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Poly(thiaheterohelicene): A Stiff Conjugated Helical Polymer Comprised of Fused Benzothiophene Rings

Tomokazu Iwasaki, Yusaku Kohinata, and Hiroyuki Nishide*

Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan

nishide@waseda.jp

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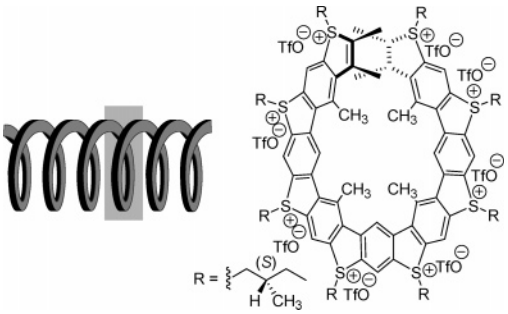
ABSTRACT



A novel helical aromatic polymer comprised of fused benzothiophene rings, poly(thiaheterohelicene), was synthesized via an intramolecular ring-closing reaction with a controlled helicity to one-sided bias. The synthetic helicity control involved the induction of the helical conformation and its fixation. The ladder polymer showed both an extended π-conjugation and planarity and a very stiff helical structure.

Helical macromolecules have a precisely ordered stereostructure and have many potential applications such as chiral separation and sensing using molecular recognition and liquid crystalline formation through molecular ordering.[1−5] π-Conjugated helical molecules comprised of fused aromatic rings are called helicenes and have often been characterized by a unique optical activities caused by their helical conjugation and by a stiff structure.[6] On the other hand, π-conjugated macromolecules with thiophene rings possess a stable doped state due to an excess π-electron conjugation on the thiophene ring and are often highly electron conductive in comparison with other π-conjugated aromatic polymers.[7,8,11c] For this work, a thiaheterohelicene, which is a helical and

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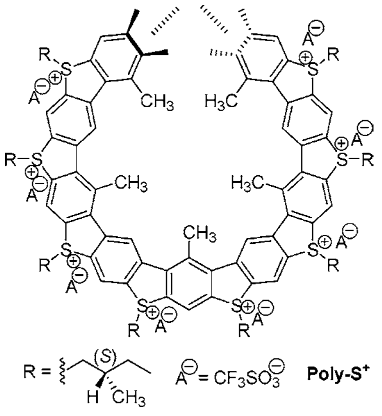


Figure 1.

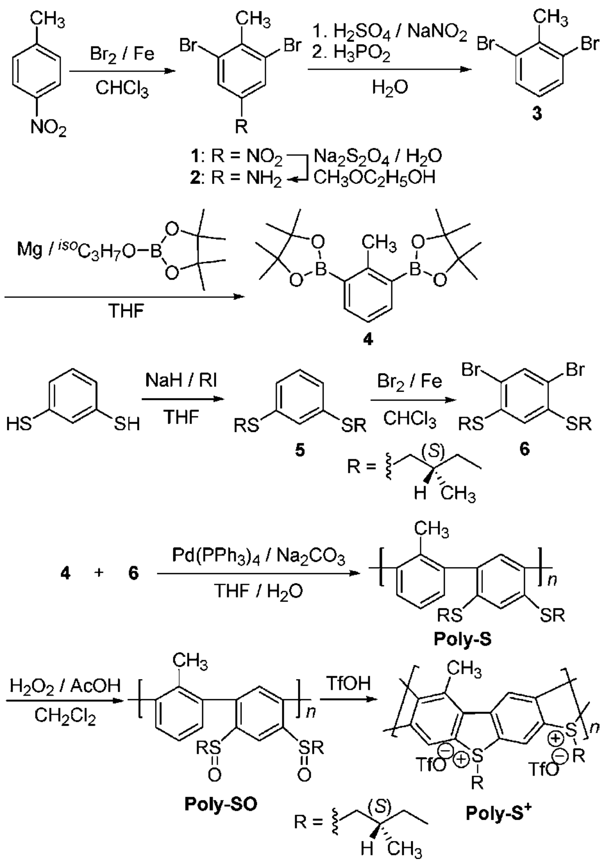
π-conjugated molecule comprised of fused sulfur-containing aromatic rings, was in this study selected as the target molecule bearing an electronic system with a helical structure. Although helical oligomers consisted of fused aromatic rings, including benzene and thiophene rings, have already been synthesized via stepwise synthetic routes,[6,9,10] there have been no reports of a helicene, including thiaheterohelicene, with a high molecular weight or a sufficient number of repeating units to form a helical structure.

An efficient synthetic route to produce poly(thiaacene)s, which are planar and ladder-type molecules, comprised of fused sulfur-containing aromatic rings, has been developed and reported by our laboratory.[11] The key step to form the poly(thiaacene)s is a quantitative intramolecular ring-closing reaction of the alkyl sulfoxide-substituted aromatic polymers. For example, ring-closing within poly[1,4-phenylene-*alt*-2,5-bis(methylsulfinyl)-1,4-phenylene] yielded poly(phenylene-2,5-dithia-1,4-diyl).[11a] This poly(thiaacene) has the fused benzothiophene units that are alternatively linked, or fused, up and down and has a significantly developed π-electron conjugation.[11]

In this study, we successfully used this synthetic method to design and synthesize a poly(thiaheterohelicene), poly[phenylene-4,6-bis(alkylsulfonio)-1,3-diyl triflate] (**Poly-S**$^+$ in Figure 1). We also present, for the first time, a “synthetic” method for controlling the helicity. Helical conformation of the chiral alkylsulfoxide-substituted poly(1,3-phenylene) (**Poly-SO**) was induced using a specific solvent with one-side bias and then was fixed to form a stiff helical structure by covalent bonds through the ring-closing reaction.

The pre-polymer (**Poly-S**) poly[4,6-bis((*S*)-(+)-2-methylbutylthio)-1,3-phenylene-*alt*-2-methyl-1,3-phenylene] was synthesized as shown in Scheme 1, based on the following molecular design. (i) Polycondensation of 2-methyl-1,3-phenylenebis(pinacol borate) (**4**) and 1,5-dibromo-2,4-bis((*S*)-(+)-2-methylbutylthio)benzene (**6**) lead to both a high molecular weight pre-polymer and the introduction of two alkylthio groups for the subsequent ring formation reaction. (ii) The presence of the 2-methyl group of **4** (or one of every other phenylene ring in **Poly-SO**) results in the selective intramolecular and electrophilic attack of the pendant sulfoxides on the favored 4 and 6 positions of adjacent phenylene rings (see the Supporting Information).

Scheme 1



2,6-Dibromotoluene (**3**) was prepared from *p*-nitrotoluene in reasonable yield[12] and converted to 2-methyl-1,3-phenylenebis(pinacol borate) (**4**). The Williamson reaction with subsequent bromination of 1,3-benzenedithiol gave another monomer, 1,5-dibromo-2,4-bis[(*S*)-(+)-2-methylbutylthio]benzene (**6**), in high yield. Pd-catalyzed polycondensation of **4** and **6**[13] yielded the chiral alkylthio-substituted poly(1,3-phenylene), poly[4,6-bis((*S*)-(+)-2-methylbutylthio)-1,3-phenylene-*alt*-2-methyl-1,3-phenylene] (**Poly-S**), which is soluble in the common solvents. The number averaged molecular weight (M_n) of **Poly-S**[14] was 1.1×10^4 ($M_w/M_n = 1.2$, degree of polymerization = 84 based on the phenylene rings), which was sufficient to form 12 helical pitches in the targeted helical polymer.

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(12) Preparation of **3** is shown in the Supporting Information.

(13) The pendant sulfides of **6** were oxidized. The obtained dibromobenzene bearing alkylsulfoxide was enantiopure (>97%) proved by ^{1}H NMR. The sulfoxide derivative was polymerized with **4** by the Suzuki coupling reaction, to afford a low molecular weight oligomer (M_w < 1000).

(14) ^{13}C NMR of **Poly-S** showed eight signals in the aromatic region.

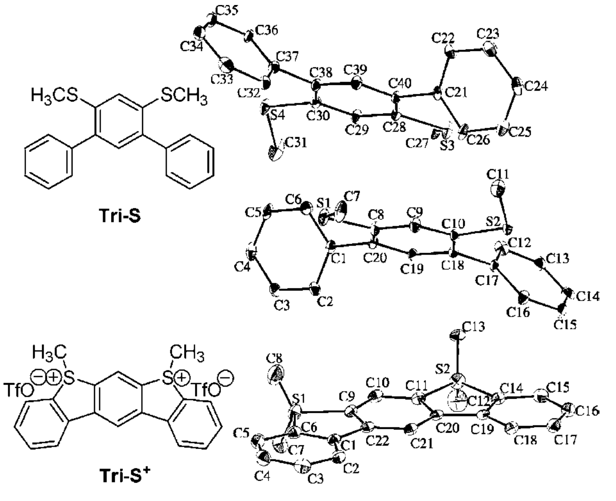

Figure 2. Molecular structure of **Tri-S** and **Tri-S**$^+$. Ellipsoids showed 30% probability levels. Dihedral angles (deg) for selected phenyl and phenylene planes: 40.3 between the C(1)−C(2)−C(3)−C(4)-C(5)−C(6) plane and the C(8)−C(9)−C(10)−C(18)−C(19)−C(20) plane for **Tri-S**; 2.05 between the C(1)−C(2)−C(3)−C(4)−C(5)−C(6) plane and the C(9)−C(10)−C(11)−C(20)−C(21)−C(22) plane for **Tri-S**$^+$.

The pendant alkyl sulfide of **Poly-S** was quantitatively oxidized using peracetic acid to afford the alkyl sulfoxide derivative.[15] Intramolecular ring-closing condensation with excess pure triflic acid or electrophilic attack of the pendant sulfoxide on the 4 or 6 position of the adjacent phenylene unit proceeded slowly in comparison with the previous ladder polymers which were prepared by research group at Waseda.[11a−c] After one week, ring closure gave a ladder polymer in which the tetrahydrothiophenium bridge between the benzene rings was formed without any structural defects based on the NMR spectroscopy.[16] **Poly-S**$^+$ is soluble in chloroform, acetonitrile, and DMF and insoluble in diethyl ether and hexane.

The UV−vis spectrum[17] of **Poly-S**$^+$ showed an absorption maximum (λ_{max}) at 315 nm with a shoulder at 343 nm, which was bathochromically shifted compared to those of the nonring-closed pre-polymer **Poly-SO** (λ_{max} = 281 nm, absorption shoulder = 318 nm), which suggested extended π-conjugation. The planarity in the structure of **Poly-S**$^+$ after ring-closure was studied by an X-ray crystallographic analysis of the trimer model compounds, **Tri-S** and **Tri-S**$^+$,[18] which were prepared via the same reactions for the corresponding polymers (Figure 2).[19] The dihedral angle between the terminal planes and the central phenyl, or phenylene, ring was estimated to be 40.3° and 2.05° for **Tri-S** and **Tri-S**$^+$, respectively. The ring-closing in **Tri-S**$^+$ caused a highly planar structure on the fused benzothiophene moieties.[20]

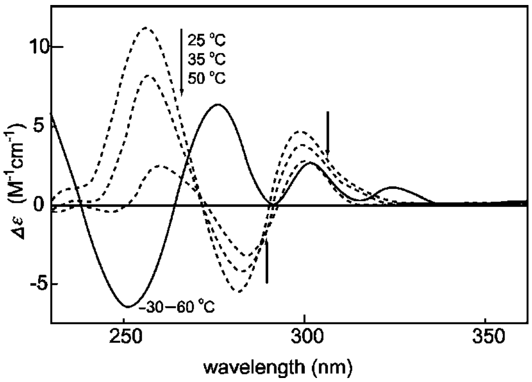

Figure 3. CD spectra of **Poly-SO** in $CHCl_3/CH_3CN$ (1/1) (dotted line) and of **Poly-S**$^+$ (obtained from intramolecular ring-closing reaction in $CHCl_3/CH_3CN$) in $CHCl_3$ (solid line in the given temperature range).

The ladder polymer **Poly-S**$^+$ did not show any Cotton effects in the circular dichroism (CD) when it was dissolved in dichloromethane, DMF, DMSO, or a mixture of three solvents with ether or hexane. This suggested that the polymer was involved equally in a mixture with a right- and left-handed helical sense. On the other hand, three Cotton effect-based CD maxima appeared at 256 (positive), 283 (negative), and 298 (positive) nm for **Poly-SO** in a mixture of chloroform and acetonitrile (a poor solvent), used as a solvent, although no Cotton effects were observed when only chloroform (a good solvent) solution was used as a solvent. CD intensity significantly decreased with solution temperature in the range from 25 to 50 °C. These results indicated that solvophobic forces induced the formation of a helix for **Poly-SO** (Figure 3).

Methods for controlling helical bias, or helicity, in helical polymers have been studied. For example, a discussion recently focused on the helical conformation of aromatic conjugated polymers with pendant chiral groups in a mixture of so-called good and poor solvents.[21,22] We intended in this

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[15] The oxidation conditions such as reaction concentration, temperature, and time were optimized. The sulfide completely disappeared in the ^1H NMR spectrum. Any peroxidation of the sulfide, such as to the sulfone, did not occur, evidenced by the absence of a peak attributed to the sulfone bond (1150, 1350 cm^{-1}) in the IR spectrum (see the Supporting Information).

[16] Ring-closing or the fused-ring formation of **Poly-S**$^+$ was proved by ^1H NMR, as follows. The signal of the methylene units adjacent to the sulfur atoms shifted to a lower magnetic field (2.99 ppm) from that of the precursor sulfoxides (2.57 ppm) due to the electron-withdrawing by the sulfonio group. Integral values of the protons derived from the phenyl ring (3H), the aryl methyl group (3H), and the methylene units on the sulfonio bridges (4H) completely agreed with those calculated for the repeating units of **Poly-S**$^+$.

[17] All of the UV−vis and CD measurements were carried out in a 0.2 mM solution.

[18] Layering the chloroform solution of **Tri-S** with hexane afforded colorless needlelike crystals suitable for an X-ray diffraction study. The colorless needlelike crystals of **Tri-S**$^+$ were obtained from an acetonitrile solution layered with diethyl ether. The details of the X-ray crystallographic data are shown in the Supporting Information.

[19] **Tri-S** was synthesized by Suzuki coupling of 1,5-dibromo-4,6-bis(methylthio)benzene (1 equiv) and phenylboronic acid (2 equiv) with Pd(PPh_3)$_4$ (1/50 equiv) in a mixture of THF and aqueous Na_2CO_3 solution (for details, see the Supporting Information).

[20] λ_{max} = 272 nm (for **Tri-S**), 299 nm (for **Tri-S**$^+$).

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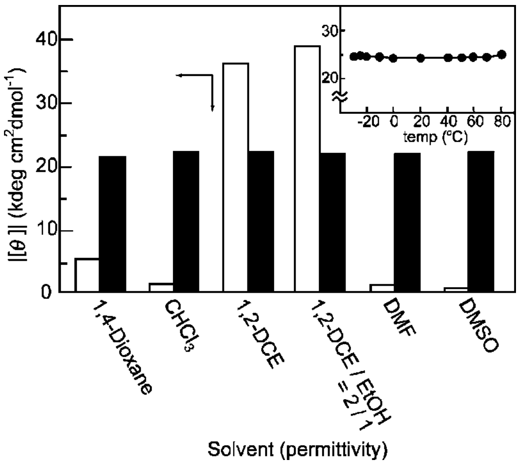

Figure 4. CD intensity of **PolyS**$^+$ (at 278 nm, solid column) and PBG (at 224 nm, open column) in various solvents; (inset) −30 to +80 °C temperature dependence of the CD absorbance for **PolyS**$^+$ in DMF (at 278 nm, solid circle). 1,2-DCE = 1,2-dichloroethane.

study to develop synthetic helicity-fixation. The helical conformation of **Poly-SO** was first induced in a mixture of chloroform and acetonitrile (v/v = 1/1), and its helicity was fixed in **Poly-S**$^+$ through the ring-closing reaction. The experimentally obtained **Poly-S**$^+$ gave four CD maxima based on the Cotton effects at 251, 275, 302, and 325 nm (negative, positive, positive, and positive, respectively) not only in the chloroform and acetonitrile mixture but also in pure chloroform. This indicated that the helicity of **Poly-S**$^+$ is maintained with a one-side bias and that **Poly-S**$^+$ possesses a stiff helical structure.

The stiffness of the π-conjugated helical structure of **Poly-S**$^+$ was studied using poly(γ-benzyl-L-glutamate) (PBG)[23] as a control example of a stiff helical polymer.[3,24] The CD intensity of **Poly-S**$^+$ (at 278 nm) and PBG (at 224 nm)[25] in several solvents and in the temperature range of −30 to +80 °C were examined and are shown in Figure 4. The CD intensity and profile of **Poly-S**$^+$ did not change even at high temperatures and did not depend on the solvent, Figure 4.[26]

In summary, a novel poly(thiaheterohelicene) **Poly-S**$^+$ comprised of fused benzothiophene rings, which has π-conjugated ladder structure, was synthesized. The helical structure was maintained over a wide range of temperatures and in a variety of solvents. We have simulated the electronic conduction of poly(thiaheterohelicene) based on a nanometer-sized electronic device,[27] and it suggested not only that electron transmittance occurs along the helical π-conjugation under a lower bias voltage (around the Fermi level of Au) but also that a solenoid-like induced magnetism occurs. Poly(thiaheterohelicene) is a good candidate for studying the one-dimensional wire in an organic molecular-based electromagnet.

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Supporting Information Available: Synthesis and characterization of the monomers and polymers and details of the X-ray crystallographic analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] Poly(γ-benzyl-L-glutamate) was purchased from the Aldrich Co., and its molecular weight was M_w = 37 000.

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[25] The CD absorptions at 278 nm (for **Poly-S**$^+$) and 224 nm (for PBG) correspond to their λ_{max} values in the UV−vis absorptions.

[26] Permittivity; 1,4-dioxane = 2.24, CHCl$_3$ = 4.90, 1,2-DCE = 10.45, DMF = 36.71, and DMSO = 48.90 (from *Chemical Safety Data Sheets*; Royal Society of Chemistry: London, 1990; Vol. 1).

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