Gas separation performance of copolymers of perfluoro(butenyl vinyl ether) and perfluoro(2,2-dimethyl-1,3-dioxole)

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A B S T R A C T
Amorphous glassy perfluorinated polymers have high gas permeability, are chemically inert, thermally stable and known for their superior separation performance for several gas pairs. In the current study, the gas separation performance of copolymers of perfluoro(butenyl vinyl ether) (PBVE) and perfluoro(2,2-dimethyl-1,3-dioxole) (PDD) with two different monomer ratios, commercially known as CyclAFlor™, was studied for the first time, both at 35 °C and at higher temperatures below their glass transition temperature. For comparison, the temperature dependence of Cytop® (a homopolymer of PBVE) was studied. The higher the mole percentage of PBVE, the lower gas permeability and the higher selectivity for all gas pairs of interest. All permeability coefficients in Cytop® were lower than those reported in the literature except for helium and hydrogen due to the annealing protocol used, enhancing He/gas and H2/gas selectivity. The poly(PBVE-co-PDD) copolymers exhibited separation performance in the vicinity of the Robeson 2008 upper bound for many gas pairs, including He/CH4, He/N2 and N2/CH4. In particular, poly(50%PBVE-co-50%PDD) was more permeable than Hyflon® AD 60 but more selective for most gas pairs of interest. Both copolymers showed increasing H2/CO2 selectivity with temperature. While permeability was stable with pressure up to 10 bar at 35 °C, a change in the activation energy of permeation of CO2 at higher temperatures suggested that changes to the polymer structure had occurred, possibly reducing the glass transition temperature. Mixed gas measurements confirmed the suitability of CyclAFlor™ copolymers for CO2/CH4 separation compared to Cytop®.

1. Introduction

With population growth and economic expansion, global problems such as water shortages and climate change are growing and are expected to exacerbate in the next few decades [1]. Membrane separation is a promising technology which has contributed solutions to these problems [2–4]. In the last few decades, a noticeable progress in polymeric membrane materials has been witnessed, which has encouraged industrial sectors to utilize them broadly in applications such as air separation, natural gas treatment and in hydrogen recovery [5], replacing more energy intensive approaches such as cryogenic distillation. Membrane technology has also found new application in natural gas dehydration and vapor recovery [2,3]. Polymeric membranes however, usually suffer from either low permeability or low selectivity and they are susceptible to physical aging and plasticization by high sorbing molecules [3,4,6,7]. Polymer chemists have thus focused on emerging advanced materials with better separation performance and increased resistance to gas phase impurities [2,3]. These polymers include polymers of intrinsic microporosity (PIMs), thermally rearranged (TR) polymers, high performance polyimides and amorphous perfluoropolymers [3,5].

Perfluoropolymers are characterized by a remarkable combination of properties which allows them to occupy a unique position within other classes of polymers [8,9]. Specifically, they possess thermal stability and remarkable resistance to aggressive chemical agents. These features have facilitated their use in a range of commercial applications, including the aerospace, electronic, chemical and medical industries [2,9,10]. Early generations of perfluoropolymers, such as polytetrafluoroethylene (PTFE) and Teflon® FEP (a copolymer of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP)) did not attract the interest of the

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membrane industry, mainly because of their semi-crystalline nature which led to low permeability and a lack of solubility in common solvents [2,9,10]. The synthesis and commercialization of amorphous perfluorinated polymers in the early 1990s, such as Teflon® AF [11], Cytop® [12] and Hyflon® AD [13], was the breakthrough in the use of this class of polymers in gas separation applications. These amorphous glassy polymers exhibit high permeability, physical aging resistance and hydrocarbon phobicity which renders these materials significantly more resistant toward plasticization by condensable hydrocarbons than conventional glassy polymers [1,9,10,13]. Perfluorinated polymers determine the upper bound for several gas pairs in Robeson’s diagrams [14–16], including He/CH₄, He/H₂, N₂/CH₄ and H₂/CH₄. This is ascribed to the unfavorable interactions between the perfluoropolymer matrix and hydrogen containing molecules (e.g. H₂ and CH₄) [9,10,17]. However, few amorphous glassy perfluorinated polymers are available for commercial use because of the difficult and expensive synthesis of this type of polymers [9].

While Teflon® AFs [10,18–20], Hyflon® ADs [13,21–23] and Cytop® [8,24] represent the most studied amorphous perfluoropolymers and are widely used as membrane materials in several gas separation applications, any perfluropolypolymer is of interest to the gas separation field. Recently, a wide range of novel perfluorinated polymers have emerged through the synthesis of homopolymers based on novel perfluorinated monomers [8,24] or copolymerization of existing perfluorinated monomers [17,22,25–27,29]. These perfluorinated polymers exhibit superior gas separation performance compared to many commercial ones, especially in helium recovery from mixed gas mixtures (e.g. natural gas and He/H₂ mixture) [8,24–26].

In the current work, we report for the first time the permeability of a series of gases in CyclAFlor™ random copolymers of perfluorobutyl vinyl ether) (PBVE) and perfluoro(2,2-dimethyl-1,3-dioxole) (PDD) (Fig. 1) with two different monomer ratios: 0.12/0.88 and 0.5/0.5 at 35 °C and temperature ranges below their glass transition temperatures (Tg). Annealed films of these perfluoropolymers (containing less than 2 wt% residual solvent) were prepared and studied. For comparison, free standing films of Cytop®, studied previously [10,24], were subjected to the same annealing protocol as used in the present study and tested. Mixed gas measurements were also performed to test the CO₂/CH₄ separation performance of the CyclAFlor™ copolymers compared to Cytop®.

2. Experimental

2.1. Materials

CyclAFlor™ copolymers with two different monomer ratios of PBVE and PDD were supplied by Chromis Technologies (USA). Poly(88% PBVE-co-12%PDD) had a molecular weight range of 115–238 kDa; while the range for poly(50%PBVE-co-50%PDD) was 395–551 kDa. Cytop® (9 wt% solution in CT-Solv.100E) was purchased from Asahi Glass Company (Japan). Engineering fluid PF-5060 (3M™) was used to dissolve the CyclAFlor™ copolymers, while CT-Solv.100E (Asahi Glass Company, Japan) was used for further dilution of the Cytop® solution. Gas cylinders of He, H₂, O₂, N₂, CO₂ and CH₄ (99.99% purity) and a 10% CO₂ in CH₄ mixture were supplied by Coregas Pty Ltd. (Australia).

2.2. Membrane preparation

 Casting solutions (3 wt%) were prepared by mixing the polymer or polymer solution and a predetermined amount of the solvent using a magnetic stirrer bar at room temperature. The casting solutions were then sonicated for 30 s and left overnight to remove any entrained gas bubbles. The bubble-free casting solution was poured on to a casting ring over a pre-wetted cellophane sheet supported on a levelled glass plate. A second glass plate was used to cover the casting ring to slow the rate of solvent evaporation (48 hr). To remove residual solvent, the film was annealed under vacuum (15 kPa absolute pressure) for 7–10 days with a gradual increase in temperature starting from 35 °C and approaching their glass transition temperature (Table 1). Finally, the membranes were annealed without evacuation at a temperature 10 °C above their Tg for 30 min to eliminate the effect of membrane preparation on the polymer morphology. The oven was then switched off to allow the membranes to cool slowly to ambient temperature. The solvent content in the annealed dense films was less than 2 wt%, as confirmed by TGA, reflecting the strong tendency of perfluoropolymers to retain the solvent during casting procedures as observed with Hyflon® AD 60 previously [23]. The membranes were stored in a vacuum desiccator for two weeks after this annealing process to reduce the impact of physical aging and then tested within the following two weeks. The thickness of the dense membranes was 40–70 μm, measured by a micrometer (Mitutoyo, Japan), giving an accuracy of approximately ±1 μm.

2.3. Gas permeation measurements

The pure gas permeabilities of He, H₂, O₂, N₂, CH₄ and CO₂ in pristine annealed films were determined using a constant volume-variable pressure apparatus described previously [30]. These measurements were conducted with a feed pressure in the range between 3 and 10 bar absolute pressure (except for O₂) at 35 °C. In addition, the permeability coefficients were measured at 6 bar absolute pressure and three different temperatures below the glass transition of the perfluoropolymers as illustrated in Table 1. Additional temperatures were measured for CO₂ permeability to better understand the trends in the data. The system was degassed by evacuation overnight and the gas was then introduced at the desired pressure to the installed membrane.

![Fig. 1. Chemical structure of Cytop® and CyclAFlor™ poly(PBVE-co-PDD).](image)

| Tg (°C) | Literature | Experimental | Calculated* |
|--------|------------|--------------|-------------|
| Cytop® | 108 [10,24] | 105 ± 5 | 35, 50, 65 and 95 |
| Poly(88% PBVE-co-12%PDD) | 115 [33] | 120 ± 2 | 116.5 |
| Poly(50% PBVE-co-50%PDD) | 149 [33] | 133 ± 3 | 158 |

*Calculated from the Flory Fox Equation \( \frac{1}{T_g} = \sum x_i \frac{1}{T_{ti}} \) [34] based on values of 108°C for Cytop and 337°C for the PDD homopolymer [33].
Gas permeability was calculated based on the steady state increase in the downstream pressure [31]. Mixed gas permeability measurements were conducted at 35 °C using a constant pressure-variable volume apparatus previously reported [32]. Helium was used as a sweep gas at an absolute pressure of 1 bar and a flow rate of 34 cm³(STP)/min. Stage cut values (the ratio of permeate gas flow rate to the feed gas flow rate) were maintained below 1% in all mixed gas experiments to avoid any concentration polarization [31]. A Micro GC 490 Gas Chromatograph with thermal conductivity detector (Agilent Technologies, Australia) and helium carrier gas was used to determine the composition of the permeate gas stream. All experiments were undertaken with at least two pristine films and each data point was the average of four different measurements on each film.

2.4. Analysis

The density of the perfluoropolymers was measured by hydrostatic weighing in toluene using a Mettler-Toledo XS205 dual range balance with 0.01 mg accuracy. The corresponding fractional free volume (FFV) of the polymers was calculated using Eq. 1

\[ \text{FFV} = 1 - \rho V_o \]  

where \( \rho \) is the polymer density (g/cm³) and \( V_o \) is the specific occupied volume (cm³/g), which is calculated as 1.3 times the Van der Waals volume estimated by the Bondi group contribution method [35].

Differential Scanning Calorimetry (Perkin Elmer DSC 8500) was used with different scanning rates (2–30 °C/min) to confirm independently the glass transition temperatures (see Table 1).

3. Results and discussion

3.1. Density and fractional free volume

The density and FFV measurements for Cytop®, CyclAFlor™ and Teflon® AF 1600 [5,10] are consistent with the reported values in the literature [10,24] (Table 2). The higher the percentage of PDD, the higher the FFV of the polymer due to the abundant bulky CF₃ substituents in PDD decreasing the chain packing and thus decreasing the polymer density.

3.2. Pure gas permeability

The pure gas permeability of all polymers at 35 °C is independent of feed pressure (Fig. 2), confirming that all tested membranes are defect-free and resistant to plasticization in the pressure range of study. Fig. 3 shows the permeability dependence on the relative proportions of PBVE and PDD. The permeability increases exponentially with the fraction of PDD due to the loss of chain packing caused by the bulky CF₃ substituents on the PDD units. With the increase of PDD, the permeability coefficients of the different gases also converge as observed in Fig. 3, leading to a loss of selectivity.

The permeability values in the annealed Cytop® membranes are noticeably lower than those in Cytop® films tested previously [10,24], except for helium and hydrogen (Table 3). The difference can be ascribed to the different conditions of film preparation, especially the annealing protocol. In the current study, a more intensive annealing protocol was used compared to the previous study, leading to lower residual solvent. Yampolskii et al. [9] have noted that this residual solvent can cause plasticization of the membrane structure, leading to higher permeability values. Macchione and co-workers similarly reported that the annealing of Hyflon® AD 60 films (T anneal: 134 °C) at 200 °C decreased CO₂, N₂, O₂ and CH₄ permeability coefficients, while the permeability of He was significantly increased [23]. The permeability reduction with annealing was attributed to the low interchain interactions of perfluoropolymers which allows efficient chain packing with annealing, decreasing the polymer FFV [23,26]. As-cast dense films of Cytop®, prepared and tested in the current work, showed greater permeability coefficients than annealed films tested in the present work for all penetrants (Table 3) For instance, the permeability coefficients of small gases, such as He and H₂ exhibited a reduction of 11% and 23%, respectively after annealing, while O₂, N₂, and CH₄ permeability coefficients showed greater falls of 240, 272, 335 and 520%, respectively. A similar annealing effect was observed by Nikiforov et al. [26] with copolymers of hexafluoropropylene(HFP) and tetrafluoroethylene (TFE).

The changes in permeability can be readily fitted to the classical free volume relationship (Eq. (2)) [36,37] (see Tables S1 and S2; and Fig. S2 in the Supplementary Information).

![Fig. 2. The effect of feed pressure on pure gas permeability of pristine dense membranes of (a) CyclAFlor™ poly(50%PBVE-co-50%PDD), (b) CyclAFlor™ poly(88%PBVE-co-12%PDD) and (c) Cytop®](image-url)
diffusivity-controlled permeation. However, carbon dioxide shows a deviation from this observed trend due to the more dominant effect of solubility on this more condensable gas, reflecting its quadrupole moment.

The common permeability and selectivity trade-off can be observed with these perfluorinated polymers (Fig. 5). An exception is Poly(50% PBVE-co-50%PDD) which is more permeable than Hyflon® AD 60 (Fig. 4), but also exhibits higher selectivity than the latter for all gas pairs of interest except the He/H₂ and O₂/N₂ pairs (Table 4). This may be related to the size and distribution of free volume elements in both polymers, or it may relate to residual solvent retention in the Hyflon® AD sample as discussed above. Yavari et al. [24] observed similar behavior, with poly(perfluoro-2-methylene-1,3-dioxolane) (poly(PFMD)) exhibiting higher permeability and selectivity for all gas pairs than Cytop®, even though both polymers had the same FFV and Tg. The same behavior was observed with Hyflon® AD 60 and poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane) (poly(PFMMMD)) [24].

The selectivity increases with the increase in kinetic diameter difference, confirming the size sieving ability of these perfluoropolymers (Table 4 and Fig.S3 in the supplementary data). However, these polymers exhibit a higher selectivity for CO₂/CH₄, H₂/CH₄ and He/CH₄ than expected from the trend of other gas pairs (pairs with no methane) (see Supplementary Information Fig.S3). This is attributed to the unfavorable interactions between perfluoropolymer matrix and hydrocarbons which offer these materials higher gas/CH₄ selectivity compared to conventional glassy polymers [9,10]. The same behavior has been observed with all perfluorinated polymers studied previously [8,20,23-27].

The position of CyclAFlor™ poly(PBVE-co-PDD) copolymers and Cytop® (this study) relative to Robeson’s upper bound [15] is a key approach to the assessment of their gas separation performance. Fig. 5 (a-f) presents such diagrams for several gas pairs, including He/H₂, He/CH₄, He/N₂, N₂/CH₄, H₂/CH₄ and CO₂/CH₄. It can be seen that Cytop® membranes tested in the present study exhibit a combination of permeability and selectivity closer to the 2008 upper bound than previously reported [10,24] for several gas pairs, including He/CH₄, He/N₂ and H₂/CH₄. This is ascribed to the removal of more of the residual solvent through the annealing process. Importantly, the behavior of the CyclAFlor™ copolymers is somewhat closer to the 2008 upper bound line for all gas pairs of interest than most of the other commercial perfluoropolymers. For He/H₂, He/CH₄ and N₂/CH₄ poly(PBVE-co-PDD)s exhibit gas separation performance in the vicinity of the 2008 upper bound line due to the combined effects of their size sieving ability and the unfavorable interactions toward hydrogen containing molecules (e.g. H₂ and CH₄) [9,10,24]. These novel copolymers are located between the two upper bound lines for the case of He/N₂ separation, while they are well below the 2008 upper bound for CO₂/CH₄ and H₂/CH₄ pairs.

In 2019, Wu et al. introduced a perfluoropolymer upper bound [16] that recognizes the uniquely unfavorable interactions between these polymers and hydrogen containing molecules. For the He/H₂ gas pair, this line actually sits below that of the 2008 upper bound. For the other three gas pairs where this bound has been determined, all polymers investigated here, including the CyclAFlor™ copolymers sit well below this new line. The polymers that appear to contribute to the higher position of these bounds are those formed from hexafluoro propylene (FHP) and its copolymers with tetrafluoroethylene [26], as well as those formed from PFMD, PFMMMD [24] or their copolymers [17,38].

### 3.3. Temperature dependence of permeability and ideal selectivity

Fig. 6 presents the He permeability as a function of temperature in the three perfluorinated polymers. The temperature dependent permeability of H₂, O₂, N₂ and CH₄ is also presented in Figs. 54-57 (supplementary material). These data can readily be fitted to Eq. (3):

\[ P = P_0 e^{-E_d/kT} \]  

where \( P \) is gas permeability (barrer), \( A \) and \( B \) are constants for a particular gas and FFV is the fractional free volume of the polymer.

The permeability coefficients mostly decrease with the critical volume of the penetrant [37] (Fig. 4 and Table S1 in the Supplementary Information). This behavior is commonly known as

![Graph showing permeability coefficients for various gases](image)

| Table 3  |
|----------|
| Permeability coefficients of gases in as-cast and annealed Cytop® at 35°C. |

| Gases | As-cast Cytop® | Annealed Cytop® |
|-------|---------------|-----------------|
|       | (this work)   | (this work)     |
| He    | 206 ± 6       | 170 ± 5         |
| H₂    | 76 ± 13       | 59 ± 16         |
| O₂    | 13.6 ± 0.2    | 16 ± 5          |
| N₂    | 3.6 ± 0.1     | 5 ± 3           |
| CO₂   | 27.8 ± 0.3    | 35 ± 5          |
| CH₄   | 1.24 ± 0.05   | 2 ± 2           |

![Graph showing temperature dependence of permeability and ideal selectivity](image)
where $P$ is the gas permeability coefficient (barrer), $P_0$ is the pre-exponential factor (barrer), $R$ is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), $T$ is absolute temperature (K) and $E_p$ is the activation energy of permeation (J mol$^{-1}$). The solution-diffusion model indicates in turn that [37]:

$$E_p = \Delta H_s + E_D$$  \(4\)
where $\Delta H$ is the heat of sorption and is usually negative, indicative of solubility declining with temperature, whereas $E_p$ is positive, indicative of diffusivity increasing with temperature. The activation energy of permeation ($E_p$) of He, H$_2$, O$_2$, N$_2$ and CH$_4$ gases in Cytop® and CyclAFlor™ copolymers were calculated based on Eq. (3) and listed in Table 5 compared to those in Teflon® AFs. The positive values of $E_p$ for these gases are indicative of $E_p$ being greater than the absolute value of $\Delta H$ and thus indicative of diffusivity dependent behavior, with permeability increasing with temperature. The values of $E_p$ in Cytop® in the present work are slightly higher than those determined by Alentiev [39] due to the lower permeability of Cytop® films tested in the present study compared to the literature (Table 3) [10,24]. Similarly, two data sets are provided for AF 2400 in Table 5 that show how membrane preparation protocols can influence the Arrhenius behaviour of penetrants in these perfluoropolymers [40,41]. Merkel et al. [41] dried their films at ambient temperature after casting, whereas Pinnau and Toy [40] dried at 150 °C under vacuum for three days. This led to permeability coefficients that differed by a factor of 1.7 and 2.0 between the two studies [41].

CO$_2$ permeability in poly(50%PBVE-co-50%PDD) decreases with temperature until 95 °C, which is typical for solubility controlled permeation (i.e. the magnitude of $\Delta H$ exceeds that of $E_p$). However, this permeability then starts to increase with temperature (Fig. 7), indicating that the diffusivity effect on permeability is becoming stronger. The CO$_2$ permeability in Cytop® and poly(88%PBVE-co-12%PDD) increases with temperature at all temperatures, but there is similarly a marked break in the Arrhenius behaviour observed at around 65 °C for these polymers (Fig. 7). These changes in the activation energy of permeation suggest that the sorption of CO$_2$ has changed the polymer structure in some manner. While the data presented in Fig. 2 would suggest that plastification by CO$_2$ is unlikely, it is possible that the interaction of the sorbed CO$_2$ along with the remaining solvent (a known plasticiser) may have caused a reduction in the glass transition temperature and thus a transition from a glassy to a rubbery state to occur at this point. It is known that upon transition from a glassy to rubbery state, penetrant diffusivity becomes more sensitive to temperature ($E_p$ increases) as observed previously with glassy polymers [42-44] and consistent with the predictions of free-volume theory [45]. Further, the heat of sorption becomes less exothermic in the rubbery region than in the glassy region as observed with Teflon® AF 1600 [46] and Teflon® AF 2400 [47].

The negative $E_p$ for CO$_2$ in the lower temperature range may reflect a low value of $E_p$ compared to a strongly exothermic $\Delta H$, which is characteristic for many glassy polymers with high FFV [20,26]. More negative values are recorded for polymers containing a larger proportion of PDD, which may also reflect the high affinity of CO$_2$ to the ether linkages in the monomer [48].

Fig. 8 illustrates the effect of temperature on the selectivity of poly (50%PBVE-co-50%PDD) for several gas pairs of interest, while similar figures for poly(88%PBVE-co-12%PDD) and Cytop® are presented in the Supplementary Information (Fig. S8 and Fig. S9). It is seen that the selectivity decreases as temperature increases for all gas pairs except for the H$_2$/CO$_2$ pair. The decrease in selectivity for most pairs is ascribed to

### Table 5

| FFV | He | H$_2$ | O$_2$ | N$_2$ | CH$_4$ | CO$_2$ | CO$_2$ testing temperature (°C) |
|-----|----|------|------|------|-------|-------|---------------------------------|
| Cytop® [9,39] | 0.210 | 12 | 11 | 14 | 16 | 24 | 9.5 | Unknown |
| Cytop® (this work) | 0.218 | 13.6 | 15.6 | 21.1 | 17.2 | 35.0 | 9 | 35-65 |
| CyclAFlor™ | 0.225 | 8.6 | 12.1 | 12.7 | 17.3 | 26.8 | 1.8 | 35-65 |
| Poly(88%PBVE-co-12%PDD) | 0.256 | 7.4 | 10.7 | 8.4 | 12.3 | 18.7 | $-2.2$ | 35-95 |
| CyclAFlor™ | 0.310 | 4.4 | 4.8 | 3.4 | 4.6 | 10.3 | $-1.8$ | 20-50 |
| Teflon® AF 2400 [40] | 0.330 | – | 3.1 | 6.3 | 8.9 | 9.8 | 0.9 | Unknown |
| Teflon® AF 2400 [41] | 0.330 | 1.6 | – | – | –2.5 | –0.4 | 1.3 | –6.7 |
| Teflon® AF 2400 [40] | 0.320 | – | 3.1 | 6.3 | 8.9 | 9.8 | 0.9 | Unknown |

Fig. 6. Temperature dependence of He permeability in CyclAFlor™ copolymers and Cytop®.

Fig. 7. Temperature dependence of CO$_2$ permeability in CyclAFlor™ copolymers and Cytop®.
the comparable increase in permeability coefficients of both penetrants with temperature rise, leading to a loss of size sieving ability. In the case of the H₂/CO₂ pair, H₂ permeability increases more rapidly than CO₂ permeability with temperature as a result of the higher Eₚ of H₂ compared to that of CO₂ (Table 5). Therefore, for both novel copolymers, H₂/CO₂ selectivity increases with temperature. This is significantly different to the behavior of Cytop®, where this selectivity falls with temperature.

3.4. Performance of CyclAFlor™ copolymers under mixed gas conditions

Mixed gas measurement is a key parameter to confirm the reliability of new materials in various gas separation applications. Yampolskii and others [9] have stated that perfluorinated polymers exhibit identical ideal and mixed selectivity for light gas mixtures (e.g. O₂/N₂, He/H₂, He/CH₄ and N₂/CH₄). However, these materials may show different selectivity under mixed conditions for gas pairs involving high sorbing molecules (e.g. CO₂ and condensable hydrocarbons) due to plasticization and competitive sorption effects. Hence, the performance of CyclAFlor™ copolymers and Cytop® was tested with a 10% CO₂-90% CH₄ mixture at 10 bar and at 35 °C, representative of a natural gas sweetening operation. The driving forces of permeation (partial pressure difference) are lower for both penetrants than these in the pure gas permeation experiments, but the ideal permeability coefficients of CO₂ and CH₄ are independent of feed pressure as noted in Fig. 2.

The difference in CO₂ and CH₄ permeability between the pure and mixed gas systems for Cytop® and poly(50%PBVE-co-50%PDD) is within the error range (see Table S1 and Table 6). However, in the case of poly(88%PBVE-co-12%PDD), both permeabilities show a significant fall (20% for CO₂ and 35% for CH₄) in the mixed gas experiments. This may be attributed to the effect of competitive sorption of each penetrant on the other.

The CO₂/CH₄ selectivity of Cytop® films under mixed conditions is comparable to the values reported previously [23,49] and is slightly higher than the pure gas value (Table 4). A noticeable increase in separation factor is also observed under mixed gas conditions for Poly(88% PBVE-co-12%PDD), while poly(50%PBVE-co-50%PDD) exhibits a comparable selectivity to the pure gas case. These increases confirm the greater impact of CO₂ sorption on CH₄ than vice versa, and the resistance of these polymers against plasticization at 35 °C as observed previously with Teflon® AFs and Hyflon® ADs [50,51].

4. Conclusions

In this study, we have demonstrated the gas separation performance of two CyclAFlor™ copolymers of perfluoro(butenyl vinyl ether) (PBVE) and perfluoro(2,2-dimethyl-1,3-dioxole) (PDD) with 88% and 50% PBVE compared to Cytop® (a homopolymer of PBVE). The investigation revealed that the higher the percentage of PBVE in the perfluorinated films, the lower permeability and the higher selectivity of these polymers. Although poly(50%PBVE-co-50%PDD) exhibits higher permeability than Hyflon® AD 60, the former is more selective than the later for most gas pairs of interest. In Robeson’s diagrams, CyclAFlor™ copolymers are located in the vicinity of the 2008 upper bound for several gas pairs, including He/CH₄, He/H₂, He/N₂ and N₂/CH₄ and somewhat closer than other commercial perfluorinated materials. This superior gas separation performance is attributed to the combination between their size sieving ability and unfavorable interactions with hydrogen containing molecules (e.g. H₂ and CH₄). All permeability coefficients increased with temperature in both Cytop® and CyclAFlor™ copolymers, except for CO₂ in poly(50%PBVE-co-50%PDD). The increase in the activation energy of CO₂ permeation for all three polymers at higher temperatures indicated a change in the Arrhenius behavior that was consistent with the glass transition temperature being exceeded. Measurements in a CO₂–CH₄ mixture showed that the performance of perfluoropolymers was stable under these mixed gas conditions.

Poly(50%PBVE-co-50%PDD) was shown to be one of the most permeable of known perfluorinated polymers and thus may be viable for several applications, including helium separation from natural gas and oxygen enriched air production for more efficient combustion. Similarly, the superior separation performance of poly(88%PBVE-co-12% PDD) makes this a promising candidate for several gas separation applications, including He/H₂, He/CH₄, N₂/CH₄ and CO₂/CH₄ separation, with performance close to, or exceeding that of commercial Cytop® membranes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2021.119401.

Author statement

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Resources; Writing - review & editing. Erich Kathmann: Resources. Whitney White: Resources. Sandra Kentish: Conceptualization; Funding acquisition; Investigation; Methodology; Project administration; Resources; Supervision; Writing - review & editing.

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