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Synthesis and chiroptical properties of helical poly(phenylacetylene) bearing optically active chiral oxazoline Pendants

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1. Introduction

In recent years, the design and synthesis of artificial helical polymers have been extensively studied in the area of macromolecular science. This is not only to mimic the nature materials, but also to produce the sophisticated functions based on the regulated structure which is similar to the biological polymers such as DNAs and proteins [1–3]. The progress in macromolecular science allows us to synthesize the artificial helical polymers with rather complex and elegant structures, such as polymethacrylates, polyisocyanides and polyisocyanates [4]. The helical polymers have been used in a wide range of applications, for example, catalysis for asymmetric syntheses, enantiomeric separation, and chiral sensing [5-8]. Apart from the helical polymers, the conjugated polymers have also attracted a large number of attention over the past decades due to their interesting properties and they become a candidate for the next generation active materials for organic-based devices such as chemical and biological sensors, or polymeric light-emitting diodes [9-11]. Polyacetylenes, one of the typical conjugated polymers, have been extensively studied for several decades by several research groups [12–17]. Furthermore, the π -conjugated polyacetylenes are known to form the helical structure with a predominantly one-handed screw sense by the introduction of the appropriate chiral groups substituted into the polymer

ABSTRACT

The novel optically active (S)-4-benzyl-2-(ethynylphenyl)-oxazoline (BnEPhOx) was successfully prepared and polymerized using rhodium catalyst ([Rh(nbd)Cl]₂) to obtain the moderate molecular weight poly(phenylacetylene)s bearing chiral oxazoline derivatives with high yields (\geq 90%). The ¹H NMR spectra demonstrated that the resulting polymers had high stereoregular structures. Moreover, the poly(phenylacetylene)s bearing chiral oxazoline exhibited better thermal stability than poly(phenylacetylene). The resulting polymers showed higher absolute values of optical specific rotation than the monomer. The polymers also exhibited intense CD signal in the region of the π - π * band of the conjugated polyacetylene backbone in chloroform solution. The results of specific rotation and CD spectroscopy indicated that all the polymers adopted higher-order structure with predominantly one-handed screw sense.In addition, the resulting polymers emitted fluorescence under UV irradiation.

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backbone, which exhibits simultaneous changes in both optical and chiroptical properties [18]. The helical polyacetylenes are interesting not only in the fundamental viewpoints regarding of synthesis and their properties, but also in their practical applications, for example, semi-conductivity, nonlinear optical properties and chiral recognition. These properties arise from their regulated secondary structure [19,20].

Chiral oxazolines are of great interest in scientific research and technological innovation because they can be easily obtained from amino alcohols, and have unique structures and significant applications. The chiral oxazoline-metal complexes were shown to be very efficient catalysts for many enantioselective organic reactions including aldol, Diels-Alder, allylicalkylation, aziridination, cyclopropanation reactions and polymerizations [21]. The advantage of the polymer-supported catalysts is that they can be easily extracted from those reactions by simple methods such as solvent precipitation [22,23]. We have previously reported a series of polymerizations of acetylene [24] and diidobenzene [25] bearing chiral oxazoline group. The polymers adopted the helical structures in a solution, evidenced by their unique induced circular dichroism (ICD) in the π - π^* transition regions of the polymer backbones. Interestingly, the Cotton effects could be induced upon the complexation of chiral oxazoline side chain with metal ions, resulting in the formation of chiral supramolecular aggregations. The resulting polymer-metal ion complexes were proposed to be used as the novel chiral polymeric catalysts in the asymmetric reactions.

We found in the previous study that polymerizability of acetylene bearing chiral oxazoline group (BnEOx) was low. This was due to the



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lower electron density of the acetylenic moiety by oxazoline side groups, which is unfavorable to the coordination with the rhodium catalyst. We expected that an introduction of a phenyl moiety into the BnEOx would increase the polymerizability, lead to obtain the high molecular weight polymers with high yield. In the continuation of our study described herein, we synthesized and polymerize a novel phenylacetylenes substituted with the chiral oxazoline derivatives (BnEPhOx) using rhodium/triethyl amine (Et₃N) catalyst to obtain optically active helical poly(phenylacetylene)s bearing chiral oxazoline in a side chain (Scheme 1). The obtained functional polymers formed the helical structure with predominantly onehandedness screw sense in a solution. Their properties were characterized by spectroscopic and thermal gravimetric methods.

2. Experimental section

2.1. Measurements

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a JNM-LA500 apparatus (JEOL, Ltd.) spectrometer using tetramethylsilane (TMS) (¹H NMR, δ 0.00) or CDCl₃ (¹³C NMR, δ 77.0) as internal reference peaks at room temperature. Infrared (IR) spectra were obtained on a FT-IR Jasco 4100 (JASCO Corporation) spectrophotometer. 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 CHRO-MATOPAC C-R7A plus (Shimadzu Corporation) 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 Corporation). Polystyrene samples were used as standards. Specific rotations were measured at concentration of 0.1–1.0 g/dL in CHCl₃ at 25 °C using a quartz cell (1.0 cm) with a JASCO DIP-1030 (JASCO Co., Ltd.). Circular dichroism (CD) spectra were measured at concentration of 0.01–0.10 g/dL in CHCl₃ at 25 °C using a quartz cell of 1.0 mm with a JASCO J-805 (JASCO Co., Ltd.). Melting points (m.p.) were measured on a YANA-GIMOTO micro melting-point apparatus. Thermogravimetric analvses were carried out using an MS-Tg/DTA220 (JEOL) at a scanning rate of 10 °C min⁻¹ under nitrogen (100 mL min⁻¹). The UV–visible spectra and photoluminescence were obtained from a Shimadzu UV-1650 PC spectrophotometer and a Jasco FP-6300 spectrofluorophotometer, respectively. Elemental analysis (JMA 10 YA: I-SCIENCE LAB CO., Ltd) was carried out at Collaborative Center for Engineering Reserch Equipment, Faculty of Engineering, Yamaguchi University.

3. Materials

All reagents were used as received without any further purification. L-Phenylalanine, cupper(I) iodide, 4-iodobenzoyl chloride, sodium hydrogencarbonate and *N*,*N*'-dimethylaminopyridine



Scheme 1. Polymerization of phenylacetylene derivatives bearing chiral oxazoline group.

(DMAP) were purchased from Wako Pure Chemical Industries, Ltd. Bis(triphenylphosphine)palladium(II) dichloride was obtained from Tokyo Chemical Industry Co., Ltd. Triethylamine (Et₃N), ptoluenesulfonyl chloride (TsCl), ammonium chloride and anhydrous magnesium sulfate were received from NACALAI TESOUE. INC. Sodium sulfate was purchased from Kanto Chemical Co. Ltd. (Bicvclo [2.2.1]hepta-2.5-diene)chloro rhodium (I) dimer ([Rh(nbd) Cll₂) and Celite[®] 545 were purchased from Sigma–Aldrich Japan. Trimethylsilylacetylene was obtained from Junsei Chemical Co. Ltd. (S)-phenylalaninol was synthesized according to the literature [26]. *n*-Hexane, ethyl acetate, tetrahydrofuran (THF), toluene, *N*,*N*'dimethylformamide (DMF), dimethyl sulfoxide (DMSO), 1,2dichloroethane, CH₂Cl₂ and CHCl₃ were dried according to the standard procedure and distilled under nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel plate 60F₂₅₄. Column chromatography was performed with silica gel 60 (0.063-0.200, MERCK).

3.1. Monomer synthesis

The typical synthesis procedure of the novel (S)-2-(3,5-diiodophenyl)-oxazoline (BnEPhOx) was given according to the strategy outline in Scheme 2.

[1] Preparation of *N*-((*S*)-1-Benzyl-2-hydroxyethyl)-4-iodobenzamide (3)

To a stirred solution of (*S*)-phenylalaniol (2) (0.85 g, 5.64 mmol) and triethylamine (0.95 mL, 6.77 mmol) in THF (10 mL), a solution of 4-iodobenzoyl chloride (1) (1.51 g, 5.64 mmol) in THF (15 mL) was added dropwise at 0 °C. The reaction mixture was stirred for 3 h. After completion of the reaction, the NaHCO_{3(aq)} (15 mL) was added, and then extracted with CH₂Cl₂. The organic layers were washed twice with NaCl_(aq), dried over sodium sulfate (Na₂SO₄), and filtrated. The filtrate was concentrated on a rotary evaporator to give white solid (1.96 g, 5.13 mmol) of hydroxyamide (3) with 91% yield. The product was used for the next reaction without any purification.

¹H NMR (CDCl₃) δ (ppm from TMS): 7.76 (d, 2H, aromatics), 7.37 (d, 2H, aromatics), 7.24–7.31 (m, 5H, aromatics), 6.22 (d, 1H, CO-HN), 4.35(m, 1H, CH), 3.70-3.81 (m, 2H, CH₂-OH), 2.98 (d, 2H, CH₂-Ph). ¹³C NMR (CDCl₃) δ (ppm from CDCl₃): 167.6, 137.8, 137.3, 129.2, 128.6, 128.4, 98.3, 64.2, 53.1, and 36.8.

[2] preparation of (S)-4-Benzyl-2-(4-iodophenyl)oxazoline (4)

To a stirred solution of hydroxyamide (3) (1.96 g, 5.13 mmol), triethylamine (2.80 g, 27.69 mmol) and DMAP (18.8 mg, 0.15 mmol) in 1,2-dichloroethane (25 mL), toluenesulfonyl chloride (TsCl) (1.47 g, 7.69 mmol) was added. The reaction mixture was refluxed for overnight. The mixture was washed twice with $NaCl_{(aq)}$, dried over MgSO₄ and the solvent was removed in vacao. The crude product was purified by column chromatography eluted with hexane/ethyl acetate (6/1, v/v) to give yellowish oil 4 (1.67 g, 4.59 mmol) with 90% yield.

¹H NMR (CDCl₃) δ (ppm from TMS): 7.79 (d, 2H, aromatics), 7.70 (d, 2H, aromatics), 7.22–7.46 (m, 5H, aromatics), 4.58 (m, 1H, CH-N), 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 CDCl₃): 163.5, 137.9, 137.4, 129.7, 129.2, 128.5, 127.2, 126.5, 98.0, 72.1, 67.8, and 41.7.

[3] Preparation of (S)-4-Benzyl-2-(4-trimethylsilylethynylphenyl) oxazoline (5)

To a solution of (*S*)-4-benzyl-2-(4-iodophenyl)oxazoline (4) (1.67 g, 4.59 mmol), bis(triphenylphosphine)palladium dichloride



Scheme 2. Synthetic route of monomer.

(0.16 g, 0.23 mmol), cupper(I) iodide (43.26 mg, 0.23 mmol) in THF (15 mL) and Et₃N (0.77 mL, 5.51 mmol) was added trimethylsilylacetylene (0.78 mL, 5.51 mmol). The reaction mixture was stirred under nitrogen atmosphere at 50 °C for overnight. After that, the mixture was filtrated, diluted with ethyl acetate, washed by saturated NH₄Cl_(*aq*) and NaCl_(*aq*) and dried over MgSO₄. The filtrate was concentrated on a rotary evaporator to give 5 (1.42 g, 4.26 mmol) of yellowish crude oil with 93% yield. The crude product was used for the next reaction without any purification.

¹H-NMR (CDCl₃) δ (ppm from TMS): 7.88 (d, 2H, aromatics), 7.55 (d, 2H, aromatics), 7.22–7.46 (m, 5H, aromatics), 4.58 (m, 1H, CH-N), 4.36 (t, 1H, CH₂-O), 4.12 (t, 1H, CH₂-O), 3.20 (dd, 1H, CH₂-Ph), 2.74 (dd, 1H, CH₂-Ph), 0.24, (s, 9H, CH₃-Si). ¹³C NMR (CDCl₃) δ (ppm from CDCl₃): 163.5, 138.1, 131.9, 129.3, 128.6, 128.2, 127.6, 126.6, 126.2, 64.2, 53.1, and 36.8.

[4] Preparation of (*S*)-4-Benzyl-2-(ethynylphenyl)oxazoline (BnEPhOx)

The (*S*)-4-Benzyl-2-(4-trimethylsilylethynylphenyl)oxazoline (5) (1.42 g, 4.26 mmol) was stirred in the presence of methanol (15 mL) and potassium carbonate (0.44 g, 3.20 mmol) at room temperature for 1 h. To the resulting solution was added diethylether (100 mL), washed 3 times with water and then dried over MgSO₄. The filtrate was concentrated on a rotary evaporator. The product was purified by column chromatography eluted with hexane/ethyl acetate (6/1, v/v) to obtain the product as a pale yellow solid (0.62 g, 2.37 mmol) with yield of 67%.

[α]_D = +23.5° in CHCl₃ (*c* = 1.0 g/dL). Melting-point: 56.5–58.8 °C, Anal. Calcd for C₁₈H₁₅NO: C 82.73%, H 5.79%, N 5.36%. Found: C 82.50%, H 5.97%, N 5.36%. ¹H NMR (CDCl₃) δ (ppm from TMS): 7.89 (d, 2H, aromatics), 7.59 (d, 2H, aromatics), 7.22–7.42 (m, 5H, aromatics), 4.58 (m, 1H, CH-N), 4.36 (t, 1H, CH₂-Q), 4.12 (t, 1H, CH₂-Q), 3.20 (dd, 1H, CH₂-Ph), 3.18 (s, 1H, H-C≡), 2.74 (dd, 1H, CH₂-Ph). ¹³C NMR (CDCl₃) δ (ppm from CDCl₃): 163.8, 137.8, 132.0, 129.2, 128.5, 128.1, 127.9, 126.5, 125.0, 83.0, 79.3, 71.9, 67.9, and 41.7.

3.2. 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 polymerization of BnEPhOx is given as follow;

The BnEPhOx (0.30 g, 1.15 mmol) was placed in a dry schlenk glass tube, which was then evacuated on a vacuum line and flushed with N₂. After this evacuation-flush procedure was repeated for three times, and anhydrous solvent (1 mL) and Et₃N (0.08 mL, 0.57 mmol) were added with a syringe. To this was added a solution of [Rh(nbd)Cl]₂ (10.58 mg, 22.96 µmol) in solvent (1.5 mL). The reaction mixture became brown from light yellow immediately. The concentrations of the monomer and the rhodium catalyst were 0.46 M and 9.18 mM, respectively. After being stirred at 50 °C for 24 h under N₂, the resultant solution was added dropwise to a large amount of *n*-hexane. The appearing precipitate was collected by filtration. Purification of the polymer was achieved from reprecipitation from CHCl₃ - henxane, and dried in vacuo at room temperature until weight constant.

Spectroscopic data of the polymers. ¹H NMR (CDCl₃) δ (ppm from TMS): 7.45–7.63 (br, 2H, aromatics) 7.00–7.23 (br, 5H, aromatics), 6.61–6.74 (br, 2H, aromatics) 5.78–5.92 (br, 1H, C]*CH*), 4.28–4.40 (br, 1H, C*H*-N), 3.98–4.17 (br, 1H, C*H*₂–O), 3.80–3.94 (br, 1H, C*H*₂–O), 3.02–3.17 (br, 1H, C*H*₂–Ph), 2.40–2.58 (br, 1H, C*H*₂–Ph).

4. Results and discussion

4.1. Monomer synthesis

The synthetic route of the novel optically active phenylacetylene bearing oxazoline derivative (BnEPhOx) is illustrated in Scheme 2. The monomer was obtained from very mild conditions, starting from coupling reaction of 4-iodobenzoyl chloride (1) with (*S*)phenylalaninol (2) in anhydrous THF with Et₃N, to obtain hydroxyamide (3). Subsequently, ring-closure reaction of hydroxyamide 3 was carried out by refluxing 1,2-dichloroethane in the presence of TsCl, Et₃N and DMAP, yielding the 4-iodobenzene which has chiral oxazoline (4). The intermediate 4 was then converted to the corresponding precursors 5 through the Sonogashira-Hagihara coupling reaction with (trimethylsilyl)acetylene (TMSA) using palladium/copper(I) catalyst system in anhydrous THF. Finally, the BnEPhOx was achieved in moderate yield from the treatment of 5 with K₂CO₃ in MeOH for deprotecting the trimethylsilyl group. The structures of all the intermediates and the monomer were confirmed by ¹H NMR, ¹³C NMR and FT-IR.

4.2. Polymerization

A novel type of poly(phenylacetylene) bearing functional oxazoline Pendant groups (poly(BnEPhOx)) was successfully synthesized by catalytic polymerization of BnEPhOx using rhodium catalyst in the presence of Et₃N under mild conditions, in accordance with a previously reported method [24]. The yellow powdery polymers were obtained from precipitation of polymeric solution into an excess of *n*-hexane. The results of the polymerizations of BnEPhOx are summarized in Table 1. Poly(BnEPhOx) with M_n ranging from 1.11 to 3.51×10^3 were obtained with 90-94% yield. Anyway, the different appearance of the polymers should be closely related to their different number-averaged molecular weight (M_n).The polymerizations were carried out under the same conditions except only the kind of solvents. Therefore, it can be proposed that the solvents had the influence on the polymerization of this type of monomer.

Here, it is important to point out that, when polymerization was carried out in DMSO as the solvent, precipitation was quite difficult to achieve the resulting polymer from the solution by directly pouring the polymer solution into a large amount of *n*-hexane as it is poor solvents (Run 3 in Table 1). Instead, a small amount of CHCl₃ should be added in the polymeric solution first before the normal procedure of the precipitation. This is to transfer the DMSO system to a CHCl₃ system.

4.3. Polymer structure

The polymers were characterized by NMR and IR spectrometers. It has been reported that rhodium catalysts can commonly provide the substituted polyacetylene with high *cis*-transoidal [27,28]. The ¹H NMR was performed to confirm the microstructure of the constitution units in the resulting polymers. The ¹H NMR spectra of poly(BnEPhOx) and BnEPhOx were shown in the same Fig. 1, for comparison. All signals could be assigned, no other unexpected signals were observed. Aromatic signals of the ethynylphenyl protons upfield shifted to 6.7 ppm after polymerization. The resonance peaks of the oxazoline moieties protons also upfield shift by ~ 0.25 ppm, which should be due to the enhanced electronic interaction between the oxazoline groups in the polymer. These are consistent with those from another study [29]. The signals of the oxazoline group of monomer were observed, i.e., signals of CH₂-Ph appeared at 2.74 and 3.18 ppm and the signal of the CH-N was also found at 4.58 ppm. The polymers displayed no signal assignable to

Table 1

Asymmetric polymerization of BnEPhOx using rhodium catalyst^a.

Run	Solvent	Yield ^b (%)	$M_{\rm n}{}^{\rm c} imes 10^{-4}$	M_w/M_n^c	$[\alpha]_D^d$ (deg.)	<i>cis</i> contents ^e (%)
1	THF	90	1.36	3.10	-244.4	99
2	Tol	91	3.51	3.18	-325.1	100
3	DMSO	90	1.11	1.78	-147.3	68
4	DMF	94	2.01	3.16	-200.2	99

Abbreviations: DMF, *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF, tetrahydrofuran; Tol, toluene.

 a (S)-4-Benzyl-2-(4-ethynylphenyl)-oxazoline (BnEPhOx) [α]_D = +23.5° in CHCl_3. Conditions: [BnEPhOx] = 1.15 mmol, [BnEPhOx]/[Rh cat.] = 50/1, polymerized at 50 °C for 24 h in solvent (2.5 mL).

^b Insoluble part in *n*-hexane.

^c THF-soluble part, determined by GPC eluted with THF calibrated by polystyrene standards.

 $^{\rm d}~c = 0.1~{\rm g/dL},~l = 1~{\rm cm},~{\rm CHCl_3}.$

^e Determined by comparing the intregation ratio of *cis* vinyl proton signal (around 5.82 ppm) and the other proton signals in the ¹H NMR spectra.

an acetylenic proton at around 3.18 ppm. Moreover, the signals of the *cis*-transoidal proton of main chain were observed at around 5.82 ppm [30,31]. All these results clearly indicate that the acetylene polymerization takes place to form the polymers composed of alternating single and double bonds. The *cis* contents of the poly(phenylacetylene)s main chain were also determined by comparing the integration ratio of *cis* vinyl proton signal (-CH = C-; H_a) with the other proton signals in the ¹H NMR spectra, which was widely used to determine *cis* content (%) of the polyacetylenes. Their *cis* contents of polymers were listed in Table 1. Almost the polymers possessed highly stereoregular *cis* structure (*cis* contents > 67.5%), like the other polymers of the same types [32–34].

Commonly, the polymerization of an acetylene monomer using rhodium catalyst provides *cis*-rich polyacetylene. There have been reported that the *cis*-trans isomerization during the acetylene polymerization is dependent on three possible factors, i.e., temperature [35], stereo-hinder of the functional groups side chain [36] and polarity of solvents [37]. In this study, the BnEPhOx was polymerized at the same temperature. Hence, the low *cis* content of the polymer obtained in DMSO should be resulted from the high polarity of the solvent.

The FT-IR measurement, a versatile method to determine the steroregularity of the polyacetylene, was carried out to determine the structure of the resulting polymers. Fig. 2 showed the FT-IR spectrum of the polymers. As can be seen in the Fig. 2, BnEPhOx clearly showed a strong absorption band at 3250 cm⁻¹ and a weak absorption band at 2150 cm⁻¹ respectively assignable to the C-H and C^C stretching vibration in the monosubstituted acetylene. No absorption bands were observed at wave number area above stretching vibration in the polymers. Moreover, the polymers showed characteristic peaks at around 1340 and 960 cm⁻¹, respectively, which were assigned to C]C and C-H vibrations in the cis-polyacetylene [38]. While the characteristic peak of the trans isomer at 1200 cm⁻¹ was not observed in this spectrum. These results indicated that the monomer was completely conversed to poly(phenylacetylene) substituted with the functional chiral oxazoline groups, which possessed highly stereoregular *cis* structure.

The solubilities of the polymers were investigated to find out that all the resulting polymers were soluble in only $CHCl_3$ and partially insoluble in THF, DMSO, DMF and toluene, while insoluble in methanol, *n*-hexane and diethyl ether.

4.4. Absorption and emission properties of the polymers

We investigated optical properties of the polymers obtained. The absorption and emission properties of poly(BnEPhOx)s along with BnEPhOx were investigated in chloroform. The UV-vis absorption spectra and photoluminescence (PL) spectra in chloroform solution are illustrated in Fig. 3. The BnEPhOx showed a strong absorption attributed to the oxazoline group in the range of 270-330 nm (Fig. 3(A)). On the other hand, the absorption of all polymers were observed at 270-520 nm. The broad absorption peaks of the polymers were assigned by comparing to the absorption spectra of the corresponding monomer. The strong absorption peaks of the polymer at 280–340 nm were definitely the signatures of the absorption of the oxazoline pendants. All the polymers showed the absorption in the longer wavelength region while the monomer did not. These were the signatures of the π - π^* interband transition of the main chain of the conjugated polyacetylene [39].

The relative photoluminescence spectra of the poly(BnEPhOx)s measured in chloroform were shown in Fig. 3(B). As depicted in Fig. 3(B), the poly(BnEPhOx) polymerized in DMSO exhibited the strongest characteristic emission peak at around 400 nm upon



Fig. 1. ¹H NMR spectra of (A) BnEPhOx and (B) poly(BnEPhOx) (run 2 in Table 1) in CDCl₃.

excitation at around 300 nm. In contrast, the poly(BnEPhOx)s obtained from toluene, DMF and THF showed only negligible weak emissions. These emission bands should be due to the stereoregular chains of the polyacetylene [40,41]. The difference in PL intensity was related to the *cis* concentrations of the resulting polymers. This result indicates that the non-radiative decay rate increases by increasing the *cis* content. The PL intensities of the polymers decrease with increasing of *cis* content; these results are consistent with those from the previous studies [41].

4.5. Chiroptical properties of the polymer

The Pendant chiral oxazoline moiety is known as a potential group to endow the main chain of polymers with a prevailing helical handedness structure [24]. So, it is anticipated that the introduction of optically active chiral oxazoline as the Pendant groups of poly(phenylacetylene) could induce an excess one handedness helical conformation in the main chain of the polymer. Subsequently, chiroptical properties of the polymers obtained were



Fig. 2. FT-IR spectra of (A) BnEPhOx and (B) poly(BnEPhOx) (run 2 in Table 1).



Fig. 3. UV-vis Absorption (A) and Emission (B) spectra of BnEPhOx and poly(BnEPhOx) measured in CHCl₃.

investigated by means of optical specific rotation ([α]_D) and circular dichroism (CD). The optical specific rotations of BnEPhOx and poly(BnEPhOx)s measured in CHCl₃ were listed in Table 1. The optical specific rotation of BnEPhOx was +23.5°. On the other hand, poly(BnEPhOx)s showed the values range from $-147.3^{\circ} \sim 325.1^{\circ}$. Poly(BnEPhOx) obtained in DMSO had the lowest absolute optical specific rotation among the other polymers. These observations were consistent with the results of the *cis* contents of polymer. The polymers which possessed highly stereoregular *cis* structure are known to have higher value of optical specific rotation.

As discussed above, the large $[\alpha]_D$ values of the polymers imply that they take a helical conformation. We conducted CD spectroscopic analysis to confirm whether the polymer chains are really spiraling in a helical sense. As shown in Fig. 4, the CD spectra of poly(BnEPhOx)s exhibited a positive Cotton effect at around 340 nm and a negative one at 270 nm. In addition, BnEPhOx showed a strong UV absorption only in the range of 270–330 nm while the polymer showed strong UV absorption over the range of 270–520 nm. Judging from the comparison between the CD and UV–vis absorption spectra of the monomers and polymers, it seems that the configurational chirality of the optically active oxazoline groups induced the Cotton effects at around 270 nm, and the polyacetylene main chain induced the ones at around 340 nm. It is considered that the CD signal of poly(BnEPhOx) arises from not only the



Fig. 4. CD spectra of BnEPhOx and poly(BnEPhOx)s measured in CHCl₃.



Fig. 5. Thermogravimetric curves of (A) poly(BnEPhOx) (run 3 in Table 1) and (B) poly(phenylacetylene) at heating rate of 10 $^{\circ}$ C/min under nitrogen.

configurational chirality of the optically active oxazoline groups but also the conformational one based on higher-order structures of polyacetylene backbone, i.e., partial helical conformation. The results of chiroptical properties obviously indicated that these polymers possess a helical structure with an excess single screw sense induced by chiral oxazoline groups in the side chain.

4.6. Thermal analysis of polymers

Thermal property of poly(phenylacetylene)s having chiral oxazoline was examined by thermogravimetric analysis (TGA) as shown in Fig. 5. The polymer showed high thermal stability. As shown in Fig. 5, the polymer showed a very small weight loss below 100 °C. This should be assigned to the loss of absorbed water. The significant weight loss of 10% was observed at around 310 °C. The char residue at 500 °C was calculated to be 62%. Poly(BnEPhOx) had higher thermal stability than poly(phenylacetylene). The polymers having an oxazoline group in the side chain are known as thermostable polymers [24]. Thermal stabilities of poly(BnEPhOx) were improved by the introduction of oxazoline group to the acetylene backbone.

5. Conclusion

In this paper, we have demonstrated the preparation of the novel poly(phenylacetylene)s bearing a chiral oxazoline group at a side chain, using rhodium catalyst ([Rh(nbd)Cl]₂) in various

solvents. The results from optical specific rotation and CD spectroscopy implied that all poly(BnEPhOx)s adopted helical structures with predominantly one-handed screw sense in chloroform solution, induced by chiral oxazoline group at the side chain. The molecular weights, yields and optical specific rotations were influenced by the polymerization solvents. The polymers exhibited good thermal stability. Poly(BnEPhOx) obtained in DMSO showed the highest PL intensity.

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