

Rapid Communication

NEW OPTICALLY ACTIVE AROMATIC POLYIMIDES
II: SYNTHESIS AND PROPERTIES OF OPTICALLY ACTIVE AROMATIC
POLYIMIDE BASED ON (R)-(+)-2, 2'-BIS(2-TRIFLUORO-4-
AMINOPHENOXY)-1,1'-BINAPHTHYL*

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Abstract Optically active (R)-(+)-2, 2'-bis(2-trifluoro-4-aminophenoxy)-1, 1'-binaphthyl was prepared from 1, 1'-bi-2-naphthol. The optically active aromatic polyimide was also successfully synthesized. This new polymer has good solubility, thermal stability etc. Its specific rotation was found to be +174°, and its chiroptical property was also studied.

Keywords Optical activity, 1, 1'-Bi-2-naphthol, Polyimide

Structurally widely varied polyimides have been designed and synthesized in recent decades for their outstanding thermal, mechanical, optical, and dielectric properties^[1-4]. Recently, we firstly reported the optically active aromatic polyimide (OAAP) prepared from chiral aromatic di(ether anhydride) containing 1, 1'-binaphthyl-2, 2'-diyl unit^[5, 6]. In our preliminary work, besides its good solubility and thermal stability, we have found that this optically active polyimide shows good chiral recognition ability toward binaphthyl derivatives when it is used as a chiral packing material for high-performance liquid chromatography (HPLC). In order to have a better understanding of the structure-property relation of the OAAP, more new kinds of polymers need to be designed and synthesized. In this communication, we report the synthesis of another new optically active aromatic polyimide derived from chiral diamine containing 1, 1'-binaphthyl-2, 2'-diyl unit.

The monomer (R)-(+)-2, 2'-bis(2-trifluoro-4-aminophenoxy)-1, 1'-binaphthyl [(R)-4] was prepared in two steps by the aromatic nucleophilic displacement reaction of (R)-(+)-1, 1'-bi-2-naphthol and 2-chloro-5-nitrotrifluorotoluene, giving the dinitro compound (R)-3, followed by reduction with hydrazine hydrate/Pd-C (see Scheme 1). The chemical structure of (R)-3 and (R)-4 were confirmed by means of NMR (Varian Unity-400), FTIR (Biorad FTS-7), elemental analyses (Elemental Analyzer MOD-1106) and MS (VG-7070E), respectively. The results are shown in Table 1.

The optical purity of the key intermediate (R)-3 was examined by HPLC via the (+)-poly(triphenylmethyl methacrylate) [(+)-PTMA]-coated silica gel column. From Fig.1, we can see that there was almost no rotational loss at that condensation condition. The specific rotation values

* This project was supported by National Natural Science Foundation of China.

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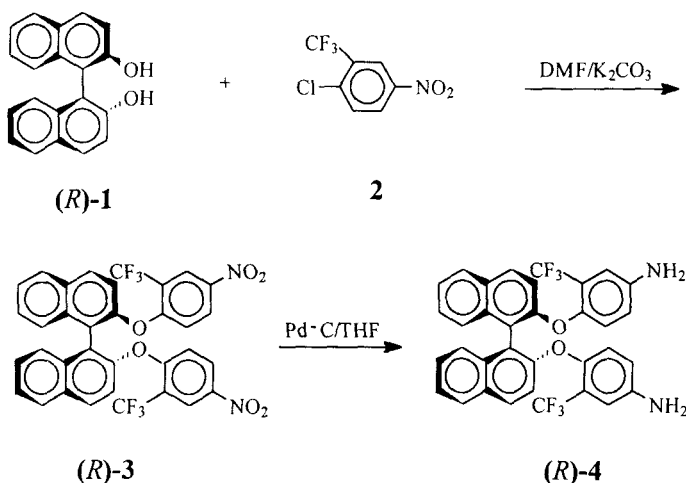
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Received October 9, 1998

of (*R*)-**3** and (*R*)-**4** are -15.4° and $+198.4^{\circ}$ (C, 0.5, THF) by Perkin-Elmer Model 241 digital polarimeter, respectively.

Table 1. Key data for the synthesized compounds (*R*)-**3** and (*R*)-**4**

Compounds	(R)-3	(R)-4
Yield	93%	80%
m.p.(°C)	109 ~ 110	282 ~ 283
Mol. Weight (by MS)	665	605
C. H. N. analyses (%):	C: 61.65(61.50); H: 2.62(2.74);	C: 67.71 (67.60); H: 3.54 (3.68);
Found (Calcd)	N : 4.18 (4.22).	N: 4.58 (4.64).
¹ H-NMR (δ , DMSO- <i>d</i> ₆)	8.33 (<i>d</i> , 2H, ⁴ <i>J</i> _{HH} =2.8 Hz), 8.10 (<i>d</i> , 2H, <i>J</i> =9.2 Hz, ⁴ <i>J</i> _{HH} =2.8 Hz), 8.03 (<i>d</i> , 2H, <i>J</i> =8.8 Hz), 7.92 (<i>d</i> , 2H, <i>J</i> =8.0 Hz), 7.48 (<i>t</i> , 2H, <i>J</i> =8.0 Hz), 7.35 (<i>t</i> , 2H, <i>J</i> =8.0 Hz), 7.32 (<i>d</i> , 2H, <i>J</i> =8.8 Hz), 7.31 (<i>d</i> , 2H, <i>J</i> =8.8 Hz), 6.97 (<i>d</i> , 2H, <i>J</i> =9.2 Hz).	8.12 (<i>d</i> , 2H, <i>J</i> =9.2 Hz), 8.07 (<i>d</i> , 2H, <i>J</i> = 8.0 Hz), 7.54 (<i>t</i> , 2H, <i>J</i> =6.8 Hz), 7.48 (<i>t</i> , 2H, <i>J</i> =6.8 Hz), 7.33 (<i>d</i> , 2H, <i>J</i> =8.4 Hz), 7.16 (<i>d</i> , 2H, <i>J</i> =9.2 Hz), 6.95 (<i>s</i> , 2H), 6.84 (<i>s</i> , 4H).
FTIR (KBr, cm ⁻¹)	1527 and 1352 (NO ₂); 1264 and 1124 (C—O—C); 1338, 1285 and 1140 (—CF ₃)	3470 and 3058 (NH ₂); 1124 and 1229 (C—O—C); 1339, 1262 and 1229 (—CF ₃).



Scheme 1

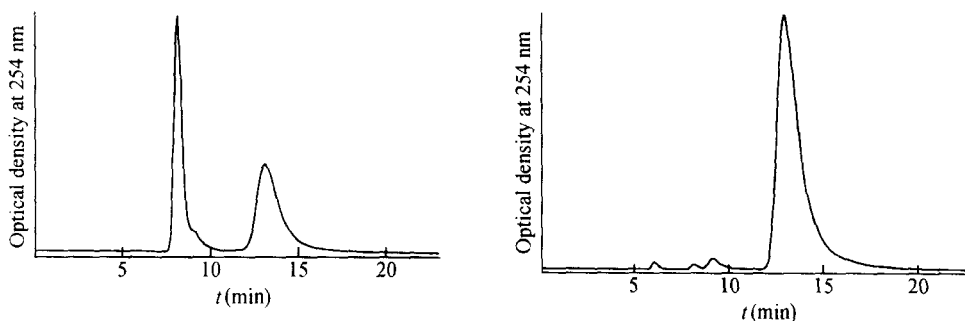
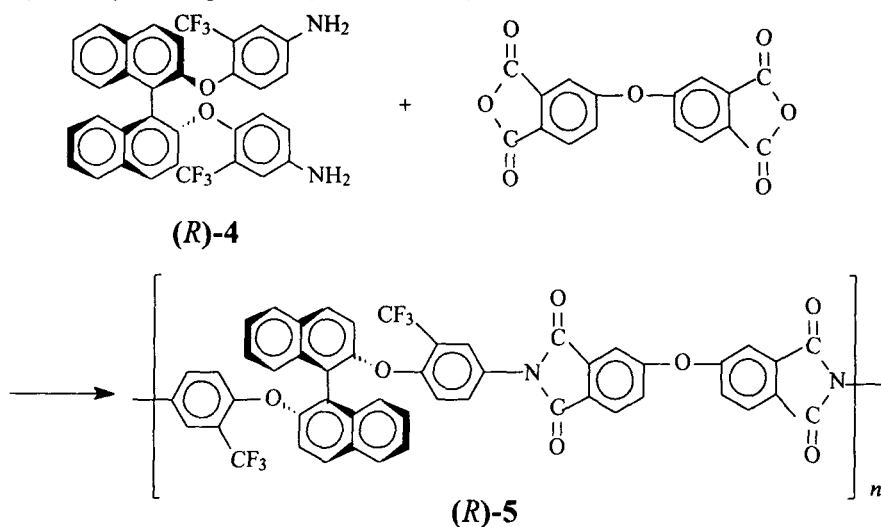


Fig.1 HPLC resolution of racemic **3** (a), and determination of optical purity of (*R*)-**3** (b) on CSP-(+)-PTrMA. Eluant: methanol; flow rate: 0.5 mLmin⁻¹ at room temperature

Optically active aromatic polyimide [(*R*)-5] was prepared from (*R*)-4 with 4, 4'-oxydianhydride by one-step method(see Scheme 2)^[4].



Scheme 2

The solubility of (*R*)-5 was improved by the incorporation of noncoplanarity in 2, 2'-substituted 1, 1'-binaphthyl units, flexible aryl ether groups and trifluoro groups. This polymer can be soluble in pyridine, DMAc and *m*-cresol etc. Its weight-average molecular weight (M_w) and polydispersity index (M_w/M_n) was found to be 3.12×10^4 and 1.53 by GPC on shimadzu HPLC-4A instrument with polystyrene as standard in THF. The FTIR spectra show characteristic absorption for the imide ring of (*R*)-5 around 1720 cm^{-1} and 1780 cm^{-1} . This polymer has a glass transition temperature of 274°C and 10 % weight loss up to 540°C . Wide angle X-ray diffraction shows that this polymer is an amorphous one despite its optical activity.

The specific rotation of (*R*)-5 is $+174^\circ$. The circular dichroism (CD) and UV spectra of this polymer were recorded on 62A DS Spectrometer (see Fig. 2). Besides a positive band at 280 nm, the CD tail in far-ultraviolet region indicated that there is another positive Cotton effect centered around 240 nm ^[6, 7], which indicates that this optically active polymer is in (*R*)-configuration.

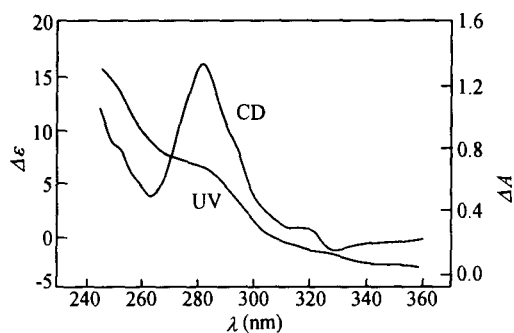


Fig.2 UV (bottom) and CD (top) spectra of (*R*)-5 in chloroform ($M \cong 1.5 \times 10^{-4}$, 1-mm cuvette)

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