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High-Intensity Circular Dichroism of Head-to-tail Regioregular Poly(1,4-phenylene)s in the Aggregated State

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Dedication ((optional))

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Abstract: Circular dichroism (CD) studies on poly(1,4-phenylene)s bearing a chiral side chain in the aggregated conditions were carried out. Little CD was observed in a solution form, while addition of a poor solvent into the polyphenylene solution induced aggregation and a strong CD was observed, accordingly. Applying the controlled degree of polymerization (DP) of poly(1,4-phenylene) in the use of bidentate diphosphine Chiraphos as a ligand for the nickel catalyst, the relationship of DP with CD strength was studied to reveal to show the highest CD at the DP = 84 (g_{abs} = *ca*. 2 x 10^{-2}). It was also found that the related aggregation was observed in good solvent 1,2-dichloroethane upon standing the solution at 4 °C for 3–23 days to observe g_{abs} = *ca*. 10^{-1}. Studies on the substituent effect of poly(1,4-phenylene) suggested that CD behaviors were dependent on the type of non-chiral substituent on the aromatic ring as well as the side-chain chirality.

Introduction

In a marked contrast to the extensive studies of π-conjugated polymers composed of a five-membered aromatic ring, such as thiophenes for use in advanced materials,[1–3] physical properties of the six-membered benzene derivative polyphenylenes have received less attention. Because of the less efficient extended π-conjugation of polyphenylenes due to the rotation of the C–C bond between benzene rings, polyphenylenes have been less focused as conductive or semiconductive materials.[4] However, polyphenylenes with an appropriately designed structure have been shown to suggest helix formation, which is applicable to a different class of functionality such as optical devices including sensors, switches, and memories that respond to chemical and physical stimuli.[5–27] Nevertheless, the preparative methodology of polyphenylenes is not sufficiently developed so far to synthesize the desired structure as expected. In particular, preparation of conjugated polymers bearing an appropriate chirality on the side chain with high degree of polymerization and a regularity in the polymer structure has been limited.

The development of a facile and efficient synthetic protocol of polyphenylenes is therefore of interest in both synthetic chemistry and materials. We have previously reported the synthesis of unprecedented regioregular poly(1,4-phenylene) **poly-1**[28,29] whose regularity is controlled in a head-to-tail manner. The reaction is carried out by the nickel(II)-catalyzed cross-coupling polymerization of bromo(chloro)benzene **1**. We have also shown that the obtained polymer exhibits circular dichroism (CD) derived from helix formation when a chiral side chain is introduced as a substituent on the benzene ring. Our preliminary studies show that circular dichroisms is observed in polyphenylene **poly-1** when a chiral side chain is introduced. However, further detailed studies have not been performed due to the preparative difficulties of the controlled polymerization reaction to yield well-defined polyphenylene. We have also shown that the use of Chiraphos **2** as a ligand for the nickel catalyst exhibits an enhanced reactivity in the polyphenylene synthesis.[29] (Figure 1) We envisaged that this finding allowed the synthesis of chiral polymers with different side chain structures as well as controlled degree of polymerization (DP).

Herein, we describe detailed studies on the CD behaviors of polyphenylene derivatives **poly-1** based on the characteristics of the molecular structure.

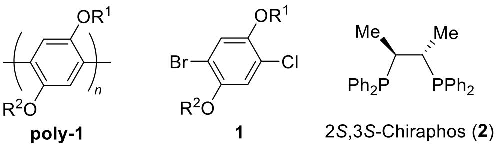
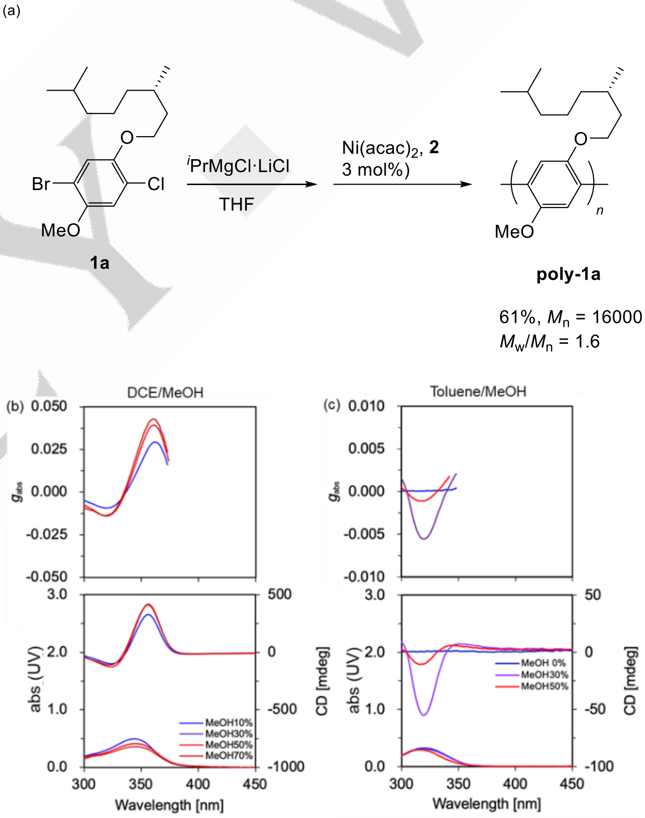


Figure 1. Structures of poly(1,4-phenylene), 1,4-bromo(chloro)benzene, and Chiraphos

Results and Discussion

Solvent effect on CD behaviors

Preparation of poly(1,4-phenylene) bearing a citronellol-derived alkoxy side chain (*S*)-(dihydro-citronellyloxy: OR^1) and methoxy (OR^2) groups, **poly-1a** was carried out as reported previously with bromo(chloro)benzene **1a** by the nickel-catalyzed cross-coupling polymerization with $Ni(acac)_2$/Chiraphos as a catalyst to afford 61% of **poly-1a** with M_n (the number average molecular weight) of 16000 (the number average degree of polymerization DP = 62) and M_w/M_n = 1.6 (M_w: weight average molecular weight).[29] (Figure 2(a)) As reported previously, a solution of **poly-1a** in 1,2-dichloroethane (DCE) did not show evident CD spectra right after the dissolution, while the Cotton effect[30] by **poly-1a** was observed in a mixed solvent system of DCE and methanol.[28] We examined the solvent effect in the CD behavior of **poly-1a**. Figure 2 (b)–(e) summarizes the results. It was also confirmed that ***ent*-poly-1a** prepared with (*R*)-dihydro-citronellol indicated opposite CD to confirm the observed CD was originated from the chiral structure. (See Supporting Information) The positive bisigned CD signal (positive Cotton effect at long wavelength and negative Cotton effect at short wavelength) was observed for the system, indicating right-handed polymer stacking according to the exciton chirality method.[31,32] The Kuhn's dissymmetry factor g_{abs} = De/e was 4.27 × 10^{-2} at 361 nm for MeOH = 70%. Since chiroptical properties of the polymer aggregate are known to be dependent on the combination and ratio of the cosolvent,[30] we studied the effect of the good solvent in the measurement of CD spectrum of **poly-1a**. Toluene, chloroform, and 1,1,2-trichloroethane were used as good solvents, and methanol was used as a poor solvent. The composition of the mixed solvent varied from 0 to 50% of methanol. The CD ellipticities and *g*-factors (g_{abs}) of the tested cosolvent systems were found to be much weaker than that in DCE. Interestingly, the toluene/methanol cosolvent system showed the opposite sign of the CD signal compared to the DCE/methanol system. In contrast, chloroform/methanol and DCE/methanol systems showed the same sign as the DCE/methanol system. This indicates the inversion of the handedness of the aggregates. Yet, it may be explained by (i) structure difference in solution state caused by solvation, electron delocalization, and steric repulsion and (ii) different stacking mode in aggregate that leads to different higher-order chiral structure. Considering that the absorption band of the **poly-1a** in toluene/methanol (λ_{max} = *ca*. 320 nm) appears in a shorter wavelength relative to DCE/methanol (λ_{max} = *ca*. 340 nm) in solution state (see below for solution state in DCE), the adjacent phenylene rings could be aligned flat for DCE/methanol compared to that in toluene/methanol cosolvent. If the **poly-1a** in DCE/methanol prefers conformer, in which the chiral side chain is located in the same direction, (Chart S1, conformer I) and that in toluene/methanol prefers the staggered conformer (Chart S1, condormer II), then the steric hindrance between the chiral side chains is less evident in conformer I and the electron delocalization stabilize the structure resulting in relatively flat adjacent phenylene rings. In contrast, the steric hindrance between the side chains becomes evident in conformer II, resulting in more twisted conformation than in conformation I.



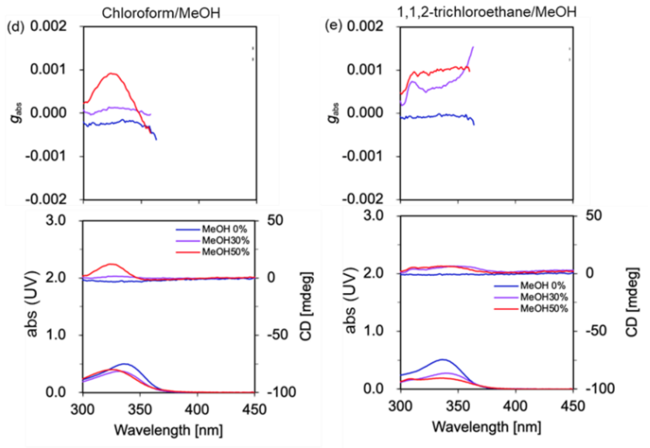


Figure 2. Preparation and spectroscopic properties of **poly-1a,** (a) Polymerization of **1a** catalyzed by nickel, (b) solvent effect of **1a** in DCE/MeOH, (c) in toluene/MeOH, (d) chloroform/MeOH, and (e) 1,1,2-trichloroethane/MeOH; The measurement was performed with a 5.0 × 10^{-4} M solution of **poly-1a** with DP = 62. The g_{abs} value is shown for regions where the absorbance is more than 0.1.

The relationship of CD behaviors with the degree of polymerization (DP)

We next investigated the effect of the degree of polymerization of polyphenylene **poly-1a** on the CD behavior. Since our recent findings on the use of a bidentate phosphine ligand Chiraphos (**2**) for the cross-coupling polymerization of bromo(chloro)benzene **1a** remarkably improved the catalytic activity of nickel(II) catalyst, the polymerization allows preparing polymer **poly-1a** with a wide range of DP by changing the ratio of monomer feed and the catalyst loading. In addition to **poly-1a** with DP = 62, 5 polymers with the range of DP = 11–168 were prepared by varying the ratio of the catalyst loading and monomer feed as 0.5–3.0 mol% (Figure 3a) (see Supporting Information) and measurements of CD spectra were performed. Figure 3b shows the DP dependence of g_{abs}. As shown in Figure 3b, which summarizes the relationship of the *g*-factor value with DP, it was revealed that the CD intensity was increased with the increase of DP up to 84. The highest g_{abs} (*ca.* 1.9 × 10^{-2}) was observed in **poly-1a** of DP = 84. On the other hand, polyphenylene **poly-1a** decreased the g_{abs} value at the range of DP > 84. It was also found that **poly-1a** with a low degree of polymerization showed a positive bisigned Cotton effect. In contrast, a high degree of polymerization showed a positive peak surrounded by two negative dips (negative trisigned Cotton effect), which became characteristic as the DP value increased. The theoretical model of a cylindrical aggregate predicts that the shape of the CD changes from bisigned to trisigned CD when the length of the aggregate increases.[33] Since poly-1,4-phenylene has rigid mesogenic main chain, the shape of the polymer is rod-like rather than globule. Therefore, the aggregate is expected to form fiber like structure resulting in similar structure as cylindrical aggregates. The polyphenylene has electric transition dipole moment along their main chain and the condition is similar to the previously reported theoretical model.[33] Similar bisiged and trisiged CD is reported for the polysilane with a chiral side chains.[8,17] The polysilane and polyphenylene are similar in that they are σ- and π-conjugated polymers, respectively, having transition dipole moment in their main chains, and they have rigid main chains. Thus, these polymers could be showing similar results explained by the theoretical model of the cylindrical aggregate. As far as we are concerned, there has not been a report on the systematic relationship of the CD intensity with the degree of polymerization of poly(1,4-phenylene)s because of its preparative difficulties in the controlled synthesis of polyphenylene with different molecular weight range.

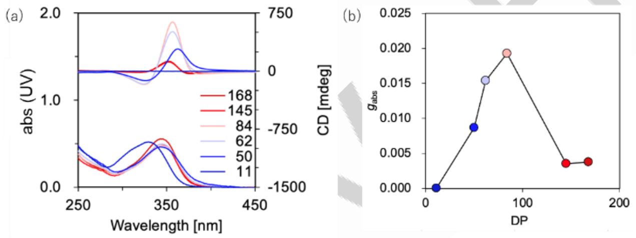


Figure 3. DP dependence of CD spectra for poly(1,4-phenylene) **poly-1a** in DCE/MeOH cosolvent with 30% methanol). (a) CD and absorption spectra of **poly-1a** (g_{abs}). (b) The relationship between the average DP and g_{abs}

The relationship with light scattering

It was found that polyphenylene **poly-1a** dissolved in DCE as prepared, which showed little CD intensity, increased the CD intensity after the thus prepared solution (3 × 10^{-4} M) was stored in refrigerator for several days. As shown in Table 1, little CD was observed in an as-prepared DCE solution of polyphenylene **poly-1a** with DP of 50–168. In contrast, increased g_{abs} were observed in these polymers after storing the solution kept at 4 °C for 3-23 days. Polymer **poly-1a** (DP = 50–168) showed comparable or slightly higher g_{abs} than those in the measurement with a mixed solution of DCE/methanol after 3 days. It should be noted that g_{abs} of **poly-1a** (DP = 84) was further improved after the storage for >10 days to 1 x 10^{-1}, which was more than 10-fold higher than the g_{abs} in the corresponding DCE/methanol. Aggregation of **poly-1a** improves helix formation by π–π stacking as standing in a DCE solution, and the result can also be related to the dynamic light scattering (DLS) of the solution of **poly-1a**. Although little scattering was found in the as-prepared DCE solution, **poly-1a** increased the average scattering after standing in the solution for three days.

Table 1. The time conversion of the g_{abs} value and light scattering of the polymer solution of **poly-1a** in DCE[a]

DP	g_{abs}[b]			Average Scattering
	3 days	10 days	23 days	as prepared after 3 days
50	6.10 ×10^{-2} (357 nm)	1.48 ×10^{-2} (362 nm)	1.91 ×10^{-2} (363 nm)	0.61 1.86
84	6.13 ×10^{-2} (361 nm)	1.19×10^{-1} (364 nm)	1.21×10^{-1} (365 nm)	0.29 50.17
168	.63 ×10^{-2} (354 nm)	1.78 ×10^{-2} (354 nm)	1.86 ×10^{-2} (354 nm)	0.37 45.76

[a] The measurement was performed in 3 × 10^{-4} M DCE after the storage of the mixture at 4 °C. [b] In parenthesis, λ_{max} at the CD maximum wavelength was shown. [c] The measurement was performed after dilution to 1.5 × 10^{-4} M.

The substituent effect of poly(1,4-phenylene)s

It was shown that a strong *g*-factor intensity was observed in the CD measurement of polyphenylene **poly-1a** bearing a chiral side-chain substituent derived from citronellol. The highest value in **poly-1a** was found to be comparable with that of the related poly(1,4-phenylene) **poly-2/SNAp** reported by Akagi (g_{abs} = 4.70 × 10^{-2}).[34] (Chart 2) Considering the structure of **poly-2/SNAp** with interactive polar functional groups at the side chain, it is noteworthy that polyphenylene **poly-1a**, which is composed only of the branched alkyl side chain, expressed a high g_{abs} value. This is probably because of the chiral substituent on all of the constituent benzene rings in **poly-1a** in a regioregular manner, while the chiral source of **poly-2/SNAp** is located in the alternating biphenyl ring.

Since the synthesis of polyphenylene using Chiraphos as a ligand for nickel(II) catalyst was in hand, the synthetic protocol allowed the synthesis of polymers with unsymmetrical side chains that were previously difficult to prepare. The reaction of 1,4-dibromobenzene **1b'** bearing chiral side chains (OR^1) at both 2 and 5-positions has not been successful in the presence of a ubiquitous nickel-bidentate phosphine complex of DPPE (1,2-diphenylphosphinoethane) or DPPP (1,3-diphenylphosphinopropane),[29] however, the use of Chiraphos **2** allowed affording polyphenylene **poly-1b**. The obtained polyphenylene **poly-1b** was also subjected to the CD spectrum measurement in DCE/methanol cosolvent. It was found that polyphenylene **poly-1b** bearing two chiral side chains at the 2,5-positions exhibited opposite Cotton effect (g_{abs} = –6.86 × 10^{-2} at 375 nm, DCE/methanol = 60/40 (v/v%)) compared with regioregular and unsymmetrical **poly-1a** (g_{abs} = 4.27 × 10^{-2} at 361 nm, DCE /methanol = 30/70 (v/v%)) as shown in Figure 4 (a). Preparation of other polyphenylenes, **poly-1c** (Z = F instead of OMe) and **poly-1d** (Z = H instead of OMe), was also carried out. These polymers were found to show the same CD sign with that of **poly-1a** bearing OMe as shown in Figure 4 (c).

The key to a high *g*-factor value would be using the citronellol-derived chiral (*S*)-dihydro-citronellyloxy side chain for poly(1,4-phenylene) **poly-1a**. Fiesel and Scherf[19,35] previously reported the CD properties of polyphenylene bearing two chiral alkoxy substituents (*S*)-2-methylbutoxy at the 2,5-positions **1e**. We therefore prepared the related polyphenylene **poly-1f** with a similar DP, and the CD properties were compared. The g_{abs} of (*S*)-**poly-1e** with the related DP (DP = 201) was found to show the opposite sign to that of (*S*)-**poly-1b** . We have also synthesized **poly-1f** (DP = 105) bearing chiral (*S*)-2-methylbutoxy and methoxy groups at the side chain and measurement of CD properties was performed under similar conditions. It was found that polyphenylene **poly-1f** also exhibited a much smaller *g*-factor (–4.2 × 10^{-4}) compared with the (*S*)-dihydro-citronellol-derived polymer **poly-1a**. These results suggest that (1) poly(1,4-phenylene) with a single chiral substituent shows opposite CD sign compared with the related symmetrical disubstituted analog and (2) the citronellol-derived chiral side chain in the regioregular manner is a suitable structure that exhibits a strong *g*-factor associated with the helix formation of poly(1,4-phenylene) **poly-1**.

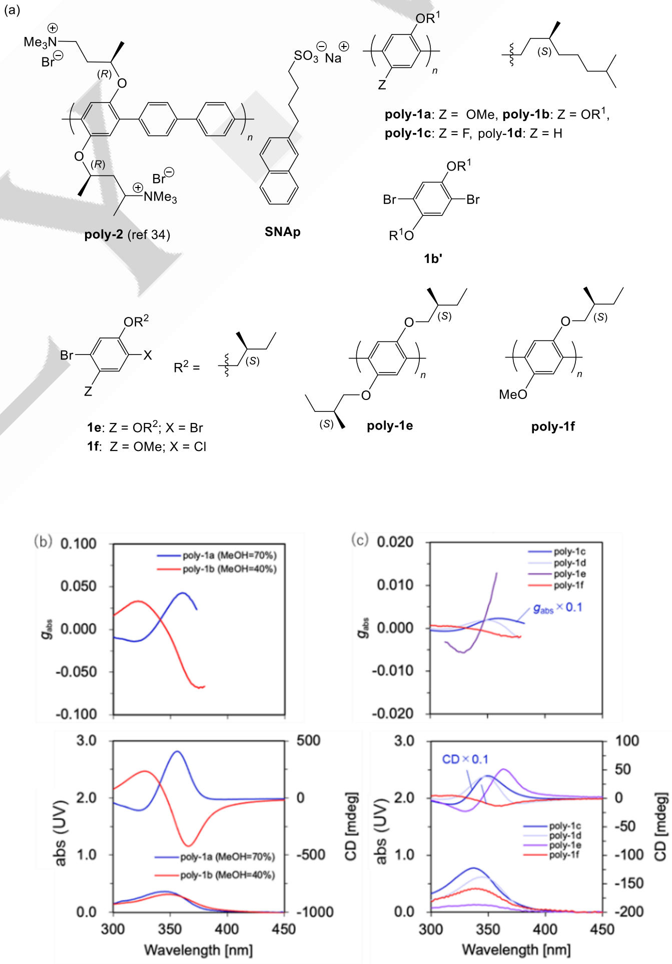


Figure 4. Structures of polypheneylenes and their synthetic precursor (a) Polymer structures of **poly-1** and **poly-2** and their synthetic precursors (dihalobenzene derivatives). (b) CD spectra of polyphenylene **1** bearing chiral (OR^1) and additional substituents (OR^2) at the 2 and 5-positions. **Poly-1a** and **poly-1b** showing opposite Cotton effect. (c) CD spectra of **poly-1c** (g_{abs} = 2.27 × 10^{-2} at 360 nm), **poly-1d** (g_{abs} = –2.44 × 10^{-3} at

377 nm), **poly-1e** (g_{abs} = 1.29 × 10^{-2} at 358 nm), **poly-1f** (g_{abs} = –2.13 × 10^{-3} at 378 nm) in DCE /methanol = 70/30 (v/v%) cosolvent*s*

Conclusion

In conclusion, we have studied the circular dichroism behavior of poly(1,4-phenylene) bearing a chiral alkoxy side chain. The CD properties were found to be influenced by the effect of solvent, degree of polymerization, and the structure of substituent. The study of such a variety of investigations ascribed to the development of polyphenylene synthesis using Chiraphos as a highly active ligand of nickel(II) complex, which allows for the synthesis of various structural derivatives with a wide range of degrees of polymerization.

Experimental Section

General

Unless otherwise noted, all the reactions were carried out using the standard Schlenk technique under an argon or nitrogen atmosphere. Melting points were measured on a Yanaco MP-J3 and were uncorrected. ^1H (400 MHz) and $^{13}C\{^1H\}$ (100 MHz) NMR spectra were measured on a JEOL ECZ 400 NMR spectrometer. The chemical shifts were expressed in ppm with tetramethylsilane (0 ppm for ^1H as an internal standard in $CDCl_3$) or D_2O (4.79 ppm for ^1H), DMSO (2.50 ppm for ^1H), $CDCl_3$ (77.16 ppm for ^{13}C), DMSO (39.52 ppm for ^{13}C). Splitting patterns were expressed as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), and br (broad peak). HRMS spectra were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. Elemental analyses were carried out at the Department of Instrumental Analysis & Cryogenics Division of Instrumental Analysis, Okayama University on a Perkin–Elmer 2400II Elemental analyzer supported by Inter-University Network for Common Utilization of Research Equipments. Concerning the calculated data of polymers their terminal structures were not taken into consideration. IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge). SEC analyses were carried out with a standard HPLC system equipped with a UV detector at 40 °C using $CHCl_3$ as an eluent with Shodex KF-405LHQ and LF-404. Molecular weights and molecular weight distributions were estimated based on the calibration curve obtained by six standard polystyrenes. Optical rotation was measured by JASCO P-2000 polarimeter, and the specific rotation was shown as $[\alpha]_D$ at the wavelength of sodium D-line (589 nm). CD spectrum was measured with a JASCO J-725 spectrometer with a JASCO PTC-348WI attachment. Dynamic light scattering (DLS) was measured with Otsuka Electronics ELSZ-2 equipped with a quartz cell (10 mm light path length). HPLC analyses with a chiral column were carried out with JASCO LC-2000 Plus with chiral column Daicel Chiralpak IF or IC (0.46 cm I.D. × 25 cm, flow rate: 0.5–1.0 mL/min) using UV and CD detectors.

Material

Preparation of **1a** bearing a chiral side chain was carried out in a manner reported previously by the reaction of 2-chloro-4-methoxyphenol and (3S)-3,7-dimethyloctanol followed by the bromination.[28] Polymerization of **1a** was performed in a manner by treatment with a Grignard reagent followed by the addition of nickel/chiraphos complex by changing the ratio of the monomer feed/catalyst loading (0.5–3.0 mol%) in our previously reported manner leading to **poly-1a**.[29] Details on the SEC analyses and spectroscopic characteristics of each DP were summarized in Table S1. Preparation of **1b** was carried out in a reported manner.[29,36] Poly(1,4-phenylene) **poly-1b** bearing two citronellol-derived chiral alkoxy side chains was synthesized in a manner with our previous report.[29] Dibromobenzene **1e** bearing two chiral side chains at the 2,5-positions was synthesized by the literature procedure with slight modification.[19] Synthesis of bromo(chloro)benzene **1f** was prepared in a manner to that of **1a**.

2-Bromo-5-chloro-4-fluorophenol (3)

Preparation of **3** was carried out similarly to that of **1a** with 3-chloro-4-fluorophenol (1.0 g, 7.0 mmol) and bromine. (93% yield) ^1H NMR ($CDCl_3$) δ 7.29 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 6.9 Hz, 1H). The obtained product was used for the following ether synthesis with chiral (*S*)-dihydro-citronellyl bromide without further purification.

(*S*)-4-Chloro-5-fluoro-2-(3,7-dimethyl)octyloxy-bromobenzene (1c)

Preparation of **1c** was carried out similarly to that of **1a** with (*S*)-3,7-dimethyl-1-bromoctane (**4**), and potassium carbonate (66% yield). ^1H NMR ($CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 6.4 Hz, 1H), 3.95–4.06 (m, 2H), 1.83–1.92 (m, 1H), 1.67–1.78 (m, 1H), 1.47–1.67 (m, 1H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.88 (s, 3H), 0.86 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 152.4 (d, $^4J_{C-F}$ = 2.9 Hz), 152.2 (d, $^1J_{C-F}$ = 245.0 Hz), 121.1 (d, $^2J_{C-F}$ = 25.0 Hz), 120.0 (d, $^2J_{C-F}$ = 19.2 Hz), 114.4, 110.3(d, $^3J_{C-F}$ = 7.7 Hz), 68.6, 39.3, 37.3, 36.0, 29.9, 28.1, 24.8, 22.9, 22.8, 19.8; IR (ATR) 2955, 2928, 2870, 1493, 1463, 1373, 1195, 1073, 865 cm^{-1}; HRMS (DART-ESI$^+$) Calcd for $C_{16}H_{23}{}^{81}Br^{35}ClFO$ $[M]^+$: 366.0584; Found *m/z* 366.0573. $[\alpha]_D^{23}$ = –1.1 (*c* 1.02, $CHCl_3$).

(*S*)-4-Chloro-2-(3,7-dimethyl)octyloxy-bromobenzene (1d)

Preparation of **1d** was carried out in a similar manner to that of **1a** with 2-bromo-5-chlorophenol, **4**, and potassium carbonate to afford **1d** in 90% yield. ^1H NMR ($CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.81 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.98–4.08 (m, 2H), 1.84–1.93 (m, 1H), 1.68-1.78 (m, 1H), 1.59–1.69 (m, 1H), 1.48–1.59 (m, 1H), 1.24–1.39 (m, 2H), 1.10–1.21 (m, 2H), 0.96 (d, *J* = 6.4 Hz, 3H), 0.88 (s, 3H), 0.86 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.2, 134.0, 133.8, 121.6, 113.7, 110.3, 67.9, 39.3, 37.3, 35.9, 29.9, 28.1, 24.8, 22.9, 22.8, 19.8; IR (ATR) 2954, 2927, 1738, 1581, 1468, 1382, 1259, 1220, 1126, 1094, 1036, 1014, 915, 837, 773, 673 cm^{-1}; HRMS (DART-ESI$^+$) Calcd for $C_{16}H_{25}{}^{81}Br^{35}ClO$ $[M+H]^+$: 349.0757; Found *m/z* 349.0744. $[\alpha]_D{}^{21}$= –1.4 (*c* 0.63, $CHCl_3$).

(*S*)-2-Chloro-1-(2-methylbutoxy)-4-methoxybenzene (5)

To 30 mL screw-capped test tube equipped with a magnetic stirring bar were dissolved 2-chloro-4-methoxyphenol (0.48 g, 3.0 mmol), potassium carbonate (0.80 g, 6.0 mmol), (*S*)-2-methyl-butan-1-yl 4-methylbenzenesulfonate (**7**, 0.66 g, 2.7 mmol) in 6 mL of acetonitrile. The mixture was stirred at 100 °C for 18 h. After cooling to room temperature, the mixture was filtrated through a celite pad. The filtrate was concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel (hexane/diethyl ether = 10/1) to afford 0.51 g of **5** as a colorless oil. (74% yield). ^{1}H NMR CDCl$_3$) δ 6.94 (d, *J* = 3.2 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 6.74 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.77 (A$_2$X, *J* = 8.8, 6.4 Hz, 2H), 3.75 (s, 3H), 4.05-3.93 (m, 2H), 1.84-1.95 (m, 1H), 1.52-1.66 (m, 1H), 1.22-1.35 (m, 1H), 1.04 (d, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 153.6, 149.1, 123.9, 116.0, 114.8, 112.9, 74.8, 55.8, 35.0, 26.2, 16.7, 11.3; IR (ATR) 2962, 2932, 2877, 1498, 1464, 1441, 1390, 1274, 1212, 1182, 1055, 1044, 1009, 887, 861, 842, 798, 782, 766 cm^{-1}; HRMS (DART-ESI$^+$) Calcd for $C_{12}H_{18}{}^{35}ClO_2$ [M+H]$^+$: 229.0995; Found *m/z* 229.0993; $[\alpha]_D^{17}$ = +8.8 (c 1.0, CHCl$_3$).

(*S*)-5-Bromo-2-chloro-4-methoxy-(2-methylbutoxy)benzene (1f)

Preparation of **1f** was carried out by the bromination of **5** with Br$_2$ to give **1f** in 77% yield. ^{1}H NMR (CDCl$_3$) δ 7.12 (s, 1H), 6.94 (s, 1H), 3.84 (s, 3H), 3.83-3.84 (m, 2H), 1.84-1.95 (m, 1H), 1.53-1.64 (m, 1H), 1.24-1.34 (m, 1H), 1.04 (d, *J* = 6.4 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H) ; ^{13}C{^{1}H} NMR (CDCl$_3$) δ 150.2, 149.4, 122.5, 118.8, 114.2, 109.5, 75.0, 57.0, 34.9 26.1, 16.6, 11.4; IR (ATR) 2962, 2933, 2876, 1497, 1464, 1440, 1391, 1366, 1274, 1213, 1182, 1075, 1033, 851, 814, 793, 772 cm^{-1}; HRMS (DART-ESI$^+$) Calcd for $C_{12}H_{16}{}^{81}Br^{35}ClO_2$ [M]$^+$: 308.0002; Found *m/z* 308.0002; $[\alpha]_D^{16}$ = +8.0 (c 1.0, CHCl$_3$).

(*S,S*)-Bis-1,4-(2-methylbutoxy)benzene (6)

To a solution of KOH (1.07 g, 18.6 mmol) in 16 mL of ethanol was added hydroquinone (0.77 g, 7.0 mmol). After stirring at room temperature for 30 min, the resulting mixture was heated at 85 °C for 30 min, followed by the addition of (*S*)-2-methylbutan-1-ol tosylate (**7**, 3.6 g, 15 mmol). Stirring was further continued at 85 °C for 16 h to form a precipitate, which was filtered off after cooling to room temperature. The filtrate was concentrated under reduced pressure to afford 1.62 g of crude **6** (66%), which was directly used for the next reaction without further purification.

(*S,S*)-2,5-Dibromo-bis-1,4-(2-methylbutoxy)benzene (1e)

Preparation of **1e** was carried out in a similar manner to that of **1b**. To a solution of the above obtained **6** (4.6 mmol) in 23 mL of dichloromethane was added bromine (0.54 mL, 9.7 mmol) at 0 °C. After stirring at room temperature, the resulting solution was poured into aqueous sodium bisulfite. Two phases were separated and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by column chromatography on silica gel using hexanes as an eluent to afford 1.35 g of **1e** (77% yield). The obtained product was identical with the authentic sample.[3] ^{1}H NMR (CDCl$_3$) δ 7.07 (s, 2H), 3.76 (A$_2$B, *J* = 8.8, 6.4 Hz, 4H), 1.84–1.96 (m, 2H), 1.54–1.64(m, 2H), 1.24–1.35 (m 2H), 1.04 (d, *J* = 6.4 Hz, 6H), 0.95 (t, *J* = 6.4 Hz, 6H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 150.2, 118.3, 111.2, 75.0, 34.1, 26.2, 16.7, 11.5.

Poly((*S*)-1-(3,7-dimethyl)octyloxy-4-methoxybenzene-2,5-diyl) (poly-1a)

To a screw-capped test tube equipped with a magnetic stirring bar were added Ni(acac)$_2$ (13.4 mg, 51 µmol), (–)-(2*S*,3*S*)-bis(diphenylphosphino)butane (23.8 mg, 55.8 µmol), and 0.5 mL of THF at room temperature under argon atmosphere. The mixture was stirred for 3 h at room temperature. The resulting solution was used for the following polymerization reaction. To a screw necked tube equipped with a magnetic stirring bar were added (*S*)-4-chloro-5-(3,7-dimethyl)octyloxy-2-methoxy-bromobenzene (**1a**, 0.120 g, 0.318 mmol), ^{i}PrMgCl·LiCl (1.3 M in THF, 0.23 mL, 0.3 mmol), and THF (0.3 mL) at room temperature under argon atmosphere. The mixture was heated at 60 ºC and stirring was continued for 1 h. The solution of the nickel catalyst (15 µL) was added to the mixture under argon atmosphere and further stirring was continued at 60 ºC for 3 h. The reaction mixture was poured into a mixture of hydrochloric acid (1.0 M, 2 mL) and methanol (5 mL) to form a precipitate, which was filtered off to leave a solid. After washing with methanol repeatedly, the solid was dried under reduced pressure to afford **poly-1a**. (M_n = 15700, M_w/M_n = 1.29) ^{1}H NMR (CDCl$_3$) δ 7.19 (d, *J* = 10 Hz, 1H), 7.07 (d, *J* = 10 Hz, 1H), 4.16–3.78 (br, 2H), 1.91–1.69 (br, 1H), 1.68–1.40 (m, 5H), 1.35–1.18 (m, 5H), 1.17–1.01 (br, 6H), 0.92–0.86 (m, 4H); IR (ATR) 2970, 2927, 2872, 1738, 1469, 1366, 1219, 773, 673 cm^{-1}; $[\alpha]_D^{23}$ = +0.3 (*c* 0.04, CHCl$_3$). Other polyphenylenes **poly-1a** with different DPs were carried out in a similar manner. Results on the characterization of obtained **poly-1a** was summarized in Table S1.

Poly((*S,S*)-1,4-bis(3,7-dimethyl)octyloxy)benzene-2,5-diyl) (poly-1b)

M_n = 16200, M_w/M_n = 1.43; ^{1}H NMR (CDCl$_3$) δ 7.12 (brs, 2H), 3.96, (br, 4H), 1.84–1.66 (m, 2H), 1.63–1.40 (m, 6H), 1.38–1.20 (m, 6H), 1.20–1.03 (m, 6H), 0.86 (t, 18H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 150.2, 127.5, 117.4, 68.2, 39.5, 37.6, 36.8, 30.2, 28.1, 24.9, 22.9, 22.8, 19.9; IR (ATR) 2954, 2926, 2869, 1490, 1468, 1382, 1366, 1256, 1206, 1056, 986, 863, 793, 764, 734 cm^{-1}; Anal. Calcd for $C_{26}H_{44}O_2$: C, 80.35; H, 11.41. Found: C, 76.33; H, 10.52.

Poly((*S*)-1-(3,7-dimethyl)octyloxy-4-fluorobenzene-2,5-diyl) (poly-1c)

M_n = 14200, M_w/M_n = 1.28; ^{1}H NMR (CDCl$_3$) δ 7.03–7.31 (m, 2H), 3.88–4.26 (m, 2H), 1.93–1.79 (m, 1H), 1.47–1.77 (m, 4H), 0.89 (d, ^1J = 6.0 Hz, 3H), 0.86 (s, 3H), 0.84 (s, 3H); ^{13}C{^{1}H} NMR

($CDCl_3$) δ 154.0 (d, ${}^1J_{C–F}$ = 240 Hz), 152.4, 131.1, 129.0, 118.2 (d, ${}^2J_{C–F}$ = 22 Hz), 115.7 (d, ${}^3J_{C–F}$ = 2.9 Hz), 68.0, 39.4, 37.5, 36.5, 29.8, 28.1, 24.8, 22.8, 22.7, 19.7; IR (ATR) 2970, 2927, 2872, 1738, 1469, 1366, 1219, 773, 673 cm^{-1}; $[\alpha]_D^{23}$ = +0.3 (*c* 0.04, $CHCl_3$).

Poly((*S*)-1-(3,7-dimethyl)octyloxybenzen-2,5-diyl) (poly-1d)

M_n = 17400, M_w/M_n = 1.49; ${}^1H$ NMR ($CDCl_3$) δ 6.76–7.56 (m, 3H), 3.93–4.22 (m, 2H), 1.80–1.95 (m, 1H), 146–1.75 (m, 3H), 1.39–1.10 (m, 7H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.86 (s, 3H), 0.84 (s, 3H); ${}^{13}C\{{}^1H\}$ NMR ($CDCl_3$) δ 155.7, 133.8, 130.3, 128.7, 122.3, 114.2, 67.0, 39.4, 37.5, 36.6, 30.1, 28.1, 24.9, 22.9, 22.8, 19.8; IR (ATR) 2926, 1739, 1470, 1379, 1306, 1219, 1147, 1066, 926, 814, 773, 673 cm^{-1}; $[\alpha]_D^{23}$ = –1.3 (*c* 0.04, $CHCl_3$).

Poly((*S,S*)-1,4-bis(2-methylbutoxy)benzene-2,5-diyl) (poly-1e)[19]

70% yield; M_n = 44700, M_w/M_n = 1.50; ${}^1H$ NMR ($CDCl_3$) 7.06 (s, 2H), 3.72–3.82 (m, 2H), 3.60–3.69 (m, 1H),.67–1.76 (m, 2H), 1.35–1.47 (m 2H), 1.08–1.21 (m, 4H), 0.88(d, *J* = 7.2 Hz, 6H), 0.84 (t, *J* = 7.2 Hz, 6H); ${}^{13}C\{{}^1H\}$ NMR ($CDCl_3$) δ 150.3, 127.9, 117.5, 74.6, 35.0, 26.3, 16.9, 11.4.

Poly((*S*)-1-(2-methylbutoxy)-4-methoxybenzen-2,5-diyl) (poly-1f)

58% yield; M_n = 20400, M_w/M_n = 1.90; ${}^1H$ NMR ($CDCl_3$) δ 7.07 (s, 1H), 7.06 (s, 1H), 3.79 (s, 3H), 3.72 (t, *J* = 7.2 Hz, 2H), 1.73–1.80 (m, 1H), 1.41–1.49 (m, 1H), 1.10–1.18 (m, 1H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.86 (t, *J* = 7.6 Hz, 3H);${}^{13}C\{{}^1H\}$ NMR ($CDCl_3$) δ 150.9, 150.4, 127.9, 127.4, 117.7, 115.2, 74.8, 56.5, 35.0, 26.2, 16.7, 11.4; IR (ATR) 2961, 2931, 2875, 1529, 1488, 1463, 1406, 1380, 1354, 1261, 1206, 1099, 1059, 1038, 863, 760 cm^{-1}.

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Keywords: poly(1,4-phenylene) • chiral side chain • aggregation • helix • circular dichroism

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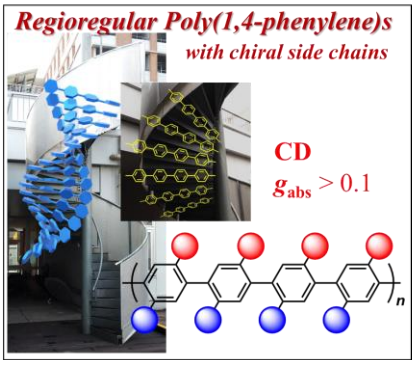

The use of nickel-Chiraphos complexe as a catalyst enables the synthesis of a variety of poly(1,4-phenylene) with a chiral side chain and provides new insights into the correlation with their helical structure through the measurement of CD spectra.

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