



Synthesis and properties of novel soluble fluorinated polyamides containing pyridine and sulfone moieties[☆]



Xiao-Ling Liu^{a,*}, Dan Wu^a, Rui Sun^b, La-Mei Yu^b, Jian-Wen Jiang^b, Shou-Ri Sheng^{a,b,**}

^a Key Laboratory of Functional Small Organic Molecule of Ministry of Education, Jiangxi Normal University, Nanchang 330022, China

^b College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China

ARTICLE INFO

Article history:

Received 20 March 2013

Received in revised form 11 May 2013

Accepted 23 May 2013

Available online 20 June 2013

Keywords:

Fluorinated polyamide

Pyridine structure

4-Trifluoromethylphenyl pendant

Sulfone linkage

Soluble

ABSTRACT

A new diamine containing pyridine and trifluoromethylphenyl groups, 4-(4-trifluoromethylphenyl)-2,6-bis(4-aminophenyl)pyridine, was synthesized and used in the preparation of the fluorinated polyamides containing pyridine and sulfone moieties with inherent viscosities of 0.70–1.06 dL g⁻¹ by the low temperature polycondensation with 4,4'-sulfonyl dibenzoyl chloride, 4,4'-[sulfonyl bis(4-phenyleneoxy)]dibenzoyl chloride, 3,3'-[sulfonyl bis(4-phenyleneoxy)]dibenzoyl chloride and 4,4'-[sulfonyl bis(2,6-dimethyl-1,4-phenyleneoxy)]dibenzoyl chloride in *N,N*-dimethylacetamide (DMAc) solution containing pyridine, respectively. All the polymers are amorphous and readily soluble in organic solvents such as DMAc, *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide, dimethyl sulfoxide, pyridine (Py), and tetrahydrofuran at room temperature. The resulting polymers showed glass transition temperatures between 280 and 318 °C and 10% weight loss temperatures ranging from 485 °C to 516 °C, and char yields at 800 °C higher than 50% in nitrogen. All polymers could be casted into transparent, flexible and strong films from DMAc solutions with tensile strengths of 72–81 MPa, elongations at break of 12–15%, and tensile moduli of 1.8–2.1 GPa. These polymers had low dielectric constants of 3.40–3.51 (1 MHz), low moisture absorption in the range of 1.08–1.28%, and high transparency with an ultraviolet–visible absorption cut-off wavelength in the 374–382 nm range.

© 2013 The Authors. Published by Elsevier B.V. All rights reserved.

1. Introduction

It is well known that aromatic polyamides are characterized as highly thermally stable polymers because of their combination of excellent thermal, mechanical and chemical properties [1–6]. However, most of them have high melting or softening temperature and are insoluble in most of organic solvents partly because of the strong interchain interaction. These properties make them generally intractable or difficult to process, thus limiting their applications. To overcome these limitations, structural modification of the polymer backbones, such as the introduction of flexible bonds (e.g., –O–, –SO₂–, etc.) [7–9], bulky pendant [10–13] or cardo groups [14–16], unsymmetrical [17–19] or non-coplanar

structures [20–23], have been used to modify the polymer properties by the design and preparation of new monomers. Among these approaches, introduction of fluorine groups into the backbone or side chain of polyamides has been considered as one of the most effective methods and attracted more and more attention from both academia and industry because the introduction of fluorine groups can provide not only enhanced solubility but also other merits such as good thermal oxidative stability, good electrical insulating and dielectric properties, low water uptake and so on [24–29]. In recent years, there have been some reports concerning the incorporation of pyridine and its derivatives into polymeric frameworks [30–33]. The rigidity based on the symmetry and aromaticity of the pyridine ring would contribute to the thermal and chemical stability, retention of mechanical property of the resulting polymer at elevated temperature, and the polarizability resulting from the nitrogen atom in pyridine ring would be suitable to improve their solubilities in organic solvents. Although polyamides based on 4-aryl-2,6-bis(4-aminophenyl)pyridines such as 4-(4-methylphenyl)-2,6-bis(4-aminophenyl)pyridine and 4-phenyl-2,6-bis(4-aminophenyl)pyridine have been previously reported [30], to our knowledge, little attention has been paid to the preparation of fluorinated polyamide from diamine monomer bearing pyridine and trifluoromethyl groups. In a continuation of our studies on easily processable high-temperature fluorinated

[☆] This is an open-access article distributed under the terms of the Creative Commons Attribution-NonCommercial-No Derivative Works License, which permits non-commercial use, distribution, and reproduction in any medium, provided the original author and source are credited.

* Corresponding author. Tel.: +86 791 88120619; fax: +86 791 88506404.

** Corresponding author at: Key Laboratory of Functional Small Organic Molecule of Ministry of Education, Jiangxi Normal University, Nanchang 330022, China. Tel.: +86 791 88120619; fax: +86 791 88506404.

E-mail addresses: liuxiaoling@jxnu.edu.cn (X.-L. Liu), shengsr@jxnu.edu.cn (S.-R. Sheng).

polyamides [16,27,28], we herein report several organosoluble aromatic polyamides containing pyridine moieties and 4-trifluoromethylphenyl substituents, along with flexible sulfone or sulfone ether linkages in the polymer main chains, based on a novel aromatic diamine monomer, 4-(4-trifluoromethylphenyl)-2,6-bis(4-aminophenyl)pyridine. The incorporation of the rigid pyridine heterocyclic ring units, bulky 4-trifluoromethylphenyl pendant groups and flexible sulfone linkages into the polymer backbone would be resulted in great benefits for improving polymer solubility and electrical and dielectric performance while maintaining thermal stability. In addition to the solubility, thermal, mechanical, optical and electric properties, the water uptakes of the obtained fluorinated poly(pyridine sulfone amide)s are also studied in this article.

2. Results and discussion

2.1. Monomer synthesis

As shown in Scheme 1, the new aromatic diamine monomer, 4-(4-trifluoromethylphenyl)-2,6-bis(4-aminophenyl)pyridine (**2**) was prepared by a two-step synthetic route. Firstly, the dinitro compound (**1**) containing pyridine heterocyclic and 4-trifluoromethylphenyl pendant group, was synthesized via a modified Chichibabin pyridine synthesis [34] from 4-trifluoromethylbenzaldehyde and 4'-nitroacetophenone in the presence of ammonium acetate. The diamine **2** was then obtained by catalytic hydrogenation of the dinitro compound **1** using hydrazine hydrate and Pd/C catalyst in refluxing ethanol.

The structures of **1** and **2** were confirmed by elemental analysis, FTIR and ^1H NMR spectroscopy. In the FTIR spectrum of the dinitro compound **1** (Fig. 1A), representative absorptions appearing around 1522 and 1350 cm^{-1} were due to symmetric and asymmetric stretching of nitro groups which disappeared after reduction. The FTIR spectrum of diamine monomer **2** (Fig. 1B) showed the characteristic bonds of amino groups at 3445 and 3358 cm^{-1} (N–H stretching) and the characteristic absorption of trifluoromethyl group at 1164 cm^{-1} , respectively. In addition, the absorption band appeared at 1621 cm^{-1} was the characteristic one of pyridine ring. In the ^1H NMR spectrum of diamine **2** (Fig. 2), the signals of aromatic protons appeared in the range of 6.77–8.04 ppm, and the characteristic resonance signal at 3.86 ppm is due to the amino group. The assignments of each proton agreed well with the proposed molecular structure of diamine monomer **2**.

2.2. Polymer synthesis

The low-temperature solution polycondensation technique was used for the synthesis of the several fluorinated polyamides containing pyridine and sulfone moieties as depicted in Scheme 2. The polyamides **4a–4d** were prepared in a one-step pathway by the direct polycondensation reaction of 1 equiv. of **2** with 1 equiv.

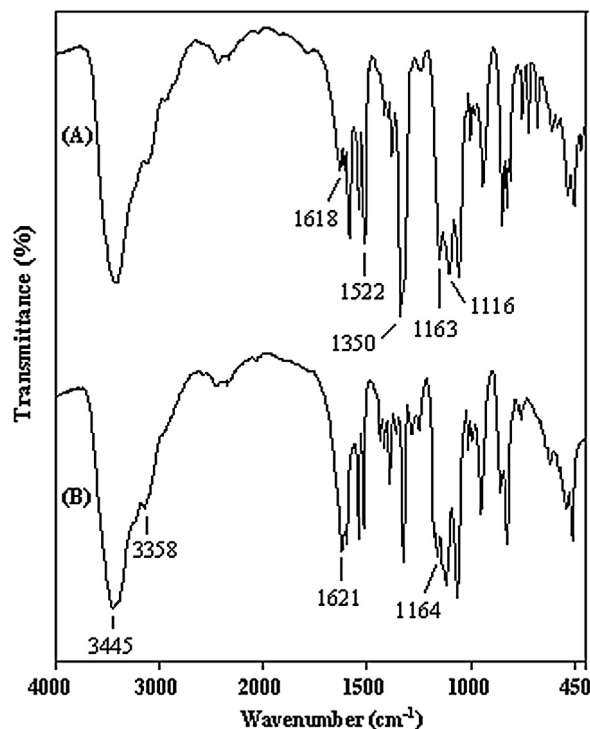
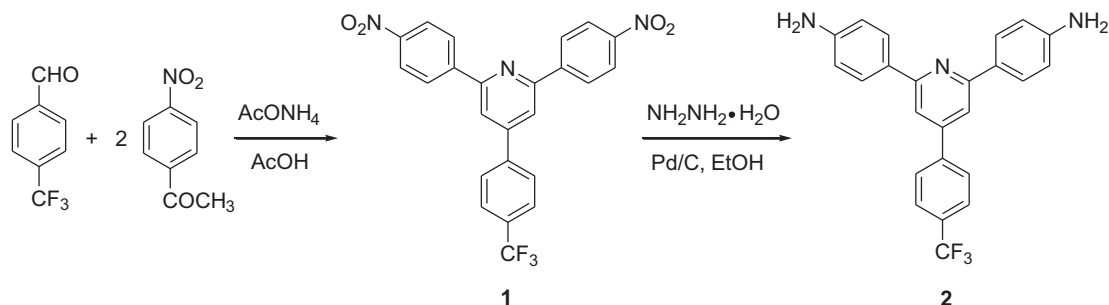


Fig. 1. FTIR spectra of the dinitro compound **1** (A) and the diamine **2** (B).

of the diacyl chloride (**3**) in DMAc solution containing a trace of pyridine cooled by an external ice–acetone bath. The reaction temperature was maintained at -10 to 0 $^{\circ}\text{C}$ in the initial 5 h. In order to obtain maximum molecular weight, the reaction was then allowed to proceed overnight at room temperature. All polymerizations proceeded homogeneously throughout the reaction, and highly viscous solutions were obtained. The polyamides **4a–4d** with inherent viscosities ranging from 0.70 to 1.06 dL g^{-1} (Table 1) were isolated as tough fibers in nearly quantitative yields, and could be solution-cast into films, indicating their high molecular weights.

As shown in Table 1, the viscosity of these polymers was in the order: **4a** > **4b** > **4c** > **4d**. This might be attributed to the presence of the more flexible ether groups in the main chains (polymers **4b** and **4c**), which decreased the intermolecular hydrogen bonding. Further, attachment of methyl substituents on the benzene ring (polymer **4d**) led to increased packing distance, introduction of lateral disorder, and decreased polar forces; thus polymer **4d** showed a lower viscosity.

Structural features of these polymers were characterized by FTIR and NMR spectroscopy. A typical FTIR spectrum for the polymer **4b** is displayed in Fig. 3. The FTIR spectra of all polymers showed the characteristic absorptions of the amide group at



Scheme 1. Synthetic route to new diamine monomer **2**.

Download English Version:

<https://daneshyari.com/en/article/7753411>

Download Persian Version:

<https://daneshyari.com/article/7753411>

[Daneshyari.com](https://daneshyari.com)