# Facile Preparation of Helical Ladder-type Polymers with Fused Phenoxathiine Rings

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Poly(3-chiral methylsulfinyl-1,2-phenyleneoxide) was synthesized, and the regioselective intramolecular ring-closing of the pendant sulfoxide on the polymer formed the corresponding helical ladder structure comprising of a fused phenoxathiine ring. The CD of the ladder polymer gave a Cotton effect which was caused by the chirality of the pendant group.

A series of helical macromolecules have been studied expecting their potential applications involving chiral separation and sensing, and liquid crystalline formation based on their precisely ordered stereostructure.[1–5] Among the helical macromolecules, helicenes, which are helical molecules comprising of fused aromatic rings, have been focused because of their unique optical activity and stiff structures derived from the aromatic fused-rings.[6–8] However, many synthetic steps and tedious procedures are often required to obtain their non-racemates. We report in this paper, for the first time, the synthesis of a phenoxathiine-based helical ladder polymer, poly[dioxa-3,6-bis(methylsulfonio)-1,2-phenylene]. The key step to form the ladder structure comprising of fused phenoxathiine ring is the one-pot quantitative ring-closing reaction of the pendant alkyl sulfoxide group on the aromatic polymer, which has been already reported by us.[9] In addition, a crucial factor to synthesize the helical molecules is how to control the helicity. In this paper, the intramolecular ring-closing reaction of the pendant sulfoxide group was regioselectively examined in order to induce a one-side bias in the helicity using a chiral hydroxy sulfonium cation, as presented in Scheme 1. Our attempt to synthetically control the helicity of the ladder polymer is also described.

Along with the molecular designing of the target helical ladder structure, the chiral sulfoxide-substituted poly(1,2-phenyleneoxide) was synthesized as the precursor polymer for the following intramolecular ring-closing reaction (Scheme 2). Because the asymmetric oxidation[10] of 4-methoxy-2-(methylthio)phenol **1** did not proceed because of the complexation of the hydroxy group of **1** with titanium tetra(*iso*-propoxide), the chiral

monomer **4**-(**R**)[11] was synthesized by the acetyl protection of **1**, the asymmetric oxidation of **2** to give **3**-(**R**), and the subsequent deprotection. **4**-(**S**)[11] was similarly prepared using (*S,S*)-diethyl tertrate.
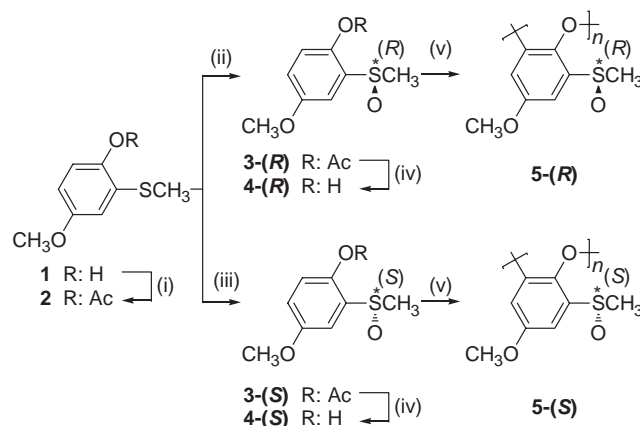
(i) Ac$_2$O, pyridine, rt, 12 h. (ii) *t*-BuOOH, Ti(O-*i*-Pr)$_4$, (*R,R*)-diethyl tartrate, CH$_2$Cl$_2$, H$_2$O, –20 °C, 24 h. (iii) *t*-BuOOH, Ti(O-*i*-Pr)$_4$, (*S,S*)-diethyl tartrate, CH$_2$Cl$_2$, H$_2$O, –20 °C, 24 h. (iv) Na$_2$CO$_3$, CH$_3$OH, H$_2$O, rt, 12 h. (v) Cu(I)Cl, pyridine, nitrobenzene, rt., 24 h.

**Scheme 2.**

The oxidative polymerization of **4**-(**R**) was examined, on the basis of the previous reports regarding the polymerization of phenol derivatives[12,13] using oxidants and oxidative catalysts such as K$_3$[Fe(CN)$_6$],[13a] Ag$_2$O,[13b] PbO$_2$,[13c] a copper-pyridine complex,[13d] and horseradish peroxidase.[13e] The Cu/pyridine-catalyzed polymerization of **4**-(**R**) afforded poly(3-(**R**)-methylsulfinyl-5-methoxy-1,2-phenyleneoxide) (**5**-(**R**))[14] with the molecular weight, $M_n$ of 1800 ($M_w/M_n = 1.2$). The degree of polymerization of ca. 10 for **5**-(**R**) as a polymer. It is enough to form two pitches of the resultant helical ladder polymer (5 benzene units in **6**-(**R**) for 1 helical pitch).

The regioselective intramolecular ring-closing of the pendant sulfoxide group on **5**-(**R**) proceeded by just the addition of triflic acid (without any further treatment) to yield the ring-closed **6**-(**R**) (Scheme 3).[15] For the obtained sample of **6**-(**R**), the $^1$H NMR signal at 2.99 ppm ascribed to the methylene unit adjacent to the sulfur atom of the parent polymer **5**-(**R**) completely disappeared and it was shifted to down-field (3.24 ppm) due to the electron-withdrawing effect of the formed sulfonio group. The signal attributed to the phenyl ring was also shifted to down-field (8.31 ppm) for **6**-(**R**) and the integration value of the proton (1H) agreed with the calculated one based on the fused-ring structure of **6**-(**R**). The UV–vis absorption maximum and shoulder of **6**-(**R**) bathochromically shifted in comparison with those of the pre-polymer **5**-(**R**) to support the extended π-

Intermediate
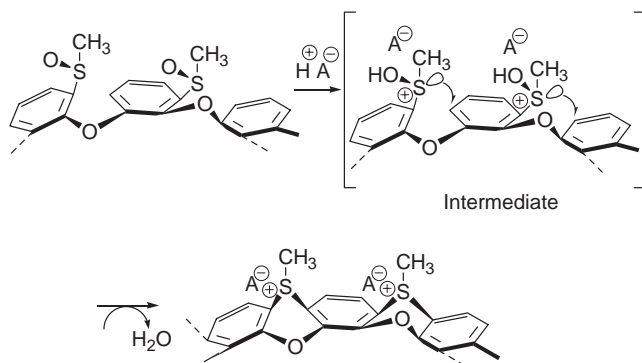
**Scheme 1.**

**Scheme 3.**
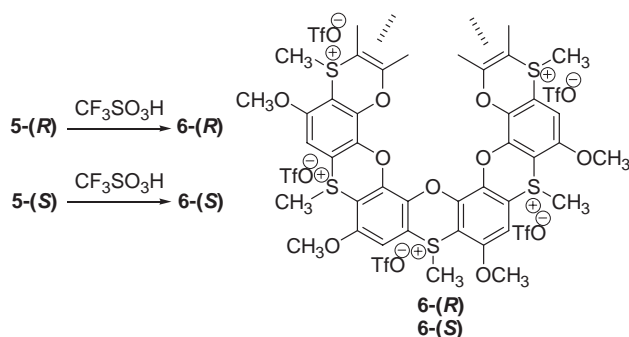
conjugation or the ladder structure of **6**-(**R**). The (**S**)-enantiomers, **5**-(**S**)[14] and **6**-(**S**),[15] were also synthesized according to the same procedure of the corresponding **5**-(**R**) and **6**-(**R**), respectively.

Circular dichroism (CD) of the monomer, **4**-(**R**) and **4**-(**S**), exhibited the peak at 239 nm ascribed to the chirality of the pendant sulfoxide, which also appeared in the CD of the precursors, **5**-(**R**) and **5**-(**S**). However, no Cotton effect was observed beyond the wavelength of 270 nm. On the other hand, **6**-(**R**) and **6**-(**S**) showed the CD extremum at 246 nm and the Cotton effect between 278–350 nm (Figure 1). The former CD extremum was attributed to the chiral sulfonio bridge and the latter broad one corresponded to the $\pi$–$\pi^*$ transition in the UV–vis absorption, suggesting the formation of a helical structure. **6**-(**R**) and **6**-(**S**) had a symmetrical CD profile in the positive and negative sides, which was not influenced by the temperature in the range of 20–50 °C. These results indicated that the helicity of the ladder polymer was caused by the chirality of the monomer. In other words, the helicity of the ladder polymer **6** could be controlled by the enantiotropy of the diethyl tartrate during the asymmetric oxidation of the monomer.
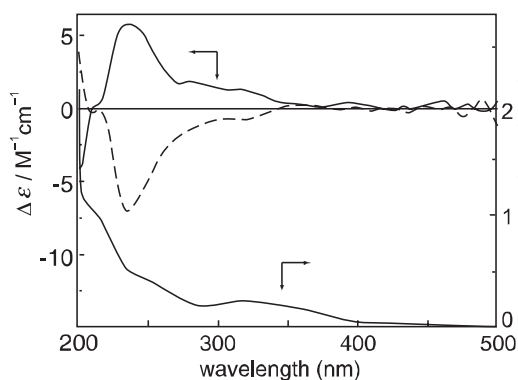


**Figure 1.** UV–vis and CD spectra of 0.1 mM **6**-(**R**) (solid line) and **6**-(**S**) (dashed line) CH₃CN solution.

In summary, a novel helical ladder polymer comprising of fused phenoxathiine ring **6** was synthesized through the regioselective intramolecular ring-closing of the pendant chiral sulfoxide in the poly(1,2-phenyleneoxide) derivative. The mechanism of the helical formation with one-sided bias could be described as follows (Scheme 1). The pendant chiral sulfoxide of **5** was protonated by the superacid to generate the chiral hydroxy sulfonium cation as an intermediate. The cation electrophilically at-

tacked oneside of the neighboring phenylene ring. The bridged chiral sulfonio group located on the oneside of the phenylene ring to yield the helical ladder structure with one-sided bias. This synthetic route is expected to be applicable for the preparation of other sulfur-containing helical ladder polymers.

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11  **4**-(**R**): $[\alpha]^{20}_D$ +87°(*c* 1.00, CHCl₃). **4**-(**S**): $[\alpha]^{20}_D$ −84° (*c* 1.00, CHCl₃).
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14  **5**-(**R**): Yield 72%. $M_n = 1800$ ($M_w/M_n = 1.2$). $[\alpha]^{20}_D$ +128° (*c* 1.00, CHCl₃). UV–vis (CH₃CN, 0.1 mM): $\lambda_{max} = 307$ nm, $\lambda_{shoulder} = 372$ nm). **5**-(**S**): Yield 77%. $M_n = 1800$ ($M_w/M_n = 1.2$). $[\alpha]^{20}_D$ −124° (*c* 1.00, CHCl₃).
15  **6**-(**R**) and **6**-(**S**): Yield: 97%. ¹H NMR (DMSO-$d_6$, 500 MHz; ppm): $\delta$ 8.31 (s, 1H), 3.91 (s, 3H), 3.24 (s, 3H). IR (KBr, cm⁻¹): 1268, 774 ($\nu_{C-F}$), 1259 ($\nu_{C-O-C}$), 1304, 1148 ($\nu_{SO_2}$). UV–vis (CH₃CN, 0.1 mM): $\lambda_{max} = 321$ nm, $\lambda_{shoulder} = 406$ nm.