Design, Synthesis and Chiroptical Properties of Optically Active Polyimides Containing Spirodilactone Unit

Lianxun GAO, Mengxian DING, Fushe HAN, and Jianqian Qu
高连勋， 丁孟贤， 韩福社， 曲建强
中国科学院长春应用化学研究所高分子物理与化学国家重点实验室
State Key Laboratory of Polymer Physics and Chemistry, Changchun
Institute of Applied Chemistry, Chinese Academy of Sciences
中国科学院、中国石化总公司高分子化学联合开发实验室
Polymer Chemistry Laboratory, Chinese Academy of Sciences
and China Petro-Chemical Corporation
Changchun 130022

1. Introduction

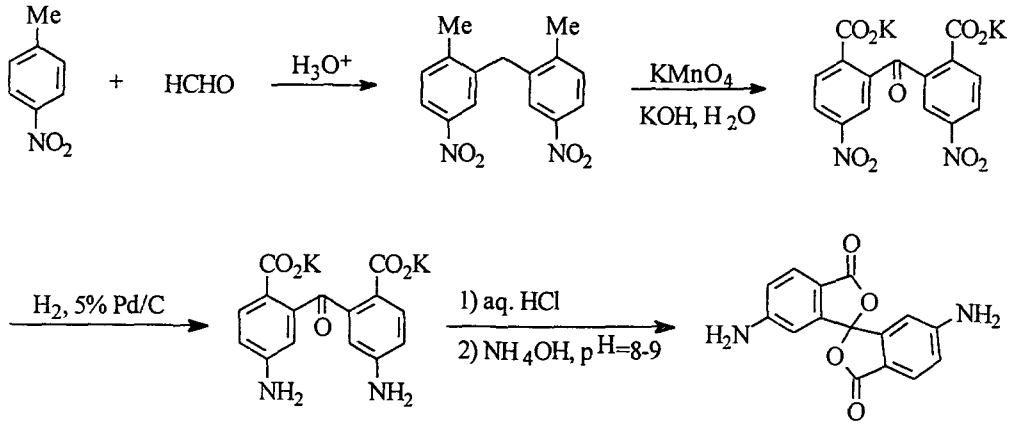
The synthesis and applications of optically active polymers are currently attracting much attention. Most naturally occurring polymers are optically active, and some of them show high performance in chiral recognition and catalytic activity, owing to their specific chiral structure as represented by genes and enzymes. In synthetic polymer chemistry, optically active polymers have found successful uses in chiral chromatographic separations and shown great potential applications in chiral catalytic systems, liquid crystals, optical switches, nonlinear optics and biomedical, etc.. In the past work, four kinds of optically active polyimides containing 1,1' -binaphthyl unit were synthesized and characterized. To systematically investigate the chiroptical properties of main chain optically active polymers, a novel type of chiral polyimides containing spirodilactone unit and were synthesized and characterized.

2. Results and Discussion

2-1. Synthesis of 6,6' -Diamino-3,3' -dioxo-[1,1]-spirodiphthalide

p-Nitrotoluene was reacted with paraformaldehyde under an acidic condition to form 2,2' -dimethyl-5,5' -dinitrodiphenylmethane, which was oxidized by KMnO4 in an aqueous potassium hydroxide solution. The dinitro functional group of the oxidized product was reduced to diamino group with hydrogen in the presence of a catalytic Pd-C in an aqueous solution. The resulted diamino intermediate was lactonized in an acidic condition to form the desired 6,6' -diamino-3,3' -dioxo-[1,1]-spirodiphthalide(Scheme 1).

Scheme 1. Synthesis of 6,6' -Diamino-3,3' -dioxo-[1,1]-spirodiphthalide



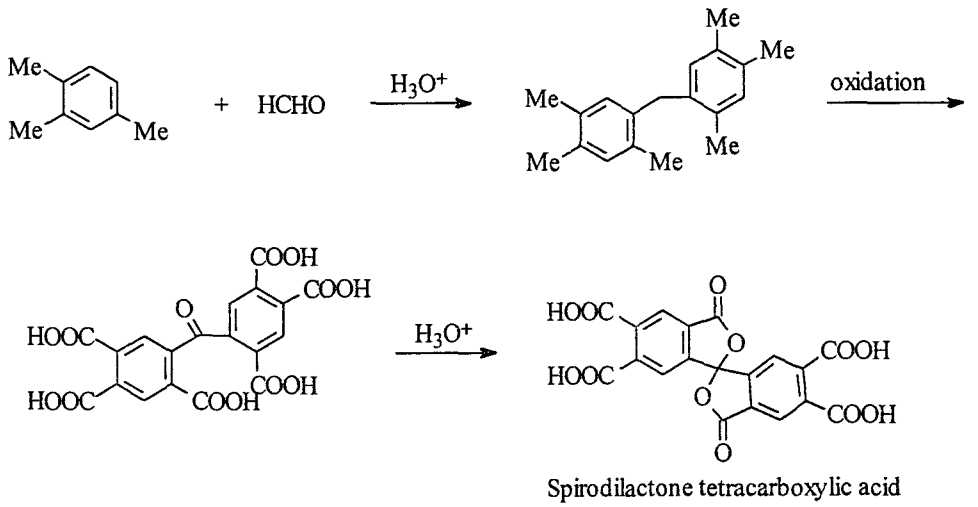
6,6'-Diamino-3,3-dioxo-[1,1]-spirodiphthalide

2-2. Synthesis of 3,3' -Dioxo-[1,1]-spirodiphthalide-5,5' ,6,6' -tetracarboxylic Acid

2,2' ,4,4' ,5,5' -Hexamethyldiphenylmethane was synthesized from the condensation of 1,2,4-trimethylbenzene and paraformaldehyde in the first step; subsequently, the diaryl methanes were oxidized by a two-stage

procedure, after that, the solution containing the oxidized products were refluxed in a acidic condition to form the spirodilactone tetracarboxylic acid. By the same method, a series of aromatic spirodilactones were prepared(Scheme 2).

Scheme 2. Synthesis of Spirodilactone Tetracarboxylic Acid



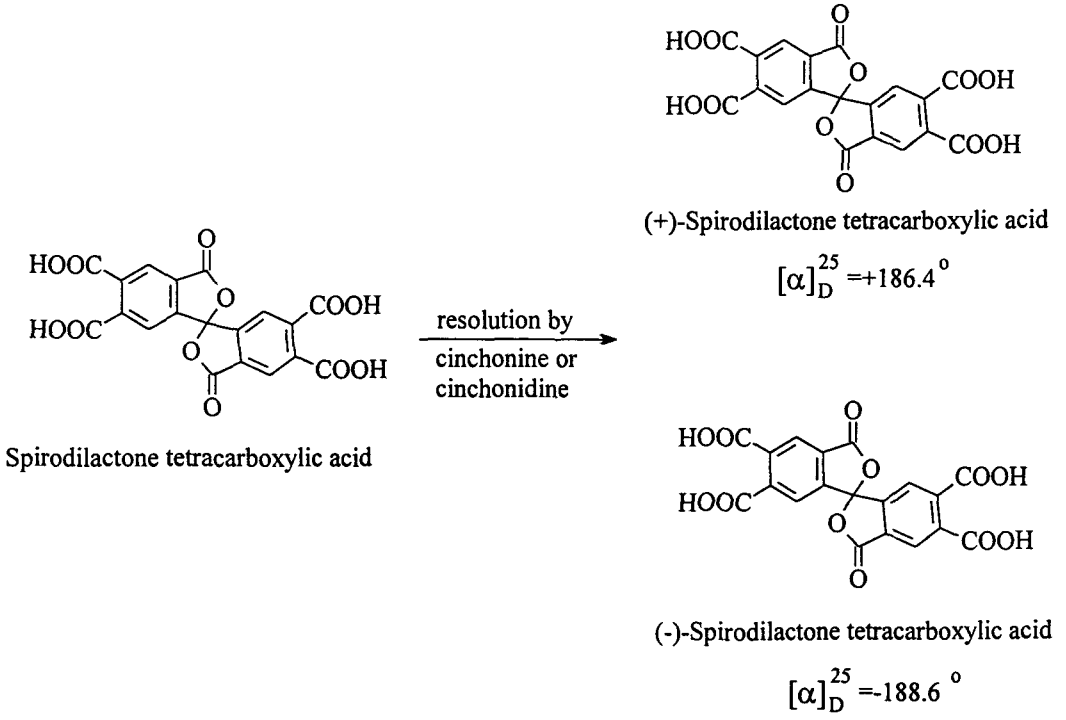
Spirodilactone tetracarboxylic acid

2-3. Resolution of 3,3' -Dioxo-[1,1]-spirodiphthalide-5,5' ,6,6' -tetracarboxylic Acid

The resolution of 3,3'-dioxo-spirodiphthalide-5,5',6,6'-tetracarboxylic acid was investigated using quinine, quinidine, cinchonine and cinchonidine, and other chiral diamines as resolving reagents. It is found that the cinchonine and cinchonidine have better efficiency than the other reagents. The enantiomer with $[\alpha]_D^{25}$=-188.6° and +186.4° were obtained after several runs of repeating resolution using cinchonine and cinchonidine, respectively(Scheme 3). According to the chiroptical methods, the enantiomer may be regard as enantiomerically pure isomer. The study of the optically active stability of the optically active tetracarboxylic acid

showed that the optical activity was unstable in the acidic and basic condition.

Scheme 3. Resolution of 3,3' -Dioxo-[1,1]-spirodiphthalide-5,5',6,6'-tetracarboxylic Acid

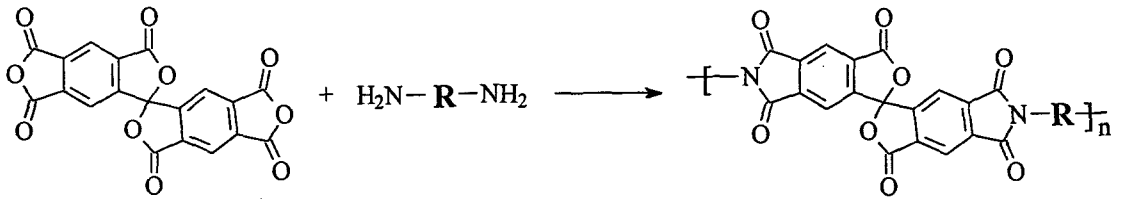


2-4. Polymerization

A type of optically active polyimides containing spirodilactone unit was prepared *via* a conventional two-stage procedure(Scheme 4 and Scheme 5). In contrast, the optically active polymers possessed the same solubilities and thermal properties as the racemic polymers. Whereas the crystallization morphology was different, as that of the racemic polymer was amorphous, while the optically active polymers were partially crystallized. The properties of the optically active stability of the optically

active polymers were close to that of the tetracarboxylic acid isomer, they are also unstable in acidic and basic conditions.

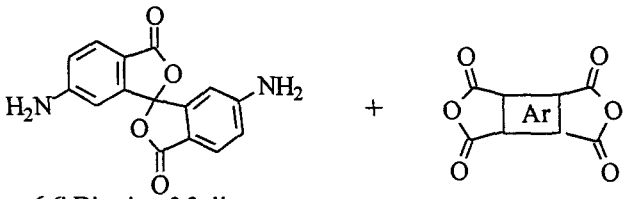
Scheme 4. Polymerization of 3,3' -Dioxo-[1,1]-spirodiphthalide-5,5' , 6,6' -tetracarboxylic Acid with Diamines



(±)-, (+), and (-)-Spirodilactone tetracarboxylic acid

(±)-, (+), and (-)-Polyimides

Scheme 5. Polymerization of 6,6' -Diamino-3,3' -dioxo-[1,1]-spirodiphthalide with Dianhydrides



6,6'-Diamino-3,3-dioxo-[1,1]-spirodiphthalide