

## Dynamic relaxation characteristics of thermally rearranged aromatic polyimides

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### ABSTRACT

The glass–rubber and sub-glass relaxation characteristics of *ortho*-functionalized aromatic polyimides and thermally rearranged polymers were investigated by dynamic mechanical and dielectric methods. Soluble polyimides (HAB–6FDA; APAF–ODPA) were synthesized by chemical and thermal imidization and subject to thermal rearrangement at elevated temperature. For the thermal exposure histories investigated, mass loss studies indicated partial conversion of the polyimide precursor, suggesting the formation of TR copolymers containing both benzoxazole units and residual imide segments. Measurement of storage modulus and loss tangent was used to follow the thermal rearrangement process *in-situ* as reflected in the suppression of the polyimide glass transition as a function of precursor structure, the nature of the *ortho* functional groups and prior thermal exposure. In addition, changes in the position and intensity of local relaxations detected across the sub-glass temperature range were correlated with the degree of thermal rearrangement in these polymers.

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### 1. Introduction

The successful application of polymer membrane technologies for selective separations often requires membrane polymers with inherently favorable permeability and selectivity characteristics that can also withstand chemically demanding environments. In a number of recent studies, modified aromatic polyimides (API) have been investigated as a promising membrane material platform for gas separation and pervaporation applications [1–9]. These polymers, which are amenable to conventional solution-based membrane casting techniques, can be converted by solid-state thermal rearrangement to insoluble polybenzoxazoles (PBO) with outstanding chemical and thermal stability [10]. Initial gas separation studies reported by Park et al. [1] reveal surprising improvements in the separation performance of thermally rearranged (TR) polymers as compared to their polyimide precursors, with the resulting gas transport properties placing these materials at or beyond the membrane upper bound as described by Robeson

[11,12]. The enhanced gas separation performance realized in the TR polymer membranes has been attributed to an unusual distribution of free volume elements formed during the rearrangement process that fosters higher permeability while retaining selectivity [1,13].

Two aromatic polyimides suitable for thermal rearrangement have been prepared with inclusion of *ortho*-positioned functional groups; the diamine (–HAB–; –APAF–) and dianhydride (–6FDA–; –ODPA–) monomers were specifically selected to foster high permeability in the resultant membranes. For the API's investigated here, different synthesis routes were undertaken for the introduction of reactive acetate or hydroxyl groups at the *ortho* positions, respectively. Upon exposure to elevated temperature, intramolecular rearrangement leads to the formation of rigid PBO's. Fig. 1 illustrates the thermal conversion of the API structures studied in this work and the corresponding changes in both composition and connectivity.

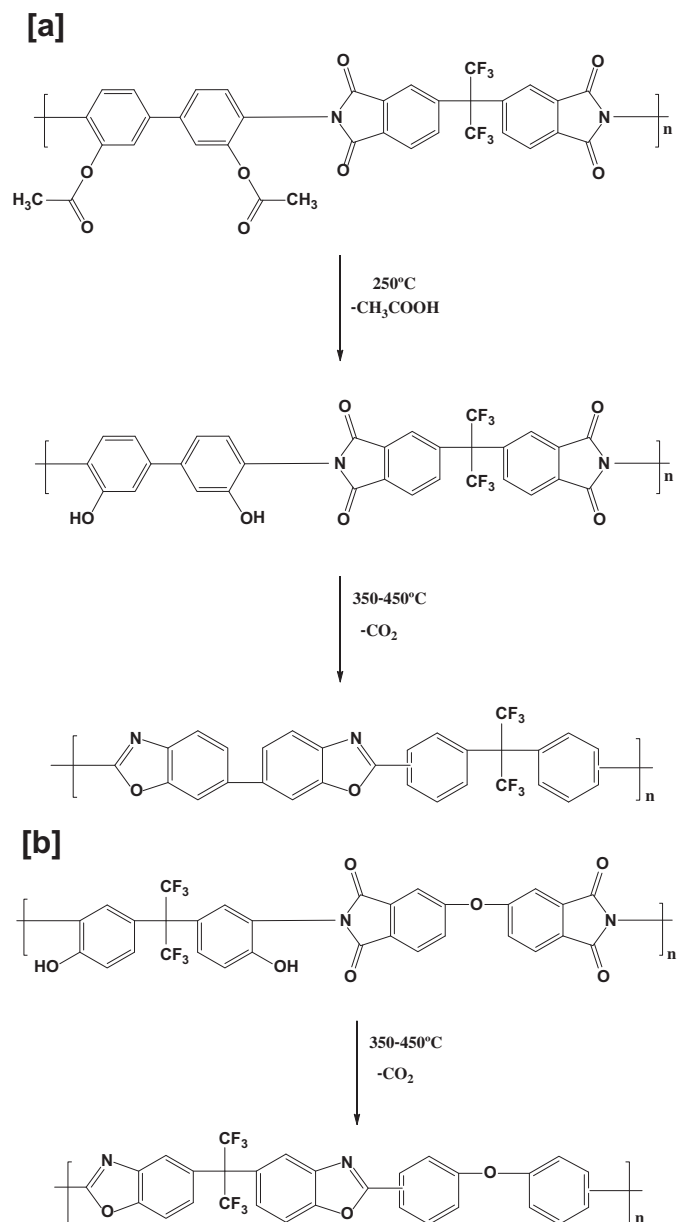
A key consideration in the preparation of TR polymers for use in membrane separations is the extent of segmental rearrangement achieved as a function of thermal exposure history. The degree of thermal rearrangement governs chain conformation and rigidity in the glassy state, and the distribution of free volume elements established during the rearrangement process. As discussed by both Sanders [6] and Smith et al. [7] for a series of HAB–6FDA

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**Fig. 1.** Chemical structures of aromatic polyimides and their corresponding polybenzoxazoles after thermal rearrangement. [a] HAB–6FDA synthesized by chemical imidization; [b] APAF–ODPA synthesized by thermal imidization.

polymer samples, thermogravimetric analysis (TGA), in combination with mass spectrometry (MS), can be used to assess the extent of intramolecular thermal rearrangement in these polymers as measured by the mass loss with corresponding identification of the loss products. While the overall mass loss can be nominally compared to a “theoretical” mass loss as predicted by reaction stoichiometry, the interpretation of the results is complicated by the numerous and typically overlapping mass loss phenomena that may be encountered upon polymer heating. These include egress of residual moisture or solvent, sequential conversion of *ortho* functional groups (*i.e.*, acetate to hydroxyl) as a prelude to rearrangement, and potential thermal degradation at high temperatures and/or extended times. In addition, inter-molecular reactions may be encountered which, while not necessarily distinguishable by TGA, could lead to the introduction of crosslinks in the polymer. As such, when attempting to correlate apparent degree of TR conversion with membrane separation performance, it is essential

to have access to a broader range of characterizations by which to evaluate the static and dynamic properties of the polymer matrix and their corresponding influence on small molecule transport. These include measurement of bulk density and estimation of fractional free volume [6], determination of free volume distribution [1,2,13], and characterization of the dynamic relaxation properties of both the as-synthesized API's and resulting PBO structures.

The dynamic relaxation behavior of aromatic polyimides has been the subject of extensive study: dynamic mechanical analysis and dielectric spectroscopy have been widely applied to determine transition temperatures, relaxation intensities, and corresponding time–temperature characteristics for the motional transitions encountered in these materials [14–30]. A brief description of the glass–rubber ( $\alpha$ ) and sub-glass ( $\gamma$ ,  $\beta$ ) relaxations typically observed in polyimides is presented in a recent study on Matrimid® [BTDA–DAPI] polyimide by Comer et al. [29]. In the current investigation, dynamic thermal analysis techniques (*i.e.*, dynamic mechanical analysis, dielectric spectroscopy) have been used to characterize the glass–rubber and sub-glass relaxation response of HAB–6FDA and APAF–ODPA *ortho*-functionalized polyimides and thermally rearranged (PBO) polymers. Across the glass–rubber relaxation range, measurements of modulus and loss tangent by dynamic mechanical methods provide insight as to the influence of prior TR exposure on polymer chain mobility, and afford an opportunity to monitor the TR process *in-situ* as manifested by backbone stiffening and shifts in the glass transition temperature. In the sub-glass region, changes in both the position and intensity of local, limited-range relaxations as a function of TR conditioning can be used as an additional basis upon which to evaluate the extent of polymer chain conversion and its impact on local mobility as related to the underlying sub-glass relaxation mechanisms.

## 2. Experimental

### 2.1. Polymer synthesis

Homopolyimides were synthesized by a two-step polycondensation using either chemical imidization or thermal imidization methods. Two distinct polyimides were prepared based on the combination of 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), and 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (APAF) with 4,4'-oxydiphthalic anhydride (ODPA). All monomers were purchased from Chriskev Company, Inc. (Lenexa, KS) and details on purification for the as-received monomers were provided previously by Ribeiro et al. [9]. For the polyimides synthesized by chemical imidization, poly(amic acid) precursors prepared by the reaction of diamine and dianhydride monomers were imidized in the presence of an excess of acetic anhydride and pyridine, leading to the esterification of hydroxyl groups originally present at the *ortho* positions of the diamine moiety (see synthetic details in Smith et al. [7]). In the case of polymers synthesized by thermal imidization, the poly(amic acid) precursors were thermally cyclized in solution at 180 °C under reflux, which led to the retention of hydroxyl groups at the *ortho* positions (re: Ribeiro et al. [9]). A total of four polymers were obtained corresponding to the chemically-imidized and thermally-imidized variants of HAB–6FDA and APAF–ODPA, respectively. The structures of the HAB–6FDA and APAF–ODPA polymers are shown in Fig. 1.

The chemical structures of the resulting polymers were confirmed by proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR; Varian INOVA-500 Spectrometer) and Fourier-transform infrared spectroscopy (FTIR–ATR; Nexus 470 Spectrometer from Thermo Nicolet). Full details on these characterizations are reported elsewhere [9].

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