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The effect of purge environment on thermal rearrangement of *ortho*-functional polyamide and polyimide

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ABSTRACT

The effects of nitrogen and air purge during thermal rearrangement of an *ortho*-functional polyamide (*o*-PA) and an *ortho*-functional polyimide (*o*-PI) towards a polybenzoxazole (PBO) structure have been investigated in terms of physicochemical changes and gas transport properties. The *o*-PA polymer was prepared from 2,2-bis(3-amino-4-hydroxyphenyl) hexafluropropane (BisAPAF) and 4,4′-biphenyl-dicarbonyl chloride (BPDC) while the *o*-PI polymer was derived from 4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 3,3′-dihydroxybenzidine (HAB). Experimental results show that the purge environment for the conditions used does not affect the thermal rearrangement of the *o*-PA film but significantly affects the thermal conversion of the *o*-PI film. Nearly identical chemical structures and pure gas permeability values are observed for *o*-PA films thermally treated at 300 °C under air or N_2. These properties become different in the *o*-PA films treated at 425 °C, which is presumed to be attributed to the influence of oxygen on the thermal stability of the derived PBO and probably the various degrees of thermal crosslinking reaction induced at a high temperature. The *o*-PI film was thermally rearranged at 425 °C because its thermal conversion takes place at a higher temperature range of 300 °C–450 °C. The *o*-PI film thermally rearranged in air exhibits improved gas permeation properties but significantly deteriorated mechanical properties. The air purge interrupts the thermal conversion of the *ortho*-functional imide to benzoxazole by oxidatively degrading the imide structure and forming the imine structure. As a result, both polymer structure and film properties change.

1. Introduction

Glassy polymer membranes continue to be of interest for gas separation applications such as H_2 purification [1,2], CO_2 capture [3,4], natural gas sweetening [5] and hydrocarbon removal [6], etc. An important challenge is the development of new high-performance materials that offer a better balance between permeability and selectivity than the typical trade-off that sometimes limits commercial success.

In recent years, many glassy materials with improved gas separation performance have been introduced. Masuda et al. [7] reported the formation of substituted polyacetylenes, e.g., poly[l-(trimethylsilyl)-1-propyne] (PTMSP) by using metal halides as the catalyst. This material was ultra permeable to all gases, but at the cost of low selectivity. Budd et al. [8,9] introduced a category of materials named polymers of intrinsic porosity (PIM) by incorporating a rigid ladder structure with contortion sites into the polymer backbone. The contortion caused by the spiro-center strongly inhibited the regular alignment of polymer chains. As a result, the fractional free volume (FFV) of the film is very high leading to the very high gas permeability. Among various PIMs reported to date, the PIM-1 polymer derived from 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane and 1,4-dicyanotetra-fluorobenzene has shown excellent gas permeation properties but its selectivity is relatively low [10]. Polyimides are another category of polymers that have been widely investigated, especially with a focus on structure–properties relationship [11–19]. Among the polyimides investigated, the one based on 4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) shows quite high gas permeability coefficients; however, the selectivity needs to be higher for most applications [19,20].

Recently, Park et al. developed another type of high-performance polymer: the so-called “thermally rearranged” (TR) polymers [21,22]. The reported TR polymers were obtained by thermally converting the solid *ortho*-positioned polyimide to heterocyclic polybenzoxazole (PBO) or polybenzothiazole (PBT), following the reaction proposed by Tullos et al. [23]. The resultant films have

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shown good separation performance for O_2/N_2, CO_2/N_2 and in particular for CO_2/CH_4 gas pairs. In addition, the plasticization characteristics of the TR films seem much improved compared to most other high-performance polymers [21]. Thus, TR polymers are considered to be a promising candidate for future applications in the industrial gas separation processes.

Several factors can influence the TR process. Park et al. [21], Wang et al. [24] and Sanders et al. [25] showed that increasing the rearrangement temperature results in a higher conversion of the precursor polymer to PBO. Ong et al. [26] claimed that the duration of thermal treatment is less influential on the conversion of the TR films compared to the effect of treatment temperature. Yeong et al. [27] demonstrated that the incorporation of a cardo moiety into the polymer backbone improves the gas separation performance of the TR polymer based on 3,3′-dihydroxybenzidine (HAB) and 4,4-(hexafluoro-isopropylidene) diphthalic anhydride (6FDA). Han et al. [28] showed evidences that different imidization routes during the synthesis process of the pristine polyimides could also affect the physical and gas separation properties of the TR polymers. Clearly, both process parameters during thermal rearrangement and precursor properties could influence the structure conversion and the separation performances of the resultant TR films.

The thermal rearrangement of an *ortho*-functional polymer is usually conducted under vacuum or in inert gas purge [21,22,24–28]. On the other hand, thermal rearrangement in air or in the presence of some amount of oxygen may be a simpler and more economical process since the absolute exclusion of oxygen will increase the cost of the membrane fabrication process. Thus, we examine the effect of purge atmosphere on the thermal rearrangement of two *ortho*-functional polymers in this study. Two purge media, nitrogen and air, were used for the thermal rearrangement. The precursors selected for this study were an *ortho*-functional polyamide and an *ortho*-functional polyimide. In addition to evaluating the pure gas separation performance of the resultant materials, the thermal transitions and chemical structure alterations were characterized by DSC, TGA, FTIR and XPS.

2. Experimental

2.1. Materials

The monomer 4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) (purity > 99.0%) was purchased from Clariant (Germany) and was further purified by vacuum sublimation prior to use. Other monomers including 2,2-bis(3-amino-4-hydroxyphenyl) hexafluropropane (BisAPAF) (>98%), 3,3′-dihydroxybenzidine (HAB) (>98%) and 4,4′-biphenyl-dicarbonyl chloride (BPDC) (>99%) were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan) and were used as received. *N*-Methyl-pyrrolidone (NMP) of analytic grade was used as the solvent for polymer syntheses and film casting. Reagents and solvents including acetic anhydride (>99.5%), anhydrous pyridine (>99.8%) and methanol (technical grade) were all used without further purification. Purified nitrogen (99.9995%) and purified air (O_2: 21% ± 1% with $CH_4 < 5$ ppm and $H_2O < 3$ ppm) used as purge gases were provided by SOXAL Pte. Ltd.

2.2. Synthesis procedures

The *ortho*-functional polyamide (*o*-PA) was synthesized from BisAPAF and BPDC as shown in Fig. 1. The typical synthesis procedures were as follows: BisAPAF (10 mmol) was dissolved in a mixture of 25 mL NMP and 2 mL pyridine in a conical flask equipped with nitrogen purge. After complete dissolution, the solution was cooled to 0 °C in an ice bath and stabilized for half an hour. Subsequently, the BPDC powder (10 mmol) was added all at once while stirring the solution. While the reaction proceeded at 0 °C for half an hour, the ice bath was removed and the viscous solution was stirred continuously at room temperature (25 °C ± 2 °C) overnight. The solution was then precipitated and washed three times in 1.5 L methanol. The polymer was filtered and dried in a vacuum oven at 60 °C overnight.

The *ortho*-functional polyimide (*o*-PI) was synthesized from 6FDA and HAB as shown in Fig. 2. The HAB (10 mmol) was dissolved

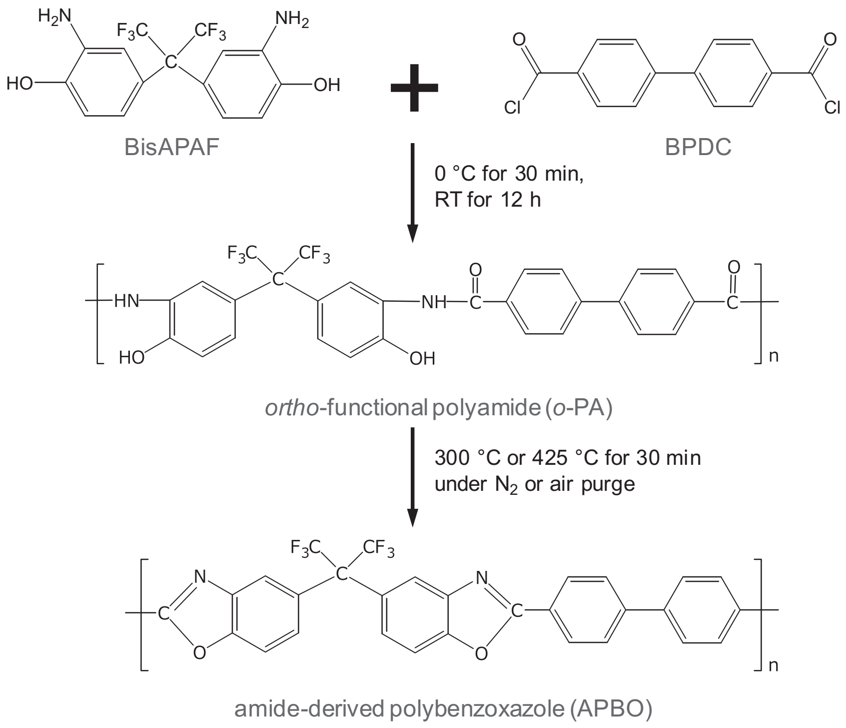

Fig. 1. Reaction schemes for the synthesis of the *ortho*-functional polyamide and its thermal rearrangement.