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**Aromatic Polyimide and Crosslinked Thermally Rearranged Poly(benzoxazole-co-imide)
Membranes for Isopropanol Dehydration via Pervaporation**

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Abstract

Novel crosslinked thermally rearranged polybenzoxazole (C-TR-PBO) membranes, which show impressive results for isopropanol dehydration, have been obtained via in-situ thermal

conversion of hydroxyl-containing polyimide precursors. The polyimide precursors are synthesized by the polycondensation of three monomers; namely, 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 3,3'-dihydroxybenzidine diamine (HAB) and 3,5-diaminobenzoic acid (DABA). Due to the incorporation of the carboxylic-group containing diamine DABA into an ortho-hydroxypolyimide precursor, the thermal induced crosslinking reaction can be achieved together with the thermal rearrangement process. Consequently, a synergistic effect of high permeability and high selectivity can be realized in one step. The resultant C-TR-PBO membrane exhibits an unambiguous enhancement in permeation flux compared to their polyimide precursors. Moreover, the newly developed C-TR-PBO membrane displays stable isopropanol dehydration performance at 60 °C throughout the continuous 200 hours. The promising preliminary results achieved in this study may offer useful insights for the selection of membrane materials for pervaporation and new methods to molecularly design next-generation pervaporation membranes.

Keywords: Poly(benzoxazole-co-imide); Pervaporation; Isopropanol dehydration; Thermal rearrangement; Thermal crosslinking

1. Introduction

Isopropanol (IPA) is an important alcohol which is used for a variety of industrial and consumer applications. For example, it can be used as an effective cleaner for electronic and optical

devices because of its non-toxicity, fast evaporation and ability to dissolve a wide range of non-polar compounds. Moreover, it is also a chemical intermediate for the production of isopropyl acetate, rubbing alcohol, vitamin B12 and a pharmaceutical additive used in hand sanitizer and disinfecting pads [1, 2]. In addition, it can be considered as an alternative fuel to alleviate global warming and slow down the depletion of fossil fuels [3, 4]. Isopropanol is produced either by the chemical reaction between propene and water or by microorganism's fermentation [4]. However, both processes require the separation of water from IPA to produce high purity IPA. Hence, the successful production and applications of isopropanol strongly depends on the development of effective dehydration technologies [5]. Currently, distillation is the dominant separation technology employed for the dehydration of IPA. However, its high energy consumption and ineffectiveness in separating azeotropic mixtures pave the way for the development of other separation technologies [6].

Pervaporation, a membrane-based separation technology, may be regarded as a promising dehydration process [7] because it offers several unique advantages over distillation. First, pervaporation is not limited by the vapor-liquid equilibrium, and thus expected to have surpassing separation efficiency, particularly in separating azeotropic and close boiling point liquid mixtures [8]. Second, it is a clean technology and can avoid cross-contamination because it does not need third components, which are commonly employed in the so-called "azeotropic distillations" [9]. Third, pervaporation is an energy-saving process because only the permeating component consumes the latent heat [10, 11]. Moreover, pervaporation has a mild operation condition by using low feed pressures and temperatures [8, 12]. Last, the compactness in module

fabrication as well as simplicity in process control are also advantageous characteristics of pervaporation [13].

In pervaporation processes, membrane is vitally important. Polymeric membranes are currently widely used in pervaporation because of their advantages in ease of fabrication and scale-up, low capital costs, and low footprint [14]. Polybenzoxazole (PBO) is a kind of glassy polymers which has a unique rigid-rod structure and possesses advantageous characteristics such as excellent solvent resistance, good thermal stability and high mechanical strength [15-21]. However, its high solvent resistance reduces its solubility in common solvents, and this brings about obstructions in membrane preparation and constrains their applications [15-17]. To solve this problem, researchers have developed an alternative PBO membrane preparation method via the in-situ thermal conversion of hydroxyl-containing polyimide precursors. In this method, an aromatic polyimide, which contains hydroxyl groups ortho to the imide nitrogen, can be converted to a polybenzoxazole through thermal rearrangement (TR) upon heating between 350 and 500 °C in an inert atmosphere or under vacuum [15-17]. This method makes the fabrication of PBO membranes more feasible.

Numerous works have focused on the application of thermally rearranged polybenzoxazole (TR-PBO) membranes for gas separation. TR-PBO membranes have shown superior gas separation properties especially in separating CO₂/CH₄ mixtures, surpassing the 2008 upper bound [22-25]. The existence of micropores and high free volume in TR polymers is the reason for the high permeability, while the rigid-rod benzoxazole structure contributes to the relatively stable selectivity [22]. Researchers have also investigated the effects of different polyimide precursor

structures [26-28], imidization methods [29], TR protocols [27, 30-32] and TR-PBO membrane thickness [33] on the free volume distribution and gas separation performance.

Although TR-PBO membranes have been widely explored for gas separation, there are limited studies on their applications for pervaporation [34, 35]. Among the limited studies, only one of them was related to alcohol dehydration where Ong et al. studied the effects of dwell duration and thermal rearrangement temperature on alcohol dehydration performance [34]. Experimental results indicated that the thermal rearrangement temperature had more significant impact on pervaporation performance than the dwell time. In addition, the TR-PBO membranes which were treated at 450°C for half an hour exhibited the highest flux with a reasonable separation factor for ethanol dehydration.

In this study, a set of crosslinked thermally rearranged polybenzoxazole (C-TR-PBO) membranes are prepared via in-situ thermal conversion of hydroxy-containing polyimide precursors and are utilized for isopropanol dehydration via pervaporation. The polyimide precursors are synthesized from the polycondensation of 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 3,3'-dihydroxybenzidine diamine (HAB) and 3,5-diaminobenzoic acid (DABA). The resultant polyimide precursors are first cast into membranes, and then converted to C-TR-PBO through the thermal treatment. The advantages of these three chosen monomers are: (1) 6FDA contains fluorine groups $-\text{CF}_3$, which are expected to prevent polymer chains from compact packing and increase the free volume of the resultant polymer; (2) HAB has a hydroxyl group ortho to the amine group, which meets the essential requirement for the TR process; and (3) DABA possesses a carboxylic group in the structure, which can undergo thermal

crosslinking during the thermal treatment. The thermally induced crosslinking mechanism for the carboxylic-group containing polyimide was proposed by Qiu et al. [36] as shown in Figure 1. Under vacuum or an inert condition and at high temperatures, the carboxylic groups of two neighboring polymer chains react to form anhydride groups. Subsequently, two phenyl free radicals are generated from the decarboxylation of the anhydride along with the release of a CO and CO₂ molecule. After that, these adjacent phenyl radicals combine to form linkages that yield biphenyl crosslinking. This would further enhance the stability and swelling resistance of resultant membranes.

The present research aims to (1) develop new polybenzoxazole membrane materials with combination of crosslinking and thermal rearrangement for pervaporation applications (2) study the synergistic effects of crosslinking and thermal rearrangement on the physicochemical properties of the membranes. To our best knowledge, this is the first time that this material is synthesized and studied for pervaporation dehydration.

2. Experimental

2.1. Materials

The 6FDA-HAB/DABA co-polyimides were synthesized from monomers 6FDA, HAB and DABA with four various diamine HAB to DABA ratios of 10:0, 9:1, 7:3 and 5:5 (abbreviated as PI-10-0, PI-9-1, PI-7-3 and PI-5-5) via the imidization reaction. The monomers 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, Clariant) and 3,5-diaminobenzoic acid (DABA, Aldrich) were purified by vacuum sublimation while 3,3'-dihydroxybenzidine diamine

(HAB, Tokyo Chemical Industry) was used without further treatments. N-methyl-2-pyrrolidone (NMP, analytical grade) from Merck (Germany) was purified by vacuum distillation. Dimethylformamide (DMF) and isopropanol from Fisher Scientific (UK), acetic anhydride and pyridine from Aldrich and methanol from Merck (Germany) of the reagent grade or higher, were used as received.

2.2. Polyimide syntheses

HAB and DABA at ratios of 10:0, 9:1, 7:3 and 5:5 were accurately weighed and dissolved in freshly distilled NMP under a nitrogen environment. The mixture was then cooled to 0 °C and an equimolar amount of 6FDA dianhydride was added. The reaction mixture was stirred for half an hour at 0 °C followed by one day at room temperature to form a viscous poly(amic acid) solution. Subsequently, in order to transform the poly(amic acid) to a polyimide, acetic anhydride and pyridine were poured into the solution. Further stirring in one day was conducted to achieve the complete imidization. The synthesis scheme is shown in Figure 2. The polyimide solution was then precipitated in methanol, washed several times with methanol and dried in an oven at 120 °C for 12 h.

2.3. Preparation of pristine polyimide dense membranes

The synthesized polyimide was dissolved in DMF to prepare a 3wt% polymer solution. The solution was then filtered through a 1 μm PTFE syringe filter and poured onto silicon wafers. The solution was left to dry at 80 °C with a monitored condition to ensure slow evaporation of the solvent. The formed membranes were then removed carefully. In order to totally remove the residual solvent, the membranes were further dried under vacuum using a gradient heating procedure: kept at 75 °C for 1h, raised to 200 °C at a rate of 25 °C/h, kept at 200 °C for 12h and naturally cooled down to room temperature. The thickness of the resultant membrane was about 20–30 μm measured by a Mitutoyo micrometer.

2.4. Thermal treatment to form crosslinked polybenzoxazole

In order to obtain a crosslinked polybenzoxazole membrane, the polyimide dense membrane was thermally treated in a Lenton horizontal vacuum tube furnace (Model VTF12/50/550) at a vacuum level of $\sim 10^{-6}$ mbar. The heating protocol was to increase temperature to 450 °C at a rate of 5 °C/min and then to keep isothermally for half an hour in a high vacuum level. After thermal treatment, the membrane was naturally cooled down to room temperature in the furnace before tests. The resultant membranes are abbreviated as C-TR-10-0, C-TR-9-1, C-TR-7-3 and C-TR-5-5. It should be noted that C-TR-10-0 means there is no crosslinking due to the absence of DABA moiety.

2.5. Membrane characterizations

The chemical structures of the newly synthesized polyimide and poly(benzoxazole-co-imide) were analyzed by Fourier transform infrared spectroscopy (Bio-Rad FTS 135) (FTIR) in the range of 500-4000 cm^{-1} in both attenuated total reflectance (ATR) and transmission modes. To examine the membranes' thermal stability, thermogravimetric analyses (TGA) were employed with a Shimadzu Thermal Analyzer (DTG-60A/TA-60WS/FC-60A) with a heating rate of 5 $^{\circ}\text{C}/\text{min}$ from 50 to 800 $^{\circ}\text{C}$ under a N_2 flow rate of 100 ml/min . In order to investigate the reactions during the thermal treatment, TGA-IR was also carried out, which consisted of a Shimadzu Thermal Analyzer (DTG-60A/TA-60WS/FC-60A) and a Shimadzu IRPrestige-21 under nitrogen atmosphere with a flow rate of 50 mL min^{-1} . All samples were pretreated from room temperature to 50 $^{\circ}\text{C}$ to remove moisture; after which, the temperature was increased to 800 $^{\circ}\text{C}$ with a rate of 10 $^{\circ}\text{C}.\text{min}^{-1}$. The released vapor was online analyzed by a scanning interval of 60 s.

Positron annihilation lifetime of the pristine polyimide and C-TR-PBO membranes were studied by bulk positron annihilation lifetime spectroscopy (PALS). This system used ^{22}Na as the source of positrons and operated at a counting rate of around 155–165 counts s^{-1} . For each spectrum, one million counts were collected. A detailed description of PALS system and experiments was depicted elsewhere [37, 38]. The PATFIT program was employed to resolve the raw data into three-lifetime components. The first one ($\tau_1 \approx 0.125 \text{ ns}$) is attributed to the annihilation of para-Positronium, the second one ($\tau_2 \approx 0.4 \text{ ns}$) is due to the free positrons, and the third one ($\tau_3 > 0.5 \text{ ns}$) is generated by the annihilation of localized ortho-Positronium (o-Ps). The o-Ps lifetime was obtained using the PATFIT program and the mean free-volume radius R ($\text{\AA}$) was determined

using an established semi-empirical correlation equation with an assumption that the cavities in the membranes are spherical, as follows [39-42]:

$$\tau_i^{-1} = 2\left[1 - \frac{R}{\Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{\Delta R}\right)\right] \quad (1)$$

where $\tau_i = \tau_3$ refers to the o-Ps lifetime. ΔR is an empirical constant (1.66 Å). Eq. (1) can be only applied for the third $\tau_3 < 10$ ns. The relative fractional free volume (*FFV*) can be determined by the following equation [41-43]:

$$FFV = \sum_i 0.0018 I_i \left(\frac{4}{3} \pi R_i^3\right) \quad (2)$$

where $I_i = I_3$ is the o-Ps intensity (%).

2.6. Solvent uptake analyses

The dense polyimide membranes and C-TR-PBO membranes were prepared in small strips. The strips were first dried in a vacuum oven at room temperature overnight to remove any moisture. The pre-weighed dry strips were subsequently immersed in pure isopropanol and water, separately. At different time intervals, the swollen strips were removed from the solvent, blotted with tissue papers to remove the excess solvent on their surfaces and their weights were determined by a digital microbalance in a closed condition. The solvent uptake data at different time intervals were recorded until there was no further notable change in their weights. This would indicate that the swollen membranes have reached sorption equilibrium. The solvent uptake ratio for each sample was determined by the weight difference between the swollen strip (M_{wet}) at the equilibrium condition and the initial strip (M_{dry}) as below:

$$\text{Solvent uptake ratio} = \frac{M_{wet} - M_{dry}}{M_{dry}} \quad (3)$$

2.7. Pervaporation performance

The pervaporation system used in this study was a lab-scale static cell as described elsewhere [44]. An aqueous 85 wt% isopropanol feed solution of 300 ml was added into a pervaporation tube in contact with the membrane. The downstream pressure was kept at less than 1 mbar by a vacuum pump. The operational temperature was 60 °C. Before the sample collection, the system was conditioned for 2 h. After that, the permeate mixtures were condensed using a cold trap submerged in liquid nitrogen. The weights of permeate samples were determined using a digital balance, and their compositions were characterized by a gas chromatography (HP-INNOWAX column, Hewlett-Packard GC 7890) and a TCD detector, respectively. Since the quantity of the feed solution was much larger than that of the permeate sample and the variation of the feed concentration was small (less than 1 wt%), it could be considered as constant throughout the experiment. In order to achieve the reproducibility of the data, all the experiments were repeated at least twice.

The total flux J was calculated by the following equation:

$$J = \frac{Q}{At} \quad (4)$$

where A , Q and t represent the effective membrane area, total mass of the permeate and operating time, respectively. Separation factor is calculated as below:

$$\alpha_{1/2} = \frac{y_{w,1}/y_{w,2}}{x_{w,1}/x_{w,2}} \quad (5)$$

where subscripts 1 and 2 represent water and isopropanol, respectively; x_w and y_w respectively indicate the components' weight fractions in the feed and permeate side.

To describe the intrinsic properties of a membrane, the permeability and mole-based selectivity are calculated based on the solution–diffusion model:

$$P_i = J_i \times \frac{l}{x_i \gamma_i P_i^{sat} - y_i P^p} \quad (6)$$

where P_i is the permeability of component i , l is the membrane thickness, J_i , P_i^{sat} and γ_i , are the flux, the saturated vapor pressure of component i and the activity coefficient, respectively. x_i and y_i are the mole fractions of component i in feed and permeate, respectively. P^p is the total pressure at the permeate side. It could be assumed as zero because the pressure in the permeate side was much smaller than the saturated vapor pressure in the feed side due to the vacuum condition. Both γ_i and P_i^{sat} were calculated based on the Wilson and the Antoine equations, respectively, using the AspenTech Process Modelling software. The membrane's mole-based selectivity was determined by the following equation:

$$\alpha_{mole} = \left(\frac{M_j}{M_i} \right) \left(\frac{P_i}{P_j} \right) \quad (7)$$

where M_i and M_j are the molecular weights of water and isopropanol, respectively.

3. Results and discussion

3.1. Characterizations of polyimide and C-TR membranes

3.1.1. FTIR analyses

In order to verify the success in synthesizing the 6FDA-HAB/DABA polyimide, ATR-FTIR analyses are carried out and the results are shown in Figure 3. The synthesized polymers possess the characteristic peaks at 1774 and 1716 cm^{-1} which are mainly attributed to typical double bands stretching of the C=O group in the imide ring [45-48]. In addition, the C–N stretching at 1365 cm^{-1} , the transverse stretching of C–N–C groups at 1084 cm^{-1} , and the out-of-plane bending of C–N–C groups at 717 cm^{-1} also characterize the presence of imide groups [34, 45, 46]. This confirms the successful fabrication of the polyimide membrane.

In contrast, for the C-TR-PBO membranes, it should be noted that the ATR-FTIR spectra show weak peak intensities due to the dark brown colour of the membranes. Therefore, a transmission mode of FTIR is used for the C-TR-PBO membranes. According to Figure 4, three new peaks for C-TR-PBO membranes can be observed at around 1477, 1554 and 1620 cm^{-1} , which characterize the vibration of benzoxazole rings [32, 49, 50]. Peaks at 1477 and 1554 cm^{-1} are the absorbing bands of benzoxazoles whereas the characteristic peak at 1620 cm^{-1} is due to C=N stretching [32, 50]. These results validate the successful formation of the polybenzoxazole structure.

3.1.2. TGA and TGA-IR analyses

Figure 5 shows the thermal behavior of the synthesized polyimides. The polyimides undergo a three-stage weight loss as the temperature increases from 100 to 700 °C. The initial weight loss (less than 1%) between 100°C to 250°C is ascribed to the elimination of residual solvents or moisture. The second stage weight loss at 250-500°C is due to the release of gas molecules produced from crosslinking and thermal rearrangement reactions. From 500°C onwards, polymer chains start to decompose which results in the last stage weight loss.

Figures 6 and 7 show the TGA curve and the simultaneous IR spectra of gases released from polyimide membranes PI-10-0 and PI-9-1 during pyrolysis, respectively. In TGA-IR spectra, yellow represents the lowest intensity of a peak, red signifies the medium intensity, and turquoise denotes the highest intensity. After about 48 min of heating corresponding to a temperature of about 420°C, the CO₂ characteristic IR peak (2250-2400 cm⁻¹) and the -C=O characteristic peak (1750 to 1850 cm⁻¹) show up in the TGA-IR spectra. The detected CO₂ comes from the thermal rearrangement process. When the temperature increases to about 520 °C, additional IR peaks including H₂O (3600-3750 cm⁻¹), CF_x (1150-1200 cm⁻¹) and -C-O (1000-1050 cm⁻¹) groups are evolved. This suggests that the polymer backbone starts to decompose at this high temperature.

Compared with the IR spectrum of PI-10-0, Figure 7 reveals that PI-9-1 experiences an earlier appearance of H₂O peak, -C=O peak, -C-O peak and CO₂ peak at a lower temperature and illustrates the distinct peak of CO molecules. According to Figure 1, water, CO₂ and CO molecules are released during the crosslinking reaction. Therefore, this phenomenon implies that

the thermally induced crosslinking reaction occurs at lower temperatures than thermal rearrangement. As temperature further increases, thermal rearrangement starts to occur, while the crosslinking process is continuing. When temperature reaches about 500 °C, decomposition of polymer chains starts, similar to the case of PI-10-0.

3.2. Solvent uptake analyses

In order to understand the affinity between the permeate molecules and the membrane, solvent uptake analyses were carried out at 60 °C. This temperature is kept the same as the pervaporation test in order to have a fair comparison. Figure 8 shows a comparison of solvent uptakes for the three polyimide precursors and their respective C-TR membranes in isopropanol and water. Both the polyimide precursors and C-TR membranes have higher affinity towards isopropanol than water, which implies that the membranes remain relatively hydrophobic. However, as the amount of carboxylic group increases, the water uptake increases while isopropanol uptake decreases for both polyimide precursors and C-TR membranes, indicating an improvement in solubility selectivity towards water. This phenomenon is attributed to the hydrophilic nature of carboxylic groups, which can play as absorption sites of water. Comparing the polyimide and its respective C-TR membrane, it can be observed that the latter absorbs less water and more isopropanol, which implies C-TR membranes have lower solubility selectivity towards water than polyimide membranes. This phenomenon corresponds well with the observation reported by Ong et al. and Wang et al. [34, 51].

3.3. Positron annihilation lifetime spectroscopy analyses

Positron annihilation lifetime spectroscopy (PALS) was applied to quantitatively analyze the free volume size and distribution for the polyimide and C-TR membrane samples. In PALS measurements, the o-Ps lifetime τ_3 and its intensity I_3 are correlated to the size and concentration of the free volume, respectively [40, 42, 52]. Figure 9 presents the PALS results. It can be observed that the polyimide membranes have τ_3 data in the range of 2.19 to 2.32 ns that corresponds to a mean cavity radius of 3.02 to 3.13 Å. After thermal rearrangement, τ_3 increases to 2.47-2.69 ns, indicating an increase in cavity sizes to 3.28-3.41 Å. This increase is attributed to the formation of cavities during the thermal rearrangement and thermal crosslinking reactions. At the same time, compared with polyimide precursors, the intensities I_3 of C-TR membranes also increase, signifying that more pores are created after the thermal treatment.

On the other hand, Figure 9 also reveals the effect of DABA content on membrane free volume. For the polyimide membranes, τ_3 and I_3 do not show significant change (4.59-4.72%) as the DABA to HAB ratio increases. This is probably because the carboxylic side chain in DABA is too small to affect polymer free volume. In contrast, the intensity I_3 of C-TR membranes decreases from C-TR-10-0 to C-TR-9-1 and subsequently increases from C-TR-9-1 to C-TR-5-5. This decrease-and-increase trend of intensity for C-TR membranes may be due to the combined effects of cavity formation during thermal treatment and crosslinking's inhibitory influence on TR [23, 24]. A similar trend was reported by Calle et al. [24].

Figure 10 indicates the calculated fractional free volume as a function of DABA to HAB ratio. Given that the lifetime τ_3 for polyimide and C-TR membranes remains relatively constant, it can be concluded that their fractional free volumes are mainly affected by the change of intensity. The fractional free volumes of polyimide membranes do not change significantly (0.96 to 1.09%) while those of C-TR membranes exhibit a V-shape in the range from 1.44 to 2.20 %.

3.4. Pervaporation performance of polyimide and C-TR membranes

Figure 11 summarizes the pervaporation performance of polyimide membranes and C-TR membranes for dehydration of 85 wt% isopropanol aqueous solutions. In order to eliminate the influence of membrane thickness, normalized flux is used in this study for comparison.

As illustrated in Figure 11, as the DABA to HAB ratio increases, the normalized flux of polyimide membranes also increases. However, their separation factor initially increases from PI-10-0 to PI-7-3 but subsequently decreases for PI-5-5. The increase in normalized flux is attributed to two factors. First, the high DABA to HAB ratio increases the hydrophilicity of the membranes, as discussed in section 3.2, which allows more water to be absorbed onto the membranes. This, in turn, results in the loosening of polymeric chains (in the wet state) and the increase in flux. Second, the membranes with a higher DABA to HAB ratio have higher fraction free volumes (PI-7-3 and PI-5-5) as indicated in Figure 10, which may lead to a higher flux in the wet state. On the other hand, when the DABA to HAB ratio increases from 10:0 to 7:3, the increase in separation factor is mainly due to the enhanced solubility selectivity as discussed in section 3.2. For the membrane PI-5-5, the slight decrease in separation factor may be attributed

to the water-induced swelling. Nonetheless, the water concentrations in permeate of all studied polyimide membranes remain higher than 99.0%, indicating good separation performance.

Although the separation factors of polyimide membranes are high, their normalized fluxes are relatively low. In order to further enhance the pervaporation performance, the polyimide membranes are thermally treated to enable thermal rearrangement and crosslinking. Figure 11 shows that the normalized fluxes of C-TR membranes are higher than those of polyimide membranes for all DABA to HAB ratios. The increase in flux of C-TR membranes is attributed to their larger free volume sizes and higher fractional free volumes. However, when compared with the polyimide membranes, the C-TR-10-0, C-TR-9-1 and C-TR-7-3 membranes have slightly lower separation factors. This is due to the decreased diffusivity selectivity when their free volume sizes are larger and decreased solubility selectivity as discussed in section 3.2. When the DABA to HAB ratio increases to 5:5; however, the separation factor of C-TR-5-5 membranes increases while that of polyimide membranes decreases, leading to the result that the former is higher than the latter. This interesting result is attributed to anti-swelling capacity of C-TR-5-5 membranes produced by the thermal crosslinking reaction among carboxylic groups. Among C-TR membranes, C-TR-5-5 displays the best separation performance with a normalized flux of 2138 $\text{g}\mu\text{m}/\text{m}^2\text{h}$ and a water concentration in permeate of approximate 99.8 wt%, as shown in Figure 11.

3.5. Performance benchmarking and stability of C-TR membranes

Table 1 compares the pervaporation performance in terms of permeability and selectivity for the membranes in this study with various pervaporation membranes available in literatures [34, 53-58]. Both the PI-5-5 and C-TR-5-5 membranes show comparable water permeability with other membranes. In terms of selectivity, C-TR-5-5 exhibits outstanding water selectivity, which is much higher than others. This superior performance opens up the opportunity of using the newly designed polybenzoxazole-based membranes for biofuel dehydration via pervaporation.

Besides having satisfactory performance, their long-term stability also needs to be addressed. Therefore, in order to evaluate the long-term stability of the C-TR membrane, the pervaporation performance is monitored continuously for 200 h at 60 °C. Figure 12 shows that the C-TR membrane displays quite stable separation performance and no obvious reduction of flux and separation factor can be observed during the entire testing duration of 200 h. The stable long-term performance has verified the benefits of crosslinking and signifies the feasibility of the C-TR membranes for pervaporation processes.

4. Conclusions

In this study, 6FDA-HAB/DABA copolyimides with four different HAB to DABA molar ratios were synthesized and subsequently thermally treated to form C-TR membranes. The science of both polyimide and C-TR membranes has been studied and their isopropanol dehydration

performance of isopropanol via pervaporation has been evaluated. The following conclusions can be drawn:

- (1) Thermal treatment of the 6FDA-HAB/DABA polyimides at 450 °C for half an hour induces thermal rearrangement and crosslinking reaction through decarboxylation. A higher fractional free volume is achieved due to more cavities formed by the release of gas molecules from both thermal rearrangement and crosslinking processes.
- (2) As the DABA to HAB ratio increases, both polyimide and C-TR membranes absorb more water and less isopropanol, which suggests an increase in solubility selectivity towards water. On the other hand, the C-TR membrane shows a higher affinity towards isopropanol than polyimide precursors, which indicates that C-TR membranes have lower solubility selectivity towards water than polyimide membranes.
- (3) C-TR membranes show a higher normalized flux than their polyimide precursor membranes due to their higher fractional free volumes. As the DABA to HAB ratio increases, both normalized flux and separation factor of C-TR membranes increase simultaneously. C-TR-5-5 exhibits the best pervaporation performance with a comparable water permeability of $0.15 \text{ mgm}^{-1}\text{h}^{-1}\text{kPa}^{-1}$ and an impressively high mole-based selectivity of 4019.
- (4) The C-TR-5-5 membrane displays stable isopropanol dehydration performance at 60 °C throughout the continuous duration of 200 h, indicating the potential of using the C-TR material for the separation and purification applications.

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Abbreviations

6FDA	: 2,2'-Bis(3,4'-dicarboxyphenyl) hexafluoropropane dianhydride
HAB	: 3,3'-dihydroxybenzidine diamine
DABA	: 3,5-diaminobenzoic acid
IPA	: Isopropanol
PVA	: Poly(vinyl alcohol)
PAA	: Poly(acrylic acid)
PBO	: Polybenzoxazole
PBO	: Polybenzoxazole Polytetrafluoroethylene
PTFE	: Polytetrafluoroethylene
DMF	: Dimethylformamide
NMP	: N-methyl-pyrrolidone
TR	: Thermal Rearrangement
ATR	: Attenuated Total Reflectance
FTIR	: Fourier Transform Infrared Spectroscopy

TGA : Thermogravimetric Analysis

PALS : Positron Annihilation Lifetime Spectroscopy

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Highlights

- Novel 6FDA-HAB/DABA polyimide and C-TR-PBO have been successfully synthesized.
- C-TR-PBO membranes exhibit impressive results for isopropanol dehydration.

- C-TR-PBO membranes show synergistic effect of high permeability and selectivity.
- C-TR-PBO membranes display a stable isopropanol dehydration performance.

Table 1. A comparison of pervaporation performance of dense membranes for isopropanol dehydration.

Membrane	Feed isopropanol concentration (wt.%)	Operating temperature ($^{\circ}\text{C}$)	Water permeability ($\text{mg m}^{-1} \text{h}^{-1} \text{kPa}^{-1}$)	Mole-based selectivity (water/isopropanol)	Reference
Matrimid	82	100	0.490	50	[53]
Torlon	85	60	0.011	3302	[54]
Ultem	85	60	0.012	683	[54]
BPADA-ODA-DABA polyimide (ODA: DABA=8:2)	80	60	0.145	9530	[55]
Chitosan crosslinked with Glutaraldehyde	90	60	0.835	609	[56]
Matrimid/MgO mixed matrix membrane	82	100	0.067	1513	[53]

PBI/ZIF-8 Mixed matrix membrane	85	60	0.358	1969	[57]
P84/ZIF-90 Mixed matrix membrane	85	60	0.166	449	[58]
Thermally rearranged polybenzoxazol e	90	80	0.299	670	[34]
C-TR-5-5	85	60	0.150	4019	This study
PI-5-5	85	60	0.129	882	This study

Figure

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