EXPLORING THE STRUCTURE-PROPERTY RELATIONSHIPS OF LINEAR AND CROSSLINKED POLY(ETHYLENE OXIDE) POLYMER MEMBRANES FOR GAS SEPARATIONS

A Dissertation

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The development of polymeric materials suitable for gas separation membrane applications is discussed in this dissertation. Compared to conventional gas separation systems, such as absorption, gas separation membrane systems are inherently smaller in size and easier to operate, and potentially, more economically viable. Membranes with high permeability (for a high gas throughput) and adequate selectivity (ability to separate a given gas from a mixture) are desired. However, due to the natural properties of polymeric materials, generally, membranes with high permeabilities unfortunately operate with low selectivities and vice versa. To combat this natural trade-off, to produce materials with both high permeabilities and sufficiently high selectivities, the chemical and physical properties of polymeric materials must be strategically designed.

The majority of this work explores strategies for incorporating rubbery poly(ethylene oxide) (PEO) into gas separation membranes. PEO is a promising material for CO₂ related-separations due to its high solubility selectively for CO₂ and its high
diffusivity, which together, give PEO-based materials excellent CO$_2$-separation performance. However, pure PEO is mechanically weak and suffers from high crystallinity which prevent its use in gas separation membranes. Therefore, this work explores strategies to incorporate PEO into copolymers, into crosslinked networks, and into semi-interpenetrating networks (s-IPNs). These systems have demonstrated improved mechanical properties, mitigated PEO crystallinity, and highly promising CO$_2$-related gas separation performance.
This is a testament to the endless love and support received by trusting in God.
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CHAPTER 1:
INTRODUCTION

1.1 Overview of Gas Separation Membranes

Significant interest in developing polymeric membranes for utilization in gas separations began in the early 1980’s by both companies and Universities [1]. Gas separation membranes have been largely developed for the purpose of removing carbon dioxide from natural gas streams, for the purification of hydrogen, and for the enrichment of oxygen [1,2]. Conventional and major competing technologies for performing these sorts of gas separations are chemical absorption, pressure swing adsorption, and cryogenic distillation [2]. However, membranes pose an attractive energy-saving (and cost-saving) alternative to the previously mentioned conventional gas separation processes due to their operation with no thermal regeneration or phase changes [3–5]. Furthermore, in contrast to these conventional separation systems, membrane separation processes typically require very little maintenance [4,6] and are significantly smaller in footprint than absorption systems [7].

In simplified description, polymeric membranes perform gas separations by acting like molecular filters which can separate one gas from another in a mixed feed stream. Gas separation membranes with different classes of molecular structures exist and their respective gas transport mechanisms are described as Knudsen-diffusion, molecular sieving, and solution-diffusion, as highlighted in Figure 1.1, among others [1,8].
However, this work focuses on nonporous polymeric membranes that perform gas separations through the solution-diffusion mechanism. Whereby, both the penetrant gas’ solubility and its diffusion characteristics determine its transport properties through the membrane [1].

Figure 1.1: Gas molecules collide with the pore walls more often than with each other in Knudsen diffusion. In molecular sieving, the larger gas is prevented from traversing due to the size of the pore. Solution-diffusion is expounded upon below.

In the solution-diffusion model, the penetrant gas first dissolves into the membrane at the high pressure feed side and then diffuses across the membrane due to a concentration gradient and then desorbs on the low pressure permeate side [9–11]. The throughput of the membrane for a pure-gas is often described by the membrane permeability, \( P \), which is the thickness normalized steady-state gas flux, \( N_A \times l \), through the membrane dived by the pressure difference across the membrane, as shown in Equation 1.1 [2]:

\[
P_A = \frac{N_A \times l}{p_2 - p_1} \tag{1.1}
\]
where $p_2$ is the upstream pressure and $p_1$ is the permeate side pressure. The most common unit of permeability is the Barrer, expressed as $(10^{-10} \text{ cm}^3 \text{ (STP) cm})/(\text{cm}^2 \text{ s cmHg})$ [12]. In principle, the permeability of a given material is intrinsic, in that it should yield the same value (exceptions exist) for a given material even if the evaluated membranes are of differing thickness or trans-membrane pressure [2].

For dense polymeric membranes operating under the solution-diffusion model, permeability can be broken into its constituent components, as given in Equation 1.2:

$$P_A = D_A \times S_A$$ (1.2)

where $D_A$ is the concentration-averaged diffusivity coefficient and $S_A$ is the solubility coefficient [2,12]. The diffusivity coefficient is a mobility-related term that corresponds to how quickly a penetrant can move in the material, while the solubility coefficient quantifies how much gas is within the material [13]. Because a membranes’ permeability characteristics are influenced by both diffusivity and solubility contributions, any factor that influences either coefficient, or both, can significantly impact the permeability of a given penetrant. For instance, a polymer material’s chain flexibility, efficiency of chain packing, free volume, and (distribution of free volume) [14] will significantly impact a given penetrants ability to diffuse through the membrane material [2]. Accordingly, smaller penetrants can often diffuse through similarly-sized intrinsic [15,16] and transient gaps within a material with less restriction, and therefore have higher diffusion coefficients compared to larger penetrants [2,12]. The solubility of a gas in a given material is largely dictated by its molecular condensability but also on specific polymer-penetrant interactions and morphological features [2,12]. Therefore, diffusion and solubility characteristics are unique to each type of penetrant and polymeric material, and
are influenced by operational conditions such as temperature and pressure [12], which results in different polymers having unique permeability characteristics for a given penetrant and operational condition. Because of these inherent membrane and penetrant properties, the ability of a given material to separate two gases (A and B) can be calculated by the ratio of the penetrants’ pure-gas permeabilities [4] and this quantity, shown as Equation 1.3, is the membrane’s ideal selectivity [2].

$$\alpha_{A/B} = \frac{P_A}{P_B}$$  \hfill (1.3)

By plugging Equation 1.2 into Equation 1.3 the ideal selectivity can be written as Equation 1.4 [12]:

$$\alpha_{A/B} = \frac{D_A}{D_B} \times \frac{S_A}{S_B}$$  \hfill (1.4)

which allows for comparing separately the diffusivity and solubility selectivity contributions to the overall membrane selectivity. Here a distinction between membrane classes can be made. When operating below the glass transition temperature (T_g) of the polymeric material, the polymer chains are rigid and semi-fixed in place due to kinetic constrains on polymer segmental motions and the material is referred to as “glassy” [2,17]. On the other hand, when operating above the T_g of a material, the polymer chains have higher mobility which gives the material “rubbery” characteristics (less rigid, more flexible, etc.) [17]. Glassy materials generally separate gases based on differences in their molecular sizes rather than differences in their solubilities and so diffusivity selectivity is important in determining overall selectivity for glassy materials [4]. Rubbery materials typically have a lower extent of size-sieving ability [17] and accordingly solubility selectivity can become more of an important factor to overall selectivity [18].
1.1.1 Glassy and Rubbery Membrane Gas Transport Correlations

For a penetrant to diffuse through a material it must be able to pass through openings, which for dense nonporous membranes requires the thermally induced random local segmental motions of polymer chains to arrange such that gaps of sufficient size are created for the passage of a given penetrant [11]. As such, the size of the penetrant gas is an important parameter because if the gaps are smaller than the penetrant then it cannot diffuse through. The parameter that best describes the “size” of light gases that is relevant for correlating gas transport properties is the kinetic diameter of the penetrant [11,17]. The kinetic diameter of a penetrant is the smallest zeolite window that the molecule can fit through [11]. With these principles in mind it is reasonable that the diffusion coefficient of a gas generally increases as the size of the penetrant molecule decreases [17]. In other words, smaller penetrants can move through the permanent or transient gaps within a nonporous material more quickly. This is true of both glassy and rubbery materials, as illustrated by Matteucci et al., where when the logarithm of the diffusion coefficients of various penetrants was plotted against the square of their kinetic diameters there is a clear linear increase in the diffusion coefficients with decreasing kinetic diameters for various glassy materials [17]. This trend appears to be somewhat less than linear for the rubbery materials, but still the diffusion coefficients increased with decreasing kinetic diameters. Not only does the size of the penetrant influence diffusion properties, but so does the type of material. For instance, the diffusion coefficient of a given penetrant, that is of a given size, can vary tremendously, even over multiple orders of magnitude [17]. Accordingly, the selection of the best material for a given gas
separation is of great importance as the gas transport properties, diffusion in this case, are strongly dictated by the type of material.

Another general trend in the transport of gases, especially in rubbery polymeric materials, is that with an increase in glass transition temperature there is a decrease in diffusion coefficients [17] and permeability [17,18]. This is illustrated by Matteucci et al. by the decrease of N\textsubscript{2} diffusion coefficient and N\textsubscript{2} permeability with increasing T\textsubscript{g} [17] and Figure 1.2 illustrates the correlation between T\textsubscript{g} and permeability in rubbery PEO as shown by Lin et al. [18]. This relationship is not as generally applicable to glassy polymeric materials because other factors, such as fractional free volume (FFV) and its distribution, become more relevant and these are only some of the constituent factors influencing T\textsubscript{g}. Accordingly, the amount of unoccupied space (free volume) within a material, (V - V\textsubscript{o}), divided by the measured volume of the polymer, V (expressed as volume per mole of repeat unit), is the fractional free volume as shown in Equation 1.5 [19]:

\[ FFV = \frac{(V-V_o)}{V} \]  \hspace{1cm} (1.5)

where V\textsubscript{o} is the volume occupied by the polymer chains, which can be estimated by Bondi’s group contribution method [19,20]. It has been found that the diffusion coefficients of penetrant gases are often related to FFV by Equation 1.6 [17]:

\[ D = Ae^{-B/FFV} \]  \hspace{1cm} (1.6)

where the empirical constants A and B vary depending on the gas and polymer. Because the solubility coefficients vary much more weekly with changing FFV than diffusion
coefficients the relationship in Equation 1.6 can be combined with Equation 1.2 such that permeability is directly correlated with FFV as shown in Equation 1.7 [17]:

\[ P = A_p e^{-B/FFV} \]  

(1.7)

here \( A_p = A \times S \). The relationships between diffusion coefficients and permeabilities with FFV of glassy materials are shown by Matteucci et al. [17], as Figure 1.3, where with increasing FFV both the diffusion coefficients and permeabilities increase. These trends hold for other gas penetrants as well [2,21], and have been observed for rubbery materials too, [21] as illustrated in Figure 1.4.

![Graph showing relationship between CO₂ permeability and T₀ of PEO phase.](image)

Figure 1.2: Relationship of permeability versus the glass transition temperature of the rubbery poly(ethylene oxide) (PEO) phase. Reprinted with permission from Elsevier.
Figure 1.3: Correlation of diffusion coefficients (a) and permeability (b) with FFV in glassy polymers. Reprinted with permission from Elsevier.

Figure 1.4: Relationship of permeability versus inverse FFV of rubbery poly(ethylene oxide) (PEO). Reprinted with permission from Elsevier and ACS Publications.
1.1.2 Prominent Literature Approaches and Challenges

The ideal gas separation membrane would be one of high permeability that has adequately high selectivity (though limits exist in how high selectivity should be due to the “pressure ratio issue”) [22]. However, for reference, the range of useful membrane selectivities recommended for CO\textsubscript{2} removal from post combustion gas streams (CO\textsubscript{2}/N\textsubscript{2}) at power plants depends on various assumptions on the cost of compressors, vacuums, membrane modules, process design, etc. but is generally in the range of 20-180 [3,22]. However, selectivity needs to be high enough to provide a useful gas separation [22]. For a given gas separation a higher permeability allows for a membrane of smaller area to be used to achieve a certain flux of gas through the membrane which corresponds to lower costs [22]. However, there are inherent material properties that lead to tradeoffs in permeability and selectivity. For instance, in 1991 Robeson plotted the selectivity vs. permeability of various gas pairs reported in the literature for polymeric membranes and noted that the data points generally fell below an empirical upper limit, where an increase in permeability correlated with a decrease in selectivity and vice versa [23]. This upper limit has since been referred to as the Robeson Upper Bound and was updated in 2008 to reflect the advancements in membrane gas separation performance noted within the literature [24]. An example of an upper bound plot for CO\textsubscript{2}/N\textsubscript{2} separation is provided in Figure 1.5 [24]. A theoretic basis for the permeability/selectivity tradeoff was developed by Freeman. Freeman noted that the most promising methods for improving the gas separation performance of polymeric membranes are to increase solubility selectivity and/or to increase polymer chain stiffness while also increasing interchain spacing. The improved solubility selectivity and/or increased chain stiffness coupled with increased
fractional free volume should allow for increased selectivity without a loss in permeability, on the other hand, permeability may also increase. With these principles in mind, the empirical upper bounds may be pushed higher until the true limits of polymeric membranes operating under the solution-diffusion mechanism are reached [11]. The upper bound was developed for homogeneous polymer films and thus its theoretical implications do not apply to heterogeneous membranes such as UV surface modified membranes, mixed matrix membranes, facilitated transport membranes, etc. [11,23,24], but regardless, the upper bounds have become common benchmarks to compare gas transport properties of various membrane materials.

![Figure 1.5: 2008 Upper bound plot for CO₂/N₂ separation. Reprinted with permission from Elsevier.](image)

1.1.3 Improving the Solubility Selectivity of Membranes for Gas Separations

As noted by Freeman, improving the solubility selectivity of membrane materials is one promising method to improve gas separation performance [11]. One of the most
heavily investigated materials for improving the solubility selectivity of CO$_2$, in particular, over other gases such as H$_2$ and N$_2$, is poly(ethylene oxide) (PEO) [10,18]. The chemical structure of PEO is illustrated in Figure 1.6. The introduction of polar groups into polymers can be used to produce materials with desirable properties such as high CO$_2$ solubility and high CO$_2$/light gas solubility selectivity. Unfortunately, though, incorporating polar groups tend to increase chain packing and cause CO$_2$ diffusion coefficients to decrease, resulting in suppressed CO$_2$ permeability [18]. However, PEO is unique in that increasing the content of polar ether oxygens can result in both improved CO$_2$ permeability and CO$_2$/light gas selectivity [18,25,26]. Such high CO$_2$/light gas selectivity values at a given CO$_2$ permeability are attainable due to the high solubility selectivity imparted by the unique affinity of CO$_2$ to the PEO segments [26]. CO$_2$ has a high quadrupole moment [27] and a high polarizability compared with other relevant light gases of interest which results in favorable affinity between CO$_2$ and polar PEO segments [26,28,29].

![Figure 1.6: General chemical structure of poly(ethylene oxide) (PEO).](image)

1.1.4 Literature Review on the Incorporation of PEO into Gas Separation Membranes

The high solubility selectivity of PEO makes this an attractive material for use in gas separation membranes. The strong interaction of the polar ether groups of PEO with the high quadrupole moment of CO$_2$ leads to relatively high solubility of CO$_2$ in PEO
compared to other light gases, which allows for CO₂ to permeate more quickly than H₂, despite that H₂ has a much smaller kinetic diameter [18,23,30,31]. Similarly, the high solubility selectivity of PEO for CO₂ enables high CO₂/N₂ perm-selectivities despite the similar size (kinetic diameters) of CO₂ and N₂ [23,26,32]. For reference, the kinetic diameters and quadrupole moments of relevant light gases are shown in Table 1.1 [23,27]. However, there exist several major drawbacks in utilizing PEO [33]. For one, pure PEO of high enough molecular weight for forming films is semi-crystalline near and above room temperature. Crystallinity is a major issue as it is generally believed that crystals are impermeable. Accordingly, the presence of crystals will act as impenetrable barriers within the polymer material and can significantly decrease the permeability of CO₂. For instance, the infinite dilution permeability of CO₂ in semi-crystalline PEO at 35 °C is 12 Barrer whereas the estimated infinite dilution CO₂ permeability in fully amorphous PEO at 35 °C is 143 Barrer – significantly larger [29]. However, several options exist in order to reduce or eliminate PEO crystallinity, such as incorporating low molecular weight PEO that remains non-crystalline, synthesizing block copolymers containing PEO, and crosslinking PEO to form network membranes [10,18]. Each prominent method of incorporating PEO into gas separation membranes has unique advantages and disadvantages, which are discussed below.
<table>
<thead>
<tr>
<th>Gas</th>
<th>Kinetic Diameter (Å)</th>
<th>Quadrupole Moment (erg$^{1/2}$ cm$^{5/2}$ $\times 10^{26}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>2.89</td>
<td>0.66</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.3</td>
<td>-4.3</td>
</tr>
<tr>
<td>O$_2$</td>
<td>3.46</td>
<td>-0.39</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.64</td>
<td>-1.52</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>3.8</td>
<td>0</td>
</tr>
</tbody>
</table>

1.1.4.1 Polyimide and Poly(ether-imide) Copolymer Membranes

Glassy polyimides are one of the main types of materials that PEO could be incorporated into. Glassy polyimide materials are well known and heavily investigated due to their often desirable properties of high fractional free volume and rigidity as well as high chemical and thermal stability and attractive mechanical properties [34–36]. However, such polymers are typically susceptible to plasticization by CO$_2$ which leads to a loss of selectivity and poorer separation efficiency [36,37]. At a high enough concentration, CO$_2$ can induce swelling of the polymer matrix which leads to an increase in free volume and segmental mobility [13,38]. Plasticization may increase permeability but often at the detrimental cost of significantly reduced selectivity [36,37,39]. Therefore, in order to make polyimide membranes more viable for CO$_2$ separations, additional efforts may be needed to mitigate or eliminate the negative effects of plasticization, such as by applying thermal treatment and crosslinking [36,37,39,40]. Furthermore, glassy polyimide materials may not be best suited for certain gas separations, such as removing CO$_2$ from H$_2$, because their size-selective operation requires the smaller, more quickly permeated H$_2$ to be recompressed following purification [18,41,42]. Additionally, in
removing CO₂ from N₂ it is beneficial to avoid the permeation of the major component (N₂) across the membrane [18]. In these sorts of instances it is preferable to more selectively permeate CO₂ across the membrane [18,42]. PEO is one of the most promising materials in order to achieve such separations due to its high solubility selectivity for CO₂ [10,18,42].

The synthesis of PEO-containing polyimide copolymer membranes by various researchers has produced materials with attractive combinations of CO₂ permeability and CO₂/gas selectivity. For instance, Okamoto et al., synthesized poly(ether imide) segmented copolymer membranes where a copolymer containing nearly 70 wt% PEO was capable of a CO₂ permeability of 140 Barrer with a CO₂/N₂ selectivity of 70 at 25 °C [26]. Even higher CO₂ permeabilities have been obtained for simple copolyetherimide polymers such as that synthesized by Krea et al., which at 80 wt% polyether content had a CO₂ permeability of 622 Barrer and a CO₂/N₂ selectivity of 44 [43]. Commendable gas separation performance has been demonstrated for separating CO₂ from H₂ as well. For instance, poly(ethylene oxide) containing copolyimides produced by Chen et al. at 65 wt% PEO content were shown to have a CO₂ permeability of 157 Barrer and a pure-gas CO₂/H₂ selectivity of 8.5. Interestingly, the CO₂ separation performance significantly improved in the mixed gas test where the CO₂ permeability was 179.3 Barrer with an accompanying CO₂/H₂ selectivity of 22.7 [33]. The CO₂ separation performance in each of these studies, and in general, increases with increasing PEO content so long as crystallinity is mitigated [25,26,33,43–45]. Unfortunately though, crystallinity can become a significant problem at too high a PEO content or PEO molecular weight [45], but moreover, the mechanical properties severely suffer at high PEO contents. The
previously mentioned PEO-containing copolyimides were noted to show significantly decreased mechanical properties with increasing PEO content [26] especially above 40 wt% PEO content [33,43]. This highlights the tradeoff in synthesizing mechanically robust and high-performance CO$_2$ separation membranes with high PEO content. However, due to the promising CO$_2$ separation performance of PEO-containing polyimide copolymers, continued research into developing mechanically robust and high-performance copolymers is encouraged.

1.1.4.2 Poly(ether-imide) Copolymer Membranes

Just as PEO has been copolymerized with rigid segments in polyimide materials, PEO has also been incorporated into polyamide materials. Perhaps the most heavily investigated group of PEO-containing polyamide materials for CO$_2$ gas separation membranes are the commercially available Pebax® thermoplastic elastomers. Pebax® is offered in various grades, with a range of crystallinity values, PEO contents, and length of rigid polyamide segments [10]. Certain Pebax® grades have demonstrated good combinations of CO$_2$ permeability and selectivity [28] which has no-doubt spurred numerous efforts to incorporate Pebax® into gas separation membranes. However, Pebax® MH 1657, one of the most commonly studied grades, does possess an inherent drawback in that it is soluble in only very few of the suitable solvents required for membrane formation [46]. Furthermore, mixed gas separation performance may be significantly different compared to pure-gas. For instance, in work done by Sutrisna et al., on Pebax® 1657, pure-gas measurements at 3 bar feed pressure and 25 °C yielded a CO$_2$ permeability of ~113 Barrer and CO$_2$/CH$_4$ selectivity of 19.4 whereas the mixed gas test at 3 bar CO$_2$ partial pressure (15 bar total) gave a CO$_2$ permeability of ~56 and a
CO₂/CH₄ selectivity of ~16 [47]. Though Pebax® is widely studied, other PEO-containing polyamides exist, and some have promising gas separation performance. For example, PEO-ran-PPO based block copolymers with tetra-amide (T6T6T) hard segments have achieved a CO₂ permeability of 470 Barrer with a CO₂/H₂ and CO₂/N₂ selectivity of 10 and 43, respectively, at 35 °C and 4 bar feed pressure [48]. These promising results motivate the continued study of PEO-polyamide copolymer membranes for CO₂-related gas separations.

1.1.4.3 Crosslinked PEO-Containing Gas Separation Membranes

Another method to incorporate high amounts of PEO into membrane materials, to increase CO₂-separation ability, while mitigating PEO crystallinity, is by crosslinking PEO segments [10,18]. PEO crystallinity in crosslinked materials is essentially eliminated when the PEO segment length between crosslink junctions is less than 1500 g/mol [49]. With PEO crystallinity reduced/eliminated and at very high PEO content, crosslinked PEO-based membranes have shown outstanding CO₂ separation performance that near or even exceed the Robeson upper bounds for CO₂/N₂ [50–53] and CO₂/H₂ [52–55] separations. Several crosslinked PEO-based membranes already have gas separation properties that make them potentially cost-competitive with conventional solvent-based CO₂ capture (MEA based absorption) at coal-fired power plants for post-combustion CO₂ capture [3]. However, not all PEO-based crosslinked membranes perform equally. For instance, when a relatively short, PEO-based dimethacrylate and monomethacrylate were photo crosslinked, the resultant film (DB10/MM9) (90/10) had a relatively high glass transition temperature of -14 °C and a CO₂ permeability of just 7 Barrer at 25 °C. However, increasing the PEO segment length of the dimethacrylate yielded a film with T₉
of -62 °C and a CO₂ permeability of 250 Barrer at 25 °C [51]. Other PEO-based crosslinked networks, such as those by Zhao et al., have attained very high CO₂ permeabilities, where the networks of poly(ethylene glycol) methyl ether acrylate (PEGMEA) and pentaerythritol triacrylate (PETA) with low crosslinker (PETA) content (5 wt%) that were very flexible (T<sub>g</sub> = -67.1 °C) and had a CO₂ permeability of 1050 Barrer at 35 °C [50]. Even though these materials primarily consist of PEO, structural (or other) variances can lead to huge CO₂ separation performance differences. As such, and especially considering the already excellent CO₂ separation capabilities of these materials, more studies investigating the structure/property relationships of crosslinked PEO-based membranes would be beneficial for future tailoring of gas separation properties. However, there are still challenges to overcome for crosslinked PEO-based materials as the mechanical properties of crosslinked PEO films are generally inferior to those of rigid polyimides and polyamides and are often not reported. Furthermore, sometimes the mechanical properties are not sufficient to be measured [50], or the crosslinked PEO is fragile and brittle [56]. Fortunately, methods to improve the mechanical properties of crosslinked PEO-based materials are being investigated with promising results [55,57].

1.1.4.4 Semi-Interpenetrating Polymer Networks (s-IPNs)

In glassy polymers, the unwanted plasticization phenomenon can be mitigated by forming semi-interpenetrating polymer networks [58,59]. S-IPNs can be produced by combining the toughness of thermoplastic materials with the chemical and thermal resistance of thermoset materials [58]. Such a system may be formed by the crosslinking of distinct monomers/oligomers to form a network around/through polymer chains of
interest. While the s-IPN platform has shown success in reducing/eliminating the selectivity losses caused by plasticization, the membrane permeability may be significantly reduced [58,59], in some cases due to the densification and restricted mobility of the material [59]. Relatively few studies have been performed on s-IPNs that combine rubbery PEO and glassy materials for performing gas separations. However, very promising results have been observed thus far in the ones that have. For instance, Saimani et al. have produced asymmetric membranes based on s-IPNs formed of commercially available poly(ether imide) (ULTEM®) and poly(ethylene glycol) diacrylate (PEGDa). These s-IPNs only incorporated up to 8 wt% PEGDa, but no selectivity losses were observed due to plasticization, as the mixed gas selectivity values matched the pure-gas selectivities for CO₂/N₂ and CO₂/CH₄ gas pairs. Furthermore, synergistic effects were observed where the selectivity values of the s-IPNs approached the higher selectivity of the two individual component materials [60]. In another work, Lillepärg et al. studied s-IPNs produced by crosslinking PEO-based oligomers about Pebax® MH 1657 as the main component. These s-IPNs showed increased CO₂ permeability and the same CO₂/N₂ selectivity as pure Pebax® MH 1657 over a range of temperatures [61]. These results show the potential for s-IPNs to combine the best performance aspects of each constituent component while reducing or negating the negative aspects of the individual components. It follows that additional research into PEO-based s-IPN’s could provide additional insights for producing high performance gas separation membranes.
1.2 Bibliography


CHAPTER 2:

STUDIES OF THE SYNERGISTIC EFFECTS OF CROSSLINK DENSITY AND CROSSLINK INHOMOGENEITY ON CROSSLINKED PEO MEMBRANES FOR CO2-SELECTIVE SEPARATIONS

2.1 Introduction

In the purification/processing of synthesis gas, after the water-gas shift reaction, and in post-combustion flue gas treatment, carbon dioxide (CO2) needs to be separated in order to allow further implementation of H2 and N2 and to reduce carbon emissions [1–3]. Pressure swing adsorption (PSA), cryogenic distillation, and amine absorption are established industrial processes for CO2 removal or carbon capture [4]. However, these processes are highly energy and cost intensive [4][5]. Membranes present a promising alternative CO2 separation strategy due to good processability, higher energy efficiency, operational simplicity, and the ability to be coupled with other gas-processing steps, for example, the water-gas shift (WGS) reaction [4][6]. Merkel et al. estimated that an Integrated Gasification Combined Cycle (IGCC) power plant can be outfitted with a CO2-selective membrane system, operating at 30 °C, downstream of the shift reactor to enable the removal and capture of 90% CO2 from syngas at an estimated increase in the levelized cost of electricity (LCOE) of just 20%, considering the membrane technology...
as of 2011 [3]. Furthermore, certain membranes have the potential to meet the CO₂ capture cost objectives of the DOE for the separation of CO₂ from post-combustion flue gas [2]. Due to the inherent advantages of membrane separation systems, research into CO₂ removal from synthesis gas (CO₂/H₂) and flue gas (CO₂/N₂) is being actively pursued [7–9]. Reverse-selective membranes are the favorable option for CO₂/H₂ separations because purified H₂ would be left in the high pressure residue stream whereby costly recompression could be mitigated or eliminated [10]. Likewise, CO₂-phillic membranes show promise for CO₂/N₂ separations where glassy membranes often suffer due to plasticization induced selectivity reduction [9].

To produce CO₂-selective membranes, poly(ethylene oxide) (PEO) is prominently used owing to its unique affinity for CO₂ due to the interaction of polar ethylene oxide (EO) units with the high quadrupole moment of the highly polarizable CO₂ molecule [11][12]. The affinity of PEO for CO₂ renders PEO-based membranes more permeable to CO₂ than to H₂ [10]. Furthermore, pure PEO or PEO-containing membranes are far more permeable to CO₂ than to N₂ [10]. However, pure PEO is not suitable for direct use for gas separation membranes due to its high crystallinity that greatly reduces permeability and poor film forming properties as well as mechanical and thermal instability [10]. To reduce or eliminate PEO crystallinity and improve gas transport, several approaches have been pursued including synthesizing PEO-containing copolymers, incorporating PEO to form blend membranes, and synthesizing PEO-based crosslinked membranes [1]. All three types of PEO-containing membranes, copolymers [13–15], blend membranes [16–18], and crosslinked membranes [7],[19–21] have shown excellent CO₂ separation performance. While crosslinked PEO membranes have shown very attractive CO₂
separation performance, the fundamental structure-property relationship remains unclear and sometimes controversial due to the complexity and ambiguities of the crosslinked structures in these randomly crosslinked membranes. In many reported cases, crosslink density alone is not able to explain the experimental observations in gas transport properties in those randomly crosslinked PEO membranes. Lin et al. reported in a study of crosslinked poly(ethylene glycol diacrylate) membranes that crosslink density does not contribute significantly to the gas permeability and diffusion coefficients of their membranes [22]. Additionally, it has been frequently observed that CO₂ separation performance varies significantly across PEO-based polymers reported by different groups even though the same PEO content was used. All these previous studies pointed to a fact that CO₂ permeability strongly depends on the detailed micro-domain morphologies, such as the spatial arrangement (e.g., the connectivity) and the shape of PEO domains, besides the simple compositional factor like crosslink density.

Due to the array of outcomes and ambiguities in crosslinked PEO systems, it would be of fundamental interest to construct model networks with well-defined crosslinking structures, wherein not only the crosslink density is precisely controlled, but also the spatial distribution of crosslinks is carefully manipulated to elucidate the effects of crosslink inhomogeneity on gas transport properties in crosslinked membranes. In fact, inhomogeneity in crosslinking has been largely unexplored in the gas separation membrane field, although it has been studied extensively in developing rubber elasticity theories and in predicting physical properties of rubbers and polymer gels [23–28].

In this work, to concurrently study the effects of crosslink density and crosslink inhomogeneity, which are independent of one another, three distinct model PEO
crosslinked systems are designed and synthesized via thermally crosslinking diamine-terminated and epoxy-terminated PEO oligomers: unimodal, bimodal, and clustered networks. Since the crosslinking occurs exclusively at the oligomer chain ends, crosslink density can be precisely controlled and systematically varied by using PEO-diamine oligomers of chosen molecular weight. By keeping the overall crosslink density comparable between systems, the distribution of crosslinks is feasibly adjusted by crosslinking PEO-diamine oligomers of various molecular weights, which leads to unimodal and bimodal distribution of intercrosslink chain length as well as clustered structure when a two-step sequential end-linking process is used. Comparative studies across these three distinct crosslinked systems are carried out to elucidate the synergistic effects of crosslink density and crosslink inhomogeneity on gas transport properties of crosslinked PEO membranes.

2.2 Experimental

2.2.1 Materials

Polyetheramines of molecular weight of 148, 600, 900, and 2000 g/mol (i.e., Jeffamine® EDR-148, ED-600, ED-900 and ED-2003) were supplied by Huntsman and used as received. For clarity, the Jeffamine® polyetheramines are referred to as PEOX in this paper, where X represents the molecular weight. Poly(ethylene glycol) diglycidyl ether with a molecular weight of 500 g/mol (referred to as PEO-epoxy) was purchased from Sigma-Aldrich, which was stored in a refrigerator and used as received. N,N-Dimethylacetamide (DMAc, 99%) was purchased from Sigma-Aldrich and used without further purification.
2.2.2 Synthesis and Film Fabrication of PEO Model Networks

Three series of PEO model networks (i.e., unimodal, bimodal and clustered) are prepared via thermally end-linking select PEO-diamines with PEO-epoxy. A simplified schematic of the three types of network structure is shown in Figure 2.1.

![Simplified schematics of unimodal, bimodal, and clustered networks.](image)

Figure 2.1: Schematics of unimodal, bimodal, and clustered networks. Bold lines in bimodal and clustered networks represent short oligomers (i.e., PEO148). PEO-epoxy part is omitted for simplicity.

For clarity, relevant to the sections below, the chemical structures of all PEO-based oligomers utilized in network formation are provided in Figure 2.2.

![Chemical structures of PEO-based oligomers.](image)

Figure 2.2: The chemical structures of all PEO-based oligomers utilized in the formation of crosslinked networks.

2.2.2.1 Unimodal Networks

The unimodal networks were synthesized by endlinking one set of PEO-diamine of a given molecular weight (i.e., PEO600, PEO900, or PEO2000) with PEO-epoxy in a
1:2 molar ratio (Figure 2.1). When PEO600 or PEO900 was used, DMAc was added to produce an approximately 15.6 wt% solution in a 20 mL disposable glass vial. No solvent was used with PEO2000. Synthesis of unimodal network of PEO600 is provided as an example. In a typical synthesis, PEO600 (0.2187 g, 0.3646 mmol) is combined with PEO-epoxy (0.3646 g, 0.7291 mmol) along with ~3.4 mL DMAc. The mixture is magnetically stirred for 50 min on a hot plate set to 50 °C. The solution is then cast onto a dried glass plate residing in a pre-heated vacuum oven set to 45 °C. An aluminum foil covering with two open sides is placed over the film to protect against dust/contaminants. Vacuum is pulled to degas and dry the film throughout the duration of crosslinking reaction. The oven temperature is then set to 90 °C and maintained for 1 h, followed by 100 °C for 1 h, and lastly 140 °C for 2 h to complete crosslinking reaction and form a film. After cooling overnight, the resulting film is peeled off of the glass plate with the aid of a razor blade. The naming scheme of the unimodal networks goes as follows: U600, U900, and U2000, where the “U” signifies unimodal and the number specifies the molecular weight of PEO-diamine used.

2.2.2.2 Bimodal Networks

For the bimodal system, two sets of PEO-diamines of short (PEO148) and long (PEO2000) chains are combined along with PEO-epoxy for end-linking reaction to introduce a bimodal distribution of inter-crosslink PEO chain length (Figure 2.1). The same 1:2 molar ratio of PEO-diamine to PEO-epoxy as that in unimodal systems is applied while no solvent is used for all bimodal systems. Crosslink density of bimodal networks is varied by adjusting the ratio of PEO148 and PEO2000 to provide the same average inter-crosslink chain length as in U600 or U900 network. Correspondingly, the
bimodal networks are thus named B600 and B900, where “B” indicates bimodal and the number specifies which unimodal system is being modeled. In a typical synthesis of a B600 network, to a disposable 20 mL glass vial, 0.1398 g (0.9449 mmol) of PEO148 and 0.6101 g (0.3051 mmol) of PEO2000 are added along with 1.2500 g (2.500 mmol) PEO-epoxy. The stirring, casting, and film forming procedure are the same as in the unimodal system.

2.2.2.3 Clustered Networks

A two-step approach involving a “clustering” process followed by end-linking is adopted to produce the clustered PEO networks (Figure 2.1). In general, a “clustering” process is first carried out by crosslinking short PEO chains (PEO148) with PEO-epoxy to produce densely crosslinked multifunctional clusters. Long PEO chains (PEO2000) and appropriate amount of PEO-epoxy are then added to the solution of preformed clusters to complete end-linking/crosslinking reaction. An example synthesis of C600 clustered network is given as follows. 0.1398 g (0.9449 mmol) of PEO148 is mixed with 0.9449 g (1.8900 mmol) PEO-epoxy in a 20 mL glass vial. The reactants are then stirred at 50 °C on a hot plate for either 50 or 90 min of “clustering” time to adjust the cluster size. Next the vial is removed from the hot plate and a mixture of 0.6101g (0.3051 mmol) of PEO2000 and 0.3051g (0.6101 mmol) of PEO-epoxy is added. The mixture is then stirred on the hot plate at 50 °C for 50 min. The casting, oven drying/crosslinking procedure, and film removal are the same as the unimodal and bimodal systems. The names C600S and C600L are given for the clustered networks produced in this work; “C” stands for clustered, “600” describes the average chain length of PEO-diamine oligomers comparable to the unimodal and bimodal systems described earlier, and “S” or “L”
relates to the size of the clusters, S for small clusters ("clustering" time of 50 min) and L for large clusters ("clustering" time of 90 min).

2.2.3 Characterizations

Molecular weight of clusters was monitored by size exclusion chromatography (SEC, Waters GPC 242System) as a function of "clustering" time. DMF was used as the eluent along with the external standard, toluene. A Waters 515 HPLC pump and three Polymer Standards Service (PSS) columns (GRAM, 10⁴, 10³, and 10² Å) were equipped in the DMF SEC at 55 °C with a DMF flow rate of 1 mL min⁻¹, and a Waters 2414 refractive index detector was connected using PSS 247 WinGPC 7.5 software.

The gel fractions of crosslinked films were obtained via gravimetric method upon solvent extraction. First, the weight of a freshly dried film (W) was acquired before it was submerged into deionized (DI) water at room temperature to extract any sol fraction; the water was replaced with fresh deionized water the next day, and after soaking at least 48 hours in total, the extracted films were was removed and dried in a vacuum oven at 75 °C for 12 h to completely remove absorbed water. The final dry, insoluble film was then weighed again (Wᵢ). Gel fraction is then calculated as:

\[ \text{Gel fraction} = \frac{W_i}{W} \times 100\% \]  

Thermogravimetric analysis (TGA) by a TGA Q500 instrument (TA Instruments) was used to determine the thermal stability of crosslinked films. Samples were first removed of moisture by drying in a vacuum oven at least at 75 °C for at least 12 h before TGA measurements. A heating rate of 10 °C/min under nitrogen purge of 60 mL/min was used. The glass transition temperature (T_g), crystallization temperature (T_c), and melting
temperature \(T_m\) were obtained by differential scanning calorimetry (DSC) using a DSC Q2000 (TA Instruments) with liquid nitrogen cooling system. All samples were first removed of moisture, weighed, and quickly transferred to the DSC to minimize atmospheric moisture exposure. Two heating-cooling cycles were applied for all samples with a heating rate of 10 °C/min and cooling rate of 20 °C/min under nitrogen purge of 50 mL/minute. Samples underwent cooling and heating between -100 °C and 150-250 °C, and the thermal transitions are reported from the second heating curve unless otherwise noted.

The densities of dried crosslinked films were obtained by the buoyancy method using an analytical balance (ML204, Mettler Toledo) and a density kit at room temperature. Heptane was chosen as the auxiliary liquid as it has little affinity for PEO [29]. A pycnometer was used to determine the room temperature density of heptane. The fractional free volume (FFV) was calculated by Bondi’s group contribution method and is given as [30][31]:

\[
FFV = \frac{(V - V_o)}{V} 
\tag{2.2}
\]

where the volume of the polymer expressed per mol of repeat unit is given by \(V\), which is obtained from the density measurements [31]. \(V_o\) is the polymer chain occupied volume obtained from the van der Waals volume \((V_w)\), where \(V_o = 1.3 \sum_{i=1}^{l} (V_w)_i\) [31].

Pure-gas permeabilities were determined for N\(_2\), H\(_2\), and CO\(_2\) using the constant-volume variable-pressure method at 35 °C [32]. Films were removed of moisture in a vacuum oven, their dried thicknesses were obtained, and permeation samples were prepared and dried an additional time at 75 °C for 14 h before loading into the gas cell.
The film is held within the gas cell and completely degassed under vacuum, at least overnight. Once degassed, the leak rate of the apparatus is measured. Next the feed gas is introduced upstream of the membrane and the permeate gas is collected in a known volume downstream. The permeability is calculated under steady state conditions by Equation 2.3,

\[ P_A = \frac{V_d l}{p_2 A R T} \left[ \left( \frac{dp_1}{dt} \right)_{ss} - \left( \frac{dp_1}{dt} \right)_{\text{leak}} \right] \] (2.3)

where the downstream volume is given by \( V_d \) and the film thickness is \( l \). The upstream absolute pressure is shown by \( p_2 \). The available area of permeable film is represented by \( A \) and the gas constant is \( R \) (0.278 cmHg cm\(^3\)/cm\(^3\)(STP) K) with the absolute temperature in Kelvin given by \( T \). In the downstream volume, at a fixed upstream pressure or under vacuum, the steady state rates of pressure increase are given by \( \left( \frac{dp_1}{dt} \right)_{ss} \) or \( \left( \frac{dp_1}{dt} \right)_{\text{leak}} \), respectively. Another vital parameter for describing gas separation performance is the membrane ideal selectivity, \( \alpha_{A/B} \), for one gas (A) over the other (B) [33], which is equal to the ratio of pure-gas permeabilities, (A is the more permeable gas):

\[ \alpha_{A/B} = \frac{P_A}{P_B} \] (2.4)

The diffusion coefficient is determined using the time lag method by [20]:

\[ D = \frac{l^2}{6\theta} \] (2.5)

where \( l \) (cm) is the film thickness and \( \theta \) (s) is the time-lag [20]. Knowing the permeability (\( P \)) and the diffusivity (\( D \)), the solubility coefficient is easily calculated by
\[ P = D \times S \] based on the solution-diffusion model for gas transport in dense polymer membranes [20].

2.3 Results and Discussion

2.3.1 Synthesis and Film Fabrication for Unimodal, Bimodal, and Clustered Crosslinked Networks

PEO-based crosslinked films with controlled crosslink density and systematically varied crosslink inhomogeneity are prepared via thermally end-linking telechelic PEO oligomers with di-epoxy or diamine end groups. In all cases, a molar ratio of 2:1 between PEO-epoxy and PEO-diamine is applied, which has proved to be the most efficient in producing ideal model networks with high gel fraction (> 95 wt%). Table 1 summarizes the composition and some structural characteristics (\( \bar{M}_c \), crosslink density, and gel fraction) of all crosslinked films in this study. As shown, all crosslinked films have > 95% gel fraction indicating successful end-linking reactions in all cases that lead to the formation of ideal model network structures. Via adjusting the composition and end-linking procedures, PEO model networks with varying crosslink density and crosslink inhomogeneity are obtained, allowing systematic and comprehensive investigation of the dependence of gas transport behavior on these two vital, yet independent and non-correlated, structure parameters in the crosslinked PEO membranes.
TABLE 2.1

COMPOSITION AND PHYSICAL CHARACTERISTICS OF CROSSLINKED PEO MEMBRANES

<table>
<thead>
<tr>
<th>Composition (in molar ratio)</th>
<th>$\bar{M}_c$ (g·mol⁻¹)ᵃ</th>
<th>Gel fractionᵇ</th>
<th>Crosslink density ($\times10^{-3}$ mol·cm⁻³)ᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>U600 PEO600 : PEO-epoxy = 1:2</td>
<td>533</td>
<td>0.97</td>
<td>1.45</td>
</tr>
<tr>
<td>U900 PEO900 : PEO-epoxy = 1:2</td>
<td>633</td>
<td>0.97</td>
<td>1.21</td>
</tr>
<tr>
<td>U2000 PEO2000 : PEO-epoxy = 1:2</td>
<td>1000</td>
<td>0.95</td>
<td>0.75</td>
</tr>
<tr>
<td>B600 PEO148 : PEO2000 : PEO-epoxy = 1:3.1:8.2</td>
<td>533</td>
<td>0.98</td>
<td>1.48</td>
</tr>
<tr>
<td>B900 PEO148 : PEO2000 : PEO-epoxy = 1:1.5:5.0</td>
<td>633</td>
<td>0.97</td>
<td>1.22</td>
</tr>
<tr>
<td>C600S PEO148 : PEO2000 : PEO-epoxy = 1:3.1:8.2</td>
<td>533</td>
<td>0.98</td>
<td>1.47</td>
</tr>
<tr>
<td>C600L PEO148 : PEO2000 : PEO-epoxy = 1:3.1:8.2</td>
<td>533</td>
<td>0.98</td>
<td>1.48</td>
</tr>
</tbody>
</table>

ᵃ example calculation of $\bar{M}_c$ is demonstrated in Appendix A.
ᵇ determined by gravimetric method described in the Experimental section.
ᶜ estimated from gel fraction data and film density. Detailed calculation procedure is given in Appendix A.
The unimodal network series which feature uniform “mesh” size and thus the least crosslink inhomogeneity are prepared to have three levels of crosslink density, i.e., average inter-crosslink chain length ($\bar{M}_c$) of 533, 633, and 1000 g/mol, by taking into account the molecular weight of PEO-epoxy (500 g/mol). For simplicity, the resulting unimodal model networks are referred to as U600, U900 and U2000 according to the PEO-diamines used in the preparation of corresponding unimodal networks.

The bimodal networks add a degree of inhomogeneity in the crosslinked PEO structure, which contains two sets of PEO chains between crosslinks via randomly end-linking PEO148 short chains and PEO2000 long chains with PEO-epoxy. To remain comparable to the unimodal system in terms of inter-crosslink chain length, the ratio of PEO148 and PEO2000 was adjusted to provide bimodal networks with the same average $M_c$ as in U600 or U900 network, i.e., B600 and B900.

The clustered system is an alteration of the bimodal system with the highest level of crosslink inhomogeneity among all crosslinked systems, wherein highly crosslinked short-chain clusters are chemically embedded in a relatively loosely crosslinked network of long PEO2000 chains. The same average $M_c$ was again maintained in the clustered networks as that in U600 and B600 networks, while the pre-clustering duration of PEO148 and PEO-epoxy was varied in order to adjust the size of densely crosslinked clusters. Experimentally, the size of the crosslinked, but still soluble, clusters is controlled by pre-crosslinking of PEO148 and PEO-epoxy at 50 °C for either 50 min (C600S) or for 90 min (C600L) before the addition of PEO2000 and PEO-epoxy chains of a predetermined amount to complete the reaction. Gel permeation chromatography (GPC) confirms that cluster molecular weight increases with increasing reaction duration.
As shown in Figure 2.3, the 50 min reaction cluster curve is broadened and shifts to faster elution times and the 90 min reaction cluster curve is the most broad and is extended to the earliest elution times, suggesting the formation of clusters and gradually increased size of clusters with reaction time.

![Figure 2.3: GPC curves of PEO-diamine and PEO-epoxy reactants at time zero and room temperature and the crosslinked clusters after reacting for 50 and 90 min at 50 °C.](image)

2.3.2 Thermal Properties of PEO Model Networks

Thermal instability and high tendency of crystallization are the two main challenges concerning PEO-based gas separation membranes [1]. In this work, good thermal stability is obtained for all crosslinked films, where the 10 wt% degradation temperature ($T_d$) is above 312 °C via TGA analysis (Table 2.1). Furthermore, PEO crystallization has been mitigated due to crosslinking, whereby the introduction of crosslink junctions decreases the conformational freedom of PEO segments reducing the ability of the PEO chains to pack into a crystalline structure [22]. It was reported that crosslinking PEO prevents significant crystallization when the molecular weight of PEO
between crosslinks is 1,500 g/mol or less, while for linear PEO at ambient conditions, crystallinity increases above a molecular weight of 600 g/mol [34]. Table 2 summarizes the thermal properties of all crosslinked films. As shown, there is no or little crystallization present for densely crosslinked networks including all 600 series and U900, suggesting that crosslinking effectively suppresses PEO crystallization. On the other hand, B900 and U2000 film show some crystallinity because of high content of long PEO2000 chains. This observation is consistent with the previously reported finding mentioned above. Crosslinking effectively disrupts PEO crystallization to reduce the melting temperature to 19 °C or lower, whereas linear PEO2000 melts significantly higher, at 43 °C [35]. Since gas permeation testing is performed at 35 °C, all films are completely amorphous when reporting their gas transport properties.
TABLE 2.2
THERMAL PROPERTIES OF CROSSLINKED PEO MEMBRANES

<table>
<thead>
<tr>
<th>Film</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_d$ (10 wt%) (°C)</th>
<th>ΔHf (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U600</td>
<td>-45</td>
<td>None</td>
<td>None</td>
<td>312</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B600</td>
<td>-49</td>
<td>-16</td>
<td>4</td>
<td>315</td>
<td>2.7</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>C600S</td>
<td>-48</td>
<td>-16</td>
<td>3</td>
<td>315</td>
<td>0.55</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>C600L</td>
<td>-48</td>
<td>-16</td>
<td>3</td>
<td>316</td>
<td>1.1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>U900</td>
<td>-49</td>
<td>None</td>
<td>None</td>
<td>322</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B900</td>
<td>-52</td>
<td>-30</td>
<td>8</td>
<td>323</td>
<td>35</td>
<td>19</td>
</tr>
<tr>
<td>U2000</td>
<td>-45</td>
<td>-5$^a$</td>
<td>19</td>
<td>331</td>
<td>45</td>
<td>24</td>
</tr>
<tr>
<td>Jeffamine ED-2003</td>
<td>43$^b$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>51$^d$</td>
</tr>
</tbody>
</table>

$^a$ Crystallization temperature obtained from the second cooling curve in DSC measurements.
$^b$ Melting temperature supplied by Huntsman Technical Bulletin [35].
$^c$ Crystallinity (%) = $\frac{\Delta H_f}{\Delta H_{f0}} \times 100\%$, where $\Delta H_f$ is the apparent heat of fusion per gram and $\Delta H_{f0}$ is taken as 188.9 J/g for the heat of fusion per gram of the perfect PEO crystal [20][36].
$^d$ Percent crystallinity data from Shao and Chung [20].

The glass transition temperature is known to be a measure of segmental mobility and rigidity [29][19] that may govern the diffusion pathway of gas molecules in the films. It follows that longer chain segments between crosslink junctions have increased mobility and thus lower $T_g$ [19]. In crosslinked PEO networks, $T_g$ has been observed to decrease linearly with decreasing crosslink density [37]. Furthermore, decreasing $T_g$ has been shown to accompany increasing CO$_2$ permeability in crosslinked PEO-based membranes [38]. Looking at the effect of crosslink density, U900 and B900 have lower $T_g$’s than their respective U600 and B600 films as expected. For U2000, considering its high molecular weight between crosslinks and thus high mobility, it is anomalous that the $T_g$ of U2000 is the same or higher than that of U600 and U900 films. However, this anomaly
is easily explained by the presence of crystallization in the U2000 film, which reduces the chain flexibility and results in an elevated \( T_g \) relative to the expected \( T_g \) when no crystals are present [39]. Interestingly, despite having the same average molecular weight between crosslink junctions, the bimodal and clustered films show slightly lower \( T_g \) than their unimodal counterparts, which is likely due to the presence of long PEO2000 chains in bimodal and clustered networks. On the other hand, the clustered C600S and C600L films have very comparable \( T_g \)’s to the B600 film since they share the same composition of long and short PEO chains.

2.3.3 Pure-Gas Permeation Properties

Nonporous polymeric membranes relevant to CO\(_2\) separations exhibit gas transport properties that are described by the solution-diffusion model [40]. In this model the permeant gas first dissolves into the membrane material on the high pressure side, diffuses through the membrane down its concentration gradient, and desorbs from the membrane on the low pressure side [40]. By combining the solution-diffusion model with Fick’s Law, the membrane permeability \( (P_A) \) is expressed by Equation. 2.6 [1]:

\[
P_A = D_A \times S_A
\]

The permeability coefficient, \( P_A \), for a gas A has units of \( 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm/cm}^2 \text{ sec cmHg} \), known as the Barrer [33]. The concentration-averaged effective diffusion coefficient is given by \( D_A \), while the gas solubility coefficient is represented by \( S_A \) [33]. The segmental motions of polymer chains produce gaps that open and close within the polymer, and gas molecules diffuse through the free volume spaces (transient open gaps) [33]. Therefore, the local segmental motions and packing of polymer chains as well as
polymer structural characteristics are critical factors of diffusion behavior [33]. For PEO membranes, high permselectivities of CO$_2$/N$_2$ and CO$_2$/H$_2$ are expected due to high CO$_2$ solubility selectivity resultant of the special affinity between highly polarizable CO$_2$ and ethylene oxide units.[19]

Pure-gas permeation results for CO$_2$, H$_2$, and N$_2$ were obtained at 3-17 bar feed pressure and 35 °C. A plot of CO$_2$ permeability as a function of feed pressure is provided as Figure 2.4 (a), and plots of feed pressure dependence of H$_2$ and N$_2$ permeabilities are provided in Figure 2.4 (b) and (c), respectively. An increasing trend in CO$_2$ permeability with feed pressure is observed for all crosslinked PEO membranes, which is indicative of membrane plasticization by highly condensing CO$_2$ gas [10][41]. Clearly shown in Figure 2.4, gas permeation properties of these PEO networks are sensitively affected by both topological characteristics, i.e., crosslink density and crosslink inhomogeneity, of crosslinked PEO membranes. Detailed analysis of respective effects of crosslink density and crosslink inhomogeneity on gas transport properties for these PEO model networks are provided in following sections.
2.3.3.1 Crosslink Density Effects on Gas Permeability and Selectivity

Within the literature, PEO-based crosslinked membranes have shown a CO$_2$ permeability dependence on crosslink density [37][42]. To evaluate the effect of crosslink density on CO$_2$ permeability in this work, a plot of CO$_2$ permeability versus crosslink density at all five feed pressures is given in Figure 2.5 (a) Similar plots for H$_2$ and N$_2$ are provided as Figure 2.5 (b) and (c), respectively. According to the average chain length
between the crosslinks, U2000 has the lowest crosslink density. The middle crosslink density films represent U900 and B900. Also, since U600, B600, C600S, and C600L films were synthesized to have the same average molecular weight between crosslinks, their crosslink densities are all comparable and plotted at the high crosslink density portion of the graph for each pressure. By plotting trendlines through the data points at each pressure, it is clear that CO₂ permeability increased linearly with decreasing crosslink density. This is the expected trend as has been observed in several previous studies[37][21][43]. The increase in CO₂ permeability can be explained by the increase in segmental mobility and flexibility accompanying the higher molecular weight PEO segments between crosslinks, i.e. decreased crosslink density [19][44].
Plasticization is also clearly evident in these membranes with increasing feed pressure [29]. As shown in Figure 2.4 (a), the CO$_2$ permeability increases significantly for all films with increasing feed pressure. CO$_2$-induced plasticization causes polymers to swell, increasing the mobility of chains, and results in increased CO$_2$ permeability [13][45]. It is expected that plasticization is more effective at loosening the already more flexible PEO chains of the lower crosslink density films, leading to further increases in
the CO₂ diffusion and solubility coefficients and increased permeability [42]. It makes sense that with less restriction points the polymer chains would swell to a greater extent.

The CO₂ diffusion and solubility coefficients have been calculated via the time-lag method to provide additional insights into the dependence of gas transport properties on crosslink density based on the solution-diffusion model. Results are provided in Figure 2.6. For given inhomogeneity level, both the CO₂ diffusion coefficients (D) and solubility coefficients (S) increased as the crosslink density decreased. For example, the diffusion coefficient of U2000 is 77% higher than that of U600 and the solubility coefficient of U2000 is 39% higher than that of U600. The increase in CO₂ diffusion and solubility coefficients with decreasing crosslink density, loosening of PEO segments, is consistent with other works [37][46].
It is expected that the loosening of PEO chains with increasing segment length between crosslinks leads to higher fractional free volume (FFV) and thus higher permeability [44]. As demonstrated in Figure 2.7, the FFV shows a 15% increase from U600 to U2000 and a 4% increase from B600 to B900. While the increase in FFV from U600 to U900 appears to be minor, the increase in CO\textsubscript{2} diffusion coefficient and decrease in T\textsubscript{g} support a significant FFV increase [19][44]. As FFV increases it is expected that permeability will also increase, as is seen with the increase in CO\textsubscript{2} permeability from U600 to U900 to U2000 [44].
Figure 2.7: FFV (grey bars, left vertical axis) and density (blue bars, right vertical axis) plotted for the unimodal and bimodal series films.

Although gas permeabilities showed the expected monotonic increasing trend with decreasing crosslink density, ideal selectivity showed a different dependence on crosslink density for different gas pairs. Figure 2.8 plots CO\textsubscript{2}/H\textsubscript{2} selectivity and CO\textsubscript{2}/N\textsubscript{2} selectivity versus crosslink density at five feed pressures. As shown previously in Figure 2.5, all three gases, CO\textsubscript{2}, H\textsubscript{2}, and N\textsubscript{2} increased in permeability following the trend of decreasing crosslink density. However, the gain in CO\textsubscript{2} permeability with decreasing crosslink density is greater than that for H\textsubscript{2}, leading to simultaneously increasing CO\textsubscript{2}/H\textsubscript{2} selectivity. It was shown previously that CO\textsubscript{2} induced plasticization could contribute to the greater gains in CO\textsubscript{2} permeability with decreasing crosslink density [41]. In addition, it has been demonstrated that as FFV increases the diffusion coefficients of larger kinetic diameter penetrants such as CO\textsubscript{2} increase more than those of smaller kinetic diameter like
H₂, leading to larger permeability gains for CO₂ relative to those of H₂ [41]. On the other hand, the CO₂/N₂ selectivity remains relatively stable (at low feed pressures) or slightly decreases (at high feed pressures, > 10 atm) with decreasing crosslink density. Consistently, it has been observed in another PEO-based crosslinked network that CO₂/N₂ selectivity remained relatively constant, albeit slightly decreased, with increased molecular weight of PEO segments between crosslink junction [42]. It is possible that the likely increased FFV of the lower-crosslink-density membranes results in larger increases to the diffusion coefficient of N₂ than to CO₂, due to N₂’s larger kinetic diameter [8][41]. Accordingly, the enhanced gains in N₂’s permeability offset the gains in CO₂’s permeability due to plasticization, leading to relatively stable CO₂/N₂ selectivity with decreasing crosslink density. In effect, longer PEO chains between crosslinks and the subsequent effects on Tₘ, FFV, and CO₂ induced plasticization, lead to improved CO₂ permeability, nearly stable CO₂/N₂ selectivity, and enhanced CO₂/H₂ selectivity.
2.3.3.2 Crosslink Inhomogeneity Effects on Gas Permeability and Selectivity

Compared to relatively established understanding on the crosslink density effects on gas transport properties, the effects of crosslink inhomogeneity remain largely unexplored although it represents a key structural parameter of crosslinked membranes. In this study, three levels of crosslink inhomogeneity were introduced in the crosslinked PEO-based membranes, namely, unimodal, bimodal and clustered networks (Figure 2.1), which feature increasing inhomogeneity in this order considering the spatial distribution of crosslink junctions in these crosslinked membranes. It should be noted that the Jeffamine® polyetheramines used in this work are not 100 % pure PEO and do contain slightly varying amounts of propylene oxide (PO) units. Consequently, the unimodal films produced in this work contain 7.2-10.5 wt % more PO units than their comparable bimodal and clustered networks. However, based on work by Reijerkerk et al. [14], this small difference in PO and EO contents between network systems will not diminish the
reliability of the results of this study regarding the effect of crosslink inhomogeneity as discussed next.

Figure 2.9 (a) compares the CO\textsubscript{2} permeability between unimodal and bimodal crosslinked membranes at various feed pressures, and similar plots for H\textsubscript{2} and N\textsubscript{2} are given in Figure 2.9 (b) and (c), respectively. For all tested gases, despite comparable crosslink density, the bimodal films showed higher permeabilities at all feed pressures than their comparable unimodal films, with the exception of B600 for H\textsubscript{2} permeability which showed no noticeable difference from U600. This observation is opposite to what would be expected from the work by Reijerkerk et al. [14], if crosslink inhomogeneity was not an important structural parameter. For instance, Reijerkerk et al. found that segmented block copolymers, with soft segment composition of 75 wt % PEO and 25 wt% PPO, displayed no significance difference in CO\textsubscript{2}/H\textsubscript{2} and CO\textsubscript{2}/N\textsubscript{2} selectivities relative to comparable block copolymers with pure PEO segments. However, the copolymers containing both PEO and PPO showed significantly higher CO\textsubscript{2} permeabilities than the ones with pure PEO segments, which is consistent elsewhere [47], due to increased soft segment flexibility, evidenced by lower T\textsubscript{g}’s [14]. Therefore, based on these previously reported results and the opposite trend (i.e., bimodal and clustered networks have higher permeabilities than the unimodal ones) observed in this study, it is evident that crosslink inhomogeneity does play an important role in influencing gas transport properties.
As such, the general trend of higher gas permeabilities for bimodal films relative to unimodal films can be ascribed to the presence of the long PEO2000 chains in bimodal networks (i.e., the inhomogeneity), which could lead to an overall more flexible chain structure and thus increased permeability [39][48]. This is evidenced by the somewhat lower Tg’s of bimodal series than unimodal ones even though their crosslink density is similar (Table 2). On the other hand, it is also reasonable that the connectivity of the free
volume microcavities plays a role in determining gas permeation properties. Likely the larger meshes formed by long PEO2000 chains in bimodal films provide pathways with lower barrier for faster diffusion of gases.

The clustered films add one more level of crosslinking inhomogeneity from bimodal series although they share the same composition and crosslink density. Comparisons across unimodal, bimodal and clustered networks provide more insight to the effects of inhomogeneity in crosslinking. Figure 2.10 (a) plots the permeability of CO\textsubscript{2} across the PEO600 series including U600, B600 and C600(S or L) films at 3 bar feed pressure, and Figure 10 (b) plots over the full feed pressure range. It is clear that the CO\textsubscript{2} permeability of C600S and C600L lie between that of U600 and B600, which is consistent with the trend of their glass transition temperatures and suggests the positive role of crosslinking inhomogeneity in enhancing gas transport. The slightly lower permeability of C600 films compared to B600 is likely due to more disrupted connectivity of free volume microcavities in the clustered films wherein the tightly crosslinked clusters formed by short PEO148 chains might act as barriers hindering gas diffusion. Similarly, the slight decrease in CO\textsubscript{2} permeability from C600S to C600L could be explained by the increased tortuosity in transport pathways imposed by the larger clusters of C600L film [49].
Figure 2.10: (a) Comparison of CO$_2$ permeability across PEO600 series of unimodal, bimodal, and clustered films at 3 bar feed pressure and (b) CO$_2$ permeability for the PEO600 series at all feed pressures.

Although introducing crosslinking inhomogeneity seems to be advantageous in improving gas permeability, its effects on selectivity are relatively less straightforward and show dependence on both the gas pairs and crosslink density. Figure 11 (a) and (b) plots the ideal selectivity of CO$_2$/H$_2$ and CO$_2$/N$_2$ gas pairs for the PEO600 and PEO900 films at 3 bar feed pressure. Plots of the ideal selectivity of CO$_2$/H$_2$ and CO$_2$/N$_2$ at each of the five feed pressures are given in Figure 11 (c) and (d), respectively. For the PEO600 series, it is seen that the CO$_2$/H$_2$ selectivity improve slightly for bimodal and clustered films compared to the unimodal U600 film suggesting the positive role of crosslinking inhomogeneity in constructing selective CO$_2$ transport pathways. The observation that clustered films (C600S and C600L) show very similar selectivities with bimodal B600 film seems to suggest that the larger meshes formed by long PEO2000 chains present in both types dominate the diffusion pathways. For the PEO900 series, a marginal increase
in CO$_2$/H$_2$ selectivity was observed in B900 over U900. For CO$_2$/N$_2$ selectivity, there is no discernable difference across both the PEO600 and PEO900 series as well as between the two series.

Figure 2.11: (a) CO$_2$/H$_2$ and (b) CO$_2$/N$_2$ selectivity for the PEO600 series (blue bars) and PEO900 series (grey bars) at 3 bar feed pressure. (c) CO$_2$/H$_2$ and (d) CO$_2$/N$_2$ selectivity for the PEO600 series (blue lines) and PEO900 series (grey lines) at all feed pressures.
2.3.3.3 Upper Bound Comparison

In a previous study on crosslinked PEO films, the effects of CO$_2$ plasticization have been shown to greatly enhance gas separation performance, allowing for both high selectivity and high permeability simultaneously [7]. Figure 2.12 and Figure 2.13 show the upper bound plots for CO$_2$/H$_2$ and CO$_2$/N$_2$ to assess the respective effect of crosslink density and crosslink inhomogeneity on membrane’s overall separation performance. As clearly shown in Figure 2.12 for the U600, U900, and U2000 films, decrease in crosslink density leads to an improvement in both CO$_2$ permeability and CO$_2$/H$_2$ selectivity for all feed pressures. It is believed that increased sorbance of CO$_2$ with increasing feed pressure leads to swelling of the polymer chains and increased CO$_2$ permeability [7]. This plasticization enhanced CO$_2$ permeability leads to the increase in CO$_2$ selectivity with increasing feed pressure, as the permeability of H$_2$ and N$_2$ remains relatively stable as feed pressure increases.
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Figure 2.12: 2008 Upper Bound plots (all five feed pressures) for (a) CO$_2$/H$_2$ separation and (b) CO$_2$/N$_2$ separation for unimodal networks of different crosslink density.

The upper bound comparison at two specific feed pressures plotted in Figure 2.13 demonstrates the effect of crosslink inhomogeneity on gas permeation properties in these crosslinked PEO membranes. As a general trend, increasing crosslink inhomogeneity improves the overall CO$_2$/H$_2$ separation performance of the membrane, given the same crosslink density and feed pressure. The same trend holds for both the PEO600 and PEO900 films that both the CO$_2$ permeability and CO$_2$/H$_2$ selectivity increase for all clustered and bimodal films relative to the comparable unimodal films at low and high pressure. However, for the CO$_2$/N$_2$ separation, the selectivity remains relatively constant within error bars for all 600 and 900 films at both low and high feed pressure levels. It is probable that synergistic effects of FFV, segment mobility, and plasticization lead to relatively stable CO$_2$/N$_2$ selectivity. The selectivity for CO$_2$ over N$_2$ has elsewhere been shown to be robust despite significant changes in PEG content, crosslink density, blending compositions, addition of PEG nanofillers, etc. [42][16][50].
As illustrated in the upper bound plots of Figure 2.12 and 2.13, these crosslinked PEO membranes exhibit excellent gas separation performance. All films approach or surpass the upper bound, especially with increasing feed pressure. The gas separation performance especially stands out for U2000 which surpasses both upper bounds for CO₂/H₂ and CO₂/N₂ separations at all tested feed pressures. Furthermore, U2000’s high CO₂/N₂ selectivity of 53 and CO₂ permeability of 376 Barrer at 3 bar feed pressure competes with or outperforms many other types of membrane materials including poly(acetylene), poly(arylene ether), polyarylate, polycarbonates, polyimides, poly(phenylene oxide), polypyrrole, polysulfones, crosslinked membranes, blend dense films, and others [51][52][47]. As such, these crosslinked PEO membrane materials are attractive for performing separations involving CO₂ in the feed. More importantly, this study provides a fundamentally new dimension in finely tuning the transport properties of crosslinked polymer membranes by adjusting the crosslink inhomogeneity, which opens
new opportunities in the design of the next generation of crosslinked membranes for energy-efficient gas separations.

In addition, in order to compare the inherent transport characteristics of these crosslinked networks, the infinite dilution penetrant permeabilities and selectivities have been estimated, as done elsewhere [10][53], such that the effects of plasticization, increasing penetrant solubility, and membrane compaction with increasing feed pressure can be excluded. The infinite dilution permeability and selectivity estimates are provided in Table 2.3 as well as plotted in Figure 2.14 and Figure 2.15. Evidently, all previously discussed trends in CO₂, H₂, and N₂ permeability and CO₂/H₂ and CO₂/N₂ selectivity, at a given feed pressure, hold for the infinite dilution permeability and selectivity estimates. This analysis adds further support that the observed gas transport differences between unimodal, bimodal, and clustered crosslinked networks originate from the fundamentally different architectural structures introduced by crosslink inhomogeneity.
**TABLE 2.3**

**INFINITE DILUTION PERMEABILITY (BARRER) AND SELECTIVITY VALUES CALCULATED FROM 35 °C PURE-GAS PERMEABILITY DATA OBTAINED AT FIVE FEED PRESSURES (3 – 17 BAR)**

<table>
<thead>
<tr>
<th>Crosslinked Network</th>
<th>$P_{CO_2}$</th>
<th>$P_{H_2}$</th>
<th>$P_{N_2}$</th>
<th>$\alpha_{CO_2/H_2}$</th>
<th>$\alpha_{CO_2/N_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>U600</td>
<td>142.8 ± 0.4</td>
<td>21.55 ± 0.08</td>
<td>3.03 ± 0.04</td>
<td>6.62 ± 0.05</td>
<td>47.1 ± 0.7</td>
</tr>
<tr>
<td>B600</td>
<td>153.7 ± 0.5</td>
<td>21.31 ± 0.08</td>
<td>3.07 ± 0.05</td>
<td>7.21 ± 0.05</td>
<td>50.1 ± 0.9</td>
</tr>
<tr>
<td>C600S</td>
<td>153.1 ± 0.4</td>
<td>21.04 ± 0.19</td>
<td>3.04 ± 0.05</td>
<td>7.28 ± 0.08</td>
<td>50.4 ± 0.9</td>
</tr>
<tr>
<td>C600L</td>
<td>148.4 ± 3.1</td>
<td>20.62 ± 0.06</td>
<td>2.96 ± 0.04</td>
<td>7.20 ± 0.17</td>
<td>50.2 ± 1.7</td>
</tr>
<tr>
<td>U900</td>
<td>200.5 ± 0.6</td>
<td>24.92 ± 0.27</td>
<td>4.02 ± 0.03</td>
<td>8.04 ± 0.11</td>
<td>49.9 ± 0.5</td>
</tr>
<tr>
<td>B900</td>
<td>215.8 ± 1.3</td>
<td>26.62 ± 0.22</td>
<td>4.52 ± 0.07</td>
<td>8.11 ± 0.12</td>
<td>47.7 ± 1.1</td>
</tr>
<tr>
<td>U2000</td>
<td>356.4 ± 1.3</td>
<td>37.60 ± 0.14</td>
<td>7.14 ± 0.10</td>
<td>9.48 ± 0.07</td>
<td>49.9 ± 0.9</td>
</tr>
</tbody>
</table>
Figure 2.14: CO₂, H₂, and N₂ permeabilities estimated at infinite dilution for PEO600 series of unimodal, bimodal, and clustered films.
Figure 2.15: CO$_2$/H$_2$ (left) and CO$_2$/N$_2$ (right) selectivity for the PEO600 series (blue bars) and PEO900 series (grey bars) at infinite dilution.
2.3.4 Measurement Error

The reporting of error in measurements has been done according to the calculations demonstrated in Appendix A for the following measurements: permeability, ideal selectivity, CO$_2$ diffusion and solubility coefficients, and fractional free volume (FFV).

2.4 Conclusions

Three distinct systems of PEO-based crosslinked membranes have been synthesized such that the respective effects of crosslink density and crosslink inhomogeneity on gas transport are determined. It was found that both crosslink density and crosslink inhomogeneity play a role in dictating gas permeation performance, though the former has more significant impact. All tested gases showed higher permeability with lower crosslink density. The CO$_2$/H$_2$ selectivity also strongly depended on crosslink density at all feed pressures in that it increased with a decrease in crosslink density. On the other hand, the CO$_2$/N$_2$ selectivity remained relatively constant regardless of variations in crosslink density. Crosslink inhomogeneity also impacted gas transport where the uneven distribution of crosslinks of the bimodal and clustered films led to enhanced CO$_2$ permeability. The CO$_2$ permeability and CO$_2$/H$_2$ selectivity were improved for bimodal and clustered films. For CO$_2$/N$_2$ separations, crosslink inhomogeneity led to increased CO$_2$ permeability for bimodal and clustered films, while no change in CO$_2$/N$_2$ selectivity was observed. Separation performance was especially attractive for U2000 which surpassed both CO$_2$/H$_2$ and CO$_2$/N$_2$ 2008 upper bounds at all tested feed pressures.
2.5 Bibliography


CHAPTER 3:

PEO-RICH SEMI-INTERPENETRATING POLYMER NETWORK (S-IPN)
MEMBRANES FOR CO₂ SEPARATION

3.1 Introduction

In the production of syngas and flue gas, CO₂ is a byproduct/contaminant that needs to be removed [1]. Conventional separation processes involving solvent-based CO₂ removal are the most mature technologies; however, high energy costs and constant operation and maintenance tasks dissuade their further implementation [1–3]. Specifically, it is estimated that an amine system used to capture 90% of CO₂ in flue gas would increase the cost of the electricity generated by the plant by 50-90%, well above the U.S. Department of Energy (DOE) target of less than 35% under these conditions [4]. Membrane-based CO₂ separation represents an attractive energy-efficient option as an alternate to absorber-stripper systems and other conventional separation processes such as pressure-swing adsorption and cryogenic distillation, because it does not require thermal regeneration or phase change [2,3,5]. Additionally, membranes show promise to outperform amine systems and to even exceed the less than 35% increase in the cost of electricity target of the DOE [4].

Aromatic polyimide-based membranes are an attractive material choice for several reasons, including high thermal resistance and excellent mechanical properties [6–10]. A challenge however with polyimides has been to improve upon their permeabilities and moderate CO$_2$/N$_2$ selectivities [11,12]. Poly(ethylene oxide) (PEO) based membranes have been demonstrated to show reverse selective (CO$_2$/H$_2$) separation ability, high CO$_2$/N$_2$ selectivity, and high CO$_2$ permeability due to favorable interactions between the ethylene oxide (EO) unit and CO$_2$ molecule [13,14]. Because linear pure PEOs have poor film forming properties as well as undesired thermal resistance and mechanical strength, copolymerizing PEOs with rigid polyimides and crosslinking have been frequently adopted in the preparation of PEO-rich membranes to address these material-related problems. For PEO-polyimide copolymer membranes, excellent CO$_2$ separation performance is obtained by increasing the content of PEO (to a point before PEO crystallization occurs) [14–16]. However, the Young’s modulus and tensile strength of the PEO-rich copolymers drop quickly with increasing PEO content, eventually reaching values too low for practical use [14]. On the other hand, crosslinking of pure PEOs has successfully been employed in various works to mitigate or even eliminate PEO crystallinity [17–19]. Crosslinked PEO membranes have shown outstanding CO$_2$ separation performance, superior to that of PEO-based block copolymers due to their nearly full PEO content [20]. Both CO$_2$/H$_2$ and CO$_2$/N$_2$ separation performance above the 2008 Robeson upper bounds have been achieved in the crosslinked PEO membranes, especially under plasticization conditions [21,22]. Unfortunately, crosslinked PEO-based membranes may not possess the necessary mechanical strength required for industrial applications [23,24].
To integrate the excellent mechanical properties of glassy polyimides and the superior CO$_2$ separation capabilities of crosslinked PEO networks, semi-interpenetrating polymer network (s-IPN) structure appears to be a promising macromolecular design strategy, wherein linear glassy polyimide chains penetrate and intertwine with the PEO networks to construct desired PEO-rich gas permeation pathways allowing for fast and selective CO$_2$ transport. PEO-based s-IPN membranes, however, are sparsely reported in the literature [25,26]. In a study of s-IPN membranes prepared from crosslinked poly(ethylene glycol) (PEG) and Ultem® 1000 polyetherimide (PEI) as the linear penetrating chains, a greatly improved CO$_2$/N$_2$ selectivity over the pure PEI was observed in the s-IPNs for both pure and mixed gas separations, while the CO$_2$ permeability of s-IPNs remained stable or slightly decreased from that of the pure PEI [25]. In another study of s-IPNs fabricated from Pebax® MH 1657 (60% PEO blocks), PEG DG 526, and Jeffamine® ED600, the s-IPN membrane that contained a higher amount of crosslinked PEO showed improved CO$_2$ permeability and approximately stable CO$_2$/N$_2$ selectivity compared to pure Pebax® over a 40-90 °C temperature range [26]. Though these s-IPNs showed promising results, systematic structure-property studies on PEO-based s-IPNs, especially those incorporating glassy polyimide and rubbery PEO networks, are not available.

In this work, PEO-rich s-IPN membranes that incorporate glassy triptycene-containing (co)polyimides and Jeffamine®-based PEO networks are prepared and studied for CO$_2$ separation. Triptycene-containing polyimide structure is chosen as the penetrating linear component in the s-IPNs because of the potential benefits of hierarchical iptycene structures in disrupting PEO crystallization as well as providing
supramolecular mechanical reinforcement in the resulting membranes as we previously reported [27]. The microstructure of s-IPNs is systematically varied by adjusting the composition of the penetrating polyimides and the crosslink density of the PEO networks such that the effects of the distribution and the connectivity of PEO domains in the s-IPN membranes on gas transport properties can be unambiguously explored.

3.2 Experimental

3.2.1 Materials

The synthesis of linear polyimides and s-IPN networks required: 4,4’-hexafluoroisopropylidene bisphthalic dianhydride (6FDA), custom-synthesized triptycene-based diamine [8], anhydrous N,N-dimethylacetamide (DMAc), acetic anhydride, anhydrous pyridine, polyetheramines of Jeffamine® ED-600 and ED-2003 by Huntsman with molecular weight of 600 and 2,000 g/mol (denoted hereafter as PEO600 and PEO2000, respectively), and poly(ethylene glycol) diglycidyl ether (denoted as PEO-epoxy, stored in a refrigerator). ¹H NMR was conducted in chloroform- d. All reagents and solvents were commercially purchased and used as received.

3.2.2 Synthesis of Linear Triptycene-PEO Polyimide Copolymers

The synthesis of triptycene-PEO polyimide copolymers is performed via two-step condensation polymerization using chemical imidization as shown in Figure 3.1 [6]. The copolymers are named as PI-PEOX, where X denotes the weight percentage of PEO in the copolymers ranging from 0 to ~ 40%. The procedure is detailed here forming PI-PEO40 as a typical example. To a flame-dried, three neck flask cooled under nitrogen,
PEO2000 (1.2411 g, 0.621 mmol) was added followed by CF$_3$-substituted triptycene-1,4-diamine monomer (0.9600 g, 1.59 mmol), which was prepared according to our previous report [8]. The flask was placed under nitrogen purge in an ice-water bath (0°C), and ~8.00 mL of anhydrous DMAc was added. Upon dissolution of the diamines, 6FDA (0.9811 g, 2.21 mmol) was added with mechanical stirring. All components stuck on the flask wall were washed down with an additional ~5 mL of anhydrous DMAc. The solution slowly warmed to room temperature and was stirred for 24 h under nitrogen to form viscous poly(amic acid) solution. If necessary, up to 5 mL of anhydrous DMAc was added to reduce viscosity. To effect chemical imidization, the ice-bath was refilled and to the poly(amic acid) solution was added pyridine (~1 mL, 13.3 mmol) and acetic anhydride (~1.3 mL, 13.3 mmol). Again, the solution slowly warmed to room temperature and was stirred for another 24 h under nitrogen purge to form the PI-PEO copolymer. The polymer product was precipitated into 400 mL of stirring methanol/water mixture (v:v = 3:1), which was collected via filtration and then dried under vacuum in stages with a final stage of 120 °C for 14 h. The synthesis of non-PEO containing triptycene-6FDA polyimide, i.e., PI-PEO0, is described in detail by Wiegand et al. [8]. The only modification from the reported procedure is that the triptycene-1,4-diamine monomer underwent an additional washing with ethyl ether to improve monomer purity for successful condensation polymerization.
Figure 3.1: General synthesis scheme for triptycene-PEO polyimide copolymers, i.e., PI-PEOX (X denotes the overall weight percentage of PEO in the copolymers).

3.2.3 Preparation of semi-Interpenetrating Polymer Networks (s-IPNs)

The general fabrication of s-IPN membranes involves the pre-crosslinking of PEO-diamine oligomers and the mixing of pre-crosslinked PEO oligomers with linear polyimide for chain penetration and final crosslinking. Two parameters were systematically adjusted. The first is the PEO segment length between crosslink junctions in the PEO networks (or crosslink density), by using either short PEO600 oligomers or long PEO2000 oligomers for crosslinking with PEO-epoxy. The second adjustable parameter is the choice of three linear (co)polyimides of varying PEO content to be incorporated, i.e., PI-PEO0, PI-PEO24, and PI-PEO34. Thus, six distinct s-IPNs were fabricated from various combinations of PEO networks and linear (co)polyimides as illustrated in Figure 3.2. The overall weight content of PEO in each s-IPN, including the PEO within any incorporated linear polyimide and the crosslinked PEO network, was carefully controlled and brought to approximately 70 wt % by adjusting the amount of
linear polyimide and crosslinkable PEO components added. The naming scheme for the s-IPNs goes as “S-X-Y”, where “S” signifies s-IPN, “X” indicates the PEO content in weight percent (wt %) within the linear (co)polyimide component, and “Y” indicates the molecular weight (g/mol) of PEO-diamine oligomers used in crosslinking (i.e., 600 or 2,000 g/mol). For example, S-34-600 represents an s-IPN network that is prepared from the PI-PEO34 linear copolymer (with 34 wt% PEO) and the PEO600-based network with an overall PEO content of ~70 wt%. In every case, the amount of solvent required is minimized to ensure high extent of crosslinking.
Figure 3.2: Schematics of six distinct semi-interpenetrating polymer networks (s-IPNs) with varied PEO content in the linear (co)polyimides and varied crosslink density in the PEO networks. Blue lines indicate the PEO segments and PEO-epoxy is omitted for simplicity.

Synthesis of the S-0-600 s-IPN membrane is provided as an example. First, the solution of linear polyimide PI-PEO0 was prepared by dissolving and stirring 0.2113 g of PI-PEO0 in ~ 1.1 mL of DMAc at room temperature. For the pre-crosslinking step, PEO600 (0.7635 g, 1.27 mmol) was mixed with PEO-epoxy (1.2724 g, 2.55 mmol) in a vial, which was then magnetically stirred at 100 °C in an oil bath. (Note, when PEO2000 was used the temperature was set to 130 °C.) Once the mixture became viscous and the stir-bar struggled to spin (~ 68 min), the vial was removed from the oil bath and cooled. 
with air, to which the previously prepared PI-PEO0 solution was immediately added. The PI-PEO0 solution vial was rinsed twice and transferred with a total of 0.55 mL of DMAc to ensure all PI-PEO0 was added. The vial containing all reaction components was then placed back in the same oil-bath now set to 50 °C and magnetically stirred for 50 min to ensure homogeneous mixing. The reaction solution was then casted onto a leveled glass slide within a vacuum oven pre-set to 45 °C. A foil covering was placed over the film to prevent dust contamination. Vacuum was pulled for the duration of the crosslinking reaction. The temperature was next set to 90 °C for 1 h, 100 °C for 1 h, and 140 °C for 2 h to complete the crosslinking and film forming. After slowly cooling overnight the film was soaked in deionized (DI) water and removed from the glass slide with the aid of a razor blade. All resulting s-IPN films were finally vacuum dried at 75 °C for 14 h to remove moisture prior to characterizing.

For mechanical property comparisons, two crosslinked network films composed entirely of PEOs without linear polyimides were prepared as a control, which had the same PEO network structures as those in the s-IPNs. Specifically, the two pure PEO network membranes were prepared following our previously reported procedures [28] via crosslinking PEO600 or PEO2000 oligomers with PEO-epoxy in a 1:2 molar ratio, which are named C600 and C2000, respectively. Synthesis of C600 pure PEO network is given as an example. To a 20 mL vial was added 0.2187 g (0.365 mmol) of PEO600 followed by 0.3646 g (0.729 mmol) of PEO-epoxy. The mixture was diluted with approximately 3.4 mL DMAc and then stirred at 50 °C on a hot plate for 50 min before being casted onto a glass slide residing in a vacuum oven pre-set to 45 °C. An aluminum foil covering with two open sides was placed over the film to mitigate dust contamination. Vacuum
was pulled for the duration that the film remained in the oven. The temperature was set to 90 °C for 1 h, followed by 100 °C for 1 h, and lastly 140 °C for 2 h. The oven temperature was then allowed to cool down slowly overnight. The film was removed with the aid of razor blade. Synthesis of C2000 network film followed the same procedure except that no solvent was used to promote completeness of crosslinking.

3.2.4 Characterizations

$^1$H NMR spectra were obtained for all linear (co)polyimides with a Bruker 400 or 500 spectrometer using deuterated chloroform (CDCl$_3$).

To evaluate the completeness of crosslinking, the gel contents in the s-IPN films were determined, as calculated in Equation 3.1. The dried films with an initial weight of $W$ were soaked in DI water for at least 48 h to extract the uncrosslinked parts, during which time the water was exchanged with fresh water at least one day before removing the films. The extracted films were allowed to air-dry and then placed into a vacuum oven for 14 h at 75 °C and weighed again as $W_i$.

$$\text{Gel content} = \frac{W_i}{W} \times 100\%$$

Equation 3.1

The degradation temperature of s-IPNs was analyzed by thermogravimetric analysis (TGA) by a Q500 TA instruments. The TGA heating rate was 10 °C/min under a 60 mL/min nitrogen purge. The glass transition temperature ($T_g$) was assessed by differential scanning calorimetry (DSC) using a DSC Q2000 from TA Instruments. Dried samples were analyzed in two cooling-heating cycles with a cooling rate of 20 °C/min and a heating rate at 10 °C/min within the range of -100 °C to 200 °C. Thermal transitions are reported from the second heating curve.
Mechanical properties of the membranes were tested in uniaxial tension at room temperature following ASTM D882-12. As-prepared membranes, 120-650 µm in thickness with less than 10 % variation along the gauge length, were cut into strips of 5 mm in width. Samples were clamped using flat knurled grips with a thin rubber facing (< 75 µm thickness). The sample gauge length was 22 mm, instead of the 100 mm specified in ASTM D882-12, due to size constraints of the as-prepared membranes. All samples were loaded to failure in uniaxial tension at displacement rate of 2.2 mm·min⁻¹ using a Bose ElectroForce 3220 electromechanical test instrument with an Interface WMC-50 50 lbf load cell at room temperature (20 °C, ~30 % humidity). The Young’s modulus, tensile strength, and percent elongation at break were calculated from force-displacement data and reported as the mean (± standard deviation) for at least four specimens per sample.

The pure-gas permeabilities of H₂, N₂, and CO₂ in s-IPN films were evaluated using the constant-volume variable-pressure method at 35 °C, under consecutive feed pressure increases from 3, 6, 10, 13, to 17 bar [29]. Immediately after being dried in a vacuum oven at 75 °C for 14 h, the permeation sample was loaded into the gas cell and degassed under vacuum at least overnight. Once the film and apparatus were degassed, the leak rate of the apparatus was determined over a duration of at least an hour. The feed gas was then introduced upstream of the membrane, and the permeate was collected downstream in a known volume. Once the rate of pressure increase downstream reached steady state, the permeability was calculated following Equation 3.2, where the permeability coefficient $P_A$ has a unit of $10^{-10}$ cm³(STP) cm/cm² sec cmHg, known as the Barrer.
\[ P_A = \frac{v_d l}{p_2 A R T} \left[ \left( \frac{dp_1}{dt} \right)_{ss} - \left( \frac{dp_1}{dt} \right)_{\text{leak}} \right] \] (3.2)

The upstream absolute pressure \( p_2 \) was increased to drive the gas to permeate across the membrane of area \( A \) and thickness \( l \). The gas constant is \( R \) (0.278 cmHg cm\(^3\)/cm\(^3\)(STP) K) and the temperature in Kelvin is given by \( T \). The steady-state rates of pressure increase in the downstream volume \( V_d \) is given by \( \left( \frac{dp_1}{dt} \right)_{ss} \) from the constant upstream pressure and \( \left( \frac{dp_1}{dt} \right)_{\text{leak}} \) is the natural leak into the system [30]. The potential ability of a membrane to separate gas A from gas B can be quantified by the ideal selectivity, \( \alpha_{A/B} \), which is equal to the ratio of pure-gas permeabilities where A is the more permeable gas:

\[ \alpha_{A/B} = \frac{P_A}{P_B} \] [30].

The time-lag method was used to determine the diffusion coefficient, \( D \), where

\[ D = \frac{l^2}{6\theta} \] The thickness of the membrane is given by \( l \) (cm) and the time-lag is given by \( \theta \) (s). Once the permeability and diffusivity are known, the solubility coefficient \( S \) is easily determined through the solution-diffusion model, i.e., \( P = D \times S \) [31].

3.3 Results and Discussion

3.3.1 Synthesis, and Physical and Mechanical Properties of s-IPN Networks

Two series of s-IPNs were prepared based on two PEO networks of different crosslink density penetrated by linear PEO-polyimide copolymers with systematically varied PEO content, yielding six distinct s-IPNs (Figure 3.2). Specifically, the two networks included the 600-series prepared from short amine-terminated PEO600 oligomers crosslinked with PEO-epoxy and the 2000-series from long PEO2000
oligomers with PEO-epoxy. Copolyimides of varied PEO content, i.e., PI-PEO0, PI-PEO24, and PI-PEO34, were incorporated as penetrating linear components in both series. The chemical structures of all linear polyimides was confirmed by $^1$H NMR and are shown in Figure 3.3. Successful incorporation of PEO into the polyimide backbone for PI-PEO24 and PI-PEO34 is confirmed by the appearance of the large peak associated with the ethylene oxide unit hydrogens at ~3.64 ppm. The exact PEO content within linear polyimides was estimated by the peak integrations in the $^1$H NMR spectra, which showed good agreement with target values. To isolate the effects of network crosslink density and PEO domain distribution, the overall PEO content was controlled to be approximately 70 wt% in all of the final s-IPN membranes by combining the appropriate amounts of crosslinkable PEO oligomers with given polyimides. The actual overall PEO content of s-IPNs was estimated based on known PEO content of incorporated polyimide, the amount of polyimide added, the amount of crosslinkable PEO oligomers added for the network formation, and the known amount of non-crosslinked PEO oligomers lost during film removal by soaking in H$_2$O. Table 3.1 provides the measured overall PEO content and actual gel content of all s-IPNs. As shown, all s-IPNs have ~ 70 wt% overall PEO content as designed and high gel fraction, allowing for reliable comparative studies to illustrate the effects of crosslink density and PEO domain distribution on the gas transport properties of s-IPNs.
Figure 3.3: $^1$H NMR spectra of linear polyimides incorporated into s-IPN networks (EO indicates the ethylene oxide unit hydrogens).
TABLE 3.1
COMPOSITION AND PHYSICAL CHARACTERISTICS OF S-IPN MEMBRANES

<table>
<thead>
<tr>
<th>Film</th>
<th>Overall PEO content (wt%)</th>
<th>Gel fraction</th>
<th>T(_g) (°C)</th>
<th>T(_d, 10) wt% (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-0-600</td>
<td>73</td>
<td>0.98</td>
<td>-31</td>
<td>318</td>
</tr>
<tr>
<td>S-24-600</td>
<td>72</td>
<td>0.98</td>
<td>-39</td>
<td>306</td>
</tr>
<tr>
<td>S-34-600</td>
<td>70</td>
<td>0.99</td>
<td>-36</td>
<td>327</td>
</tr>
<tr>
<td>S-0-2000</td>
<td>71</td>
<td>0.98</td>
<td>-40</td>
<td>346</td>
</tr>
<tr>
<td>S-24-2000</td>
<td>70</td>
<td>0.97</td>
<td>-40</td>
<td>332</td>
</tr>
<tr>
<td>S-34-2000</td>
<td>70</td>
<td>0.93</td>
<td>-42</td>
<td>352</td>
</tr>
</tbody>
</table>

As shown in Figure 3.4, these s-IPN membranes show good uniformity and high flexibility.

Figure 3.4: Images highlighting the uniformity and dexterity of s-IPN membranes. S-34-600 is shown as a representative example.
All s-IPNs show good thermal stability, where the 10 wt % degradation temperature is above 300 °C (Table 3.1). The second heating curve of DSC, provided as Figure 3.5, shows no crystallization or melting peaks, indicating that these s-IPN films are completely amorphous, thus overcoming the issue of PEO crystallinity that is frequently observed in PEO-rich copolymers and even crosslinked PEOs [15,19,32].

![Figure 3.5: Second heating traces of DSC analysis for all s-IPNs. The glass transition temperatures are marked with a vertical dash.](image)

Shown in Table 3.1, all s-IPN films are rubbery due to a high overall PEO content of ~ 70 wt%, and the glass transition temperatures, ranging from -42 to -31 °C, show some dependence on the structural and compositional characteristics of s-IPNs. In particular, given the same polyimide composition and overall PEO content, the 2000 series have slightly lower T_g’s than the 600 series, likely due to less constrained chain motion in the 2000 series with longer PEO segments. Additionally, within the 600 series,
s-IPNs that incorporate PEO-containing linear copolyimides (i.e., S-24-600 and S-34-600) seem to have slightly lower T_g’s than the S-0-600 that utilizes non-PEO-containing homopolyimide as the penetrating component, which is consistent with the expectedly higher PEO chain mobility in the linear component than in the networks. This effect is less obvious in the 2000 series possibly due to the high overall chain mobility.

To obtain excellent CO_2 separation performance, PEO-based membrane materials may have to sacrifice their mechanical properties in achieving high PEO content [14]. It is often found that mechanical properties of PEO-containing soft/hard copolymer membranes significantly decrease when PEO content surpasses 40 wt% [14,33]. There are cases for PEO-polyimide copolymer membranes where the mechanical properties were not even sufficient to be measured [14]. Similarly, crosslinked PEO-based membranes can suffer from weak mechanical properties. High PEO-content crosslinked membranes produced by Kwisneń et al., have a tensile modulus below 1.0 MPa [24] while for other crosslinked PEO-based membranes the mechanical properties are too poor to be measured [22].

In this study, representative s-IPNs incorporating PI-PEO0 polyimide (i.e., S-0-600 and S-0-2000) were tested for Young’s modulus, tensile strength, and elongation at failure, which are compared with respective crosslinked pure PEO membranes (i.e., C600 and C2000). For reference, the mechanical properties are provided in Table 3.2. It was found that the incorporation of PI-PEO0 polyimide clearly enhanced the tensile strength of crosslinked pure PEO membranes by 282% in going from C600 to S-0-600 and by at least 603% from C2000 to S-0-2000 (the maximum tensile strength of S-0-2000 could not be determined as the elongation of the material exceeded the expansion capabilities of
the testing apparatus). The s-IPN structures also significantly reduced the brittleness of crosslinked pure PEO membranes. For example, S-0-600 film had an elongation at failure that is more than three times of that of C600 film while S-0-2000 features an elongation at failure at least 27 times that of C2000 film – limited by the maximum apparatus expansion capacity. Even though the overall PEO content of all s-IPNs is high (~70 wt %), the s-IPNs (S-0-600 and S-0-2000) showed mechanical properties that exceed those of some previously mentioned PEO-containing copolymers and weak PEO-based crosslinked membranes [14,22,24].

**TABLE 3.2**

**MECHANICAL PROPERTIES OF PURE PEO CROSSLINKED NETWORKS AND CORRESPONDING S-IPNS INCORPORATING PI-PEO0 LINEAR POLYIMIDE**

<table>
<thead>
<tr>
<th>Film</th>
<th>Young’s Modulus (MPa)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Tensile Strength (MPa)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Elongation (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C600</td>
<td>2.67 ± 0.04</td>
<td>0.53 ± 0.13</td>
<td>22.52 ± 6.04</td>
</tr>
<tr>
<td>S-0-600</td>
<td>4.08 ± 0.23</td>
<td>2.04 ± 0.42</td>
<td>72.66 ± 18.40</td>
</tr>
<tr>
<td>C2000</td>
<td>1.75 ± 0.01</td>
<td>0.23 ± 0.03</td>
<td>13.95 ± 1.77</td>
</tr>
<tr>
<td>S-0-2000</td>
<td>1.16 ± 0.16</td>
<td>&gt; 1.62&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&gt; 383&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Data is reported as the mean (± standard deviation) for at least four specimens per sample.

<sup>b</sup> Values are limited by the maximum apparatus expansion capability.

3.3.2 Pure-Gas Permeation Properties

All s-IPN films were tested for pure-gas permeability for CO₂, H₂, and N₂ at various feed pressure and 35 °C to evaluate their potentials as separation membranes for
carbon capture (CO$_2$/N$_2$) and reverse-selective membranes for hydrogen purification (CO$_2$/H$_2$). Figure 3.6 plots the gas permeability at each of the five feed pressures for all s-IPNs. As shown, it is of note that the CO$_2$ permeability increased with increasing feed pressure across all s-IPNs. On the other hand, the permeability of H$_2$ and N$_2$ remained relatively stable or slightly decreased with increasing feed pressure. The increase in CO$_2$ permeability with increasing feed pressure for all s-IPNs is indicative of plasticization that has been typically observed in PEO-rich membranes [34]. Plasticized materials undergo CO$_2$ induced chain packing disruption leading to increased chain mobility and higher FFV, whereby higher diffusion coefficients and higher permeability [35]. For glassy polymeric membranes, CO$_2$ plasticization typically leads to a significant loss of gas selectivity; [34] thus various membrane modification methods have been investigated to suppress the effects of plasticization, such as crosslinking and producing s-IPNs [35,36]. However, for PEO-containing rubbery polymers, CO$_2$-induced plasticization has been shown to enhance separation performance for CO$_2$/H$_2$ separations [21]. The observed slight decrease in H$_2$ and N$_2$ permeability with increasing feed pressure is likely due to pressure-induced compaction of the soft membranes, which has been observed in the crosslinked PEO membranes reported previously [37]. The H$_2$ and N$_2$ permeability decrease most strongly for the s-IPNs synthesized with PEO2000 networks indicating their transport pathways are more susceptible to compaction largely due to their higher chain mobility as reflected in their lower T$_g$’s than the 600 series.
Figure 3.6: Pure-gas permeability of (a) CO$_2$, (b) H$_2$, and (c) N$_2$ as a function of feed pressure for all s-IPN membranes.
The combined effects of CO\(_2\) plasticization and membrane compaction naturally led to increased ideal selectivity for CO\(_2\) over H\(_2\) and N\(_2\) with increasing feed pressure. For reference, upper bound plots are provided in Figure 3.7 for all s-IPNs where the CO\(_2\)/H\(_2\) selectivity and CO\(_2\)/N\(_2\) selectivity are plotted against CO\(_2\) permeability. Each s-IPN has five data points, corresponding to the five feed pressures tested. As shown, the 2000 series of s-IPNs has good separation performance, especially for CO\(_2\)/H\(_2\) separations as all s-IPNs surpassed the upper bound with feed pressure above 10 bar. For CO\(_2\)/N\(_2\) separations, though none of the s-IPNs cross the upper bound, but by increasing feed pressure, crosslinking with PEO2000, and utilizing PEO-containing polyimide copolymers, significant improvement in gas permeability is achieved that led to a close approach to the upper bound. While mixed gas conditions were not used in these s-IPN permeation experiments, previous studies of other PEO containing s-IPNs have shown no loss in CO\(_2\)/N\(_2\) selectivity under mixed gas conditions compared to pure-gas permeation [25].
Figure 3.7: Upper Bound (2008) comparison of s-IPNs for (a) CO$_2$/H$_2$ and CO$_2$/N$_2$ gas pairs as a function of feed pressure.
As apparently seen from Figure 3.6 and Figure 3.7, gas separation performance of the s-IPNs is sensitive to the compositional and morphological characteristics of the s-IPNs. To better understand the structure-property relationship for these s-IPNs, the gas permeation results obtained at 3 bar, 35 °C are tabulated in Table 3.3 for detailed discussion. As illustrated, two trends are readily apparent. First, it is clear that the 2000-series s-IPNs have significantly higher permeabilities than the 600-series even they share almost the same overall PEO content. For example, the CO\textsubscript{2} permeability of the S-24-2000 film (90.3 Barrer) is more than twice that of the S-24-600 film (41.3 Barrer) while both have very similar overall PEO content of ~ 70 wt%. Looking back at Figure 3.6 (a), this trend is consistent for all five feed pressures and seems to be more obvious at high feed pressure. The higher permeability in the 2000 series is likely attributed to enhanced diffusion coefficients, as will be discussed later. Additionally, the 2000 series of s-IPNs also show apparently higher CO\textsubscript{2}/H\textsubscript{2} selectivity than their PEO600 counterparts, while no clear trend can be tracked for the CO\textsubscript{2}/N\textsubscript{2} selectivity between the two series. The second trend observable in Table 3.3 is that within the 600 or 2000 series, as the content of PEO in the penetrating linear polyimides increases, the permeability of CO\textsubscript{2}, H\textsubscript{2}, and N\textsubscript{2} increases in the s-IPNs. For example, given the same overall PEO content, incorporating 34 wt% PEO in the penetrating linear polymer (S-34-600) led to a ~36% increase in CO\textsubscript{2} permeability as compared to S-0-600 wherein the penetrating linear polyimide contains no PEO. Similarly, S-24-2000 has a CO\textsubscript{2} permeability that is ~22% higher than that of the S-0-2000 film. This observation clearly indicates that the distribution and connectivity of PEO domains (in linear component or in the networks) play a critical role in regulating the gas transport in PEO-containing membranes. Since the overall PEO
content is fixed, incorporating PEO in both the linear component and the networks seems to provide better connectivity in gas transport pathways allowing for fast diffusion. However, the exception is that of S-34-2000, which based on the trend would be expected to have the highest permeabilities. In Table 3.1 it can be seen that the gel fraction of S-34-2000 is markedly lower than the rest of the s-IPNs and therefore retains more unreacted PEO2000 and/or PEO-epoxy oligomers, which points to a possible disruption of the transport pathways within S-34-2000 leading to compromised gas permeability. This observation again emphasizes the importance of the structure of transport pathways. While the gas permeability shows strong dependence on the compositional and structural characteristics of s-IPNs, the ideal selectivity remains relatively constant within the 600 or 2000 series of s-IPNs, though a slight increase in CO₂/H₂ selectivity with increase PEO content in the linear component was observed within both 600 and 2000 series. It seems to suggest that the ideal selectivity of the s-IPNs is primarily dominated by the overall PEO content in the membranes.
TABLE 3.3
PURE-GAS PERMEABILITY AND IDEAL SELECTIVITY OF ALL S-IPN MEMBRANES AT 3 BAR FEED, 35 °C

<table>
<thead>
<tr>
<th>Film</th>
<th>P (CO₂)</th>
<th>P (H₂)</th>
<th>P (N₂)</th>
<th>α (CO₂/H₂)</th>
<th>α (CO₂/N₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-0-600</td>
<td>40.0 ± 0.9</td>
<td>9.8 ± 0.2</td>
<td>0.8 ± 0.02</td>
<td>4.1 ± 0.2</td>
<td>51.6 ± 2.7</td>
</tr>
<tr>
<td>S-24-600</td>
<td>41.3 ± 0.9</td>
<td>10.2 ± 0.2</td>
<td>0.8 ± 0.02</td>
<td>4.1 ± 0.2</td>
<td>49.2 ± 2.5</td>
</tr>
<tr>
<td>S-34-600</td>
<td>54.3 ± 1.6</td>
<td>12.2 ± 0.4</td>
<td>1.0 ± 0.04</td>
<td>4.4 ± 0.3</td>
<td>52.1 ± 3.5</td>
</tr>
<tr>
<td>S-0-2000</td>
<td>73.9 ± 1.8</td>
<td>14.1 ± 0.3</td>
<td>1.5 ± 0.04</td>
<td>5.2 ± 0.3</td>
<td>49.0 ± 2.5</td>
</tr>
<tr>
<td>S-24-2000</td>
<td>90.3 ± 1.9</td>
<td>15.5 ± 0.3</td>
<td>1.9 ± 0.04</td>
<td>5.8 ± 0.2</td>
<td>46.2 ± 2.0</td>
</tr>
<tr>
<td>S-34-2000</td>
<td>86.3 ± 2.0</td>
<td>15.0 ± 0.3</td>
<td>1.9 ± 0.05</td>
<td>5.7 ± 0.3</td>
<td>46.2 ± 2.3</td>
</tr>
</tbody>
</table>
Analysis of the CO₂ diffusion and solubility coefficients of s-IPNs (3 bar, 35 °C) are illustrated in Figure 3.8 to help understand the fundamentals of gas transport in these s-IPN films. As shown, the diffusion coefficients show the same general trends as those in the CO₂ permeability discussed above. Moreover, the solubility coefficients are relatively constant across all s-IPNs, suggesting the dominant role of kinetic diffusion for the gas transport in these PEO-based s-IPNs. Specifically, between comparable s-IPNs (i.e., S-0-600 vs. S-0-2000, S-24-600 vs. S-24-2000, and S-34-600 vs. S-34-2000), the CO₂ diffusion coefficients increased 78%, 85%, and 31%, respectively, from the 600 series to 2000 series s-IPNs. Typically, under conditions leading to increased diffusion coefficients, larger kinetic diameter penetrants exhibit relatively larger gains in permeability than do smaller penetrants [38]. This is the expected trend based on the kinetic diameters of these gases. The order of relative permeability enhancement between comparable PEO600-based s-IPNs and PEO2000-based s-IPNs goes as N₂ > CO₂ > H₂, consistent with their respective kinetic diameters [39]. This relative permeability enhancement can be used to explain the trends in CO₂/H₂ and CO₂/N₂ selectivity in Table 2, wherein all 2000-series s-IPNs have higher CO₂/H₂ selectivity than 600-series and no trend can be concluded in the case of CO₂/N₂ selectivity.
In Figure 3.8, CO₂ diffusion coefficient (grey bars, left axis) and CO₂ solubility coefficient (blue bars, right axis) for s-IPN membranes (3 bar, 35 °C).

In Figure 3.9, a comparison between the CO₂ separation performance of s-IPNs and their constituent linear (co)polyimides is made at 3 bar feed pressure. The arrows aid in following the structural change from linear PEO-containing polyimides to s-IPNs and the increase in overall PEO content from 0% in PI-PEO0 polyimide up to 70 wt% in the s-IPNs. It is clear that for the linear polyimides that CO₂ selectivity is increased with increasing PEO content but at the expense of decreased CO₂ permeability relative to PI-PEO0. On the other hand, all s-IPNs feature significantly enhanced CO₂ selectivity and CO₂ permeability compared to their constituent linear polyimides (the exception being S-34-2000, which has a similar CO₂/N₂ selectivity to PI-PEO34).
Figure 3.9: Upper Bound (2008) comparison for all s-IPNs and constituent polyimides for (a) CO$_2$/H$_2$ selectivity and (b) CO$_2$/N$_2$ selectivity versus CO$_2$ permeability. (PI-PEO0 data adapted from our previous report [8].)
For reference, the gas transport properties of C600 and C2000 are provided in Table 3.4. By comparison between Figure 3.9 and Table 3.4 it can be noted that the CO$_2$ permeabilities of these s-IPNs fall between that of their constituent linear (co)polyimides and neat PEO crosslinked networks.

TABLE 3.4
PERMEABILITY (BARRER) AND SELECTIVITY VALUES CALCULATED FROM 35 °C PURE-GAS PERMEABILITY DATA OBTAINED AT 3 BAR FEED PRESSURE

<table>
<thead>
<tr>
<th>Crosslinked Network</th>
<th>$P_{CO_2}$</th>
<th>$P_{H_2}$</th>
<th>$P_{N_2}$</th>
<th>$\alpha_{CO_2/H_2}$</th>
<th>$\alpha_{CO_2/N_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C600</td>
<td>152.5 ± 2.8</td>
<td>21.3 ± 0.4</td>
<td>2.95 ± 0.06</td>
<td>7.17 ± 0.27</td>
<td>51.7 ± 2.0</td>
</tr>
<tr>
<td>C2000</td>
<td>375.6 ± 5.6</td>
<td>37.2 ± 0.7</td>
<td>7.04 ± 0.15</td>
<td>10.09 ± 0.34</td>
<td>53.4 ± 2.0</td>
</tr>
</tbody>
</table>

3.3.3 Measurement Error

The calculation of error for data reporting is explained in Appendix A for various measurements, such as permeability, selectivity, and CO$_2$ diffusion and solubility coefficients.

3.4 Conclusions

In this work, a series of PEO-rich s-IPNs with systematically varied structural and compositional characteristics was produced, which successfully combined the good
mechanical properties of glassy polyimides and the excellent CO$_2$ separation performance of crosslinked PEO-based membranes. Specifically, the tensile strength of s-IPNs is nearly 4-fold (in some cases more than 7-fold) higher than that of the crosslinked pure PEO membranes. Simultaneously, the semi-interpenetrating network structure led to greatly augmented CO$_2$ permeability, CO$_2$/H$_2$ and CO$_2$/N$_2$ selectivity, compared to their constituent linear polyimides due to its capability to incorporate high PEO content. The separation performance of s-IPNs shows strong dependence on the structural and compositional characteristics of both the penetrating linear polyimides and the networks, suggesting the critical role of the distribution and connectivity of PEO domains in PEO-containing membranes. In general, incorporating PEO segments in the penetrating linear polyimides and utilizing PEO networks with low crosslink density led to significantly improved (up to 25 fold) CO$_2$ permeability, higher CO$_2$/H$_2$ selectivity, and nearly stable CO$_2$/N$_2$ selectivity, which demonstrates great potential of the PEO-based s-IPN membrane platform for high performance CO$_2$ separation applications.

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CHAPTER 4:

HARD-SOFT SEGMENTED COPOLYMERS CONTAINING TRIPTYCENE MOIETIES AND PEO SEQUENCES FOR CO₂ SEPARATION MEMBRANES

4.1 Introduction

The enormous amount of electricity produced by utility-scale facilities in the United States in a given year, at 4.01 trillion kWh, was for example, mostly generated by fossil fuels (63%) in 2017, according to preliminary data [1]. It has been recognized by the Intern-governmental Panel on Climate Change that the proliferous CO₂ emissions from burning fossil fuels must be decreased in order to reduce the steep rise in atmospheric CO₂ concentrations [2,3]. Relevant to CO₂ emissions, in the specific process of producing syngas by the water-gas shift reaction, CO₂ is generated as a byproduct [4]. It follows that, to reduce emissions, to further use N₂ from post-combustion flue gas, and to further utilize H₂ after the water-gas shift reaction, CO₂ must be removed [4–7]. Established absorber-stripper separation systems are one option for performing these separations, however their inherent drawbacks of complex operation, high cost, chemical solvent use, and large footprint encourage seeking other separation technologies [8,9]. Thus, an alternative gas separation technology that mitigates these drawbacks would be promising, and membranes possess such advantageous properties, [6,10] especially for mitigating CO₂ emissions [11].

Many polymeric materials exist that could be considered for use as gas separation membranes, however polyimides are among the most studied for such applications [10,12,13] due to their typically high thermal stability and desirable gas separation
performance compared to other membrane materials, such as conventional cellulose acetate [14,15]. Polyimides that incorporate 4,4’-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA), often demonstrate promising combinations of permeability and selectivity due to the bulky CF$_3$ groups which, disrupt chain packing leading to higher FFV, while providing chain stiffness due to steric hinderances [12,14]. Of note is the polyimide 6FDA-DATRI synthesized by Cho and Park [16]. This polyimide incorporated both 6FDA and the triptycene moiety which gave 6FDA-DATRI the highest FFV of any known 6FDA-based polyimide at that time. It was believed that the high FFV was in part contributed by the tiny void spaces inherent between the “blades” of the triptycene moiety, which was reasoned based on the observation that the d-spacing for 6FDA-DATRI was actually smaller relative to other 6FDA-based polyimides [16].

Even though polyimides have been produced with good combinations of FFV and rigidity, leading to attractive gas separation properties, polyimides are not best suited for all types of CO$_2$ removal [17]. In the case of separating CO$_2$ from H$_2$, polyimides generally have higher permeability for H$_2$, as a result of their size-selective nature. This results in having to recompress H$_2$ before it can be used elsewhere, which is expensive [5,17]. It would be advantageous for the membrane material to more quickly permeate CO$_2$ compared to H$_2$ that way recompression of H$_2$ could be minimized. Poly(ethylene oxide) (PEO) is a promising material for this application due to its higher permeability of CO$_2$ compared to H$_2$ as well as to other light-gases such as N$_2$ and CH$_4$ [5,17]. The unique affinity between PEO’s polar ethylene oxide groups and CO$_2$ is believed to be a result of dipole-quadrupole interactions, [5] which impart PEO with high solubility selectivity towards CO$_2$ [5,17,18]. Unfortunately though, PEO has several inherent issues
that hamper its direct use in gas separation membranes. For one, PEO tends to have high crystallinity at ambient temperatures, and for another, PEO has relatively low thermal stability and poor mechanical properties [19]. The issue with crystallinity is that crystalline PEO is considered to be impermeable [6] and accordingly even semi-crystalline PEO shows significantly reduced CO\textsubscript{2} permeability compared to fully amorphous PEO, as highlighted by Lin et al [5]. These researchers estimated a CO\textsubscript{2} permeability of 143 Barrer for fully amorphous PEO at infinite dilution, while that of the semi-crystalline PEO was estimated to be just 12 Barrer [5]. Though pure, linear-type PEO may not be satisfactory for use as stand-alone gas separation membranes, PEO can still be incorporated into gas separation membranes by strategic methods, such as blending with low molecular weight PEO [20–24], forming crosslinked or branched PEO membranes [17,25–31], and by synthesizing PEO-containing copolymers [19,32–39] that incorporate hard segments [5,19].

Copolymers of flexible PEO-segments and rigid-segments have been shown to improve the mechanical properties relative to pure PEO as well as to mitigate PEO crystallinity and impart favorable solubility selectivity [18] to yield membranes with high CO\textsubscript{2} separation performance [19,40,41]. Copolymers have been produced that feature higher CO\textsubscript{2} permeability (179.3 Barrer) than their constituent soft PEO (143 Barrer) or constituent rigid polyimide homopolymers (1.14 Barrer) [5,19]. Furthermore, copolymer selectivity for CO\textsubscript{2} can likewise exceed that of the constituent PEO and rigid homopolymers [41]. These properties of PEO-based copolymers demonstrate that the benefits of either the soft PEO or rigid homopolymers can be combined into one material while reducing or eliminating the drawbacks of either component on their own. It follows
that excellent CO$_2$ separation performance has been obtained by PEO-containing copolymers, even exceeding the CO$_2$/H$_2$ upper bound [19].

For PEO-containing copolymers, the properties of the hard segment significantly influences membrane properties, including CO$_2$ separation ability and thermal and mechanical properties [41]. Furthermore, for PEO-containing copolymers, incorporating structures that increase the micro-phase separation between the hard and soft segments, such as those with longer soft/hard-segments, higher PEO content, increased rigidity of the hard-segment, higher crystallinity of the hard-segments, and those with increased hydrogen bonding between the hard segments, can result in improved thermal and mechanical properties [42–44] and improved gas separation performance [37,41,45,46]. We have previously shown [47] in a 60 wt% PEO-containing copolymer that contains the very bulky pentiptycene moiety in its backbone, that it’s Young’s modulus is more than 15 times greater than that of the structurally similar copolymer, 6FDA-ODA-PEO1 (60) [19], which does not contain the pentiptycene moiety. The pentiptycene and PEO-containing copolymer just mentioned did not exhibit micro-phase separation but instead featured unique PEO chain threading and interlocking supramolecular interactions, due to the presence of pentiptycene units, which significantly improved its mechanical properties compared to 6FDA-ODA-PEO1 (60) [19,47].

Another iptycene, triptycene, which is less complex and less bulky than pentiptycene, has also been utilized to improve mechanical properties and even reduce crystallinity in polyester based copolymers [48,49]. The presence of triptycene allows the polyester segments to undergo chain threading through the clefts between the “blades” of the tiptycene moieties and this allows for an interlocking of triptycene units while the
material is under strain which allows for better dispersion of the load as well as improved stiffness, ductility, and strength [48–50]. However, it is not known if triptycene incorporation will likewise lead to improved mechanical properties in PEO-containing polyimide copolymers and what the effect of PEO chain threading will be on the thermal and gas transport properties. In this work, three series of PEO-containing polyimide copolymers have been synthesized where the PEO content and chemical structure of the hard-segment (i.e. containing triptycene or not and 6FDA or not) are systematically varied such that the role of varying degrees of supramolecular interactions, hard-segment rigidity, and PEO content can be elucidated with respect to thermal properties, qualitative mechanical properties, and gas transport properties.

4.2 Experimental

4.2.1 Materials

The triptycene-1,4-diamine monomer utilized in this work was synthesized with the materials reported in our previous work [51].

The materials required for the synthesis of triptycene-containing PEO-based copolyimides were reported in Chapter 3, section 3.2.1 Materials, where in this case only Jeffamine® ED-2003 (PEO2000), with a molecular weight of 2000 g/mol, was used.

The additional materials for the synthesis of non-triptycene containing, PEO-based copolymers are 2,4,6-trimethylbenzene-1,3-diamine (DAM) and pyromellitic dianhydride (PMDA), purchased from commercial sources. Both were used as received without additional purification.
4.2.2 Synthesis of PEO-Polyimide Segmented Copolymers

The synthetic scheme of PEO-polyimide copolymers in this work is given in Figure 4.1. The copolymers are denoted as “X-PEOY,” where “X” identifies the composition of the rigid segment and “Y” describes the weight percent (wt%) of PEO in the copolymer. All copolymers in this work were synthesized using the same polyetheramine, PEO2000.

4.2.3 Synthesis of 6FDA-Triptycene and PEO-Containing Copolymers

The general synthesis strategy of this series of copolymers has been described in our work on semi-interpenetrating polymer networks [52]. However, the reaction scheme of the two-step polycondensation with chemical imidization, is shown in Figure 4.1. To provide a simplified naming scheme the triptycene-diamine monomer is denoted as “T.” Furthermore, Jeffamine® ED-2003 polyetheramine is referred to as “PEO” and hexafluoroisopropylidinedibisphtalic dianhydride (6FDA) is simply denoted as “6.” These monomers were used to synthesize the “6T-series” copolymers which comprise three distinct copolymers, each with a unique PEO content.

4.2.4 Synthesis of 6FDA-DAM and PEO-Containing Copolymers

The synthetic procedure for the 6T-series copolymers was adapted and applied here. The reaction scheme is highlighted in Figure 4.1 and the monomer 2,4,6-trimethyl-1,3-diaminobenzene (DAM) is denoted as “D.” Here, two copolymers were synthesized, the “6D-series” copolymers, which each have a distinct PEO content.
4.2.5 Synthesis of PMDA-DAM and PEO-Containing Copolymers

As before, the synthetic procedure for the 6T and 6D-series copolymers was used here, as shown in Figure 4.1. The “PD-series” copolymers contain pyromellitic dianhydride (PMDA), referred to as “P,” and each of the three copolymers of the series has a unique PEO content.

4.2.6 Membrane Formation

The solution casting method was used for all copolymers to produce membranes. The DMAC solution for film casting contained 6 – 25 wt% copolymer and was heated up to 115 °C, if needed, to dissolve the copolymer. The solution was then passed through a 0.45 μm PTFE syringe filter directly onto a glass plate and an infrared lamp was used to evaporate most of the solvent. The film was then transferred to a vacuum oven and dried at 100 °C for at least 14 h under vacuum. If the glass transition temperature was sufficiently high, the films could be peeled off the glass plates with a razor blade, otherwise the films were soaked in water before being peeled off. The water-soaked films were then dried under vacuum overnight at room temperature. Thermogravimetric analysis (TGA) was used to confirm complete solvent removal.

4.2.7 Polymer and Membrane Characterizations

The chemical structures of all copolymers were confirmed by H¹ nuclear magnetic resonance (¹H NMR) with a Bruker 400 MHz or 500 MHz instrument, using DMSO-"d₆" or CDCl₃.
A TGA Q500 instrument was used to perform thermogravimetric analysis on all films in order to determine their thermal stability and to confirm complete solvent removal. Samples were heated at 10 °C/min. under a nitrogen purge of 60 mL/min.

Physical properties of the films, the glass transition temperature (T_g) and crystallization (T_c) and melting temperature (T_m), were analyzed with a differential scanning calorimeter (DSC). Samples were dried in vacuum oven and then loaded into the DSC Q2000 (TA Instruments) with a liquid nitrogen cooling system. A nitrogen purge of 50 mL/min. was used along with a heating rate of 10 °C/min. and cooling rate of 20 °C/min. All reported thermal transitions are taken from the second heating curve unless otherwise noted and the temperature range employed varied between -100 °C and 300 °C.

The small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) data were obtained by the Chemical and Materials Science group at Argonne National Laboratory. The Advanced Photon Source (APS) synchrotron beamline 12-ID-B utilized an X-Ray beam wavelength of 0.9322 Å at a photon energy of 13.3 keV. A silver behenate standard was used to calibrate the q-range and the distance between the sample and the detector was 2013 mm for the SAXS detector and 430.15 mm for the WAXS detector. An exposure time of 1 second was used and the resulting two-dimensional (2D) spectra were collected with a Pilatus 2M camera for SAXS samples and with a Pilatus 300 camera for WAXS samples. The 2D spectra were converted to 1D spectra by azimuthal integration. All spectra were corrected for transmission and background scattering and analyzed using Igor Pro-Irena SAS package to display arbitrary SAXS or
WAXS intensity versus the scattering vector $q$, where $q = (4\pi/\lambda) \sin(\theta/2)$, and $\lambda$ is the X-ray wavelength and $2\theta$ is the scattering angle.

The pure-gas transport properties for $N_2$, $H_2$, and $CO_2$ were evaluated at 35 °C using the constant-volume variable-pressure method, [53] as is described in Chapter 2 section 2.2.3 Characterizations, utilizing Equation 2.3, which is provided below as Equation 4.1. The thickness of all films was determined after the films were dried in a vacuum oven. The films were next sealed within the permeation cell and the testing apparatus was degassed under strong vacuum for at least 12 hours. The leak rate of the apparatus was then determined followed by permeation testing at steady state as described in Chapter 2 section 2.2.3 Characterizations.

$$P_A = \frac{V_{dl}}{T_{2ART}} \left[ \left( \frac{dp_1}{dt} \right)_{ss} - \left( \frac{dp_1}{dt} \right)_{leak} \right]$$

(4.1)

The ratio of the pure-gas permeabilities of more permeable gas (A) over another gas (B) provides the ideal selectivity, Equation 4.2, of the membrane.

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

(4.2)

The apparent $CO_2$ diffusion coefficients were estimated by the time-lag method using Equation 4.3. Here, $l$ (cm) represents the film thickness and $\theta$ (s) is the time-lag [29]. The $CO_2$ solubility coefficients ($S$) are then easily extracted from the following relation to permeability, $P = D \times S$ [29].

$$D = \frac{l^2}{6\theta}$$

(4.3)
Figure 4.1: Synthesis scheme for PEO-containing segmented copolymers, i.e., X-PEOY (“X” identifies the composition of the rigid segment (6T, 6D, PD) and “Y” provides the weight percent of PEO in the copolymers). Copolymer composition, i.e., PEO weight content, was adjusted by varying the feed ratio of PEO2000.
4.3 Results and Discussion

4.3.1 Synthesis of PEO-Polyimide Copolymers

Three series of PEO-containing copolymers were synthesized with distinct hard segments composed of specific combinations of diamines and dianhydrides so that the effects of varying degrees of supramolecular interactions and hard-segment rigidity could be evaluated over a range of PEO contents. The 6T-series incorporates triptycene moieties which are expected to promote PEO chain threading supramolecular interactions. The 6D-series contains no triptycene units in its hard segments, thus removing supramolecular interactions, but instead incorporates DAM and removes the flexible either linkages, whereby increasing its hard-segment rigidity compared to the 6T-series. The PD-series utilizes PMDA instead of 6FDA whereby further increasing the hard-segment rigidity compared to the 6D and 6T-series PEO-containing copolymers.

All PEO-polyimide copolymers were synthesized by the typical two-step polycondensation reaction with chemical imidization. To produce three distinct series of copolymers, the choice of rigid segment dianhydride and diamine were systematically varied. Furthermore, the stoichiometry of monomers was appropriately adjusted to achieve copolymers with varied PEO content. Accordingly, each copolymer series was differentiated by its distinct rigid segment composition (“m” segment in Figure 4.1), and within each series at least two copolymers with discrete PEO contents (“n” segment in Figure 4.1) were produced. $^1$H NMR was used to confirm the chemical structure of each copolymer. The $^1$H NMR spectra for each of the target 50 wt% PEO copolyimides is provided for reference in Figure 4.2. Furthermore, to illustrate the control of PEO content in these copolymers, the $^1$H NMR of the 6T-series copolymers is provided for reference
in Figure 4.3. The actual PEO content was estimated by $^1$H NMR and reported in Table 4.1, where it is noted that the estimated PEO content does not perfectly match the target content but is sufficiently close for the purposes of this study. For all copolymers, Table 4.1 provides the monomer molar feed ratio as well as the targeted PEO content and $^1$H NMR estimated PEO content.

Figure 4.2: Reference $^1$H NMR spectra of target 50 wt% PEO copolyimides.
Figure 4.3: $^1$H NMR spectra (CDCl$_3$) of the 6T-series copolymers normalized to all have the same PEO-peak intensity.
TABLE 4.1

MONOMER MOLAR FEED RATIO, TARGET PEO CONTENT, AND $^1$H NMR ESTIMATED PEO CONTENT OF ALL COPOLYMERS

<table>
<thead>
<tr>
<th>Film</th>
<th>Monomer Molar Feed Ratio (Dianhydride : Diamine : PEO2000)</th>
<th>Target PEO wt%</th>
<th>Estimated PEO wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>6T-PEO20</td>
<td>(5.205 : 4.205 : 1.000)</td>
<td>30</td>
<td>24</td>
</tr>
<tr>
<td>6T-PEO30</td>
<td>(3.559 : 2.559 : 1.000)</td>
<td>40</td>
<td>34</td>
</tr>
<tr>
<td>6T-PEO50</td>
<td>(2.572 : 1.572 : 1.000)</td>
<td>50</td>
<td>46</td>
</tr>
<tr>
<td>6D-PEO50</td>
<td>(3.835 : 2.835 : 1.000)</td>
<td>50</td>
<td>52</td>
</tr>
<tr>
<td>6D-PEO60</td>
<td>(2.644 : 1.644 : 1.000)</td>
<td>60</td>
<td>62</td>
</tr>
<tr>
<td>PD-PEO60</td>
<td>(6.447 : 5.447 : 1.000)</td>
<td>50</td>
<td>57</td>
</tr>
<tr>
<td>PD-PEO70</td>
<td>(4.444 : 3.444 : 1.000)</td>
<td>60</td>
<td>67</td>
</tr>
<tr>
<td>PD-PEO80</td>
<td>(3.014 : 2.014 : 1.000)</td>
<td>70</td>
<td>76</td>
</tr>
</tbody>
</table>

4.3.2 Thermal Properties of PEO-Copolyimides

The glass transition temperature of each copolymer is provided in Table 4.2. Despite the varying rigid segment compositions and PEO contents, all copolymers synthesized in this work show only one $T_g$ during DSC analysis (Figure 4.4) in the second heating curve. This suggests that all copolymers synthesized here are non-phase-separated. The non-phase-separated morphology, at least for the target 50 wt% PEO copolyimides, is confirmed by SAXS analysis. It is apparent in the SAXS/WAXS spectra of the three copolymer series at comparable (~50 wt%) PEO content in Figure 4.5 that no scattering peaks exist that would suggest phase-separation if present.
Figure 4.4: The second DSC heating curve of all copolymers with the $T_g$’s indicated by a vertical line.
Figure 4.5: SAXS/WAXS spectra of each copolymer series at ~50 wt% PEO.

It is also apparent from Table 4.2 that the triptycene moiety significantly impacts the T_g of the copolymer. For instance, the T_g of 6T-PEO50 is a staggeringly 52 °C higher than that of 6D-PEO50, which has the same PEO content but the triptycene moiety replaced with DAM. Similarly, the T_g of 6T-PEO50 is much higher than that of other PEO-containing polyimide copolymers within the literature (-23 °C to -61 °C) of similar PEO content [35,37,54]. However, it should be noted that clearly defined T_g’s are not present in the second heating curve during DSC analysis of the 6T-series copolyimides, but rather, the T_g of each copolymer in the 6T-series is taken as the point where the slope of the heating curve simply changes. The relatively high T_g of 6T-PEO50 is consistent with other works considering that elsewhere, controlled triptycene incorporation has systematically increased T_g values [55,56] and has been used to elevate the T_g above polymer degradation temperatures (> 500 °C) [49]. Triptycene incorporation has been
shown to impart other unique physical properties to polymers. For example, when the triptycene moiety was sufficiently dispersed on a polyetherolefin backbone, no phase separation was observed, likely as a result of the threading of polymer chains through the open spaces of the triptycene clefts due to the minimization of intermolecular free volume mechanism [56]. Furthermore, polymer ductility and stiffness have simultaneously been enhanced due to triptycene incorporation, thanks to chain threading [55]. It is also believed that this chain threading mechanism is at least in part responsible for the relatively high T_g values for pentiptycene based PEO copolymers synthesized by Luo et al. [47]. Considering these previously mentioned studies involving iphtycene incorporation, it is consistent that the 6T-PEO50 copolymer exhibits a relatively high T_g value, due to the high degree of mixing of hard and soft-PEO segments as a result of the threading of PEO segments through the triptycene clefts, which restrict the mobility of the PEO segments and increase the overall backbone rigidity [34].

The glass transition temperatures of these copolymers indicate that the non-triptycene-containing 6D and PD-series have a higher extent of micro-phase separation than do the 6T-series copolymers. While it is believed that all copolymers synthesized in this work do not have a fully micro-phase separated morphology, because only one T_g is observed for all copolymers, the actual extent of micro-phase separation may differ for each copolymer. By the two-phase model, the Fox equation can be modified, shown as Equation 4.4, and utilized to estimate the content of the hard segment in the soft domain (W_HS) of the copolymer membrane.[37] In this equation, T_{g,c} is the glass transition temperature of the copolymer and T_{g,s}^* and T_{g,h}^* are the glass transition temperatures of
the pure soft and hard segments, respectively [37]. It follows that the better the miscibility between the hard and soft segments the higher the $W_{HS}$ values.

$$\frac{1}{T_{g,c}} = \frac{1-W_{HS}}{T_{g,S}^*} + \frac{W_{HS}}{T_{g,H}^*}$$  \hspace{1cm} (4.4)

In order to utilize Equation 4.4, the $T_g$’s of the hard segment homopolymers have been provided in Table 4.2. For clarity, the homopolymers are triptycene-6FDA, 6FDA-DAM, and PMDA-DAM, which have been renamed according to the previous naming scheme as 6T-PEO0, 6D-PEO0, and PD-PEO0, to signify that these do not contain PEO. The content of the hard segment in the soft domain for 6T-PEO50 is estimated at 43 wt%. This is significantly higher than the degree of mixing for 6D-PEO50 at only 16 wt% and for PD-PEO60 which has at most 16 wt% (depending on the actual $T_g$ of PD-PEO0) contamination of the hard segment in the soft domain. This analysis reveals that supramolecular inter-chain interactions due to the triptycene moieties are likely increasing the extent of micro-phase mixing. In addition, the strikingly 52 °C higher $T_g$ of 6T-PEO50 compared to both 6D-PEO50 and PD-PEO60 suggests that the triptycene units have significantly impeded the mobility of threaded PEO segments due to supramolecular interactions.

The copolymers of this work are amorphous, except for those of the PD-series with very high PEO content. For instance, PD-PEO80 has the highest crystallinity at 14.6%, in the second DSC heating curve, but its melting temperature is 25 °C and so the membrane is completely amorphous during permeation testing at 35 °C.
TABLE 4.2
THERMAL PROPERTIES OF ALL COPOLYMER MEMBRANES AND HOMOPOLYIMIDES

<table>
<thead>
<tr>
<th>Film</th>
<th>T_g (°C)</th>
<th>T_c (°C)</th>
<th>T_m (°C)</th>
<th>T_d (10 wt%)</th>
<th>Crystallinity (%)</th>
<th>W_HS (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6T-PEO0</td>
<td>290 ^a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6T-PEO20</td>
<td>136 ^b</td>
<td>None</td>
<td>None</td>
<td>364</td>
<td>0</td>
<td>77</td>
</tr>
<tr>
<td>6T-PEO30</td>
<td>82 ^b</td>
<td>None</td>
<td>None</td>
<td>352</td>
<td>0</td>
<td>64</td>
</tr>
<tr>
<td>6T-PEO50</td>
<td>20 ^b</td>
<td>None</td>
<td>None</td>
<td>355</td>
<td>0</td>
<td>43</td>
</tr>
<tr>
<td>6D-PEO0</td>
<td>395 ^c</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6D-PEO50</td>
<td>-32</td>
<td>None</td>
<td>None</td>
<td>374</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>6D-PEO60</td>
<td>-36</td>
<td>None</td>
<td>None</td>
<td>375</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>PD-PEO0</td>
<td>&gt; 400 ^d</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PD-PEO60</td>
<td>-32</td>
<td>None</td>
<td>None</td>
<td>371</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>PD-PEO70</td>
<td>-46 ^e</td>
<td>i</td>
<td>i</td>
<td>377</td>
<td>&lt; 5.6 ^f</td>
<td>8.4</td>
</tr>
<tr>
<td>PD-PEO80</td>
<td>-47</td>
<td>8</td>
<td>25</td>
<td>376</td>
<td>14.6</td>
<td>7.8</td>
</tr>
</tbody>
</table>

^a The T_g of the rigid component of the 6T series is taken from Wiegand et al. [51].
^b No obvious T_g, but instead a mere change in slope of the DSC curve.
^c The T_g of the rigid component of the 6D series is taken from Qui et al. [57].
^d The T_g of the rigid component of the PD series is taken from Álvarez et al. No T_g was observed up to 400 °C [58].
^e The T_g was dependent upon the final temperature of the previous heat cycle and ranged between -41°C and -50 °C.
^f The T_c, T_m, and crystallinity (%) depended on the final temperature of the previous heat cycle.

4.3.3 Qualitative Mechanical Properties of PEO-Copolyimides

All films were produced via the solution casting method from the synthesized copolymers. Interestingly, the highest PEO content achieving for a copolymer that resulted in a robust film significantly varied depending on the composition of the hard segment. Contrary to the previous reports about enhanced mechanical properties with triptycene incorporation, [50,55,56] the high PEO-content copolymers of the 6T-series
suffered from mechanical weakness compared to the PD-series copolymers. The 6T-series copolymers could not form handleable films at 60 wt% PEO or higher as the films became extremely soft and stretchable. On the contrary, the PD-series copolymers, which do not contain triptycene but feature the most rigid hard segments, could form mechanically stable and handleable films at nearly 80 wt% PEO. The relatively weak mechanical properties of the 6T-series copolymers at high PEO contents could be due to two potentially related factors. The first factor is that the rigid segment of the 6T-series contains flexible ether linkages whereas the rigid segment of the PD-series does not. Therefore, it is possible that the higher rigidity of the PD-series rigid segment, suggested by its significantly higher $T_g$, is enhancing its mechanical properties of the high PEO content PD-series copolymers. The second potentially related factor, is the degree of micro-phase separation. It was previously estimated, by Equation 4.4, that 6T-PEO50 has significantly more mixing of the hard and soft phases than do any of the PD-series copolymers. While even PD-PEO80 did not show complete micro-phase separation, a higher degree of micro-phase separation (which it has compared to 6T-PEO50) could influence its physical properties to increase them [37,41]. This can also be used to explain the significant difference in mechanical stability of the 6D-series copolymers compared to the PD-series copolymers at high PEO contents. The 6D-series cannot form films that are handleable above 60 wt% PEO (still higher than the 6T-series). Even though both the 6D and PD-series do not contain flexible ether linkages in their hard segments, it is likely that the PD-series has an even more rigid hard segment evidenced by its glass transition temperature of PD-PEO0 being apparently higher than 400 °C. As such, it is estimated that PD-PEO80, for instance, only contains at most 8 wt% hard segments in the soft
domain, whereas 6D-PEO60 contains 14 wt%. Thus, due to higher rigidity hard segments and potentially a higher degree of micro-phase separation, the PD-series copolymers can form mechanically robust films at very high PEO contents.

4.3.4 Pure-Gas Permeation Tests

The gases CO₂, H₂, and N₂ were utilized in pure-gas permeation tests at 35 °C over a pressure range of 3–17 bar. The resultant permeability and CO₂/gas ideal selectivity values for tests conducted with a feed pressure of 3 bar are provided in Table 4.3.

<table>
<thead>
<tr>
<th>Film</th>
<th>P (CO₂)</th>
<th>P (H₂)</th>
<th>P (N₂)</th>
<th>α (CO₂/H₂)</th>
<th>α (CO₂/N₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6T-PEO20</td>
<td>4.6</td>
<td>5.9</td>
<td>0.13</td>
<td>0.79</td>
<td>35</td>
</tr>
<tr>
<td>6T-PEO30</td>
<td>6.4</td>
<td>4.7</td>
<td>0.16</td>
<td>1.4</td>
<td>41</td>
</tr>
<tr>
<td>6T-PEO50</td>
<td>25</td>
<td>8.4</td>
<td>0.58</td>
<td>3.0</td>
<td>43</td>
</tr>
<tr>
<td>6D-PEO50</td>
<td>30</td>
<td>9.0</td>
<td>0.63</td>
<td>3.3</td>
<td>48</td>
</tr>
<tr>
<td>6D-PEO60</td>
<td>53</td>
<td>12</td>
<td>1.0</td>
<td>4.5</td>
<td>53</td>
</tr>
<tr>
<td>PD-PEO60</td>
<td>13</td>
<td>4.8</td>
<td>0.24</td>
<td>2.6</td>
<td>53</td>
</tr>
<tr>
<td>PD-PEO70</td>
<td>40</td>
<td>8.4</td>
<td>0.75</td>
<td>4.7</td>
<td>53</td>
</tr>
<tr>
<td>PD-PEO80</td>
<td>81</td>
<td>13</td>
<td>1.5</td>
<td>6.2</td>
<td>53</td>
</tr>
</tbody>
</table>
4.3.4.1 Influence of PEO Content on Gas Permeability

Figure 4.6 displays the CO\textsubscript{2} permeability of all copolyimides at 3 bar feed pressure. It is clear that for all series of copolymers an increase in PEO content resulted in greatly increased CO\textsubscript{2} permeability. Within each copolymer series, the CO\textsubscript{2} permeability nearly doubled for each \textsim 10 wt\% increase in PEO content, with the exception of the relatively small CO\textsubscript{2} permeability increase between 6T-PEO\textsubscript{20} and 6T-PEO\textsubscript{30} where both copolymers are in the glassy state at such low PEO contents. The comparatively small increase in CO\textsubscript{2} permeability in going from 6T-PEO\textsubscript{20} to 6T-PEO\textsubscript{30} could be due to the threading of PEO segments through the clefts of the triptycene moieties which would confine the PEO segments and restrict the otherwise expected significant increase in the CO\textsubscript{2} diffusion coefficient with increasing PEO content.

![Figure 4.6: Pure-gas CO\textsubscript{2} permeability at 3 bar feed pressure and 35 °C for all copolymer membranes.](image)
The trend of increasing CO$_2$ permeability with increasing PEO content also holds for the other tested gases, H$_2$ and N$_2$, as shown in Figure 4.7. Similarly, the exception to significant H$_2$ and N$_2$ permeability increases with increasing PEO content is demonstrated in going from 6T-PEO20 to 6T-PEO30. This limited permeability increase effect is more likely to happen at low PEO contents as there are many voids about the triptycene moieties of the 6T-series copolymers available to be filled by PEO chain threading, however, once the cavities are filled, the typically large increases in permeability with increasing PEO content resumes as demonstrated by the large permeability increase in going from 6T-PEO30 to 6T-PEO50. The restricted permeability increase for triptycene-containing 6T-series with low PEO content has been observed in other iptycene-containing PEO copolymers. For example, for pentiptycene containing PEO copolymers, those with 40 wt% PEO content actually had lower CO$_2$, H$_2$, O$_2$, N$_2$, and CH$_4$ permeabilities than the copolymer with only 20 wt% PEO. This observation was believed to be a result of the lower fractional free volume of the copolymer with 40 wt% PEO due to the filling of molecular cavities about the pentiptycene moieties with PEO segments [47]. Due to the structural similarities between the 6T-series copolymers studied in this work and the pentiptycene-containing PEO copolymers studied previously, both the pentiptycene-PEO copolymers and the pentiptycene-6FDA homopolymer (Pent-6FDA) will be included in the following discussions.
Figure 4.7: Pure-gas H$_2$ (a) and N$_2$ (b) permeability at 3 bar feed pressure for all copolymer membranes.
4.3.4.2 Influence of the Hard Segment Composition on Gas Permeability

The FFV and gas transport properties of the non-PEO-containing homopolyimides (the hard-segments of the copolymers) have been provided in Table 4.4 as these properties are helpful for elucidating their role as hard segments in the PEO-containing copolymers. The non-PEO-containing rigid segment components of the copolymers discussed in this work have been provided in Table 4.4. As shown in Table 4.4, PMDA-DAM (PD) has a much higher CO$_2$ solubility coefficient compared to Trip-6FDA (6T) and Pent-6FDA and 6FDA-DAM (6D) has a much higher CO$_2$ diffusion coefficient than Trip-6FDA and Pent-6FDA, and these factors make the CO$_2$ permeabilities of the iptycene-containing homopolyimides far lower than those of PMDA-DAM and 6FDA-DAM.
<table>
<thead>
<tr>
<th>Film</th>
<th>FFV</th>
<th>$P_{CO_2}$ (Barrer)</th>
<th>$D_{CO_2}$ ($10^{-8}$ cm$^2$/s)</th>
<th>$S_{CO_2}$ ($10^2$ cm$^3$(STP)/(cm$^3$ cmHg))</th>
<th>Gas Transport Testing Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMDA-DAM (PD) [58]</td>
<td>0.166</td>
<td>526</td>
<td>9.2</td>
<td>57</td>
<td>(3 bar, 30 °C)</td>
</tr>
<tr>
<td>6FDA-DAM (6D)</td>
<td>0.182 [59]</td>
<td>431 [59] 870 [61] 900 [61] 299 [60]</td>
<td>54 [59]</td>
<td>8.0 [59]</td>
<td>(10 atm, 35 °C) [59] (200 torr, 30 °C) [61] (2 atm, 35 °C) [60]</td>
</tr>
<tr>
<td>Trip-6FDA (6T)</td>
<td>0.183 [51]</td>
<td>20 [51]</td>
<td>2.1 [62]</td>
<td>9.7 [62]</td>
<td>(130 psig, 35 °C) [51] (2 atm, 35 °C) [62]</td>
</tr>
<tr>
<td>Pent-6FDA</td>
<td>0.197 [63]</td>
<td>132 [63]</td>
<td>9.3 [64]</td>
<td>11 [64]</td>
<td>(10 atm, 35 °C) [63][64]</td>
</tr>
</tbody>
</table>
As shown in Table 4.4, the CO\textsubscript{2} solubility coefficients vary widely depending on the homopolyimide. For instance, 6FDA-DAM has a CO\textsubscript{2} solubility coefficient of 8.0 while that of PMDA-DAM is 57. However, these vast difference in CO\textsubscript{2} solubility coefficients seem to disappear once each homopolyimide has been copolymerized with PEO. As shown in Figure 4.8, the CO\textsubscript{2} solubility coefficients hover near a value of 2 for all copolymers, regardless of PEO content or rigid segment composition. This illustrates that compared to the homopolyimides the CO\textsubscript{2} solubility is actually severely limited by the presence of PEO, even for 6T-PEO20, which only has about 24 wt% PEO. Therefore, due to the effect of PEO on the CO\textsubscript{2} solubility coefficient alone, the PEO phase significantly impacts the CO\textsubscript{2} permeability of these copolymers. On the other hand, the CO\textsubscript{2} diffusion coefficients of these copolymers significantly varies depending on both the composition of the rigid segment and the amount of PEO incorporated into the copolymer. The significant differences in CO\textsubscript{2} diffusion coefficients within and between these copolymer series suggest that factors which are able to influence the mobility of the flexible PEO segments can strongly impact the permeability by their effects on diffusivity.
As previously discussed, all copolymers synthesized in this work do not have distinct micro-phase separated morphology. As a result of the mixing of hard and soft phases, different compositions of the rigid segment could be expected to influence the mobility of PEO to differing degrees, which influences the gas transport properties of these respective segmented copolymers. To investigate the effects of the rigid segment composition in more detail, the CO₂ permeability of the target 50 wt% PEO copolymers of each series has been plotted versus feed pressure in Figure 4.9. For added discussion, the permeation data from the pentiptycene-containing copolymer (46.8 wt% PEO) previously studied [47] has been added to Figure 4.9. The copolymer, PD-PEO60, has also been included in Figure 4.9 because its estimated PEO content of 57 wt% is
appropriately close to that of the ~50 wt% PEO containing copolymers for the purposes of this analysis. In Figure 4.9 it is observed that 6T-PEO50 has a lower CO$_2$ permeability than 6D-PEO50 at all feed pressures. The ~6 wt% lower PEO content of 6T-PEO50 compared to 6D-PEO50 can sufficiently explain the lower CO$_2$ permeability of 6T-PEO50, rather than this being a consequence of differing rigid segment compositions. However, it is most striking that PD-PEO60, which has a higher actual PEO content than all other series in Figure 4.9, has by far the lowest CO$_2$ permeability (~2.5 times less than 6D-PEO50) at all feed pressures, despite that its corresponding homopolyimide hard segments (i.e., PMDA-DAM) has a much higher CO$_2$ permeability than the other homopolyimides (potentially besides 6FDA-DAM due to wide ranging reported values) (Table 4.4). These results are discussed below.
Figure 4.9: Pure-gas permeability of CO$_2$ as a function of feed pressure for target 50 wt% PEO-containing copolymer membranes with different hard segments. The data of pent-PI-PEO2000 (50%) were taken from ref. [47]. The numbers in parentheses are the actual PEO weight content determined from $^1$H NMR.

Generally, for PEO-containing polymers, the CO$_2$ permeability decreases as the glass transition temperature increases, due to the decreased mobility of polymer segments and decreased FFV [18]. Following this typical trend it would be expected that the triptycene-containing copolymer, 6T-PEO50, with its relatively very high $T_g$, (52 °C higher than that of 6D-PEO50 and PD-PEO60) would have by far the lowest CO$_2$ permeability compared to 6D-PEO50 and PD-PEO60 [18,37]. From Figure 4.9 this is clearly not the case as the CO$_2$ permeability of 6T-PEO50 falls between that of 6D-PEO50 and PD-PEO60 at all five feed pressures. This anomaly might be explained by the unique PEO chain threading apparent with triptycene incorporation in 6T-PEO50, as such
threading could lead to two competing effects on CO\textsubscript{2} permeability. For instance, the threading of PEO segments would presumably reduce the mobility of PEO segments as well as fill the otherwise empty clefts of the triptycene moieties which would decrease the FFV and together decrease CO\textsubscript{2} permeability. Such consequences of PEO threading could be a major factor in why 6T-PEO50 has a lower CO\textsubscript{2} permeability than 6D-PEO50. However, the threading of PEO segments may also have a positive effect on CO\textsubscript{2} permeability by producing well-connected, low-barrier transport pathways for CO\textsubscript{2} diffusion. This proposed positive effect of PEO chain threading could help explain why 6T-PEO50, with its relatively very high T\textsubscript{g}, has a higher CO\textsubscript{2} permeability than PD-PEO60. Furthermore, compared to the other target 50 wt% PEO copolymers, PD-PEO60 is the least affected by CO\textsubscript{2} induced plasticization, illustrated by its lowest amount of relative CO\textsubscript{2} permeability increase in going from 3 to 17 bar feed pressure. It would appear that the more rigid PMDA and DAM hard segments of PD-PEO60 are able to restrict the mobility of PEO chains more so than in 6D-PEO50, for instance. Interestingly though, this restricted mobility is not reflected in the glass transition temperatures of these membranes. That is, 6T-PEO50 actually has the highest T\textsubscript{g} (normally most restricted mobility) and 6D-PEO50 and PD-PEO60 have the same T\textsubscript{g} values. This could be due to a complicated interplay of factors, such as varying extents of micro-phase separation and unique PEO chain threading with triptycene moieties. Another possibility for the low permeability of PD-PEO60 would be if it has the lowest FFV. Unfortunately, attempts to estimate the FFV of these copolymers by the group contribution method yielded non-sensical results, probably due to the ill-defined structure of PEO. However, based on the relatively low FFV of PMDA-DAM, it would not be surprising if PD-
PEO60 has a lower FFV than does 6D-PEO50 or possibly 6T-PEO50. In any case, PD-PEO60 has the lowest CO\textsubscript{2} diffusion coefficient of 6.9 compared to 6D-PEO50 and 6T-PEO50 which have CO\textsubscript{2} diffusion coefficients of 15.0 and 11.2, respectively. The copolymer PD-PEO70 even has a much lower CO\textsubscript{2} diffusion coefficient than 6D-PEO60 and is similar in magnitude to the CO\textsubscript{2} diffusion coefficient of 6D-PEO50. Because the CO\textsubscript{2} solubility coefficient remains about the same for all copolymers, differences in CO\textsubscript{2} permeability are due to changes in the CO\textsubscript{2} diffusion coefficients.

Furthermore, 6T-PEO50 has a higher CO\textsubscript{2} permeability than the structurally similar pentiptycene-containing copolymer, as shown in Figure 4.9. This result might not be initially expected considering that the homopolyimide Pent-6FDA \cite{63,64} has a much higher CO\textsubscript{2} permeability (132 Barrer) than Trip-6FDA \cite{51,62} (20 Barrer), including higher CO\textsubscript{2} diffusion and solubility coefficients and a higher FFV. However, because pentiptycene has even larger “clefts” and more inherent internal free volume than triptycene it is sensible that the pentiptycene-containing copolymer would facilitate more PEO chain threading and residing within the pentiptycene moieties than the triptycene-containing copolymer. As such, at the same PEO content, it could be expected that pentiptycene-containing PI-PEO2000 (50\%) would have a lower CO\textsubscript{2} permeability than 6T-PEO50 due to its elevated extent of PEO chain threading and consequential more severe reduction in fractional free volume due to the filling of cavities by the PEO segments.

As done with CO\textsubscript{2}, the permeability of H\textsubscript{2} and N\textsubscript{2} for each target 50 wt% PEO-containing copolymer is plotted versus feed pressure in Figure 4.10. It is apparent for H\textsubscript{2} and N\textsubscript{2} that their permeability trends are the same as those for CO\textsubscript{2} where 6D-PEO50 has the highest permeabilities and PD-PEO60 has the lowest, with the iptycene-containing
copolymers in between. However, for H₂ and N₂ there is no plasticization with increasing feed pressure, as expected, as their permeability remains constant as the feed pressure rises. The same factors used to explain the trends in CO₂ permeability of each copolymer are applicable here to explain the similar trends of H₂ and N₂ permeability.
Figure 4.10: Pure-gas permeability of H₂ (a) and N₂ (b) versus feed pressure for target 50 wt% PEO-containing copolyimides.
4.3.4.3 Influence of PEO Content on Ideal-Gas Selectivity

For PEO-containing materials within the literature, the typical trend for CO$_2$/H$_2$ selectivity is that the selectivity increases as the content of PEO in the material increases because the chain rigidity decreases [19,33]. Similarly, for each of the copolymer series of this work, increasing the PEO content resulted in increased the CO$_2$/H$_2$ selectivity, which is demonstrated in Figure 4.11 (a) This is the expected trend because the size-sieving ability of the membrane should decrease as the amount of flexible PEO increases, [65,66] because this allows for the larger CO$_2$ molecules to experience a more significant decrease in size-restricted permeability compared to H$_2$ [65]. As shown in Figure 4.11 (b), the PEO content had a much lesser effect on the CO$_2$/N$_2$ selectivity of these copolymers. At 3 bar feed pressure, there was only a small increase in CO$_2$/N$_2$ selectivity in going from 6T-PEO20 to 6T-PEO50. However, the fact that there was a noticeable change at all could be because 6T-PEO20 has such a low PEO content that there is likely noticeable contribution of the hard segments to the gas transport properties. In other words, the gas transport in 6T-PEO20 is relatively less dominated by the PEO phase and so its CO$_2$/N$_2$ selectivity was especially low, at only 35 [67]. For the higher PEO content copolymers, no change in CO$_2$/N$_2$ selectivity was observed (outside the error bars) in the 6D and PD-series copolymers with increasing PEO content. This finding is consistent with other works that show relatively stable CO$_2$/N$_2$ selectivity over a range of PEO contents for PEO-containing materials [33,37,41].
Figure 4.11: Pure-gas CO$_2$/H$_2$ (a) and CO$_2$/N$_2$ (b) selectivity at 3 bar feed pressure for all copolyimides.
4.3.4.4 Influence of Rigid Segment Composition on Ideal-Gas Selectivity

The composition of the rigid segment of these copolymers also plays a significant role in determining the CO$_2$/H$_2$ selectivity. For instance, as shown in Figure 4.12, even for copolymers of ~50 wt% PEO content, the CO$_2$/H$_2$ selectivity varies greatly depending on the type of rigid segment. At 3 bar feed pressure, the CO$_2$/H$_2$ selectivity for PD-PEO60 is 2.6, which is only 79% of the selectivity of 3.3 for 6D-PEO50. 6D-PEO50 has a much higher CO$_2$ diffusion coefficient than PD-PEO60 and accordingly, it would be expected that the size-sieving ability of 6D-PEO50 would be lower, which promotes higher CO$_2$/H$_2$ selectivity [65]. Even at higher PEO contents, 6D-PEO60 has a CO$_2$/H$_2$ selectivity that is 73% higher than that of PD-PEO60 and is almost as high as that of PD-PEO70. Consistently, other 60 wt% PEO containing copolyimides within the literature have CO$_2$/H$_2$ selectivities that vary from 5.0 to 8.1, depending on the composition of the rigid segment [19]. In contrast to before, where the CO$_2$/N$_2$ selectivity remained relatively stable over differing PEO contents, the composition of the rigid segment has a sizeable effect on the CO$_2$/N$_2$ selectivity of these copolymers, at least at ~50 wt% PEO content. For example, the pent-PI-PEO2000 (50%) has a CO$_2$/N$_2$ selectivity of 36, which is much less than that of 6D-PEO50 at 48. The iptycene-containing PEO copolymers, at least at 50 wt% PEO, have lower CO$_2$/N$_2$ selectivities than 6D-PEO50 and PD-PEO60 copolymers. The much higher CO$_2$/N$_2$ selectivity of PD-PEO60, is probably not due to higher PEO content, but rather to its likely much higher diffusivity selectivity based on its much lower CO$_2$ diffusion coefficient. However, the reason the iptycene-containing 50 wt% PEO-based copolymers have lower CO$_2$/N$_2$ selectivities compared to 6D-PEO50 and PD-PEO60 is less straight-forward. This result can be explained by a combination of
opposing factors. For instance, the higher $T_g$’s of the iptycene-containing copolymers suggests higher overall rigidity and better diffusivity selectivity than 6D-PEO50 and PD-PEO60 but PEO chain threading may lead to the formation of less size-selective gas transport pathways that may substantially lower the CO$_2$/N$_2$ selectivity of the iptycene-containing copolymers.
Figure 4.12: Pure-gas CO\textsubscript{2}/H\textsubscript{2} (a) and CO\textsubscript{2}/N\textsubscript{2} (b) selectivity as a function of feed pressure for target 50 wt% PEO-containing copolymers.
4.3.4.5 Comparison with the Upper Bounds

The CO$_2$/H$_2$ and CO$_2$/N$_2$ ideal selectivities of these copolymers at all five feed pressures have been plotted versus CO$_2$ permeability compared to the 2008 upper bounds [68], as shown in Figure 4.13 (a) and (b), respectively. High amounts of CO$_2$ induced plasticization are shown in these copolymer membranes where both the ideal gas CO$_2$ permeability and CO$_2$/gas selectivity increased with increasing feed pressure. However, 6T-PEO20, with its low PEO content, did not exhibit plasticization as its high content of rigid segments prevented PEO swelling at least up to 17 bar feed pressure. For PEO-containing membranes, CO$_2$ induced plasticization is often observed, but in contrast to glassy materials, plasticization does not necessarily mean that gas separation performance in mixed-gas tests will suffer. On the other hand, there are cases where CO$_2$ plasticization in mixed gas tests resulted in separation performance that was essentially unchanged from pure-gas tests [67] or even improved in mixed-gas tests [19,69]. It is also worth noting the promising gas separation performance is demonstrated by PD-PEO80, however, this is only the case because of the very high PEO content that this material is able to achieve with good mechanical robustness. The PD-series copolymers, at a given PEO-content, had the lowest CO$_2$ permeability, so it would be very interesting to observe if the gas separation properties of the 6T and 6D-series copolymers would be even better than those of PD-PEO80 at PEO contents of ~80 wt%, but unfortunately due to their poor mechanical properties at such high PEO contents, this was not possible.
Figure 4.13: Upper Bound (2008) comparison of all copolymer membranes for (a) \( \text{CO}_2/\text{H}_2 \) and \( \text{CO}_2/\text{N}_2 \) gas pairs as a function of feed pressure.
4.3.5 Measurement Error

The calculation of error for data reporting is explained in Appendix A for various measurements, such as permeability, selectivity, and CO\(_2\) diffusion and solubility coefficients.

4.4 Conclusions

The PEO-containing polyimide copolymers of this work featured a non-micro-phase separated morphology. That is, there was significant mixing of the hard and soft domains of these copolymers. As such, the composition of the copolymer rigid segment of each copolymer series impacted CO\(_2\) separation performance. Likewise, within each copolymer series, the content of PEO dictated the CO\(_2\) separation ability, where increasing PEO content yielded higher CO\(_2\) permeability, relatively stable CO\(_2\)/N\(_2\) selectivity and higher CO\(_2\)/H\(_2\) selectivity, which is consistent with other PEO-based materials [19,46,67]. For the 6T-series copolymers that contain triptycene moieties, it is believed that PEO chain threading through the clefts of the triptycene units resulted in decreased FFV, lower PEO-segmental mobility and higher \(T_g\), and, at 50 wt% PEO content – lower CO\(_2\) permeability compared to the 50 wt% PEO-containing copolymer 6D-PEO50. However, there may be a beneficial aspect of PEO chain threading where such threading may allow for regions of well-connected gas transport pathways that resulted in 6T-PEO50 still having a higher CO\(_2\) permeability than PD-PEO60. The low extent of micro-phase separation of the 6T-series copolymers coupled with its flexible ether linkages in the hard segments may be responsible for the relatively poor mechanical properties of the 6T-series copolymers at high PEO contents above 50 wt%. Similarly,
the 6D-series copolymers were not mechanically robust enough to form handleable films above 60 wt% PEO content.

However, the 6D-series copolymers, with their relatively low $T_g$ values (highly mobile PEO segments) and high CO$_2$ diffusivity coefficients, yielded the best CO$_2$ separation performance at a given PEO content. This highlights a tradeoff observed with these copolymers where the PD-series copolymers at a given PEO content had the lowest CO$_2$ permeability, but with its extremely rigid hard segments and relatively high extent of micro-phase separation was able to form mechanically stable films at nearly 80 wt% PEO content, which gave PD-PEO80 the highest combination of CO$_2$ permeability and CO$_2$/gas selectivity of any of the copolymers in this study. Based on the findings of this study, at least for PEO-containing copolyimides of non-completely micro-phase separated morphologies, it is important that the PEO segments have high mobility but also that a hard segment is incorporated that is rigid enough to provide the mechanical robustness to allow for copolymers with very high PEO contents to be produced.

4.5 Bibliography


CHAPTER 5:
INTERFACIALLY POLYMERIZED PEO-CONTAINING COPOLYAMIDES WITH
VARIED HARD SEGMENT COMPOSITION, INCLUDING TRIPTYCENE-BASED,
FOR CO₂ SEPARATIONS

5.1 Introduction

The enormous scale of CO₂ emissions, largely contributed by power generation, points toward improving and enacting carbon capture technologies [1,2]. To perform CO₂ capture, membranes may be well suited and are a promising alternative technology to conventional solvent-based separation systems [3–5]. The type of polymer utilized in gas separation membranes makes a significance difference to the gas separation performance but one of the prominent class of materials studied for CO₂ separations is poly(ethylene oxide) (PEO)-containing polyamides [6]. For segmented copolymers, made up of hard and soft blocks, certain properties of the constituents allow them to microphase separate. For instance, incompatibilities as a result of differences in the degree of polymerization, volume fraction, Flory-Huggins interaction parameter, and hydrogen bonding can lead to a microphase separated structure [7–10]. This ability to microphase separate is often desired, as microphase-separated morphologies (or at least partially microphase-separated) lead to improved mechanical properties [8][9][11]. Additionally, for PEO-containing copolymers, including polyether-block-polyamide (PEBA) polymers, it appears that such microphase separated morphologies lead to higher gas permeabilities [12–14]. Of the PEBA polymers, Pebax® MH 1657 in particular is heavily studied for performing membrane-based CO₂ separations due to its microphase separated
morphology and attractive combination of mechanical robustness and good CO₂ separation ability [15]. Despite these promising characteristics of Pebax, any further improvements to the physical and CO₂-separation properties of such PEO-containing materials is welcomed for reducing operational costs and other hindrances to widespread industrial implementation. As such, polyamides are a good material option for further study because such materials can often be synthesized by very facile interfacial polymerization methods [16–20], which is in contrast to the more intensive synthesis of Pebax [9] or many polyimide materials.

It has been shown that the gas transport properties, as well as the physical and thermal properties of PEO-based copolymers are dependent on the amount of PEO within the copolymer and the chemical structure of the hard segment [12,21,22]. Differences in the PEO content or hard-segment composition can lead to varying degrees of microphase-separation which can lead to various physical properties of the material [12]. Because of the vast tunability of physical and gas separation properties of PEO-containing materials it is important to widen the knowledge of physical/property relationships by studying novel PEO-containing polyamides. Of significant interest is the effect of the triptycene moiety in the backbone of PEO-containing polyamides. Triptycene has been shown in glassy polymers to push gas separation performance to new heights as demonstrated in the ultra-microporous PIM-polyimides by Ghanem [23] and in thermally rearranged polymers in our previous study [24]. Such excellent gas separation performance (above the 2008 upper bounds for H₂/H₂, H₂/N₂, CO₂/CH₄, and O₂/N₂) is possible in these materials because the bulky triptycene units act to simultaneously disrupt the packing of polymer chains while adding chain rigidity, all while incorporating ultra-microporosity [23,24].
Not only has triptycene incorporation been shown to lead to membranes with outstanding gas separation performance, but when it was integrated into the backbone of polyesters their mechanical properties significantly improved. This finding is believed to be a result of the unique threading of polymer chains about the triptycene moieties due to the minimization of internal free volume mechanism; such threading allowed for the triptycene units to interlock when the material was under strain for better dispersion of the load [25–27]. Similarly, when pentaptycene was incorporated into the backbone of a 60 wt% PEO-containing polyimide copolymer, its Young’s modulus was ~15 times higher than the analogous copolymer, 6FDA-ODA-PEO1 [28], synthesized elsewhere, which did not include the iptycene structure [29]. However, the triptycene moiety has not yet been incorporated into PEO-containing polyamide copolymers. It is not known if the mechanical properties will likewise be improved due to chain threading and if this threading will lead to a loss of microphase separation and a loss of flexibility of the PEO segments. Such losses would likely decrease gas permeabilities, but if the mechanical properties are improved, perhaps higher PEO contents could be achieved to still provide excellent gas separation performance. In this work, four series of copolymers have been synthesized through facile interfacial polymerization techniques. Each series of copolymer contains a distinct hard segment composition (some with more triptycene or no triptycene incorporated) and within each series, the content of PEO is varied. These compositional changes allow for studying the effects of triptycene incorporation and PEO content on the qualitative mechanical properties as well as on the physical, thermal, and CO₂ separation performance of these copolyamides.
5.2 Experimental

5.2.1 Materials

The triptycene-based diacid chloride monomer utilized in this work is simply referred to as “T,” but the synthesis of this monomer has been previously reported.[24] The required materials are Anthracene (97%), potassium carbonate, Pd/C 10 wt % catalyst, and anhydrous \(N,N\)-dimethylformamide (DMF) were purchased from Alfa Aesar. \(p\)-Benzoquinone (≥98%), 4-nitrobenzonitrile (97%), thionyl chloride (≥99%), potassium hydroxide, hydrochloric acid (ACS reagent 37%), hydrobromic acid (48 wt %), glacial acetic acid (GR ACS Grade), xylenes, and toluene were purchased from Sigma-Aldrich. Methanol was purchased from BDH. Ethanol (200 proof) was purchased from KOPTEC.

The triptycene-based diamine is also referred to as “T” in this study, but the synthesis of this monomer was reported in our previous work.[30] For completeness the required materials are given here as follows: Anthracene (97%), 2-chloro-5-nitrobenzotrifluoride (98%), potassium carbonate, and Pd/C 10 wt % catalyst were purchased from Alfa Aesar. \(p\)-Benzoquinone (≥98%), hydrazine monohydrate, hydrobromic acid (48 wt %), glacial acetic acid (GR ACS Grade), xylenes, and \(N,N\)-dimethylformamide were purchased from Sigma-Aldrich. Methanol was obtained from BDH and ethanol (alcohol) was obtained from EMD.

The diacid chloride monomer, 6FC, is referred to as “6” in this study, and its synthesis has previously been reported.[31] The materials utilized in the synthesis of “6” are as given as follows: 2,2’-bis (4-carboxyphenyl)hexafluoropropane (6FAC, ≥98%)
purchased from TCI Chemicals. Thionyl chloride (≥99%) was obtained from Sigma-Aldrich and hexanes was purchased from EMD.

The remaining materials for the synthesis of PEO-containing polyamide copolymers are: Polyetheramine, Jeffamine® ED-2003 (2000 g/mol), supplied by Huntsman Co. and will be referred to as “PEO2000.” 2,4,6-trimethylbenzene-1,3-diamine (DAM, referred to as “D”) and Terephthaloyl chloride (Tc) were purchased from commercial sources. Dichloromethane (DCM) was supplied by Sigma-Aldrich.

The solvent used for film casting was N,N-dimethylacetamide (DMAc) purchased from Sigma-Aldrich or Alfa Aesar.

All reactants and reagents obtained from commercial sources were used as received without further purification.

5.2.2 Synthesis of PEO-Containing Copolyamides

All PEO-containing copolyamides of this study were synthesized by interfacial polymerization techniques. For reference, the general synthetic scheme for all copolymers is provided in Figure 5.1 and each series is denoted as “TT, 6T, 6D, or TcD” to describe the content of the hard segment.

5.2.2.1 Synthesis of PEO-Containing Copolyamides with “TT” Hard Segments

The first series of PEO-containing copolyamides features a hard segment that incorporates both the triptycene diacid chloride and diamine-based monomers, as illustrated in Figure 5.1. To synthesize these copolymers, the synthesis of TT-PEO50 (targeting 50 wt% PEO content) is described as a representative example. First, PEO2000 (0.3609 g, 0.180 mmol) was added into a 20 mL glass vial. To this same vial, NaOH
(0.0353 g, 0.857 mmol) was washed in with 3.25 mL of water. To a separate vial, triptycene diacid chloride (0.2415 g, 0.429 mmol) was added along with 11.83 g of DCM. The triptycene-diamine monomer (0.1500 g, 0.248 mmol) was added to a third vial along with 7.35 g DCM. Each solution was stirred separately and after as much dissolution as possible of the monomers at room temperature, the solution containing PEO2000 was transferred via pipette to the stirring solution of triptycene diacid chloride. These two monomers were allowed to react for at least 20 minutes before the solution of triptycene-diamine was added to this reaction vial with stirring. The reaction with all three monomers was carried out for at least 1 h (normally 2 h) and afterward the reaction vial contents were poured into and washed into a round-bottom flask with DCM and water. This flask was placed into a roto-evaporator to remove the DCM, after which the fully precipitated copolyamide product was collected by decanting the remaining water and washing with fresh water. The obtained TT-PEO50 copolymer was dried at 70 °C in a vacuum oven. To purify the product, TT-PEO50 was dissolved in DMAc to form a 10 wt% solution and precipitated by pouring into 80 mL of water. The purified copolyamide was then dried in a vacuum oven for 14 h at 120 °C.

5.2.2.2 Synthesis of PEO-Containing Copolyamides with “6T, 6D, or TcD” Hard Segments

The synthesis of the 6T, 6D, and TcD-series copolyamides follows the same general workup, precipitation, and vacuum oven drying procedures as the TT-series copolyamides, unless noted below. Exceptions to the general procedure are that the TcD-series copolyamides were finally vacuum dried at 70 °C for 10 h and that TcD-PEO70 was precipitated into warm water (60 °C), which prevented this particular copolyamide
from dissolving. Furthermore, to dissolve TcD-PEO60 in DMAc, prior to precipitation purification, LiCl had to be added to promote dissolution. Other points of interest pertain to the “at least 20 minutes” reaction step; for the 6T-series, this reaction occurred between 6FC and PEO2000 before the triptycene-diamine monomer was added; For the 6D-series, this reaction was done between 6FC and PEO2000 before DAM was added; For the TcD-series, this reaction was performed between Tc and PEO2000 before DAM was added.

5.2.3 Membrane Formation

The solution casting method was used to produce all membranes. The solubility of each copolymer varied in DMAc and therefore the solution concentration for film casting was varied as necessary for each copolyamide (8 – 23 wt% copolyamide in solution). The exception is that TcD-PEO60 and TcD-PEO70 had to be dissolved in DMSO for film casting, due to limited solubility in DMAc. Otherwise, all copolyamide solutions for film casting were stirred between room temperature and 115 °C as necessary to dissolve the copolyamide. Once dissolved, the solutions were filtered with 0.45 μm PTFE syringe filters. Each filtered solution was cast onto a level glass plate and the solvent was mostly evaporated overnight with an infrared lamp. To remove the remaining solvent, the films were dried at a final temperature of 100 °C for 14 h under vacuum. To aid in removing the films from the glass plates, each were submerged into water until they could be peeled off the plates with razor blade assistance. The soaked films were air-dried overnight and then placed into a vacuum oven to dry overnight at R.T. before characterizations. The resultant films were 77 – 145 μm in thickness.
5.2.4 Characterizations

A Bruker 400 or 500 MHz instrument was used to analyze the chemical structure of all copolyamides by $^1$H nuclear magnetic resonance with DMSO-$d_6$ solvent.

To confirm solvent removal and to determine thermal stability, a thermogravimetric analysis instrument (TGA Q500 TA Instruments) was used. Films were heated at 10 °C/min from R.T. up to 600 °C under a 60 mL/min nitrogen purge. A DSC Q2000 (TA Instruments) instrument was used to determine any glass transition temperature ($T_g$), crystallization temperature ($T_c$), or melting ($T_m$) temperature. Liquid nitrogen was used for cooling and the films were maintained under a 50 mL/min nitrogen purge. The films were cooled at a rate of 20 °C/min and heated at a rate of 10 °C/min. Films were first cooled to -100 °C, then heated to ~200 °C, cooled to -100 °C, and finally heated to 300 °C. All reported values were obtained from the second heating curve to eliminate thermal history effects.

The small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) data were obtained by the Chemical and Materials Science group at Argonne National Laboratory. The Advanced Photon Source (APS) synchrotron beamline 12-ID-B utilized an X-Ray beam wavelength of 0.9322 Å at a photon energy of 13.3 keV. A silver behenate standard was used to calibrate the q-range and the distance between the sample and the detector was 2013 mm for the SAXS detector and 430.15 mm for the WAXS detector. An exposure time of 1 second was used and the resulting two-dimensional (2D) spectra were collected with a Pilatus 2M camera for SAXS samples and with a Pilatus 300 camera for WAXS samples. The 2D spectra were converted to 1D spectra by azimuthal integration. All spectra were corrected for transmission and background
scattering and analyzed using Igor Pro-Irena SAS package to display arbitrary SAXS or WAXS intensity versus the scattering vector \( q \), where \( q = (4\pi/\lambda) \sin(\theta/2) \), and \( \lambda \) is the X-ray wavelength and \( 2\theta \) is the scattering angle.

The pure-gas permeabilities of CO\(_2\), H\(_2\), and N\(_2\) were evaluated at 35 °C by the constant-volume variable-pressure method [32]. The permeability of gas A, \( P_A \), is here calculated by Equation 5.1, and the parameters are described in Chapter 2 section 2.2.3.

\[
P_A = \frac{V_d l}{P_2 A RT} \left[ \left( \frac{dp_1}{dt} \right)_{ss} - \left( \frac{dp_1}{dt} \right)_{leak} \right] \tag{5.1}
\]

The films were first dried in a vacuum oven and then their thicknesses were obtained. The films were prepared utilizing a printer-paper support and then placed into the gas cell. After each film was loaded, the apparatus and film were degassed under strong vacuum (<0.1 torr) overnight. After degassing, the leak rate was determined and afterward the high-pressure feed stream was introduced upstream of the film. Once steady-state pressure increase occurs downstream, the permeability is calculated by Equation 5.1.

The ideal selectivity [33], \( \alpha_{A/B} \), was calculated by Equation 5.2 to determine the separation capability of each copolyamide film.

\[
\alpha_{A/B} = \frac{P_A}{P_B} \tag{5.2}
\]

The apparent CO\(_2\) diffusion coefficient, \( D \), of each copolyamide membrane was estimated by the time-lag method with Equation 5.3 [22]. In this equation, the time-lag is given by \( \theta \) (s) and the thickness of the membrane is \( l \) (cm). Once the diffusion coefficient
is estimated, the solubility coefficient, $S$, is easily determined by the relation $P = D \times S$ [22].

$$D = \frac{l^2}{6\theta}$$ (5.3)
Figure 5.1: General synthetic scheme for PEO-containing polyamide copolymers, i.e., X-PEOY (“X” describes the composition of the rigid segment (TT, 6T, 6D, or TcD) and “Y” denotes the overall weight percent of PEO in the copolymers).
5.3 Results and Discussion

5.3.1 Synthesis of PEO-Containing Copolyamides

All copolyamides were polymerized interfacially with DCM and water as the two immiscible phases. In order to achieve the desired PEO content within each copolyamide a two-step synthetic approach was utilized. For instance, during the synthesis of each copolyamide, the diacid chloride and PEO-diamine monomers were first reacted together for approximately 20 minutes. After this initial reaction, that to some extent endcaps the PEO-diamines with the acid chloride moieties, the rigid diamine monomers are added to the reaction vial with vigorous stirring. After collection and drying, explained in Sections 5.2.2.1 and 5.2.2.2, each copolymer was analyzed by $^1$H NMR to confirm that the correct PEO content and correct chemical structure were obtained. The $^1$H NMR estimated PEO contents are provided in Table 5.1 were it is clear that the estimated PEO contents match well with the target contents. Figure 5.2 is also provided as a representative example that shows the $^1$H NMR spectra of each 60 wt% PEO-containing copolyamide from each of the four copolyamide series.
TABLE 5.1
TARGET PEO CONTENT AND $^1$H NMR ESTIMATED PEO CONTENT OF ALL COPOLYAMIDES

<table>
<thead>
<tr>
<th>Film</th>
<th>Target PEO wt%</th>
<th>Estimated PEO wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TT-PEO50</td>
<td>50</td>
<td>53</td>
</tr>
<tr>
<td>TT-PEO60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>6T-PEO50</td>
<td>50</td>
<td>49</td>
</tr>
<tr>
<td>6T-PEO60</td>
<td>60</td>
<td>61</td>
</tr>
<tr>
<td>6D-PEO50</td>
<td>50</td>
<td>47</td>
</tr>
<tr>
<td>6D-PEO60</td>
<td>60</td>
<td>58</td>
</tr>
<tr>
<td>6D-PEO70</td>
<td>70</td>
<td>67</td>
</tr>
<tr>
<td>TcD-PEO60a</td>
<td>60</td>
<td>61</td>
</tr>
<tr>
<td>TcD-PEO70</td>
<td>70</td>
<td>68</td>
</tr>
</tbody>
</table>

*aWould not completely dissolve in DMSO-$d_6$. 
Figure 5.2: $^1$H NMR spectra (DMSO-$d_6$) of target 60 wt% PEO-containing copolyamides.
5.3.2 Thermal Properties of PEO-Containing Copolyamides

The thermal properties of each copolyamide, from TGA and DSC analysis, are reported in Table 5.2. According to TGA, the temperature of the 10 wt% loss for these copolymers is above 350 °C, with the analysis starting from 100 °C to ensure that absorbed moisture from the atmosphere has been removed. DSC analysis reveals that all copolyamides have just one T\text{g}, as shown in Figure 5.3, despite the various hard segment compositions and various PEO contents. The presence of only one T\text{g} for each copolymer indicates that all copolyamides here do not exhibit a micro-phase separated morphology [34].

### TABLE 5.2

**THERMAL PROPERTIES OF ALL COPOLYAMIDES**

<table>
<thead>
<tr>
<th>Film</th>
<th>T\text{g} (°C)</th>
<th>T\text{c} (°C)</th>
<th>T\text{m} (°C)</th>
<th>Crystallinity (%)</th>
<th>T\text{d}(10 wt%) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TT-PEO50</td>
<td>31</td>
<td>-7</td>
<td>397</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TT-PEO60</td>
<td>-7</td>
<td>391</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6T-PEO50</td>
<td>29</td>
<td>393</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6T-PEO60</td>
<td>-10</td>
<td>387</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6D-PEO50</td>
<td>-44</td>
<td>383</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6D-PEO60</td>
<td>-45</td>
<td>362</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6D-PEO70</td>
<td>-50</td>
<td>-9</td>
<td>22</td>
<td>17.9</td>
<td>376</td>
</tr>
<tr>
<td>TcD-PEO60\text{a,b}</td>
<td>-53</td>
<td>-29</td>
<td>18</td>
<td>~13.7</td>
<td>371</td>
</tr>
<tr>
<td>TcD-PEO70</td>
<td>-52</td>
<td>-15</td>
<td>18</td>
<td>15.6</td>
<td>369</td>
</tr>
</tbody>
</table>

\text{a} Not fully soluble in DMSO for film casting.

\text{b} Soaked in methanol to remove DMSO solvent.
Figure 5.3: The second heating traces of DSC analysis for all copolyamides and the non-PEO-containing pure hard-segment, 6T-PEO0, of the 6T-series.

The 60 wt% PEO-containing copolyamides were analyzed by SAXS/WAXS, as shown in Figure 5.4 (a), and the absence of scattering peaks indicative of micro-phase separation confirm, at least for the 60 wt% PEO-containing copolyamides, that fully micro-phase separated morphologies do not exist. It should be noted that the spectra for TcD-PEO60 in Figure 5.4 (a) and (b) may not be reliable for analysis because this sample was unexpectedly found to contain ~7 wt% residual DMSO solvent from film casting.
The remaining solvent may be the cause of the striking sharp peaks in the WAXS spectral region highlighted in Figure 5.4 (b). However, the typical PEO crystallization peaks at 2θ = 19° and 23° (q ~2.22 Å⁻¹ and ~2.69 Å⁻¹) cannot be observed in this limited-range WAXS spectra for any of the 60 wt% PEO-containing copolyamides [28,35,36]. The absence of crystallinity is confirmed in the DSC analysis for these 60 wt% PEO-containing copolyamides as no crystallization peaks were present, except for TcD-PEO60, however this specific sample underwent an additional step of methanol soaking, compared to the SAXS/WAXS sample, to remove residual DMSO and this additional workup could have led to the appearance of PEO crystallization in the DSC run. As tabulated in Table 5.2, no crystallinity is observed for these copolyamides except for TcD-PEO60 and the 70 wt% PEO-containing copolyamides. This finding is typical, as other PEO-containing copolymers within the literature also begin to show significant PEO crystallinity near and above a PEO content of 60 wt% [14,21,28,37]. However, under gas permeation testing all films are believed to be fully amorphous at a temperature of 35 °C as even the highest melting temperature of 22 °C for 6D-PEO70 is sufficiently below the testing temperature.
Figure 5.4: (a) SAXS/WAXS spectra and (b) WAXS spectra of the ~60 wt% PEO-containing copolyamides from each copolymer series. “Sample contains ~7 wt% residual DMSO solvent.

An interesting result is apparent when observing the glass transition temperatures of these copolyamides. At a given PEO content, for example at 50 or 60 wt%, the copolyamides that incorporate the triptycene moiety into their hard segments display significantly higher $T_g$’s than the copolyamides that do not include triptycene. Related results have been observed elsewhere, where triptycene incorporation led to higher $T_g$’s [26,38] or to relatively very high $T_g$ values [25,29]. It is likely that the same mechanisms that give rise to the relatively high $T_g$ values of triptycene-including polymers also give rise to their often improved mechanical properties. It is believed that triptycene incorporation promotes polymer molecular threading and molecular interlocking interactions which act to enhance the mechanical properties of polymers that include triptycene within their backbones [25,26,29,38]. In light of these results of other triptycene including polymers, it appears that the minimization of internal free volume mechanism, which promotes polymer chain threading through the cavities of the
triptycene moieties [26], is acting on the PEO segments of the TT and 6T-series copolyamides to confine them by the triptycene moieties during chain threading to significantly increase their $T_g$’s above those of the comparable 6D and TcD-series copolyamides of the same PEO contents. For instance, the $T_g$ of TT-PEO50 is a striking 75 °C higher than that of 6D-PEO50, even though both contain 50 wt% PEO.

At a given PEO content the triptycene-containing copolyamides have by far the highest $T_g$ values of the copolyamides investigated in this study. Such a result may be due to the TT and 6T-series copolyamides having a lower extent of micro-phase separation compared to the 6D and TcD-series copolyamides. By the two-phase model and the Fox equation, the content of the copolyamide hard segment in the soft segment domain can be estimated by Equation 5.4 [12].

$$\frac{1}{T_{g,c}} = \frac{1 - W_{HS}}{T_{g,s}} + \frac{W_{HS}}{T_{g,h}}$$ (5.4)

In Equation 5.4, $T_{g,s}^*$ and $T_{g,h}^*$ are the glass transition temperatures of the pure soft and hard segments, respectively, and $T_{g,c}$ is the observed lower glass transition temperature (if two $T_g$’s are present) of the copolymer. This equation is solved for $W_{HS}$, which is the content of the hard segment in the soft segment domain. Unfortunately, the glass transition temperatures of the pure TT, 6D, and TcD-series hard segments are not known. This means that this analysis can only be carried out for the 6T-series copolymers as the $T_g$ of the pure 6T-series hard segment was found to be 287 °C, as shown in Figure 5.3. Regardless, for the 6T-series copolyamides there is a very high presence of hard segments of the 6T-series in the soft domains at 47 wt% and 30 wt% for 6T-PEO50 and 6T-PEO60, respectively. Such high extent of mixing of the hard and soft segments of the
6T-series copolyamides is consistent with the idea of PEO segment threading through the cavities between the triptycene “blades.” A drawback to this mixing estimation is that it cannot take into consideration supramolecular inter-chain interactions due to the triptycene moiety and as such may or may not provide an accurate estimation. Regardless, it is still reasonable to explain the relatively high \( T_g \) values of the TT and 6T-series copolyamides as a result of chain-threading and therefore hard and soft segment mixing. In other words, at a given PEO content, the extent of micro-phase separation, though not complete, is higher for the 6D and TcD-series copolyamides; evidence for this claim is that their significantly lower \( T_g \)’s approach that of pure Jeffamine® ED-2003 (-59.0 °C) [39], which is expected with more micro-phase separation [9,40]. The extent of micro-phase separation is important because it can influence every physical property, including mechanical properties, as discussed below [9,12,41].

5.3.3 Qualitative Mechanical Properties of Copolyamides

The ability to form mechanically robust, handleable films from these copolyamides varied significantly depending on the composition of the hard segment at high PEO contents. In opposition to the previously highlighted studies of iptycene-enhanced mechanical properties, the triptycene-containing copolyamides (TT and 6T-series) were the most limited mechanically at high PEO contents. While the TT and 6T-series copolyamides at just 60 wt% PEO content were relatively soft and tacky and could not form handleable films at higher PEO contents, the 6D and TcD-series copolyamides could easily form robust films up to and including 70 wt% PEO content. The significantly improved mechanical properties, at high PEO content, of the 6D and TcD-series copolyamides is likely due to two related factors that influence micro-phase
separation. As discussed in the previous section on thermal properties, it is believed that the 6D and TcD-series copolyamides exhibit much higher degrees of micro-phase separation compared to the triptycene-containing TT and 6T-series copolyamides. As mentioned previously, this could enhance their mechanical properties. Another potentially contributing factor is the presence of flexible ether linkages in the backbone of the hard segments of the TT and 6T-series copolyamides. It has been observed in other PEO-containing copolymers that incorporating dianhydrides with higher rigidity led to increased micro-phase separation and improved mechanical properties [21]. Such findings can be used to highlight how important chain rigidity can be, even in PEO-containing materials, and the potential mechanical downside of including flexible ether linkages in the backbone of the hard segments of these copolyamides.

5.3.4 Pure-Gas Transport Properties of PEO-Containing Copolyamides

Pure-gas permeation tests were conducted at 35 °C for CO₂, H₂, and N₂ at five distinct feed pressures between 3 and 17 bar. The 3 bar permeability and selectivity data for all copolyamide membranes is provided in Table 5.3.
TABLE 5.3

PURE-GAS PERMEABILITY AND IDEAL SELECTIVITY (3 BAR, 35 °C)

<table>
<thead>
<tr>
<th>Film</th>
<th>P (CO₂)</th>
<th>P (H₂)</th>
<th>P (N₂)</th>
<th>α (CO₂/H₂)</th>
<th>α (CO₂/N₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TT-PEO50</td>
<td>6.0</td>
<td>4.6</td>
<td>0.13</td>
<td>1.3</td>
<td>47.0</td>
</tr>
<tr>
<td>TT-PEO60</td>
<td>11.0</td>
<td>6.8 – 4.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.36</td>
<td>2.6&lt;sup&gt;b&lt;/sup&gt;</td>
<td>30.3</td>
</tr>
<tr>
<td>6T-PEO50</td>
<td>13.3</td>
<td>8.3</td>
<td>0.28</td>
<td>1.6</td>
<td>48.3</td>
</tr>
<tr>
<td>6T-PEO60</td>
<td>NA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10.2 – 7.9&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.52</td>
<td>NA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>NA&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>6D-PEO50</td>
<td>24.0</td>
<td>7.8</td>
<td>0.58</td>
<td>3.1</td>
<td>41.5</td>
</tr>
<tr>
<td>6D-PEO60</td>
<td>52.3</td>
<td>11.9</td>
<td>1.22</td>
<td>4.4</td>
<td>42.7</td>
</tr>
<tr>
<td>6D-PEO70</td>
<td>100.6</td>
<td>16.1</td>
<td>2.25</td>
<td>6.3</td>
<td>44.6</td>
</tr>
<tr>
<td>TcD-PEO60</td>
<td>83.2</td>
<td>12.7</td>
<td>1.69</td>
<td>6.6</td>
<td>49</td>
</tr>
<tr>
<td>TcD-PEO70</td>
<td>120.1</td>
<td>17.1</td>
<td>2.52</td>
<td>7.0</td>
<td>47.7</td>
</tr>
</tbody>
</table>

<sup>a</sup>Membrane exhibited unusual decrease in permeability with time.
<sup>b</sup>Pure-gas selectivity increased with time.
<sup>c</sup>The membrane ruptured under permeation testing and steady state data is not available.

5.3.4.1 Effects of PEO Content on Gas Permeability

In Figure 5.5 it can be seen that within each copolyamide series, the CO₂ permeability significantly increased with increasing PEO content, which is expected based on other PEO-containing copolymers [12,28,39,42]. For the TT and 6T-series copolyamides the CO₂ permeability nearly doubled each time the overall content of PEO increased by 10 wt%. The TcD-series also shows a large increase in CO₂ permeability in going from TcD-PEO60 to TcD-PEO70, but this increase is only a factor of 1.44 instead of ~2. However, this discrepancy could be due to the limited solubility of TcD-PEO60 for film casting and its unique film-submersion in methanol to remove residual DMSO.
Figure 5.5: CO$_2$ permeability (Barrer) of all copolyamides at 3 bar feed pressure. Data is not available for 6T-PEO60.

To more deeply investigate the factors influencing the permeation properties of these copolyamides, the CO$_2$ diffusion and solubility coefficients have been calculated by the time-lag method and are graphically represented in Figure 5.6. Especially when the error bars are considered, there is very little difference between CO$_2$ solubility coefficients within and between each copolyamide series. However, the CO$_2$ solubility coefficient is anomalously low for 6D-PEO70 and the reason is unknown however, its actually solubility coefficient is expected to be similar to those of 6D-PEO50 and 6D-PEO60. Regardless, differences in CO$_2$ permeability between series, at a given PEO content, are primarily due to differences in the CO$_2$ diffusion coefficients. Similarly, within each copolyamide series, the significant CO$_2$ permeability increase with increasing
PEO content is primarily a result of increasing CO\(_2\) diffusion coefficients. This result is consistent with the lower \(T_g\) values and higher segmental mobility [43] at higher PEO contents. Furthermore, other works have shown that the CO\(_2\) diffusion coefficients significantly increase with increasing PEO content with relatively little change to CO\(_2\) solubility coefficients [12,28].

![Figure 5.6: CO\(_2\) diffusion coefficient (left axis) and CO\(_2\) solubility coefficient (right axis) of copolyamide membranes (3 bar, 35 °C).](image)

As with CO\(_2\) permeability, significant increases in both H\(_2\) and N\(_2\) permeabilities were observed with increasing PEO content within each copolyamide series, as highlighted in Figure 5.7. Another interesting finding that can be seen in Figure 5.7 (a) is that for TT-PEO60 and 6T-PEO60 the H\(_2\) permeability significantly decreased from their original values. For both copolyamides, H\(_2\) permeability tests were conducted as normal
on the first day going through all 5 feed pressures up to 17 bar and then degassed overnight. However, the H₂ permeability decreased with time and with increasing pressure. To investigate this unusual trend, the H₂ permeability for these two copolyamides was again tested on the next day. The arrows in Figure 5.7 (a) for TT-PEO60 and 6T-PEO60 show the change in the H₂ permeability at 3 bar feed pressure on the first day to the obtained H₂ permeability at 3 bar feed pressure on the second day. After all permeation tests were conducted on these two copolyamides it was found that both films had been driven into their filter-paper supports. This clearly shows the limited mechanical strength of these two copolyamides, at 60 wt% PEO content, which suffered severe membrane deformation and presumably compaction. Thus, the decreasing H₂ permeabilities with time and pressure of these two copolyamides is likely due to membrane compaction and effects of being driven into the filter paper support.
Figure 5.7: Pure-gas $\text{H}_2$ (a) and $\text{N}_2$ (b) permeability of all copolyamides (3 bar, 35 °C).
5.3.4.2 Effects of Copolyamide Hard Segment Composition on Gas Permeability

Despite the relatively high CO$_2$ permeabilities and often excellent gas separation performance of glassy polymers that incorporate tryptycene [23,44,45] those characteristics were not observed for the TT and 6T-series copolyamides of this work.

As shown in Figure 5.8, at a given PEO content of either 50 wt% or 60 wt% the triptycene-containing copolyamides maintain the lowest CO$_2$ permeabilities, compared to the 6D and TcD-series, at all feed pressures. It is striking that at 50 wt% PEO, the copolyamide 6D-PEO50 has a CO$_2$ permeability that is ~4 fold that of TT-PEO50, over the entire feed pressure range. Even at 60 wt% PEO content, 6D-PEO60 keeps a 4.6 – 5 fold improvement in CO$_2$ permeability compared to TT-PEO60 over the 3 – 17 bar feed pressure range. However, some of this improved CO$_2$ permeability for 6D-PEO60 is possibly due to the weak mechanical properties of TT-PEO60 which lead to membrane compaction and deformation into the filter paper. Furthermore, the CO$_2$ permeability of 6T-PEO50, which has an intermediate amount of triptycene, falls between that of TT-PEO50 and 6D-PEO50. Taken together, these results are consistent with the higher T$_g$ values of the triptycene-containing copolyamides which are believed to exhibit PEO chain threading and restricted chain mobility that leads to overall lower permeabilities. Therefore, it is consistent in these copolyamides that as the content of triptycene increases, and PEO threading increases, the CO$_2$ permeability decreases.
Figure 5.8: CO$_2$ permeability for the 50 wt% PEO content (a) and 60 wt% PEO (b) copolyamide membranes as a function of feed pressure
Even at higher PEO contents of 70 wt%, there are differences in the CO$_2$ permeabilities between the 6D and TcD-series copolyamides. As shown in Figure 5.9, the composition of the rigid segment still plays an important role, even when only making up only 30 wt% of the copolymer. The CO$_2$ permeability of TcD-PEO70 is approximately 20 % higher than that of 6D-PEO70 at every feed pressure. The T$_g$ of TcD-PEO70 at -52°C, is 2 °C lower than that of 6D-PEO70 and this is at least some evidence of more flexible and mobile polymer segments for TcD-PEO70, which is known to increase permeability [46,47]. The comparison between TcD-PEO60 and 6D-PEO60 is more ambiguous however due to the solubility issue of TcD-PEO60 in DMSO for film casting and due to the unique methanol soak that TcD-PEO60 experienced. Regardless, the CO$_2$ permeability for TcD-PEO60 was about 60 % higher than that of 6D-PEO60 and this is consistent with the much lower T$_g$, and thus more mobile segments, of TcD-PEO60 at -53°C compared to that of 6D-PEO60 at -45 °C. Unfortunately, how much the unique workup procedure contributes to this higher permeability of TcD-PEO60 is not known and thus the effects of differences in hard-segment compositions on permeability is not explicit.
The composition of the hard segment impacts CO₂ permeability by primarily influencing the CO₂ diffusion coefficients, rather than CO₂ solubility coefficients, of these copolyamides. Again, referencing Figure 5.6, it appears that the higher the triptycene content, at a given PEO content, the lower the CO₂ diffusion coefficient. For example, the CO₂ diffusion coefficients of TT-PEO50, 6T-PEO50, and 6D-PEO50 are 4.3, 7.1, and 14.3 \(10^{-8}\) cm\(^2\)/s, respectively, which makes the CO₂ diffusion coefficient of TT-PEO50 less than one-third that of 6D-PEO50. Similarly, even at 60 wt% PEO content, the CO₂ diffusion coefficient of TT-PEO60 is only one-fifth that of 6D-PEO60 (6.1 compared to 30.4 \(10^{-8}\) cm\(^2\)/s)). The relatively low CO₂ diffusion coefficients of the TT and 6T-series copolyamides at a given PEO content are consistent with the high T\(_g\)'s due to chain threading and restricted PEO segmental mobility of the TT and 6T-series.
copolymers. These findings further support the importance of incorporating chemical structures into the polymer backbone that will allow for non-restricted PEO-segmental mobility to increase CO₂ permeability.

5.3.4.3 Influence of PEO Content and Hard-Segment Composition on CO₂/Gas Selectivity

The CO₂/H₂ and CO₂/N₂ selectivities are plotted in Figure 5.10 for the 6D-series copolyamides (the only series with three distinct PEO contents) versus feed pressure. However, for 6D-PEO70 the permeability of H₂ and N₂ (for selectivity calculations) were only evaluated at 3 bar feed pressure. As shown in Figure 5.10 (a), the CO₂/H₂ selectivity increased as the content of PEO increased, which is consistent with other PEO-containing materials [22,28,48]. As the PEO content increases in these copolyamides, the chain flexibility also increases, as evidenced by lower T_g values, which reduces the size-sieving ability to increase CO₂/H₂ selectivity [49,50]. On the other hand, as shown in Figure 5.10 (b) the CO₂/N₂ selectivity remains relatively stable with increasing PEO content, which is also observed in other PEO-containing materials [12,21,48]. Stable CO₂/N₂ stability with increasing PEO content is frequently observed due to the competing effects of increased CO₂ solubility (selectivity) and diffusivity with increasing PEO content and the increased chain flexibility which more-so favors the mobility of larger N₂ molecules [48].
Figure 5.10: Pure-gas CO$_2$/H$_2$ (a) and CO$_2$/N$_2$ (b) selectivity versus feed pressure for the 6D-series copolyamides.
The composition of the hard segment, at a given PEO content, does impact the CO\textsubscript{2}/H\textsubscript{2} selectivity as shown in Figure 5.11. For example, in Figure 5.11 (a), the non-triptycene containing 6D-PEO50 copolyamide, at 3 bar feed pressure, has a CO\textsubscript{2}/H\textsubscript{2} selectivity that is 92% higher than that of 6T-PEO50 and 138% higher than that of TT-PEO50. Furthermore, at 3 bar feed pressure, even at 60 wt% PEO content the CO\textsubscript{2}/H\textsubscript{2} selectivity of 6D-PEO60 is still 66% higher than that of TT-PEO60, and that of TcD-PEO60 is 149% higher than that of TT-PEO60. It is apparent from these trends, in combination with the relatively high T\textsubscript{g}’s and low CO\textsubscript{2} diffusion coefficients of the triptycene-containing copolyamides that the TT and 6T-series copolyamides have stronger size-sieving capability than do the 6D and TcD-series copolyamides. However, differences due to hard-segment composition seem to strongly lessen or even disappear (if error bars are taken into account) at 70 wt% PEO content. As shown in Figure 5.11 (c) the CO\textsubscript{2}/H\textsubscript{2} selectivity of TcD-PEO70 is only 12% higher than that of 6D-PEO70 and the overlapping error bars make this difference less confident. It is reasonable that at such high PEO contents, the CO\textsubscript{2}/H\textsubscript{2} separation characteristics would converge towards those of pure PEO.
Figure 5.11: Pure-gas CO$_2$/H$_2$ selectivity versus feed pressure for 50 wt% (a), 60 wt% (b), and 70 wt% (c) PEO-containing copolyamides.
In contrast to the large differences in CO\textsubscript{2}/H\textsubscript{2} selectivity between the copolyamide series at 50 wt% PEO content, there are no significant differences in CO\textsubscript{2}/N\textsubscript{2} selectivity at 50 wt% PEO content between series, as shown in Figure 5.12 (a). For the 60 wt% PEO-containing copolyamides there is a very small difference in CO\textsubscript{2}/N\textsubscript{2} selectivity at low feed pressures between the 6D and TcD-series copolyamides but this subtle difference narrows with increasing feed pressure to be essentially negligible when the error bars are considered. However, the CO\textsubscript{2}/N\textsubscript{2} selectivity of TT-PEO60 is anonymously low and a satisfactory explanation has not been determined. In any case, at 70 wt% PEO content, as shown in Figure 5.12 (c), there are little or no appreciable differences in CO\textsubscript{2}/N\textsubscript{2} selectivity between the 6D and TcD-series copolyamides. For this copolyamides there is in general very little difference in CO\textsubscript{2}/N\textsubscript{2} selectivity between series at a given PEO content. This observation can in part be rationalized because the N\textsubscript{2} and CO\textsubscript{2} have more similar kinetic diameters (3.64 vs. 3.30, respectively) than do H\textsubscript{2} and CO\textsubscript{2} (2.89 vs. 3.30, respectively) [51] which suggests that size-sieving effects would be less pronounced for CO\textsubscript{2}/N\textsubscript{2} than for CO\textsubscript{2}/H\textsubscript{2}.
Figure 5.12: Pure-gas CO$_2$/N$_2$ selectivity versus feed pressure for 50 wt% (a), 60 wt% (b), and 70 wt% (c) PEO-containing copolyamides.
5.3.4.4 Upper Bound Comparison

The CO$_2$ gas permeabilities and CO$_2$/H$_2$ and CO$_2$/N$_2$ selectivities for all copolyamides are plotted on the 2008 upper bounds [52] in Figure 5.13 (a) and (b), respectively. Each copolyamide is plotted with five data points, one for each of the five feed pressures tested (except for 6D-PEO70 which was only tested at 3 bar feed pressure). For all copolyamides tested here, the trend of increasing CO$_2$ permeability with increasing CO$_2$/gas selectivity was observed with increasing feed pressure from 3 to 17 bar for these pure-gas tests, which is indicative of CO$_2$-plasticization. The copolyamide, TcD-PEO70, displayed the best CO$_2$-separation performance and surpassed the CO$_2$/H$_2$ upper bound at all feed pressures and approached the CO$_2$/N$_2$ upper bound at the highest feed pressures. The blue arrows on the upper bound plots indicate the performance of Pebax® MH 1657 [43], which is one of the most prominently studied PEO-containing copolyamides utilized in blend and mixed matrix membranes due to its attractive CO$_2$ separation properties; it is noted that TcD-PEO70 exhibits nearly identical CO$_2$ separation performance to Pebax® MH 1657 for CO$_2$/H$_2$ and CO$_2$/N$_2$ separations.
Figure 5.13: All copolyamide membranes plotted on the Upper Bound (2008) for CO₂/H₂ (a) and CO₂/N₂ (b) separations at all feed pressures tested. Arrows point to the separation performance of Pebax® MH 1657 at 35 °C and 7 bar feed pressure [43].
5.3.5 Measurement Error

The calculation of error for data reporting is explained in Appendix A for various measurements, such as permeability, selectivity, and CO\textsubscript{2} diffusion and solubility coefficients.

5.4 Conclusions

This work utilized facile interfacial polymerization methods to synthesize four distinct series of PEO-containing copolyamides, where each series contained a hard segment of unique composition. Furthermore, within each copolyamide series, the PEO content was systematically varied so that the effects on the physical, thermal, and gas separation properties of these copolyamides could be related to their hard segment compositions and PEO contents. Of high interest was the effect of incorporating the triptycene moiety into PEO-containing copolyamides. Unexpectedly, incorporating triptycene into the backbone of these copolyamides did not qualitatively improve the mechanical properties as it had done in other polymers [25–27,29]. On the other hand, these findings are consistent with the chain-threading mechanism that would be expected to limit the micro-phase separation of the rubbery and glassy domains of these copolyamides, which may also limit their mechanical properties [8,9,11,12,21,41]. Further evidence in support of PEO chain-threading through the triptycene moieties is that the triptycene-containing copolyamides, at a given PEO content, had significantly higher glass transition temperatures, lower CO\textsubscript{2} diffusion coefficients, and lower CO\textsubscript{2} permeabilities than the non-triptycene containing copolyamides at the same PEO contents. The non-triptyene containing copolyamide, TcD-PEO70, that remained
mechanically stable at 70 wt% PEO content yielded the best CO$_2$ separation performance that was above the 2008 upper bound for CO$_2$/H$_2$ and approached the CO$_2$/N$_2$ upper bound. Furthermore, the CO$_2$/H$_2$ and CO$_2$/N$_2$ separation performance of TcD-PEO70 was nearly identical to that of the heavily investigated PEO-containing polyamide, Pebax® MH 1657.

5.5 Bibliography


6.1 Conclusions

Crosslinked poly(ethylene oxide) (PEO) networks were studied in Chapter 2. It was found in these membranes that the CO$_2$ separation performance could be significantly enhanced by decreasing the crosslink density. When the average PEO-segment length between crosslink junctions was increased from 533 to 1000 g/mol, the CO$_2$ permeability improved from 153 Barrer to 376 Barrer, the CO$_2$/H$_2$ selectivity improved from 7.2 to 10.1, and the CO$_2$/N$_2$ selectivity remained stable, all at 3 bar feed pressure. These results were due to the combined effects of increasing CO$_2$ diffusion and solubility coefficients with decreasing crosslink density. Furthermore, the introduction of crosslink inhomogeneity was also able to enhance CO$_2$ separation ability. The uneven distribution of crosslinks resulted in the bimodal and clustered films having higher CO$_2$ permeability, higher CO$_2$/H$_2$, and the same CO$_2$/N$_2$ selectivity as the counterpart unimodal films.

In Chapter 3, semi-interpenetrating polymer networks (s-IPNs) of PEO-based polymers are reported. The s-IPN platform yielded membranes that combined the good mechanical properties of glassy, linear polyimide constituents and the excellent CO$_2$ separation performance of purely crosslinked PEO into stand-alone membranes with well-rounded properties. It was found that incorporating PEO into the linear penetrating polyimides and decreasing the PEO crosslink density both improved the CO$_2$ permeability and CO$_2$/H$_2$ and maintained the CO$_2$/N$_2$ selectivity. These results highlight
the critical role of the distribution and connectivity of PEO domains and segments in PEO-containing membranes. The s-IPN platform is thus shown as a very viable way of mitigating the drawbacks of weak mechanical properties of purely crosslinked PEO and the potentially low CO$_2$ permeabilities of linear polyimides, all while providing attractive CO$_2$ separation performance.

Hard-soft segmented polyimide copolymers incorporating PEO are studied in Chapter 4. Three series of copolymers were studied where the composition of the hard-segments was varied from one series to another. Furthermore, within each series, the content of PEO within the copolymers was systematically varied to allow for comparisons between series. These copolymers exhibited non-micro-phase separated morphologies. It was found that no matter the composition of the hard-segment, increasing the content of PEO resulted in significantly increased CO$_2$ permeability, increased CO$_2$/H$_2$ selectivity, and relatively stable CO$_2$/N$_2$ selectivity. The 6T-series copolymers, those that included triptycene moieties in the hard-segments, showed evidence of PEO chain threading. The PEO chain threading resulted in much higher glass transition temperatures for the 6T-series at a given PEO content than those of the 6D and PD-series copolymers. Furthermore, due to chain threading it is believed that the CO$_2$ permeability was reduced in the 6T-series compared to the 6D-series but that such threading may also provide efficient CO$_2$ transport pathways that resulted in improved CO$_2$ permeabilities compared to the PD-series. Furthermore, the mechanical properties varied widely between series. The triptycene-containing 6T-series did not show the expected improved mechanical properties as the significant extent of PEO chain threading resulted in high degrees of mixing of the hard and soft domains, which
decreased the mechanical properties. On the other hand, the PD-series copolymers incorporated very rigid hard segments that led to less mixing of the hard and soft domains, which is believed to have enabled for much better mechanical properties that allowed for forming robust films at very high, nearly 80 wt% PEO content.

Interfacially polymerized polyamide-based PEO-containing copolymers are studied in Chapter 5. This work demonstrates the utility in employing facile interfacial polymerization techniques for producing PEO-containing polyamide copolymers. Similarly to Chapter 4, this work studies the effects of varied PEO-contents and varied hard-segment compositions in copolyamides. The triptycene-containing copolyamides showed much evidence for PEO chain threading as their CO$_2$ diffusion coefficients and CO$_2$ permeabilities were lower and their T$_g$’s were significantly higher, at a given PEO content, compared to the non-triptycene-containing copolyamides. Regardless of the composition of the hard-segment, increasing the PEO content resulted in improved CO$_2$ separation performance. Furthermore, the composition of the hard-segment significantly impacted the mechanical properties, where for example, the triptycene-containing copolyamides could not form mechanically stable films at and above 60 wt% PEO content, whereas the TcD-series copolyamides could easily form robust films at 70 wt% PEO content that displayed excellent CO$_2$ separation properties, comparable to those of the commercially available copolyamide, and heavily studied, Pebax® MH 1657.

6.2 Recommendations

The CO$_2$ separation properties of membranes containing poly(ethylene oxide) (PEO) have been demonstrated in this work to be very attractive. For crosslinked PEO
membranes, the results of this study indicate that in order to improve CO\textsubscript{2} separation performance the crosslink density should be reduced. Reducing the crosslink density can be accomplished by using longer PEO-segments between crosslink junctions or perhaps by forming partially crosslinked and partially branched network membranes. In addition, further improvements in CO\textsubscript{2} separation performance can be achieved at a given crosslink density by introducing inhomogeneity in the distribution of crosslink junctions. Introducing inhomogeneity may disrupt chain packing and provide efficient CO\textsubscript{2} transport pathways for enhanced CO\textsubscript{2} separation performance.

The semi-interpenetrating network (s-IPN) platform is very encouraging for combining the desirable mechanical properties of glassy polymers with the excellent CO\textsubscript{2} separation properties of purely crosslinked PEO. Further improvements in CO\textsubscript{2} separation performance could potentially be achieved by reducing the crosslink density and/or by further increasing the PEO-content in the linear penetrating polyimide components. In addition, s-IPNs do not have to include polyimide-based linear components and thus polyamide or other polymer types could be explored. There is reason to believe for s-IPNs that utilizing linear components that already display high CO\textsubscript{2} separation performance may increase the CO\textsubscript{2} separation abilities of s-IPNs at a given PEO content and crosslink density.

As demonstrated in this work, polyimide- and polyamide-based PEO-containing copolymers of hard and soft segments can also display very promising CO\textsubscript{2} separation performance with qualitatively good mechanical properties. To increase the CO\textsubscript{2} permeability and separation performance, PEO-containing copolymers should be produced with the highest amount of non-crystallized PEO as possible while still
maintaining necessary mechanical properties. However, at a given PEO content, the composition of the hard-segment can significantly impact CO₂ separation performance. Accordingly, hard-segments that promote micro-phase separation between the soft PEO domain and the hard-segment domain should be utilized. Hard-segments that incorporated the triptycene moiety led to PEO chain-threading, reduced micro-phase separation and weak mechanical properties at high PEO contents. Non-triptycene-containing and very rigid hard-segments led to higher degrees of microphase separation and also yielded membranes that could support higher PEO contents while remaining mechanically robust. Thus, future work should focus on maximizing micro-phase separation and/or structural factors that allow PEO to exhibit high mobility and potentially higher FFV.
APPENDIX A:

PROPERTY CALCULATIONS AND ERROR CALCULATIONS

A.1 Calculation of the Average Inter-Crosslink Chain Length ($\bar{M}_c$)

The calculations of the $\bar{M}_c$ of U600, B600, and C600S are provided as representative examples. For each crosslinked network, $\bar{M}_c$ is calculated by dividing the moles of PEO-diamine plus the moles of PEO-epoxy added, for film formation, (both multiplied by their respective molecular weights) dived by the total moles of PEO-diamine and PEO-epoxy added.

\[
\text{U600: } \bar{M}_c = \left( \frac{0.3646 \times 600 + 0.7291 \times 500}{1.0937} \right) = 533 \text{ g mol}^{-1}
\]

\[
\text{B600: } \bar{M}_c = \left( \frac{0.9449 \times 148 + 0.3051 \times 2000 + 2.500 \times 500}{3.75} \right) = 533 \text{ g mol}^{-1}
\]

\[
\text{C600S: } \bar{M}_c = \left( \frac{0.9449 \times 148 + 1.8900 \times 500 + 0.3051 \times 2000 + 0.6101 \times 500}{3.75} \right) = 533 \text{ g mol}^{-1}
\]

A.2 Crosslink Density Calculation

The crosslink density of all films is estimated and not experimentally determined. This estimate cannot take into account dangling chain ends or partially crosslinked oligomers that form linear chains rather than crosslink junctions and is only a rough guideline. The estimate begins by approximating the weight of non-reacted oligomers within the film, which is done by taking the difference of the total weight of reactant oligomers added and the total weight of reactant oligomers added multiplied by the gel
fraction. It is approximated that the weight difference corresponds to the weight loss of non-crosslinked oligomers in a stoichiometric ratio to their addition. Therefore, the mols of PEO-diamine that did not react can be estimated and accordingly the number of mols of non-formed crosslinks is twice the number of mols of non-reacted PEO-diamine. The number of mols of non-formed crosslinks is subtracted from the maximum possible (twice the number of mols of PEO-diamine added) to yield the number of mols of crosslinks in the film. Since the density of the film is known, as is the weight of reactants added, the volume can be estimated. The number of mols of crosslinks is then divided by the volume to yield the crosslink density in (mol/cm³).

A.3 Calculation of Pure-Gas Permeability Error

The error in permeability takes into account all sources of error such as error in measured downstream volume size, error in measured membrane thickness, error in measured membrane area, error in measured operating temperature, error in upstream pressure reporting, error in the slope of the plot of downstream pressure increase versus time, and error of the slope of the leak rate graph of downstream pressure increase versus time. In mathematical form, the error in permeability is calculated as:

\[ \pm \text{permeability} \times \left( \frac{\text{downstream volume error}}{\text{downstream volume}} + \frac{\text{membrane thickness error}}{\text{membrane thickness}} + \frac{\text{membrane area error}}{\text{membrane area}} + \frac{\text{temperature error}}{\text{temperature}} + \frac{\text{upstream pressure error}}{\text{upstream pressure}} + \frac{\text{error of slope of downstream pressure increase} + \text{error of the slope of the leak rate}}{(\text{slope of downstream pressure increase} - \text{slope of leak rate}) \times 0.1} \right) \]
A.4 Calculation of Ideal Selectivity Error

The calculation of the error in ideal selectivity is given as follows:

\[ \pm \text{selectivity} \times \left( \frac{\text{permeability error of more permeable gas}}{\text{permeability of more permeable gas}} + \frac{\text{permeability error of less permeable gas}}{\text{permeability of less permeable gas}} \right) \]

A.5 CO₂ Diffusion and Solubility Coefficient Calculations Accounting for Measurement Error

In order to calculate the diffusion coefficient according to \( D = \frac{l^2}{6\theta} \), the time-lag must be estimated. When beginning a gas permeation test, a plot of downstream pressure versus time can be made. The time-lag, \( \theta \), is then extracted from this plot by solving the plot equation, \( y = m\theta + b \), for \( \theta \), where “\( y \)” is the initial downstream pressure before the gas of interest has permeated through the membrane, “\( m \)” is the slope of the graph of the steady state region of constant slope, and “\( b \)” is the intercept of the steady state region. The error in relevant values must also be taken into account. For instance, the downstream pressure transducer has an error of 0.25% and reports to three decimal places. Accordingly, the error in downstream pressure reporting is calculated as:

\[ \pm ((\text{downstream pressure}) \times 0.0025) + 0.0005 \]. The slope error and intercept error were calculated using OriginPro 9.1. The error in the time-lag is calculated as:

\[ \pm \text{Timelag} \times \left( \frac{\text{downstream pressure error}}{\text{downstream pressure-intercept}} + \frac{\text{intercept error}}{\text{downstream pressure-intercept}} + \frac{slope \text{ error}}{slope} \right) \]. To calculate the error in the diffusion coefficient, the error in membrane thickness measurement must be determined. The error in membrane thickness is calculated by taking the standard deviation of multiple thickness measurements (at least
10) divided by the square root of the number of thickness measurements. The error in the
diffusion coefficient can then be calculated as: \( \pm \text{diffusion coefficient} \times \ \left( \frac{2\times\text{thickness error}}{\text{thickness}} + \frac{\text{timelag error}}{\text{timelag}} \right) \). The error in the solubility coefficient can finally be
calculated as: \( \pm \text{solubility coefficient} \times \left( \frac{\text{permeability error}}{\text{permeability}} + \ \frac{\text{diffusion coefficient error}}{\text{diffusion coefficient}} \right) \).

A.6 Calculation of Fractional Free Volume (FFV) Error

The error in FFV is calculated as follows:

\[ \pm \text{FFV} \times \left( \frac{\text{error of volume of repeat unit (cm}^3\text{/mol)}}{\text{volume of repeat unit (cm}^3\text{/mol)}} \right) \]. The error of the volume of repeat
unit (cm\(^3\)/mol) is calculated by: \( \pm \text{volume of repeat unit} \times \left( \frac{\text{density error}}{\text{density}} \right) \).