



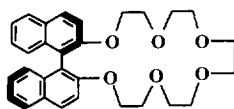
The First Sterically Regular Chiral Conjugated Crown Ether Polymer

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Abstract: The coupling of (*S*)-6,6'-dibromo-2,2'-binaphtho-20-crown-6 with 1,4-diethynyl-2,5-dioctadecyloxybenzene in the presence of Pd(PPh₃)₄ and CuI catalysts leads to the formation of the first sterically regular chiral conjugated crown ether polymer. This polymer is soluble in organic solvents. GPC analysis shows that the molecular weight of this polymer is $M_w = 10,500$ and $M_n = 5,300$ (PDI = 2.0). $[\alpha]_D = 120.9$ ($c = 0.95$, THF). Another soluble crown ether polymer has also been made from the racemic binaphthyl monomers. Its molecular weight is $M_w = 27,900$ and $M_n = 11,500$ (PDI = 2.4). Copyright © 1996 Elsevier Science Ltd

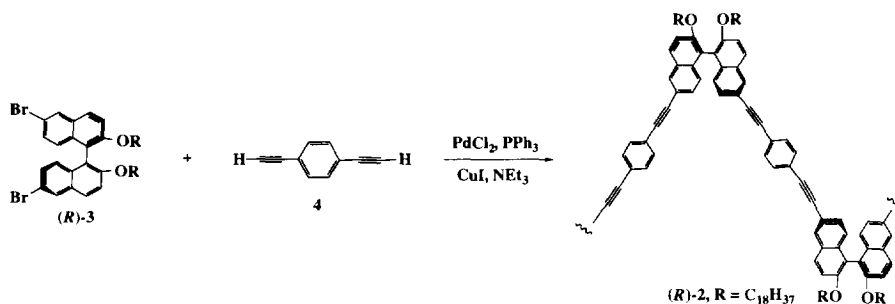
The molecular recognition capability of chiral binaphthyl crown ethers such as (*R*)-2,2'-binaphtho-20-crown-6, (*R*)-**1**, has been studied extensively by Cram *et al.*¹ These molecules have shown enantioselective



(*R*)-**1**

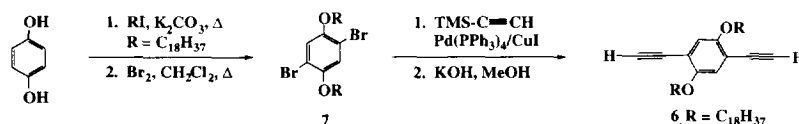
recognition of chiral amino acids^{1a} and have been used to catalyze the asymmetric Michael addition.^{1b} The binaphthyl crown ether functions have also been covalently bonded to the sterically irregular polystyrene backbone for enantioselective separation of amino acids.^{1c} Recently, a poly(binaphthyl crown ether) coated electrode prepared by electropolymerization of the racemic crown ether, *rac*-**1**, on platinum has been used as a sensor to selectively detect catecholamines that are known as important neurotransmitters.² However, no spectroscopic and structural information about this electrochemically generated polybinaphthyl crown ether has been obtained. Herein, our synthesis and spectroscopic characterization of the first sterically regular chiral conjugated crown ether polymer is reported.

We have used the optically active binaphthyl compounds to construct the main chain chiral conjugated polymers as novel electrical and optical materials^{3a-c} and as a new generation of polymeric catalysts.^{3d} For example, a sterically regular chiral poly(aryleneethynylene) (*R*)-**2** has been obtained by using the PdCl₂/CuI catalyzed polymerization of a chiral binaphthyl dibromide monomer (*R*)-**3** with 1,4-diethynylbenzene, **4** (Scheme 1).^{3a} In order to synthesize the desired binaphthyl crown ether polymers, both racemic and (*S*)-6,6'-dibromo-2,2'-binaphtho-20-crown-6, *rac*-**5** and (*S*)-**5**, are prepared from the reaction of 6,6'-dibromo-1,1'-bi-2-naphthol with pentaethylene glycol ditosylate.^{1d} However, when *rac*-**5** is polymerized with **4** in the presence of Pd(PPh₃)₄/CuI catalysts, the resulting polymer is insoluble in regular organic solvents.



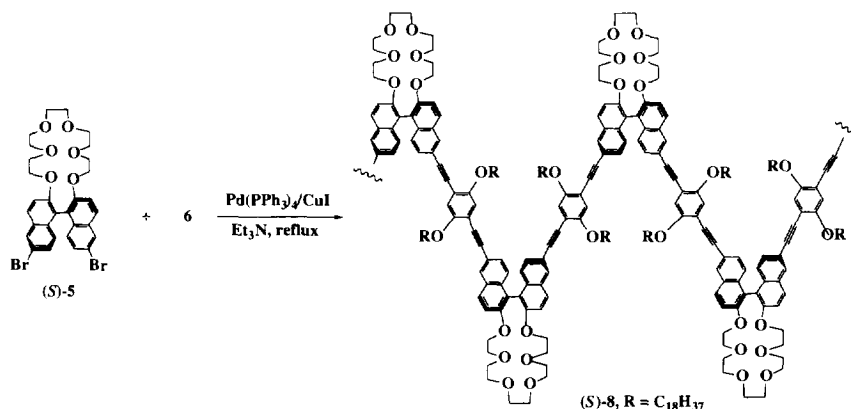
Scheme 1. An Optically Active Poly(aryleneethynylene) (R)-2.

To make soluble crown ether polymers, long chain alkyl groups are introduced to the conjugated linker molecule **4**. From hydroquinone, 1,4-diethynyl-2,5-dioctadecyloxybenzene, **6**, is prepared (Scheme 2).⁴ Alkylation of hydroquinone with excess iodoctadecane followed by bromination gives **7**. The cross coupling



Scheme 2. Synthesis of an Alkylated Bishynylbenzene Linker.

of **7** with trimethylsilyl acetylene followed by desilylation with base produces **6**. This long chain alkyl substituted linker molecule is polymerized with (*S*)-**5** to generate a crown ether polymer (*S*)-**8** (Scheme 3). The optical purity of (*S*)-**5** is greater than 99.9% as determined by HPLC analysis using a Chiralcel OD column made by Chiral Technologies Inc. Under nitrogen, a mixture of (*S*)-**5** (124.1 mg, 0.192 mmol), **6** (127.0 mg, 0.192 mmol), Pd(PPh₃)₄ (10.8 mg, 0.0093 mmol) and CuI (5.1 mg, 0.027 mmol) in triethyl amine (9.5 mL) was heated at reflux for 2.5 d. After filtration of the resulting triethylammonium salt, the solvent was removed.



Scheme 3. Synthesis of the Sterically Regular Chiral Conjugated Crown Ether Polymer (*S*)-**8**.

The residue was dissolved in methylene chloride and precipitated with methanol three times to give polymer (*S*)-**8** as a brown solid in 86% yield. (*S*)-**8** is the first sterically regular chiral conjugated crown ether polymer where all of the binaphthyl units have one *S* configuration in the rigid polymer chain. This polymer is soluble in regular organic solvents such as methylene chloride, chloroform and THF. Gel permeation chromatography (GPC) analysis of (*S*)-**8** relative to polystyrene standards shows its molecular weight is $M_w = 10,500$ and $M_n = 5,300$ (PDI = 2.0). In our earlier report, the LLS study of (*R*)-**2** indicates that the actual molecular weights of these binaphthyl-based poly(aryleneethynylene)s are normally higher (by ca. 1.4 - 2.5 times) than what are measured by GPC analysis relative to polystyrene standards.^{3a} The specific optical rotation of (*S*)-**8** is $[\alpha]_D = 120.9$ ($c = 0.95$, THF), the opposite sign of the optical rotation of the monomer (*S*)-**5** $\{[\alpha]_D = -8.3$ ($c = 0.95$, THF) $\}$. The ^1H NMR spectrum of this polymer displays three resonance regions: the aromatic protons at δ 7-3, the methylene protons adjacent to the oxygen atoms at δ 3-4, and the alkyl protons at δ 1-2. The ^{13}C NMR spectrum of (*S*)-**8** shows two multiplets at δ 86.1 and 95.5 corresponding to the alkyne carbons in the polymer. In the UV spectrum of (*S*)-**8** in methylene chloride solution, absorption maxima are observed at 240, 296, 334 and 378 nm. This polymer is a strongly fluorescence material with emission maxima at 420, 445 and 455 nm when excited at 378 nm in methylene chloride solution.

(*S*)-**8** also exhibits strong Cotton effects in its circular dichroism (CD) spectrum (Figure 1). The molecular ellipticity of this polymer is: $[\theta]_\lambda = -3.72 \times 10^5$ (233 nm), 1.88×10^5 (251 nm), 5.21×10^4 (285 nm), -8.86×10^3 (349 nm), 3.46×10^4 (398 nm). Figure 2 is the CD spectrum of the monomer (*S*)-**5** with Cotton effects: $[\theta]_\lambda = -8.55 \times 10^5$ (233 nm), 9.12×10^5 (246 nm), -6.25×10^4 (293 nm) and -2.73×10^4 (331 nm). The major difference between the monomer and the polymer is that a long wavelength CD effect at 398 nm is observed for the polymer due to its more extended conjugation.

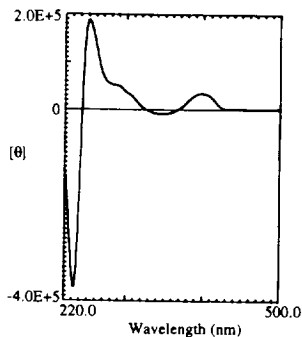


Figure 1. The CD Spectrum of (*S*)-**8**.

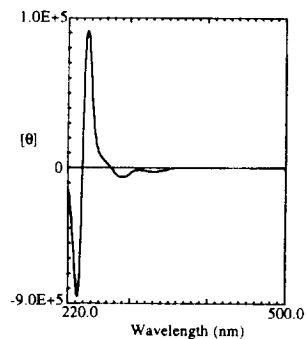
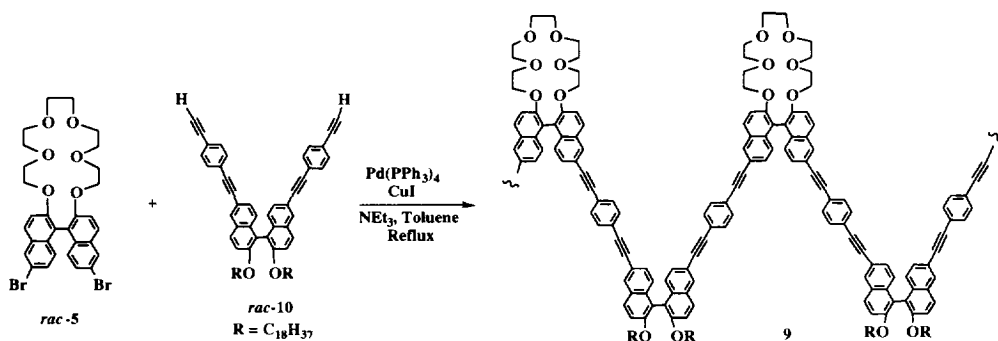


Figure 2. The CD Spectrum of (*S*)-**5**.

A higher molecular weight poly(binaphthyl-crown-ether), **9**, is obtained from the polymerization of *rac*-**5** with *rac*-**10**, another racemic binaphthyl monomer⁵ (Scheme 4). This polymerization is carried out in a refluxing triethylamine-toluene solution in the presence of $\text{Pd}(\text{PPh}_3)_4$ and CuI catalysts. The resulting polymer **9** has a molecular weight of $M_w = 27,900$ and $M_n = 11,500$ (PDI = 2.4) as measured by GPC. **9** is also soluble in regular organic solvents. Two multiplets at δ 89 and 92 are observed for the alkyne carbons of this polymer in its ^{13}C NMR spectrum. The UV spectrum of **9** shows $\lambda_{\text{max}} = 246, 300$ and 354 nm. (*S*)-**8** absorbs at significantly longer wavelength than **9** because of the two extra alkoxy donors in the repeat unit of (*S*)-**8**.



Scheme 4. Synthesis of a Soluble and Optically Inactive Crown Ether Polymer **9**.

In summary, binaphthyl-based rigid crown ether polymers have been synthesized. These materials are soluble in common organic solvents and have been characterized by various spectroscopic methods. Strong CD effects are observed for the sterically regular chiral crown ether polymer. Recently, Swager *et al.* have shown that conjugated polymers containing molecular receptors such as crown ethers and cyclophanes can be used as efficient conductivity sensors and fluorescence sensors.⁶ With the incorporation of chirality into conjugated polymers, polymers like (*S*)-**8** are potentially useful as novel chiral sensors. These polymers can be also applied in asymmetric catalysis.

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