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Synthesis of an Optically Active Poly(aryleneethynylene) Containing Extended Conjugation in the Repeat Unit.

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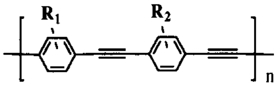
Abstract: A binaphthyl-based chiral poly(aryleneethynylene) (*R*)-**9** that contains significantly longer conjugated repeat unit than the previously reported such materials has been synthesized. GPC analysis of (*R*)-**9** shows that its molecular weight is Mw = 38,200 and Mn = 29,000 (PDI = 1.3). The specific optical rotation of this polymer is $[\alpha]_D = -288.6$ (c = 0.5, CH_2Cl_2). Although the conjugated repeat unit of (*R*)-**9** contains a total of 54 π electrons, this polymer is still soluble in regular organic solvents. The polymer made of racemic binaphthyl units is also prepared. Copyright © 1996 Elsevier Science Ltd

The study of polyaryleneethynylenes, e.g., **1**, has been carried out and these materials have exhibited interesting electroluminescent property as well as nonlinear optical property.[1] Recently, we have synthesized the optically active poly(aryleneethynylene)s[2a] such as (*R*)-**2** by using the palladium catalyzed coupling of binaphthyl monomers, e.g., (*R*)-**3**, with *para*-phenylene linker molecules, e.g., 1,4,-bisethynylbenzene **4** (Scheme 1). (*R*)-**2** represents a class of novel main chain chiral conjugated polymers prepared in our laboratory.[2] These materials are potentially useful in asymmetric electrosynthesis, chiral catalysis and chiral



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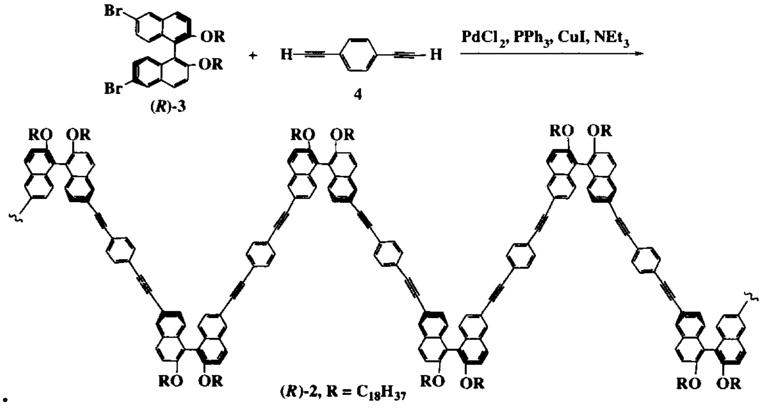
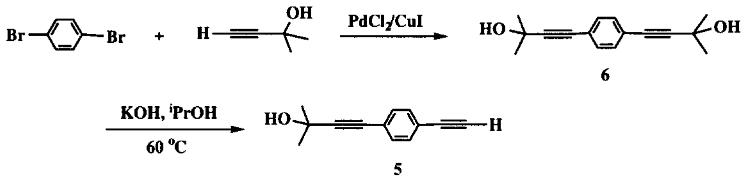


Scheme 1.

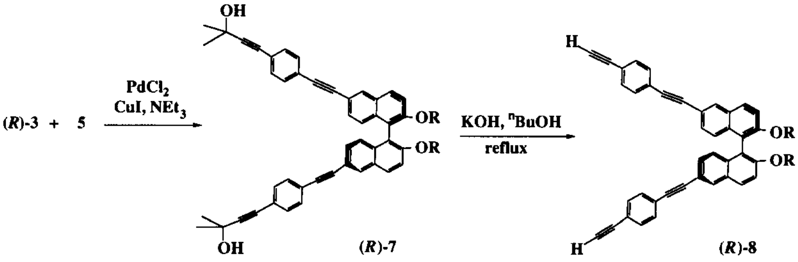
sensing. Herein, we report our synthesis and characterization of a chiral poly(aryleneethynylene) that contains a much more extended conjugation in its repeat unit than (*R*)-**2**.

A monoprotected 1,4-bisethynylbenzene **5** is prepared for the synthesis of the monomer for the polymerization (Scheme 2). The cross-coupling of 1,4-dibromobenzene with 2-methyl-3-butyn-2-ol in the presence of $PdCl_2$/CuI gives **6**. Partial deprotection of **6** by heating its isopropanol solution at 60 °C in the presence of potassium hydroxide produces **5** in 65% yield.[3,4]



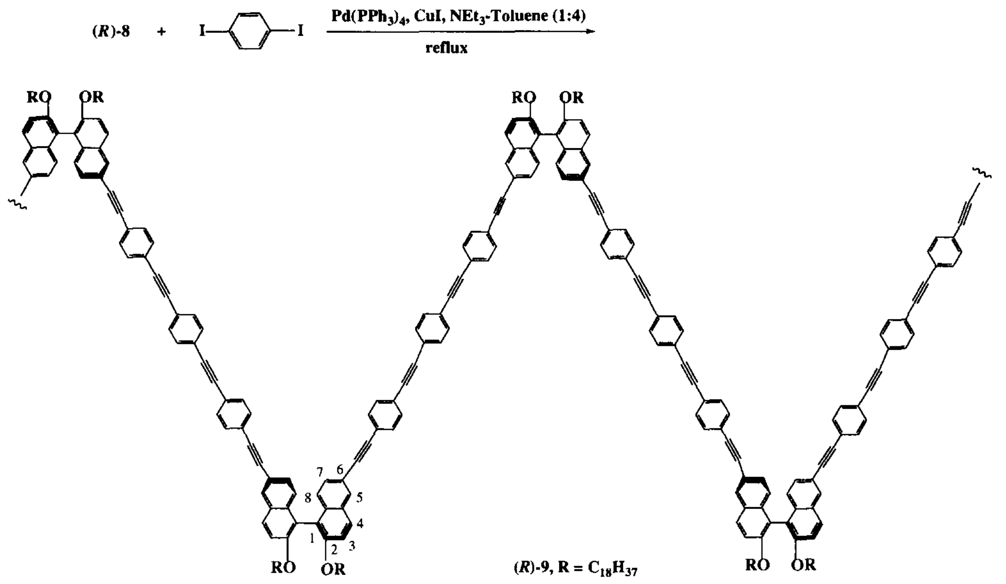
Scheme 2. Synthesis of Monoprotected 1,4-Bisethynylbenzene **5**.

Coupling of **5** with (*R*)-**3** gives (*R*)-**7**. Base-promoted deprotection of (*R*)-**7** produces a chiral binaphthyl monomer (*R*)-**8** (Scheme 3).[3] The structure of (*R*)-**8** is characterized by high resolution fast atom bombardment mass spectroscopy, IR and NMR analyses. The ^1H NMR signal of the terminal alkyne protons is observed at δ 3.18 (s). The IR spectrum of (*R*)-**8** displays a medium absorption at 3302 cm^{-1} for the alkyne C-H stretch and two weak absorptions at 2204 and 2108 cm^{-1} for the triple bond stretch. The specific optical rotation of (*R*)-**8** is $[\alpha]_D = -176.3$ ($c = 1.0$, CH_2Cl_2). The UV spectrum of (*R*)-**8** in methylene chloride shows $\lambda_{max} = 240$, 298 and 334 nm. The optical purity of (*R*)-**8** is greater than 99% as determined by HPLC analysis using a Chiralcel OD column made by Chiral Technologies Inc.



Scheme 3. Synthesis of the Chiral Binaphthyl Monomer (*R*)-**8**.

This chiral binaphthyl monomer is polymerized with 1,4-diiodobenzene to generate (*R*)-**9** (Scheme 4). The reaction is carried out by adding tetrakis(triphenylphosphine)palladium(0) (5 mol %) and cuprous iodide (5 mol %) to a triethyl amine-toluene (1:4) solution of (*R*)-**8** (0.25 mmol) and 1,4-diiodobenzene (0.25 mmol). The resulting mixture is heated at reflux under nitrogen for 25 h and is then filtered to remove the produced insoluble triethylamine hydrobromide salt. The polymer (*R*)-**9** is purified by dissolution in methylene chloride and precipitation with methanol multiple times. The yield of the polymer is 98%. Gel permeation chromatography (GPC) analysis of (*R*)-**9** using THF eluent and polystyrene standards shows that the molecular weight of this polymer is $M_w = 38,200$ and $M_n = 29,000$ (PDI = 1.3). A laser light scattering study of (*R*)-**2** has been carried out earlier[2a] which indicates that the GPC results of this class of poly(aryleneethynylene)s using polystyrene as the standard are normally smaller (by ca. 1.4 to 2.5 times) than the actual molecular weights of these materials.



Scheme 4. Synthesis of the Conjugation Extended Chiral Poly(aryleneethynylene) (*R*)-**9**.

Although the conjugated repeat unit of (*R*)-**9** contains a total of 54 π electrons (!), this polymer is still soluble in regular organic solvents such as chloroform, methylene chloride and THF. We have found that longer reaction time will produce insoluble polymers because the molecular weights may be too high. The specific optical rotation of (*R*)-**9** is $[\alpha]_D = -288.6$ ($c = 0.5$, CH_2Cl_2). The ^1H NMR spectrum of (*R*)-**9** is fairly well-resolved. In the aromatic region, 6 major signals are observed for the polymer. The singlet at δ 8.06 is assigned to H-5 of the binaphthyl unit. Four doublets at δ 7.91, 7.42, 7.30 and 7.11 with a coupling constants of ca. 8.6 Hz are the signals of the remaining two pairs of adjacent protons on the binaphthyl unit. A broad and intense signal at δ 7.50 is due to the 1,4-phenylene protons. Although in the ^1H NMR spectrum of (*R*)-**9**, no difference can be observed between the phenylene protons, four distinctive ^{13}C NMR signals at δ 92.4, 91.2, 90.8 and 88.8 are observed for the four kinds of alkyne carbons in the polymer. These NMR analyses support the structure of the polymer. The IR spectrum of (*R*)-**9** shows a weak absorption at 2205 cm^{-1} for the alkyne triple bonds in the polymer. The UV-vis spectrum of (*R*)-**9** in methylene chloride solution displays absorption maximums at $\lambda_{max} = 238$ and 366 nm. Strong fluorescence of this polymer is observed at 420, 464 and 500 (sh) nm.

The racemic monomer *rac*-**8** has also been polymerized with 1,4-diiodobenzene to generate *rac*-**9** by applying the same condition used for the preparation of (*R*)-**9**. This polymer is also soluble in organic solvents.

GPC analysis shows the molecular weight of *rac*-**9** is Mw = 42,000 and Mn = 20,000 (PDI = 2.1). The spectroscopic data of *rac*-**9** are almost identical to those of the optically active polymer (*R*)-**9**.

The circular dichroism (CD) spectrum of (*R*)-**9** in methylene chloride solution shows strong Cotton effects. The molecular ellipticity of the polymer is [θ] = +4.46 x 10^5 (235 nm), -7.74 x 10^4 (262 nm), -1.21 x 10^5 (284 nm), +3.94 x 10^4 (338 nm) and -2.03 x 10^5 (385 nm). As shown in Figure 1 where the CD spectra of (*R*)-**9** and (*R*)-**2** are compared, due to the more extended conjugation in (*R*)-**9**, it has significantly larger negative Cotton effect at the longer wavelength. Further study of this polymer will be carried out.

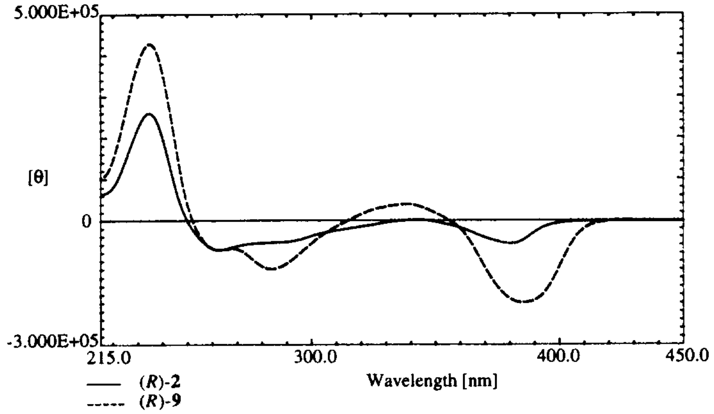


Figure 1. Comparison of the CD Spectra of (*R*)-**9** with (*R*)-**2** in Methylene Chloride Solution.

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4. Characterization of **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 3.16 (s, 1H), 2.02 (s, 1H), 1.63 (s, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 131.9, 131.5, 95.6, 82.7, 81.6, 78.8, 64.8, 31.4.

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