Highly transparent and hydrophobic fluorinated polyimide films with *ortho*-kink structure

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A B S T R A C T

This study focuses on the synthesis and characterization of new polyimide films with *ortho*-kink structures based on trifluoromethyl-containing diamines and hexafluoroisopropylidene-containing dianhydrides. High-temperature solution polycondensation reactions via conventional two-stage process involving the thermal imidization of the poly(amic acid) precursors resulted in polyimides with high molecular weights. The structures of the monomers and the corresponding polymers were fully confirmed by infrared and nuclear magnetic resonance spectroscopy. All polyimides were easily soluble in convenient organic solvents and showed excellent thermal stability, up to 345 °C. Transparent thin films were obtained therefrom, some of them having a porous structure. The polyimides presented good optical properties with high transparency and low cut-off wavelength. Their aggregation behavior followed by fluorescence spectroscopy was discussed in correlation with the chemical structure. The high hydrophobic character of these fluorinated polyimides was evidenced by the values of water contact angle to the polymer film surfaces. All these properties recommend their use in opto-electronic devices as transparent flexible substrates.

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1. Introduction

In our days there is a trend to find, by researching and developing, new materials capable of overcoming specific problems, and improving or reducing the cost of present-day industrial processes. In contrast to conventional polymeric materials, high-performance materials are characterized by specific criteria, such as higher thermal resistance, higher mechanical strength, lower specific density, higher conductivity, higher thermal, electrical or sound insulation properties, and superior flame resistance [1,2]. Accordingly, aromatic polyimides are regarded as high-performance materials due to their superior thermal and mechanical properties, which make them useful for advanced technologies [3–6]. They are distinguished from other high-performance polymers by the solubility of the polyamidic acid precursor form, which can be cast into uniform films and quantitatively converted to the polyimide structure. Their strength, heat and chemical resistance are so great that these materials often replace glass and metals, such as steel, in many demanding industrial applications. For these reasons, polyimides have found wide use as insulating thin films and coatings in microelectronic, advanced composites in the aerospace and armament industry, asbestos substitutes in thermal isolation units, advanced fabrics and non-woven materials for industrial filters, protective and sport clothing, among others.

However, fully aromatic polyimides have rigid chains and strong interchain interactions originating from intra-

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and interchain charge transfer complex (CTC) formation and electronic polarization, which result poor solubility and difficult processing. The introduction of thermally stable aromatic and non-aromatic fluorine-containing structures into the polymer backbone is a promising way to modify the desirable properties of polyimides, especially their solubility [7]. The incorporation of fluorine into polyimide structures has been intensively explored in the past decade with the hope of fine-tuning several properties of particular interest. Fluorine incorporation has been found to generally lower the dielectric constant [8] and moisture absorption [9], to bring about desirable changes to optical properties [10] and also, to increase the thermal stability in some cases [11]. While there have been occasional forays into more complex fluorinated structures with valuable results, most work has concentrated on the incorporation of the hexafluoroisopropylidene moiety (6F) into dianhydride and diamine components [12,13] or of perfluorinated groups on benzene rings [14].

Also, the introduction of kink structures into polymer chains can prevent chains' alignment and disrupt the formation of efficient charge transfer complexes (CTCs). As a consequence, polymers with substantially improved solubility and easy to be processed from their solutions by common casting or spin-coating techniques could be obtained [15,16]. The kink structure can also result in the formation of colorless polymer films with high transmittance.

Combining these structural modifications, i.e. the incorporation of flexible groups, as hexafluoroisopropylidene or trifluoromethyl, and kink structure in the polymer backbones, minimizes the trade-off between the processability and properties of wholly aromatic polyimides. As part of our continuing efforts in developing easy processable, highly thermostable polymers with potential ability for use as advanced materials, it appeared interesting to us to synthesize new *ortho*-kink aromatic polyimides containing hexafluoroisopropylidene in the main chain and trifluoromethyl units on the aromatic rings. The basic properties of these kink polyimides such as solubility, molecular weight, thermal stability, as well as, the photo-optical properties, films quality and wettability were investigated.

2. Experimental

2.1. Starting materials

2-Nitro-4-(trifluoromethyl)-chlorobenzene, piperazine (99%), triethylamine (⩾99%), 1,4-dihydroxybenzene (ReagentPlus®, ⩾99%), hexafluoroisopropylidene-bis(phthalic anhydride) (6FDA) (99%), hexafluoroisopropylidene-bis(phenol) (97%), 4-nitrophthalonitrile (99%), dimethylsulfoxide (99.7%; DMSO), dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (HPLC grade; NMP), chloroform (anhydrous, ⩾99%) were purchased from Sigma–Aldrich (Taufkirchen, Germany). Acetic anhydride (98%; GC) and tin chloride dihydrate (>99.99%) were purchased from Merck (Darmstadt, Germany). Hydrochloric acid (37%) and potassium carbonate (reagent grade) were purchased from Chimopar (Bucharest, Romania). Potassium hydroxide (p.a.) was purchased from Chemical Company (Iasi, Romania). All reagents, except 6FDA, were used without further purification. Solvents were purified by standard procedures and handled in a moisture-free atmosphere.

2.2. Synthesis of monomers

1,4-Bis[2-amino-4-(trifluoromethyl)phenyl]piperazine (**M1**) was prepared in two steps starting from 2-nitro-4-(trifluoromethyl)chlorobenzene. The highly activated chlorine atom in 2-nitro-4-(trifluoromethyl)chlorobenzene was replaced with piperazine unit by aromatic nucleophilic substitution reaction, in the presence of triethylamine as catalyst. The reduction of the resulting dinitro compound with $SnCl_2$/HCl as the reducing agent lead to the corresponding diamine **M1**. After purification by extraction with chloroform, **M1** was obtained in a yield of 90%.
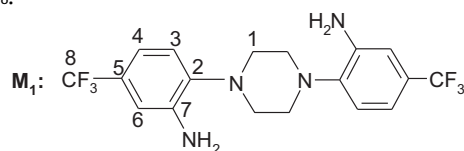
M1: ^1H NMR ($CDCl_3$, 25 °C), δ (ppm): 3.13 (8H, bs, H-1), 4.20 (4H, bs, −NH_2), 6.97 (2H, bs, H-6), 7.02 (2H, d, 8.4 Hz, H-4), 7.10 (2H, d, 8 Hz, H-3). ^{13}C NMR ($CDCl_3$, 25 °C), δ (ppm): 51.2 (C-1), 111.7 (quartet, 3.5 Hz, C-6), 115.5 (quartet, 4 Hz, C-4), 119.7 (C-3), 124.4 (quartet, 272 Hz, C-8), 126.8 (quartet, 32 Hz, C-5), 141.6 (C-2), 141.7 (C-7). ^{19}F NMR ($CDCl_3$, 25 °C), δ (ppm): −62.2. ^{15}N NMR (*acetone-d6*, 25 °C), δ (ppm): 52–53 (both nitrogen atoms).

1,4-Bis[2-amino-4-(trifluoromethyl)phenoxy)]benzene (**M2**) was prepared in a similar way as described for **M1**. The aromatic nucleophilic substitution reaction of the chlorine from 2-nitro-4-(trifluoromethyl)chlorobenzene with 1,4-dihydroxybenzene, in the presence of K_2CO_3, gave the corresponding dinitro compound which was further reduced with $SnCl_2$/HCl to give diamine **M2**. After purification by extraction with chloroform, **M2** was obtained in a yield of 92%.
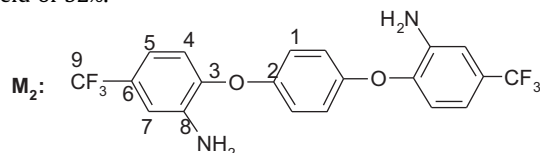
M2: ^1H NMR ($CDCl_3$, 25 °C), δ (ppm): 4.07 (4H, bs, −NH_2), 6.84 (2H, d, 8.4 Hz, H-4), 6.95 (2H, d, 8.4 Hz, H-5), 7.03 (4H, bs, H-1), 7.05 (2H, bs, H-7). ^{13}C NMR ($CDCl_3$, 25 °C), δ (ppm): 112.7 (quartet, 3.7 Hz, C-7), 115.4 (quartet, 4 Hz, C-5), 117.8 (C-4), 120.0 (C-1), 124.2 (quartet, 272 Hz, C-9), 126.3 (quartet, 32 Hz, C-6), 138.2 (C-8), 146.7 (C-3), 152.2 (C-2). ^{19}F NMR ($CDCl_3$, 25 °C), δ (ppm): −62.0. ^{15}N NMR (*acetone-d6*, 25 °C), δ (ppm): 49 (NH_2).

Hexafluoroisopropylidene-bis(phthalic anhydride) (6FDA, **M3**) was provided from a commercial source and it was purified by recrystallization from acetic anhydride followed by thoroughly washing with anhydrous diethylether.