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The evolution of physicochemical and gas transport properties of thermally rearranged polyhydroxyamide (PHA)

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ABSTRACT

The evolution of physicochemical and gas transport properties of thermally rearranged polyhydroxyamide (PHA) as a function of temperature have been systematically investigated in the present work. Besides the degree of conversion, it is revealed that thermal cyclization temperature plays the other determining factor during the rearrangement process since not only could it affect the degree of thermal conversion, but also influences thermal history and introduces thermal crosslinking. By thermally cyclizing the PHA precursor membranes at different temperatures in the range of 300–450 °C, similar degrees of chemical structure conversion (~91%) have been achieved, while enhanced gas separation properties are found in the membrane thermally cyclized at a higher temperature. Analyses based on membrane physical properties and glass transition behavior prove that the aforementioned phenomenon is attributed to the suppression of polymer chain segmental rotation and the lower chain packing density induced by a higher thermal cyclization temperature. The gas sorption and diffusion characteristics of CO_2/CH_4 further elucidate that the amplification of membrane fractional free volume has a greater impact on diffusivity selectivity than solubility selectivity. The dual-mode sorption data confirm that the transformation of gas transport properties is attributed to the changes in both Henry's molecular dissolution and Langmuir sorption, which are closely related to the membrane physical properties.

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1. Introduction

As a new category of polymers with microporosity, thermally rearranged (TR) polymers have greatly stimulated the research interests in the field of polymer science and technology due to their excellent gas separation performance as well as strong chemical and thermal resistance [1–5]. In general, TR polymer films are obtained by thermally cyclizing the *ortho*-positioned aromatic polyimide precursor at a temperature above 300 °C under vacuum or nitrogen purging condition. During the thermal cyclizing process, the *ortho*-positioned group reacts with the polyimide ring, which finally results in a more rigid heterocyclic structure. Depending on the functional groups at *ortho* position (–OH, –SH or $-NH_2$) of the precursors, the resultant thermally rearranged structures can be in the form of polybenzoxazoles (PBO), polybenzothiazoles (PBT) or polypyrrolones (PPL), etc. [1,5,6].

In order to achieve superior separation performance and explore the mechanism of thermal rearrangement process, several works have been well designed and conducted. Park et al. [1,5] declared that the ultrahigh gas permeabilities in TR polymers are attributed to the micro-pores formed during thermal rearrangement and proposed that the hour-glass shaped cavities may contribute to the outstanding gas permselectivities. By introducing copolymerization to the TR precursors, Jung et al. [3] demonstrated that the fractional free volume of the thermally rearranged membranes can be fine tuned by varying the copolymerization composition after studying a series of TR poly(benzoxazole-co-imide) and Choi et al. [4] reported that ideal selectivities can be effectively enhanced by copolymerized poly(benzoxazole-co-pyrrolone). Besides, Han et al. [7] investigated the effect of precursor synthesis routes and announced that the imidization route of the precursor also influences on the properties of the TR membranes, though the starting monomers are the same. Calle and Lee [2] studied the structure–property relationship by incorporating an ether group into the hydroxyl-containing polyimide (TR precursor). The results showed that the ether group has introduced flexibility to the polymer backbone. Furthermore, it was shown that both higher final temperature and longer thermal dwell time could result in a higher degree of conversion. Recently, Wang et al. have studied the property changes of a poly(hydroxyamide amic acid) which exhibits a stepwise thermal cyclization behavior. It is revealed that the enhancement of gas transport properties is more pronounced in membranes obtained by cyclodecarboxylation at a higher temperature rather than in those obtained by cyclodehydration induced at a lower temperature. It is well accepted that property alterations are closely associated to the degree of conversion [8].

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The literature studies have proven that the degree of thermal conversion is a key factor that affects the gas performance directly and it is known that the degree of conversion usually increases along with thermal treatment temperature [1,8,9]. However, at present, the effects other than the degree of thermal cyclization are yet to be studied separately.

In this work, we aim to investigate the effect of thermal cyclization temperature on the thermal rearrangement process of *ortho*-positioned polymers. In order to exclude the effect of thermal cyclization degree, a polyhydroxyamide (PHA) was employed as the precursor since PHA can reach a high conversion rate (>90%) at a significantly lower temperature (300 °C) and decomposes at a high temperature (>500 °C). The thermal cyclization of PHA membranes was conducted at four temperatures, 300 °C, 350 °C, 425 °C and 450 °C. In order to understand the effect of temperature, chemical structure transformation, thermal stability, physical properties, gas transport performance and sorption behavior of the resultant membranes were characterized thoroughly and reported in details. Overall, this work will elucidate the fundamentals of thermal cyclization and molecularly illuminate the temperature-induced chain rearrangement along with solid evidences.

2. Experimental

2.1. Materials

2,2-bis(3-amino-4-hydroxyphenyl)hexafluropropane (BisAPAF) (>98%) and 4,4′-biphenyl-dicarbonyl chloride (BPDC) were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). Prior to synthesis, BisAPAF was purified via recrystallization in diethylene glycol dimethyl ether (Singapore-Aldrich Co., Singapore) at 60 °C whereby BPDC was used as received. N-methyl-2-pyrrolidinoe (NMP) was distilled under reduced pressure at 70 °C. Anhydrous pyridine (99.8%) from Sigma–Aldrich Co. (Singapore), dimethylformamide (DMF), methanol and ethanol were all used as received.

2.2. Polymer synthesis procedures

The polymer precursor, polyhydroxyamide (PHA), was synthesized via the polycondensation routine. 15 mmol of purified BisAPAF was dissolved in 35 mL of NMP in a 100 mL conical flask equipped with nitrogen purging inlet and outlet. After complete dissolution, 33 mmol of pyridine was added into the solution dropwise. Then, the solution was cooled to 0 °C in an ice-water bath, followed by the addition of 15 mmol of BPDC powder. HCl generated from the reaction between amine and carbonyl dichloride was neutralized immediately by the excess pyridine in the solution. The ice-water bath was then removed after 1 h of polymerization and the viscous solution was stirred continuously under nitrogen blanket for 8 h at room temperature. The resultant solution was precipitated and the polymer was washed in methanol for 3 times in order to remove the solvent, unreacted monomers and the impurities. Subsequently, the polymer was filtered and dried in a conventional oven at 60 °C for 12 h.

2.3. Membrane fabrication and thermal rearrangement procedures

The dense film was obtained from the solution casting method. A 5 wt% solution was prepared by dissolving 1 g of polymer into 19 g of DMF. After being stirred overnight, the solution was filtered by a 0.45 μm PTFE membrane filter and cast into a 15-cm Petri dish. Then the solution was covered with an aluminum foil sheet and held in a conventional oven at 80 °C for 24 h to evaporate the solvent. In order to remove the residual solvent completely, the nascent film was peeled off, sandwiched between two wire mesh sheets and further dried in a Heraeus vacuum oven (Thermo Fisher Scientific Inc.) by practicing the following protocol: (a) hold at 75 °C for 4 h, (b) increase the temperature at a rate of 25 °C/2 h till 200 °C, (c) hold at 200 °C for 24 h and (d) naturally cool down to room temperature. The obtained films are of a thickness in the range of 30–50 μm.

Thermal cyclization of the membrane was carried out in a Centurion^{TM} Neytech Qex high vacuum furnace (ultimate vacuum: 0.002 mbar, chamber volume: ~500 cm^3). The furnace was preheated to the target temperature (300 °C, 350 °C, 425 °C or 450 °C) followed by the insertion of the pristine PHA membrane. The membrane was held at the temperature for 0.5 h and immediately quenched at room temperature. The characterizations and gas transportation property measurements were carried out within 24 h.

Except the precursor PHA, the samples are named as PBO300, PBO350, PBO425 and PBO450 where PBO indicates the polymer type (polybenzoxazole) while the numbers denotes the thermal cyclization temperature. The reaction schemes for polymer synthesis and thermal cyclization reaction are shown in Fig. 1.

2.4. Membrane characterizations

The chemical structure of PHA was confirmed by a Bruker Avance 300 (AV300) NMR spectroscopy at a resonance frequency of 300 MHz and DMSO-d6 was employed as the solvent. A gel permeation chromatography (GPC) (Waters GPC system comprising a Waters 2414 refractive index detector and a Waters 1515 isocratic HPLC pump) was used to determine the molecular weight of PHA. 10 mg of PHA was dissolved into 10 mL of DMF to prepare the testing sample and its molecular weight was obtained by comparing the sample retention time with that of a set of equal-concentration standard polystyrene solutions. The inherent viscosity (IV) of PHA was measured by a Ubbelohde viscometer (Schott Gerate, Mainz, Germany) with a polymer solution concentration of 0.5 g/dL at 25 °C. NMP was used as the reference solvent.

The chemical transformations of the membranes were investigated by an attenuated total reflection (ATR)-FTIR spectroscopy (Bio-Rad FTS-3500) with 32 scans over the wave number range of 400–4000 cm^{-1}. The sample chamber was purged with continuous nitrogen flow at a rate of 10 mL/min.

The elemental analyses to C, N and H contents were conducted by an Elementar Vario Micro Cube while the contents of F were measured by the Ion Chromatography (IC) analysis with a Metrohm modular IC system.

X-ray Photoelectron Spectroscopy measurements were conducted by an AXIS His spectrometer (Kratos Analytical Ltd., England) to characterize the chemical binding energy levels of C, N, O, F. The monocharomatized Al Kα source at a dwell time of 100 ms was used.

The thermal cyclization process and the thermal stability of materials were characterized by TGA (TGA 2050, TA instrument) over a temperature range of 25–700 °C. Besides, TGA isothermal experiments were also conducted to each sample by following the protocol: (1) ramp from 25 °C to 200 °C at a rate of 10 °C/min; (2) isotherm at 200 °C for 30 min to remove trace amounts of solvents and moisture; (3) ramp from 200 °C to the respective thermal cyclization temperature at a rate of 100 °C/min and (4) isotherm for 30 min. These experiments are to simulate the thermal treatment process.

The glass transition temperatures (T_g) of films were measured by DSC (DSC 822^e (Mettler Toledo)) over a temperature range from 25 °C to the thermal rearrangement temperature for the respective PBO samples except for PBO300 which was ramped to 350 °C since its T_g was not detected till 300 °C. For PHA, the DSC operating

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