

Conjugated Polymers with Main Chain Chirality. 1. Synthesis of an Optically Active Poly(arylenevinylene)[†]

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Conjugated polymers such as polyacetylene, poly(*p*-phenylene), and poly(*p*-phenylenevinylene) have attracted considerable attention during the past two decades. These materials have demonstrated remarkable electronic and optical properties including electroluminescence, nonlinear optical effects, and high conductivities upon doping.² Optically active conjugated polymers are potentially useful materials. For example, they can be used to prepare ferroelectric liquid crystals and to prepare chiral electrodes for asymmetric electrosynthesis. However, remarkably few studies in this area have been reported.³ Recently, Grubbs *et al.* described the synthesis of soluble chiral polyacetylenes.^{3a} In their system (Scheme 1), a cyclooctatetraene substituted with an optically active alkyl group undergoes ring-opening metathesis polymerization by reaction with a tungsten carbene catalyst to give a chiral conjugated polyacetylene. The chiral side groups in the polymer are observed to twist the main chain in predominantly one screw sense to generate a disymmetric chromophore. Other examples of chiral conjugated polymers have been prepared including polypyrrroles and polythiophenes containing optically active functional groups.^{3b-d} In all cases, these polymers have their chirality derived from chiral side groups. In our laboratory, we are interested in the synthesis of conjugated polymers with main chain chiral configuration. We anticipate that these novel materials will provide enhanced chiral induction in asymmetric electrosynthesis due to their main chain chirality.

We chose 1,1'-bi-2-naphthol, **1**, and its derivatives as building blocks in the construction of main chain chiral conjugated polymers because of their outstanding asymmetric differentiation properties.⁴ The chirality of binaphthyl compounds is derived from the restricted rotation of the two naphthalene rings. The angle between the two naphthalene rings ranges from 60° to 120°.^{4d} The chiral configuration of binaphthyls is remarkably stable. For certain optically active binaphthyl molecules, no significant racemization in solution is observed at temperatures in excess of 200 °C.⁵ These molecules have been used in a number of asymmetric processes either as chiral ligands for metal catalysts or as chiral reagents.⁴ Optically active binaphthyls have also been applied to make chiral packing materials for enantioselective chromatographic separations.⁶ Racemic **1** (*rac-1*) can be obtained by using a copper(II)-catalyzed oxidative coupling of 2-naphthol in air.⁷ By

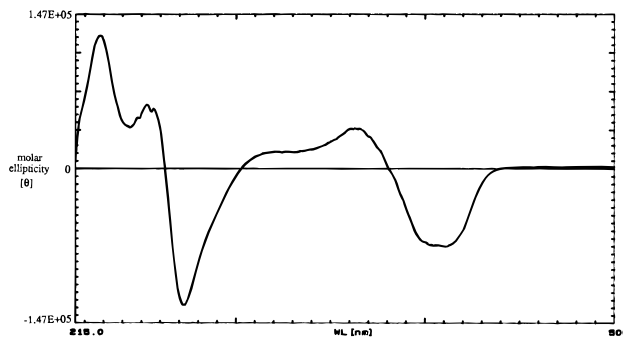


Figure 1. CD spectrum of (*R*)-7.

using (8*S*,9*R*)-(-)-*N*-benzylcinchonidinium chloride, **2**, as an inclusion crystallization agent, optically pure (*R*)-**1** can be obtained from *rac-1*.⁸ We have improved this method to obtain both (*R*)-**1** and (*S*)-**1** with high optical purities and on a large scale.⁹ In a typical experiment, 60 g of *rac-1* is resolved to give 22.5 g of (*R*)-**1** (>99% ee) and 21 g of (*S*)-**1** (>99% ee). The chiral resolving agent **2** is recovered in 80% yield.

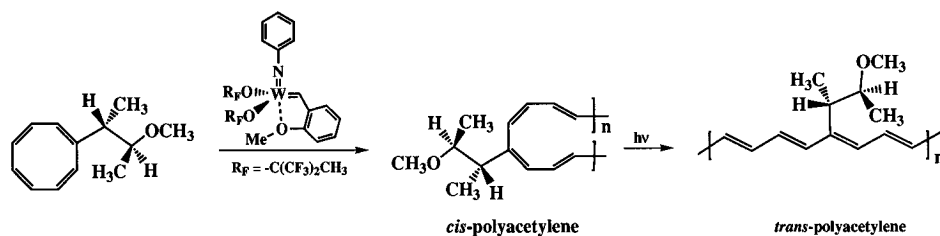
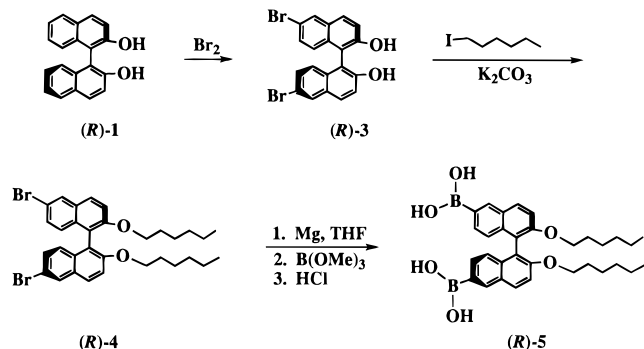
We generate chiral conjugated polymers from (*R*)-2,2'-bis(hexyloxy)-1,1'-binaphthyl-6,6'-diboronic acid, (*R*)-**5**, which can be readily prepared from (*R*)-**1** (Scheme 2). Bromination of (*R*)-**1** gives 6,6'-dibromo-1,1'-bi-2-naphthol, (*R*)-**3**, in 95% yield.^{6a,10} Reaction of (*R*)-**3** with 1-iodohexane in the presence of base produces the alkylated product (*R*)-**4** {[α]_D = 25.9° (*c* = 0.52, THF)} in 95% yield. (*R*)-**4** can be converted to (*R*)-**5** in 50% yield by reaction with magnesium to form a bifunctional Grignard reagent followed by treatment with trimethyl borate and acidic hydrolysis.^{11,12} The optical rotation of (*R*)-**5** is [α]_D = 35.6° (*c* = 0.22, DMSO).

The palladium-catalyzed Suzuki coupling of (*R*)-**5** with 1,4-bis(*p*-bromostyryl)benzene (*E:Z* = 1:1.2),¹³ **6**, leads to an optically active conjugated polymer (*R*)-**7** (Scheme 3).¹⁴ Analysis of the polymer by GPC (THF, polystyrene standard) shows *M*_n = 20 000 and *M*_w = 67 000 (PDI = 3.4). This polymer is soluble in common organic solvents (e.g., THF, benzene, toluene, pyridine, chlorobenzene, methylene chloride, chloroform, and 1,2-dichloroethane). Self-standing films can be prepared by evaporation of the solvent from a polymer solution. The polymer contains a mixture of *cis* and *trans* double bonds. In the ¹H NMR spectrum of (*R*)-**7**, a broad peak at δ 6.61 is assigned to the *cis* protons of the vinylenes and the *trans* proton signals overlap with aromatic signals (> δ 7). The NMR integration indicates a *trans*:*cis* ratio of 1:0.45 for the polymer. The optical rotation of the polymer is [α]_D = -351° (*c* = 0.38, THF). Figure 1 is the circular dichroism (CD) spectrum of (*R*)-**7** in THF (2.73×10^{-5} M).¹⁵ The observed CD effects are consistent with a chiral conjugated π system for (*R*)-**7**.^{3a}

Following a similar procedure, *rac-7* has been prepared from the Suzuki coupling of the racemic monomer, *rac-5*, and **6**. *rac-7* is most likely composed of a mixture of diastereomeric polymers containing both *R* and *S* binaphthyl units. Analysis of *rac-7* by GPC shows *M*_n = 17 000 and *M*_w = 48 000 (PDI = 2.8). The *trans*:*cis* ratio of *rac-7* is the same as that of (*R*)-**7** based on ¹H NMR analysis. Both (*R*)-**7** and *rac-7* are green solids. The UV spectra of (*R*)-**7** and *rac-7* show an absorption maximum at λ_{max} = 390–392 nm. The fluorescence spectra of the polymers show a maximum emission at λ = 468 nm when excited at 390 nm. These polymers emit strong blue light under a UV lamp. The fluores-

[†] Dedicated to Professor Henry Taube at Stanford University on the occasion of his eightieth birthday.

Scheme 1. Ring-Opening Metathesis Polymerization of an Optically Active Cyclooctatetraene

Scheme 2. Synthesis of the Chiral Monomer (*R*)-5

cence quantum yield of *rac*-7 in toluene solution is about 50% by comparison to that of 9-anthracenecarboxylic acid.¹⁶ Interestingly, the fluorescence quantum yield of (*R*)-7 in toluene is greatly enhanced to 80%. Thus, the optically active polymer has a much greater fluorescence quantum efficiency than the polymer derived from the racemic monomer. Thin films of the polymers that have been spin-coated onto glass slides can be oxidatively doped by exposure to an acetonitrile solution of NOBF₄. The doped conductivities for both (*R*)-7 and *rac*-7 range from 4×10^{-5} to 7×10^{-5} S cm⁻¹.

Thermogravimetric analysis (TGA) shows that (*R*)-7 is stable up to 340 °C under N₂. Differential scanning

calorimetry (DSC) indicates a glass transition temperature (*T*_g) for (*R*)-7 at 210 °C. Analysis of *rac*-7 by TGA suggests that (*R*)-7 is less stable than *rac*-7, which begins to lose mass at 390 °C. The *T*_g of *rac*-7 is observed at 203 °C.

To characterize the packing and microscopic structure of these polymers, we have conducted a systematic atomic force microscopy (AFM) study.¹⁷ Figure 2 shows the AFM images of thin films of (*R*)-7 and *rac*-7 spin-coated on mica. Mica is chosen because of its atomically flat (0001) surface.¹⁸ Therefore, any corrugations observed in the AFM images can be attributed to the polymers instead of the substrate.^{17b} Each mica surface is freshly cleaved before spin-coating to avoid contamination. As can be seen from the topographic images of (*R*)-7 and *rac*-7, the two films exhibit different surface morphologies. Although both are somewhat rough and porous, (*R*)-7 films have larger domains (thousands of angstroms) separated by pits or holes ranging from 50 to >200 Å in depth. *rac*-7, on the other hand, is composed of smaller domains, only hundreds of angstroms, and the corrugation is only tens of angstroms. Scans of areas smaller than those shown in Figure 2 are taken systematically by zooming into the polymer domains. No long-range order (or periodicity) is found, however, on either of the films.

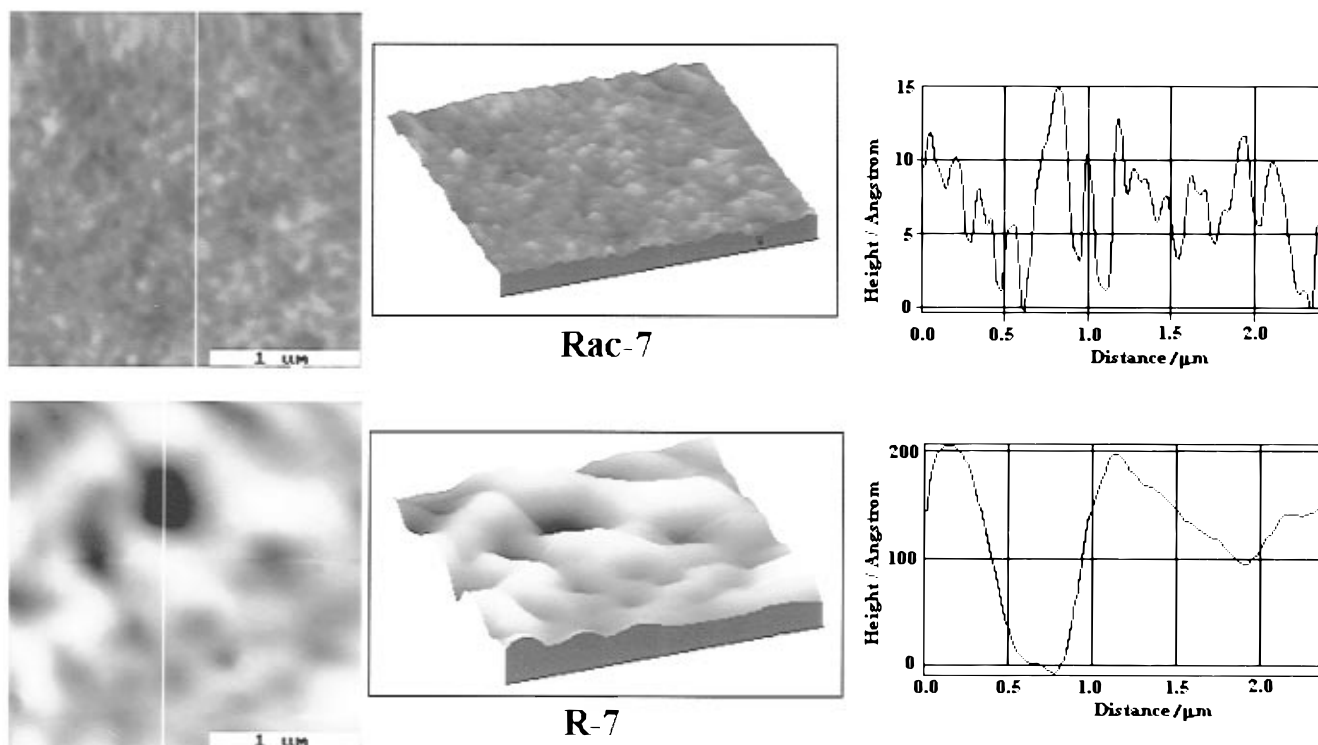


Figure 2. AFM images ($2 \times 2 \mu$ scans) of *rac*-7 (top) and (*R*)-7 (bottom). Images were taken under ambient conditions using a home-built AFM¹⁸ and a Digital cantilever with a force constant of 0.58 N/m. The force (or load) used for the two images is 6 nN. Both images were raw data with only background correction.

