

Optical and electrochemical properties of oligo(1,5-dialkoxynaphthalene-2,6-diyl)s with self-assembled ordered structures in solid state

Isao Yamaguchi, Kanako Yamauchi

Department of Material Science, Faculty of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan

Correspondence to: I. Yamaguchi (E-mail: iyamaguchi@riko.shimane-u.ac.jp)

ABSTRACT: Oligo(1,5-dialkoxynaphthalene-2,6-diyl)s were synthesized by Ni(cod)₂ (cod = 1,5-cyclooctadiene)-promoted condensation reactions of 1,5-dialkoxy-2,6-dibromonaphthalenes. The UV-Vis, photoluminescence (PL), and powder X-ray diffraction (XRD) measurements suggested that the oligomers have a self-assembling ordered structure in the solid state. The oligomers underwent electrochemical oxidation (p-doping), which occurred at lower potentials for films than for acetonitrile solutions containing [Et₄N]BF₄. This effect is caused by the longer π -conjugation lengths of the oligomers in films, which was attributed to molecular self-assembly leading to ordered structures in the solid state. The electrochemical reaction of the oligomers was accompanied by electrochromism.

© 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41840.

KEYWORDS: conducting polymers; electrochemistry; optical properties

Received 3 August 2014; accepted 1 December 2014

DOI: 10.1002/app.41840

INTRODUCTION

π -Conjugated polymers have attracted considerable attention owing to their interesting chemical properties and practical applications.¹ The molecular self-assembly of π -conjugated polymers into ordered structures in the solid state considerably affects their chemical properties.^{2–18} It has been reported that π -conjugated polymers consisted of a rigid main chain with long alkyl side chains often self-assemble into ordered structures in the solid state.^{2–18}

Well-defined π -conjugated oligomers have attracted considerable attention because of their utility for understanding the chemical and physical properties of the related polymeric materials as well as for investigating structure–property correlations.^{19–22} It has been reported that oligonaphthalenes (ONPs) exhibit strong photoluminescence (PL) and thermal stability, and they were convertible to ladder-type ONPs by an intramolecular Friedel-Crafts reaction.^{23–25} ONPs with long alkyl side chains may self-assemble into ordered structures in the solid state. However, controlling the chain lengths of ONPs is often difficult because it requires multi-step coupling reactions. In this study, we aim to synthesize ONPs with various degrees of oligomerization (DOs) in a one-pot reaction; Ni(cod)₂-promoted dehalogenation of 1,5-dialkoxy-2,6-dibromonaphthalenes was conducted for various reaction times. Investigation of the DO dependence on the chemical properties of ONPs with ordered structures in

the solid state will provide useful information for the development of new functional materials. To the best of our knowledge, there is no report on the synthesis of ONPs by a one-pot reaction and on their chemical properties caused by the molecular self-assembly of the oligomers into ordered solid-state structures.

Herein, we report the synthesis of oligo(1,5-dialkoxynaphthalene-2,6-diyl)s and a comparison of their optical and electrochemical properties in films and the solution phase. In addition, model 1,5-dialkoxynaphthalenes compounds were also synthesized to compare their chemical properties to those of the corresponding oligomers.

EXPERIMENTAL

General

Solvents were dried, distilled, and stored under nitrogen. 2,6-Dibromo-1,5-dihydroxynaphthalene was synthesized according to the literature.²⁶ Other reagents were purchased and used without further purification. Reactions were carried out with standard Schlenk techniques under nitrogen.

IR and NMR spectra were recorded on a JASCO FT/IR-660 PLUS spectrophotometer with a KBr pellet and a JEOL AL-400 spectrometer, respectively. Elemental analysis was conducted on a Yanagimoto MT-5 CHN corder. GPC analyses were carried out on a Jasco 830 refractometer with polystyrene gel columns

(K-803 and K-804) with a RI detector using chloroform as an eluent. UV-Vis and PL spectra were obtained using a JASCO V-560 spectrometer and a JASCO FP-6200, respectively. Quantum yields were calculated by using a diluted ethanol solution of 7-dimethylamino-4-methylcoumarin as the standard. Cyclic voltammetry was performed with a Hokuto Denko HSV-110. Powder X-ray diffraction measurement was conducted using a Rigaku RINT 2500 generator with CuK α irradiation.

Synthesis of Monomer-1

2,6-Dibromo-1,5-dihydroxynaphthalene (2.5 g, 7.9 mmol) and potassium hydroxide (1.4 g, 24 mmol) were dissolved in 50 mL of anhydrous ethanol, and the mixture was refluxed until potassium hydroxide dissolved in the solvent. After 1-bromohexane (3.4 mL, 24 mmol) was added dropwise to the solution, the reaction solution was refluxed for 36 h. The precipitate was removed by filtration, and the filtrate was washed with brine. The organic layer was dried over sodium sulfate and the solvent was removed under vacuum. The resulting solid was purified by silica gel column chromatography with an eluent of hexane/chloroform ($v/v = 2/1$) and then recrystallized from a solution of chloroform and methanol ($v/v = 1/1$). **Monomer-1** was collected by filtration, dried under vacuum, and obtained as a light yellow crystal (0.83 g, 22%). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.74 (d, $J = 8.8$ Hz, 2H), 7.60 (d, $J = 8.8$ Hz, 2H), 4.07 (t, $J = 6.6$ Hz, 4H), 1.94 (m, 4H), 1.57 (m, 4H), 1.40 (m, 8H), 0.93 (t, $J = 6.8$ Hz, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 152.79, 131.04, 130.07, 119.36, 113.78, 74.67, 31.71, 30.24, 25.70, 22.64, 14.10. Calcd for $\text{C}_{22}\text{H}_{30}\text{Br}_2\text{O}_2$: C, 54.34; H, 6.22. Found: C, 54.59; H, 6.10.

Synthesis of Monomer-2

Monomer-2 was synthesized by the reaction of 2,6-dibromo-1,5-dihydroxynaphthalene with 1-bromooctane in a similar manner.

Data of **monomer-2**: Yield = 46%. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.74 (d, $J = 8.8$ Hz, 2H), 7.60 (d, $J = 9.2$ Hz, 2H), 4.07 (t, $J = 6.6$ Hz, 4H), 1.94 (m, 4H), 1.36 (m, 20H), 0.89 (m, 6H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 152.78, 131.02, 130.05, 119.34, 113.76, 74.64, 31.84, 30.26, 29.46, 29.27, 26.03, 22.66, 14.10. Calcd for $\text{C}_{26}\text{H}_{38}\text{Br}_2\text{O}_2$: C, 57.57; H, 7.06. Found: C, 57.70; H, 6.89.

Synthesis of Oligomer-1a

$\text{Ni}(\text{cod})_2$ (1.3 g, 4.8 mmol) and 2,2-bipyridyl (0.75 g, 4.8 mmol) were dissolved in 5 mL of dry DMF under nitrogen. To the solution was added a DMF solution (5 mL) of **monomer-1** (0.98 g, 2.0 mmol) at 60°C. The reaction solution was stirred at 85°C for 100 h. The precipitate was collected by filtration, washed with an aqueous solution of ammonia (two times), an aqueous solution of 2,2',2'',2'''-(ethane-1,2-diyl)dinitrilo)tetraacetic acid, 0.1N HCl(aq), methanol, and dried under vacuum to give **oligomer-1a** as a yellowish green powder (0.46 g, 48%). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.11 (H^b , 2H), 7.85 (H^b , d, $J = 8.8$ Hz, 0.18H), 7.77 (H^a , 2H), 7.44 (H^c , t, $J = 8.4$ Hz, 0.18H), 6.86 (H^a , d, $J = 7.6$ Hz, 0.18H), 4.18 (0.36H), 3.74-3.81 (4H), 2.17 (0.36H), 1.63 (4H), 1.41 (0.36H), 1.15-1.25 (12.36H), 0.95 (0.54H), 0.78 (6H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 152.95, 152.91, 152.55, 130.11, 130.06, 130.00,

129.71, 129.52, 129.43, 128.68, 127.81, 127.50, 127.42, 126.67, 117.92, 117.80, 117.31, 114.75, 73.93, 68.24, 31.67, 31.54, 30.27, 30.21, 29.33, 26.00, 25.66, 25.61, 22.67, 22.54, 14.09, 14.02, 13.96.

Synthesis of Oligomer-1b, Oligomer-2a, and Oligomer-2b

Oligomer-1b, **oligomer-2a**, and **oligomer-2b** were synthesized analogously.

Data of **oligomer-1b**: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.11 (H^b , 2H), 7.85 (H^b , d, $J = 7.6$ Hz, 0.29H), 7.78 (H^a , 2H), 7.44 (H^c , t, $J = 8.4$ Hz, 0.29H), 6.87 (H^a , d, $J = 8.0$ Hz, 0.29H), 4.18 (0.58H), 3.74-3.81 (4H), 1.96 (0.58H), 1.52-1.62 (2H), 1.13-1.25 (12.58H), 0.95 (0.58H), 0.75-0.79 (6H).

Data of **oligomer-2a**: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.09 (H^b , 2H), 7.85 (H^b , d, $J = 8.4$ Hz, 0.15H), 7.77 (H^a , 2H), 7.43 (H^c , t, $J = 8.0$ Hz, 0.15H), 6.87 (H^a , d, $J = 7.6$ Hz, 0.15H), 4.17 (0.30H), 3.73-3.80 (4H), 0.95 (0.30H), 1.44-1.64 (4H), 1.08-1.25 (20.75H), 0.90 (0.45H), 0.86 (6H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 153.37, 152.88, 129.98, 129.50, 127.75, 127.43, 125.84, 117.88, 114.70, 73.90, 73.86, 68.22, 38.81, 30.30, 29.44, 29.32, 29.20, 26.32, 26.00, 25.93, 22.69, 22.63, 14.12.

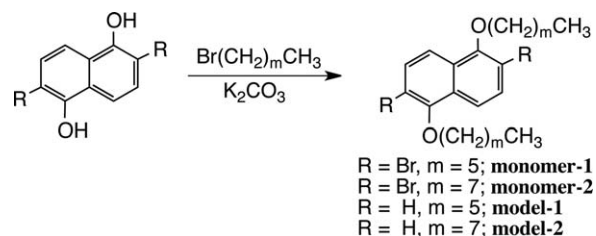
Data of **oligomer-2b**: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.11 (H^b , 2H), 7.85 (H^b , d, $J = 8.4$ Hz, 0.32H), 7.77 (H^a , 2H), 7.43 (H^c , t, $J = 8.0$ Hz, 0.32H), 6.87 (H^a , d, $J = 7.6$ Hz, 0.32H), 4.17 (0.30H), 3.73-3.80 (4H), 0.95 (0.32H), 1.44-1.64 (4H), 1.08-1.25 (21.6H), 0.90 (0.48H), 0.85 (6H).

Synthesis of Model-1

1,5-dihydroxynaphthalene (2.6 g, 16 mmol) and potassium hydroxide (2.7 g, 48 mmol) were dissolved in 50 mL of anhydrous ethanol, and the mixture was refluxed until potassium hydroxide dissolved in the solvent. After 1-bromohexane (4.2 mL, 47 mmol) was added dropwise to the solution, the reaction solution was refluxed for 36 h. The precipitate was removed by filtration, and the filtrate was washed with brine. The organic layer was dried over sodium sulfate and the solvent was removed under vacuum. The resulting solid was purified by silica gel column chromatography with an eluent of hexane/chloroform ($v/v = 2/1$) and then recrystallized from a solution of chloroform and methanol ($v/v = 1/1$). **Model-1** was collected by filtration, dried under vacuum, and obtained as a light yellow crystal (1.31 g, 25%). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.84 (d, $J = 8.4$ Hz, 2H), 7.36 (t, $J = 8.0$ Hz, 2H), 6.83 (d, $J = 8.0$ Hz, 2H), 4.11 (t, $J = 6.4$ Hz, 4H), 1.92 (m, 4H), 1.26-1.38 (m, 12H), 0.90 (m, 6H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 154.67, 126.78, 125.04, 114.02, 105.21, 68.15, 31.63, 29.28, 25.94, 22.63, 14.06. Calcd for $\text{C}_{22}\text{H}_{32}\text{O}_2$: C, 80.44; H, 9.82. Found: C, 80.65; H, 9.59.

Synthesis of Model-2

Model-2 was synthesized analogously. Data of **Model-2**: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.84 (d, $J = 8.4$ Hz, 2H), 7.34 (t, $J = 8.0$ Hz, 2H), 6.82 (d, $J = 8.0$ Hz, 2H), 4.11 (t, $J = 6.4$ Hz, 4H), 1.91 (m, 4H), 1.29-1.39 (m, 20H), 0.89 (m, 6H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 154.68, 126.76, 125.05, 114.01, 105.20, 68.14, 31.86, 29.43, 29.32, 29.29, 26.28, 22.69, 14.15. Calcd for $\text{C}_{26}\text{H}_{40}\text{O}_2$: C, 81.20; H, 10.48. Found: C, 81.49; H, 10.13.



Scheme 1. Synthesis of monomers and model compounds.

RESULTS AND DISCUSSION

Synthesis

Monomer-1 and **monomer-2** were synthesized by the reaction of 2,6-dibromo-1,5-dihydroxynaphthalene with 1-bromohexane and 1-bromooctane, respectively (Scheme 1). Model compounds, **model-1** and **model-2**, were synthesized by the reaction of 1,5-dihydroxynaphthalene with 1-bromohexane and 1-bromooctane, respectively (Scheme 1).

The dehalogenative oligomerization reactions of **monomer-1** and **monomer-2** were carried out using Ni(cod)₂ as a condensation reagent for 100 h and 48 h, respectively, resulting in the formation of **oligomer-1a**, **oligomer-1b**, **oligomer-2a**, and **oligomer-2b** in 48%, 15%, 35%, and 25% yields, respectively. The synthesis results are summarized in Table I (Scheme 2).

Oligomer-1a, **oligomer-1b**, **oligomer-2a**, and **oligomer-2b** were soluble in chloroform and tetrahydrofuran (THF) at room tem-

perature, but were insoluble in polar organic solvents such as *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).

The M_n and M_w values of the obtained oligomers, determined by GPC measurements, are summarized in Table I. The M_n and M_w values of the chloroform solutions of **oligomer-1a**, **oligomer-1b**, **oligomer-2a**, and **oligomer-2b** were 4690 and 5630, 3210 and 3530, 6080, and 7170, and 3250 and 3580, respectively. These values suggest that the DOs of the oligomers depended on reaction times.

The η_{sp}/c values of **oligomer-1a** in chloroform and a mixture of MeOH and chloroform ($v/v = 6/4$) at 30°C were 0.14 dL g⁻¹ and 0.19 dL g⁻¹, respectively. MeOH is a poor solvent for the oligomer. The higher η_{sp}/c value of the oligomer in MeOH/CHCl₃ than in chloroform is ascribed to the self-assembled structure of the oligomer in MeOH/CHCl₃. It was reported that the addition of poor solvent into the solutions of poly(3-alkylthiophene-2,5-diyl)s caused the self-assembly of the polymers.¹⁰ The self-assembly of the oligomers obtained in this study are also described in the UV-Vis and photoluminescence spectra and solid state structure sections.

IR and ¹H-NMR Spectra

Figure 1 shows the IR spectra of **model-1**, **monomer-1**, **oligomer-1a**, and **oligomer-1b**. The IR spectrum of **monomer-1** contained a peak corresponding to the stretching vibration of a C-Br bond at 920 cm⁻¹; this peak was not present for the IR spectrum of **oligomer-1a** and **oligomer-1b**. Similarly, the C-Br

Table I. Synthesis Results

	Yield (%)	M_n^a	M_w^a	Absorption (nm)		PL (nm)		Oxidation potential (V) ^d	
				In CHCl ₃ ^b	In film	In CHCl ₃	In film	In film ^e	In solution ^f
Oligomer-1a	48	4690	5630	277 (4.06), 341 (3.57)	277, 346	386	444, 477, 498 ^c	0.40	1.00
Oligomer-1b	14	3210	3530	277 (4.50), 341 (4.09)	278, 345	386	408, 440, 468, 498 ^c	0.42	1.05
Oligomer-2a	35	6080	7170	278 (5.02), 341 (4.53)	278, 341	387	387, 408, 439, 467, 497 ^c	0.39	0.97
Oligomer-2b	25	3250	3580	277 (4.06), 344 (4.52)	276, 341	388	387, 409, 440, 498 ^c	0.48	0.99
Model-1	25			244 (4.00), 300 (4.06), 314 (4.00), 328 (3.87)		336 ^c , 348, 369 ^c			
Model-2	14			244 (3.98), 300 (3.92), 314 (3.99), 328 (3.85)		336 ^c , 349, 369 ^c			

^a Determined by GPC (vs. polystyrene standards). Eluent was chloroform.

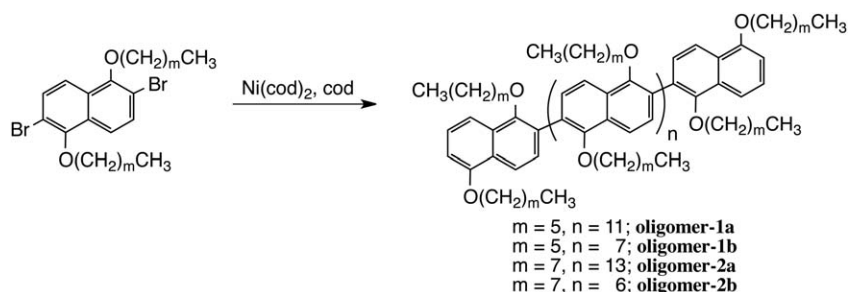
^b log ϵ values are shown in parenthesis.

^c Shoulder peak.

^d Measured by cyclic voltammetry. Sweep rate was 50 mV s⁻¹.

^e Cast film on a Pt plate.

^f In an acetonitrile solution of [Et₄N]BF₄ (0.1M).



Scheme 2. Synthesis of oligomers.

peak was not present in the IR spectra of **oligomer-2a** and **oligomer-2b**. The disappearance of the C—Br peak suggests that the expected condensation reactions were successful.

Figure 2 shows the $^1\text{H-NMR}$ spectra of **model-1**, **monomer-1**, **oligomer-1a**, and **oligomer-1b** in CDCl_3 . The peak assignments are shown in the figure. **Oligomer-1a** and **oligomer-1b** have 1,5-dihexyloxy-naphthyl-2-yls as the end-terminal groups. The replacement of a C—Br bond with a C—H bond as the end-terminal group may occur during purification with dilute HCl. The analytical results suggested that the oligomers did not contain bromine atom. The NMR chemical shifts of the peaks corresponding to the terminal naphthyl (H^a , H^b , and H^c) and hexyloxy (H^d - H^h) protons of the oligomers are consistent with those of **model-1**. The $^1\text{H-NMR}$ spectra of **oligomer-2a** and

oligomer-2b exhibited peaks corresponding to the protons of the main chain and terminal groups at similar chemical shifts to those of **oligomer-1a** and **oligomer-1b**. The integral ratios of the main chain and terminal groups peaks suggested that the degree of oligomerization (DOs) of **oligomer-1a**, **oligomer-1b**, **oligomer-2a**, and **oligomer-2b** were 11, 7, 13, and 6, respectively. The molecular weights of **oligomer-1a**, **oligomer-1b**, **oligomer-2a**, and **oligomer-2b** calculated from the DOs are ~ 4240 , 2930, 5730, and 3060, respectively. These values are nearly consistent with the M_n values estimated from the GPC analysis.

UV-Vis and Photoluminescence Spectra

Optical data are summarized in Table I. Figure 3 shows the UV-Vis spectra of **monomer-1**, **model-1**, and **oligomer-1a** in chloroform.

The onset positions (λ_{onset}) for the absorption spectra of **oligomer-1a** and **oligomer-1b** were longer than those of **monomer-1** and **model-1**; this suggests that a longer π -conjugation system present in the oligomer chain. Observation of longer absorption wavelengths for **oligomer-1a** and **oligomer-2a** than for **oligomer-1b** and **oligomer-2b** was attributed to the longer chain lengths of **oligomer-1a** ($n = 11$) and **oligomer-2a** ($n = 13$) than those of **oligomer-1b** ($n = 7$) and **oligomer-2b** ($n = 6$). Naphthalene is reported to have three absorption bands (I, II, and III), exhibiting the characteristic absorption maxima (λ_{max}) at 221, 266, and 301 nm in methanol, respectively. In addition to the peak at 266 nm, three other peaks at 248, 257, and 275 nm were observed for Band II because of the presence of hyperfine structures of naphthalene. Introduction of electron-donating substituent(s), alkyl and amino groups, at the 1- and 5-positions of naphthalene caused bathochromic shifts in the peaks of the three absorption bands. As shown in Figure 3, **model-1** exhibited absorptions at 244 nm and in the range 300–328 nm, corresponding to Band I and Bands II and III of the naphthalene ring, respectively. These wavelengths are longer than those of naphthalene because of hyperconjugation between the electron-donating substituents and the naphthalene ring. Hyperfine splitting in Band II of **monomer-1** and **oligomer-1a** is not present because of the symmetric substitution at the 1-, 2-, 5-, and 6-positions of the naphthalene ring. Introduction of the substituents at 2- and 6- (or 7-) positions of naphthalene is reported to cause bathochromic shifts in the peaks corresponding to the three bands, accompanied by a collapse of the hyperfine splitting in Band II.²⁷

To investigate the solid state optical properties, the films of the oligomers were prepared by casting their chloroform solutions on a quartz glass plate. As shown in Figure 4, the cast films of **oligomer-1a** and **oligomer-2a** had absorption peaks at longer

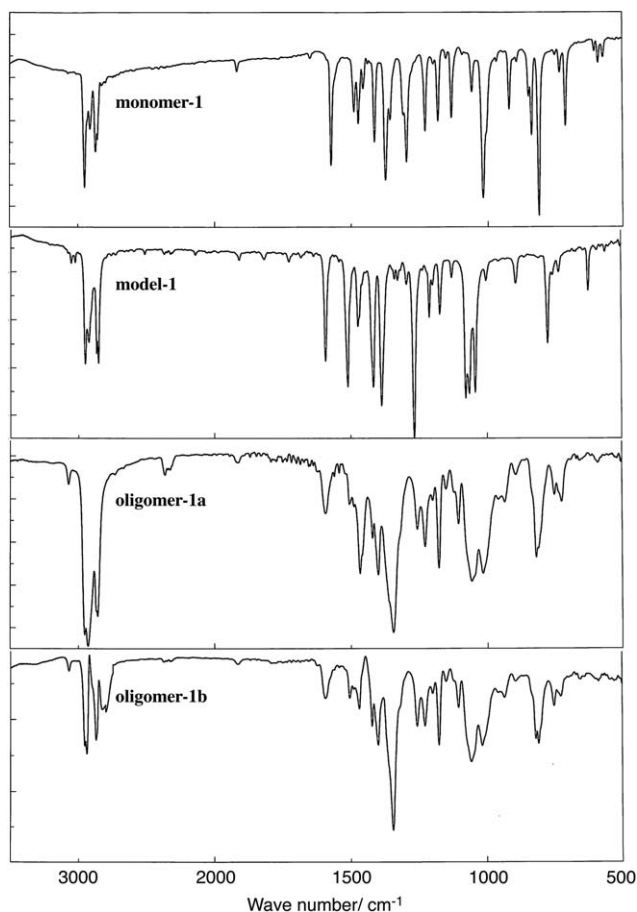


Figure 1. IR spectra of monomer-1, model-1, oligomer-1a, and oligomer-1b.

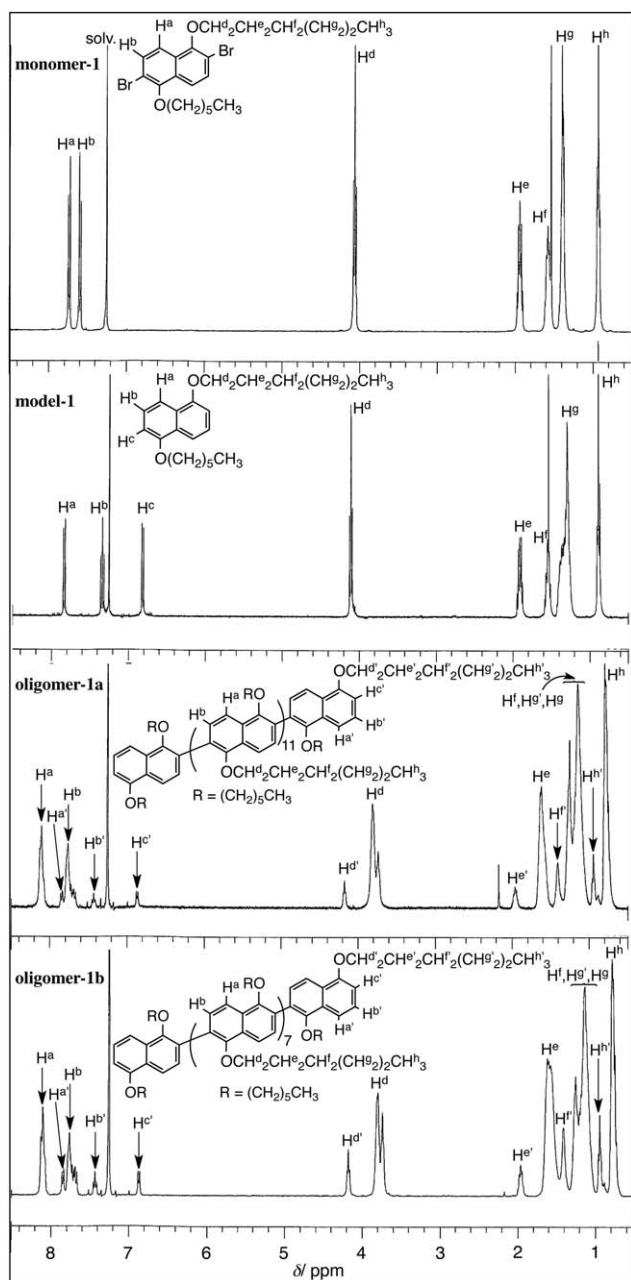


Figure 2. $^1\text{H-NMR}$ spectra of monomer-1, model-1, oligomer-1a, and oligomer-1b in CDCl_3 .

wavelengths than those taken in chloroform. It has been reported that π -conjugated polymers, which form π -stacked structures in the solid state often show a bathochromic shift of λ_{max} . Based on these results, it can be concluded that the oligomers likely form ordered structures in the solid state.

To obtain more information on the formation of the self-assembly ordered structures of the oligomers, we carried out the UV-Vis measurements of the chloroform solutions of **oligomer-1a** in the presence of various amounts of MeOH. The absorptions shifted to longer wavelengths as the MeOH/ CHCl_3 ratios increased. The spectral changes are shown in Figure 5. The absorption positions of the oligomer in MeOH/ CHCl_3 ($v/v = 6/4$) were almost the same as those of the cast film of the

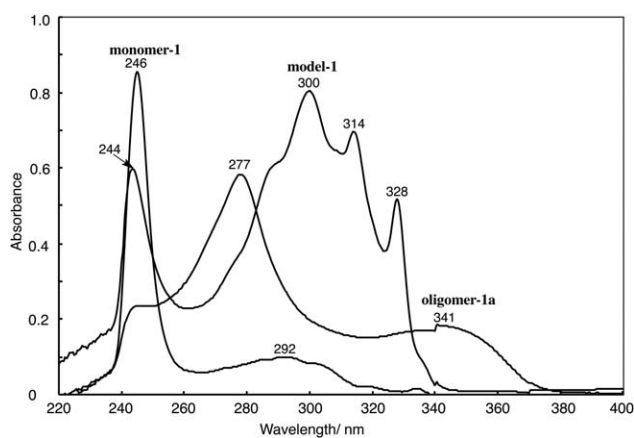


Figure 3. UV-Vis spectra of monomer-1, model-1, and oligomer-1a in chloroform.

oligomer. It has been reported that regioregular poly(3-alkylthiophene)s (PRTs) in MeOH/ CHCl_3 system show similar spectral changes because of the formation of the self-assembly ordered structures in the colloidal solutions and they take the self-assembly ordered structures in film.¹⁰

Both the solution and thin films of the monomers, model compounds, and oligomers obtained were photoluminescent when irradiated with UV light. Figure 6 shows the photoluminescence spectra of the chloroform solutions and films of **oligomer-1a** and **oligomer-1b**. The PL peak positions of the chloroform solutions of **oligomer-1a** ($\lambda_{\text{em}} = 386$ nm) and **oligomer-1b** ($\lambda_{\text{em}} = 387$ nm) were longer than those of **model-1** ($\lambda_{\text{em}} = 348$ nm), which was attributed to the larger π -conjugated system present in the oligomer chain. These observations are consistent with the results that the $\beta\sigma\pi\pi\sigma$ of the oligomers were observed at longer wavelengths than those of the model compounds. The PL spectra of films of **oligomer-1a** and **oligomer-1b** exhibited strong peaks at 477 and 440 nm, with small and shoulder peaks at longer wavelengths. The appearance of the small and shoulder peaks may be the signature of π - π interactions between the interchain species, which have well-defined vibronic structures. The peaks corresponding

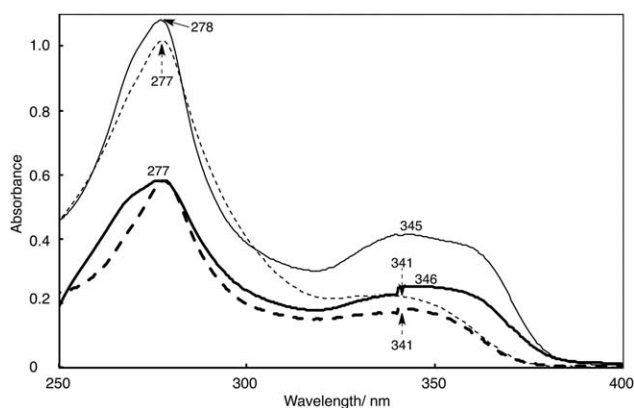


Figure 4. UV-Vis spectra of oligomer-1a in chloroform (bold dotted curve) and film (bold solid curve) and oligomer-1b in chloroform (thin dotted curve) and film (thin solid curve).

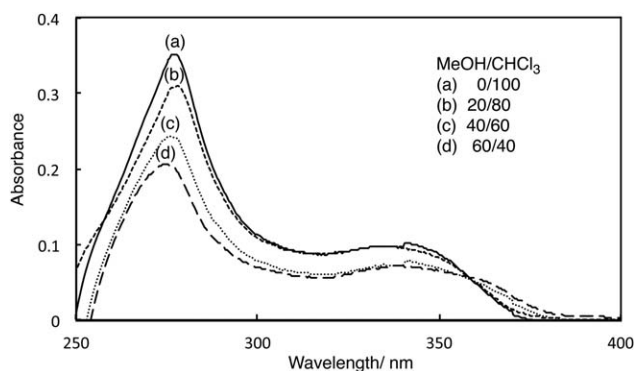


Figure 5. UV-Vis spectra of oligomer-1a in the mixtures of chloroform and methanol in various volume ratios.

to the vibronic structures are often observed in the PL spectra of π -conjugated polymers and oligomers with self-assembled ordered structures in films.^{28–30} The PL peak wavelengths of the oligomers were also longer in films than in the chloroform solution because of the ordered structures in the former. The quantum yields of the PL of **oligomer-1a**, **oligomer-1b**, **oligomer-2a**, and **oligomer-2b** in chloroform were 21, 15, 31, and 16%, respectively. These values are larger than those of **model-1** ($\Phi = 4\%$) and **model-2** ($\Phi = 7\%$).

Solid State Structure

As previously described, shifts in the UV-Vis and PL peaks of the films (Figures 4–6) suggest that the oligomers assume self-assembled ordered structures in the solid state. The powder X-ray diffraction (XRD) pattern of **oligomer-1a**, shown in Figure 7, supports this assumption. The XRD pattern of **oligomer-1a** was similar to those of the π -conjugated oligomers and polymers with ordered structures in the solid state and exhibited a strong sharp peak in a low-angle region and a medium broad peak in the range $2\theta = 24–26^\circ$. The peaks with $d_1 = 16.4 \text{ \AA}$ and $d_2 = 4.0 \text{ \AA}$ in Figure 6 likely correspond with the distances

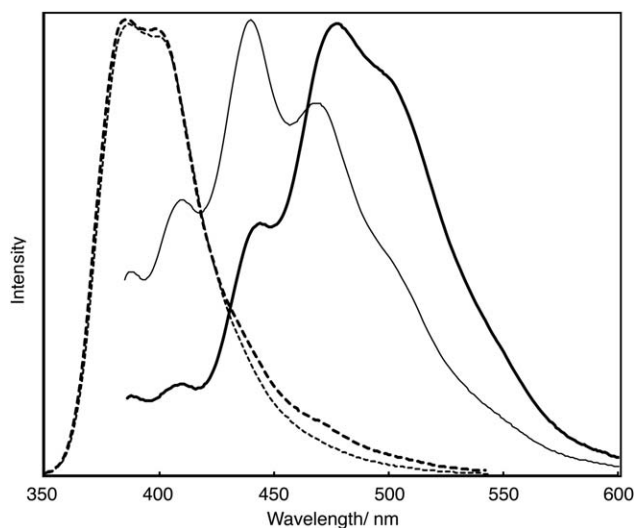


Figure 6. PL spectra of oligomer-1a in chloroform (bold dotted curve) and film (bold solid curve) and oligomer-1b in chloroform (thin dotted curve) and film (thin solid curve).

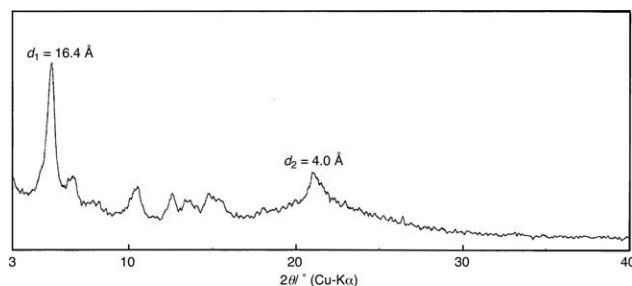


Figure 7. Powder X-ray diffraction (XRD) pattern of oligomer-1a.

between the oligomer chains separated by the hexyl side chains and the face-to-face distance of the oligomer chain, respectively. These distances are comparable to the self-assembled π -conjugated polymers such as regioregular poly(3-hexylthiophene-2,5-diyl) ($d_1 = 16.7 \text{ \AA}$ and $d_2 = 3.8 \text{ \AA}$)¹⁰ and poly(hexyl-substituted *p*-phenyleneethynylene) ($d_1 = 16.4 \text{ \AA}$ and $d_2 = 3.8$ and 4.1 \AA)³¹ in the solid state. Figure 8 shows a schematic drawing of the possible ordered structure of **oligomer-1a** in solid state.

Cyclic Voltammograms

Figure 9(a,b) shows the cyclic voltammograms of the cast films of **oligomer-1a** and **oligomer-1b** in an acetonitrile solution containing $[\text{Et}_4\text{N}]\text{BF}_4$ (0.10M) and electrolyte solutions of the oligomers, respectively. The oxidation potentials of the oligomers are summarized in Table I. The solutions of **oligomer-1a**, **oligomer-1b**, **oligomer-2a**, and **oligomer-2b** exhibited peaks at 1.00 V, 1.05 V, 0.97 V, and 0.99 V (E_{pa} vs. Ag^+/Ag), respectively, while the cast films showed peaks at 0.40 V, 0.42 V, 0.39 V, and 0.48 V (E_{pa} vs. Ag^+/Ag) corresponding to the electrochemical oxidation of the oligomer backbone, respectively. The larger oxidation potentials of the cast films of the oligomers than the

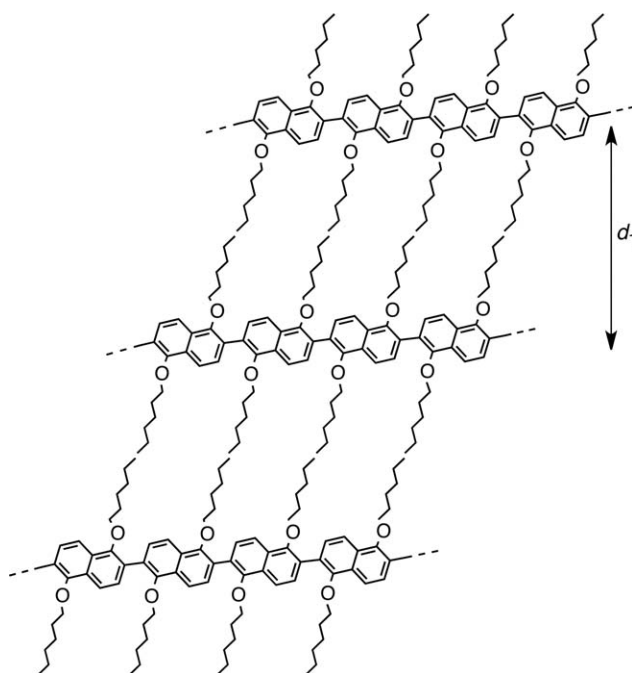


Figure 8. A schematic drawing of the possible ordered structure of oligomer-1a in solid state.

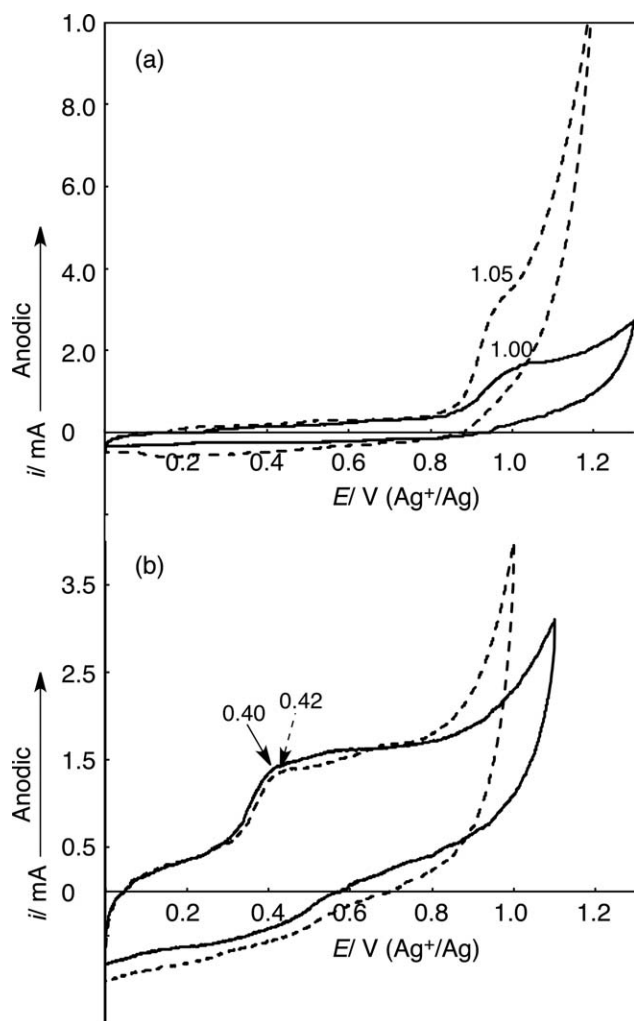


Figure 9. Cyclic voltammograms of (a) oligomer-1a (solid curve) and oligomer-1b (dashed curve) in an acetonitrile solution containing $[\text{Et}_4\text{N}]\text{BF}_4$ (0.10M) and (b) cast films of oligomer-1a (solid curve) and oligomer-1b (dashed curve) in an acetonitrile solution containing $[\text{Et}_4\text{N}]\text{BF}_4$ (0.10M).

solutions correspond to the longer π -conjugated systems in the films than in solutions. These results are consistent with the UV-Vis and PL results. The light brown films of the oligomers became dark brown after the electrochemical oxidation and regained their light brown color after crossing the E_{pc} peak.

CONCLUSIONS

Oligo(1,5-dialkoxy-naphthalene-2,6-diyl)s were synthesized by the $\text{Ni}(\text{cod})_2$ -promoted reactions of 1,5-dialkoxy-2,6-dibromonaphthalenes; their DOs could be controlled by altering the reaction times. The UV-Vis spectra of the oligomers exhibited absorption peaks at longer wavelengths than the monomers, revealing that the π -conjugation system expanded along the oligomer chain. The PL peaks of the oligomers in the films were also observed at longer wavelengths than in solution, which was attributed to the molecular self-assembly of the oligomers into ordered structures in the solid state. This conclusion was supported by XRD analysis. Cyclic voltammetry of the

oligomers showed that their electrochemical oxidation potentials depended on the DOs. From the results obtained in this study, it can be concluded that π -conjugated oligomers with controlled chain lengths can be obtained by $\text{Ni}(\text{cod})_2$ -promoted reactions of dibromoaromatic compounds for effective development of new functional oligomeric materials.

REFERENCES

- List, E. J. W.; Scherf, U. In *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T.; Reynolds, J. Eds.; CRC Press: New York, 2007.
- Malawi, H. S., Ed. *Handbook of Organic Conductive Molecules and Polymers*, Wiley: Chi Chester, UK, 1997; Vol. 2.
- Sengmany, S.; Ceballos, C.; Belhadj, R.; Cachet-Vivier, C.; Gall, E. L.; Brissault, B.; Penelle, J.; Léonel, E. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 900.
- Lee, K.-H.; Morino, K.; Sudo, A.; Endo, T. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1190.
- Lee, K.-H.; Lee, H.-J.; Kuramoto, K.; Tanaka, Y.; Morino, K.; Sudo, A.; Okauchi, T.; Tsuge, A.; Endo, T. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 234.
- Yamamoto, T.; Sato, T.; Iijima, T.; Abe, M.; Fukumoto, H.; Koizumi, T.; Usui, M.; Nakamura, Y.; Yagi, T.; Tajima, H.; Okada, T.; Sasaki, S.; Kishida, H.; Nakamura, A.; Fukuda, T.; Emoto, A.; Ushijima, H.; Kurosaki, C.; Hirota, H. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 896.
- Sato, T.; Yagi, T.; Tajima, H.; Fukuda, T.; Yamamoto, T. *React. Funct. Polym.* **2008**, *68*, 369.
- Kishida, H.; Hirota, K.; Wakabayashi, T.; Okamoto, H.; Kokubo, H.; Yamamoto, T. *Appl. Phys. Lett.* **2005**, *87*, 121902.
- Yamamoto, T.; Arai, M.; Kokubo, H.; Sasaki, S. *Macromolecules* **2003**, *36*, 7986.
- Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B.-L.; Suganuma, H.; Asakawa, N.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; Matsuda, H. *J. Am. Chem. Soc.* **1998**, *120*, 2047.
- Craley, C. R.; Zhang, R.; Kowalewski, T.; McCullough, R. D.; Stefan, M. C. *Macromol. Rapid Commun.* **2009**, *30*, 11.
- Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202.
- Jeffries-El, M.; Sauvé, G.; McCullough, R. D. *Macromolecules* **2005**, *38*, 10346.
- Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649.
- Brustolin, F.; Goldoni, F.; Meijer, E. W.; Sommerdijk, N. A. J. M. *Macromolecules* **2002**, *35*, 1054.
- Langeveld-Voss, B. M. W.; Waterval, R. J. M.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1999**, *32*, 227.
- Adachi, T.; Brazard, J.; Ono, R. J.; Hanson, B.; Traub, M. C.; Wu, Z.-Q.; Li, Z.; Bolinger, J. C.; Ganesan, V.; Bielawski, C. W.; Bout, D. A. B.; Barbara, P. F. *J. Phys. Chem. Lett.* **2011**, *2*, 1400.

18. Merlo, J. A.; Frisbie, C. D. *J. Phys. Chem. B* **2004**, *108*, 19169.
19. Tour, J. M. *Chem. Rev.* **1996**, *96*, 537.
20. Martin, R. E.; Diederich, F. *Angew. Chem. Int. Ed.* **1999**, *38*, 1350.
21. Carroll, R. L.; Gorman, C. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 4378.
22. Schenning, A. P. H. J.; Meijer, E. W. *Chem. Commun.* **2005**, 3245.
23. Chen, J.-C.; Lee, T.-S.; Lin, C.-H. *Chem. Eur. J.* **2008**, *14*, 2777.
24. Tanemura, K.; Suzuki, T.; Horaguchi, T. *J. Appl. Polym. Sci.* **2013**, *127*, 4524.
25. Lu, B.; Liu, C.; Li, Y.; Xu, J.; Liu, G. *Synth. Met.* **2011**, *161*, 188.
26. Wheeler, A. S.; Ergle, D. R. *J. Am. Chem. Soc.* **1930**, *52*, 4872.
27. Clar, E. *Spectrochim. Acta* **1950**, *4*, 116.
28. Kreyenschmidt, M.; Klaerner, G.; Fuhrer, T.; Ashenurst, J.; Karg, S.; Chen, W. D.; Lee, V. Y.; Scott, J. C.; Miller, R. D. *Macromolecules* **1998**, *31*, 1099.
29. Romaner, L.; Pogantsch, A.; Freitas, P. S.; Sherf, U.; Gaal, M.; Zojer, E.; List, E. J. W. *Adv. Funct. Mater.* **2003**, *13*, 597.
30. List, E. J. W.; Guentner, R.; Freitas, P. S.; Sherf, U. *Adv. Mater.* **2002**, *14*, 374.
31. Huang, W. Y.; Gao, W.; Kwei, T. K.; Okamoto, Y. *Macromolecules* **2001**, *34*, 1570.