

Facile Synthesis of Chiral Conjugated Polymer Based on BINOL Skeleton

Chun E DONG^{1,*}, Yong Gang ZHI¹, Zuo Long YU¹, Liang Fu ZHANG¹,
Albert. S. C. CHAN²

¹Chengdu institute of organic chemistry Academ Sinica Chengdu 610041

²Hong Kong Polytechnic University, HongKong

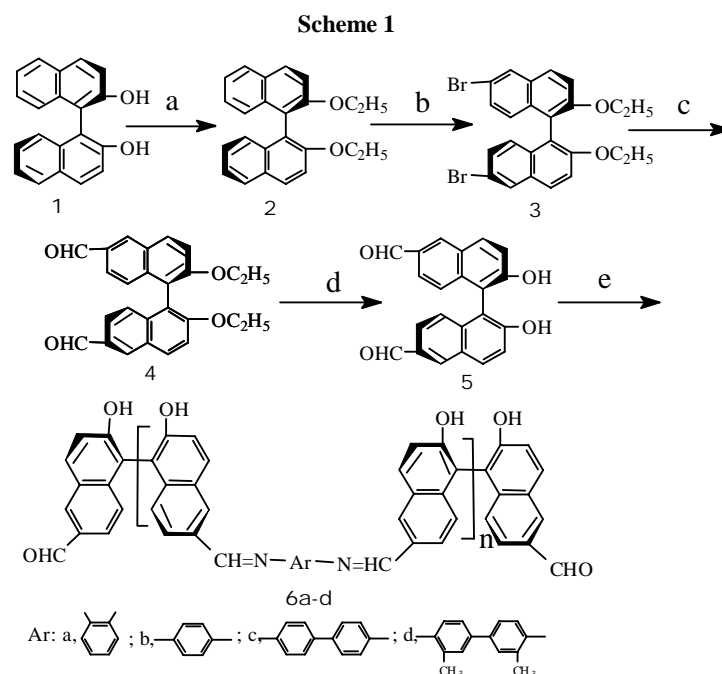
Abstract: A new type of chiral conjugated polymers **6a-d** has been synthesized by the reaction of (R)-2,2'-dihydroxy-1,1'-binaphthyl-6,6'-dicarbaldehyde **5** with corresponding diamine in the presence of acetic acid.

Keyword: Chiral conjugated polymers, synthesis, BINOL.

The study of polymer supported chiral catalysts has attracted very extensive attention in recent years¹. The intrinsic advantages of these catalysts in organic synthetic chemistry are that they can be separated with the products by simple filtration. Traditionally, polymer chiral catalysts are prepared by attaching chiral ligand to sterically irregular polymer backbone². In this system, the catalytic sites are randomly oriented along the polymer chain which makes it very difficult to systematically modify the microenvironment of the catalytic centers to optimize the reactivity and stereoselectivity of the catalysts. Thus preparation of chiral conjugated polymers where the catalytic centers are highly organized is necessary. However, synthesis of chiral conjugated polymers for catalytic purpose is scarce. As far as we know, the method for preparation of chiral conjugated polymer is limited to transition metal catalyzed Suzuki-coupling reaction³.

Owing to its excellent chiral induction in a number of organic transformation, optically active 1,1'-bi-2,2'-naphthols (**BINOL**) play a major role in asymmetric catalytic synthesis⁴. Therefore we chose optically active **BINOL** as starting material to synthesize a new type of chiral conjugated polymers.

The synthetic route is outlined in **Scheme 1**. By the published method⁵, optically active **1** was obtained in large scale with e.e. up to 96%. Alkylation of **1** with bromoethane in boiling acetone and anhydrous potassium carbonate for 3 days gave **2** in 95% yield. Selective bromination of **2** using bromine in CH₂Cl₂ at 0 °C afforded **3** in nice yield. **3** was lithiated in THF at -70 °C using an excess of n-BuLi, after 6 h an excess of DMF was added and subsequent hydrolysis to gave (R)-2,2'-diethoxy-1,1'-binaphthyl-6,6'-dicarbaldehyde **4**. A 0.2 mol.L⁻¹ CH₂Cl₂ solution of **4** was added to 1.0 mol.L⁻¹ CH₂Cl₂ solution of boron tribromide at r.t, the mixture was stirred overnight, followed by hydrolysis with water to give **5** in 93% yield. Reaction of **5** with diamine at 100 °C gave polymers **6a-d** in 56% ~80% yield.



The polymers showed weak absorption at 1670cm^{-1} which indicates that there are aldehyde end groups. The representative polymer **6a** reprecipitated three times from THF-methanol gave data as follow: $[\alpha]_D^{25} = -240$ ($c = 0.2 \text{ CH}_3\text{OH}$), IR, cm^{-1} : 3360, 1670, 1282, 818, 751; UV-Vis (CH_3OH), nm: 242, 333, 420, ^1H NMR (DMSO-d_6 , 200MHz), ppm, 5.32 (s, 2H, OH), 7.17~8.03 (m, 10H, C_6H_5), 8.87 (s, 1H, $\text{CH}=\text{N}$) 10.2 (s, 1H, CHO). The structures of **2-5** were confirmed by IR, ^1H NMR, MS spectra.

Both solvent and temperature are important factors affecting the yield of **6**. THF/acetic acid=1:4 is preferable to THF.

A simple method was demonstrated to synthesize chiral conjugated polymers. They will be used to catalyze the reaction of aldehydes with diethylzinc, Mukaiyama, aldol condensation, asymmetric cyanosilylation of aldehydes *etc.*

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References and Notes

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