Cu-Catalyzed Couplings

Novel Pathways for the Formation of Chiral Binaphthyl Polymers: Oxidative Asymmetric Phenolic Coupling Alone and in Tandem with the Glaser–Hay Coupling**

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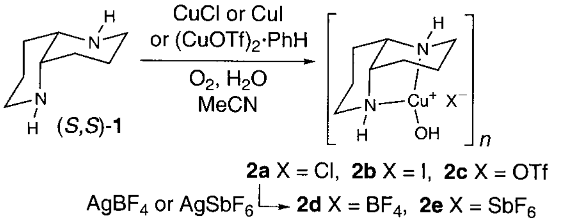
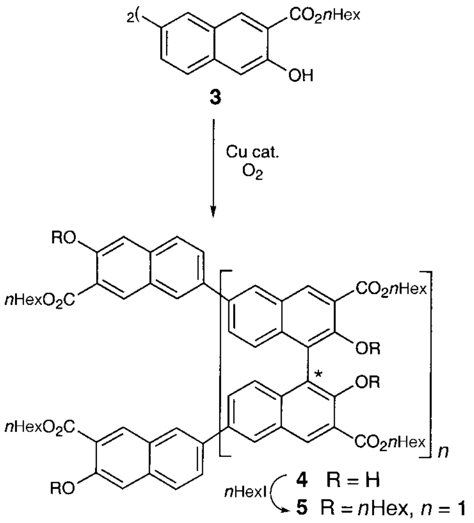
Conjugated polymers have exhibited a number of notable properties including high doped conductivity, electroluminescence, and optical nonlinearity.[1] Optically active versions are potentially important; however, few have been studied. Because of the important properties[2] that chiral polybinaphthyls[3] exhibit as well as their successful applications in asymmetric catalysis,[4] the synthesis of binaphthyl polymers with different functionality and the development of new methods for more efficient polymerization are important.

In this communication we describe the synthesis of new ester-functionalized chiral 1,1′-binaphthol polymers by oxidative coupling of achiral components with 1,5-diaza-*cis*-decalin catalysts **2** (Scheme 1).[5] Prior reports of the preparation of chiral binaphthyl polymers begin with chiral 1,1′-binaphthyl monomers. To our knowledge, the enantioselective synthesis of chiral polybinaphthyls has not been reported.[6]



Scheme 1. Preparation of chiral catalysts **2**. Tf = trifluoromethanesulfonyl.

Oxidative coupling of polymer precursor **3** with the achiral catalyst CuCl(OH)·TMEDA (**6**, TMEDA = tetramethylethylenediamine) yielded two fractions, **4a** and **4b**, with different molecular weight distributions (Scheme 2, Table 1, entry 1). The number-average molecular weights M_n from the integrations of the NMR signals for the internal and terminal units correlate with the data from gel-permeation chromatography (GPC).[7] When **3** was polymerized with the chiral CuI catalyst **2b** (Scheme 1) which we reported previously,[5] the reactivity was poor; a low molecular weight material **4c** (50–52 % yield) was obtained which contained *ortho*-iodinated by-products.



Scheme 2. Polymerization of 6,6′-linked naphthalenes.

In a search for more reactive catalysts that would not cause substrate halogenation, we synthesized the new complexes **2c–e** (Scheme 1). It was necessary to effect halogen exchange to **2d,e** from the Cu^{II} complex **2a** as the metal complexes formed by in situ oxidation of the Cu^I diamine adducts with Ag^I salts were characterized by poor catalytic activity. Reactions with the resultant CuOTf and $CuSbF_6$ catalysts were relatively slow. However, the $CuBF_4$ catalyst was as selective as the CuI catalyst and substantially more reactive. With **3** (Table 1, entries 2 and 3), the yield and the degree of polymerization to give the new ester-functionalized polymers **4d** were substantially higher.

In undertaking these polymerizations, we were concerned whether the chiral biaryl from the first enantioselective coupling would influence the stereochemical outcome of the subsequent diastereoselective couplings. Work by Okamoto et al.[6] showed that such substrate diastereocontrol alters the stereochemical induction obtained with a chiral catalyst in related systems. To measure asymmetric induction in these polymerizations, **3** was treated with (*S,S*)-**2d** under milder conditions (3 h, 60 °C) to provide the dimer (*R*)-**4e** and trimer (*R,R*)-**4f**. CSP (chiral stationary phase) HPLC of the bisether **5** (Scheme 2) revealed that dimer **4e** formed with 85 % *ee*. While HPLC resolution of the trimer was not possible, the ^{1}H NMR spectrum showed 70–75 % *de*. Enantioselectivity of 85 % *ee* in each biaryl coupling would lead to 72 % *de* [85.5 % (*R,R*)-**4f**, 14.0 % (*S,R*)-**4f**, 0.5 % (*S,S*)-**4f**], consistent with this NMR measurement. Thus, each biaryl coupling in the polymerization is independent, proceeding with 85 % *ee*; stereocontrol from catalyst **2d** prevails over substrate diastereocontrol. The CD spectra[7] of the enantiomeric polymers **4d** show mirror Cotton effects, indicating that the enantiomeric catalysts indeed produce enantiomeric polymers. The spectra of the polymer are very similar to those of dimer **4e**

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Table 1: Treatment of **3** with selected Cu catalysts (Scheme 2).[a]

Entry	Cat.	Prod.	Yield [%]	M_w[b]	M_n[b]	PDI[b,c]	$[\alpha]_D^{RT}$	Int:term[b,d]
1	**6**	**4a**	37	4800	3100	1.56	–	4.7:1
		4b	25	8500	5800	1.48	–	9.6:1
2	(*R*,*R*)-**2d**	(*S*)$_n$-**4d**	74	10500	4900	2.14	+78	8.1:1
3	(*S*,*S*)-**2d**	(*R*)$_n$-**4d**	78	12300	5400	2.29	−89	8.9:1

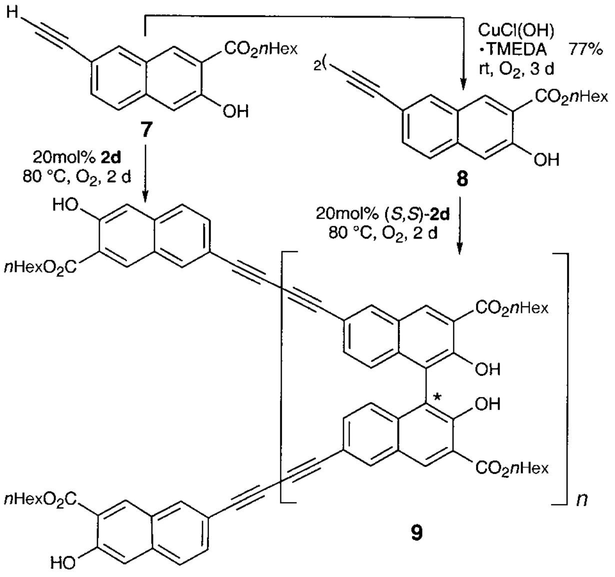
[a] Reactions were 2–5 d at 40–80 °C with 10–20 mol% catalyst. [b] Determined by GPC with a polystyrene standard. [c] PDI = M_w/M_n. [d] Ratio of internal to terminal units.

and trimer **4f** (same maxima and minima) except that the signals are more intense owing to the greater number of naphthalene units in the chain.[8]

Chiral polybinaphthyls typically contain naphthalene units that are linked by means of 1,1′-bonds and 2,2′-, 3,3′-, or 6,6′-connections. In prior reports and the work described above, polybinaphthyls are constructed from "monomers" in which one set of these linkages is already formed. A more efficient method for preparing such polymers would be to create both sets of linkages simultaneously. To test this proposal we prepared monomers **7** and **10**, which contain two sites that we hypothesized would react in the presence of **2d**—an alkyne terminus and a naphthol.

The Glaser–Hay coupling[9] of the terminal arylalkynes is very rapid and occurs prior to the phenolic coupling, as demonstrated by the formation of **8** (77% yield) upon treatment of **7** with CuCl(OH)·TMEDA (Scheme 3). Further polymerization by phenolic coupling was accomplished by subjecting diyne **8** to (*S,S*)-**2d** to provide **9** in 90% yield (Table 2). When monomer **7** was subjected to these same conditions, polymer **9** (73% *ee* for each biaryl coupling) was produced directly (Table 2). The UV and CD spectra[7] of polymer **9** generated from either **7** or **8** were identical, which indicates that catalyst **2d** can effect both the alkynyl and phenolic coupling cleanly (Figure 1). No cross-coupling and no interference by alkynylcopper intermediates on the stereochemical course of the biaryl coupling were observed. Finally, when a substituted 1,1′-binaphthol corresponding to the repeating unit of **9** (Scheme 3) was polymerized through alkyne–alkyne coupling, the structure of the resultant product was identical to that of polymer **9** from either **7** or **8** (Figure 1), even though the termini are alkynyl instead of naphthalenyl.

With alkyl alkynes we discovered that the Glaser–Hay coupling is slower than the phenolic coupling. For example, treatment of alkyl alkyne monomer **10** with 10 mol% CuCl(OH)·TMEDA at room temperature provided only the simple biaryl coupling product (±)-**11** (61% yield,



Scheme 3. Polymerization of arylalkynyl-2-naphthols.

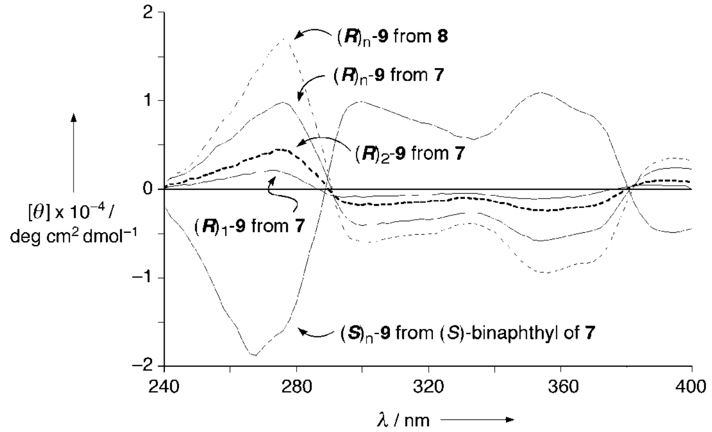
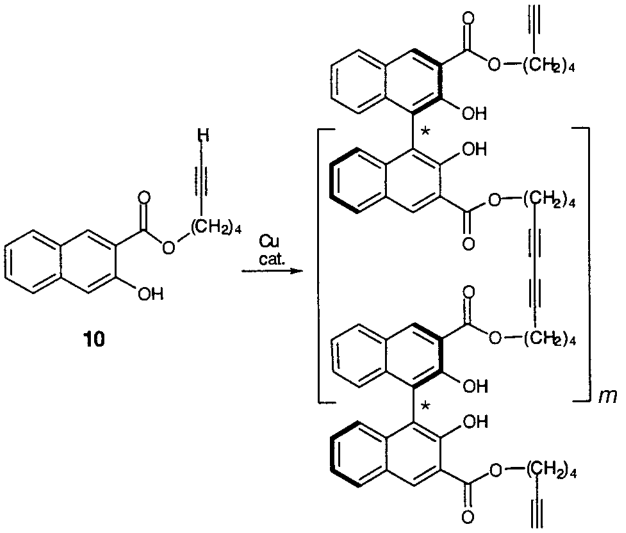


Figure 1. CD spectra of **9** (2×10^{-5} M in CH_2Cl_2).

Table 2: Treatment of **7**, **8**, and **10** with catalyst **2d** (Schemes 3 and 4).[a]

Monomer	**2d**	Product	Yield [%]	M_w[b]	M_n[b]	$[\alpha]_D^{RT}$
8	(*S*,*S*)	(*R*)$_n$-**9**	90	12900	4400	−248
7	(*S*,*S*)	(*R*)$_n$-**9**	80	9200	4900	−168
7	(*R*,*R*)	(*S*)$_n$-**9**	86	15100	6800	+174
10	(*R*,*R*)	(*S*)$_n$-**11**	60	10300	3900	−180

[a] Reactions were 2 d at 80 °C with 20 mol% catalyst. [b] Measured by GPC with a polystyrene standard.



10

$(S)_n$-**11**, $n = m+1$

Scheme 4. Polymerization of alkylalkynyl-2-naphthols.

Scheme 4). The polymeric form incorporating both alkyl alkynyl and binaphthol coupling, $(S)_n$-**11**, could be generated directly from **10** by using 20 mol% (R,R)-**2d** (Scheme 4, Table 2, entry 4). Interestingly, the optical rotation of polymer $(S)_n$-**11** is negative while the optical rotation of the related polymer $(S)_n$-**9** (Scheme 3) is positive (Table 2, entry 3). Even though both compounds possess the same binaphthol configurations and a diyne unit, the optical absorption properties are substantially different due to the location of the linking units. This conclusion is supported by the CD spectra of these polymers; one negative absorption ($\lambda = 270$ nm) and two positive absorptions (302, 356 nm) are observed for $(S)_n$-**9**, while $(S)_n$-**11** is characterized by two strong negative absorptions (252, 262 nm) and one weaker positive absorption (308 nm).

The mirror Cotton effects from the CD spectra of polymers **9** (Figure 1) and **11** indicate that the enantiomeric catalysts indeed produce enantiomeric polymers. In addition, the CD spectra of **9** and **11** largely resemble those of their corresponding dimeric and trimeric forms, which indicates that the diyne-linked polymers described herein do not adopt a secondary helical conformation beyond the individual chiral binaphthyl units.

In conclusion, we report the first enantioselective synthesis of functionalized chiral polybinaphthyls from achiral starting materials. We use chiral copper catalysts to effect enantioselective oxidative biaryl coupling of 2-naphthols alone and in tandem with Glaser–Hay coupling. Since the functional group tolerance is high,[10] a large number of structures are accessible with this method. The CD and UV spectra (see Supporting Information) of the functionalized polybinaphthyls support the formation of chiral polybinaphthyls, with different linking units giving rise to different overall structures. The relative reaction rates of various substrates with the chiral catalysts follows the order: benzyl cyanides[11] ≫ aryl alkynes[9] > electron-rich 2-naphthols > electron-deficient 2-naphthols > alkyl alkynes.[9] Since the chemoselectivity of each coupling is remarkably high, substrates can be selected which assemble in a defined order under a single set of reaction conditions exposing selected terminal groups, allowing selective cross-linking, or generating more complex architectures.

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Keywords: asymmetric catalysis · chirality · copper · coupling reactions · polymerization

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