

Resolution of 3,3'-Dioxo-1,1'(3H,3'H)spirobi[isobenzofuran]-5,6,5',6'-tetracarboxylic acid and Optically active Polyimides thereof

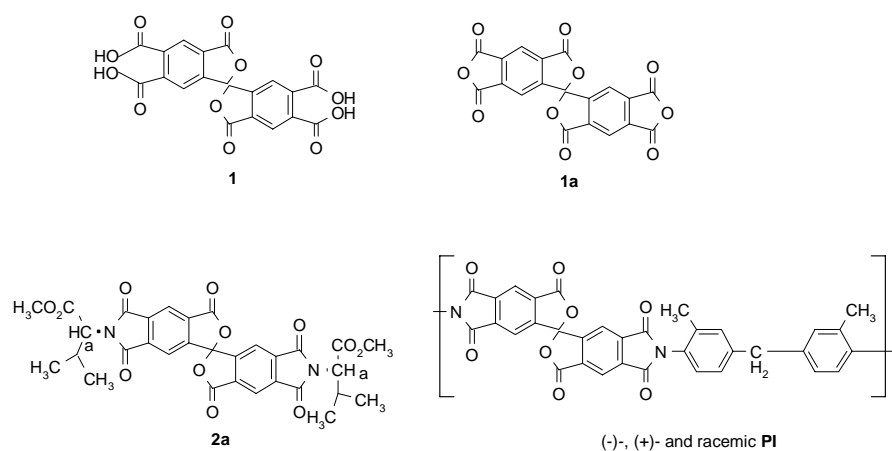
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Abstract: 3,3'-Dioxo-1,1'(3H,3'H)spirobi[isobenzofuran]-5,6,5',6'-tetracarboxylic acid **1** was resolved successfully and the corresponding optically active polyimides **PI** were synthesized. The properties of the optically active **PI** and the racemic one were investigated. The results showed that the specific rotation of (-)-**PI** was about two times to that of the (+)-**PI**, and the regularity of the optically active **PI** was higher than that of the racemic one.

Keywords: Resolution, spirodilactone tetracarboxylic acid, optically active polyimide.

Previously, we have reported a novel type of polyimides prepared from 3,3'-dioxo-1,1'(3H,3'H)spirobi[isobenzofuran]-5,6,5',6'-dianhydride **1a** and a variety of diamines¹. Considering that a spiral compound is planar asymmetry², we recently studied the resolution of **1**, and thereof, synthesized the optically active polyimides. To our knowledge, optically active polyimides containing a planar asymmetric monomers have not been reported thus far.



Cinchonidine and cinchonine base were proved to be an efficient agents for the resolution of **1** when the molar ratio of **1** to resolving agents was 1:1 and the mixture of ethanol and butanone(v/v=1:1) was used as solvent. Typically, a solution of the diastereomeric salts transformed from the racemic **1** and resolving agent was cooled at -15°C for 12 h, white precipitate was filtered, the filtrate was concentrated to remove about 1/4 volume of the solvent, and subsequently, was allowed to recrystallize at -15°C . After seven runs of repeated recrystallization of the salts, it gave an acid of constant specific rotation if the diastereomerically enriched salt obtained from the filtrate was decomposed with 6% aqueous HCl. Accordingly, a pair of enantiomers possessed the specific rotation of -188.6 and $+186.4^{\circ}$ might be obtained by using cinchonidine and cinchonine base as resolving agents, respectively. It suggested that the enantiomers were optically pure.

We have failed to determine the optical purity of optically active **1** quantitatively by HPLC and NMR method^{4,5}. However, for the corresponding dianhydride **1a**, after screening of a series of chiral derivatizing agents (CDAs), such as amino acid esters and amines, we finally discovered that the enantiomeric purity of dianhydride **1a** could be satisfactorily evaluated by using the *L*-valine methyl ester as CDAs.

Figure. 1 ^1H NMR spectra of the phthalimide methine protons (Ha) of **2a**:
a, (-)-**1a** was enriched; **b**, racemic **1a**; **c**, (+)-**1a** was enriched.

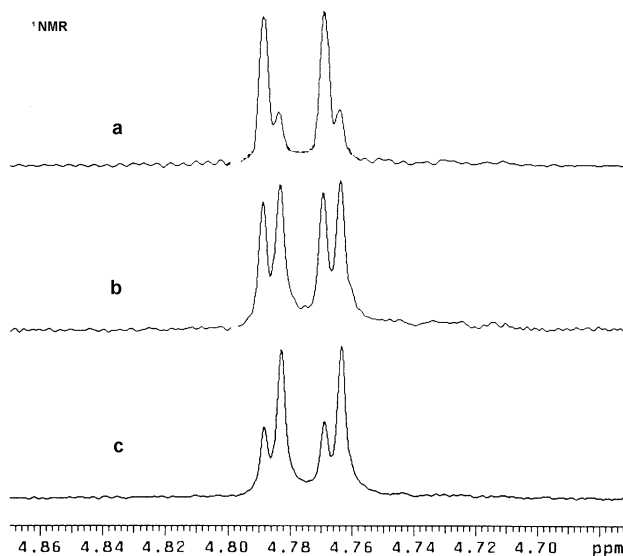


Figure.1 was the ^1H NMR spectra of phthalimide methine proton (Ha) of the derivative

2a⁶ prepared from the racemic **1a** (**b** in **Figure.1**), enantiomerically enriched (-)-**1a** (**a** in **Figure. 1**) and (+)-**1a** (**c** in **Figure.1**) with *L*-valine methyl ester. The well resolved signals for the methine proton(Ha) of the **2a** was observed. It indicated that the diimide derivatives **2a** might be used for the determination of the enantiomeric purity of the chiral **1a**. However, this result can not be used to judge quantitatively the enantiomer purity of **1** since racemization occurs when **1** was transformed to **1a**. As the experiment showing, when chiral **1** was refluxed in acetic anhydride for 3 h, the optical rotation was close to zero, and also, when chiral **1** was heated at above 230°C, the optical rotation was observed to diminish gradually with the extension of the heating time. The detailed results about the optical stability of the chiral **1** will be reported elsewhere in due course.

A type of optically active polyimides was prepared from the optically active dianhydride **1a**, which was converted from the corresponding optically pure **1** by thermal dehydration at 240°C for 2h, and bis-(3,3'-dimethyl-4,4'-diaminophenyl)methane (DMMDA). As **Table 1** shows, the specific rotation of monomers (-)-**1a** and (+)-**1a** was -155.2 and +157.6⁷, while that of the corresponding polymers was -94.0 and +50.8, respectively. The causes of the difference between the specific rotation of (-)-**PI** and (+)-**PI** is being studied in our laboratory.

Table 1. Specific rotation of (-), (+)-**1a** and **PI**, and the inherent viscosities of **PI**

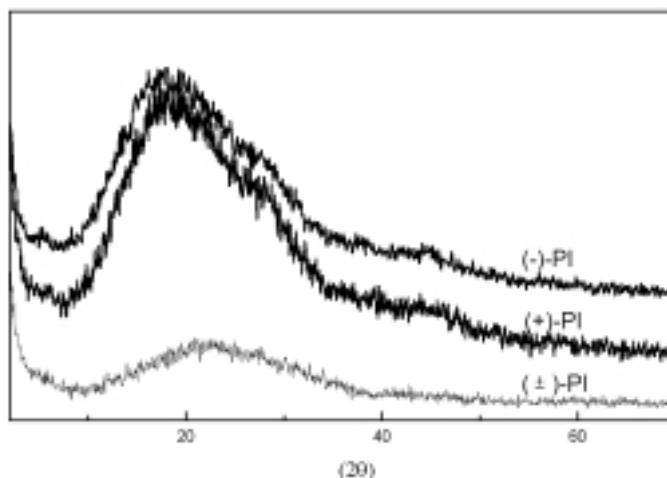
	(-)- 1a	(+)- 1a	(-)- PI	(+)- PI	(±)- PI
η_{inh} (dL/g) ^a	–	–	0.25	0.23	0.21
$[\alpha]_D^{25}$ ^b	-155.2°	+157.6°	-94.0°	+50.8°	–

^a Measured at a concentration of 0.25 g/dL in N,N-dimethyl acetamide(DMAc) at 30°C using a Ostwald viscometer;

^b Determined at a concentration of 0.0025 g/mL.

The optical stabilities of the optically active polyimides in the acidic condition was higher than that in the basic condition, since the specific rotation of (+)-/(-)-**PI** were observed to become 0 and –0.8, respectively, in about 12 h in the presence of NaOH in DMAc solution, whereas that of (+)-/(-)-**PI** were stable in the concentrated hydrochloric acid. Besides, the specific rotation of the optically active polyimides were invariable when the polyimides were heated at 310°C for 5 h.

The optically active polyimides possessed the same solubilities as the racemic one. They were soluble in DMAc, DMF, DMSO, NMP, THF *etc.*, and partially soluble in CH₂Cl₂ and CHCl₃. The thermal properties of the optically active polyimides, such as Tg and loss of weight, were also close to the racemic one. However, as **Figure.2** shows, the crystallinities of the optically active polyimides were higher than that of the racemic one, this may be due to the regularity of the polymer chain for the optically active polyimides was higher than that of the racemic one.

Figure. 2 X-ray diffractogram for (-)-, (+)- and (±)-PI**Acknowledgment**

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References and notes

1. F.S. Han, M.X. Ding., L.X. Gao, *Polymer*, **1999**, *40*(13), 3809.
2. W.H. Mills., C.R. Nodder, *J. Chem. Soc.*, **1921**, *119*, 2095 .
3. Unless otherwise noted, the specific rotation($[\alpha]_D^{25}$) was measured by 341 LC Polarimeter using N,N-dimethyl acetamide (DMAc) as solvent, $t=25^\circ\text{C}$, $c=0.005$ g/ml.
4. The HPLC resolution of **1** was performed on: (a) a 4.0 mm ID×250mm analytical column , the stationary phase was Chiralcel OD (cellulose tri(3,5-dimethylphenyl) carbamate), the mobile phase were hexane+3% isopropanol, and the flowing rate was 0.3 ml/min; (b) a 4.6 mm ID×300mm analytical column , the stationary phase was PTrMA ((+)-Poly(triphenylmethyl methacrylate), the mobile phase was acetonitrile (A.R.), and the flowing rate was 0.5 ml/min; UV detection at 254nm.
5. The ^1H NMR was recorded on a Varian Unity 400 spectrometer. The Chiral Lanthanide Shift Reagents (CLSRs) was $\text{Eu}(\text{tfc})_3$, and solvent was DMSO-d_6 and $\text{C}_2\text{D}_6\text{CO}$, separately.
6. **2a** yield 98.3%; ^1H NMR (400Hz, $\text{C}_2\text{D}_6\text{CO}$): δ 8.608 (s, 2H), 8.506 (s, 2H), 4.779 (d, 1H, $J=7.6\text{Hz}$), 4.774 (d, 1H, $J=7.6\text{Hz}$), 3.771 (d, 6H, $J=4.4\text{Hz}$), 2.701 (m, 2H), 1.235 (d, 6H, $J=6.4\text{Hz}$), 1.017 (d, 6H, $J=6.8\text{Hz}$).
7. The e.e value was 83% and 85%, respectively, as determined by the quantitative ^1H NMR.

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