

Synthesis and Characterization of Optically Active Aromatic Polyimides Having Axially Dissymmetric 1,1'-Binaphthalene-2,2'-diyl Units

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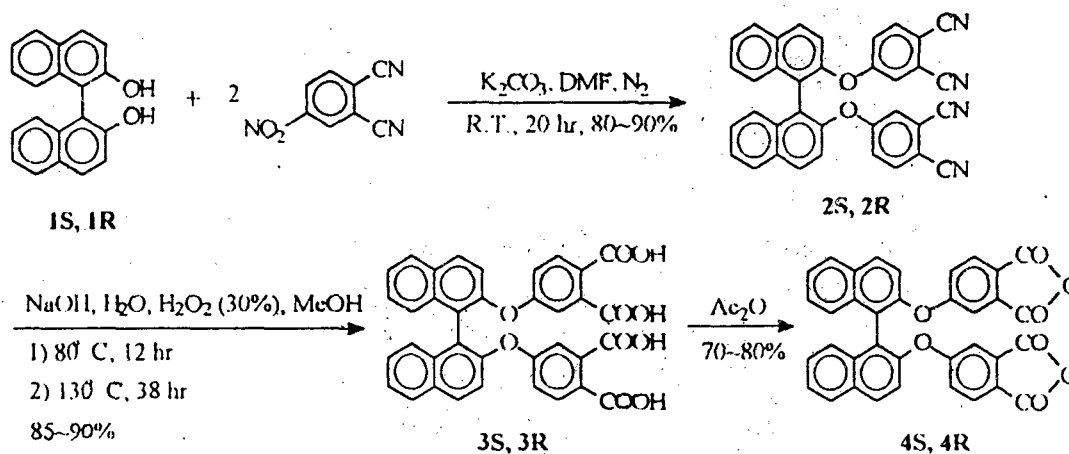
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ABSTRACT

The optically active aromatic diether dianhydride containing C_2 symmetric auxiliary were synthesized firstly by a series of reactions. New optically active aromatic polyimide was prepared from the newly prepared the chiral diether dianhydrides. All the polymers were soluble in common organic solvents such as chloroform, pyridine, NMP etc. These polymers had the same high glass transition temperature (274°C) as the binary blend and good thermal stability. Furthermore, the racemization of the optically active polymers was not observed at the temperature as high as 250°C for 96 h in air atmosphere that showed optical stability resulted from the perpendicularity between the rotation axis and the macromolecular chain. The sign of CD spectra showed the opticochiral properties for the obtained polyimides.

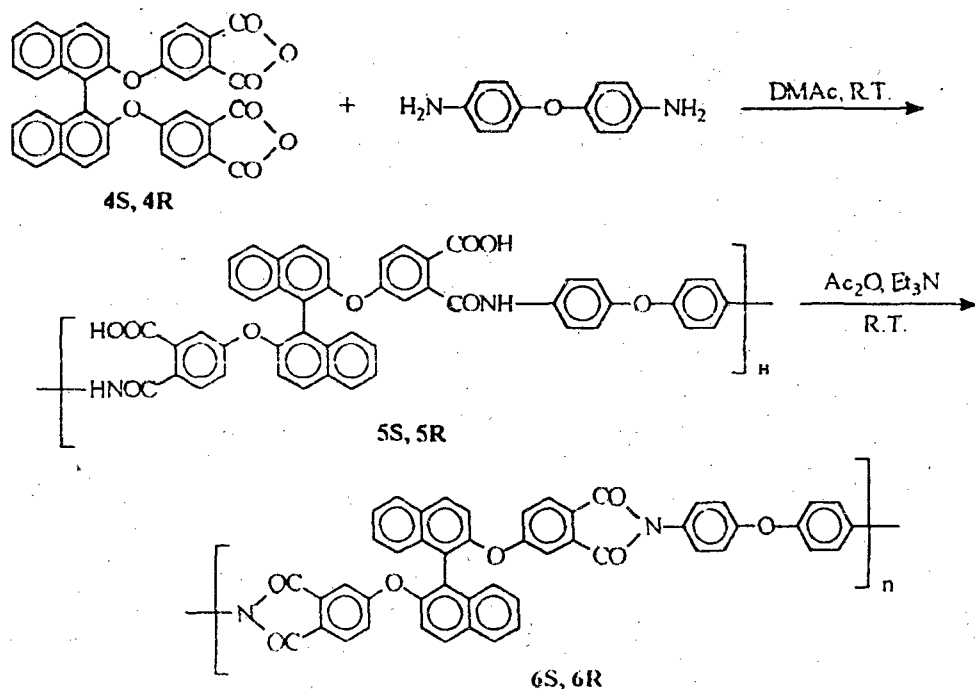
Aromatic polyimides have been extensively studied in recent decades as high performance polymer materials for applications in integrated optoelectronic circuits and aerospace devices due to their unique thermal, mechanical, optical and dielectric properties. In spite of this growing importance in many areas, however, there has been no report to date of an optically active aromatic polyimides. Optical activity in polymers can be achieved by three means: (1) Optical activity is the result of chiral centers in the main chain; (2) Optical activity resides in the side chain; (3) Optical activity results from a super-molecular structure. The largest group of optically active polymers derive their chirality from the single-handedness of the helices they form.

Here, we report the first syntheses of a type of optically active aromatic polyimides possessing optically active (-)-S- or (+)-R-1,1'-bi-2-naphthyl unit and, in particular, important results on their high optical rotation, excellent solubility and good thermal oxidative stability.



Scheme 1. Preparation of optically active aromatic diether dianhydride

In synthesizing optically active compounds from starting optically pure materials, it is important to avoid racemization at each reaction step. The rigid, bulky optically active (-)-S- and (+)-R-1,1'-bi-2-naphthanol (*IS* and *IR* respectively), see Scheme 1, were chosen as the starting materials, since their optical stability has been well studied in the past¹. The design of the synthetic route shown in Scheme 1 was based on the known optical stability of these and other binaphthyl derivatives. The optical purity of the compounds at each monomer reaction step was examined by HPLC that recovered that the production had little or no rotational loss. Thus, optically active aromatic bis(ether anhydride)s (*4S* and *4R*) were prepared by reaction of *IS* or *IR* with 4-nitrophthalonitrile in the presence of potassium carbonate, and subsequent hydrolysis of the resultant tetranitrile derivatives *2S* and *2R* to the corresponding tetraacid derivatives *3S* and *3R* with NaOH in H₂O, CH₃OH and H₂O₂, which were in turn converted to by acetic anhydride. These structures supported by ¹H-NMR (400 MHz), FT-IR, mass spectra (EI⁺ technique) and Elemental Analysis. In the above procedures, optical activity appears to have been preserved.



Scheme 2. Preparation of optically active aromatic polyimides

The syntheses of optically active aromatic poly(ether imide)s (6S and 6R) are outlined in Scheme 2 by the conventional two-step procedure by the condensation reaction of 4S or 4R with 4,4'-oxydianiline to form processable poly(amic acid)s precursor in the first step, followed by the second step which poly(amic acid)s are cured by either thermal or chemical treatment to obtain polyimides. These optically active polymers have high optical rotation ($[\alpha]_{\text{D}}^{20} - +182^\circ$, $c=0.5$, THF). Surprisingly, these polymers have high Tg (274°C) and decomposition temperature (499°C, 5%, in air), and show no appreciable weight loss up to 400°C in both air and nitrogen. In particular, they are soluble in many common organic solvents such as CH₂Cl₂, CHCl₃, THF, Py, DMSO, DMAc, DMF, NMP, *m*-cresol et.. The molecular weights of the polymers with inherent viscosities of 0.35~0.60 can be estimated by Gel Permeation Chromatography (GPC). These polymers were completely amorphous examined by Wide-angle X-ray diffraction. We will continue to research about the photoelectronic properties of these optically active polymers and then compared with their corresponding racemic polymers in details.

In conclusion, we have been first successfully synthesized the optically active dianhydride monomers and the corresponding OAAPIs, containing chiral binaphthyl units. The resulting OAAPIs possess high optical rotation, excellent solubility and good thermo-oxidative stability. The obvious advantages of the syntheses monomers method cover the problem of the optical rotation loss. We are interested in continuing to develop this type of optically active aromatic polyimides system.

REFERENCES

1. E. B. Kyba et al., *J. Org. Chem.*, 1977, **42**: 4173.
2. D. R. Heath et al., US Patent 3,730,946 (1973); 3,787,475 (1974).