Optically Active Aromatic Polyimides Having Axially Dissymmetric 1,1′-Binaphthalene-2,2′-diyl Units

Qiding Mi, Lianxun Gao, and Mengxian Ding*

Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences,
Changchun 130022, P. R. China

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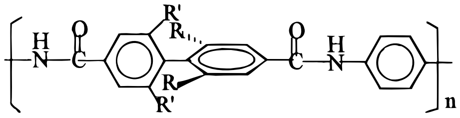
Aromatic polyimides (APIs) have been extensively studied in recent decades as high-performance polymers for their unique thermal, mechanical, dielectrical, and optical properties and are widely used as engineering plastics, matrix resins, insulating materials, and various materials for microelectronics.[1] On the other hand, the synthetic optically active polymers today have also become of great interest owing to their chiral structure which may play an important role in molecular arrangement and assembly, that is critical for optoelectronics supermolecular structure.[2] However, there has been no report to date of an optically active API. As part of our overall goal to study great potential physical properties of APIs controlled directly or indirectly by chirality, the particular interest for us is to understand the behaviors of the optically active APIs compared with their corresponding racemic APIs. In a previous paper,[3] we have reported the synthesis of racemic APIs derived from (±)-1,1′-binaphthalene-2,2′-diyl units. In this communication, we wish to report the first synthesis of a type of thermally stable API possessing *(R)*-(+)- or (*S*)-(−)-1,1′-bi-2-naphthalene units in the main chain, along with some of their important properties.

Atropisomeric polyamides containing chiral biphenylene units (**1**) have been reported by Overberger et al.[4] The chirality of the polyamides results from the twisted biphenylene moieties, and the rotatory stability depends on the substitutents *R* and *R′*. In this work, we chose the C_2 dissymmetry of 1,1′-bi-2-naphthalene as the units of the macromolecular chain under the consideration that the rotation axis of the two naphthalene rings was perpendicular to that of the macromolecular chain, so that the optical stability at high temperatures could be expected[5] because the racemization resulting from the rotation around the axis of the two binaphthalene rings would be highly hindered by the long chain stretching out on both sides.[6] Although optically active polyamides derived from 2,2′-diamino-1,1′-binaphthalene or 2,2′-bis(chlorocarboxy)-1,1′-binaphthalene have also been reported,[7] these polyamides have low viscosity values due to the steric hindrance of those binaphthalene monomers. Therefore, introduction of ether linkages into the dianhydride was considered for avoiding the steric hindrance.



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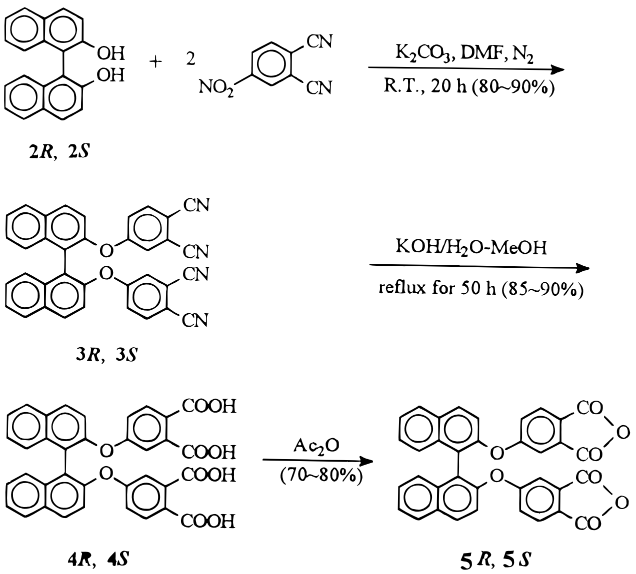
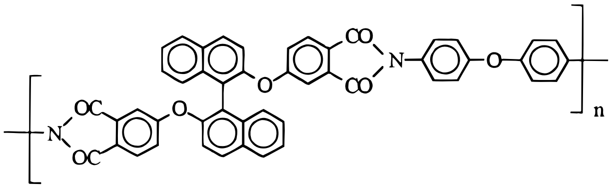
The key monomers, optically active (*R*)-(+)- or (*S*)-(−)-2,2′-bis(3,4-dicarboxyphenoxy)-1,1′-binaphthalene dianhydrides (**5***R* and **5***S*), were prepared by the reactions[8,9] (see Scheme 1) of optically active (*R*)-(+)- or (*S*)-(−)-1,1′-bi-2-naphthol (**2***R* and **2***S*, respectively) with 4-nitrophthalonitrile in the presence of potassium carbonate in DMF to give tetranitrile derivatives **3***R* and **3***S*,[10a,11] which were then hydrolyzed to obtain corresponding tetracarboxylic acids **4***R* and **4***S*[10] with methanolic potassium hydroxide and finally dehydrated in acetic anhydride.[11]

Scheme 1



The optically active APIs (**6***R* and **6***S*) were prepared by the polycondensation of **5***R* and **5***S* with 4,4′-oxydianiline, respectively, to form the corresponding poly(amic acid)s and subsequent chemical imidization with acetic anhydride-triethylamine. Equimolar amounts of **6***R* and **6***S* were mixed in DMAc to form a binary blend, **6***R*/**6***S*. The chemicals prepared in this work were characterized by ^{1}H-NMR, IR, mass spectra (EI+), and elemental analysis.[12] The optical purities of **3***R* or **3***S* and **4***R* or **4***S* were found to be preserved during the synthesis course according to the HPLC analysis via a chiral column and comparative experiments.[6,8,10]



6*R*, **6***S*

The solubilities of the resulting polyimides were greatly improved by the introduction of the axially dissymmetric 1,1′-bi-2-naphthalene units into the polymer backbone. These polymers were soluble in many common organic solvents such as methylene chloride, chloroform, THF, pyridine, DMSO, DMAc, NMP, etc. The weight-averaged molecular weight (M_w) of 2.21×10^4 for **6***R* with a polydispersity index of 1.51 was obtained by GPC in THF (polystyrene as the standard).[12]

6*R***,** **6***S* and **6***R*/**6***S* showed primarily similar thermal behaviors. These polymers were fairly stable up to 450 °C by TGA.[12] The T_g value, at 274 °C by DMA,[12,13a] for **6***R*/**6***S* was about the same as those of its components (**6***R* and **6***S*), which seems to imply that there was no stereocomplex formed as for the other optically active polymers.[14] **6***R*, **6***S*, and **6***R*/**6***S* were glassy amorphous

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* Corresponding author. Fax: 86-0431-5685653.

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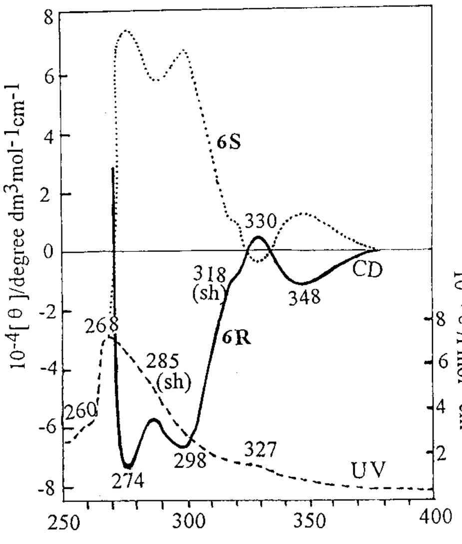

Figure 1. Absorption spectra (bottom) of **6***R* (- - -) in DMF and circular dichroism spectra (top) of **6***R* (—) and **6***S* (···) in DMF. The spectra were recorded at [**6***R* or **6***S*]/*M* $\approx 2.7 \times 10^{-5}$ using a 0.5-mm cuvette.

polymers despite their optical activity. Optical rotations[15] of **6***R* and **6***S* remained unchanged after heating at 250 °C in the air for 96 h. However, the samples became insoluble in methylene chloride, chloroform, THF, and DMSO but were still soluble in DMAc and NMP, which indicates the presence of an additional intermolecular interaction between the polymer chains after heat treatment. Figure 1 shows the UV absorption and CD spectra of **6***R* and **6***S*. A pair of perfect symmetrical curves of **6***R* and **6***S* shown in the CD spectra indicates that the two polymers are in opposite configurations.[16]

References and Notes

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(8) The following information is already known concerning compounds related to this study: (a) Current synthetic methods for bis(ether anhydride)s are usually by nitro displacement between either a diphenoxide and a nitrophthalimide to form a bis(ether phthalimide), which is then converted to a bis(ether anhydride), or a diol and a nitrophthalonitrile to form a tetranitrile derivative, which is then also converted to a bis(ether anhydride). However, we recently studied that the first method involves the use of higher temperatures (reaction temperature ≥ 110 °C), with a lower yield (ca. 40−50%) and partial racemization, while the second method is preferred due to the reaction at lower temperatures (reaction temperature, room temperature), higher yield (ca. 80−90%) and no racemization.[10a] (b) When **3***S* and **3***R* were hydrolyzed to obtain the corresponding tetraacids, no racemization was observed when heated to reflux in the presence of 20% KOH (H_2O) in methanol for 50 h.[6c,10b]

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(10) In the present study, the optical purity of **5***R* and **5***S* was determined as followed: (a) **3***R* or **3***S* was recovered from HPLC via the (+)-PTrMA coated silia gel column (eluant, methanol) and showed only one peak which indicates no rotational loss in the condensation treatment. (b) When **4***S* was heated to reflux additionally in 20% KOH (H_2O) for 48 h, no rotation loss was observed. In addition, the sample of **4***S* was recovered by acidifying with 6 N HCl and then was heated to reflux in 50% H_2SO_4 for 10 h. The $[\alpha]_{589}^{20}$ of the recovered **4***S* was +86.6°, compared to +86.4° for the original **4***S*.[12]

(11) In the process of recrystallization, a very different crystallization behavior was observed between the optically active tetranitrile derivatives (**3***R* and **3***S*), dianhydrides (**5***R* and **5***S*), and their corresponding racemates. Namely, the racemic tetranitrile could be easily crystallized from acetonitrile−methanol, whereas the optical pure tetranitriles were very difficult, and the racemic dianhydride could be easily crystallized from acetic anhydride, while the optical pure dianhydrides were not.

(12) Purification and analytical data on new compounds. **3**: white solid, recrystallized twice from acetonitrile−methanol.[8a] Anal. Calcd for $C_{36}H_{18}O_2N_4$: C, 80.27; H, 3.37; N, 10.41. Found for 3*R*: C, 79.95; H, 3.30; N, 10.43. Found for 3*S*: C, 80.41; H, 3.34; N, 10.49. **5**: white solid, recrystallized twice from acetic anhydride−toluene. Anal. Calcd for $C_{36}H_{18}O_8$: C, 74.74; H, 3.14. Found for 5*R*: C, 74.58; H, 2.98. Found for 5*S*: C, 74.50; H, 3.01. Anal. Calcd for $(C_{48}H_{26}O_7N_2)_n$, **6**: C, 77.62; H, 3.53; N, 3.77. Found for 6*R*: C, 76.81; H, 3.34; N, 4.49. Found for 6*S*: C, 77.11; H, 3.34; N, 4.32. $[\alpha]_{589}^{20}$= −20.0, +20.1, −86.3, +86.4, +68.5, −68.4, +202.8, −202.5 (*c* 0.5, DMAc) for **3***R*, **3***S*, **4***R*, **4***S*, **5***R*, **5***S*, **6***R*, and **6***S*, respectively. The parent ion peaks at 539 (M^+) for **3** and 579 (M^+) for **6**. The FTIR spectrum (KBr) (Biorad FTS-7) showed absorptions at 2232 cm^{-1} (−C≡N) for **3**; 1776, 1721 cm^{-1} (carbonyl groups of imide), 1373 cm^{-1} (C−N), and 1240 cm^{-1} (C−O−C) for **6**. Mp: 177−178 °C for **3**, 141−142 °C for **5**. ^1H NMR (400 MHz, DMSO-d_6; $CDCl_3$ for **3** and **4**), δ: **3** 8.03 (d, 2H, *J* = 8.8 Hz), 7.93 (d, 2H, *J* = 8.0 Hz), 7.51 (t, 2H, *J* = 7.2 Hz), 7.46 (d, 2H, *J* = 8.4 Hz), 7.36 (t, 2H, *J* = 7.2 Hz), 7.28 (dd, 2H, *J* = 8.8 Hz), 7.20 (d, 2H, *J* = 8.4 Hz), 7.00−7.05 (m, 4H); **4** δ 8.01 (d, 2H, *J* = 8.8 Hz), 7.91 (d, 2H, *J* = 8.0 Hz), 7.69 (d, 2H, *J* = 8.4 Hz), 7.48 (t, 2H, *J* = 7.2Hz), 7.33 (t, 2H, *J* = 8.4Hz), 7.30 (d, 2H, *J* = 8.8 Hz), 7.25 (d, 2H, *J* = 8.0 Hz), 7.18−7.20 (m, 4H); **5** δ 8.15 (d, 2H, *J* = 9.2 Hz), 8.03 (d, 2H, *J* = 8.4Hz), 7.80 (d, 2H, *J* = 8.8 Hz), 7.49 (td, 2H, *J* = 7.2 Hz), 7.39 (d, 2H, *J* = 9.2 Hz), 7.35 (t, 2H, *J* = 7.2 Hz), 7.27 (td, 2H, *J* = 8.4 Hz), 7.10−7.13 (m, 4H); **6** δ 8.2 (s, 2H), 8.1 (s, 2H), 7.3−7.7 (m, 12H), 7.0−7.3 (m, 8H), 6.9 (s, 2H). Inherent viscosities (dL/g) in DMAc at 30 °C (*c* 0.5 g/dL): 0.30 for **6***R*, 0.29 for **6***S*. T_g:[13a] 274 °C for **6***R*, **6***S*, and **6***R*/**6***S*. T_g:[13b] 534 °C for **6***R* and 530 °C for **6***S* in nitrogen, 520 °C for **6***R* and 510 °C for **6***S* in air atmosphere.

(13) (a) T_g was determined by DMA at heating rate 5 °C/min under nitrogen. (b) Temperature at which 5% weight loss was determined by TGA at heating rate 10 °C/min under air or nitrogen.

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(15) The $[\alpha]_D^{20}$ (*c* 0.5, DMAc) were determined to be +202.8°, +202.4°, +202.6°, +202.2°, and 202.6° as the **5***R* heated at 250 °C for 0, 24, 48, 72, and 96 h, respectively.

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