Chiral Oxazoline Substituted Optically Active Poly(*m*-Phenylene)s: Synthesis and Coupling Polymerizations of (*S*)-4-Benzyl-2-(3,5dihalidephenyl) Oxazoline Using Transition Metal Catalysts

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ABSTRACT: Optically active poly(*m*-phenylene)s substituted with chiral oxazoline derivatives have been synthesized by the nickel-catalyzed Yamamoto coupling reaction of optically active (*S*)-4-benzyl-2-(3,5-dihalidephenyl)oxazoline derivatives (X = Br or I). The structures and chiroptical properties of the polymers were characterized by spectroscopic methods and thermal gravimetric analyses. The polymers showed higher absolute optical specific rotation values than their corresponding monomer, and showed a Cotton effect at transition region of conjugated main chain. The optical activities of the polymers should

INTRODUCTION Functional π -conjugated polymers have attracted much considerable interest during the past decades. These functional polymers exhibit unique structure and interesting properties owing to the π -conjugation in the backbone chains, which allow them to be served for many applications including optical and electronic devices.¹⁻³ Meanwhile, the artificial helical polymers have been also one of the major research subjects of polymer chemistry because of their secondary structure and backbone conformation, which are similar to the structure of natural macromolecules, that is, DNAs and proteins. There have been many reports on the sophisticated design and synthesis of artificial helical polymers.⁴⁻⁸

It is well understood that a prevailing screw sense of polymers could be achieved by the introduction of appropriate chiral substitute groups into the polymer backbone. The secondary structures of those polymers are generated and stabilized by interactions such as steric repulsion, hydrogen bonds, and van der Waals forces.^{9,10} Interestingly, π -conjugated polymers constructed from the monomer with molecular shape like *m*-phenylene are known to fold into helical conformations in a process thermodynamically driven by solbe attributed to the higher order structure such as helical conformations. Moreover, the helical conformation could be induced by addition of metal salts into polymer solutions. The polymers showed good thermal stabilities, which was attributable to the oxazoline side chains. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1315–1322

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vophobic effects and bended linkage. These were demonstrated by the previous studies, namely $poly(m-phenylene)s^{11,12}$ and $poly(m-phenylene ethynylene)s^{13,14}$ In addition, an interaction between chiral side groups is sometime required to induce an excess screw sense for the helical polymers. We have previously reported the induction of a prevailing screw sense of helical polyacetylene by complexation of chiral oxazoline side chain with metal ions in a solvent, resulted in the formation of chiral supramolecular aggregation as evidenced by induced Cotton effects.¹⁵

To the best of our knowledge, there are relatively few reports on the synthesis of helical poly(*m*-phenylene)s bearing an optically active side chain. Therefore, the present study is devoted to the design and synthesis of a series of optically active *m*-phenylene substituted with chiral oxazoline derivatives, which were polymerized by Yamamoto coupling reaction to obtain the optically active poly(*m*-phenylene)s bearing chiral oxazoline at the side chains (Scheme 1). The obtained polymers are expected to fold into helical conformation due to incurvated linkage backbones and chiral oxazoline groups at the side chain. This includes an induction of helical sense of the polymers by the complexation

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SCHEME 1 Polymerization of 3,5-dihalidebenzene derivatives bearing chiral oxazoline group.

with metal ions in a solvent. All the obtained polymers are then also characterized by spectroscopies and thermogravimetric analysis (TGA).

EXPERIMENTAL

Measurements

 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ nuclear magnetic resonance (NMR) spectra were recorded on a JNM-LA500 apparatus (JEOL) spectrometer using tetramethylsilane (TMS) (¹H NMR, δ 0.00 ppm) or CDCl₃ (¹³C NMR, δ 77.0 ppm) as internal reference peaks at room temperature. The number- and weight-average molecular weight $(M_n \text{ and } M_w)$ of polymers were determined by gel permeation chromatographic (GPC) on a LC-10AS and CHROMA-TOPAC C-R7A plus (Shimadzu) using HSG-40H, HSG-20H, HSG-15H, and HSG-10H columns (THF as an eluent at flow rate of 1.0 mL/min, 50 °C) equipped with an ultraviolet (UV) detector SPD-10A (Shimadzu) on the basis of standard polystyrene samples. Thermo gravimetric analyses were carried out using an MS-Tg/DTA220 (JEOL) at a scanning rate of 10 °C/min under nitrogen (100 mL/min). Melting points (mp) were measured on a Yanagimoto micromelting point apparatus. Specific rotations were measured on the concentration of 0.1-1.0 g/dL in THF at 25 °C using a quartz cell (1.0 cm) with a JASCO DIP-1030 (JASCO). Circular dichroism (CD) spectra were measured on the concentration of 0.01-0.10 g/dL in THF at 25 °C using a quartz cell of 1 mm with a JASCO J-805 (JASCO). Infrared (IR) spectra were performed on a FTIR Jasco 4100 (JASCO) spectrophotometer. Thermo gravimetric analyses were carried out using an MS-Tg/DTA220 (JEOL) at a scanning rate of 10 °C/min under nitrogen (100 mL/min). Elemental analysis was done MICRO CORDER JM10 (J-SCIENCE LAB) at the Collaborative Center for Engineering Research Equipment, Faculty of Engineering, Yamaguchi University.

Materials

All reagents were used without any further purification. Sodium nitrite, triethylamine, toluenesulfonyl chloride (TsCl), and anhydrous magnesium sulfate were received from Nacalai Tesque (Kyoto, Japan). 3,5-Aminobenzoic acid was obtained from Merck (Darmstadt, Germany). L-Phenylalanine (**2**), 3,5-dibormobenzoic acid (**5a**), sulfuric acid, urea, cupper iodide, potassium iodide, N,N'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were purchased from Wako Pure Chemical Industries. Sodium sulfate and bis(1,5-cyclooctadiene) nickel (0) were received from Kanto Chemical. Celite® 545 was purchased from Sigma-Aldrich Japan. 1,5-Cyclooctadiene were obtained from Tokyo Chemical Industry. 2,2'-Bipyridyl (α,α' -) were received from Kishida Reacgents Chemicals (Osaka, Japan). 3,5-Diiodobenzoic acid (**5b**)¹⁶ and (*S*)-phenylalaninol (**2**)¹⁷ were synthesized according to the literatures. *n*-Hexane, toluene, tetrahydrofuran, ethyl acetate, *N,N*-dimethylformamide, dimethylsulfoxide, 1,2dichloroethane, CH₂Cl₂, and CHCl₃ were dried according to the standard procedure and distilled under nitrogen atmosphere. Column chromatography was performed with silica gel 60 (0.063–0.200, MERCK). Analytical thin-layer chromatography was performed on Merck silica gel plate 60F₂₅₄.

Monomer Synthesis

The typical synthesis procedures of optically active (*S*)-4-benzyl-2-(3,5-dihalidephenyl)oxazoline derivatives (DXPhBnOx, X = Br or I) were given according to strategy outline in Scheme 2.

(S)-Phenylalaninol (3)

To a stirred suspension of NaBH₄, (10.0 g, 264.4 mmol) in THF (100 mL) was added L-phenylalanine (16.53 g, 100.0 mmol). The flask was immersed in an ice-water bath, and a solution of concentrated H₂SO₄, (6.6 mL, 120 mmol) in diethyl ether (20 mL) was added dropwise (addition time ca. 3 h). Stirring of the reaction mixture was continued at room temperature overnight. The excess borane was quenched by slow addition of MeOH (70 mL) until gas bubble stopped carefully. The mixture was concentrated to about 70 mL and 5N NaOH (100 mL) was added. After removing the organic solvent, the mixture was heated at reflux for 6 h. The resulting two-phase mixture was cooled and filtered through a thin pad of Celite which was washed with water and CH₂Cl₂.¹⁷ The filtrate was extracted three times with CH₂Cl₂ (30 mL), and then washed with saturated NaCl (aq) (30 mL \times 3). The combined organic phase was dried over anhydrous sodium sulfate, followed by evaporation of the solvent left solid phenylalaninol, which was recrystallized from ethyl acetate and hexane to yield 12.64 g (84.6 mmol, 84.6% yield) as colorless needle crystal.

Mp: 90–91 °C, $[\alpha]_D$ –18.0° (1.0 g/dL, l = 10 cm, THF). ¹H NMR (CDCl₃) δ (ppm from TMS): 1.57 (br, 5H, NH₂), 2.54 (dd, 1H, CH₂—OH), 2.81 (dd, 1H, CH₂—OH), 3.13 (m, 1H, CH), 3.38 (dd, 1H, CH₂-Ph), 3.64 (dd, 1H, CH₂-Ph), 7.18–7.34 (m, 5H, Ph).

3,5-Diiodobenzoic Acid (5b)

To an ice-cooled, stirred suspension of 3,5-diaminobenzoic acid (3.00 g, 19.7 mmol) in a mixture of concentrated sulfuric acid (30 mL) and water (15 mL) was added sodium nitrite powder (3.26 g, 47.2 mmol) with the temperature controlled between -5 and 0 °C. After 1 h, urea (0.251 g, 4.18 mmol) was added, and then a cold solution of potassium iodide (32.8 g, 198 mmol) in 30 mL of water was added dropwise. The black-brown mixture was stirred for another 3 h with the temperature between -5 and 0 °C and heated to 60 °C for 30 min. Then the warm suspension was poured into 150 mL of ice-cold water. The precipitate was washed six times with water by decantation. The resulting brown



SCHEME 2 Synthetic route of monomer.

precipitate was collected by vacuum filtration, dried, and then dissolved in diethyl ether (150 mL).¹⁶ The resulting dark brown diethyl ether solution was washed with aqueous Na₂S₂O₃ until a pale yellow color was observed. The organic phase was dried over anhydrous magnesium sulfate, followed by evaporation of the solvent to give orange crystal 3.44 g (7.03 mmol, 35.7% yield).

¹H NMR (DMSO- d_6): δ (ppm from TMS): 8.33 (s, 1H, 4-H), 8.15 (s, 2H, 2, 6-H).

N-((S)-1-Benzyl-2-hydroxyethyl)-3,5-dibromobenzamide (6a)

To a stirred solution of 3,5-dibromobenzoic acid (2.00 g, 7.14 mmol) in 25 mL of dry THF was added *N*-hydroxysuccinimide (NHS) (1.02 g, 8.91 mmol) and DCC (1.77 g, 8.56 mmol) sequentially. The mixture was continued to stir at room temperature under nitrogen atmosphere for 3 h. Then, a solution of (*S*)-phenylalaninol (1.19 g, 7.87 mmol) in 25 mL of dry THF was added to the mixture via syringe. After being stirred for overnight at room temperature, the mixture was then filtrated using aspirator and the solvent was removed out at reduced pressure. The residue was taken up with EtOAc, washed twice with NaCl_(aq), dried over sodium sulfate (Na₂SO₄), and filtration. The organic layer was removed on a rotary evaporator. The product was purified by column chromatography eluted with hexane/ethyl acetate (7/3, v/v) to obtain the product as white solid in 2.90 g (7.02 mmol, 98% yield).

¹H NMR (CDCl₃) δ (ppm from TMS): 7.10–7.00 (m, 5H, Ph), 6.22 (d, 1H, *H*—N), 4.35(m, 1H), 3.70 (m, 2H, CH₂—OH), 2.69 (d, 2H, CH₂-Ph).

N-((*S*)-1-Benzyl-2-hydroxyethyl)-3,5-diiodobenzamide (6b) This compound was synthesized according the general procedure described above, starting from 3,5-diiodobenzoic acid

(2.14 g, 5.72 mmol), NHS (0.82 g,7.15 mmol), DCC (1.42 g, 6.87 mmol), and (*S*)-phenylalaninol (0.95 g, 6.30 mmol) in 50 mL of dry THF. The crude product was purified by silica gel column chromatography eluted with hexane/ethyl acetate (7/ 3, v/v) to give a white solid (1.62 g, 3.31 mmol) in 58% yield.

¹H NMR (CDCl₃) δ (ppm from TMS): 7.10–7.00 (m, 5H, Ph), 6.22 (d, 1H, *H*–N), 4.35(m, 1H), 3.70 (m, 2H, CH₂–OH), 2.69 (d, 2H, CH₂-Ph).

(S)-4-Benzyl-2-(3,5-dibromophenyl)oxazoline (1a: DBrPhBnOx)

To a stirred solution of hydroxyamide **6a** (2.90 g, 7.02 mmol), triethylamine (3.80 g, 37.65 mmol) and DMAP (0.0149 g, 0.116 mmol) in 25 mL of 1,2-dichloroethane was added TsCl (1.996 g, 10.47 mmol) at 0 °C. The reaction mixture was stirred at reflux temperature for 12 h. After that, the mixture was washed twice with saturated NaCl_(aq), dried over MgSO₄, and removed solvent *in vacao*. The crude product was purified by column chromatography eluted with hexane/ethyl acetate (10/1, v/v) to give 1.50 g (3.81 mmol) of yellowish oil in 54% yield.

¹H NMR (CDCl₃) δ (ppm from TMS): 8.30 (s, 1H, 4-H), 8.17 (s, 2H, 2,6-H), 7.21–7.33 (m, 5H, Ph), 4.58 (m, 1H, CH), 4.36 (t, 1H, CH₂—O), 4.12 (t, 1H, CH₂—O), 3.20 (dd, 1H, CH₂-Ph), 2.74 (dd, 1H, CH₂-Ph). ¹³C NMR (CDCl₃) δ (ppm from TMS): 161.58, 137.51, 136.69, 129.93, 129.27, 128.44, 126.63, 122.84, 72.38, 67.93, 41.71. [α]₄₃₅ = -11.9°, [α]_D = -5.0° (c = 1.0 g/dL, l = 10.0 cm, THF). ELEM. ANAL: Calcd. for C₁₆H₁₃NOBr₂: C, 48.64%; H, 3.32%; N, 3.55%. Found: C, 49.10%; H, 3.43%; N, 3.49%.

(S)-4-Benzyl-2-(3,5-diiodophenyl)oxazoline (1b: DIPhBnOx) This compound was synthesized according the general procedure described above, starting from hydroxyamide **6b** (1.62 g, 3.31 mmol), triethylamine (1.75 g, 17.25 mmol),



TABLE 1 Yamamoto Homocoupling-Polymerizations of DXPhBnOx^a

Run	DXPhBnOx	Solvent ^{b)} (mL)	Temp. (°C)	Time (h)	Yield ^{c)} (%)	M_n^{d}	$M_{\rm w}/M_{\rm n}^{\rm d}$	$[\alpha]_{435}^{e)}$ (°)
1	1a	Tol/DMF (3.0/3.0)	80	24	33.0	1250	1.19	+313.2 ^f
2	1a	Tol/DMF (3.0/3.0)	80	48	54.7	1080	1.14	+258.8
3	1b	Tol/DMF (3.0/3.0)	80	24	21.9	1310	1.24	+301.0
4	1b	Tol/DMF (3.0/3.0)	80	48	37.7	1090	1.22	+240.6
5	1a	Tol (6.0)	80	48	31.0	760	1.24	$+54.3^{f}$
6	1a	DMF (6.0)	80	48	19.3	950	1.24	+791.7
7	1a	DMSO (6.0)	80	48	20.0	840	1.24	+27.3

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^a (S)-4-Benzyl-2-(3,5-dibromophenyl)oxazoline(DBrPhBnOx), $[\alpha]_{435}$

 $\begin{array}{l} -11.9^\circ, [\alpha]_D=-5.0^\circ \text{ in THF (1a), (S)-4-benzyl-2-(3,5-diiodophenyl)oxazoline} \\ (DIPhBnOx), [\alpha]_{435}=-3.2^\circ, [\alpha]_D=-1.23^\circ \text{ in THF (1b), conditions: 1a}=1b=\\ 0.8 \text{ mmol, bpy}=0.90 \text{ mmol, COD}=0.90 \text{ mmol, Ni(COD)}_2=1.2 \text{ mmol.} \\ ^b \text{ Solvents; Tol, toluene, DMF: N,N-dimethylformamide, DMSO: di-$

methyl sulfoxide.

DMAP (0.0117 g, 0.10 mmol), and TsCl (0.9136 g, 4.79 mmol) in 25 mL of 1,2-dichloroethane. The crude product was purified by silica-gel column chromatography eluted with hexane/ethyl acetate (15/1, v/v) to give 0.9396 g (1.92 mmol) of yellowish solid in 58% yield.

¹H NMR (CDCl₃) δ (ppm from TMS): 8.30 (s, 1H, 4-H), 8.17 (s, 2H, 2,6-H), 7.21–7.33 (m, 5H, Ph), 4.58 (m, 1H, CH), 4.36 (t, 1H, CH₂—O), 4.12 (t, 1H, CH₂—O), 3.20 (dd, 1H, CH₂-Ph), 2.74 (dd, 1H, CH₂-Ph). ¹³C NMR (CDCl₃) δ (ppm from TMS): 160.76, 147.34, 137.12, 135.90, 130.72, 128.89, 128.28, 126.30, 93.98, 71.87, 67.60, 41.20. FTIR (/cm): 2970, 2910, 1650, 1540, 1350, 1300, 955, 710, 555. mp: 72.3–73.7 °C, [α]₄₃₅ = -3.2° , [α]_D = -1.23° (c = 1.0 g/dL, l = 10.0 cm, THF). ELEM. ANAL: Calcd for C₁₆H₁₃NOI₂: C, 39.29%; H, 2.68%; N, 2.86%. Found: C, 39.61%; H, 2.78%; N, 2.84%.

Polymerization

The polymerizations were carried out in a Schlenk glass tube equipped with three-way stopcock under an inert nitrogen atmosphere according to Scheme 1. A typical experimental procedure for Yamamoto homocoupling polymerization of **1a** is given as follow:

A mixture of **1a** (0.32 g, 0.80 mmol), 2,2'-bipyridyl (0.14 g, 0.90 mmol), 1,5-cyclooctadiene (0.97 g, 0.90 mmol), and Ni(COD)₂ (0.33 g, 1.2 mmol) in anhydrous solvent 6 mL was replaced with N₂. The mixture was continued to stir at 80 °C for 12 and 48 h under nitrogen atmosphere. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (100 mL). The organic layer was washed with 1N HCl (3 × 100 mL) and H₂O (3 × 100 mL), and then dried over MgSO₄, and the solvent was removed solvent at reduced pressure. The residue distilled with THF (0.5 mL) was slowly added dropwise into a large amount of diethyl ether. Purification of the polymer was performed with reprecipitation from a THF-diethyl ether system and dried under reduced pressure at room temperature until constant weight.

RESULTS AND DISCUSSION

Monomer Synthesis

A series of optically active monomers containing an oxazoline derivative were obtained from two main steps via the ^c Et₂O insoluble part.

^d By GPC (eluent: THF) with poly(styrene) standard.

 $^{\rm e}$ c = 0.01 g/dL, l = 10.0 cm in THF.

 $^{\rm f}$ c = 0.1 g/dL, I = 10.0 cm in THF.

sequence of reactions described in Scheme 2. The reaction took place under very mild conditions, starting from coupling reaction of 3,5-dibromobenzoic acid (**5a**) or 3,5-diiodobenzoic acid (**5b**) with L-phenylalaninol (**3**), followed by a ring closure reaction of hydroxyamide (**6a**) and (**6b**) to obtain the monomer (**1a**) and (**1b**). The structure of monomers was confirmed by ¹H NMR, ¹³C NMR, and FTIR spectroscopy.

Polymerization

Table 1 summarized the conditions and results of the polymerization. Monomers were used in Yamamoto coupling reactions to prepare poly(m-phenylene) bearing a chiral oxazoline. The reactions were carried out at 80 $^\circ\text{C}$ for 24 and 48 h in toluene, DMF, DMSO, and a mixture of toluene/DMF using a nickel catalyst in the presence of 2,2'-bipyridyl and 1,5-cyclooctadiene, in accordance with our method reported previously.¹⁸ Powdery polymers were obtained by precipitation of polymer solution into an excess of diethyl ether. The polymers were obtained in 20-55% yields, having number average molecular weight (M_w) range from 760 to 1310 relative to polystyrene standard. As shown in the table, the polymers obtained from mixed solvent systems and longer polymerization times were obtained in higher yields, and had higher M_w than otherwise. These indicated that yields and $M_{\rm w}$ were influenced by the polymerization conditions such as solvents and reaction time.

The low polymerizability could be explained by two possible reasons. First, it is due to the solubility of polymers. The polymers showed low solubility, resulting in the precipitation during polymerizations. Coupling reactions of aryl compounds substituted at *o- or m-*position yield cyclic compounds such as porphyrin, phthalocyanine, calixarene, and cyclic [n] *m*-phenyleneacetylenes. Cyclic phenylene derivatives direct-coupled by aryl units bonded to an *o-*position.^{19,20} To our knowledge, macrocyclic compounds synthesized by direct-coupling reaction of *m*-aryldihalide derivatives have not been reported previously. The second reason should be attributed to the steric hindrance of bulky substitutes. Hashimoto et al.²¹ reported the synthesis and polymerization



FIGURE 1 ¹H NMR spectra of (A) DIPhBnOx and (B) poly(PhBnOx) (run 4 in Table 1) in CDCl₃.

of a series of substituted 2,5-dichlorobenzoates. They found that polymerization of monomers substituted with the bulky groups proceeded to give polymers with relative low M_w and yield. The steric hindrance of bulky substitutes definitely affected the degree of polymerizations. Therefore, low polymerizability of current study should be resulted from the bulky chiral oxazoline derivative as well.

Polymer Structure

The structures of the polymers were characterized and confirmed by ¹H NMR, ¹³C NMR, and IR spectra. These spectroscopic methods usually provide valuable information about the monomer and polymer structures. ¹H NMR charts of the polymer and monomer measured in CDCl₃ are given in Figure 1. The polymers and monomer gave satisfactory analysis data corresponding to their expected molecular structure. Signals of chiral oxazoline derivatives were detected for both a monomer and a polymer, that is, the signals of CH—N was found at 4.58 ppm and the signal of CH₂-Ph were appeared at 2.74 and 3.18 ppm. It should be pointed out that resonance peaks in the ¹H NMR spectra of the polymer were broader than the monomer, indicating that the monomer was successfully polymerized.

Figure 2 shows ¹³C NMR of the polymer and monomer. The polymer showed all important peaks when compared with that of monomer. The quaternary carbons to iodide in monomer at 93.98 ppm shifted to a low magnetic field (139–143 ppm) in the spectrum of the polymer. In addition, the polymer showed characteristic peak of the quaternary carbon of the poly(*m*-phenylene) backbone at around 141 ppm.²² These confirmed that the monomer was successfully converted to polymer as expected.

FTIR was also carried out to confirm the structure of the monomer and polymers. Figure 3 indicates the FTIR spectra. The spectrum of polymer was almost similar to the monomer. The C=N stretching bands of oxazoline groups at 1543/cm were detected for both polymer and its monomer.



FIGURE 2 ¹³C NMR spectra of (A) DIPhBnOx and (B) poly(PhBnOx) (run 4 in Table 1) in CDCl₃.



FIGURE 3 FT IR spectra of (A) DIPhBnOx and (B) poly(PhBnOx) (run 3 in Table 1).

The difference was what of only the monomer showed a strong absorption band at 500/cm due to the C-I bending vibrations absorption bands while the polymer did not, implying that the nickel catalyst is effective to polymerize this type of monomers.

Chiroptical Properties of Polymers

It is well understood that the helical structure of the polymer could be induced by introduction of suitable chiral groups into the polymer backbones. There are evidences that the presence of optically active chiral oxazoline derivatives side group could induce the polymer main chain with an enantiomeric excess in the helical conformation.^{23,24} This study expects that the main chain of the poly(*m*-phenylene)s could be endowed to form higher order structure with a prevailing helical handedness as well. The chiroptical activities of the polymers were then examined by means of optical specific rotation and CD.

As given in Table 1, the values of optical specific rotation ([α]₄₃₅) of DBrPhBnOx and DIPhBnOx are -11.9° and -3.2° , respectively. In contrast to the monomers, their corresponding polymers have positive optical specific rotation value

 $([\alpha]_{435})$ range from +27.3° to +791.7°. The larger value of specific rotation of the polymer, compared with monomer is commonly accepted as evidence of the presence of a chiral higher order structure such as helical conformations with a predominantly one-handed screw sense.^{25–27} The lower values of optical specific rotation of the polymers obtained in run 5 and run 7 should signify the less higher order structures, compared with the other polymers, which agreed with those results of CD measurement and GPC.

Figure 4 showed CD and UV spectra of polymers along with those of monomers measured in THF at room temperature. The polymers showed a UV absorption band over a wavelength range from 220 to 300 nm, having maximum absorption (ε_{max}) at around 250 nm. These could be assigned to the conjugation of the poly(*m*-phenylenes) backbones, which was in agreement with those of reported previously.²⁸⁻³⁰ In addition, the monomers showed almost no induced Cotton effects, while almost the polymers showed intense CD signal in the transition area of the conjugated polymer backbone. This could be concluded that the polymers possess a higher-order structure, a partial helical structure, in view of their comparatively low specific rotations and low molecular weights.

Next, we further investigated the responsiveness of the polymer to metal ions in a solution. As shown in Figure 5, the addition of Zn(II) salt to a polymer solution brought to the dramatically changes in both CD and UV spectra patterns. The formation of Zn(II)-induced complexes has been evidenced by the CD. The $[\theta]_{max}$ of the polymer at 288 nm were found to be increased with an increase of Zn(II) contents, whereas almost no change was observed in the case of monomer. There have been evidences that addition of metal salts into the solution of chiral oxazoline substituted polymers produced chiral aggregations with a handedness.^{31,32} In this study, the increase in CD intensities observed in the π - π * transition region of the polymer backbones may also cause the formation of chiral supramolecular aggregates with handedness likewise.



FIGURE 4 CD and UV-vis spectra of DXPhBnOx and poly(PhBnOx); (A): (a) DBrPhBnOx, (b) DIPhBnOx, (c) run 1, (d) run 2, (e) run 3, (f) run 4, (g) run 5, (h) run 6, and (i) run 7 in Table 1; (B) expanded CD spectra at 240–360 nm.



Thermal Properties of the Polymer

Thermal stability of polymer was investigated using TGA under nitrogen atmosphere, and compared with its monomer (Fig. 6). The first slight weight loss of the polymer and its monomer were observed at below 100 °C, which should be assigned to the loss of absorbed moisture. Another noticeable feature is that the degradation profile of the polymer is not similar to that of monomer. The significant weight loss (5%) of the polymer began around 275 °C, and gradually decrease up to 500 °C while the monomer showed poor thermal stability profile. The temperature for which the weight loss is 5%, 10%, and maximum weight loss temperature of polymer were observed at higher value than that of the monomer. It is notable to conclude that poly(*m*-phenylene) bearing chiral oxazoline derivatives show good thermal stability, attributed from the oxazoline pendants.^{11,13}

CONCLUSIONS

We have successfully prepared the novel poly(*m*-phenylene) bearing chiral oxazoline derivatives at the side chain from (S)-4-benzyl-2-(3,5-dihalidephenyl)oxazoline derivatives (DXPhBnOx, X = Br or I) through the Yamamoto coupling reaction using Ni(COD)₂ and 2,2'-bipyridyl as catalytic system. The yields, molecular weight, specific rotation of the polymers were influenced by polymerization conditions such as solvent and temperature. The polymers exhibit good thermal stability with 5% weight loss temperature above 275 °C. The polymers having higher values of specific rotation showed the Cotton effect in the transition region of the π - π * in THF solution. These indicated that the polymers possessed higher order structure such as helical conformations, driven by bended linkage backbones and a chiral oxazoline group at a side chain. Moreover, the helical conformation of the polymers could be induced by complexation of chiral oxazoline groups with the Zn(II) ion in a solution, resulting in the formation of chiral supramolecular aggregations.



FIGURE 5 CD and UV-vis spectral changes of poly(PhBnOx) (run 3 in Table 1) in the presence of $Zn(OTf)_2$ in THF.



FIGURE 6 TGA curves of (A) DIPhBnOx and (B) poly(PhBnOx) (run 3 in Table 1) at heating rate of 10 °C/min.

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