



Investigation of the chemical and morphological structure of thermally rearranged polymers



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ABSTRACT

Reacting *ortho*-functional poly(hydroxyimide)s via a high-temperature (i.e., 350 °C–450 °C) solid-state reaction produces polymers with exceptional gas separation properties for separations such as CO₂/CH₄, CO₂/N₂, and H₂/CH₄. However, these reactions render these so-called thermally rearranged (TR) polymers insoluble in common solvents, which prevent the use of certain experimental characterization techniques such as solution-state nuclear magnetic resonance (NMR) from identifying their chemical structure. In this work, we seek to identify the chemical structure of TR polymers by synthesizing a partially soluble TR polymer from an *ortho*-functional poly(hydroxyamide). The chemical structure of this TR polymer was characterized using 1-D and 2-D NMR. By use of cross-polarization magic-angle spinning ¹³C NMR, the structure of the polyamide-based TR polymer was compared to that of a polyimide-based TR polymer with a nearly identical proposed structure. The NMR spectra suggest that oxazole functionality is formed for both of these TR polymers. Furthermore, gas permeation results are provided for the precursor polymers and their corresponding TR polymer. The differences in transport properties for these polymers result from differences in the isomeric nature of oxazole-aromatic linkages and morphological differences related to free volume and free volume distribution.

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1. Introduction

Thermally rearranged (TR) polymers were first investigated for CO₂/CH₄ separations, and these polymers have shown exceptional permeabilities, selectivities, and a resistance to CO₂ plasticization

[1]. These polymers are synthesized via a solid-state reaction of aromatic poly(hydroxyimide)s (PIs), whereby the *hydroxy*-functional group must be *ortho*-positioned to the polyimide diamine. Upon reacting these polyimides to their corresponding TR polymers, the resulting materials become insoluble in all known solvents, and their insolubility prevents the use of traditional characterization techniques, such as solution-state nuclear magnetic resonance (NMR), to confirm their precise chemical structure.

The outstanding transport properties of TR polymers have spurred significant interest in identifying their chemical structure. Tullos et al. drew correlations between the reaction of small molecule hydroxy-imides to form oxazoles with the reaction of PIs to form polybenzoxazoles (PBOs) [2,3]. Han et al. confirmed through mass spectrometry that CO₂ is evolved during thermal rearrangement, also supporting the reaction mechanism of PIs to form PBOs [4]. Calle et al. used Fourier Transform Infrared

Abbreviations: PI, poly(hydroxyimide); PA, poly(hydroxyamide); PBO, polybenzoxazole; TGA, thermogravimetric analysis; DSC, differential scanning calorimetry; PALS, positron annihilation lifetime spectroscopy; FTIR, Fourier transform infrared spectroscopy; SEC, size exclusion chromatography; NMR, nuclear magnetic resonance; COSY, correlation spectroscopy; HSQC, heteronuclear single quantum correlation; HMBC, heteronuclear multiple bond correlation; CP-MAS, cross-polarization magic-angle spinning; TOSS, total suppression of spinning sidebands; APAF, 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane; 6FCI, 2,2'-bis(4-carboxy-phenyl)hexafluoropropane diacid chloride; 6FDA, 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride.

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Spectroscopy (FTIR) to confirm the PBO structure of samples synthesized from PIs and poly(hydroxyamide)s (PAs) [5].

Nevertheless, alternative chemical structures have been proposed. Hodgkin et al. used FTIR and molecular simulation results to suggest that PI precursors react to form poly(biphenylene bisimide)s instead of PBOs [6,7]. Kostina et al. used FTIR and minimization of potential reaction energies to suggest that the predominant chemical structure of TR polymers is an aromatic lactam [8].

The thrust of this work is to identify the structure of TR polymers through 1-D and 2-D NMR experiments. To accomplish this end, we have employed traditional synthesis techniques described by Han et al. [9] to prepare a partially soluble, fluorinated TR polymer based on 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (APAF) and 2,2'-bis(4-carboxy-phenyl)hexafluoropropane diacid chloride (6FCl) (PA-TR). With the exception of a structural isomer, the proposed APAF-6FCl PA-TR is identical in chemical structure to that of a TR polymer prepared from APAF and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) (PI-TR, cf., Scheme 1).

Solution-state ^1H NMR and ^{13}C NMR coupled with correlation spectroscopy (COSY), heteronuclear single quantum correlation (HSQC) spectroscopy, and heteronuclear multiple bond correlation (HMBC) spectroscopy aids in identifying PBO peak assignments for the soluble fraction of the PA-TR. Moreover, we have employed cross-polarization magic-angle spinning (CP-MAS) ^{13}C NMR to compare the solution NMR spectra for the PA-TR with the solid-state spectra for the PA-TR and PI-TR samples. These results indicate the formation of oxazole functionality for polyimide and polyamide-based TR polymers.

We also determined gas permeability for several gas pairs for the PA, PA-TR, PI, and PI-TR polymers. From these results, TR polymers formed from polyimides have higher permeabilities and similar selectivities to TR polymers formed from polyamides.

Confirmation that PBOs can be synthesized via PIs has broad implications for designing new polymers for a variety of applications. In addition to gas separation membranes, PBOs and related structures, such as polybenzimidazoles and polybenzothiazoles, are actively being investigated as high-temperature proton exchange membranes in fuel cells [10–12], nanoporous materials for CO_2 capture and H_2 storage [13,14], and photoresist polymers in the microelectronics industry [15–17]. Using the thermal rearrangement process to form new PBOs may facilitate discovery of new adsorbent materials, polymer electrolytes, photosensitive polymers with low dielectric constants, and gas separation membranes.

2. Materials and methods

2.1. Synthesis of the poly(hydroxyimide) (PI)

Poly(hydroxyimide) (PI) monomers were purified using vacuum sublimation. The diamine, 2,2-bis(3-amino-4-hydroxyphenyl)-

hexafluoropropane (APAF, Chriskev, CAS # 83558-87-6) was sublimated at 220 °C and the dianhydride, 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA, Sigma Aldrich, CAS # 1107-00-2) was sublimated at 235 °C. Crystals were used for synthesis immediately after sublimation.

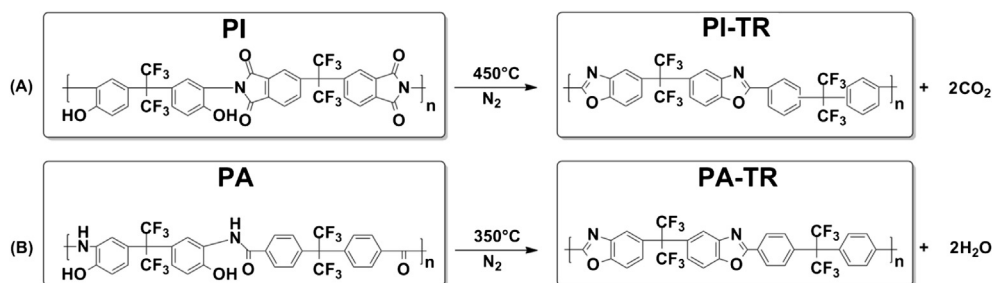
Lozano et al. have reported that higher molecular weight polyamides can be synthesized by first silylating diamines prior to amidization [18]. In addition to polyamides, this synthesis technique has been applied to PIs similar to those considered in this work [4,5]. Therefore, in addition to monomer sublimation, silylation was used to produce a PI with sufficient molecular weight to cast films.

In a typical synthesis batch, 25 mmol of APAF was added to a three-neck flask fitted with an overhead mechanical stirrer and purged with nitrogen (Airgas, 99.999%). Nitrogen was flushed through a Drierite column (W.A. Hammond Drierite Co., Ltd., Xenia, OH) to remove water vapor before reaching the reaction flask. Anhydrous N-methyl-2-pyrrolidinone (NMP) (38 mL, Sigma Aldrich, P/N 328634) was used to dissolve the diamine, and, after the diamine was fully dissolved, an ice bath was used to chill the reaction vessel. Chlorotrimethylsilane (CTMS, 14.4 mL, Sigma–Aldrich, P/N 92361) and pyridine (12 mL, Sigma–Aldrich, P/N 270407) were added to the reaction flask as the silylating and activating agents, respectively. Approximately 4.4 mol of CTMS and pyridine were used per mole of APAF. Silylation was allowed to proceed for approximately 30 min.

After silylation, 25 mmol of 6FDA were slowly added to the reaction vessel. Because the APAF diamine contains strongly electron withdrawing hexafluoroisopropylidene groups, a small amount of co-base, 4-dimethylaminopyridine (DMAP), was added to the reaction mixture to improve reactivity [19]. The amount of DMAP added to the reaction vessel was 10% of the molar ratio of pyridine used in the reaction. An additional 38 mL of anhydrous NMP was added to the reaction flask to make a 20% solution, and the poly(amic acid) reaction proceeded for 24 h. Unless otherwise noted, all concentration percents for polymer solutions are reported as the total mass of monomer in g per total volume of solvent in mL.

To imidize the poly(amic acid), 1,2-dichlorobenzene (27 mL, Sigma–Aldrich, P/N 240664) and additional anhydrous NMP (7 mL) were added to the reaction flask to make a 15% solution. The volume of 1,2-dichlorobenzene to total volume of solvent added was 1:4. The reaction solution was then heated to 180 °C for 24 h to imidize the poly(amic acid).

Following imidization, the reaction solution was precipitated as thin, light pink fibers in deionized water. Approximately 10 mL aliquots of polymer solution were precipitated in approximately 400 mL aliquots of deionized water, which were left stirring in a blender. To extract solvent, the polyimide fibers were rinsed with water and then left stirring in a 70:30 mixture of deionized water:methanol for 24 h. The methanol was purchased from VWR (P/N BDH-1135). The polymer fibers were then filtered and rinsed



Scheme 1. Proposed reactions of (A) APAF-6FDA, an *ortho*-functional poly(hydroxyimide) (PI), to form a polybenzoxazole (PI-TR) and (B) APAF-6FCl, an *ortho*-functional poly(hydroxyamide) (PA), to form a polybenzoxazole (PA-TR).

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