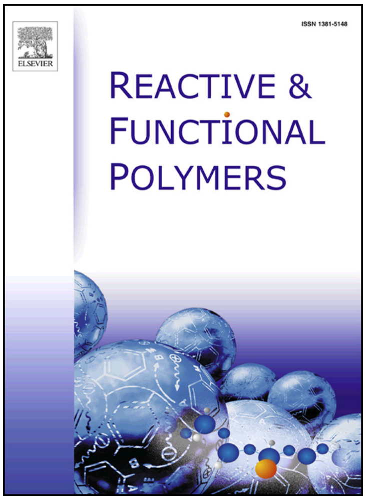

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Synthesis and ion responsiveness of optically active polyacetylenes containing salicylidene Schiff-base moieties

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ABSTRACT

Acetylenic monomers containing salicylidene Schiff-base groups (**1a** and **1b**) as well as Schiff-base and hydroxy groups (**1c**) were synthesized and polymerized with $[(\mathrm{nbd})\mathrm{RhCl}]_2/\mathrm{Et}_3\mathrm{N}$ catalyst to afford the corresponding polymers **2a**-**c** with high molecular weights ($M_\mathrm{n} = 2.6–7.2 \times 10^5$) in high yields (75–97%). Polarimetric, circular dichroism (CD), and UV-vis spectroscopic analyses indicated that the polymers formed helical structures with a predominantly one-handed screw sense. The addition of metal ions to salicylidene Schiff-base-containing polymers **2a** and **2b** produced insoluble polymer/metal complexes through ionic cross-linking as a result of salicylaldimine-metal ion complexation. Polymers **2b** and **2c** underwent a helix-coil transition upon the addition of $\mathrm{HSO_4}^-$, whereas these polymers did not exhibit responsiveness to other anions, such as F^-, Cl^-, and Br^-.

Keywords: Conjugated polymer; Polyacetylene; Helix; Stimuli-responsive; Polymerization

1. Introduction

The development of novel artificial helical polymers continues to be a topic of considerable interest and importance in the area of macromolecular science from both fundamental and application-oriented perspectives [1-6]. Over the past decades, tremendous strides have been made in the field of synthetic helical polymer chemistry, and a variety of helical polymers have been successfully synthesized not only to mimic biological helices but also for their potential applications in chiral recognition, asymmetric catalysis, chemical sensors, and so forth [7–10]. Among these polymers, conjugated helical polymers, such as polyisocyanides, polysilanes, and polyacetylenes, are of great interest and are intensively studied because of their unique functions resulting from their helical structures and conjugated main chains.

As a class of typical π-conjugated polymers, polyacetylene and its derivatives exhibit interesting chemical and physical properties [11-13]. Substituted polyacetylenes can form helical structures with a predominantly one-handed screw sense through the introduction of appropriate chiral substituents into the side chain or through the helix-sense-selective polymerization of achiral monomers [14–22]. Polyacetylene derivatives adopt a dynamic helical conformation due to the relatively low energy barriers for helix reversal [3]. These derivatives can undergo helix/random coil transitions and/or helix inversions in response to external stimuli, such as temperature, light, and change of medium conditions, including polarity and pH, which is attractive in a wide variety of fields, including life sciences, pharmacy, and chemical engineering. Although various helical polyacetylenes have been reported, sophisticated studies are still being performed to design and tailor desired polymer properties.

Salicylidene Schiff bases, which are an important and versatile class of ligands, have attracted considerable attention because of their facile preparation via salicylaldehyde-amine condensation, easy modification of their steric and electronic properties, and high binding affinity toward various metal ions [23-25]. Various salicylidene Schiff-base/metal complexes have been synthesized and have found potential applications in optic materials, chemical sensors, biological probes, and efficient catalysts for organic reactions [26-29]. However, compared with the extensively studied low-molecular-weight systems, the synthesis and applications of salicylidene Schiff-base-containing polymers are quite limited. Lu and coworkers prepared “light-controllable” fluorescent polystyrene micelles via salicylaldimine-Zn^{2+} complexation [30]. Theato and coworkers prepared thermo- and light-responsive polyacrylamides that contained different amounts of salicylideneaniline chromophores [31]. Cai and coworkers reported the synthesis of metal-functionalized polymer micelles through Co^{2+}-salicylaldimine coordination [32]. The above-mentioned salicylidene Schiff-base-containing polymers were synthesized through the side-chain modification of polymers via aldehyde-amine condensation. In contrast, the direct polymerization of salicylidene Schiff-base-containing monomers is a simple and straightforward route for the synthesis of well-defined polymers with salicylidene Schiff-base pendant groups. We recently reported that (*S*)- and (*R*)-*N*-(4-ethynylbenzylidene)-1-phenylethanamine, which are Schiff-base-functionalized acetylenic monomers, polymerize with $[(nbd)RhCl]_2/Et_3N$ catalyst to afford helical polyacetylenes [33]. Thus, we can potentially prepare novel functional helical polyacetylenes bearing salicylidene Schiff-base groups through direct polymerization of the corresponding monomers, which could exhibit interesting properties as a result of the combination of the unique characteristics of the salicylidene Schiff base and the higher-order structure of the polyacetylene backbone.

The present study focuses on the synthesis and polymerization of novel acetylenic monomers containing salicylidene Schiff-base moieties (**1a** and **1b**) as well as a monomer containing both Schiff-base and hydroxy groups (**1c**) for comparison (Scheme 1). The secondary structures of the resulting polymers were investigated in detail, and their responsiveness to metal ions and tetra-*n*-butylammonium hydrogen sulfate was examined.

(*insert Scheme 1 here*)

2. Experimental section

2.1. Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-400 spectrometer. IR spectra were recorded on a BRUKER Vertex-70 spectrophotometer. The number- and weight-averaged molecular weights (M_n and M_w) of the polymers were determined using a gel permeation chromatograph equipped with a Waters 515 HPLC pump and a Waters 2414 differential refractometer using THF as the eluent at a flow rate of 1.0 mL/min and calibrated with polystyrene standards. Elemental analysis of the monomers was performed at the Analytical Center of Dalian University of Technology. Specific rotations ($[\alpha]_D$) were measured using a JASCO DIP-1000 digital polarimeter. CD and UV-vis spectra were recorded on a JASCO J-810 spectropolarimeter.

2.2. Materials

THF, which was used as the polymerization solvent, was distilled over sodium prior to use. Triethylamine was distilled and dried over potassium hydroxide. 4-Bromobenzaldehyde (Aladdin Co.), 5-bromosalicylaldehyde (J & K), (*R*)-1-phenylethanamine (Aldrich), (*R*)-2-phenylglycinol (Aladdin Co.), trimethylsilylacetylene (Acros), bis(triphenylphosphine)palladium(II) dichloride (Aldrich), and $[(nbd)RhCl]_2$ (Aldrich) were used as received. Other solvents, such as methanol, toluene, and $CHCl_3$, were of high purity and were used without further purification. 4-Ethylnylbenzaldehyde and 5-ethynylsalicylaldehyde were synthesized following methods reported in the literature [34,35].

2.3. Monomer synthesis

*2.3.1. (R)-4-Ethynyl-2-((1-phenylethylimino)methyl)phenol (**1a**)*

A 100-mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar. (*R*)-1-Phenylethanamine (0.61 g, 5 mmol) and 5-ethynylsalicyclaldehyde (0.73 g, 5 mmol) were dissolved in toluene (60 mL). The reaction mixture was heated at reflux temperature for 10 h. The generated water was separated using a Dean-Stark apparatus. Then, toluene in the reaction mixture was removed by evaporation, and the crude product was purified by recrystallization from ethanol to afford bright yellow crystals in 55% yield; $[\alpha]_D = +23°$ (c = 0.2 g/dL, $CHCl_3$, room temperature). ^1H NMR (400 MHz, $CDCl_3$): δ 13.8 (s, 1H, O*H*), 8.31 (s, 1H, C*H*=N), 7.42–6.88 (m, 8H, Ar*H*), 4.54 (q, 1H, N-C*H*), 2.97 (s, 1H, *H*C≡C), 1.61 (m, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (*C*H=N), 162.0, 143.5, 136.1, 135.5, 128.9, 127.6, 126.5 118.7, 117.6, 112.3, 83.3, 75.9, 68.4, 24.9. IR (cm^{-1}, $CHCl_3$): 3278, 3107, 2927, 1630 (CH=N), 1583, 1485, 1396, 1289, 973, 830, 770, 701. Anal. Calcd for $C_{17}H_{15}NO$:

C, 81.90; H, 6.06; N, 5.62. Found: C, 81.78; H, 6.21; N, 5.87.

*2.3.2. (R)-4-Ethynyl-2-((2-hydroxy-1-phenylethylimino)methyl)phenol (**1b**)*

This monomer was prepared using the same method as for monomer **1a** but with (*R*)-2-phenylglycinol rather than (*R*)-1-phenylethanamine to afford orange crystals in 50% yield; $[\alpha]_D = +9°$ (c = 0.1 g/dL, $CHCl_3$, room temperature). ^1H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H, C*H*=N), 7.44–6.90 (m, 8H, Ar*H*), 4.47 (t, 1H, N-C*H*), 3.91 (m, 2H, CH_2OH), 2.99 (s, 1H, *H*C≡C). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7 (*C*H=N), 145.1, 136.8, 132.4, 128.6, 128.3, 127.1, 126.8, 124.3, 83.5, 79.0, 70.0, 25.0. IR (cm^{-1}, $CHCl_3$): 3287, 3061, 2925, 2867, 1633 (CH=N), 1586, 1487, 1383, 1287, 1068, 893, 830, 760, 700. Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.73; H, 5.65; N, 5.47.

*2.3.3. (R)-N-(4-Ethynylbenzylidene)-2-phenylglycinol (**1c**)*

This monomer was prepared using the same method as for monomer **1a** but with (*R*)-2-phenylglycinol and 4-ethynylbenzaldehyde rather than (*R*)-1-phenylethanamineand 5-ethynylsalicylaldehyde to afford light yellow crystals in 54% yield; $[\alpha]_D = +125^o$ (c = 0.1 g/dL, $CHCl_3$, room temperature). ^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H, C*H*=N), 7.69–7.29 (m, 9H, Ar*H*), 4.50 (t, 1H, N-C*H*), 3.98 (m, 2H, CH_2-O), 3.22 (s, 1H, *H*C≡C). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (*C*H=N), 140.6, 135.9, 132.4, 129.0, 128.8, 127.7, 126.9, 126.6, 126.3, 124.7, 83.4, 79.4, 67.8, 62.4. IR (cm^{-1}, $CHCl_3$): 3286, 3062, 3029, 2923, 2868, 1641 (CH=N), 1604, 1493, 1452, 1383, 839, 759, 701. Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.60; H, 5.99; N, 5.55.

(*insert Scheme 2 here*)

2.4. Polymerization

The polymerizations were conducted in a glass tube equipped with a three-way stopcock under dry nitrogen. [(nbd)RhCl]$_2$ and Et$_3$N were added to a monomer solution in THF under nitrogen, and the resulting solution ([M]$_0$ = 0.5 mol/L, [Rh]/[M]$_0$ = 100, [Et$_3$N]/[Rh] = 50) was maintained at 30 °C for 4 h. The formed polymers were isolated by precipitation into a large amount of *n*-hexane and dried to a constant weight under reduced pressure; the polymer yields were gravimetrically determined.

2.5. Spectroscopic data of the polymers

2a: ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.01 (br, 1H, C*H*=N), 7.57–6.65 (br, 9H, Ar*H*), 5.81 (br, 1H, *H*C=C), 4.28 (br, 1H, NC*H*), 2.95–2.79 (br, 2H, C*H*$_2$OH). IR (cm^{-1}, CHCl$_3$): 3501, 3111, 2955, 2927, 2863, 1632 (HC=N), 1558, 1489, 1456, 1395, 822, 760, 697. **2b**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.40 (br, 1H, C*H*=N), 7.56–6.63 (br, 8H, Ar*H*), 5.61 (br, 1H, *H*C=C), 4.48 (br, 1H, NC*H*), 3.91–3.74 (br, 2H, C*H*$_2$OH). IR (cm^{-1}, CHCl$_3$): 3426, 3257, 3030，2949, 2871, 1631 (HC=N), 1586, 1489, 1442, 1373, 1105, 1062, 827, 783, 698. **2c**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.11 (br, 1H, C*H*=N), 7.57–7.05 (br, 9H, Ar), 5.78 (br, 1H, *H*C=C), 4.51 (br, 1H, NC*H*), 4.07–4.3 (br, 2H, C*H*$_2$OH). IR (cm^{-1}, CHCl$_3$): 3383, 3060, 3027, 2923, 2863, 1640 (HC=N), 1602, 1562, 1492, 1452, 1384, 826, 760, 701.

2.6. Preparation of polymer/metal ion complexes

The polymer/metal ion complexes were prepared by adding metal acetate to the polymer solutions. Copper acetate, zinc acetate, and chromium acetate were used as metal acetate hydrates. A detailed procedure is as follows: **2a** (49.8 mg, 0.2 mmol in terms of repeat unit) was placed in a flask and completely dissolved in THF (10 mL). A solution of copper acetate [Cu(CH$_3$COO)$_2$·H$_2$O, 20 mg, 0.1 mmol] in ethanol (3 mL) was added dropwise, and the resulting mixture was stirred overnight at room temperature. During that time, the color of the suspension changed from orange to brown, and a large amount of solid precipitated from the solution. The precipitate was filtered and repeatedly washed with THF and methanol, and it was dried to constant weight under reduced pressure.

3. Results and discussion

3.1 Monomer synthesis and polymerization

Acetylenic monomers **1a**-**c** were synthesized via the salicylaldehyde-amine condensation reaction according to Scheme 2. The structures of the monomers were identified by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis.

Rhodium catalysts can efficiently polymerize various monosubstituted acetylenes to afford polymers with high molecular weights and stereoregularity even though the monomers possess polar and functional groups [36-39]. Thus, the polymerizations of monomers **1a**-**c** were conducted with $[(nbd)RhCl]_2/Et_3N$ catalyst in THF, and the results are summarized in Table 1. The corresponding polymers **2a**-**c** with fairly high molecular weights ($M_n = 2.6–7.2 \times 10^5$) were obtained in high yields (75–96%). All of the polymers were soluble in common organic solvents, such as $CHCl_3$, CH_2Cl_2, THF, and DMF. The polymer structures were examined using IR and ^{1}H NMR spectroscopy. The monomers exhibited an absorption band at approximately 3280 cm^{-1} assignable to the ≡C–H stretching vibration, which disappeared in the IR spectra of the polymers. However, the absorption band due to HC=N at approximately 1640 cm^{-1} remained intact in the polymers. These results indicate that the polymerization occurs to form polymers composed of alternating single and double bonds and with no change in the Schiff-base group in the resulting polymers. However, we could not determine the *cis*-contents of polymers from the integration ratio of *cis*-vinyl proton and the other proton signals due to the broadness of the peaks in the ^{1}H NMR spectra. Because the polymerization of acetylenic monomers with Rh-based catalysts generally affords *cis*-rich polyacetylenes, it is assumed that the geometric structure of **2a**-**c** is also the same. This was further confirmed by laser Raman analysis (Fig. S1), in which intense peaks at 1556 cm^{-1} (C=C stretching) and 1340 cm^{-1} (C-C stretching) attributable to the *cis*-polyacetylene structure were observed.

(*insert Table 1 here*)

3.2 Chiroptical properties of the polymers

The chiroptical properties of the polymers were examined by polarimetry, CD, and UV-vis spectroscopy. As shown in Table 1, the polymers exhibited $[\alpha]_D$ values 5–20 times larger than those of the corresponding monomers, suggesting that the polymers adopt helical structures with a predominantly one-handed screw sense in $CHCl_3$. This result was further confirmed by the CD and UV-vis spectra of the obtained polymers measured in $CHCl_3$ at 20 °C (Fig. 1). The monomer exhibited stronger Cotton effects at 300–370 nm than its corresponding polymer, and a similar result was observed in a previous study [40]. The polymers exhibited split-type intense Cotton effects at approximately 330 and 390 nm. Although the optical configuration of **1a** was inverted to those of **1b** and **1c**, the polymers exhibited helical structures with the same screw senses. These results might be due to the presence of $–CH_2OH$ groups in the cases of **2b** and **2c**, thereby influencing their chiroptical properties. In addition, whereas monomer **1a** exhibited a strong UV absorption only in the range of 300–370 nm, the polymers showed strong UV absorptions over the wide range of 280–500 nm. These results suggest that the chiral Schiff-base groups induced the Cotton effects at approximately 330 nm and that the polyacetylene main chain induced the ones approximately 385 nm. Thus, it is concluded that the CD signals of **2a**–**c** arise from not only the configurational chirality of the Schiff-base groups but also from the conformational one based on the higher-order structures of the polyene backbone.

(*insert Fig. 1 here*)

Fig. 2 presents the CD and UV-vis spectra of the polymers measured in various solvents. **2a** showed similar CD signals in both nonpolar and polar solvents, indicating that the helical structure of the polymers originates from steric effects. **2b** and **2c** exhibited similar results, but the solvent effects were somewhat larger. Although the reason is not yet clear, these results might be due to the presence of $–CH_2OH$ groups, leading to more sensitive solvent effects. A certain change in Cotton effects with solvents suggests that the helix of the present polymers is dynamic.

(*insert Fig. 2 here*)

Fig. 3 shows the effects of temperature on the CD and UV-vis spectra of the polymers. In the cases of **2a** and **2b**, the intensities of the Cotton effect were only slightly decreased by increasing the temperature from 0 to 80 °C. The present temperature dependence of the helix and the slight decrease in UV-vis absorption might be due to randomization of the chain conformation activated by thermal perturbation. Additionally, the temperature effect on the CD and UV-vis spectra of **2a** and **2b** was smaller than that of **2c**. The higher thermal stability of the helicity of **2a** and **2b** might be due to the formation of a six-membered pseudo-aromatic ring via the hydrogen bond of $O–H\cdots N$, which forms between the hydroxy group of the phenol ring and the nitrogen atom of imine, leading to a larger steric effect [41]. In addition, in all cases, the CD and UV–vis spectral changes were reversible with increasing and decreasing temperature. Similar results were observed in the cases of other helical polyacetylene derivatives [3, 32-44]

(*insert Fig. 3 here*)

3.3 Responsiveness of 2a to metal ions

Polymers that contain coordinative groups in their main and side chains can coordinate with metal ions to form functional polymer/metal complexes that exhibit interesting properties. For example, (*R*,*R*)-salen/salan-based polymers could be used as fluorescence sensors for Zn^{2+}detection [45], and a Schiff-base-anchored polystyrene/Cr^{3+} complex exhibited good microbial ability [46]. In the present study, the complexation of **2a** with various metal ions was investigated. Upon the addition of Cu^{2+} ions to a THF solution of **2a**, a precipitate formed in the system, suggesting that intra- and inter-molecular cross-linking reactions occurred, and as gravimetrically determined, a quantitative conversion concerning complexation was attained. The resulting product was insoluble in $CHCl_3$, CH_2Cl_2, THF, and DMF, in which **2a** exhibited good solubility. Similar results were observed in the cases of **2b** and **2c** and other metal cations such as Zn^{2+} and Cr^{3+}. It is known that low-molecular-weight salicylidene Schiff-base derivatives can coordinate with metal ions through bidentate bonding to form bis-complexes, that is, one metal ion coordinates with two salicylaldimine ligands [47-50]. According to the IR spectra (Fig. 4), the absorption peak of the imine C=N moiety of **2a** appears at 1619 cm^{-1} after the addition of Cu^{2+} ions, which is clearly red-shifted compared to that of **2a** (1630 cm^{-1}), indicating that the nitrogen atom of the imine coordinates to the Cu^{2+} ion. Furthermore, the weak peak at 527 cm^{-1} assignable to ν(Cu–O) suggests that the hydroxy groups are involved in the formation of the polymer/metal complex [51]. Therefore, the cross-links in the present study were likely generated by the formation of a metal-ligand complex, as proposed in Fig. 5. Although the resulting polymer/metal complexes were insoluble, they might serve as potential heterogeneous catalysts for asymmetric catalysis, and this study is currently in progress.

(*insert Fig. 4 and Fig. 5 here*)

*3.4 Responsiveness of **2c** to anions*

Fig. 6 shows the changes in the CD and UV-vis spectra upon the addition of tetra-*n*-butylammonium hydrogen sulfate (n-$Bu_4N^+HSO_4^-$) to a solution of **2c** in THF. The CD signals at 330 nm and 390 nm gradually decreased with increasing amount of n-$Bu_4N^+HSO_4^-$, and they completely disappeared upon the addition of 1.0 equivalent of HSO_4^-. This result indicates that **2c** underwent a helix-coil transition. In contrast, other anions such as F^-, Cl^-, and Br^- did not result in detectable changes in the CD spectra. A similar result was observed in the case of **2b** (Fig. S2), whereas **2a** did not exhibit responsiveness to HSO_4^-. Due to the broad peaks of the polymer in the ^1H NMR spectra, we measured ^1H NMR spectra using (R)-2-(benzylideneamino)-2-phenylethanol as a model compound in the absence and presence of n-$Bu_4N^+HSO_4^-$. As shown in Fig. S3 in the Supporting Information, the peak intensity of the hydroxy proton of the model compound decreased and finally disappeared with increasing amounts of n-$Bu_4N^+HSO_4^-$. Although the detailed mechanism of this transition is not clear, it is hypothesized that the formation of hydrogen bonds between the pendent groups of the polymer and HSO_4^- changes the shape and bulkiness of the side groups [52], leading to a helix-coil transition.

(*insert Fig. 6 here*)

4. Conclusion

In the present study, we have demonstrated the synthesis and polymerization of novel optically active, substituted acetylenic monomers containing both Schiff-base and hydroxy groups using [(nbd)RhCl]$_2$/Et$_3$N catalyst. The produced polymers exhibited optical rotations that were 5–20 times larger than those of the corresponding monomers and intense CD signals at the absorption region of the conjugated polyacetylene backbone, indicating that they form predominantly one-handed helical structures. Polymers **2a** and **2b** containing salicylidene Schiff-base moieties afforded cross-linking polymer/metal complexes through salicylaldimine-metal ion complexation. Taking the advantage of the optical activity and insolubility of these polymer complexes, they are promising as heterogeneous asymmetric catalysts. Polymers **2b** and **2c** exhibited a helix-coil transition upon the addition of HSO_4^-, whereas no detectable CD signal changes were observed in the cases of F^-, Cl^-, and Br^- ions.

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Captions for schemes and figures

Scheme 1. Synthesis of poly(phenylacetylene) derivatives **2a-c**.

Scheme 2. Synthesis of monomers **1a-c**.

Fig. 1. CD and UV-vis spectra of **1a** and **2a**-**c** measured in $CHCl_3$ at 20 °C (c = 0.05 mg/mL).

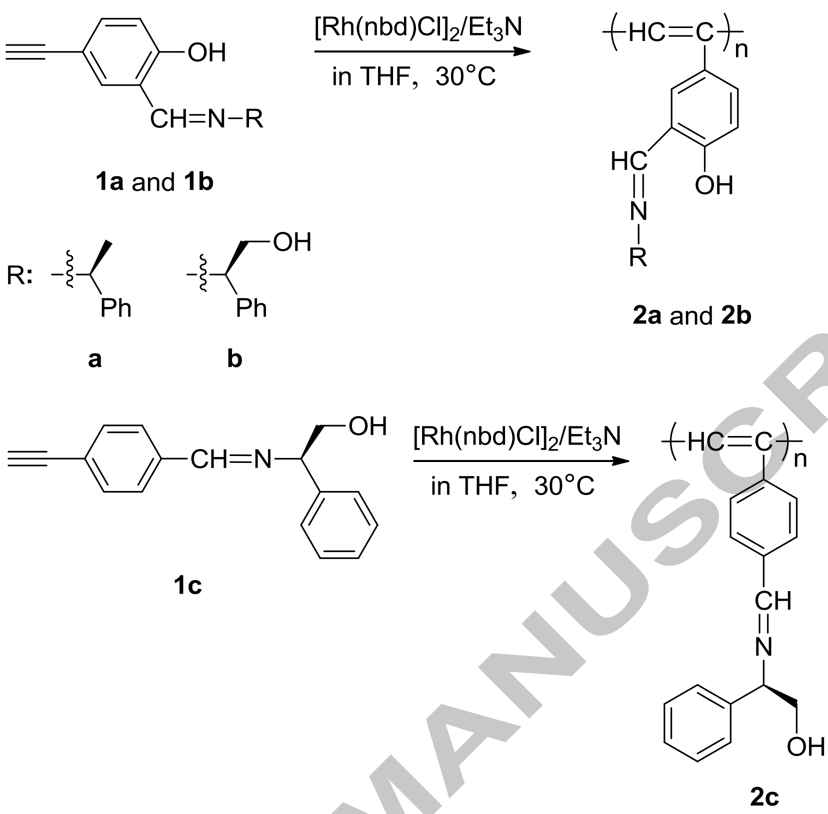
Fig. 2. CD and UV-vis spectra of **2a**-**c** measured in various solvents at 20 °C (c = 0.05 mg/mL).

Fig. 3. CD and UV-vis spectra of **2a**-**c** measured in $CHCl_3$ at various temperatures (c = 0.05 mg/mL).

Fig. 4. IR spectra of **2a** and **2a**/Cu^{2+} complex

Fig. 5. Schematic drawing of **2a**/metal ion complex formed by the coordination of metal ionto **2a**.

Fig. 6. CD and UV-vis spectra of **2c** upon addition of HSO_4^- measured in THF at 20 °C (c = 0.05 mg/mL).



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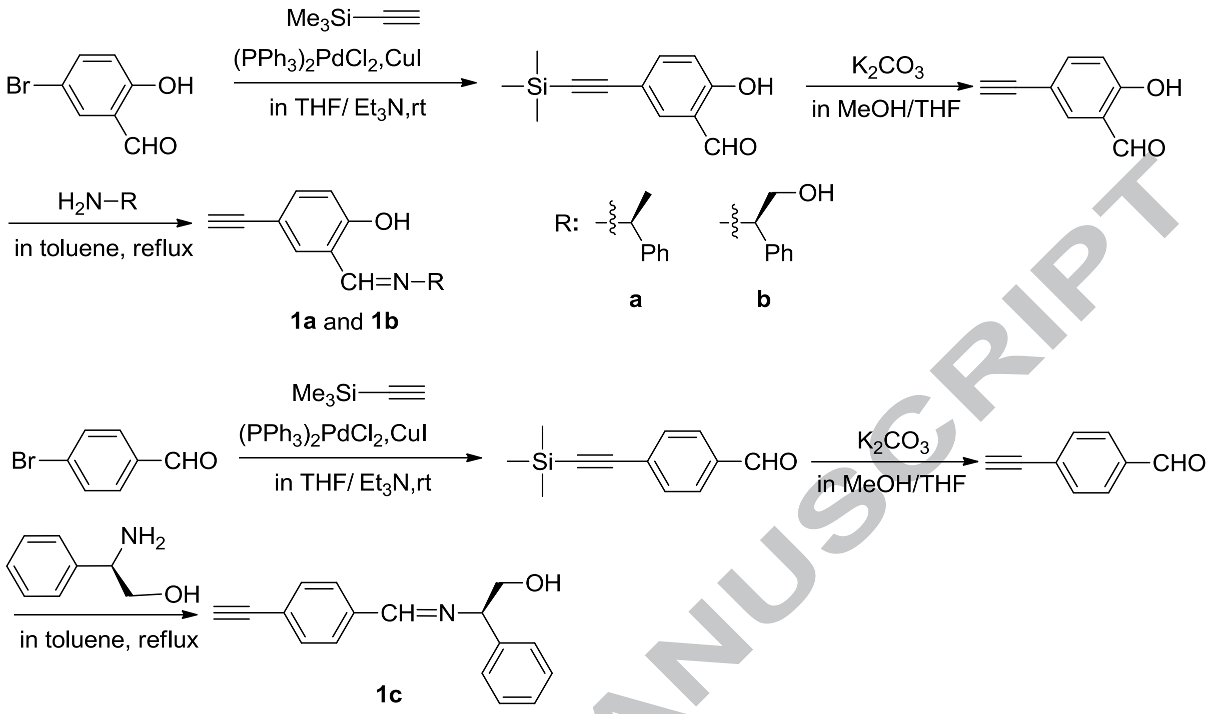
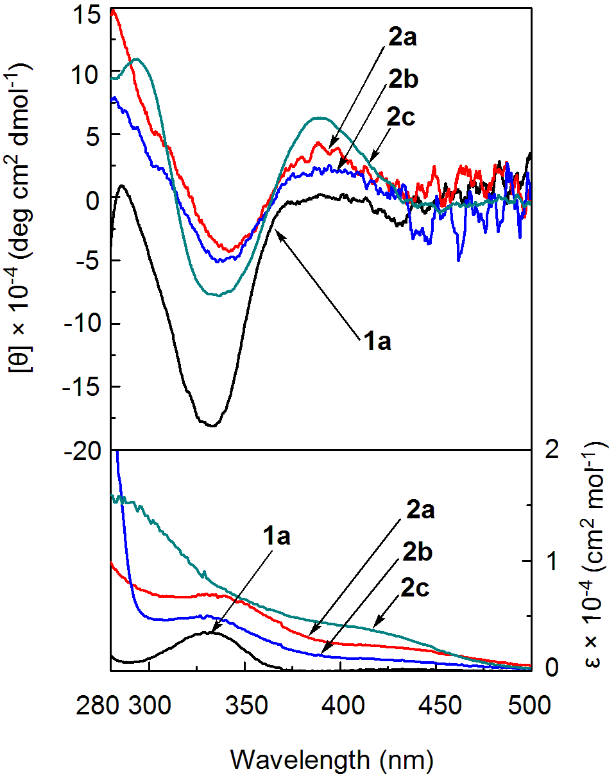


Scheme 2. Synthesis of monomers **1a-c**.



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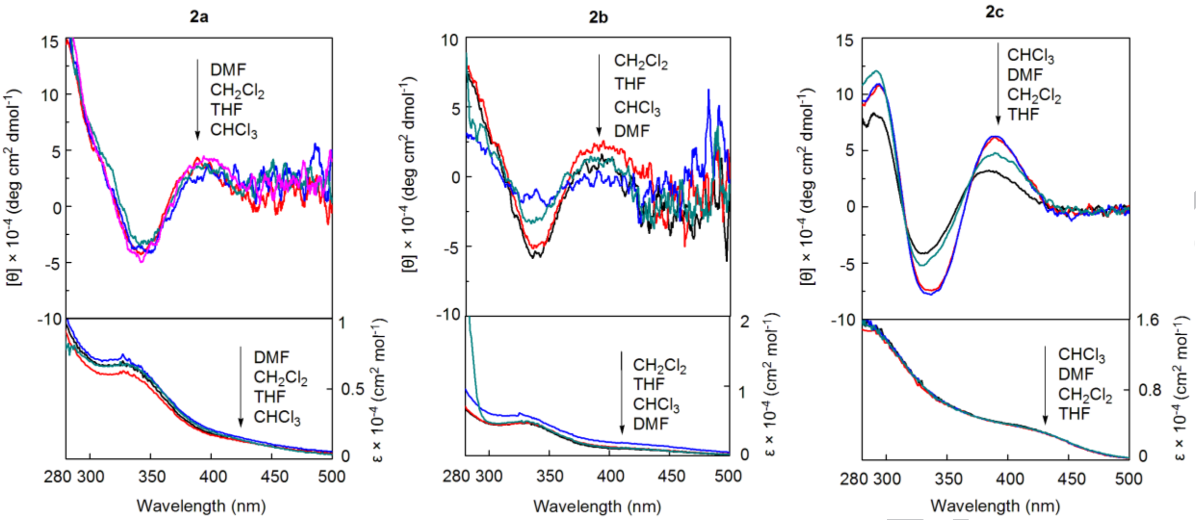
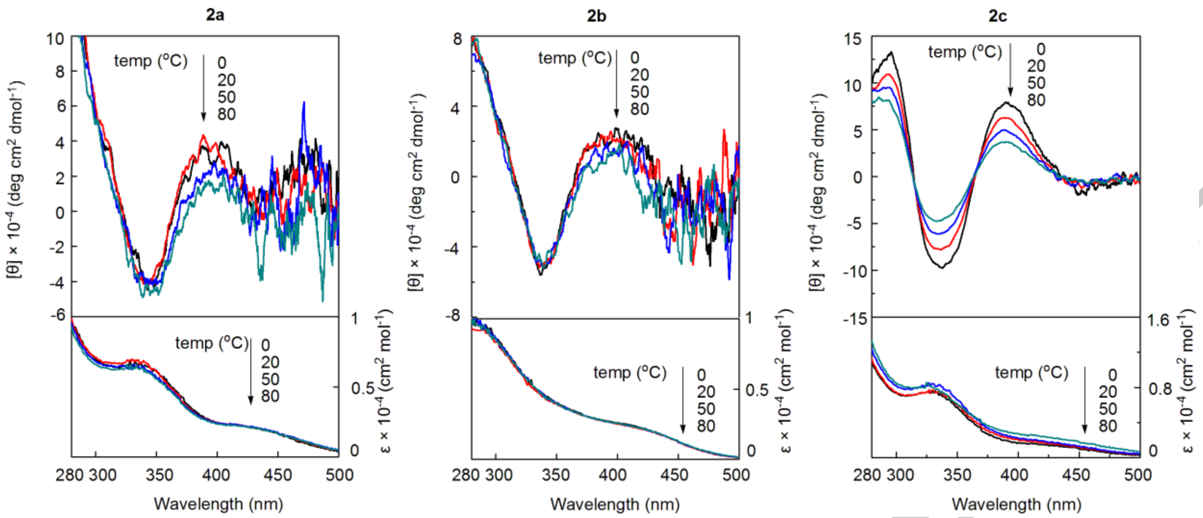


Fig. 2. CD and UV-vis spectra of **2a-c** measured in various solvents at 20 °C (c = 0.05 mg/mL).



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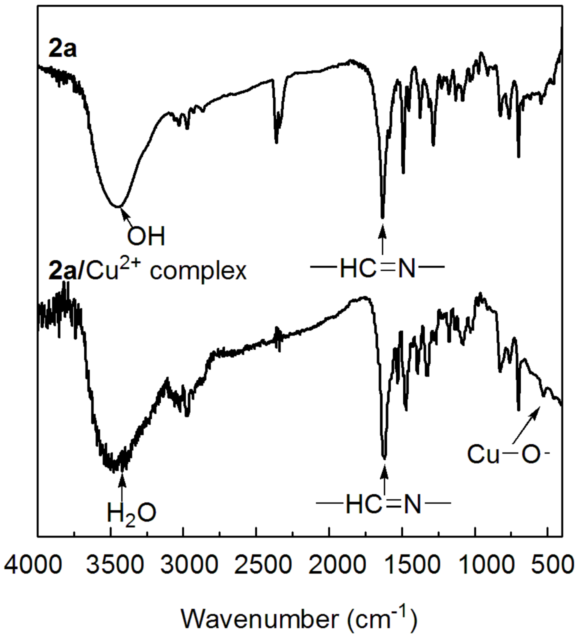

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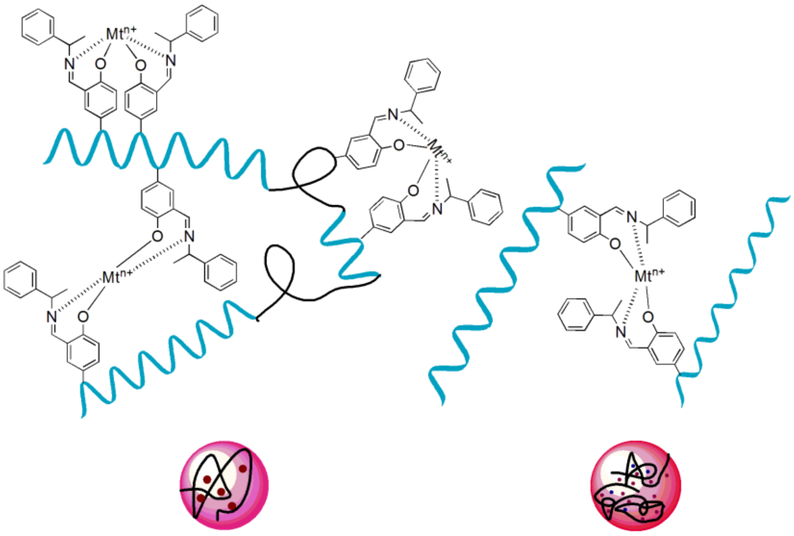

Fig. 5. Schematic drawing of **2a**/metal ion complex formed by the coordination of metal ion to **2a**.

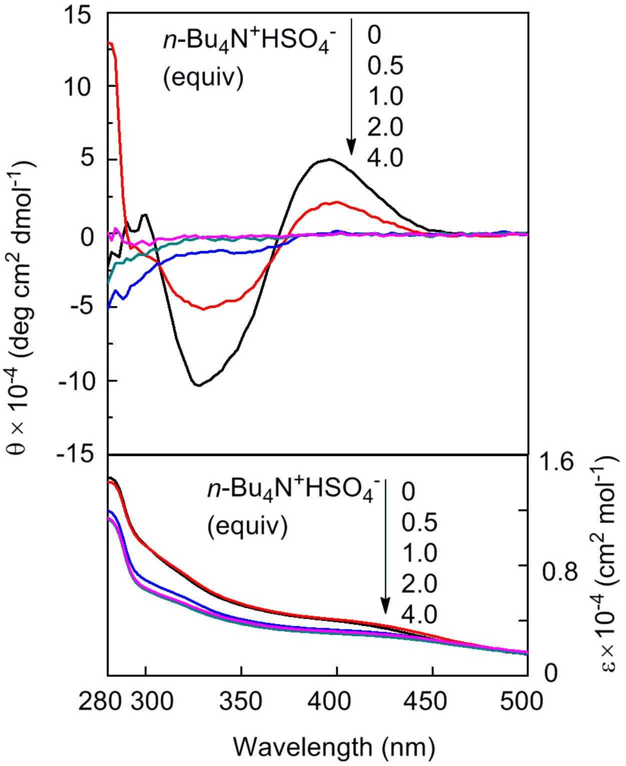

Fig. 6. CD and UV-vis spectra of **2c** upon addition of HSO_4^- measured in THF at 20 °C (c = 0.05 mg/mL).

Table 1

Polymerization of monomers **1a**-**c**.[a]

				$[\alpha]_D$[d] (deg)	
Monomer	Yield[b] (%)	$M_n \times 10^{-5}$[c]	M_w/M_n[c]	Monomer	Polymer
1a	80	3.3	1.1	+23	+291
1b	75	2.6	1.1	+9	+197
1c	96	7.2	1.2	+125	+718

[a] Polymerization conditions: in THF at 30 °C for 4 h, $[M]_0$ = 0.5 mol/L, $[M]_0$/[Rh] = 100.

[b] *n*-Hexane-insoluble part.

[c] Determined by GPC using THF as eluent with a polystyrene calibration.

[d] Measured by polarimetry at 20 °C, c = 0.20 g/dL in $CHCl_3$.