

SYNTHESIS OF POLYBINAPHTHOLS INCORPORATING CHIRAL (*R*)-1,1'-BI-2,2'-NAPHTHOL ENTITIES WITH *p*-DIVINYLBENZENE BY Pd-CATALYZED HECK REACTION

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Abstract Polymer (I) and polymer (II) were obtained by the polymerization of (*R*)-6,6'-dibromo-2,2'-binaphtho-20-crown-6 (M-1) and (*R*)-6,6'-dibromo-2,2'-di(methoxyethoxymethoxy)-1,1'-binaphthyl (M-2) with *p*-divinylbenzene under Pd-catalyzed Heck reaction. The UV, fluorescence and CD spectra of polymer (I) and (II) are similar due to the same linkers present in their polymer chain. Polymers (I) and (II) can emit strong blue fluorescence and are expected to have potential applications in polarized blue-light emitting sensors. The chiral conjugated polymers (I) and (II) exhibit a strong Cotton effect in their circular dichroism (CD) spectra, indicating a high rigidity of polymer backbone.

Keywords (*R*)-BINOL, Chiral conjugated polymer, Heck reaction

INTRODUCTION

(*R*) or (*S*) 2,2'-binaphthol (BINOL) have often been used as the starting materials for obtaining chiral binaphthyl compounds. The 2,2'-hydroxyl groups of BINOL can be easily converted into other functional groups and the 3,3'-and 6,6'-positions of naphthyl skeletal structure of BINOL can be selectively functionalized, leading to a variety of binaphthyl derivatives which can exhibit remarkably stable chiral configuration as well as high chiral induction in many asymmetric processes^[1–4]. The multibinaphthyl hosts developed for molecular recognition purposes are mainly focused on crown ethers and cyclic amides. These macrocycle molecules either undergo complexation-induced organization in the presence of guest molecules or preorganize cavities based on rigid structures^[5, 6]. Pu has undertaken further investigations on the design and synthesis of a series of novel binaphthyl-based chiral conjugated polymers used as the Lewis acid to carry out highly enantioselective organic reactions, such as the additions of aldehydes, hetero-Diels-Alder reactions, 1,3-dipolar cycloadditions, reductions of ketones, and others. These rigid and sterically chiral polybinaphthyl polymers also represent a new generation of materials for applications in asymmetric catalysis, chiral sensors, polarized light emission and nonlinear optical materials^[7–10]. But polymers (I) and (II) have not been reported so far. In this study polymers (I) and (II) were obtained by the polymerization of (*R*)-6,6'-dibromo-2,2'-binaphtho-20-crown-6 (M-1) and (*R*)-6,6'-dibromo-2,2'-di(methoxy-ethoxymethoxy)-1,1'-binaphthyl (M-2) with *p*-divinylbenzene with Pd-catalyzed Heck reaction.

EXPERIMENTAL

All reactions were performed under a nitrogen or argon atmosphere using Schlenk tube techniques. NMR spectra in deuterated chloroform solution were recorded on a Bruker AC-200 spectrometer.

IR-spectra were determined with a Perkin-Elmer SPECTRUM 1000 FT-IR spectrometer. Optical rotations were measured on a Perkin-Elmer polarimeter 241. Fluorescent spectra were determined on P.E. Model 8100

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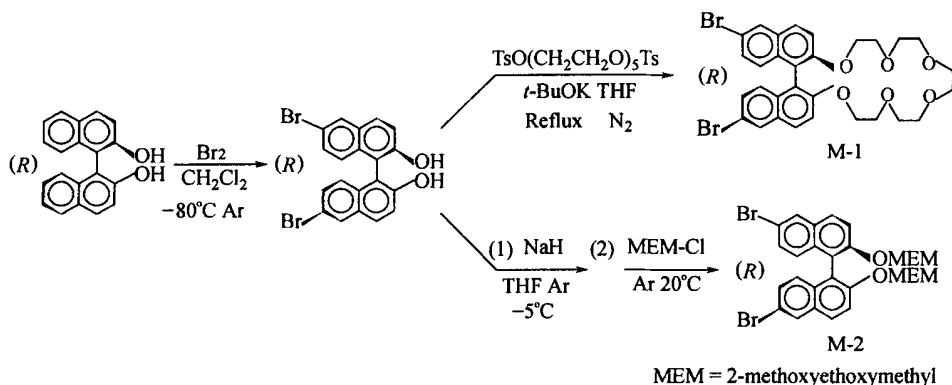
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spectrometer. Circular dichroism (CD) spectra were measured with a JASCO J-810 spectropolarimeter. Molecular weight was determined by gel permeation chromatography (GPC) on Waters 510 HPLC pump with THF as solvent and relative to polystyrene standards. (*R*)-1,1'-Bi-2-naphthol (BINOL) and 2-methoxyethoxymethyl chloride (MEM-Cl) were purchased from Aldrich and Sigma respectively, and directly used without purification. Dried solvents were required in experiments, THF and diethyl ether were distilled from sodium-benzophenone, DMF was distilled from CaH₂ and CH₂Cl₂ was distilled from P₂O₅.

Monomer Synthesis

The preparation of *p*-divinylbenzene was carried out as same as the procedures described in the literature^[11].

M-1, (*R*)-6,6'-Dibromo-2,2'-binaphtho-20-crown-6 and M-2, (*R*)-6,6'-dibromo-2,2'-di(methoxyethoxymethoxy)-1,1'-binaphthyl were synthesized from (*R*)-BINOL (Scheme 1) according to the literature^[12, 13], and pentaethyleneglycolditosylate [TsO(CH₂CH₂O)₅Ts] was synthesized according to the literature^[14].



Scheme 1 Synthesis procedures of monomer (I) and monomer (II)

Polymer (I) Synthesis^[15, 16]

p-Divinylbenzene (130 mg, 1 mmol) was dissolved in 9 mL DMF and an equimolar amount of M-1 (647 mg, 1 mmol) was dissolved in 9 mL DMF, and they were mixed. 0.4% Pd(OAc)₂ (1.1 mg) and 2.4% PPh₃ (7.1 mg), 5 molar equivalent Et₃N (0.85 mL)/M-1 were added to the above mixture solution. The solution was stirred and heated at 110°C for 10 h under N₂, and then refluxed at 145°C for 2 h. The reaction mixture was cooled down to room temperature. The solution was filtered through a short silica gel column, and then the solution was mixed with 200 mL methanol to precipitate out the polymer (Scheme 2). The brown crude polymer was washed with methanol several times and dried in vacuo. The final yield is 65% (402 mg). The polymer is an air stable solid and shows a moderate to good solubility in THF, CH₂Cl₂ and CHCl₃. Polymer (I) has *M_w* = 12700, *M_n* = 8200, PDI = 1.54. [α]_D²⁵ = -419.9 (*c* 0.5, THF), FT-IR (KBr pellet, cm⁻¹): 2916, 2847, 1586, 1262, 1090 and 800. H-NMR (CDCl₃, δ): 3.40–3.60 (m, 16 H), 4.07–4.21 (m, 4 H), 7.01–7.16 (m, 10 H), 7.22–7.30 (m, 2 H), 7.47–7.51 (m, 2 H) and 8.02–7.83 (m, 4 H).

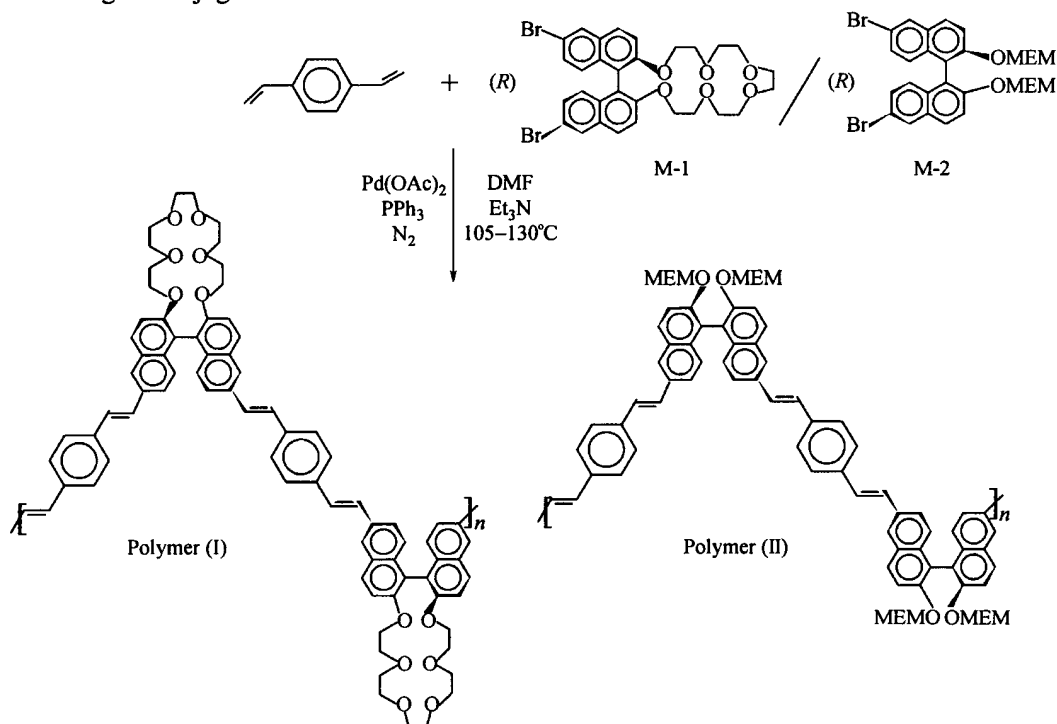
Polymer (II) Synthesis

The synthesis of polymer (II) was carried out in the same way as that of polymer (I). The polymer has *M_w* = 26000, *M_n* = 11500, PDI = 2.13. [α]_D²⁵ = -649.4 (*c* 0.5, THF), FT-IR (KBr pellet, cm⁻¹): 2867, 1589, 1474, 1229, 1104, 1015 and 813. H-NMR (CDCl₃, δ): 3.28–3.37 (m, 14 H), 3.43–3.46 (m, 4 H), 5.15 (d, *J* = 24.6, 6.7, 2 H), 7.07–7.31 (m, 10 H), 7.47–7.52 (m, 4 H), 7.62 (d, *J* = 8.8, 2 H) and 7.94 (d, *J* = 12.5, 2 H).

RESULTS AND DISCUSSION

UV spectra of the polymers (I) and (II) in THF are similar (Fig. 1), and their absorption maxima $\lambda_{\max}$ appear at 387 nm ($\epsilon_{387} = 4.9 \times 10^4$ L · mol⁻¹ · cm⁻¹) and 385 nm ($\epsilon_{385} = 6.0 \times 10^4$ L · mol⁻¹ · cm⁻¹), respectively. But the UV absorption maxima $\lambda_{\max}$ of M-1 and M-2 appear at 283 nm ($\epsilon_{283} = 1.22 \times 10^4$ L · mol⁻¹ · cm⁻¹) and 285 nm ($\epsilon_{285} = 1.92 \times 10^4$ L · mol⁻¹ · cm⁻¹) nm, respectively. It was concluded that there is a large red-shift in the

electronic absorptions of the conjugated polymer due to the effective π conjugated segment of *p*-divinylbenzene and naphthyl group in the main chain^[1, 8]. Polymers (I) and (II) can emit very strong blue light under ultraviolet light (366 nm) even in very low concentration, but the fluorescent wavelength of M-1 and M-2 does not show visible fluorescence. Their fluorescent wavelengths $\lambda_{\text{max}}^{\text{F}}$ appear in the ultraviolet region^[17]. The fluorescent wavelengths $\lambda_{\text{max}}^{\text{F}}$ of polymer (I) in THF solution appear at 430 and 456 nm, and those of polymer (II) at 431 and 456 nm (Fig. 2 and 3). The fluorescent spectra of polymer (I) and polymer (II) are similar due to the same conjugated linker unit *p*-divinylbenzene in the polymer main chain. The wavelength of polymer (I) in KBr pellet has a larger red shift to 474 nm, while polymer (II) has a larger red shift to 480 nm (Fig. 2 and 3). This can be attributed to a higher conjugated chain in the solid state than in solution^[18].



Scheme 2 Synthetic route for polymer (I) and polymer (II)

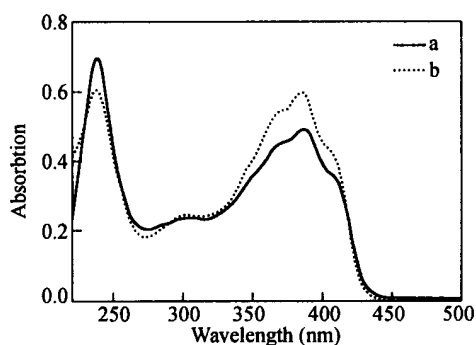


Fig. 1 UV spectra of
 a) Polymer (I); b) Polymer (II)

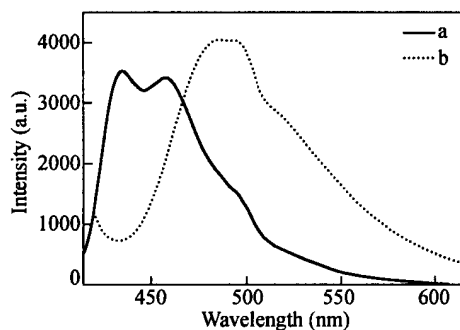


Fig. 2 Fluorescence spectra of polymer (I)
 a) THF solution, $\lambda_{\text{ex}} = 415 \text{ nm}$
 b) KBr pellet, $\lambda_{\text{ex}} = 422 \text{ nm}$

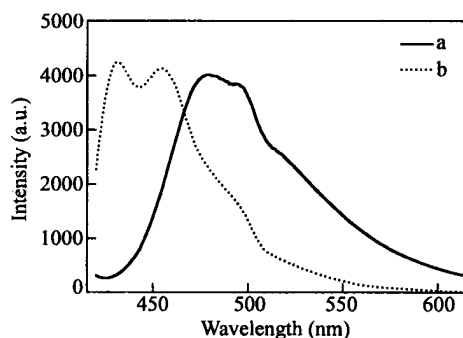


Fig. 3 Fluorescence spectra of polymer (II)
a) THF solution, $\lambda_{\text{ex}} = 410$ nm; b) KBr pellet, $\lambda_{\text{ex}} = 425$ nm

The optical rotation ($[\alpha]_{\text{D}}^{25} = -649.4$) of polymer (II) was larger than that of polymer (I) ($[\alpha]_{\text{D}}^{25} = -419.9$). Both polymers can exhibit strong Cotton effects in their circular dichroism (CD) spectra (Fig. 4). The molecular ellipticity of polymer (I) is: $[\theta]_{\lambda} = -4.43 \times 10^4$ (250 nm), $+0.384 \times 10^4$ (353 nm), -1.01×10^4 (396 nm), -1.06×10^4 (414 nm), and the molecular ellipticity of polymer (II) is: $[\theta]_{\lambda} = -3.37 \times 10^4$ (251 nm), $+1.53 \times 10^4$ (355 nm), -3.21×10^4 (396 nm), -3.66×10^4 (409 nm). CD spectra of polymer (I) and polymer (II) are similar due to their similar UV absorption, but their molecular ellipticities $[\theta]_{\lambda}$ are different, especially on higher wavelength region. The molecular ellipticity $[\theta]_{\lambda}$ of polymer (II) is larger than the polymer (I). It can be assumed that the chain structure of polymer (II) is more flexible than that of polymer (I) because polymer (I) has a higher rigidity of polymer backbone due to crown ether molecular structure leading to increased hindrance to free rotation at the pivotal 1-1'-bond^[19].

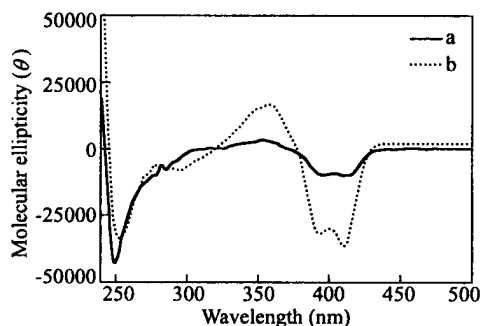


Fig. 4 CD spectra of (a) polymer (I) and (b) polymer (II)

CONCLUSIONS

Pd-catalyzed Heck reaction was found to offer a simple access to the chiral (*R*)-BINOL polymers (I) and (II). The similarity of UV, fluorescence and CD spectra of polymer (I) and (II) is attributed to the same linker unit in the polymer main chain. The difference of the molecular ellipticity $[\theta]_{\lambda}$ of polymer (I) and (II) in CD spectra is attributed to the higher rigidity of crown ether structure in polymer (I). Both polymer (I) and (II) can emit strong blue fluorescence and are expected to have potential applications in polarized blue-light emitting sensors.

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