Effect of thermal treatment on the structure and gas transport properties of a triptycene-based polybenzoxazole exhibiting configurational free volume

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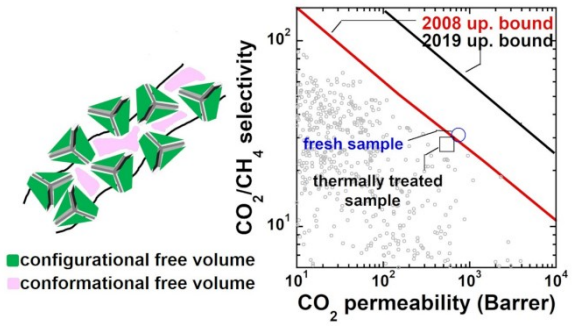
Graphical Abstract



Highlights

- Thermal treatment at 220°C for 240h influences polymer chain mobility
- Thermal treatment does not cause accelerated physical aging
- Configurational free volume makes TPBO's transport properties highly stable
- Thermal treatment affects solely Henry's mode diffusivity

Abstract

The effect of thermal treatment at 220°C for 10 days on the structure and transport properties of a triptycene-based polybenzoxazole (TPBO) was investigated experimentally and theoretically. Gas and water vapor sorption in TPBO is virtually unaffected by thermal treatment, while diffusion and permeability coefficients decrease by just 20%. Remarkably, the CO_2/CH_4 selectivity exhibit a negligible change. Fluorescence spectroscopy, WAXD and FTIR analysis indicate that, in sharp contrast with typical behavior of glassy polymers, TPBO does not experience accelerated physical aging, and rule out formation of intermolecular charge transfer complexes upon thermal treatment. According with this physical picture, the diffusion coefficient of penetrant molecules sorbed in the Langmuir's mode, D_H, does not change after treatment. Small molecule diffusivity and permeability decline is caused by a decrease in polymer chain mobility, which makes more difficult opening gaps to allow penetrant diffusion jumps. According to this picture, the Henry's mode diffusion coefficient, D_D, substantially decreases upon thermal treatment. The higher stability exhibited by TPBO relative to other high T_g glassy polymers is ascribed to the presence of configurational free volume, which is not related to the non-equilibrium transient conformation, but to the molecular configuration and, as such, it is not relaxed upon protracted exposure to high temperatures.

Keywords: thermal treatment, configurational free volume, chain mobility, sorption, permeability

1. Introduction and motivation

In 2017, the US Environmental Protection Agency (EPA) estimated that a more rational use of membrane-based separations would save $4 billion/year and 100 million tons of CO_2 emissions [1]. To be suitable for large scale applications, robust membranes exhibiting stable transport properties even in the harsh environments typically encountered in the chemical and petrochemical industry are needed [2]. Polymer membranes exhibiting high stability at temperatures higher than 200°C would improve the thermal and economic efficiency of hydrogen separation from pre-combustion syngas in the Integrated Gasification Combustion Cycle (IGGC), as well as of H_2/CH_4 separation from refinery processes, where high operation temperatures are needed to prevent condensation of hydrocarbon impurities [3, 4].

Recently, thermally rearranged polybenzoxazoles containing hierarchical triptycene units (TPBOs) exhibited unprecedented permeability and selectivity for H_2 purification and CO_2 separation [5, 6]. Triptycenes are three-dimensional structures formed by three aromatic rings arranged in a paddlewheel-like configuration [7, 8]. Their hierarchical fused-ring structure makes triptycenes attractive building blocks for preparing polymers with exquisitely tailored free volume architecture [6, 8, 9]. Due to their highly rigid structures, TPBOs exhibit high thermal stability up to 400°C, a T_g above the degradation temperature, and ultra-high permeability and selectivity, which positions them close or above the 2008 upper bounds in several separations of practical interest [6, 10]. A unique feature of triptycene-containing polymers is the combination of conformational and configurational free volume [5, 6, 11, 12]. Indeed, once inserted into a polymer backbone, triptycene groups provide their internal free volume (i.e., the clefts defined by the shape of the triptycene skeleton), which greatly enhances gas permeability and selectivity [6]. Unlike in conventional glassy polymers, the internal free volume provided by triptycene units is not related to the non-equilibrium, transient

conformation, but to the molecular configuration. Configurational free volume is intrinsic to the polymer structure and, as such, it is non collapsible, similar to the case of inorganic molecular sieves [12]. The presence of configurational free volume is expected to make transport properties of TPBOs more stable compared to other rigid, high T_g glassy polymers, such as Matrimid® and polymers of intrinsic microporosity (PIMs), which loose up to 50% of their permeability upon exposure to high temperature for a few hours. However, information about the actual stability of configurational free volume is scarce and, specifically, the effect of protracted exposure to high temperatures is essentially unexplored.

The fundamental hypothesis that motivates this study is that the unique combination of configurational and conformational free volume provides not only exceptional size sieving ability, but also a potential solution to mitigate the accelerated physical aging exhibited by conformational free volume in existing polymer membranes upon exposure to high temperatures for long times [13-16]. To shed fundamental light on this aspect, in this study we provide a thorough experimental investigation of the effects of thermal treatment on TPBO-0.25, a thermally rearranged polybenzoxazole prepared from a co-polyimide precursor (TPHI-0.25), i.e., triptycene-dianhydride(0.25)−6FDA(0.75)−6FAP(1.0) [6]. Selected membrane samples, about 40 μm thick, were exposed to temperatures as high as 220°C for 240 hours (10 days) under full vacuum. Structural analysis, as well as sorption, diffusion and permeation experiments were exploited to track the effects of thermal treatment. The treatment temperature, 220°C, was selected for two reasons: *i)* it mimics reasonably well the typical temperature of IGCC and water-shift processes, and *ii)* it was the highest temperature attainable in our laboratories using vacuum ovens.

Interestingly, gas and water vapor sorption are barely affected by thermal treatment, while diffusion and permeability coefficients decrease by just 20% upon membrane exposure at

220°C for 10 days. Thermal treatment has negligible effects on the CO_2/CH_4 selectivity, so that the overall performance of thermally treated sample still positions very close to the 2008 upper bound. FTIR, fluorescence spectroscopy, and WAXD analysis indicate that no relevant structural changes take place during the thermal treatment, and suggest that changes in transport properties are not ascribable to accelerated physical aging, but to a decrease in polymer chain mobility. This picture is quantitatively confirmed by the dual mode analysis of transport data [17].

Remarkably, TPBO exhibits better stability compared to other rigid glassy polymers upon protracted exposure to high temperatures. For example, Ansaloni reported a 50% decrease of CO_2 and CH_4 permeability and diffusivity upon thermal treatment of Matrimid® polyimide at 150°C for 24h [18]. Swaidan reported that propane permeability in an intrinsically microporous polyimide, PIM-6FDA, decreases by 45% upon annealing at 250°C for 24h [19]. The excess free volume exhibited by conventional glassy polymers is related to the non-equilibrium transient conformation and, as such, it is highly unstable. Exposure to high temperatures influences polymer chain dynamics and accelerates the relaxation of non-equilibrium free volume, which is consistent with the results reported by Ansaloni and Swaidan [18, 19]. The superior stability exhibited by TPBO is ascribed to configurational free volume [5, 6, 12].

2. Theoretical background

Small molecule permeability coefficient through a membrane, P_i, is defined as follows [20]:

$$P_i = \frac{N_i \ell}{\Delta p} \qquad \text{(Eq. 1)}$$

where N_i is the steady-state penetrant flux, ℓ is the membrane thickness, and Δp is the pressure difference across the membrane. Based on the solution-diffusion model, permeability coefficient is the product of the sorption coefficient, S_i (i.e., the ratio between penetrant concentration in the upstream membrane face and the upstream pressure), and the concentration-averaged diffusion coefficient, $\bar{D}_i$ [20]:

$$P_i = \bar{D}_i \times S_i \qquad \text{(Eq. 2)}$$

The ideal selectivity for component *i* relative to component *j*, α_{ij}, is defined as [21]:

$$\alpha_{ij} = \frac{P_i}{P_j} \qquad \text{(Eq. 3)}$$

where P_i and P_j represent the permeability coefficients of pure components *i* and *j* at fixed pressure and temperature. Ideal selectivity can be expressed as the product of the diffusion selectivity, α_D, which measures the membrane size-sieving ability, and the sorption selectivity, α_S, which measures the membrane ability to separate molecules based on their condensability or affinity for the membrane material [22]:

$$\alpha_{ij} = \frac{\bar{D}_i}{\bar{D}_j} \times \frac{S_i}{S_j} = \alpha_D \times \alpha_S \qquad \text{(Eq. 4)}$$

According to the dual mode model, gas sorption in glassy polymers is expressed as the sum of the Henry's sorption mode (C_D), analogous to the case of gas dissolution in rubbery polymers, and the Langmuir's mode (C_H), which is peculiar of glassy polymers and represents gas absorption in the excess free volume [17]:

$$C = C_D + C_H = k_D p + \frac{C_H' b p}{1 + b p} \qquad \text{(Eq. 5)}$$

In Eq. 5, k_D is the Henry's constant, C_H' is the Langmuir sorption capacity, b is the Langmuir affinity parameter, and p is the pressure in the external gas phase, respectively. Paul and Koros hypothesized that gas molecules sorbed in the Langmuir's mode are partially immobilized, so that only a fraction of these molecules, F, exhibit the same mobility as those sorbed in the Henry's mode. Based on the dual mode picture, the pressure dependence of gas permeability in glassy polymers is expressed as follows [17]:

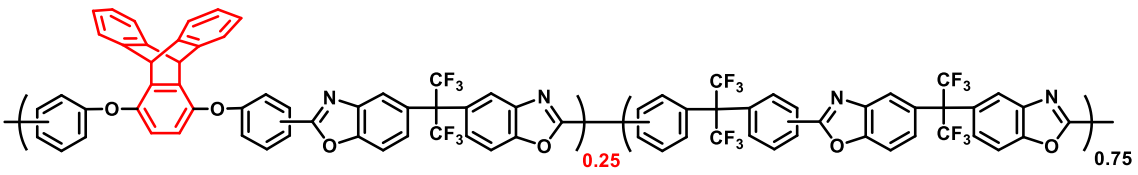
$$P = k_D D_D \left(1 + \frac{FK}{1+bp}\right) \qquad \text{(Eq. 6)}$$

where p is the upstream pressure, and D_D and D_H are the diffusion coefficients of penetrant molecules sorbed in the Henry's and Langmuir's mode, respectively, which are supposed to not change with pressure [23]. Finally, $F = \frac{D_H}{D_D}$ and $K = \frac{C_H' b}{k_D}$ [17].

3. Experimental

3.1 Precursor synthesis. Details about the precursor (i.e., TPHI) synthesis were provided elsewhere [6], and are briefly summarized in the Supporting Information. The thermally rearranged polymer, TPBO-0.25, is insoluble in any solvents. Its structure and relevant chemical-physical properties are reported in Table 1.

Table 1. *Structure and properties of TPBO-0.25 [5, 6].*



density (g/cm³)	glass transition T	conversion (%)
1.393 ± 0.002	> 400°C	100

3.2 Film casting, thermal conversion, and thermal treatment. The TPHI-0.25 precursor film was fabricated via the solution-casting method [6]. A 7 wt% solution of TPHI-0.25 in NMP was prepared, filtered using a 0.45 μm Teflon syringe filter, and cast on a leveled glass plate. A free-standing film was formed by allowing slow evaporation of NMP under an infrared lamp for overnight at 70°C. The nascent membrane was dried in a vacuum oven at 180°C for 24hr to remove the residual solvent. The thermal conversion from TPHI-0.25 to TPBO-0.25 was performed by sandwiching the TPHI-0.25 film between two porous ceramic plates and transferring it in a muffle furnace for 1h at 300°C under constant nitrogen flow. The temperature was further raised to 450°C for 30 min, with a rate of 30 °C/min. The resulting film, about 40 μm thick, was allowed to cool down to ambient temperature at a cooling rate of 10°C min^{-1}.

Selected membrane samples were thermally treated at 220°C for 10 days under vacuum, using a VWR oven (model 89508-426). Once the thermal treatment was complete, the samples were slowly cooled to room temperature under vacuum. Following this procedure, structural characterization and gas and vapor sorption/permeation tests were run immediately.

3.3 FTIR spectroscopy. Time-resolved FTIR-ATR spectra were collected on the same sample, before and after thermal treatment, using a 6700 Nicolet spectrophotometer. Instrumental parameters were set as follows: resolution = 4 cm^{-1}, spectral range = 4000/600 cm^{-1}, number of scans = 64.

3.4 Fluorescence spectroscopy. Fluorescence spectroscopy analysis of both fresh and thermally treated TPBO-0.25 films was performed using Jobin Yvon Horiba Fluorolog-3 spectrofluorometer. 0.5 cm × 2 cm samples from each of the fresh and annealed TPBO-0.25 films were prepared using a razor blade and fit in the cuvette for the subsequent analysis. A 360 nm filter and excitation wavelength of 350 nm were selected for the fluorescence measurements, which gave the best emission signal outputs in the emission range 350-550 nm.

3.5 WAXD measurement. Wide-angle X-Ray Diffraction (WAXD) patterns were generated using a Bruker Advanced Davinci X-Ray diffractometer in reflection mode by Cu Kα radiation (wavelength, λ = 1.54 Å). The X-Ray generator has voltage and current of 40kV and 40 mA, respectively, with step increment of 0.02° and scan speed of 7s per step in 2θ range of 5-45°. The *d*-spacing was calculated from the Bragg's law, based on diffraction peak maxima [24].

3.6 Solubility and permeability measurement. Gas and water vapor sorption was measured at 35°C using two separate constant-volume, barometric systems [5]. Gas permeability was measured at 35°C using a constant-volume, variable-pressure system. Details are provided in the Supporting Information.

4. Results and discussion

4.1 FTIR, Fluorescence Spectroscopy and WAXD analysis. FTIR spectra (cf. Fig. 1A) indicate that thermal treatment did not produce any detectable change in the polymer chemical structure.

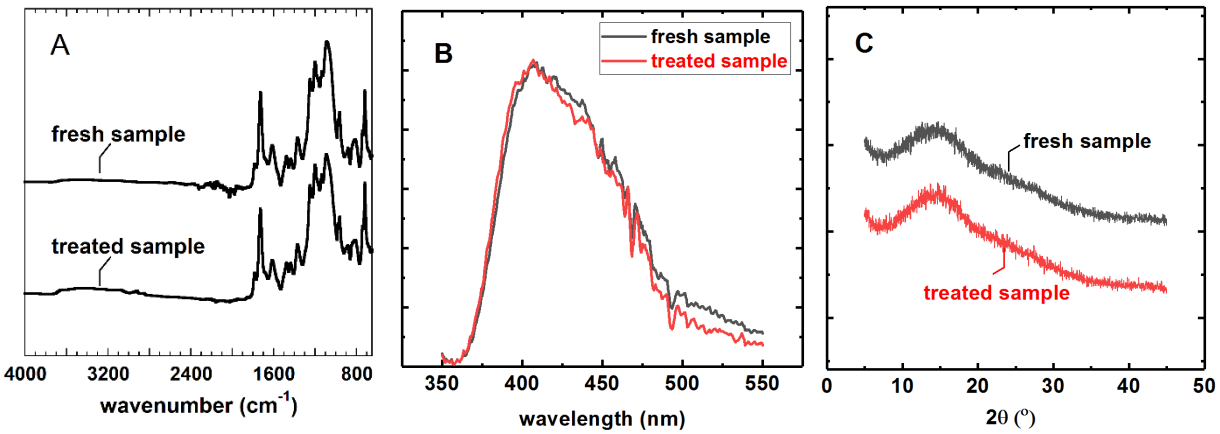


Figure 1. *FTIR spectra (A), fluorescence spectra (B), and WXRD diffraction pattern (C) of freshly cast and thermally treated TPBO-0.25 films.*

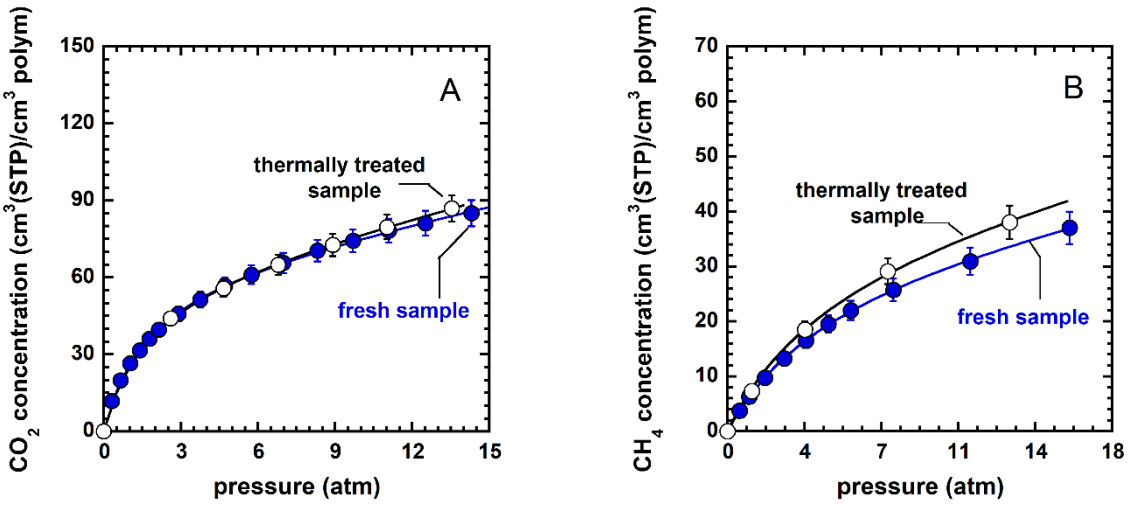
Fluorescence spectroscopy and wide angle X-ray diffraction analysis (WAXD) were exploited to study the effect of thermal treatment on the polymer chains conformation and packing.

Fluorescence spectroscopy reveals basic electronic properties of polymers, which strongly depend on the conformation and packing of polymer chains in the solid state [25]. This approach has been used for the analysis of annealing effect in several membrane materials [19, 26-28]. TPBO fluorescence spectra before and after treatment (cf. Fig. 1B) display broad emission range between 350 and 550 nm, which is in the range of many reported rigid-rod like conjugated polymer structures [29-31]. An almost identical emission maxima at ~408 nm was observed in both spectra, which is consistent with typical features of polybenzoxazoles [32, 33]. Generally, shifts in the peak position indicate a change in the electronic structure of the sample, and changes in the peak intensity indicate a change in the density of emitting complexes. In the specific case of TPBO, none of these effects is observed, as peak's position and intensity do not change upon thermal treatment, which rules out any change in the polymer chain conformation and packing after 10-day of intensive high temperature treatment. In sharp contrast with this behavior, Koros and co-workers reported a marked red-shift of the 6F-PAI fluorescence peak to higher wavelengths (> 50 nm shift) after thermal treatment, accompanied by an intensity change, which was indicative of formation of charge transfer complexes [27]. The extent of π-stacking interactions between planar benzoxazole rings in polybenzoxazoles has been widely discussed in the literature, in order to explain fluorescence spectroscopy results [33-35]. Even though a fundamental analysis of fluorescence properties of polybenzoxazoles is beyond the scopes of this study, the lack of π-stacking interactions in TPBOs could be attributed to the presence of bulky triptycene units, which hamper the formation of charge transfer complexes for steric reasons.

Results of this study support the conformational rigidity of triptycene-containing PBO structures, and their capability to retain gas transport properties even under harsh operation conditions.

WAXD is a complementary technique to assess polymer chain packing. Consistently with the fluorescence pattern, WAXD diffraction pattern (cf. Fig. 1C) of TPBO does not show noticeable differences between the fresh and treated samples. The average *d*-spacing, calculated from the Bragg's law, changes from 6.02 to 5.97 Å. Since this difference (-0.83%) is not statistically significant, it can be concluded that chain packing is unaffected by thermal treatment. Therefore, the annealed TPBO sample exhibits almost unchanged chain conformation and packing patterns relative to the freshly cast film, which highlights the superior stability of TPBO.

4.2 Gas and water vapor sorption. CO_2 and CH_4 sorption isotherms at 35°C in freshly cast and thermally treated TPBO samples are shown in Fig. 2A-B as a function of pressure, along with the dual mode fitting. Experimental uncertainty (5% for CO_2 sorption, 8% for CH_4 sorption) was calculated using the error propagation method, taking into account the uncertainty on *i)* the two pressure signals, *ii)* the charge-chamber and sorption-chamber volumes, and *iii)* the polymer density. The larger uncertainty on CH_4 sorption data is ascribable to the much lower CH_4 solubility in TPBO relative to CO_2. In the pressure range inspected, 0-15 atm, pressures and fugacities match fairly well to each other, therefore sorption and transport data are reported as a function of pressure.



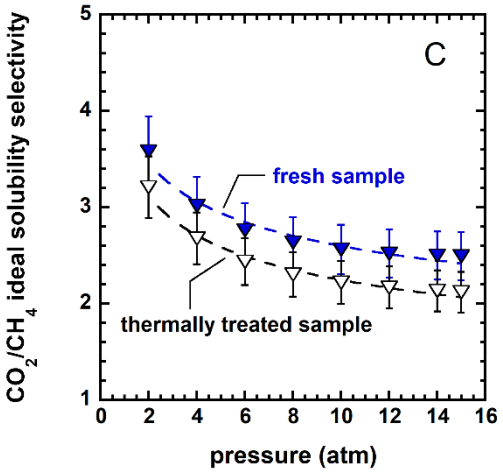


Figure 2. *CO_2 (A) and CH_4 (B) sorption isotherms at 35°C in freshly cast and thermally treated TPBO-0.25. Open and filled circles are experimental points, and continuous lines represent the dual mode best fit. (C) Ideal CO_2/CH_4 solubility selectivity at 35°C. Dashed lines represent a guide for the eye.*

CO_2 sorption isotherms before and after thermal treatment match very well to each other, which is consistent with the structural characterization discussed above. Indeed, the treatment does not cause any detectable structural change, and, consistently, it does not affect the polymer sorption capacity.

Although CH_4 sorption in the thermally treated sample looks somehow higher than in the freshly cast sample, the difference is not statistically significant (cf. Fig. 2B). Therefore, if we account for the uncertainty affecting CH_4 sorption data, we have to conclude that the treatment does not produce any significant change in CH_4 sorption in TPBO. Ideal CO_2/CH_4 solubility-selectivity at 35°C is shown in Fig. 2C as a function of pressure. If we account for the experimental uncertainty, which was calculated from that on CO_2 and CH_4 sorption data using the error propagation method [36], CO_2/CH_4 solubility-selectivity does not change significantly upon thermal treatment.

As for CO_2 and CH_4, water vapor sorption in TPBO at 35°C is unaffected by thermal treatment (cf., Fig. 3).

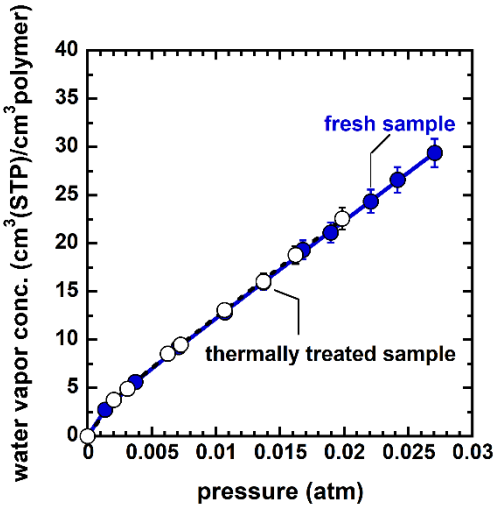


Figure 3. *Water vapor sorption at 35°C in TPBO-0.25 as a function of pressure. Filled circles represent water vapor sorption in the freshly cast TPBO-0.25 sample. Open circles represent water sorption in thermally treated TPBO sample. Lines represent the dual mode best fit.*

The dual mode model has been used to describe experimental CO_2, CH_4 and water vapor sorption isotherms in TPBO. Sorption isotherms in the freshly cast sample were fit as described in our previous study [5]. To reduce the degrees of freedom, sorption data for the thermally treated sample were fit by allowing just k_D and C_H' to change, while *b* was assumed equal to the value found for the freshly cast sample. The assumption that penetrant affinity for the Langmuir's sites (i.e., *b*) does not change upon thermal treatment is supported by the results of structural analysis discussed above, as well as by the fact that experimental solubility isotherms before and after treatment are perfectly superimposed in the low pressure range, where sorption in the Langmuir's mode is predominant. The dual mode parameters and their uncertainty are summarized in Table 2.

Table 2. *Dual mode parameter for CO_2, CH_4 and water vapor sorption at 35°C in freshly cast and thermally treated TPBO-0.25. Uncertainty was calculated as reported in ref. [37].*

	CO_2		CH_4		water vapor	
	fresh	*treated*	*fresh*	*treated*	*fresh*	*treated*
k_D *(cm³(STP)/(cm³ atm))*	*2.01± 0.12*	*2.30± 0.15*	*0.76± 0.20*	*0.88*	*1001±5*	*1015±7*
C_H' *(cm³(STP)/cm³)*	*63.8± 2.0*	*61.2± 0.9*	*33.0± 4.0*	*36.5*	*2.42±0.15*	*2.45±0.08*
b *(atm⁻¹)*	*0.59±0.02*	*0.59±0.02*	*0.20± 0.02*	*0.20*	*963±117*	*963±117*

Despite the uncertainty on the CH_4 dual mode parameters in thermally treated TPBO was not calculated, due to the limited amount of experimental data, it is expected to be much larger than that on CO_2 and water dual mode parameters. Therefore, changes in k_D and C_H' for CH_4 upon thermal treatment are expected to not be statistically significant. Finally, the CO_2 and water vapor dual mode parameters are essentially the same for the two TPBO samples.

4.3 Gas and water vapor transport. CO_2 permeability and CO_2/CH_4 ideal selectivity at 35°C and 10 atm are shown in the Robeson diagram in Fig. 4 [10, 38]. Permeability decreases by just 20% upon thermal treatment. If the experimental uncertainty is accounted for [36], the change in CO_2/CH_4 selectivity is negligible. Permeability data of CO_2 and CH_4 as a function of pressure at 35°C for both fresh and treated samples are shown in Fig. S1, Supporting Information.

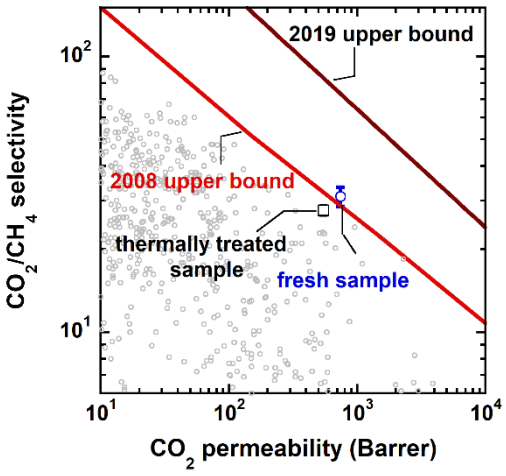


Figure 4. *A) CO_2/CH_4 ideal selectivity vs. CO_2 permeability at 10 atm and 35°C for a freshly cast and thermally treated TPBO-0.25 sample.*

CO_2 and CH_4 concentration-averaged diffusion coefficients at 35°C, $\bar{D}$, were calculated as a function of pressure (cf. Figs. 5A-B) using the solution-diffusion model (i.e., as P/S). $\bar{D}$ is defined as follows [39]:

$$\bar{D} = \frac{1}{C_0}\int_0^{C_0} D_{eff}\, dC \qquad \text{(Eq. 7)}$$

where C_0 is the penetrant concentration in the upstream membrane face, and D_{eff} is the local, effective diffusion coefficient [40]. During a permeation experiment, the downstream pressure is always below 10 Torr, therefore penetrant concentration in the downstream membrane face is essentially zero.

CO_2 and CH_4 concentration-averaged diffusion coefficients decrease upon thermal treatment (cf. Figs. 5A-B). The decrease in diffusivity, which is ultimately responsible for the corresponding decrease in permeability, is ascribable to a reduction in polymer chain mobility, rather than physical aging. Indeed, as discussed in the previous section, the *d*-spacing change upon thermal

treatment is negligible. Diffusion coefficient is much more sensitive to free volume distribution and polymer chain dynamics than sorption coefficient, therefore while thermal treatment does not influence gas solubility, it produces a detectable effect on gas diffusivity [27].

Interestingly, CO_2 and CH_4 diffusivity decrease by a similar extent, therefore CO_2/CH_4 diffusivity-selectivity in TPBO does not change upon thermal treatment (cf. Fig. 5C).

Gas selectivity in PIM-1 and its derivatives substantially increases upon thermal treatment [14, 15]. Accelerated physical aging, which produces a decrease of conformational free volume and an increase in polymer stiffness, has been invoked to explain the decrease in permeability and increase in selectivity exhibited by PIM-1 and other glassy polymers upon thermal treatment [14, 15, 41]. In contrast, the 20% decrease in permeability observed in TPBO is not accompanied by an increase in selectivity and, as such, it should simply be ascribed to a decrease in polymer chain mobility instead of physical aging. Indeed, reduction of chain mobility makes more difficult for the penetrant molecules to execute diffusion jumps. Reduced chain mobility could be ascribed to short range segmental motions or side group motions which cannot be captured by standard structural analysis. Local motion of side groups has been reported in a series of triptycene-containing polyimides [42]. The lack of selectivity change suggests that the size-sieving ability of TPBO is essentially provided by the configurational free volume which, being intrinsic to the polymer structure, is highly stable and it is not influenced by thermal treatment.

Water vapor concentration-averaged diffusion coefficients were estimated as a function of pressure at 35°C by fitting the experimental sorption kinetics to the Fick's law, and are shown in Fig. 5D [43, 44]. An example of water vapor sorption kinetic in TPBO is shown in Fig. S2, Supporting Information. As observed for CO_2 and CH_4, thermal treatment does not influence water vapor sorption, although it causes a decrease of water vapor diffusion coefficient.

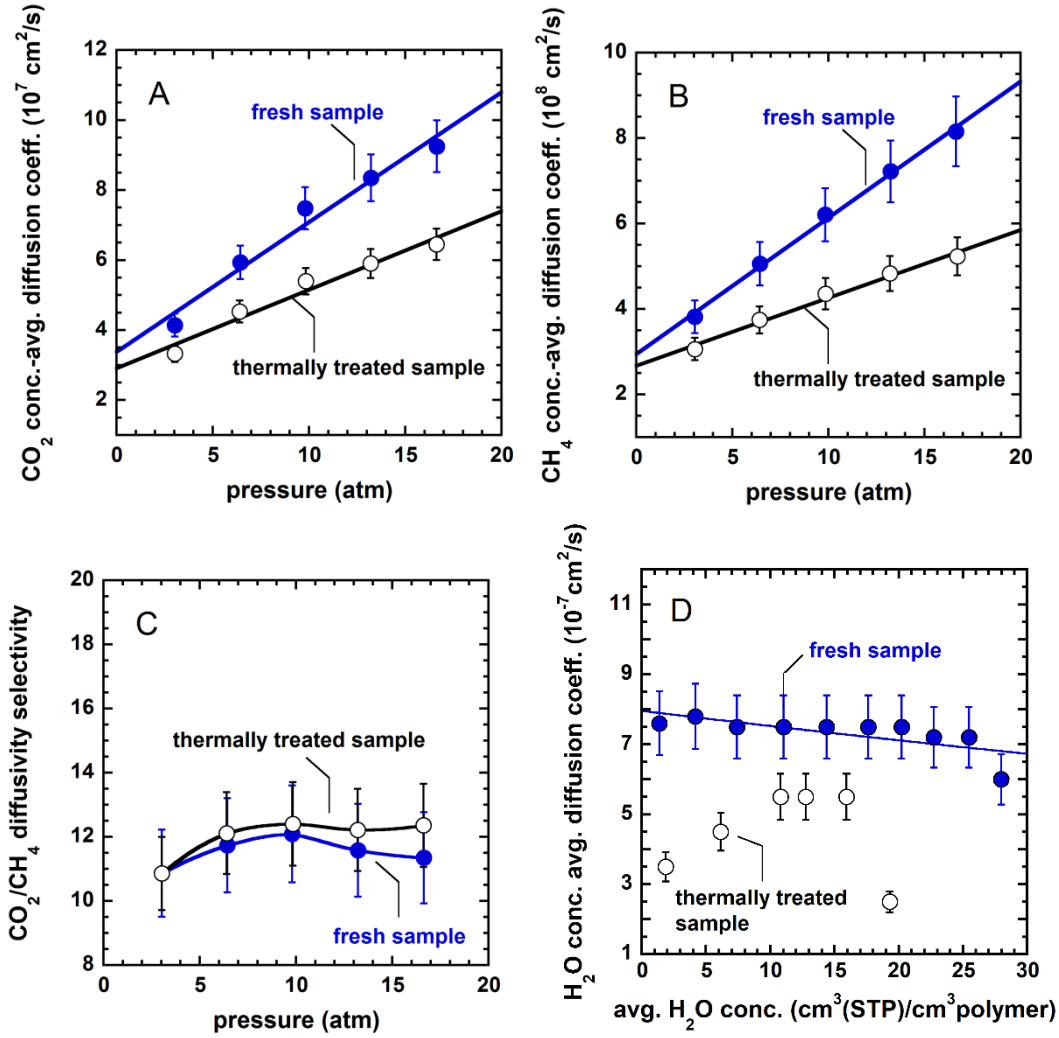


Figure 5. *CO_2 (A) and CH_4 (B) diffusion coefficient at 35°C in freshly cast and thermally treated TPBO-0.25 as a function of pressure. C) CO_2/CH_4 diffusivity-selectivity at 35°C. D) water vapor diffusion coefficient at 35°C in freshly cast and thermally treated TPBO-0.25 as a function of pressure. Lines are drawn to guide the eye.*

The experimental findings were rationalized using the dual mobility model. Once the dual mode parameters for sorption are known, penetrant diffusion coefficients in the Henry's mode (D_D) and in the Langmuir's mode (D_H) can be estimated by fitting Eq. 6 to experimental permeability vs. pressure data [17]. Specifically, permeability is plotted vs. *1/(1+bp)* to obtain a straight line, whose slope gives D_H and whose intercept to the y-axis gives D_D. As shown in Fig. S3, Supporting Information, CO_2 experimental permeability is linear vs. *1/(1+bp)*, with R^2 exceeding 0.95 for both TPBO samples. The linear increase of CO_2 permeability as a function of *1/(1+bp)* rules out the

occurrence of polymer plasticization, which would cause a decrease of permeability vs. *1/(1+bp)* [17, 23, 45]. As discussed in our recent study, the increase of diffusion coefficient with pressure (cf. Figs. 5A-B) can be interpreted based on the dual mobility model, and it is not indicative of polymer plasticization [5].

Since the dual mode parameters for CH_4 exhibit a much larger uncertainty relative to CO_2, we limited the dual mobility analysis to CO_2 transport data.

The CO_2 D_D and D_H values in the freshly cast and thermally treated TPBO samples are shown in Table 3. Based on the error propagation method [36], the uncertainty on D_D and D_H was estimated to be about 15%. D_D exceeds D_H by one order of magnitude, which indicates that CO_2 molecules sorbed in the Langmuir mode are endowed with a very low mobility. This picture is consistent with the high rigidity of triptycene units, and with the fact that their internal free volume size is comparable to the penetrant molecular size [5]. D_H experiences a negligible change upon thermal treatment. Specifically, it apparently increases by 7%, even though this change is not statistically significant, as the uncertainty on D_H is 15%. Therefore, this result confirms that free volume relaxation does not take place during thermal treatment. In contrast, the 39% decrease exhibited by D_D is statistically significant, as it largely exceeds the uncertainty. Therefore, the observed decrease in diffusion coefficient upon thermal treatment, which is responsible for the corresponding decrease in permeability, is solely due to a decrease in D_D. The latter phenomenon is due to a reduction in polymer chain mobility, which makes more difficult opening gaps to allow penetrant molecules diffusion, instead of accelerated physical aging. Interestingly, results of the dual mobility model mirror the behavior of gas sorption isotherms before and after thermal treatment. As shown in Figs. 2A-B, differences between samples are larger at high pressure. At medium-low pressures, when sorption occurs essentially in the Langmuir domain, the isotherms before and after thermal treatment are completely overlapped. Differences between the fresh and treated

sample are more evident at high pressure, when sorption and transport occur essentially in the Henry's mode, which suggests, consistently with the results of structural characterization, that no change in free volume occurs during thermal treatment, so that differences between the treated and virgin sample are only due to a change in the Henry's mode sorption/transport behavior, which is ascribed to a decrease in chain mobility. Although TPBO exhibits a very stiff, probably cross-linked structure which inhibits long range chain motions, very local short range segmental motions or side group motions, which cannot be captured by standard thermal analysis, can still take place [42]. These local motions do not produce any detectable T_g or sub-T_g transitions (i.e., α and β transitions).

Table 3. *CO_2 diffusion coefficient in the Henry's (D_D) and Langmuir's (D_H) region at 35°C, calculated using the dual mobility model. Uncertainty on D_D and D_H is about ±15%.*

	D_D (cm²/s)	D_H (cm²/s)
freshly cast TPBO-0.25	2.3×10^{-6}	1.3×10^{-7}
treated TPBO-0.25	1.4×10^{-6}	1.4×10^{-7}

TPBO behavior substantially departs from that exhibited by other rigid glassy polymers containing fused aromatic rings. For example, Ansaloni measured CO_2 and CH_4 permeability in Matrimid® polyimide before and after thermal treatment at 150°C for 24 hours [18]. Both CO_2 and CH_4 permeability decreased by approximately 50% compared to the freshly cast sample, with a slight increase in selectivity. Analogously to the case of TPBO, the decay in CO_2 diffusivity and permeability at 35°C were comparable to each other. Unfortunately, the authors didn't attempt to rationalize these findings in a more fundamental light, and did not measure gas sorption [18].

Despite the more aggressive treatment (10 days instead of 1 day), CO_2 and CH_4 permeability in TPBO decrease by only 20%, which is far below the 50% decrease observed for Matrimid® polyimide [18]. We attribute the relatively high stability exhibited by TPBO to the presence of triptycene units. Unlike in conventional glassy polymers, the internal free volume provided by iptycene units is not related to the non-equilibrium, transient conformation, but to the molecular configuration. Configurational free volume is intrinsic to the polymer structure and, as such, it is non collapsible, similar to the case of inorganic molecular sieves [5, 6, 12]. Moreover, the bulky size of triptycene units, as well as chain threading and interlocking, might slow down the physical aging of the conformational portion of free volume. These unique structural features are ultimately responsible for the relatively high stability exhibited by TPBO in response to a very harsh thermal treatment. Other highly permeable, microporous glassy polymers, such as 6FDA-TMPD, suffer from severe physical aging even at room temperature, which makes their transport properties and separation performance highly unstable and hampers their use in the industrial practice [46]. Noteworthy, TPBO exhibits higher stability compared to conventional thermally rearranged polymers (i.e., polybenzoxazoles) without triptycene-groups, which suffer from non-negligible physical aging [47, 48]. A detailed study of the physical aging behavior of thin films of TPBO is underway.

5. Conclusions

The effect of thermal treatment at 220°C for 10 days on the structure and transport properties of a triptycene-based polybenzoxazole (TPBO-0.25) was investigated experimentally and theoretically. The observed 20% decrease in CO_2 and CH_4 permeability coefficients after thermal treatment is solely due to a decrease in the diffusion coefficient, while sorption coefficient does not exhibit any detectable change. Moreover, the freshly cast and thermally treated samples exhibit a fairly similar CO_2/CH_4 selectivity.

Fluorescence spectroscopy, WAXD and FTIR analysis indicate that, in contrast with the typical behavior of glassy polymers, TPBO does not experience any relevant structural change upon thermal treatment, such as accelerated physical aging, and rule out formation of intermolecular charge transfer. The dual mode analysis of transport data indicates that the diffusion coefficient of penetrant molecules sorbed in the Langmuir's mode, D_H, does not change upon thermal treatment, which is consistent with the idea that accelerated physical aging does not take place. This result is remarkable, especially if we consider the severity of pre-treatment, and it points out the superior stability exhibited by TPBO, which is ascribed to the presence of configurational free volume. In contrast, the Henry's mode diffusion coefficient, D_D, decreases upon thermal treatment, indicating that the gas diffusivity and permeability decline is caused by a decrease in polymer chain mobility upon exposure to 220°C for 10 days, which makes more difficult to open gaps needed for the penetrant to execute diffusion jumps.

The higher stability exhibited by TPBO relative to other rigid high T_g polymers, such as Matrimid® and PIMs, is ascribed to the presence of configurational free volume, i.e., the empty space between the benzene blades in the triptycene units. Unlike in common glassy polymers, the internal free volume provided by iptycene units is not related to the non-equilibrium, transient conformation, but to the molecular configuration and, as such, it is non collapsible, which helps justify the lack of accelerated physical aging exhibited by TPBO upon protracted exposure to high temperatures.

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References

[1] U.S. Environmental Protection Agency (EPA), https://www.epa.gov/, 2017 (accessed May 30 2019).

[2] M. Galizia, W.S. Chi, Z.P. Smith, T.C. Merkel, R.W. Baker, B.D. Freeman, 50th anniversary perspective: Polymers and mixed matrix membranes for gas and vapor separation: A review and prospective opportunities, Macromolecules, 50 (2017) 7809-7843.

[3] K.A. Stevens, J.D. Moon, H. Borjigin, R. Liu, R.M. Joseph, J.S. Riffle, B.D. Freeman, Influence of temperature on gas transport properties of tetraaminodiphenylsulfone (TADPS) based polybenzimidazoles, J. Membr. Sci., (2019) 117427.

[4] D. Wang, K. Li, W. Teo, Preparation and characterization of polyetherimide asymmetric hollow fiber membranes for gas separation, J. Membr. Sci., 138 (1998) 193-201.

[5] V. Loianno, S. Luo, Q. Zhang, R. Guo, M. Galizia, Gas and water vapor sorption and diffusion in a triptycene-based polybenzoxazole: effect of temperature and pressure and predicting of mixed gas sorption, J. Membr. Sci., 574 (2019) 100-111.

[6] S. Luo, Q. Zhang, L. Zhu, H. Lin, B.A. Kazanowska, C.M. Doherty, A.J. Hill, P. Gao, R. Guo, Highly selective and permeable microporous polymer membranes for hydrogen purification and CO2 removal from natural gas, Chemistry of Materials, 30 (2018) 5322-5332.

[7] Y.J. Cho, H.B. Park, High performance polyimide with high internal free volume elements, Macrom. Rapid Comm., 32 (2011) 579-586.

[8] J.R. Weidman, R. Guo, The use of iptycenes in rational macromolecular design for gas separation membrane applications, Ind. Eng. Chem. Res., 56 (2017) 4220-4236.

[9] J.R. Wiegand, Z.P. Smith, Q. Liu, C.T. Patterson, B.D. Freeman, R. Guo, Synthesis and characterization of triptycene-based polyimides with tunable high fractional free volume for gas separation membranes, J. Mater. Chem. A, 2 (2014) 13309-13320.

[10] L.M. Robeson, The upper bound revisited, J. Membr. Sci., 320 (2008) 390-400.

[11] V. Loianno, Q. Zhang, S. Luo, R. Guo, M. Galizia, Modeling Gas and Vapor Sorption and Swelling in Triptycene-Based Polybenzoxazole: Evidence for Entropy-Driven Sorption Behavior, Macromolecules, 52 (2019) 4385-4395.

[12] T. Corrado, R. Guo, Macromolecular Design Strategies Toward Tailoring Free Volume in Glassy Polymers for High Performance Gas Separation Membranes, Molecular Systems Design & Engineering, (2019) DOI: 10.1039/C9ME00099B.

[13] P. Bernardo, F. Bazzarelli, F. Tasselli, G. Clarizia, C. Mason, L. Maynard-Atem, P. Budd, M. Lanč, K. Pilnáček, O. Vopička, Effect of physical aging on the gas transport and sorption in PIM-1 membranes, Polymer, 113 (2017) 283-294.

[14] R. Swaidan, B. Ghanem, E. Litwiller, I. Pinnau, Physical aging, plasticization and their effects on gas permeation in "rigid" polymers of intrinsic microporosity, Macromolecules, 48 (2015) 6553-6561.

[15] R.R. Tiwari, J. Jin, B. Freeman, D. Paul, Physical aging, CO2 sorption and plasticization in thin films of polymer with intrinsic microporosity (PIM-1), J. Membr. Sci., 537 (2017) 362-371.

[16] R. Swaidan, B. Ghanem, E. Litwiller, I. Pinnau, Effects of hydroxyl-functionalization and sub-T_g thermal annealing on high pressure pure-and mixed-gas CO_2/CH_4 separation by polyimide membranes based on 6FDA and triptycene-containing dianhydrides, J. Membr. Sci., 475 (2015) 571-581.

[17] D.R. Paul, W. Koros, Effect of partially immobilizing sorption on permeability and the diffusion time lag, J. Polym. Sci.: Polym. Phys. Ed., 14 (1976) 675-685.

[18] L. Ansaloni, M. Minelli, M.G. Baschetti, G. Sarti, Effects of thermal treatment and physical aging on the gas transport properties in Matrimid®, Oil & Gas Science and Technology–Revue d'IFP Energies nouvelles, 70 (2015) 367-379.

[19] R.J. Swaidan, X. Ma, E. Litwiller, I. Pinnau, Enhanced propylene/propane separation by thermal annealing of an intrinsically microporous hydroxyl-functionalized polyimide membrane, J. Membr. Sci., 495 (2015) 235-241.

[20] T. Merkel, V. Bondar, K. Nagai, B.D. Freeman, I. Pinnau, Gas sorption, diffusion, and permeation in poly (dimethylsiloxane), J. Polym. Sci. B: Polym. Phys., 38 (2000) 415-434.

[21] J.G. Wijmans, R.W. Baker, The solution-diffusion model: a review, J. Membr. Sci., 107 (1995) 1-21.

[22] H. Lin, B.D. Freeman, Gas solubility, diffusivity and permeability in poly (ethylene oxide), J. Membr. Sci., 239 (2004) 105-117.

[23] P. Li, T. Chung, D.R. Paul, Gas sorption and permeation in PIM-1, J. Membr. Sci., 432 (2013) 50-57.

[24] A. Bishnoi, S. Kumar, N. Joshi, Wide-Angle X-ray Diffraction (WXRD): Technique for Characterization of Nanomaterials and Polymer Nanocomposites, in: Microscopy Methods in Nanomaterials Characterization, Elsevier, 2017, pp. 313-337.

[25] B.J. Schwartz, Conjugated polymers as molecular materials: How chain conformation and film morphology influence energy transfer and interchain interactions, Ann. Rev. Phys. Chem., 54 (2003) 141-172.

[26] J.K. Lee, H.-J. Kim, T.H. Kim, C.-H. Lee, W.H. Park, J. Kim, T.S. Lee, A new synthetic approach for polybenzoxazole and light-induced fluorescent patterning on its film, Macromolecules, 38 (2005) 9427-9433.

[27] J.T. Vaughn, W.J. Koros, J. Johnson, O. Karvan, Effect of thermal annealing on a novel polyamide–imide polymer membrane for aggressive acid gas separations, J. Membr. Sci., 401 (2012) 163-174.

[28] F. Zhou, W.J. Koros, Study of thermal annealing on Matrimid® fiber performance in pervaporation of acetic acid and water mixtures, Polymer, 47 (2006) 280-288.

[29] Z. Chen, J. Bouffard, S.E. Kooi, T.M. Swager, Highly emissive Iptycene− fluorene conjugated copolymers: synthesis and photophysical properties, Macromolecules, 41 (2008) 6672-6676.

[30] J.J. Intemann, J.F. Mike, M. Cai, S. Bose, T. Xiao, T.C. Mauldin, R.A. Roggers, J. Shinar, R. Shinar, M. Jeffries-El, Synthesis and Characterization of Poly (9, 9-dialkylfluorenevinylene benzobisoxazoles): New Solution-Processable Electron-Accepting Conjugated Polymers, Macromolecules, 44 (2010) 248-255.

[31] E.E. Nesterov, Z. Zhu, T.M. Swager, Conjugation enhancement of intramolecular exciton migration in poly (p-phenylene ethynylene) s, J. Am. Chem. Soc., 127 (2005) 10083-10088.

[32] S. Wang, H. Lei, P. Guo, P. Wu, Z. Han, Novel conjugated polymer poly (benzobisoxazole-2, 6-diylvinylene): synthesis and evidence of aggregate formation in methanesulfonic acid, Eur. Polym. J., 40 (2004) 1163-1167.

[33] S. Wang, P. Wu, Z. Han, Random conjugated polybenzazole copolymers: Synthesis, characterization, and exciton confinement effects in photophysical properties, J. Mater. Sci., 39 (2004) 2717-2726.

[34] S. Park, S. Kim, J. Seo, S.Y. Park, Strongly fluorescent and thermally stable functional polybenzoxazole film: excited-state intramolecular proton transfer and chemically amplified photopatterning, Macromolecules, 38 (2005) 4557-4559.

[35] S. Wang, P. Guo, P. Wu, Z. Han, Supramolecular regulation of photophysical properties and electron paramagnetic resonance studies of novel rod− coil ordered copolymers based on poly (p-phenylene benzobisoxazole), Macromolecules, 37 (2004) 3815-3822.

[36] P.R. Bevington, D.K. Robinson, Data Reduction and Error Analysis for the Physical Sciences, 3rd ed., McGraw-Hill, Boston, 2003.

[37] M.S. Caceci, Estimating error limits in parametric curve fitting, Analytical Chemistry, 61 (1989) 2324-2327.

[38] B. Comesaña-Gándara, J. Chen, C.G. Bezzu, M. Carta, I. Rose, M.-C. Ferrari, E. Esposito, A. Fuoco, J.C. Jansen, N.B. McKeown, Redefining the Robeson upper bounds for CO_2/CH_4 and CO_2/N_2 separations using a series of ultrapermeable benzotriptycene-based polymers of intrinsic microporosity, En. Environ. Sci., 12 (2019) 2733-2740.

[39] A. Singh, B.D. Freeman, I. Pinnau, Pure and mixed gas acetone/nitrogen permeation properties of polydimethylsiloxane [PDMS], J. Polym. Sci. B: Polym. Phys., 36 (1998) 289-301.

[40] K.P. Bye, V. Loianno, T.N. Pham, R. Liu, J.S. Riffle, M. Galizia, Pure and mixed fluid sorption and transport in Celazole® polybenzimidazole: Effect of plasticization, J. Membr. Sci., 580 (2019) 235-247.

[41] Y. Huang, D. Paul, Physical aging of thin glassy polymer films monitored by gas permeability, Polymer, 45 (2004) 8377-8393.

[42] J.R. Weidman, S. Luo, C.M. Doherty, A.J. Hill, P. Gao, R. Guo, Analysis of governing factors controlling gas transport through fresh and aged triptycene-based polyimide films, J. Membr. Sci., 522 (2017) 12-22.

[43] J. Crank, The mathematics of diffusion, Oxford university press, 1979.

[44] M. Galizia, M.G. De Angelis, E. Finkelshtein, Y.P. Yampolskii, G.C. Sarti, Sorption and transport of hydrocarbons and alcohols in addition-type poly (trimethyl silyl norbornene). I: Experimental data, J. Membr. Sci., 385 (2011) 141-153.

[45] P. Li, T. Chung, D.R. Paul, Temperature dependence of gas sorption and permeation in PIM-1, J. Membr. Sci., 450 (2014) 380-388.

[46] S. Kanehashi, T. Nakagawa, K. Nagai, X. Duthie, S. Kentish, G. Stevens, Effects of carbon dioxide-induced plasticization on the gas transport properties of glassy polyimide membranes, J. Membr. Sci., 298 (2007) 147-155.

[47] Q. Liu, M. Galizia, K.L. Gleason, C.A. Scholes, D.R. Paul, B.D. Freeman, Influence of toluene on CO_2 and CH_4 gas transport properties in thermally rearranged (TR) polymers based on 3, 3′-dihydroxy-4, 4′-diamino-biphenyl (HAB) and 2, 2′-bis-(3, 4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), J. Membr. Sci., 514 (2016) 282-293.

[48] H. Wang, T.-S. Chung, D.R. Paul, Physical aging and plasticization of thick and thin films of the thermally rearranged ortho-functional polyimide 6FDA–HAB, J. Membr. Sci., 458 (2014) 27-35.