Evolution of glassy polymers used for gas separation following ion beam irradiation

Jeffery B. Ilconich
The University of Toledo
A Dissertation

entitled

Evolution of Glassy Polymers used for Gas Separation following Ion Beam Irradiation

by

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Submitted as partial fulfillment of the requirements for

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Advisor: Dr. Maria Coleman

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An Abstract of

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Commercial gas separation membranes are typically polymeric because of low cost, processibility and wide range of available properties. However, while much work has been done to develop improved polymers for membranes, these materials have limitations for many applications. Therefore, much work has been focused in post-formation modification of polymer membrane. In this work, two very different polymers were modified by ion irradiation to evaluate the evolution in chemical structure, microstructure and permeation properties. A specific focus was on the impact of ion choice on properties of a specific polymer.

The first part of study focused on evolution in a typical commercial membrane polymer, polysulfone, following $H^+$ irradiation. Ion irradiation of polysulfone resulted in significant evolution in chemical structure at intermediate $H^+$ doses. There was a general decrease in permeance with little improvement in selectivity following irradiation.
Modification of asymmetric polysulfone membranes by H⁺ and C⁻ irradiation resulted in significant damage to the porous substrate of the membranes. Therefore, these membranes exhibited larger decreases in permeance then could be attributed to changes in the selective layer.

The polyimide, 6FDA-6FpDA, was irradiated with three different ions, (H⁺, N⁺ and F⁺) to investigate impact of ion mass and energy transfer mechanisms. As expected the polymer responded different to the different ions at similar overall doses and total energy transfer. In general, more damage to the polymer matrix was achieved with larger mass ions. The larger relative evolution to microstructure was attributed to the greater nuclear loss mechanism for N⁺ and F⁺ relative to H⁺. Significant evolution in permeation properties corresponded to this change in chemical structure and microstructure. While the ions exhibited similar trends in evolution in permeation properties, there were large differences in scale of modification. For example, at high dose H⁺ irradiation, the gas pair He/CH₄ exhibited significant increase in both permeance and permselectivity. However, F⁺ irradiation at high doses exhibited drastic decreases in permeance for all gases. Several irradiated samples exhibited permeation properties that were beyond the trade-off curve for tradition polymers. Therefore, with additional research, ideal conditions may be selected to optimize the changes in permeation properties.
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Chapter 1: Introduction

Ion irradiation is an easily controlled method that can significantly modify the structure and properties of a thin polymer surface layer. Modification occurs when energy is transferred from the ion to the polymer matrix. The energy is transferred by two different mechanisms, electronic and nuclear energy loss mechanism. There are many controllable factors that determine how the polymer is modified such as virgin polymer structure, ion type, and ion energy.

The effect of irradiation on the polymer’s structure includes emission of small gas molecules, bond breaking, and formation of graphite like materials at higher fluences[1-12]. The changes in the polymer chemical structure cause changes in other properties such as microstructure, electrical and transport.

While the evolution of the transport properties, chemical structure and microstructure of polymeric membrane with increasing ion irradiation fluence are not clearly understood, preliminary result with polyimide (6FDA-6FpDA) have shown that a simultaneous increase in the permselectivity and permeance can be achieved [2, 3, 5, 13-15].

Two very different polymeric materials, polysulfone and the polyimide, 6FDA-6FpDA were used in this study. Polysulfone was chosen for this project because it is very well characterized and is used in commercial membranes. 6FDA-6FpDA was chosen because it has inherently good transport characteristics, as well as, bulky groups
to hold open the volume. Also, 6FDA-6FpDA had favorable results in preliminary studies.

Using several qualitative and quantitative techniques, a systematic study was performed to evaluate the evolution of the gas transport properties, chemical structure and microstructure of PSF and 6FDA-6FpDA. The study also studied how different ions affect the polymers.
Chapter 2: Research Objectives

The overall objective of this project was to investigate the effect of ion beam irradiation at increasing fluences on two glassy polymeric (polysulfone, and 6FDA-6FpDA) membrane materials.

1. Determining the effect the virgin polymer structure plays by characterization of the transport properties, chemical structure and microstructure of two membrane polymers following $H^+$ irradiation over a wide range of doses.

A detailed investigation was required to determine the effect of initial polymer structure has on structure and properties of irradiated polymers. The gas permeation properties, chemical structure and microstructure of PSF, and 6FDA-6FpDA were studied following $H^+$ irradiation at increasing fluences using the methods mentioned in Table 2.1.

2. Systematic characterization of the transport properties, chemical structure and microstructure of the polyimide, 6FDA-6FpDA, using $H^+$, $N^+$ and $F^+$ over a wide range of doses.

Ions, depending on their atomic number and mass, transfer energy in different mechanisms. For example, in the energy range used in this study, $H^+$ irradiation exhibits a highly electronic mechanism loss and is very small in size. $N^+$ and $F^+$ irradiation are similar in size and both contain a significantly higher use of the nuclear mechanism to
lose energy. The difference between the N$^+$ and F$^+$ ion is that fluorine ion is potentially reactive.

The evolution in the transport properties, chemical structure, and microstructure, with increasing ion fluence was examined using qualitative and quantitative procedures. Table 2.1 shows the various techniques that were used, along with the information that is provided and the type of film that was used.

**Table 2.1.** Techniques used to study evolution of irradiated samples

<table>
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<tr>
<th>Technique</th>
<th>Type of Data</th>
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<td>Microstructure</td>
<td>Asymmetric/Composite</td>
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<td>Positron Annihilation Spectroscopy</td>
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<td>Asymmetric/Composite</td>
</tr>
<tr>
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<td>Permeation</td>
<td>Composite</td>
</tr>
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Chapter 3: Literature Review

3.1 Gas Separation using Membranes

A wide range of high purity and enriched gas streams used for commercial application requires gas separation systems. For example, enriched oxygen can be recovered from air to aid those with breathing problems and ultra high pure hydrogen gas is valuable for use in fuel cell where impurities, such as carbon monoxide, can deactivate the fuel cell membrane, and make it less effective [16-22]. Other examples of gas separation include the removal of carbon dioxide from hydrocarbons [20, 21, 23]. There are several methods that can effectively separate gases, including adsorption, cryogenic distillation and polymeric membranes [19]. The economic viability of these applications depends upon system and scale of separation.

Gas adsorption is a semi-batch process that is typically run with multiple columns so that the process can be operated continuously. Typically, pressure swing or temperature swing adsorptions are used for commercial gas separations. Cryogenic distillation is similar to regular distillation, but is performed at temperatures where gases are in liquid form. While very high purities can be achieved with cryogenic distillation, it is a very energy intensive technique. Gas separation through membranes is a continuous process in which two purified product streams, penetrate and retentate, are produced.

Membrane systems typically consist of membrane modules, which contain a large number of hollow fiber membranes. These modules can be configured either in parallel
to enhance system capacity, or series to increase product purity. Advantages of membranes include low capital cost, relative low energy usage and ease of increasing capacity with addition of modules [19, 20, 24]. Most membranes for gas separation consist of a dense polymeric selective layer on a porous support. Since polymeric membranes were the base materials for this project, the remainder of the background section on gas separation will focus on transport characterization of these materials.

3.1.1 Polymeric Membrane Transport Characterization

The invention of the asymmetric integrally skinned cellulose acetate reverse osmosis membrane by Leob and Sourirajan in 1960 led to a great interest in the field of membranes separation [17]. Gas transport through the dense polymer layer occurs through a solution-diffusion mechanism where the penetrate molecules sorb into the high-pressure side, diffuse across the membranes, and finally desorb into the low pressure downstream. The permeability is defined as the thickness and pressure-normalized flux of the gas molecule through the membrane. The permeability can be expressed in terms of solubility and diffusion by Equation 3.1:

\[
P = S \cdot D
\]

where \( P \) is the permeability, \( S \) is the solubility coefficient and \( D \) is the diffusivity coefficient.

For a given polymer, various gases permeate through the membrane at different rates. For example at 35 °C and 2 atm., oxygen permeates through polysulfone 5.6 times faster then nitrogen. The selectivity is a measure of the ability of a polymer to provide a permselective barrier between two gases [18, 19, 25]. The ideal selectivity can be
expressed as the ratio of the pure component permeability and can be expanded to the ratio of the product of the sorption and diffusion coefficient as seen in Equation 3.2:

$$\frac{\alpha^*_A}{\alpha^*_B} = \frac{P_A}{P_B} = \frac{S_A}{S_B} \times \frac{D_A}{D_B}$$ (3.2)

The solubility of the penetrant into the membrane is largely dependent on the condensibility of the gas and polymer free volume [19]. Therefore, a good indicator of relative solubility of two different gases is the difference of the critical temperature, $T_c$ [19]. For example, CO$_2$ with a $T_c$ of 302K is more soluble than He with a $T_c$ of 5.2 K. While the critical temperature is the key property for the solubility coefficient, the relative kinetic diameters of gas penetrants correlate well with the diffusivity [19]. For example, He with a kinetic diameter of 2.6 Å diffuses more readily through polymeric membranes than CH$_4$ with a kinetic diameter of 3.8 Å.

Diffusion occurs when the penetrant molecule is able to move through a gap from one opening to another. This jump occurs when the polymer chain segments form gaps larger than the sieving size of the penetrant. Increasing the temperature causes more movement of the polymer chains and increases the number of gaps which the gas penetrant can move through. Synthesizing polymer that can limit or increase the chain mobility will affect the diffusivity within the polymer [19, 26].

3.1.2 Polymeric Membrane Materials

Considerable work has been done to correlate the polymer’s chemical structure to gas transport properties [13, 19, 22, 27-29]. When developing polymers for use as membranes, the polymer’s fractional free volume and rigidity are important. In general, an increase in fractional free volume results in an increase in the permeability of a gas
through increase in both the diffusivity and solubility coefficient [19]. For example, adding “bulky” side groups tends to increase the chain spacing and the size of penetrate gaps available for diffusion [19]. However, this increase in free volume will typically result in larger relative increases in diffusivity for large molecules so there is a net decline in the diffusivity selectivity. Maintaining rigidity of the polymer backbone is critical for increasing the diffusivity selectivity and the permselectivity of the membrane [19]. When a polymer is more rigid, the average penetrate gaps are smaller and less frequent with a net result of decreased diffusivity and increase diffusivity selectivity. Essentially, more energy is required to open gaps large enough for the larger particles to diffuse through the matrix. Therefore one successful approach has been to synthesize polymer with bulky groups in backbone that both increase spacing and rigidity. This gives an increase in diffusivity without a loss in diffusivity selectivity.

Aromatic polysulfones and polyimides are two classes of polymers with favorable gas transport properties. Polysulfones are glassy materials with high $T_g$ with outstanding properties such as, environmental stability, physical properties, and solubility. The polysulfones also have very good mechanical characteristics such as, rigidity at elevated temperature and flexibility [30]. The polysulfones also have positive chemical properties such as, phenyl groups provide high degree of resonance, the sulfone group provides a sink for the electrons for the aromatic groups, and the aromatic moeties are resistance to

$$\text{CH}_3\text{C}\left(\text{O} - \text{C} - \text{O} - \text{S} - \text{O} - \text{O}\right)_n$$

Figure 3.1. The repeat unit for the polymer, polysulfone.
high energy irradiation [30]. Polysulfone repeat unit and physical properties are shown in Figure 3.1 and Table 3.1.

Table 3.1: Properties of Bulk Polysulfone [31]

<table>
<thead>
<tr>
<th>$T_g$ (°C)</th>
<th>Density (g/cm$^3$)</th>
<th>$P_{O_2}^a$</th>
<th>$P_{CO_2}^a$</th>
<th>$P_{He}^a$</th>
<th>$\alpha_{O_2/\text{N}_2}$</th>
<th>$\alpha_{CO_2/\text{CH}_4}$</th>
<th>$\alpha_{He/\text{CH}_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>1.240</td>
<td>1.4</td>
<td>5.6</td>
<td>13</td>
<td>5.6</td>
<td>14.9</td>
<td>27.4</td>
</tr>
</tbody>
</table>

\[
a = 1\text{Barrer} = 10^{-10} \frac{cm^3 (STP) \cdot cm}{cm^2 \cdot s \cdot cmHg}
\]

Polyimides are also a glassy polymer with a very high $T_g$ with good gas transport properties. Polyimides are used in many different situations [32, 33]. For example, the fluorinated polyimide Teflon is used as a non-stick surface. The polyimide, 6FDA-6FpDA, which was used in this study is not readily available and had to be synthesized. The 6FDA-6FpDA repeat unit and its physical properties are shown in Figure 3.2 and Table 3.2. 6FDA-6FpDA contains groups that limit mobility and bulky groups which opens the structure up. 6FDA-6FpDA was used as basis of this project because of these attractive inherent properties.

Table 3.2 Bulk Properties of 6FDA-6FpDA [19]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
<th>Density (g/cm$^3$)</th>
<th>$P_{O_2}^a$</th>
<th>$P_{CO_2}^a$</th>
<th>$P_{He}^a$</th>
<th>$\alpha_{O_2/\text{N}_2}$</th>
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<th>$\alpha_{He/\text{CH}_4}$</th>
</tr>
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<tbody>
<tr>
<td>6FDA-6FpDA</td>
<td>320</td>
<td>1.466</td>
<td>16.3</td>
<td>63.9</td>
<td>137</td>
<td>4.7</td>
<td>40</td>
<td>85.6</td>
</tr>
</tbody>
</table>

\[
a = 1\text{Barrer} = 10^{-10} \frac{cm^3 (STP) \cdot cm}{cm^2 \cdot s \cdot cmHg}
\]
3.1.3 Other membrane materials and processes

Ideally, a polymer with combined high permeability and selectivity would be used in industrial applications. However, there is a tradeoff between high permselectivity and permeability for polymers that results in an upper bound of the properties for large class of polymers [34, 35]. Figure 3.3 shows an example of a tradeoff curve for the gas pair O₂/N₂ with the value for 6FDA-6FpDA shown. Many polymers have been synthesized in an attempt to surpass this tradeoff curve. While synthesizes of novel polymers have shifted the tradeoff curve up and to the right, there now seems to be an upper limit. While there are benefits to synthesizing new polymers there are also disadvantages. With synthesizing new polymers, specific components can be placed in the repeat unit, such as big bulky groups to increase the free volume and/or chain rigidity [19]. However, the disadvantages of this process are that synthesizing new polymers is both time consuming and expensive [36].

While polymeric membranes are used in many current commercial applications, to exceed current upper bound condition, new materials are required [37]. There are several types of inorganic materials that have been studied as membranes materials, such as precipitated oxides (silica based), zeolites and carbon molecular sieves [38]. While the
transport properties of these inorganic materials are very good, these materials do not exhibit good mechanical stability.

As for post-formation modifications, several techniques including fluorination and pyrolysis have been used to attempt to improve transport properties beyond the current trade-off curve [19, 39-44]. Pyrolysis is the process of heating the membrane to a very high temperature for extended amount of time. Pyrolysis causes the polymer loses some or all functional groups until everything except the carbon atoms are removed. This is the process used to make carbon molecular sieve membranes. While carbon molecular sieve membranes can be very productive and selective there are several disadvantages. First of all, pyrolysis is a very energy extensive process. In addition
carbon molecular sieves are very fragile and can break easily. Most commercial membranes are asymmetric and contain a porous support, which will also be modified by pyrolysis [45]. Therefore, a technique that allows modification of the selective layer but maintains stability of the support is of considerable interest.

Barsema [46] reported that as the temperature increased during pyrolysis of Matrimid®, the sample weight decreased about to 35% of the original sample and H₂, CO, CO₂, CH₄ and N₂ were evolved from the sample. FTIR showed the reduction of numerous peaks of functional groups with increased temperature and time, and that there was an evolution in the chemical structure toward a carbon-like structure. This carbonization corresponds to an increase in density[46]. The permeability for oxygen through the heat-treated membranes decreased while O₂/N₂ selectivity increased at lower temperatures, but decreased at higher temperatures.

Fuertes [47] made carbon membranes by pyrolysing the polyimides, Kapton® and Matrimid® polyimide membranes. The results for Matrimid® showed minimal improvements in the permeability for oxygen and selectivity for O₂/N₂. Kapton® pyrolysis resulted in permeabilities of about 6 – 8 times higher the Matrimid pyrolysis but with a lower permselectivities.

3.2 Ion Irradiation

Ion irradiation is an easily controlled method to modify the structure and properties of thin polymeric surface layers through the transfer of energy from the energetic ion to the polymer backbone. In irradiation the ions, formed in one of several ways, are energized to desired energy travels through the chambers towards the target.
The ions penetrate into the target and transfer energy to target molecules. The ions can either be generated from a gas or a solid source.

The energy transferred from the ion to target molecules occurs by electronic and nuclear mechanisms. Electronic energy loss occurs when an electron is either raised to a higher energy (electron excitation), or an electron is “ejected from the atom” (electron ionization) [10]. Nuclear energy loss is caused from collision of the ion with an atom of the polymer chain and can result in the recoil of the target atom. The recoil atoms transfer energy to neighboring atoms through both electronic and nuclear mechanisms [10]. For lighter ions (low atomic number and mass) (ie. H$^+$ and He$^+$), nuclear stopping is negligible, however, with heavier ions (high atomic number and mass) nuclear mechanism is important and can dominate relative to electronic loss, as will be explained in detail below [10]. There is considerable difference in the extent of modification of polymers resulting from electronic and nuclear loss mechanism. In this study, the polyimide, 6FDA-6FpDA was irradiated with ions that exhibit a range of transfer mechanism. For example, H$^+$ irradiation was used to isolate effect the of the electronic energy transfer, while N$^+$ was used to provided contribution from both nuclear and electronic energy loss mechanisms. F$^+$ should have similar nuclear and electronic loss mechanism to N$^+$ but is potentially reactive.

Several studies over the past decade have focused on impact of ion irradiation on polymer structure and properties [1, 5, 7-9, 12, 15, 36, 48-96]. Ion beam modification of the polymer structure can include, removal of function groups, formation of small volatile gases, crosslinking, chain scission, formation of double and triple bonds, and at high fluences, formation of a graphite-like material. Because of this modification to chemical
structure, ion irradiation can have a wide range of effect on the polymer’s properties, such as, optical, mechanical, or conductivity \[52, 55, 64, 94\]. This project takes advantage of evolution in microstructure to modify gas transport properties of polymers.

There are three regions of modification resulting from ion irradiation, low, medium and high \[14, 81\]. The result of low dose modification includes small changes in chemical structure and morphology, medium dose modification includes significant crosslinking and modification, while high dose modification of the polymer causes formation of graphite like material. Even though there are defined modification ranges, there are no set doses for the ranges do to the fact that ion dose is only one factor that determines the amount of modification. The extent of modification depends on several key parameters such as ion energy, ion type, dose, virgin polymer structure, and current density. The impact of these parameters on the energy transfer to the polymer can be estimated using the SRIM Monte Carlo simulation.

Ion energy plays an important role in determining the depth and amount of modification to the polymer matrix. Figure 3.4 (a and b) shows two Monte Carlo simulations of \(\text{H}^+\) irradiation of 6FDA-6FpDA at 180 keV and 450 keV, respectively \[97, 98\]. The x-axis represents the depth into the polymer from the surface, while the y-axis represents the energy transfer per ion per angstrom. There are two key differences between the two energy profiles (i) the shape of the profiles are significantly different and (ii) the depth of modification is deeper for the higher energy profile. The different shapes of the energy profile can lead to substantial differences in the amount of energy transferred to the matrix. For example, at the same fluence, the sample irradiated with 180 keV would have more energy transfer than the sample at 450 keV. This is because
Figure 3.4. Monte Carlo simulation of H$^+$ irradiation of 6FDA-6FpDA at 180 keV (a) and 450 keV (b) with electronic (●) and nuclear (□) energy loss mechanism.
that the profile for the 180 keV Monte Carlo simulation contains a higher ev/ion/angstrom in the lower region than the other. The relationship between depth of modification and beam energy is important to insure that the entire thickness is modified.

3.2.1 Factors affecting Irradiation

As mentioned earlier, ion choice plays an important role in determining the relative importance of energy loss mechanism and depth of modification. Much work has been done with lighter ions, where the electronic energy loss mechanism dominates and with increasing heavier ions, where the ions exhibit increasing relative nuclear energy loss mechanism [1, 7, 8, 48, 53, 56-58, 60, 61, 65, 68, 70-78, 80-83, 85, 87, 89-91, 93]. The type of energy loss mechanism plays an important role in determining the form and extent of structural modification. For example, Hu showed that Matrimid® exhibited significantly more damage following N⁺ irradiation relative to H⁺ at similar total energy transfer, but higher nuclear energy transfer [99]. In addition, the choice of ion determines the amount of energy that is deposited into the target. Figure 3.5 (a and b) shows a Monte Carlo simulation of the energy loss profile as a function of depth for 450 keV H⁺ and 400 keV N⁺ irradiation, respectively, of 6FDA-6FpDA. At similar ion energies, there are several important key points from Figure 3.5. First of all, hydrogen ions transfer less energy per angstrom of depth than nitrogen ions. This allows for a lower fluence for N⁺ to achieve the same amount of energy transfer. Secondly, the amount of nuclear energy transfer is significantly higher with nitrogen irradiation than hydrogen irradiation, which results in different evolution of properties and structure. Finally, at the same ion energy, the depth of penetration is significantly greater for hydrogen irradiation. While either
Figure 3.5. Monte Carlo simulation 6FDA-6FpDA irradiated with $H^+$ at 450 KeV (a) and $N^+$ at 400 KeV (b) with electronic (●) and nuclear (□) energy loss mechanism.
mechanism can cause chain scission and crosslinking, an ion with high electronic energy loss typically causes more crosslinking while nuclear energy loss is more responsible for chain scission [10].

The virgin polymer structure and properties also play an important role in determining structure, microstructure and properties of irradiated polymers. The density of the polymer affects the depth of irradiation where depth of irradiation is greater at the same condition with lower density polymer. Also, some polymer structures are more resistance to modification than others. For example, a polymer that contains several aromatic groups is able to transfer the charge better than an aliphatic polymer, because it is highly conjugated.

Following irradiation, significant modification in the chemical structure can occur including, release of small gas molecules, degradation of bonds, and formation of crosslinks [1, 7, 8, 48, 51, 53, 57, 65, 78, 92, 93, 96]. Crosslinking between polymer chains is primarily associated with the electronic energy loss mechanism [10, 11, 71]. For example polyethersulphone, exhibited significant degree of crosslinking following alpha irradiation at shallow depth.

3.2.2 Ion Irradiation of Polymer

Guenther [49] irradiated several polyimides and polyethersulfone with B⁺ at several doses. Polyethersulfone is similar to structure to polysulfone and one of the polyimides contained 6FDA, which is used in 6FDA-6FpDA. B⁺ irradiation of polyethersulfone resulted in improvements of electrical conductivity, values of optical constants, and E-modulus. B⁺ irradiation of the polyimide, 6FDA-ODA, resulted in
removal of CF₃ groups, along with an increase conductivity of several orders of magnitudes.

Saha [92] irradiated polypropylene with C⁺ and caused significant chemical modification. Based on UV-VIS, there was a shift in the maximum peak, which is believed to be caused by conjugation of bonds. This formation of unsaturated linkage was confirmed by FTIR. The gas evolved from polypropylene included hydrogen, and hydrocarbons between C₁Hₓ and C₄Hₓ. With the observation of release of heavy hydrocarbons, it can be concluded that C⁺ irradiation caused main chain scission of polypropylene.

3.2.3 Ion Irradiation of Polymeric Membranes

The modification of the chemical structure and microstructure can affect the transport properties of the material. For example, crosslinking of the polymer chains produces a more rigid matrix and typically increase selectivity. At low doses, there is a loss of functional groups that can result in an increase in fractional free volume with corresponding increase in ion dose.

In the past decade, some work was been done on the subject of irradiation of polymeric membranes and the effect on the permeance and permselectivity. Since most of the reported studies used very different experimental procedure, their results do not directly compare to this work or each other.

Won et al. [81] modified polysulfone and Matrimid® with Ar⁺, N⁺ or He⁺ at relative low energies. Dense films of 30 – 40 µm were modified over a wide range of fluences. With a combination of fairly thick film and low irradiation energies, only a low percentage of the film thickness was modified. Therefore a large percent of the transport
through the films was through the virgin materials. The carbon dioxide, helium and nitrogen permeances decrease for most cases, with an increase in CO$_2$/N$_2$ selectivity.

Hu [99], a member of this research group, reported that modification of several different polyimides, resulted in significant change in permeance and permselectivity. Matrimid®, 6FDA-6FmDA, and the co-polymer 6FDA-6FmDA-6FpDA were irradiated with H$^+$. Note that the 6FDA polyimides used by Hu are isomers of the 6FDA-6FpDA used in this study. These membranes were spin coated onto ceramic support and tested prior to and after irradiation in the same method used for this study. The increase in normalized permeance for H$^+$ irradiated 6FDA co-polymer, for all gases tested with increasing ion fluence, however the largest increases were seen for CO$_2$ and methane with only modest increase for He. The normalized permeance for CO$_2$ and CH$_4$ was $\sim$15 and 13 times greater, respectively, while He saw only $\sim$ 4 fold increase. This caused a decrease in the normalized selectivity for He/CH$_4$. On the other hand the selectivity for O$_2$/N$_2$ saw a slight increase in permeance when compared to the virgin membranes.

Hu [99] also showed that H$^+$ irradiation of 6FDA-6FmDA resulted in dramatic changes in the permeances for five different gases. Oxygen, nitrogen, methane and carbon dioxide exhibited similar results following low dose with a slight decrease to $\sim$0.9 of the virgin value. At higher doses there was an increase in permeance with increase ion fluence with a maximum of $\sim$3.3. Helium exhibited the smallest increase in permeance and was less dramatic than the other gases.

Hu [99] also showed that N$^+$ irradiation caused more modification in permeance than H$^+$ irradiation on the polyimide, Matrimid®. With N$+$ irradiation, the normalized permeance resulted in the maximum increase followed by a sharp decrease with
increasing fluences. Helium and oxygen had the greatest increase in normalized permeance, while carbon dioxide, oxygen and nitrogen had the greatest decrease. $H^+$ irradiation of Matrimid® resulted in initial decrease in permeance followed by an upward trend. Helium had the highest increase in relative permeance of $\sim 1.8$.

Preliminary results from our group showed that 6FDA-6FpDA irradiated with $H^+$ show simultaneous increase in the permeance and permselectivity for several different gas pairs [15]. Polymer solution was deposited onto ceramic supports. The membranes were tested prior to and after irradiation. Specifically, with increase irradiation the permeance for oxygen increased 7.3 folds and the permselectivity for $O_2/N_2$ increase 3.0 folds.
Chapter 4: Experimental

4.1 Materials

Polysulfone and the polyimide, 6FDA-6FpDA, were the polymers used for this research. The structure and bulk properties of these polymers are given in Figure 4.1 and Table 4.1. Polysulfone was chosen for this research because it is a very well characterized membrane material that is currently used for commercial applications [31]. 6FDA-6FpDA has inherently good transport characteristics, as well as, bulky groups to hold open the volume [19]. In addition, 6FDA-6FpDA was chosen because of the favorable results in preliminary studies [15]. High molecular weight polysulfone was purchased from Aldrich Chemical Company. The 6FDA-6FpDA was synthesized using a well-established method [100]. The solvents and reagents were purchased from a chemical company, such as, Aldrich Chemical Company.

Figure 4.1 Repeat units for (A.) PSF and (B) 6FDA-6FpDA
Table 4.1. Bulk Properties of Polysulfone[31] and 6FDA-6FpDA[19]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (ºC)</th>
<th>Density (g/cm$^3$)</th>
<th>$P_{O_2}^g$</th>
<th>$P_{CO_2}^g$</th>
<th>$P_{He}^g$</th>
<th>$\alpha_{O_2}/\sqrt{N_2}$</th>
<th>$\alpha_{CO_2}/\sqrt{CH_4}$</th>
<th>$\alpha_{He}/\sqrt{CH_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6FDA-6FpDA</td>
<td>320</td>
<td>1.466</td>
<td>16.3</td>
<td>63.9</td>
<td>137</td>
<td>4.7</td>
<td>40</td>
<td>85.6</td>
</tr>
<tr>
<td>PSF</td>
<td>190</td>
<td>1.240</td>
<td>1.4</td>
<td>5.6</td>
<td>13</td>
<td>5.6</td>
<td>14.9</td>
<td>27.4</td>
</tr>
</tbody>
</table>

The polyimide, 6FDA-6FpDA was synthesized by a method reported by Husk at al.[100]. The monomers were purchased from Aldrich Chemical Company and were purified through sublimation. Prior to synthesis, DMAC was heated at reflux over calcium hydride for several hours. Then, DMAC was distilled onto activated molecular sieves. The acetic anhydride and triethylamine were distilled shortly before use.

For polyimide synthesis, a round bottom reaction flask was charged with equimolar quantities of 6FDA and 6FpDA (5-15 mmol). Then 50 ml of DMAC was added and the solution was stirred. After dissolution the flask was heated to 50-58 ºC for three hours. The solution was cooled to ~45 ºC and 40 mmol of both acetic anhydride and triethylamine was added to the flask. The temperature of the mixture was increased to 50 ºC for one hour and then 100 ºC for 20 minutes. The solution was cooled slightly and poured into 1000 ml of methanol. The precipitated polymer was filtered and placed into 500 ml of methanol and blended. The polymer powder was filtered and dried under vacuum at 80 ºC for several hours followed by heating at ~ 200 ºC under vacuum for 16 hours. The synthesis of 6FDA-6FpDA was confirmed by FTIR. The spectrum of the synthesized polyimide was compared to the known spectrum.
4.2 Membrane and Film Formation

Both membranes and dense freestanding films were used in this study to investigate the impact of ion irradiation on polymer structure and properties. A membrane or film was used depending on the analysis technique. Membranes were typically used to test the modified properties associated with the gas transport evolution, while dense films were used to analyze the microstructure and chemical structure of the polymers.

4.2.1 Membranes

Two types of membranes were used in this study. Asymmetric membranes were used to determine the effect of irradiation on membrane properties and composite membranes were used to isolate the effect on polymer properties.

4.2.1.1 Preparation of Asymmetric PSF Membranes

Asymmetric membranes consist of multiple layers of a particular polymer and are the typical form used for commercial applications. Figure 4.2 shows a SEM photo of an asymmetric membrane. The upper surface of an asymmetric gas separation membrane is a dense resistance layer where all of the gas separation occurs. The lower layer is porous with minimal resistance to gas transport and is used to provide mechanical support. The porous support contains a gradient from small to large pores, starting below the dense layer.

Asymmetric membranes of PSF were made using a dry-wet inversion technique reported by Pesek et al.[101]. A solution of ~22% PSF, 29% NMP (solvent), 29% THF (solvent) and 20% ethanol (non-solvent) by weight was prepared. The viscous solution was poured onto a glass plate and a micrometer doctor’s blade was pulled over the
solution to produce a uniform thickness for the membrane sheet. The solution was allowed to set for 2 minutes in air and the glass plate with the membrane was submerged into distilled water for 10 minutes to remove the solvent and nonsolvents. The membrane was transferred to a methanol bath for 2 hours followed by air-drying for 12 hours. Additional drying was done at 40°C in vacuum for 2 hours. The thickness of the skin layer (selective layer) of the asymmetric membranes was estimated using oxygen permeance measurements and assuming the selective layer permeability was equivalent to bulk properties. Only asymmetric membranes with an O₂/N₂ selectivity of at least 80% (α = 4.48) of the bulk properties were used.

Figure 4.2. An SEM photo of an asymmetric PSF Membrane at 1000 magnification
4.2.1.2 Preparation of Composite membranes

While asymmetric membranes investigate ion beam irradiation effects on entire membrane as a whole (support and selective layer), composite membranes isolate the effect of ion beam irradiation on the permeation properties of the polymer because the ceramic support is not modified. Composite membranes were cast from a 3-10 weight percent polymer solution in methylene chloride using a spin coater (P-6000 Spin Coater from Specialty Coating Systems, Inc.). For each membrane, a Whatman® anodisc ceramic membrane with 0.02 µm pore diameter was fixed onto a metallic wafer support. The support was centered on the vacuum chuck of the spin coater. The solution was poured onto the anodisc membrane while spinning at 70 – 80 RPM. The sample’s speed was increased to a defined rate (400 – 700 rpm) and spun for a predetermined time (300 – 900 seconds). The membranes were masked because of the size of the ion beam. The 47 mm anodisc and membrane was masked with an permeation opening of 2.85 cm². The back of the anodisc was also masked to improve mechanical stability and prevent cracking of the ceramic support. The mask size for the back of the membrane was an outside diameter of ~4.45 cm and an inside diameter of ~2.54 cm. The membranes were dried in an oven at 40° C under vacuum for 2 hours.

4.2.2 Dense Free-Standing Film

Thin freestanding films (2 – 6 µm) of polysulfone and 6FDA-6FpDA were used for the FTIR, and dissolution studies. Films were cast using one of the following two methods: (1) standard solution casting method or (2) spin coating onto a silicon wafer support. For solution casting the films were cast into a dish from a polymer /methylene chloride solution in a solvent-enriched environment to slow the rate of solvent
evaporation. Following evaporation of the solvent, the films were masked with aluminum foil tape and placed in distilled water to allow the films to float out of the dishes. The films were dried for 24 hours in a vacuum oven at 100°C.

For spin coating onto silicon wafer, a 2 – 6 weight percent polymer solution in methylene chloride was made and filtered several times. A silicon wafer was cleaned and centered on the vacuum chuck. The solution was poured onto the disk so that the entire surface area is covered. The disks were spun for approximately 900 seconds and masked with aluminum foil tape. The entire disk was submerged into a warm water bath and the film was floated from the silicon wafer. The film was dried for 24 hours in a vacuum oven at 100°C. All films were stored in desiccators to reduce uptake of water. The mask for all films had a diameter of at least 1.9 cm. The films were sandwich between two metal plates with a hole in the middle of both plates.

4.3 Ion irradiation

Ion beam irradiation was performed using a Tandem Accelerator at The University of Western Ontario, London Ontario, Canada, as shown in Figure 4.3. All ion beam irradiation was performed at room temperature within a vacuum chamber at a pressure of less than $1.0 \times 10^{-7}$ torr. Lowering the pressure of the chamber provides a clear path for the beam from the source to the target by removing gas particles. The beam-current density was maintained at low levels ($< 1 \mu A/cm^2$) to avoid heating of the samples. Heating of the sample can cause modification of the polymer structure and properties not indicative of irradiation. The incident beam was perpendicular to the surface of the samples. Well-known computer software “The stopping and range of ions in Matter” (SRIM) was used to determine the appropriate energy for the implantation
[97]. The ion energy level used for membranes was chosen in each case to ensure modification of polymer selective layer and to minimize penetration into porous substrate. Thus the impact of irradiation on the transport properties of the polymer selective layer could be isolated. For dense films irradiated with either N$^+$ or F$^+$, the sample must be irradiated from both sides. The implantation energy for the dense films was high enough to produce a near uniform modification of the entire thickness. The ion beam size is one inch in diameter and rastered back and forth to ensure uniform modification of the sample.
4.3.1 Changing Ion Energy

Depending on the samples that were irradiated, different ion energies were required. As shown in Figure 4.4 for H⁺, the change in ion energy effects several different aspects, such as depth of modification, and profile of energy transferred per ion.

Figure 4.4. A SRIM Monte Carlo simulation of H⁺ irradiation of 6FpDA-6FDA at (a) 180 keV and (b) 2400 keV with electronic (●) and nuclear (□) energy loss mechanism.
The depth of penetration increases for a given ion with increased energy. The energy chosen for modification was dependent on the type of sample to be modified. For example, the energy used for modification for an asymmetric membrane should be sufficient to modify the selective layer, but not to penetrate the support. At higher energy, the greater depth of modification will cause damage to the porous substructure. On the other hand, higher energies can be used on freestanding dense films and composite membranes because the support will not be affect by ions for conditions used for this study.

4.3.2 Changing Ions

As discussed in the background, different ion affects the polymer matrix in very different ways. Specifically, ions can transfer energy by two different mechanisms, electronic or nuclear. The relative extent of nuclear to electronic energy transfer is largely dependent on the atomic number and mass of the ion. Figure 4.5 (a and b) shows SRIM simulations for two different ions, H\(^+\) and N\(^+\), irradiating the same polymer, 6FDA-6FpDA, at the same energy. The depth of modification is significant lower for the larger ion, nitrogen. Also, the amount of energy transfer to the polymer matrix per ion per angstrom is significantly higher for nitrogen irradiation. Finally, the nuclear mechanism plays a more significant role in the transfer of energy for N\(^+\) irradiation. Fluorine irradiation, which has a similar size to N\(^+\), was also be used to modify the polymers. Fluorine was been shown to be very reactive [102], so impact of F\(^+\) irradiation was investigated.
Figure 4.5. A Monte Carlo Simulation of (a) H\(^+\) and (b) N\(^+\) of 6FDA-6FpDA at 2400 keV
4.3.3 Normalization of Samples Modified at Different Conditions

Samples irradiated under different conditions, such as ion or energy, are difficult to compare directly by using ion dose or fluence. This is due to the fact the energy transferred per ion are not the same from one condition to another. However, the total energy transferred for each sample can be used to compare samples irradiated under different conditions. To estimate the total energy transfer a SRIM simulation must first be performed for each ion used at a different energy and different polymer. After the SRIM simulation was been performed, the thickness of the sample is plotted as a vertical line on the graph. The average of the total energy transfer per ion per angstrom is estimated for the region left of the vertical line. The total energy transferred to the polymer matrix per angstrom is the average energy transferred to the polymer matrix per angstrom for each ion multiplied by the ion fluence. The total electronic energy transfer per angstrom and total nuclear energy transfer per angstrom can be estimated using a similar approach.

4.4 Measurement of Permeance

The effect of ion irradiation on the rate of gas transport within the composite and asymmetric membranes will be quantified using permeance and permselectivities. The permeance is the pressure-normalized flux of a gas through a membrane material as shown in Equation 4.1:

\[
\text{Permeance} = \frac{P_A}{l} = \frac{F_A}{\Delta p_A}
\]  

(4.1)

where \(P_A\) is the permeability of species A, \(l\) is the thickness of the selective layer, \(F_A\) is the molar flux of the gas and \(\Delta p_A\) is the difference in pressure between the feed and permeate sides of the membrane. The permeance is typically used to describe membrane
systems with very thin selective layers in which the thickness is difficult to measure. The permeability is a measure of the rate of gas transport of the molecule within a particular material and is determined solely by material properties. However, the permeance is a function of both the material selected and the thickness of the selective layer. Additionally, the relative separation ability of the membrane will be monitored using an ideal selectivity. The ideal selectivity, \( \alpha_{AB} \), is defined as the ratio of the pure component permeabilities or permeances.

The pure gas permeances of several industrially important gases (oxygen, nitrogen, helium, methane and carbon dioxide) were measured for the virgin and irradiated membranes at 35 °C using standard permeation cells and well-established techniques [103, 104]. Prior to permeation measurements, the membranes were masked on the upstream face using multiple layers of foil tape to define the permeation area. An area was selected to correspond to the size of the incident beam to ensure that the entire membrane surface was evenly irradiated. In the case of the composite membranes, the foil mask provided additional mechanical support that allowed ease of handling of the ceramic membranes.

4.4.1 Constant Volume\ Variable Pressure Cell

The pure gas permeances of thicker samples or low permeability materials (i.e. polysulfone) at 35 °C were measured in standard constant volume\ variable pressure (CV\VP) permeation cells with pressurized upstream and evacuated downstream. A pressure transducer (0-10 torr) on the down-stream side was used to monitor pressure with time when the down-stream side was isolated from vacuum. Figure 4.6 shows a diagram of a CV\VP permeation cell used in this study. The standard method used for
characterizing polymers over a wide pressure range was modified to prevent stress on the fragile ceramic porous support. For these experiments, the upstream membrane face was not evacuated prior to pressurizing, but was purged at low pressure with the feed gas for several minutes. Next the downstream was slowly evacuated, and the upstream purge was closed and pressure slowly increased to 50 psia. The system was allowed to sit for at least eight hours to ensure steady state. Oxygen, nitrogen, methane, helium and carbon dioxide at 50 psia at 35 °C were used in these permeation studies. The membranes were tested prior to and after irradiation.

4.4.2 Constant Pressure\ Variable Volume Cell

The pure gas permeances of thinner samples or high permeability materials (i.e. 6FDA-6FpDA) at 35 °C were measured using Constant Pressure\ Variable Volume (CP\VV) permeation cells and a bubble flow meter with well-established methods [104]. Figure 4.7 shows a diagram of CP\VV permeation cell used in this study. The upstream was slowly vented with the feed gas for several minutes, pressurized to 40 PSIG and
allowed to sit for at least eight hours to ensure steady state. A bubble flow meter on the
downstream membrane face was used to determine the volumetric flow rate of gas
through the membrane. Several tests were run for each gas to ensure steady state.
Oxygen, nitrogen, methane, helium and carbon dioxide at 40 PSIG at 35 °C were used in
these permeation studies. The membranes were tested prior to and after irradiation.

![Diagram of Constant Pressure/Variable Volume permeation cell.](image)

**Figure 4.7. A schematic of Constant Pressure/Variable Volume permeation cell.**

### 4.5 Variable Energy Positron Annihilation Spectroscopy

Positron annihilation spectroscopy analysis was performed by Professor Peter Simpson’s group at the Positron Beam Laboratory, Department of Physics and Astronomy, University of Western Ontario. Positron annihilation spectroscopy analysis shows the free volume as a function of depth. Positrons emitted from a $^{22}$Na source of activity 50 mCi was moderated to energies of about 3 eV and electrostatically accelerated to pre-selected energies between 500 eV and 60 keV, then guided onto the sample by an axial magnetic field. With the vacuum system usually not being baked, the measurements were performed at a pressure of about $10^{-7}$ Torr. The $\gamma$ spectrometer was a 210 cm$^3$ HP Ge detector, with an energy resolution of about 1.3 keV at 511 keV.

Positrons were implanted into the sample, where they lose their kinetic energy in
about 10 ps, subsequently diffusing randomly at thermal energy before finally
annihilating with an electron provided by a sample atom. The majority of annihilation
events generate two $\gamma$ quanta with energies of about 511 keV, emitted into nearly
opposite directions. Because not only the total energy, but also the total momentum of the
positron-electron pair must be conserved in the annihilation process, the resulting $\gamma$ peak
exhibits Doppler broadening. However, as the momentum contribution of the thermalized
positrons is negligible compared to the momenta of the electrons, both the width and the
detailed shape of the annihilation peak are independent of the positron source and the
positron implantation process, and are dependent only on the electronic environment in
which the positrons annihilate (i.e., the physical and chemical structure of the sample
material). In particular, the positron is a sensitive probe of open volumes. Due to the
absence of positive ion cores, open volumes provide an attractive potential well for the
positron. Therefore, if the positron during its random diffusion in the sample encounters
a vacancy, it gets trapped there, and finally annihilates with an electron inside the
vacancy. The probability of annihilation with valence electrons (compared with core
electrons) is greater for positrons trapped by vacancies, and, thus, the average momentum
of the annihilation electron is lower and a narrower annihilation $\gamma$ line results. The line
width is usually characterized by a parameter S, defined as the number of counts in a
central region of the peak (e.g., between 510.3 and 511.7 keV) divided by the total counts
in the peak region (in our case between 504.5 and 517.5 keV). The energy reported will
correspond to depth into the membrane from the surface.

4.6 Scanning Electron Microscopy (SEM)

A cross-section of PSF asymmetric membranes with both the irradiation modified
and virgin areas was characterized using a Scanning Electron Microscopy (JOEL 6100) at
the Instrumentation Center, Department of Chemistry, University of Toledo. Specifically any modification of the porous substrate resulting from irradiation was evaluated. Prior to analysis, samples were soaked in water for several minutes and placed into liquid nitrogen. The membranes were then snapped and a crisp edge was produced. The samples were sputtered with gold under an argon atmosphere and were characterized using SEM.

4.7 Fourier Transform Infrared (FTIR) Spectroscopy

The evolution in chemical structure with ion fluence was monitored using FTIR, with a Nicolet 5DX Spectrometer at the Department of Chemistry, University of Toledo. The FTIR spectra of each sample was measured prior to and following irradiation. Dense freestanding films of several microns were used. The thickness of the film was limited to several microns (~ 3 - 4 \( \mu \)m) because a thicker film would absorb the IR laser and a weak signal would be reported. If possible, spectrums of virgin polymer were compared to published standards. The irradiated samples spectrum was compared to the same sample prior to irradiation. The area under the peak was calculated for the irradiated samples for each peak of interest and normalized by the virgin area. This allows for comparison of membranes of slightly different area.

4.8 Dissolution Analysis

Crosslinking was qualitatively observed through dissolution studies. Irradiated dense films, used for FTIR analysis were placed into an excess amount of methylene chloride. Methylene chloride readily dissolves the virgin polymer used in this study. Samples were observed for two weeks to determine if the irradiated polymers dissolve, partially dissolve, or does not visually change in the solvent.
Chapter 5: Ion Irradiation of Polysulfone

5.1 Introduction

Over the past few decades, much work was been done to improve gas separation membranes\[20, 24, 25\]. These include synthesis of new materials, polymer based post synthesis modification such as ion irradiation, fluorination and pryolsis. Ion irradiation is a method to control the modification of polymeric materials and thus influence the gas permeation properties \[2, 3, 5, 7, 8, 10, 14, 15, 46, 63, 69, 81, 90, 99, 105, 106\]. Ion irradiation transfers energy from the ion to the polymer and can be used to modify a thin layer of the polymer and can significantly change the chemical and microstructure.

In this chapter, effect of H$^+$ irradiation on polysulfone will be reported. Polysulfone was chosen for this research because it is a very well characterized membrane material \[31\] that is currently used for commercial applications. The structure and properties of PSF are shown in Table 5.1 and Figure 5.1. The microstructure was monitored before and after the dense films irradiated with H$^+$ at 400 KeV for doses between 1 X 10$^{13}$ to 6 X 10$^{15}$ ions/cm$^2$. The evolution in bulk permeability was examined using composite PSF membranes irradiated with H$^+$ between 1 X 10$^{13}$ to 1 X 10$^{15}$ ions/cm$^2$. Finally, the permeance and microstructure of PSF asymmetric membranes were investigated after irradiation with H$^+$ at 100 keV between 1 X 10$^{13}$ to 4 X 10$^{15}$ ions/cm$^2$. Additionally, C$^-$ irradiation at 40 keV was used to modify the permeability of PSF asymmetric membranes for permeance studies.
Table 5.1: Properties of Bulk Polysulfone [31]

<table>
<thead>
<tr>
<th>$T_g$ (°C)</th>
<th>Density (g/cm$^3$)</th>
<th>$P_{O_2}^a$</th>
<th>$P_{CO_2}^a$</th>
<th>$P_{He}^a$</th>
<th>$\alpha_{O_2/\ N_2}$</th>
<th>$\alpha_{CO_2/\ CH_4}$</th>
<th>$\alpha_{He/\ CH_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>1.240</td>
<td>1.4</td>
<td>5.6</td>
<td>13</td>
<td>5.6</td>
<td>14.9</td>
<td>27.4</td>
</tr>
</tbody>
</table>

$a = 1$ Barrer $= 10^{-10} \frac{cm^3}{cm^2 \cdot s \cdot cmHg}$

5.2 Results and Discussion

5.2.1 FTIR Analysis

Seven PSF freestanding dense thin films were irradiated with H$^+$ at 400 KeV between 1 X $10^{13}$ to 2 X $10^{15}$ H$^+/cm^2$. These samples were used for both FTIR and dissolution studies. Figure 5.3 shows the virgin PSF spectrum for the region of 400 to 4000 cm$^{-1}$. The evolution in irradiated spectrums for five specific peaks shown in Table 5.2 was examined in detailed. Figure 5.4 shows the virgin spectrum of PSF along with three irradiated samples in the wavenumber range of 400 to 2000 cm$^{-1}$. There was a general decrease the height of all of the peaks with increasing irradiation fluence. However, the largest decrease was seen in the spectrum when the fluence increased from 1 x $10^{14}$ to 4 x $10^{14}$ H$^+/cm^2$. At the higher fluences most of the peaks were either greatly reduced in size or undistinguishable from the base line.
Table 5.2. The peak identification for virgin PSF

<table>
<thead>
<tr>
<th>ID</th>
<th>Function group</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Aliphatic C-H</td>
<td>~2972</td>
</tr>
<tr>
<td>B</td>
<td>SO(_2) Doublet</td>
<td>~1300</td>
</tr>
<tr>
<td>C</td>
<td>COC</td>
<td>~1224</td>
</tr>
<tr>
<td>D</td>
<td>COC</td>
<td>~1020</td>
</tr>
<tr>
<td>E</td>
<td>SO(_2)</td>
<td>~550</td>
</tr>
</tbody>
</table>

As shown in Figure 5.4, the sulfone peak at 550 cm\(^{-1}\) (peak E) is isolated from other peaks and is therefore easily distinguishable. This sulfone peak is clearly

Figure 5.3. FTIR Spectrum of virgin PSF with specific peaks pointed out and annotated in Table 5.3.
decreasing with increasing ion fluence. The sulfone doublet peak at 1300 cm\(^{-1}\) (peak B) shows a similar trend with increasing ion fluence. The impact of irradiation on the structure of PSF will be monitored in terms of relative peak area. Relative peak areas are reported to account for any differences in properties of virgin films and to allow direct comparison between the irradiated samples. The relative area is defined as the ratio of the irradiated film area to the virgin film area where a value of 1 indicates no change. The relative peak areas for irradiated to virgin sample of sulfone peaks are shown in Figure 5.5 as a function of increasing ion dose. There is little modification in either peak
at low fluences followed by a sharp decrease in relative area at increase fluences. While the sulfone peak is not visible at higher fluences, it does not mean that the complete functional group is removed. Marletta and Iacona suggested that the sulfone group (-SO$_2$-) in polyethersulfone was either completely eliminated or that the oxygens were removed and the group was reduced to a sulfide (-S-) depending on the severity of irradiation [107]. Since FTIR does not show a sulfide peak, Raman spectroscopy would be needed to investigate the mechanism for the sulfone group in PSF.

Figure 5.5. The relative area under a FTIR peak for a sulfone singlet at 550 cm$^{-1}$ (O) and a sulfone doublet at 1300 cm$^{-1}$ (x).
The asymmetrical vibration (1244 cm$^{-1}$) and the symmetrical vibration (1020 cm$^{-1}$) for the aromatic ether (COC) exhibit a strong correlation between the peaks and a moderate decrease with increasing ion fluence. However, at the highest dose there was a slight increase in the relative area. As shown in Figure 5.6, the relative peak area for the asymmetrical and symmetrical aromatic ether vibrations are in good correlation. At the highest fluence the relative peak area drops to approximately 50% of the virgin sample. A potential mechanism for degradation of the aromatic ether may be breaking the oxygen-carbon bond on one side, followed by removal of the oxygen other phenol group. The

![Figure 5.6. The relative area under a FTIR peak for an asymmetric C-O-C bond at 1244 cm$^{-1}$ (O) and a symmetric C-O-C bond at 1040 cm$^{-1}$ (x).]
oxygen can form diatomic oxygen or possible water. The separate ends of the phenol groups can react in a number of ways. For example, hydrogen reacts with the end of the phenol group and thus cause chain scission. Another possibility is that the open phenol groups reacts with the methene group from the methyl group or the tertiary carbon in the backbone. This would result in formation of crosslinks, but no chain scission. While some chain scissions may occur, crosslinking is more prevalent in PSF, particularly at higher ion fluences. Therefore, the mechanism of phenol groups bonding with methene is more probable.

The C-H stretches of the methyl groups are at 2962 and 2872 cm$^{-1}$. As shown in Figure 5.7, the relative area of the peak at 2962 cm$^{-1}$ shows a decrease with increasing fluence. The peak at 2872 cm$^{-1}$ is a very small peak and is very similar to the peak at 2962 cm$^{-1}$. The samples that were irradiated at or below $1 \times 10^{14}$ H$^+/cm^2$ had a very similar spectrum to the virgin polymer. The samples that were irradiated above this fluence show a sharp decrease in peak area. This could be from the formation of methene groups that have a very similar wavenumber. Therefore it is difficult to determine the difference in methyl and methene signals and it is possible for a methyl group to transform into a methene group.

Figure 5.8 shows a comparison of the relative peak areas for several function groups. Significant modification of the chemical structure begins to occur at doses greater $1 \times 10^{14}$ H$^+/cm^2$. The spectrums of polysulfone at or above this fluence show a significant decrease in peak area. The general trends for all peaks are similar with an initial slow decrease in peak area at low fluences followed by a sharp decrease at elevated fluences. The methyl and ether groups show similar trends and maintain approximately
Figure 5.7. The relative area under a peak for FTIR of the CH$_3$ at 2982 cm$^{-1}$.
Figure 5.8. A comparison of the rate at which the relative area for the methyl group (x), sulfone group (o) and the C-O-C (●).
45% of the virgin peak area at the highest fluences. There was a plateau in the relative peak area in both cases at fluences up to $2 \times 10^{15} \text{ H}^+/\text{cm}^2$ followed by a sharp decrease. By contrast, the SO$_2$ peaks exhibited a sharp decrease in peak area at lower initial fluences ($4 \times 10^{14} \text{ H}^+/\text{cm}^2$) and had decreased more rapidly. There is little degradation in the size of the peak area for the methyl group in the region between $4 \times 10^{14} \text{ H}^+/\text{cm}^2$ and $1 \times 10^{15} \text{ H}^+/\text{cm}^2$.

5.2.2 Dissolution Studies

A qualitative study of dissolution in methylene chloride was performed on the irradiated samples used for FTIR studies to examine crosslinking. Table 5.3 shows the results of the dissolution study. The lower dose samples ($1 \times 10^{13} – 1 \times 10^{14}$) dissolved instantly in the solvent. Samples irradiated in the intermediate range showed slight dissolution, while samples irradiated at or above $1 \times 10^{15} \text{ H}^+/\text{cm}^2$ exhibited no visible dissolution. No change was noted beyond the initial dissolution. Crosslinking occurred at doses in the intermediate and high dose ranges (those at and above $1 \times 10^{14} \text{ H}^+/\text{cm}^2$). Crosslinking will cause the polymer to be more rigid and is expected to increase selectivity, resistance to temperature and solvents.

**Table 5.3 Dissolution Results**

<table>
<thead>
<tr>
<th>Result</th>
<th>Ion Dose (H$^+/\text{cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete Dissolution</td>
<td>Virgin – $1 \times 10^{14}$</td>
</tr>
<tr>
<td>Partial Dissolution</td>
<td>$4 \times 10^{14} – 8 \times 10^{14}$</td>
</tr>
<tr>
<td>No Dissolution</td>
<td>$1 \times 10^{15}$ and greater</td>
</tr>
</tbody>
</table>
5.2.3 Permeation Properties of Composite Membranes

Composite membranes with thin PSF layers on a porous ceramic membrane were used to investigate the impact of irradiation on bulk polymer properties. A ceramic membrane was used because it provided no resistance to gas transport and would not be modified by ion irradiation. The permeances and permselectivities of the virgin composite membranes and estimated selective layer thickness are given in Table 5.4. The selective layer thickness of the virgin membranes, estimated using the $O_2$ permeance and the $O_2$ bulk permeability, ranged from 4.2 $\mu$m to 5.7 $\mu$m. Additionally the $O_2/N_2$ selectivities of the virgin membranes were between 63 and 80% of the bulk polymer value. The composite membranes were not considered to be completely defect free. The composite membranes were irradiated with $H^+$ ions at 450 keV at doses from $1 \times 10^{13}$ to $4 \times 10^{15}$ $H^+/cm^2$. This energy was used to ensure modification of the entire polymer selective layer thickness. The permeances and permselectivities of the irradiated membranes are given in Table 5.5.

Table 5.4: Permeation Properties of Virgin PSF Composite Membranes

<table>
<thead>
<tr>
<th>Film ID</th>
<th>$(\frac{P_{O_2}}{T})_{a}$</th>
<th>$(\frac{P_{CO_2}}{T})_{a}$</th>
<th>$(\frac{P_{He}}{T})_{He}$</th>
<th>$\alpha_{O_2/N_2}$</th>
<th>$\alpha_{CO_2/CH_4}$</th>
<th>$\alpha_{He/CH_4}$</th>
<th>Estimated Thickness ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>0.34</td>
<td>1.7</td>
<td>2.8</td>
<td>4.7</td>
<td>19.3</td>
<td>32.0</td>
<td>4.1</td>
</tr>
<tr>
<td>H</td>
<td>0.32</td>
<td>1.6</td>
<td>2.6</td>
<td>3.8</td>
<td>15.2</td>
<td>24.0</td>
<td>3.6</td>
</tr>
<tr>
<td>I</td>
<td>0.25</td>
<td>1.1</td>
<td>1.9</td>
<td>3.5</td>
<td>11.0</td>
<td>18.4</td>
<td>5.7</td>
</tr>
<tr>
<td>J</td>
<td>0.32</td>
<td>1.5</td>
<td>2.5</td>
<td>3.6</td>
<td>8.9</td>
<td>14.8</td>
<td>4.3</td>
</tr>
</tbody>
</table>

\[ a = 1GPU = 10^{-6} \frac{cm^3(STP)}{cm^2 \cdot s \cdot cmHg} \]
Table 5.5: Permeation Properties of Irradiated PSF Composite Membranes

<table>
<thead>
<tr>
<th>Film ID</th>
<th>Film Modification (H+/cm²)</th>
<th>( \left( \frac{P}{T} \right)_{O_2} )</th>
<th>( \left( \frac{P}{T} \right)_{CO_2} )</th>
<th>( \left( \frac{P}{T} \right)_{He} )</th>
<th>( \alpha_{O_2}/N_2 )</th>
<th>( \alpha_{CO_2}/CH_4 )</th>
<th>( \alpha_{He}/CH_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>1x10^{13}</td>
<td>0.364</td>
<td>1.50</td>
<td>2.73</td>
<td>4.50</td>
<td>14.9</td>
<td>27.4</td>
</tr>
<tr>
<td>H</td>
<td>1x10^{14}</td>
<td>0.316</td>
<td>1.30</td>
<td>2.58</td>
<td>2.80</td>
<td>10.2</td>
<td>20.0</td>
</tr>
<tr>
<td>I</td>
<td>4x10^{14}</td>
<td>0.361</td>
<td>1.50</td>
<td>3.11</td>
<td>4.60</td>
<td>12.2</td>
<td>25.4</td>
</tr>
<tr>
<td>J</td>
<td>4x10^{15}</td>
<td>0.311</td>
<td>1.02</td>
<td>2.33</td>
<td>2.50</td>
<td>6.4</td>
<td>14.7</td>
</tr>
</tbody>
</table>

\( a = 1 GPU = 10^{-6} \frac{cm^3 (STP)}{cm^2 \cdot s \cdot cmHg} \)

The normalized permeance for the gases helium, carbon dioxide and oxygen and the gases methane and nitrogen are shown in Figures 5.9(a) and (b), respectively. Figures 5.10 (a) and (b) shows the normalized permselectivity for the gas pairs oxygen/nitrogen and helium/methane. The normalized properties are defined as the ratio of the irradiated membrane to the virgin membrane properties. Normalized permeances and permselectivities are reported to account for any differences in properties of virgin membranes and to allow direct comparison between the irradiated samples.

In general, H⁺ irradiation resulted in small to moderate increases in oxygen permeance for the PSF composite membranes with corresponding small decreases in the O₂/N₂ permselectivity. The increase in permeance and decrease in permselectivity could be attributed to a slightly more open structure and could be accomplished by removal of functional groups, such as methyl or the oxygens from the sulfone groups. However, after significant amounts of functional groups are removed, the polymer matrix could collapse. Crosslinking not only makes the polymer matrix more rigid, it can also prevent
Figure 5.9 A. Relative permeance oxygen (x), carbon dioxide (o) and helium (●) for H⁺ irradiation of composite polysulfone membranes.

Figure 5.9 B. Relative permeance for nitrogen (x) and methane (O) for H⁺ irradiation of composite polysulfone membranes.
Figure 5.10 A. Relative oxygen permeance ($x$) and permselectivity for $O_2/N_2$ (O) for C$^+$ irradiation of composite polysulfone membranes.

Figure 5.10 B. Relative helium permeance ($x$) and permselectivity for He/CH$_4$ (O) for H$^+$ irradiation of composite polysulfone membranes.
the matrix from collapsing to some extent. At increasing ion doses the energy could cause a complete collapse of the polymer matrix significant drops in permeance. Since transport properties of irradiated PSF membranes showed little improvement, no further studies were done.

5.2.3 Permeation Properties of Asymmetric Membranes

While the permeation study on PSF composite membranes was used to understand the effect on the bulk polymer, asymmetric membranes were used to study the effect on a membrane that could be used commercially.

The pure gas permeances were measured for six asymmetric PSF membranes prior to and following irradiation with 100 keV $H^+$ ions at doses from $1 \times 10^{13}$ to $4 \times 10^{15} \text{ H}^+/\text{cm}^2$ to correspond to irradiation range of composite membranes. Seven asymmetric membranes were irradiated with 40 keV $C^-$ at doses from $4.4 \times 10^{12}$ to $1.3 \times 10^{15} \text{ C}^-/\text{cm}^2$. Along with the seven permselective asymmetric membranes modified with $C^-$, two blanks, or non-selective membranes were irradiated with $C^-$ at $4.4 \times 10^{13}$ and $4.4 \times 10^{14} \text{ C}^-/\text{cm}^2$. The blanks were cast so no thin selective layer was formed on the surface. The virgin membranes were defect free and had a selective layer thickness of approximately 60 nm (Table 5.6) and 100 to 300 nm (Table 5.7) for $H^+$ and $C^-$ irradiation, respectively. The permeances and permselectivities at 35 °C for the $H^+$ and $C^-$ irradiated membranes are reported in Tables 5.8 and 5.9.
The normalized permeance of H⁺ irradiated PSF asymmetric membranes for several gases as a function of ion dose are shown in Figures 5.11 (a and b). The normalized permeance and permselectivity for oxygen/nitrogen is shown in figure 5.12. Following H⁺ irradiation of PSF asymmetric membranes at lower doses, the permeances and permselectivities were similar to the virgin membranes. At doses greater than 1x10¹⁴ H⁺/cm², irradiation of PSF asymmetric membranes resulted in simultaneous large decreases in permeance and permselectivity for most gas pairs. For example, there was
an 85% decrease in the permeance of O₂ and a 48% decrease in the O₂/N₂ selectivity following irradiation at 4\times 10^{14} \text{ H}^+/\text{cm}^2.

Table 5.8: Permeation Properties of Irradiated H⁺ PSF Asymmetric Membranes

<table>
<thead>
<tr>
<th>Film ID</th>
<th>Film Modification (H⁺/cm²)</th>
<th>( \frac{P}{T} )\textsubscript{O₂}</th>
<th>( \frac{P}{T} )\textsubscript{CO₂}</th>
<th>( \frac{P}{T} )\textsubscript{He}</th>
<th>( \alpha_{O₂/N₂} )</th>
<th>( \alpha_{CO₂/CH₄} )</th>
<th>( \alpha_{He/CH₄} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1\times 10^{13}</td>
<td>23.0</td>
<td>83.7</td>
<td>164</td>
<td>4.78</td>
<td>20.3</td>
<td>39.8</td>
</tr>
<tr>
<td>B</td>
<td>1\times 10^{14}</td>
<td>26.3</td>
<td>102</td>
<td>212</td>
<td>3.29</td>
<td>12.0</td>
<td>25.0</td>
</tr>
<tr>
<td>C</td>
<td>4\times 10^{14}</td>
<td>3.9</td>
<td>15.2</td>
<td>54.4</td>
<td>3.07</td>
<td>19.1</td>
<td>68.4</td>
</tr>
<tr>
<td>D</td>
<td>8\times 10^{14}</td>
<td>2.8</td>
<td>10.3</td>
<td>52.1</td>
<td>1.90</td>
<td>9.67</td>
<td>48.8</td>
</tr>
<tr>
<td>E</td>
<td>1\times 10^{15}</td>
<td>3.6</td>
<td>14.7</td>
<td>57.6</td>
<td>2.80</td>
<td>17.8</td>
<td>70.0</td>
</tr>
<tr>
<td>F</td>
<td>4\times 10^{15}</td>
<td>1.9</td>
<td>7.09</td>
<td>33.0</td>
<td>1.65</td>
<td>7.84</td>
<td>36.6</td>
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</table>

\( a = 1 \text{GPU} = 10^{-6} \frac{\text{cm}^3 \text{(STP)}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}} \)

Table 5.9: Permeation Properties of Irradiated PSF Asymmetric Membranes used for C⁻ irradiation

<table>
<thead>
<tr>
<th>Film ID</th>
<th>Film Modification (C/\text{cm}²)</th>
<th>( \frac{P}{T} )\textsubscript{O₂}</th>
<th>( \frac{P}{T} )\textsubscript{CO₂}</th>
<th>( \frac{P}{T} )\textsubscript{He}</th>
<th>( \alpha_{O₂/N₂} )</th>
<th>( \alpha_{CO₂/CH₄} )</th>
<th>( \alpha_{He/CH₄} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>4.4\times 10^{12}</td>
<td>5.2</td>
<td>24.2</td>
<td>80.0</td>
<td>5.0</td>
<td>40.3</td>
<td>133.3</td>
</tr>
<tr>
<td>J</td>
<td>2.2\times 10^{13}</td>
<td>2.4</td>
<td>12.8</td>
<td>74.9</td>
<td>3.6</td>
<td>34.1</td>
<td>200.1</td>
</tr>
<tr>
<td>L</td>
<td>4.4\times 10^{13}</td>
<td>2.0</td>
<td>2.0</td>
<td>48.0</td>
<td>4.8</td>
<td>7.2</td>
<td>170.0</td>
</tr>
<tr>
<td>M</td>
<td>8.8\times 10^{13}</td>
<td>1.4</td>
<td>2.9</td>
<td>26.0</td>
<td>3.8</td>
<td>14.1</td>
<td>126.3</td>
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<tr>
<td>N</td>
<td>1.9\times 10^{14}</td>
<td>0.9</td>
<td>1.3</td>
<td>18.7</td>
<td>2.4</td>
<td>4.9</td>
<td>69.0</td>
</tr>
<tr>
<td>O</td>
<td>4.4\times 10^{14}</td>
<td>1.7</td>
<td>1.6</td>
<td>28.6</td>
<td>1.1</td>
<td>1.1</td>
<td>19.1</td>
</tr>
<tr>
<td>P</td>
<td>1.3\times 10^{15}</td>
<td>2.1</td>
<td>3.4</td>
<td>30.0</td>
<td>1.2</td>
<td>2.0</td>
<td>17.4</td>
</tr>
<tr>
<td>Q</td>
<td>4.4\times 10^{13}</td>
<td>83.2</td>
<td>NA</td>
<td>NA</td>
<td>1.1</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>R</td>
<td>4.4\times 10^{14}</td>
<td>31.2</td>
<td>NA</td>
<td>NA</td>
<td>1.2</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

\( a = 1 \text{GPU} = 10^{-6} \frac{\text{cm}^3 \text{(STP)}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}} \)
Figure 5.11 A. Relative permeance for oxygen (x) carbon dioxide (O) and helium (●) for H⁺ irradiation of asymmetric polysulfone.

Figure 5.11 B. Relative permeance for nitrogen (x) and methane (O) for H⁺ irradiation of asymmetric polysulfone membranes.
The normalized permeance of C- irradiated PSF asymmetric membranes for several pure gases as a function of ion dose are shown in Figures 5.13 (a and b). The normalized permeance and permselectivity for several gas pairs are shown in figure 5.14 (a and b). The permeance for the fast gases (Figure 5.13 a), oxygen, helium and carbon dioxide, decrease significantly at fluences greater than ion dose of $1.9 \times 10^{14} \text{ C}^-/\text{cm}^2$. After this dose, the permeance increased for the faster gases, with helium and oxygen increasing the most. Carbon dioxide had only a minor increase in permeance at the higher doses. The slow, large gases (Figure 5.13 b), methane and nitrogen, exhibited a very similar trend as the faster gases. However, at the highest doses, the increase is around two folds of the
Figure 5.13 A. Relative permeance for oxygen (x), carbon dioxide (o) and helium (●) for C⁻ irradiation of asymmetric polysulfone membrane.

Figure 5.13 B. Relative permeance of nitrogen (x) and methane (O) for C⁻ irradiation of asymmetric polysulfone membranes.
Figure 5.14 A. Relative oxygen permeance (x) and permselectivity for O₂/N₂(O) for C⁻ irradiation of asymmetric polysulfone membranes.

Figure 5.14B. Relative helium permeance (x) and permselectivity for He/CH₄(O) for C⁻ irradiation of asymmetric polysulfone membranes.
original values. This resulted in a permselectivity that had minimal decrease at the lowest doses, but had significant decreases at the highest doses.

5.2.4 Analysis of Asymmetric Membrane Microstructure

Ten PSF asymmetric membranes were prepared and irradiated with H\(^+\) using the same method that was used for the membranes for the permeation studies. The O\(_2\)/N\(_2\) selectivity of each virgin membrane was at least 82% of the bulk polymer, which indicates that the membranes were essentially, defect free. PAS analysis was performed on each membrane prior to and following H\(^+\) irradiation at 100 keV at ion doses from 1x10\(^{13}\) to 4x10\(^{15}\) H\(^+\)/cm\(^2\). Unlike the commonly used positron annihilation lifetime spectroscopy, PAS provides information about average free volume as a function of depth but does not allow analysis of free volume distribution. For this reason, PAS is ideal for this study because it allows analysis of the evolution in free volume of the porous substrate as a function of both dose and depth into the membrane surface.

Sample PAS spectra for one virgin and four irradiated membranes that represent the full range of doses are shown in Figure 5.15. The energy on the X-axis corresponds to depth into the membrane surface and the S-parameter corresponds to free volume. In general, an increase in the S-parameter corresponds to an increase in free volume[108-111]. The depth of penetration of the positrons is determined by the density of the material. Since the density of the polysulfone in the asymmetric membranes is a complex function of depth, the results will be presented in terms of the energy. Finally, a vertical line is incorporated in the graph at the approximate depth of the selective layer in virgin membranes. Note that because of the depth of penetration, the positron studies focused primarily on the evolution in the porous substrate and provide little detail about the free
volume of the selective layer because the selective layer was so thin. The PAS curves for all of the virgin membranes were very similar which indicates that there is little difference in free volume characteristics of the porous substrate prior to irradiation. Any variations in PAS spectra for irradiated membranes can, therefore, be attributed to the impact of ions on the membrane microstructure.

Four samples were chosen to represent membranes following low, intermediate and high dose irradiation to demonstrate the trends that were seen for the entire membrane.
series. While the microstructure packing was modified well beyond the dense selective layer of each membrane, at higher energies (depths) the curves returned to those for the virgin membranes. Therefore, ion irradiation at 100 KeV did not modify the entire thickness. At lower doses (< 1 x 10^{14} H^+/cm^2), the extent of modification was fairly small and the samples were similar to those for the virgin membranes. As the ion dose was increased to 4x10^{14} H^+/cm^2, there was a significant decrease in the S-parameter. This corresponds to the dose at which there was a sharp decrease in both permeance and selectivity in asymmetric membranes, for each gas pair studied. As the ion fluence was further increased, there was a continuing trend of a decrease in the S-parameter (free volume).

Following PAS analysis, the irradiated membranes were used for SEM analysis to produce a direct image of the membrane cross-section. The PAS technique would produce only very slight irradiation damage to the material [112]. SEM photos of the non-irradiated sections of each membrane were also taken. SEM photos of virgin and irradiated membranes are shown in Figure 5.16 (a-d). These photos represent membranes irradiated at low, medium and high doses. All of the virgin samples had similar images and a dense layer thickness that corresponded with those estimated from the permeation studies. All membranes are shown skin side up and have the same magnification of 1000. There was an apparent formation of a region of compaction below the selective layer in the irradiated membranes, which increased in thickness for higher irradiation doses. The formation of a compacted region is particularly clear in the image of the membrane following irradiation at 4x10^{15} H^+/cm^2.
Figure 5.16: SEM pictures at 1000 magnification of side of (a) virgin membranes and membranes irradiated at (b) $1 \times 10^{14}$ H$^+$/$\text{cm}^2$, (c) $4 \times 10^{14}$ H$^+$/$\text{cm}^2$, (d) $4 \times 10^{15}$ H$^+$/$\text{cm}^2$. 
5.2.6 Analysis of asymmetric membranes

The sharp decrease in permeance following irradiation at high doses for asymmetric membranes can be attributed to (i) a decrease in the permeability of the polysulfone that makes up the dense selective layer, and/or (ii) compaction of the intermediate porous substrate to form a non-selective layer with Knudsen type resistance and selectivity.

As discussed earlier, the impact of H\(^+\) irradiation on the transport properties of bulk polymer was investigated using a series of PSF-composite membranes. The composite membranes consisted of a PSF selective layer on a porous ceramic support that was not affected by the irradiating ions. Therefore, the permeation properties of the polymer layer can be separated from any affect on the asymmetric membrane substrate.

While there was little change in the permeance of the composite membranes following irradiation, there was a sharp decrease in permeance of the asymmetric membranes following irradiation at doses at or above \(4 \times 10^{14} \text{ H}^+/\text{cm}^2\). As shown in Figure 5.17 for the normalized permselectivity for O\(_2\)/N\(_2\) the composite and asymmetric membranes, irradiated with H\(^+\), exhibited similar decreases in permselectivity following irradiation at lower doses. However, as the ion dose was increased beyond \(1 \times 10^{14} \text{ H}^+/\text{cm}^2\), there was a significant deviation in the impact of irradiation on the permselectivities of these membranes. While the composite membrane exhibited a slight increase in permselectivity following irradiation at \(4 \times 10^{14} \text{ H}^+/\text{cm}^2\), the permselectivity in the asymmetric membrane was about 55% of the virgin value. Additionally, there was a continuing trend of decreasing permselectivity with increasing ion dose in the asymmetric membrane that did not occur in the bulk polymer.
In the second scenario, penetration of the ions beyond the dense selective layer can result in the formation of an additional resistance layer with Knudsen separation properties. SRIM Monte Carlo Simulations were used to estimate the depth of penetration of ions in materials of a specified chemical structure and density. The estimated depth of penetration of H\textsuperscript{+} at 100 keV in polysulfone films with bulk density was at least 1.2 µm, which is well beyond the selective layer thickness. These simulations do not account for the much lower polymer density in the porous substrate region so that the depth of H\textsuperscript{+} penetration would be greater than the estimate based on
bulk density. Since the selective layer of these membranes is quite thin, there is considerable energy transfer from the ions to the PSF porous substrate. This energy transfer may result in collapse of the microstructure of the irradiated porous region, which would form a nonselective region with Knudsen resistance.

A recent report by Rezac et al., attributed the large decreases in permeance and permselectivity following heating of PSF asymmetric membranes at a temperature near the glass transition temperature to a collapse of the porous substructure of the membrane [113]. The large decrease in permselectivity was a result of the addition of a resistance layer with Knudsen selectivities. A series resistance model, which included the resistance due to an initial dense selective layer as well as a non-selective resistance layer, was applied to permeability of the heated asymmetric membranes. This model accurately described the evolution in permeation properties of the asymmetric membranes on heating and agreed well with supplemental results.

Rezac et al. showed that heating asymmetric PSF membranes near the glass transition temperature resulted in a compaction of the porous substrate which led to simultaneous decreases in permeance and permselectivity [113]. A series resistance model assuming Knudsen diffusion in the compacted region of the porous materials agreed well with the variation in gas transport properties of the heated membranes. A simulated model will be used to provide insight into the impact of H+ irradiation on the permeance and permselectivity of the asymmetric membranes. The permeance of a gas through an asymmetric or composite membrane can be described in terms of a series resistance model as shown in Equation 5.1:

$$\frac{1}{P_{Total}} = \frac{1}{P_{Selective}} + \frac{1}{P_{Substrate}}$$ (5.1)
where \[ \left( \frac{1}{P} \right)_{\text{Total}} \] is the overall resistance to gas transport, \[ \left( \frac{1}{P} \right)_{\text{Selective}} \] is the resistance of the permselective layer, and \[ \left( \frac{1}{P} \right)_{\text{Substrate}} \] is the resistance of the porous substrate. Since the porous support has extremely high permeabilities, the resistance in the substrate is typically neglected and separation occurs solely in the selective layer. The ideal selectivity is defined as the ratio of the pure component permeances and can be described using the following expression.

\[
\alpha_{AB} = \frac{\left( \frac{1}{P} \right)_A + \left( \frac{1}{P} \right)_{\text{Select}}}{\left( \frac{1}{P} \right)_{\text{Sub}} + \left( \frac{1}{P} \right)_{\text{Select}}} = \frac{\left( \frac{1}{P} \right)_A}{\left( \frac{1}{P} \right)_B} \tag{5.2}
\]

where \( \alpha_{AB} \) is the ideal selectivity. In order to independently calculate the permeance in the substrate, measured values of the porosity and tortuosity of the porous substrate would be required. Since this data cannot be isolated for the porous region within the modified asymmetric membrane, an alternative method was used to apply the series resistance model to the data for the irradiated membranes. Specifically, the \( \text{O}_2 \) permeance of the porous substrate following irradiation was defined in terms of the permeance of the unmodified selective layer and a resistance ratio as defined in Equation (5.3):

\[
R = \frac{\left( \frac{1}{P} \right)_{\text{Sub}}}{\left( \frac{1}{P} \right)_{\text{Select}}} \tag{5.3}
\]

where \( R \) is the resistance to \( \text{O}_2 \) transport of the substrate relative to the unmodified selective layer. While preliminary results with the composite membranes indicate that there is an evolution in the permeation properties of polysulfone following irradiation, the
relative resistance $R$ in the modified asymmetric membranes was defined in terms of the virgin membrane properties to simplify the analysis.

As a first step, the value $R$ and $\left(\frac{l}{P}\right)_{Substrate}$ that is required to decrease the virgin membrane permeance to the value of the irradiated membranes were calculated from the $O_2$ permeances using Equations 1 and 3. The $N_2$ permeance for the irradiated membranes in the porous support was calculated from $\left(\frac{l}{P}\right)_{Substrate}$ for $O_2$ and a Knudsen selectivity of $O_2/N_2$ of 0.94. Finally, an estimated ideal selectivity for the $O_2/N_2$ system was calculated using Equation 5.3. A plot of the estimated permselectivities using the series resistance models and the experimental values for the irradiated membranes as a function of estimated $R$ is shown in Figure 5.18. The line represents a series resistance model in which an $O_2$ permeance of 25 and selectivity of 5.6 were used to provide a representation of the general trend. While the permselectivities are generally a bit higher than the predicted values, the series resistance model followed similar trends to the real system. Note that for these simple calculations the impact of irradiation on the bulk polymer properties was not considered. Since the virgin membranes had some variability in permeation properties it is expected that there would be some deviation from the calculated values.
The PAS results support the hypothesis that an additional layer of reduced average free volume (i.e. S-parameter) is formed following ion irradiation at higher doses as shown in Figure 5.15. The collapse of the microstructure was greatest near the irradiated surface with the S-parameter returning to the virgin spectrum values at greater depths. The impact of irradiation on the near-surface porosity was greater following irradiation at increasing doses. The dose range at which there was a decrease in the S-parameter corresponds very well with the doses in which the permeances were sharply decreased.
For example, following H\(^+\) irradiation at 1 x 10\(^{13}\)/cm\(^2\), there was no decrease in the permeances and the S-parameter corresponded with that of the virgin membrane. However, following irradiation at or above 4 x 10\(^{14}\) /cm\(^2\) there was a decrease in permeance and the S-parameter in the near surface region was much lower indicating a reduction in free volume. The SEM pictures (Figure 5.16) also indicate that there is formation of a collapsed porous region at the surface below the selective layer.

Modification of a separate set of PSF asymmetric membranes by irradiation with C\(^-\) ions resulted in large decreases in permeances and permselectivities that were similar to the H\(^+\) irradiated asymmetric membranes. To test the impact of irradiation on the porous support, two asymmetric membranes without selective layers were modified with C\(^-\) at 4.4 x 10\(^{13}\) and 4.4 x 10\(^{14}\) ions/cm\(^2\). Prior to irradiation, the O\(_2\)/N\(_2\) selectivity for the two blanks was approximately 1.0. Following irradiation there was a sharp decrease in the O\(_2\) permeance of the membranes with little change in the O\(_2\)/N\(_2\) selectivity. There was a slight increase in selectivity for the membrane blanks following irradiation but these membranes still had very low selectivities. At 4.4 x 10\(^{13}\) C\(^-\)/cm\(^2\) the relative oxygen permeance is greater for the blank than that of the corresponding membrane, while at 4.4 x 10\(^{14}\) C\(^-\)/cm\(^2\) the relative oxygen permeance is lower for the blank. There are several possible factors for that can contribute to this result. The first reason is that the ions damaged the support and caused the pores to collapse at the higher fluence. The ions penetrated deeper into the support for the blanks than the membranes because there is no dense selective layer and the ions penetrate further into a less dense material.

While H\(^+\) irradiation had little impact on the permeance of the bulk polymer, there was a general decrease in the permselectivity following irradiation at doses at or greater
than $4 \times 10^{14}$/cm$^2$. The normalized permeance in the composite membranes following high dose irradiation does not follow the trend that is seen for the asymmetric membranes as shown in Figure 5.19. However, some of the decrease in selectivity of the asymmetric membranes may be the result of decreases in selectivity of the bulk polymer following irradiation. While irradiation resulted in a significant modification to the porous substructure of the asymmetric membrane as well as the properties of the polymer selective layer, the simultaneous decrease in permeance and permselectivity can be attributed primarily to a collapse of the porous substrate. In all cases the irradiated membranes were mechanically stable and exhibited no brittleness.

5.2.7 Comparison of $H^+$ and $C^-$ irradiated asymmetric membranes

As mentioned earlier, the SRIM for $H^+$ ions primary exhibit primarily electronic energy loss mechanism. The $C^-$ ions exhibits both some nuclear energy loss and a large portion of electronic energy loss mechanism. The depth of penetration for 100 keV $H^+$ is 1.3 $\mu$m compared to 40 keV $C^-$ 0.3 $\mu$m estimated on bulk polymer density. Since the porous support has a much lower density, there would be ion penetration into the support layer and modification of porous layer. Therefore, the modification of the $H^+$ set of asymmetric membranes would be significantly deeper into the membrane.
Analysis of H+ irradiated samples of PSF thin dense films indicated that there is a significant evolution in the chemical structure. H+ irradiation caused crosslinking to free standing dense films at fluences above 1 X 10^{14} H+/cm^2. Irradiation below this dose had little effect on the chemical structure, while irradiation at higher doses resulted in a gradual loss in function groups. The most significant changes in the FTIR spectrum and the dissolution results occurred at the dose of 4 x 10^{14} H+/cm^2 and above.

A series of polysulfone asymmetric membranes were irradiated with H+ ions at 100 keV and doses ranging from 1x10^{13} to 4x10^{15} ions/cm^2. While irradiation at low doses
resulted in little change in the permeation properties of these membranes, there was a sharp decrease in both permeance and permselectivity following irradiation at higher doses. Positron annihilation spectroscopy and SEM were used to analyze the evolution in microstructure of asymmetric membranes following \( \text{H}^+ \) irradiation. In both cases, the formation of a compacted region in the porous substrate was indicated. Irradiation of composite membranes allowed isolation of the effect of irradiation on the permeation properties of the bulk polymer. There were small changes in the permeance for the smaller gas molecules, but a general trend of decrease in permselectivity for the bulk polysulfone with increasing fluence. However, the decrease in permselectivity for the asymmetric membrane was much larger than that seen for the bulk polymer following irradiation at similar doses. The large simultaneous decrease in permeance and permselectivity in asymmetric membranes can, therefore, been attributed to the formation of a non-selective resistance layer following penetration of the energetic ions into the polysulfone porous support of the membrane.

Irradiation with \( \text{H}^+ \) ions at high energy resulted in penetration of the ions well into the porous substrate, which led to the formation of a nonselective resistance layer. Recently developed plasma immersion ion implantation (PIII) [114] offers many advantages over conventional beamline ion implantation including the ability to implant complex shaped surfaces (such as the hollow fiber membranes systems that are typically used for commercial applications) combined with a lower capital and operating cost. Since PIII is a low energy irradiation method (< 100 keV), the depth of modification can easily be limited to the selective layer thickness for membrane modification [114]. This will avoid
problems of energy transfer to the porous support and formation of nonselective resistance layers.
Chapter 6: H\textsuperscript{+} Irradiation of 6FDA-6FpDA Films and Membranes

6.1 Introduction

As discussed in Chapter 5, H\textsuperscript{+} irradiation caused significant modification to polysulfone’s microstructure, chemical structure and permeation properties at doses of 1 x 10\textsuperscript{14} H\textsuperscript{+}/cm\textsuperscript{2} and greater. While polysulfone is an attractive commercial membrane material, it did not exhibit significant improvements in gas transport properties following irradiation. Since polyimides have been shown to respond positively to pyrolysis treatment [32, 40, 43, 47, 115], the remainder of this project focused on irradiation of the polyimide, 6FDA-6FpDA. The polyimide, 6FDA-6FpDA, was chosen for the detailed study because of the favorable preliminary results of simultaneous increase for permeance and permselectivity following H\textsuperscript{+} irradiation [15]. The bulky carbon trifluorines off of the main polymer chain prevents significant chain packing in the polyimide and will hold it open following ion dose irradiation. In addition, there is considerable steric hindrance along backbone of 6FDA-6FpDA, which results in much higher T\textsubscript{g}. This combined open microstructure and chain rigidity results in material with high permeability and reasonable selectivities for most gas pairs. This chapter presents a study of impact of H\textsuperscript{+} irradiation structure and permeation properties of 6FDA-6FpDA. The structure and bulk properties of the 6FDA-6FpDA are given in Figure 6.1 and Table 6.1. Table 6.2 shows the modification range, energy, type of media and tests.
Table 6.1 Bulk Properties of 6FDA-6FpDA [19]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T_g (°C)</th>
<th>Density (g/cm³)</th>
<th>$P_{O_2}^a$</th>
<th>$P_{CO_2}^a$</th>
<th>$P_{He}^a$</th>
<th>$\alpha_{O_2/\alpha}/N_2$</th>
<th>$\alpha_{CO_2/\alpha}/CH_4$</th>
<th>$\alpha_{H_2/\alpha}/CH_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6FDA-6FpDA</td>
<td>320</td>
<td>1.466</td>
<td>16.3</td>
<td>63.9</td>
<td>137</td>
<td>4.7</td>
<td>40</td>
<td>85.6</td>
</tr>
</tbody>
</table>

*1Barrer = $10^{-10} \frac{cm^3(STP) \cdot cm}{cm^2 \cdot s \cdot cmHg}$

Figure 6.1. The repeat unit for the polyimide, 6FDA-6FpDA.

Table 6.2 Experimental Summary

<table>
<thead>
<tr>
<th>Type of Film</th>
<th>Energy (keV)</th>
<th>Fluence Range (H⁺/cm²)</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite Membranes</td>
<td>180</td>
<td>$1 \times 10^{14} - 1 \times 10^{16}$</td>
<td>Permeation</td>
</tr>
<tr>
<td>Free Stand Dense Film</td>
<td>450</td>
<td>$5 \times 10^{13} - 1 \times 10^{15}$</td>
<td>FTIR, Dissolution</td>
</tr>
</tbody>
</table>

6.2 Results and Discussion

6.2.1 Dissolution and FTIR Analysis

Seven 6FDA-6FpDA freestanding dense films were irradiated with H⁺ at 450 KeV at fluences between $5 \times 10^{13}$ and $4 \times 10^{15}$ H⁺/cm². These samples were used for both FTIR and dissolution studies. However the highest fluence samples broke during irradiation and were used only for dissolution. Thin freestanding dense films were masked and analyzed using FTIR prior to irradiation. Thin films were used to ensure entire thickness was modified by ion beam irradiation.
A qualitative study of dissolution in methylene chloride was performed on the irradiated samples following FTIR analysis to determine if crosslinking had occurred. The results of the dissolution study are given in Table 6.3. The lower dose sample (5 X 10^{13} H+/cm^2) dissolved instantly. Samples irradiated in the intermediate range showed slight dissolution, while samples irradiated at or above 6 X 10^{14} H+/cm^2 exhibited no visible dissolution. No change was noted beyond the initial dissolution. Therefore crosslinking occurred at doses in the intermediate and high dose ranges (those at and above 1 X 10^{14} H+/cm^2). Crosslinking, which will typically cause the polymer to be more rigid is expected to increase selectivity and increase resistance to temperature and solvents effect on transport properties.

**Table 6.3 Dissolution Results**

<table>
<thead>
<tr>
<th>Result</th>
<th>Ion Dose (H+/cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete Dissolution</td>
<td>Virgin – 5 X 10^{13}</td>
</tr>
<tr>
<td>Partial Dissolution</td>
<td>1 X 10^{14}</td>
</tr>
<tr>
<td>No Dissolution</td>
<td>6 X 10^{14} and greater</td>
</tr>
</tbody>
</table>

Figure 6.2 shows the virgin 6FDA-6FpDA spectrum in the region of 400 to 4000 cm^{-1}. The virgin spectra for all samples were consistent. Figure 6.3 shows the virgin spectrum of 6FDA-6FpDA, along with three irradiated samples in the wavenumber range of 400 – 2000 cm^{-1}. The evolution in the irradiated spectrums for the six specific peaks shown in Table 6.4 will be discussed in this section in detail.

Overall, there was a decrease in most of the peaks in the spectrum along with disappearance of several shoulder peaks with increasing irradiation. For example, the shoulder peak of the 1372 cm^{-1} (CNC peak) disappeared at higher ion fluence. Unlike the
Figure 6.2  Virgin spectrum of 6FDA-6FpDA with annotated points for use with Table 6.4

Figure 6.3  Fingerprint region of 6FDA-6FpDA virgin spectrum along with three irradiated samples over range of ion dose
PSF discussed in Chapter 5, the spectrum of H\textsuperscript{+} irradiated 6FDA-6FpDA still resembles the virgin spectrum over the entire range of doses used in this study. Therefore the 6FDA-6FpDA is more resistant to irradiation than PSF.

**Table 6.4** Functional Group for FTIR with use with Figure 6.2

<table>
<thead>
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<th>Number</th>
<th>Wavenumber (cm\textsuperscript{-1})</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1778</td>
<td>C=O Symmetric</td>
</tr>
<tr>
<td>2</td>
<td>1725</td>
<td>C=O Asymmetric</td>
</tr>
<tr>
<td>3</td>
<td>1372</td>
<td>CNC Axial Stretch</td>
</tr>
<tr>
<td>4</td>
<td>1128-1250</td>
<td>CF Stretching</td>
</tr>
<tr>
<td>5</td>
<td>720</td>
<td>CF\textsubscript{3} Bending</td>
</tr>
<tr>
<td>6</td>
<td>828</td>
<td>Para Connected aromatic CH out of plane bending</td>
</tr>
</tbody>
</table>

The peak at 720 cm\textsuperscript{-1} represent CF\textsubscript{3} bending and the peaks at 1128 – 1250 cm\textsuperscript{-1} represent CF stretching for CF, CF\textsubscript{2} and CF\textsubscript{3} in 6FDA-6FpDA. The relative area of these peaks with increasing H\textsuperscript{+} irradiation is shown in Figure 6.4. The relative area is defined as the ratio of the area for irradiated sample to area of the virgin sample to allow for comparison of slightly different samples. Both peaks exhibited similar trends of gradual decrease in area with increasing H\textsuperscript{+} fluence. At the lowest doses, there was a slight decrease in the relative area of CF\textsubscript{3} bending with a decreasing trend to 66% of the virgin sample area at the highest fluences studied. While the CF stretching results in a maximum decrease to 71% at the highest fluences. It is difficult to distinguish if the stretch was for CF, CF\textsubscript{2}, or CF\textsubscript{3}. While the CF\textsubscript{3} bending measures only CF\textsubscript{3} groups, the CF stretch measures CF, CF\textsubscript{2}, or CF\textsubscript{3}, and therefore, the reduction of a CF\textsubscript{3} to a CF\textsubscript{2} or CF and would still be recorded by FTIR at some point.

The relative areas of the imide C=O for asymmetric stretch at 1728 cm\textsuperscript{-1} and symmetric stretch at 1778 cm\textsuperscript{-1} as a function of increasing fluence are shown in Figure 6.5. The two imide peaks exhibited very similar results following H\textsuperscript{+} irradiation with increasing irradiation. In both cases at low to intermediate fluences there was minimal
Figure 6.4. Relative area of CF$_3$ bending (□) and CFs stretching (●) with increasing H$^+$ fluence.

Figure 6.5 Relative area of symmetric (□) and asymmetric (●) C=O functional group with increasing H$^+$ fluence.
decrease in peak area followed by a sharp drop off at fluences greater than $7 \times 10^{14}$ H$/\text{cm}^2$. The C=O group showed minimal loss at the lower fluences. At higher fluences, there was additional damage to C=O groups which resulted in a loss of about 25% of the relative area for both peaks at the highest fluences. Therefore, there is significant evolution in the C=O group between $6 \times 10^{14}$ and $8 \times 10^{14}$ H$/\text{cm}^2$.

The para out of plane stretching for C-H has a peak at a wavenumber at 828 cm$^{-1}$ and the CNC axial stretch at 1372 cm$^{-1}$. Figure 6.6 shows the relative area for both peaks with increasing ion irradiation. At the highest H$^+$ fluence, the relative area was less than 60% of the original for the para out of plane stretching for C-H. There was a gradual decrease in area with increasing doses for this peak. The CNC group follows a very similar trend to that of the C=O peaks where there is a slight initial drop followed by a minimal decrease with increasing H$^+$ irradiation. At the highest fluences the relative areas are about 75% of the virgin areas.

Figure 6.7 shows the six relative areas for peaks discussed earlier to allow for comparison of the various functional groups. For the most part, the six relative areas can be split into two sets, (i) gradual decrease in area with dose. The first set, significant decreases at $6 \times 10^{14}$ H$/\text{cm}^2$, which includes both CF groups along with C-H out of plane bending and (ii) constant values followed by a sharp decrease at $8 \times 10^{14}$ H$/\text{cm}^2$, which includes the C=O groups and the CNC stretching. While the functional groups do not act identical to others in their set, they show similar trends.

At the lowest fluence, $1 \times 10^{14}$ H$/\text{cm}^2$, all of the functional groups reacted similarly by losing $\sim 10\%$ of the relative area. However, at $6 \times 10^{14}$ H$/\text{cm}^2$, the functional groups form two distinct regions, minimal addition loss of relative area, and
Figure 6.6. Relative area of para connected aromatic of CH out of plane stretching (□) and CNC axial stretch (●) functional groups with increasing H⁺ fluence.

Figure 6.7. Comparison of the relative area of symmetric C=O (○), asymmetric C=O (●), CF₃ (□), CF (■), para connected out of plane bending (Δ) and CNC stretching (▲) with increasing H⁺.
significant loss of relative area. The C=O bonds for both asymmetric and symmetric stretching and the CNC group exhibited minimal additional loss. The other groups, CF₃, CF, and para out of plane stretching for C-H, had reduction of relative area to ~73%. Irradiation at 8 × 10¹⁴ H⁺/cm² resulted in sharp decreases in relative area for the functional groups of both C=O groups and CNC, while CF₃, CF, and para out of plane stretching for C-H had minimal additional decrease. At the highest fluence, 1 × 10¹⁵ H⁺/cm², there was minimal additional loss of relative area for all of the functional groups except CF₃, and para out of plane stretching for C-H. The para out of plane stretching for C-H was decrease to ~ 57% of the virgin area. To generalize the results, the para out of plane stretching for C-H was the most susceptible while the C=O was the least susceptible to H⁺ irradiation.

6.2.2 Crosslinking Mechanism

Based on crosslinking studies, significant crosslinking occurred at fluences at or above 1 × 10¹⁴ H⁺/cm². However, the irradiated polymer becomes insoluble in methylene chloride at 6 × 10¹⁴ H⁺/cm². As mentioned previously the CFs functional groups along with the C-H out of plane stretching exhibited a significant reduction in relative area at 6 X 10¹⁴ H⁺/cm², which coincides with a point of noticeable crosslinking. On the other hand, there was negligible loss of area for the CNC and C= groups of imide linkage at this dose. Therefore, crosslinking likely occurs at the four carbon trifluro groups at the ion doses. A proposed mechanism for crosslinking is discussed below as seen in Figure 6.8 (a). The proposed mechanism starts with the formation of a free radical following the removal of a fluorine from a CF₃ group. In addition, a CF₃ from a neighboring polymer
Figure 6.8. Two potential crosslinking mechanisms for 6FDA-6FpDA irradiated with H⁺
chain is cleaved to form a free radical. The two free radicals can react with and form a crosslink along with a CF₄ molecule.

Another potential mechanism would be formation of a crosslink at C=O groups as shown in Figure 6.8 (b). This could be accomplished by breaking one of the double bonds from two groups on neighboring polymer chains and two C-O-C groups would be formed. This mechanism is not supported by FTIR because there is no peak growth in the area of C-O-C bonds. In addition, this mechanism is unlikely due to steric hindrance.

6.2.3 Modification of the microstructure

The modification of the polyimide chemical structure by ion irradiation should result in evolution in microstructure, specifically packing defects and chain rigidity. This section provides a proposed evolution in the microstructure packing of materials based on knowledge of virgin microstructure and chemical structure evolution. In addition, the expected impact on gas transport properties will be discussed and compared with permeation data in the next section.

Virgin Material

The polyimide, 6FDA-6FpDA has been very well characterized in regard to microstructure [19, 33]. As shown in Table 6.1, 6FDA-6FpDA has a very high free volume and relatively high Tₛ. The high FFV has been attributed to a combination of (1) large bulky groups along the backbone (ie CF₃) that prevent close chain packing and (2) large planar groups along chain which results in regions of high free volume in combination with densely packed regions. This combined rigidity and free volume results in a high permeability (from high diffusivity and solubility) combined with high permselectivity. The solid line in Figures 6.9 (a-c) represents a sample of distribution of
dynamic free volume for virgin polymer. The average dynamic free volume results from a combination of average chain spacing, molecular scale packing defects and chain mobility. It represent general size of gaps available for diffusion and sorption versus concentration of these gaps. On the x-axis, represent a dynamic volume of openness, while the y-axis represents the number of each specific volume.

Low Dose (1 X 10^{14} \text{ H}^+/\text{cm}^2 and below)

At low dose H^+ irradiation, a small amount of CF_3 is removed and minimal amount of crosslinking occurs. The removal of a small amount of fluorines or CF_3 groups would causes an increase in the free volume, specifically, formation of microstructure and therefore increase in permeance. Since there is only a small reduction in FTIR area for the CF groups, the impact of functional groups on the free volume and free volume distribution will be fairly small at this point. In addition, the 6FDA-6FpDA is a high free volume polymer with a large percentage of free volume in form of packing defects. These materials are prone to physical aging which results in loss of some of these packing defects with losses in free volume [17, 116]. This will tend to result in shifting of the free volume distribution to smaller sizes and some narrowing of the distribution. In addition, the transfer of energy from ions to polymer chains may cause some rearrangement of polymer chains is a process that is similar to aging. The net result would be small changes in free volume with slight shift to lower free volumes with losses in permeance and minimal change in selectivity.

Medium Dose (6 X 10^{14} – 2 X 10^{15} \text{ H}^+/\text{cm}^2)

Based on structural evolution studies at medium fluence of range of H^+ irradiation of 6FDA-6FpDA there is considerable loss of CF_3 and considerable formation of
crosslinks. However, there is still sufficient CF$_3$ groups present to hold the polymer matrix open. Crosslinking would cause the polymer matrix to be more rigid and which, effectively reduces dynamic free volume, particularly at the larger end. When both crosslinking and the removal of fluorines and CF$_3$ occur the free volume can changes dramatically. Figure 6.9 (b) shows a cartoon of how the free volume may changes at the intermediate range of H$^+$ irradiation. Larger gases could see the most improvement due to the size of the new voids and the rigidity from the crosslink to keep them open. Therefore the selectivities would decrease for several gas pairs.

**High Dose (greater than 2 X 10$^{15}$ H$^+/cm^2$)**

In the high dose region of H$^+$ irradiation for 6FDA-6FpDA, FTIR was not performed because samples were broken during irradiation. However, based on trends for lower doses, it is expected that there were be gradual loss of CF$_3$ and other groups. In addition, the polymer matrix was considerable crosslinked. The removal of a large amount of flourines and CF$_3$ would eventually causes the matrix to collapse because there is no support or bulky groups to keep the matrix open. Also, with the reduced mobility caused by increased crosslinking, the effective free volume is significantly reduced at higher fluences. Figure 6.9 (c) shows a schematic of the change in free volume distribution following high dose of H$^+$ irradiation. The collapse of microstructure at high dose could result in formation of numerous smaller size defects, which are not accessible to larger gases (i.e. nitrogen and methane). The permeance of the larger gases, such as, methane and nitrogen, could decrease significantly, while small molecules would be expected to increase. This results in a large increase in selectivity for some gas pairs at high fluences.
Figure 6.9 Schematic of the free volume distribution of three regions of irradiation of 6FDA-6FpDA, low (a), medium (b) and high (c). The irradiation polymer matrix (---) is compared to the virgin material (—).
6.2.4 Permeation Studies

The pure gas permeances were measured for five 6FDA-6FpDA composite membranes prior to and following H\(^+\) irradiation. The set was modified with 180 keV H\(^+\) ions at doses from 1 \(\times 10^{14}\) to 1 \(\times 10^{16}\) \(\text{H}^+ / \text{cm}^2\). Each sample had an \(\text{O}_2 / \text{N}_2\) selectivity that was at least 88% of the bulk value prior to irradiation and was considered defect free. The selective layer thickness was estimated using virgin oxygen permeance and the bulk polymer permeability reported in literature \[19\]. All selective layer thicknesses were between 0.5 and 0.9 \(\mu\text{m}\). The virgin permeances and permselectivities for all five membranes, along with the estimated thickness of the selective layer are given in Table 6.5. The permeance and permselectivities at 35 °C for irradiated membranes are reported in Table 6.6.

### Table 6.5 Virgin Permeance and Estimated Thickness of Selective layer

<table>
<thead>
<tr>
<th>Film ID</th>
<th>(\frac{P}{l}_{\text{O}_2})</th>
<th>(\frac{P}{l}_{\text{CO}_2})</th>
<th>(\frac{P}{l}_{\text{He}})</th>
<th>(\alpha_{\text{O}_2/\text{N}_2})</th>
<th>(\alpha_{\text{CO}_2/\text{CH}_4})</th>
<th>(\alpha_{\text{He}/\text{CH}_4})</th>
<th>Estimated Thickness ((\mu\text{m}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>32.8</td>
<td>114.1</td>
<td>204.6</td>
<td>4.5</td>
<td>49.7</td>
<td>89.1</td>
<td>0.5</td>
</tr>
<tr>
<td>B</td>
<td>24.3</td>
<td>106.8</td>
<td>179.7</td>
<td>4.2</td>
<td>51.9</td>
<td>87.4</td>
<td>0.7</td>
</tr>
<tr>
<td>C</td>
<td>17.6</td>
<td>73.4</td>
<td>139.2</td>
<td>4.1</td>
<td>61.8</td>
<td>117.2</td>
<td>0.9</td>
</tr>
<tr>
<td>D</td>
<td>17.3</td>
<td>73.3</td>
<td>136.2</td>
<td>4.2</td>
<td>59.5</td>
<td>110.7</td>
<td>0.9</td>
</tr>
<tr>
<td>E</td>
<td>16.0</td>
<td>69.8</td>
<td>130.3</td>
<td>4.2</td>
<td>63.8</td>
<td>119.0</td>
<td>0.9</td>
</tr>
</tbody>
</table>

\(a = 1\text{Barrer} = 10^{-10} \frac{\text{cm}^3 (\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}\)

### Table 6.6 Permeance and permselectivity for irradiated samples

<table>
<thead>
<tr>
<th>Film ID (ion type)</th>
<th>Film Modification (ions/cm(^2))</th>
<th>(\frac{P}{l}_{\text{O}_2})</th>
<th>(\frac{P}{l}_{\text{CO}_2})</th>
<th>(\frac{P}{l}_{\text{He}})</th>
<th>(\alpha_{\text{O}_2/\text{N}_2})</th>
<th>(\alpha_{\text{CO}_2/\text{CH}_4})</th>
<th>(\alpha_{\text{He}/\text{CH}_4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(1 \times 10^{14})</td>
<td>15.1</td>
<td>69.6</td>
<td>114.4</td>
<td>4.3</td>
<td>61.5</td>
<td>101.0</td>
</tr>
<tr>
<td>B</td>
<td>(1 \times 10^{15})</td>
<td>36.0</td>
<td>181.6</td>
<td>259.1</td>
<td>4.6</td>
<td>44.9</td>
<td>64.0</td>
</tr>
<tr>
<td>C</td>
<td>(2 \times 10^{15})</td>
<td>27.8</td>
<td>119.1</td>
<td>191.2</td>
<td>6.3</td>
<td>83.8</td>
<td>134.4</td>
</tr>
<tr>
<td>D</td>
<td>(5 \times 10^{15})</td>
<td>11.8</td>
<td>65.1</td>
<td>292.8</td>
<td>5.6</td>
<td>86.3</td>
<td>388.0</td>
</tr>
<tr>
<td>E</td>
<td>(1 \times 10^{16})</td>
<td>7.2</td>
<td>46.2</td>
<td>264.7</td>
<td>6.0</td>
<td>157.8</td>
<td>904.3</td>
</tr>
</tbody>
</table>

\(a = 1\text{Barrer} = 10^{-10} \frac{\text{cm}^3 (\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}\)
The irradiated membranes exhibited similar trends in modification of permeation of each gas studied with an initially decrease in permeance at low fluences, followed by an increase in the intermediate range and a decrease at high fluences. However, the maximum increase in permeance occurred at slightly different fluences for each gas, which resulted in significant variation in selectivity. The results are reported in terms of normalized permeances and permselectivities to account for any differences in properties of virgin membranes and to allow for comparison between irradiated samples. The normalized properties are defined as the ratio for property of the irradiated membrane to the virgin membrane property. Figure 6.10 shows the normalized permeance plotted against increasing ion fluence for all five gases studied. All of the gases showed a significant decrease in permeance at the lowest fluence, followed by an increase in the intermediate range. At the highest fluences studied, helium continued to increase in relative permeance while all of the other gases exhibit a significant decrease relative to virgin membrane. The largest gases, methane and nitrogen, exhibited the largest drop in relative permeance. For example, helium had a normalized permeance of 2.0 at $1 \times 10^{16}$ H$^+$/cm$^2$, while, methane had a normalized permeance of 0.3 at the same fluences. This leads to a large increase in selectivities at higher fluences.

Both the normalized permselectivities and relative permselectivities for O$_2$/N$_2$ as a function of ion dose is shown in Figure 5.11. The relative permselectivities were used to compare irradiated membranes to bulk materials. It is defined as the ratio selectivity of irradiated membranes to the reported bulk value. As shown in Figure 5.10, oxygen exhibited a maximum relative permeance of $\sim$1.6 at $2 \times 10^{15}$ H$^+$/cm$^2$. While nitrogen exhibited a permeance increase at the same fluence, the increase was less than for
Figure 6.10 The relative permeance for $\text{O}_2$ (●), $\text{CO}_2$ (○), $\text{He}$ (▼), $\text{N}_2$ (△) and $\text{CH}_4$ (X) with increasing ion fluence.

Figure 6.11 Relative selectivity for $\text{O}_2$/$\text{N}_2$ with respect to bulk (x) and with respect to virgin sample (●) with increasing $\text{H}^+$ fluence.
oxygen. This corresponds to minimal change to normalized permselectivity at the lowest doses, but an increase of around 1.4 times the virgin selectivity for the doses at or above $2 \times 10^{15} \text{ H}^+/\text{cm}^2$. At $2 \times 10^{15} \text{ H}^+/\text{cm}^2$, there was a significant combined increase of permeance and permselectivity where the $\text{O}_2/\text{N}_2$ irradiated selectivity was 6.3 relative to 4.7 for bulk polymer. The relative permselectivities shows a very similar trend to that of the normalized permselectivities, but are slightly lower in value. Overall, oxygen and nitrogen permeances react very similarly following irradiation. This is not unexpected as oxygen and nitrogen are similar in shape and size and have relative similar solubilities.

As discussed earlier, the relative permeance of helium decreased to 50% of virgin values following low fluence irradiation followed by a steady increase with increasing fluences (Figure 6.10). The methane permeance also decreased at low fluences exhibited a large increase at intermediate fluence with a maximum at $1 \times 10^{15} \text{ H}^+/\text{cm}^2$. As dose was further increased, the relative permeance of methane decreased sharply. As shown in Figure 6.12, the relative He/CH$_4$ relative and normalized permselectivities exhibited small changes at the lowest fluences, followed by a sharp increase to over 7.5 times the virgin selectivity at the highest dose. At the highest dose, He/CH$_4$, there was significant increase in both the He permeance and permselectivity where the irradiated selectivity was $\sim 900$. The increase is not unexpected at higher doses where the microstructure has collapsed so that larger molecules are prevented from diffusing through the membranes.

6.2.5 Permeance and Microstructure

For the most part, the relative permeances had initial decreases followed by an increase to a maximum then a decrease with increasing ion dose. The peak location and
height varied depending upon gas and different dose would be used to modify membranes for specific separation. Therefore, there would be an optimal ion fluence to maximize the productivity and selectivity for a given gas pair, while this study identified general trends.

The differences in shape of relative permeances of the gases are due to original microstructure, evolution in polymer microstructure and size and shape of the penetrants. Following irradiation at low doses, there may have been rearrangement of the polymer matrix, in a process similar to aging, which resulted in better-packed material. This would cause the permeance for large gases to decrease because it is more difficult to diffuse through the membrane. Larger gases would see a larger decrease in permeance if
this were the only result from ion irradiation. In addition, removal of small amount of CF$_3$ would result in void formation that increases the free volume. These voids would increase the diffusion of gas molecules; specifically the larger voids would significantly increase the larger gases permeances. Therefore, the permeance data supports that there is an overall loss in free volume, as described in Figure 6.9 (a).

In the medium ion fluence range (6 X 10$^{14}$ – 2 X 10$^{15}$ H$^+$/cm$^2$), there was considerable modification of the microstructure, which resulted in significant evolution in the transport properties. In this region irradiation of the polymer matrix resulted in removal of more functional groups, which would increase the free volume and a larger amount of crosslinking which leads to a more rigid material. This would be expected to result in an increase in permeance for all gases with general increase in selectivity. However, the impact of structural evolution on the selectivity would be complex. Depending on gases there may be an increase or decrease. As shown in Figure 6.9 (b), the permeance of all of the gases tested had an increase at some point in this range. For example, at 1 X 10$^{15}$ H$^+$/cm$^2$, methane and nitrogen had about 2 and 1.3 times, greater permeance than the virgin material, respectively. However, at 2 X 10 H$^+$/cm$^2$, methane and nitrogen had 1.2 and 1.0 times, higher permeance, than the virgin material, respectively. Beyond this dose, the permeance of these large molecules decreased sharply.

At higher fluences (greater than 2 X 10$^{15}$ H$^+$/cm$^2$), additional functional groups were removed along with addition crosslinking. At lower fluence the removal of functional groups would lead to in opening of the matrix, eventually, the removal of to many functional groups would result in a collapse of the matrix. There would be a
decrease in void volume, specifically, large sized voids, and along with increased
crosslinking. Therefore, at very high doses, the irradiated polymer would be rigid and a
more closed material. This would result in a decrease in the permeances of gases through
the membrane, specifically larger penetrantes. Figure 6.9 (c) shows a schematic of a
proposed free volume distribution of polymer irradiated at high fluence. There is a
narrowing of free volume distribution with a shift to higher values at low free volume
end. This would result in sharp increase in He permeance while all of the other gases
exhibit large decreases in permeance, especially the larger gases, nitrogen and methane.

The high permeability of He is due to a very high diffusivity with a negligible
solubility at 35°C. Therefore any change in permeance of He is due to a change in
diffusivity. Carbon dioxide had a very high solubility in 6FDA-6FpDA and therefore is
more susceptible to change in solubility. Table 5.7 shows the diffusivity and solubility
coefficient in 6FDA-6FpDA for the five gases used in this study. At $1 \times 10^{15}$ and $2 \times
10^{15} \text{ H}^+/\text{cm}^2$, both helium and carbon dioxide permeances increase to $\sim 1.3$ and $1.6$,
respectively. Therefore, both the solubility and diffusivity increased in the region even
though there was a decrease at the previous ion fluence. This is probably due to the
increase in free volume, because, in this region there is significant crosslinking that
increases the rigidity. At the highest fluences, there is large difference in the relative
permeances for helium and carbon dioxide; therefore, the solubility and diffusivity of the
polymer are also very different. For helium, the increase must again, be from an increase
in free volume. However, carbon dioxide the decrease also corresponds to decrease free
volume, therefore there must be a sharp increase in the free volume between the kinetic
diameter of helium and carbon dioxide.
Methane and nitrogen are both larger gases and are very different than helium and oxygen. As mentioned earlier nitrogen permeability is highly dependent on the diffusion coefficient while methane permeability is more dependent on the solubility. At the lowest fluence, $1 \times 10^{14} \text{ H}^+/\text{cm}^2$, the permeance for both gases decrease similarly to helium and carbon dioxide. This could be attributed to a more uniform packing matrix along with some crosslinking that prevents chain mobility. In the intermediate range ($1 \times 10^{15}$ and $2 \times 10^{15} \text{ H}^+/\text{cm}^2$) methane relative permeance is higher than nitrogen, similar to carbon dioxide to helium. Therefore, the contribution was less affected than the diffusivity coefficient in this region. At the highest fluences, the relative permeance for methane and nitrogen sharply decreases.

### 6.3 Conclusions

There was significant modification of the chemical structure, microstructure and gas permeance of 6FDA-6FpDA following H$^+$ irradiation. FTIR and dissolution studies showed that irradiation resulted in progressive removal of functional group and crosslinking. The extent of modification was dependent upon functional groups. The para out of plane stretching for C-H connected bonds was the most susceptible to irradiation, while imide linkage was the most resistant based on relative peak area. In addition, there was significant loss of CF$_3$ in lower dose region. Crosslinking occur at doses at or greater than $1 \times 10^{14} \text{ H}^+/\text{cm}^2$. A mechanism for crosslinking was proposed based upon combined dissolution and FTIR data. Specifically, crosslink formation occurs between two CF$_3$.

The permeation properties were significantly modified following H$^+$ irradiation. The general trend was an initial decrease in normalized permeance at low doses, followed
by an increase to a maximum and then decrease at increasing fluences. Helium was an exception to this trend since it did not exhibit a decrease in normalized permeance at high fluences. However, with additional ion fluence, the permeance for helium could decrease and follow the trend. The larger gases (i.e. N$_2$ and CH$_4$) had very large decreases in permeance at high dose. This resulted in significant increase in the selectivities for gas pairs such as He/CH$_4$ and He/N$_2$. 
Chapter 7: 6FDA-6FpDA Chemical and Microstructure Modified by H⁺, N⁺ or F⁺ Ions

7.1 Introduction

As discussed in Chapter 6, H⁺ irradiation over a range of doses resulted in evolution in chemical structure, microstructure and permeation properties of 6FDA-6FpDA. 6FDA-6pDA freestanding dense films initially dissolved into methylene chloride, but with increasing H⁺ irradiation, the films became more resistant to dissolution, and eventually there was no sign of dissolution. This indicates that with increase H⁺ irradiation, crosslinking occurs in 6FDA-6FpDA. Through FTIR the chemical structure evolution was monitored and indicated significant decay of several functional groups. To generalize the results, the para out of plane stretching for C-H is the most susceptible while the C=O are the least susceptible to H⁺ irradiation. The permeation results show that for all gases expect helium, the relative permeance initially decrease, increase to a maximum, and was followed by a sharp peak. Helium’s relative permeance did not reach a maximum, which led to significant increases in both helium’s permeance and permselectivity for He/CH₄ at higher H⁺ doses.

While H⁺ irradiation resulted in significant evolution of the structure and properties of 6FDA-6FpDA, incomplete modification was achieved at practical doses. In addition, H⁺ irradiation has a nearly exclusive electronic energy transfer mechanism, with very little contribution from nuclear loss. Therefore, the next two chapters will focus on
impact of ion irradiation of 6FDA-6FpDA with ions of different mass. Chapter 6 discusses effect of dose and ion type (i.e. $H^+$, $N^+$, $F^+$) on chemical structure. Chapter 7 will focus on evolution in permeation properties following irradiation with the same ions used in chemical structure studies. The repeat unit of 6FDA – 6FpDA and bulk properties are shown in Figure 7.1 and Table 7.1, respectively. Results will be discussed in terms of ion dose, total energy transfer, as well as the electronic and nuclear contributions to transfer. Table 7.2 shows the ion, modification range, energy, type of media and test performed on them.

**Table 7.1** Bulk Properties of 6FDA-6FpDA

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
<th>Density (g/cm$^3$)</th>
<th>$\bar{P}_{O_2}$</th>
<th>$\bar{P}_{CO_2}$</th>
<th>$\bar{P}_{He}$</th>
<th>$\alpha_{O_2}/N_2$</th>
<th>$\alpha_{CO_2}/CH_4$</th>
<th>$\alpha_{He}/CH_4$</th>
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</thead>
<tbody>
<tr>
<td>6FDA-6FpDA</td>
<td>320</td>
<td>1.466</td>
<td>16.3</td>
<td>63.9</td>
<td>137</td>
<td>4.7</td>
<td>40</td>
<td>85.6</td>
</tr>
</tbody>
</table>

$^a = 1 \text{Barrer} = 10^{-10} \text{cm}^3\text{(STP)} \cdot \text{cm} \cdot \text{s} \cdot \text{cmHg}$

**Table 7.2** Experimental Summary

<table>
<thead>
<tr>
<th>Ion</th>
<th>Type of Film</th>
<th>Energy (KeV)</th>
<th>Dose Range</th>
<th>Data</th>
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<tr>
<td>$H^+$</td>
<td>Free Stand Dense Film</td>
<td>450</td>
<td>$5 \times 10^{13} - 1 \times 10^{15}$</td>
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</tr>
<tr>
<td>$N^+$</td>
<td>Free Stand Dense Film</td>
<td>2400</td>
<td>$8.33 \times 10^{11} - 3.33 \times 10^{13}$</td>
<td>FTIR, Dissolution</td>
</tr>
<tr>
<td>$F^+$</td>
<td>Free Stand Dense Film</td>
<td>2400</td>
<td>$6.66 \times 10^{11} - 1.67 \times 10^{13}$</td>
<td>FTIR, Dissolution</td>
</tr>
</tbody>
</table>

The electronic and nuclear energy transfer as a function of depth for samples irradiated with $N^+$ 2400KeV is shown in Figure 7.2 (a). Because of the large energy loss...
as a function of depth, N⁺ and F⁺ irradiation at the energies available would not uniformly modify the entire depth of the freestanding films. Therefore, samples were irradiated on both sides to ensure uniform modification for the entire thickness of the films. Figure 7.2 (b) shows individual energy transfer for samples irradiated from each side. The combined energy transfer for each mechanism is shown in Figure 7.2 (c). The level of energy transfer is relatively constant through the entire thickness of the membrane, which allows for consistent modification of the films. For the thin films irradiated with N⁺ and F⁺, the samples had to be irradiated from both sides to ensure a uniform modification. Figure 7.3 shows the energy transferred for the final irradiation of both sides from the SRIM simulations for F⁺ of 6FDA-6FpDA.
Figure 7.2. The Monte Carlo simulation of N⁺ at 2400 KeV for (A) single side irradiation, (B) dual side irradiation and (C) the sum of dual irradiation for electronic (o) and nuclear (□) energy transfer mechanism.
The impact of H\textsuperscript{+} irradiation on structural evolution was discussed in detail in Chapter 6. The following section gives brief results of evolution in structure following irradiation with each type of ion. 6FDA-6FpDA freestanding dense films were irradiated with H\textsuperscript{+} at 450 KeV, N\textsuperscript{+} at 2400 KeV or F\textsuperscript{+} at 2400 KeV over a wide range of fluences. These samples were used for both FTIR and dissolution studies. Figure 7.4 shows the virgin 6FDA-6FpDA FTIR spectrum in the region of 400 to 4000 cm\textsuperscript{-1}. The evolution in the irradiated spectrums for six specific peaks shown in Table 7.3 were examined in detailed.

7.2 Results

The impact of H\textsuperscript{+} irradiation on structural evolution was discussed in detail in Chapter 6. The following section gives brief results of evolution in structure following irradiation with each type of ion. 6FDA-6FpDA freestanding dense films were irradiated with H\textsuperscript{+} at 450 KeV, N\textsuperscript{+} at 2400 KeV or F\textsuperscript{+} at 2400 KeV over a wide range of fluences. These samples were used for both FTIR and dissolution studies. Figure 7.4 shows the virgin 6FDA-6FpDA FTIR spectrum in the region of 400 to 4000 cm\textsuperscript{-1}. The evolution in the irradiated spectrums for six specific peaks shown in Table 7.3 were examined in detailed.
Table 7.3 Functional Group for FTIR with use with Figure 7.4

<table>
<thead>
<tr>
<th>Number</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1778</td>
<td>C=O Symmetric</td>
</tr>
<tr>
<td>2</td>
<td>1725</td>
<td>C=O Asymmetric</td>
</tr>
<tr>
<td>3</td>
<td>1372</td>
<td>CNC Axial Stretch</td>
</tr>
<tr>
<td>4</td>
<td>1128-1250</td>
<td>CF Stretching</td>
</tr>
<tr>
<td>5</td>
<td>720</td>
<td>CF₃ Bending</td>
</tr>
<tr>
<td>6</td>
<td>828</td>
<td>Para Connected aromatic CH out of plane bending</td>
</tr>
</tbody>
</table>

7.2.1 H⁺ Irradiation

A qualitative study of dissolution in methylene chloride was performed on the irradiated samples used for FTIR studies to examine crosslinking. Table 7.4 shows the results of dissolution study for H⁺. The lower dose samples (below 5 X 10¹³ H⁺/cm²) dissolved instantly in the solvent. Samples irradiated in the intermediate range showed
slight dissolution while samples irradiated at or above $4 \times 10^{14}\ H^+/\text{cm}^2$ exhibited no visible dissolution. This indicates that significant crosslinking is starting to occur at $1 \times 10^{14}\ H^+/\text{cm}^2$. No change was noted in samples beyond the initial dissolution.

<table>
<thead>
<tr>
<th>Table 7.4 Dissolution Results for $H^+$ Irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Result</strong></td>
</tr>
<tr>
<td>Complete Dissolution</td>
</tr>
<tr>
<td>Partial Dissolution</td>
</tr>
<tr>
<td>No Dissolution</td>
</tr>
</tbody>
</table>

Figure 7.5 shows the decay of the six specific peaks as a function of $H^+$ dose. FTIR studies showed that irradiation resulted in progressive removal of functional group. Relative peak areas are reported to account for any differences in properties of virgin films and to allow direct comparison between the irradiated samples. The relative area is defined as the ratio of the irradiated film to the virgin film property where a value of 1 indicates no change. At the lowest dose, $1 \times 10^{14}\ H^+/\text{cm}^2$, all of the functional groups reacted similarly with approximately 10% loss in the relative area. However, at $6 \times 10^{14}\ H^+/\text{cm}^2$, the functional groups form two distinct regions of loss of relative area and therefore rate of decay. The C=O bonds for both asymmetric and symmetric stretching and the CNC group resulted in minimal additional loss, with the CNC group’s relative area decreasing the most to ~86% of the original area. The other groups, CF$_3$, CF, and para out of plane stretching for C-H, exhibited larger reduction of relative area to ~73%. Irradiation at $8 \times 10^{14}\ H^+/\text{cm}^2$ resulted in sharp decreases in relative area for the functional groups of both C=O groups and CNC, while CF$_3$, CF, and para out of plane stretching for C-H had minimal addition decrease. At the highest fluence, $1 \times 10^{15}\ H^+/\text{cm}^2$, there was minimal addition loss in relative area for all of the functional groups.
except CF$_3$, and para out of plane stretching for C-H. The para out of plane stretching for C-H was decreased to less than 60% of the virgin area. To generalize the results, the para out of plane stretching for C-H was the most susceptible while the C=O was the least susceptible to H$^+$ irradiation. The results are discussed in detail in Chapter 6.

7.2.2 Impact of N$^+$ irradiation on Structure

Five 4 µm thick dense freestanding samples of 6FDA-6FpDA were irradiated with N$^+$ at 2400 KeV from both sides. Table 7.5 shows the qualitative description of dissolution for sample following N$^+$ irradiation. At the doses used for N$^+$ irradiation, no sample had complete dissolution; however, some samples (below N$^+/\text{cm}^2$) resulted in partial dissolution. Sample irradiated above N$^+/\text{cm}^2$ resulted in no noticeable dissolution. Figure 7.6 shows the virgin spectrum in the wave number range of 400-2000 cm$^{-1}$ of 6FDA-6FpDA, along with three N$^+$ irradiated samples over range of doses used. The
The figure shows that with increasing N⁺ irradiation, several peaks decrease, and at the highest dose, the spectra is significantly different than that of the virgin spectra. For example, the CF₃ stretch at 720 cm⁻¹ is significantly reduced at the highest fluence. However, several peaks resemble the virgin spectra, such as the C=O peak at 1720 cm⁻¹.

**Table 7.5** Dissolution Results for N⁺ Irradiation

<table>
<thead>
<tr>
<th>Result</th>
<th>Ion Dose (N⁺/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete Dissolution</td>
<td>Virgin</td>
</tr>
<tr>
<td>Partial Dissolution</td>
<td>8.33 X 10¹¹ - 1.83 X 10¹²</td>
</tr>
<tr>
<td>No Dissolution</td>
<td>6.66 X 10¹² and greater</td>
</tr>
</tbody>
</table>

As shown in Figure 7.7, the asymmetric and symmetric peaks for C=O shows similar trends following to N⁺ irradiation. At low doses (less the 2 X 10¹² N⁺/cm²) there was minimal loss of C=O peak area, however at medium and higher doses (above 5 X 10¹² N⁺/cm²) there was substantial loss in area. Figure 7.8 shows the relative area loss for CF₃ bends and CF₅ stretches irradiated with N⁺. At lower and medium doses both the CF₃ bends and CF₅ stretches are affected minimally and reacted very similarly. However at the highest doses, the CF₅ stretches were less affected than the CF₃ bends. At the highest dose the CF₅ bend relative area is reduced to approximately 12% of the virgin material. The larger area reduction of CF₃ peak can be attributed to loss of CF₃ peak where any single fluorine atom to form CF₂. In case of CF, the loss of a fluorine atom will result in small reduction of peak area, but the remain CF₂ will provide a full signal. Figure 7.9 shows the relative area for CNC and C-H out of plane peaks. The general trends hold true for each type of peak with little change at low to intermediate doses and a sharp drop at higher doses. Note that both groups exhibit similar levels of decrease in peak area at each dose.
Figure 7.6. The FTIR of virgin 6FDA-6FpDA along with three samples irradiated with increasing $N^+$. 

Figure 7.7. Relative area for $N^+$ irradiated 6FDA-6FpDA for the C=O groups at 1778 cm$^{-1}$ (○) and 1725 cm$^{-1}$ (■).
Figure 7.8. Relative area for N\textsuperscript{+} irradiated 6FDA-6FpDA for the CF\textsubscript{3} bend (○) and CFs stretches (■).

Figure 7.9. Relative area for N\textsuperscript{+} irradiated 6FDA-6FpDA for the CNC group (○) C-H out of plane stretching (■).
7.2.3 Impact of F$^+$ irradiation on Structure

Five freestanding dense films were irradiated on both sides with 2400 KeV F$^+$. Table 7.6 provides a qualitative description of dissolution for F$^+$ irradiation. At the doses used for F$^+$ irradiation, no sample exhibited complete dissolution; however, samples irradiated below F$^+/\text{cm}^2$ resulted in partial dissolution. Beyond this point there was no noticeable dissolution. The virgin spectrum of 6FDA-6FpDA, along with three F$^+$ irradiated samples over wide range of doses in the wave number range of 400-2000 cm$^{-1}$ is shown in Figure 7.10. Similar trends are seen in F$^+$ irradiation as those that were seen from N$^+$ irradiation. For example, F$^+$ irradiation resulted in a significant reduction of the CF$_3$ stretch similar to that shown from N$^+$ irradiation.

<table>
<thead>
<tr>
<th>Result</th>
<th>Ion Dose (F$^+/\text{cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete Dissolution</td>
<td>Virgin</td>
</tr>
<tr>
<td>Partial Dissolution</td>
<td>$6.66 \times 10^{11} - 8.33 \times 10^{11}$</td>
</tr>
<tr>
<td>No Dissolution</td>
<td>$1.83 \times 10^{12}$ and greater</td>
</tr>
</tbody>
</table>

The relative area as a function of ion dose for the asymmetric and symmetric stretch for C=O is shown in Figure 7.11. At the lowest dose, there is minimal change in the relative area for both peaks. The peak at 1725 cm$^{-1}$ had moderate losses until the highest dose, where the relative area was approximately 67% of the virgin. The C=O peak at 1778 cm$^{-1}$ had a moderate decrease in relative area at $8.33 \times 10^{11}$ F$^+/\text{cm}^2$, with significant decreases in relative area at increasing doses beyond this point. The relative area for CF$_3$ bends and CF$_2$ stretches for F$^+$ irradiation of 6FDA-6FpDA are shown in Figure 7.12. At the lowest dose, there is minimal loss in relative area for both peaks, however, with additional F$^+$ irradiation a steady decrease in relative area. The decrease in peak area were similar for CF$_3$ and CF$_2$. Figure 7.13 shows the relative area of the C-H
Figure 7.10. The FTIR of virgin 6FDA-6FpDA along with three samples irradiated with increasing F⁺.

Figure 7.11. Relative area for F⁺ irradiated 6FDA-6FpDA for the C=O groups at 1778 cm⁻¹ (○) and 1725 cm⁻¹ (■).
Figure 7.12. Relative area for F⁺ irradiated 6FDA-6FpDA for the CFs stretch (○) and CF₃ bend (■).

Figure 7.13. Relative area for F⁺ irradiated 6FDA-6FpDA for the C-H out of plane stretching (○) and the CNC group (■).
out of plane stretching and CNC peak. At doses up to $1.66 \times 10^{12}$ and $6.66 \times 10^{12}$ F$^+$/cm$^2$ for the C-H out of plane stretching and CNC peaks, respectively, the decrease in relative area was minimal. With additional irradiation, the relative area for both peaks decreased significantly when compared to the virgin material.

7.3 Discussion

As discussed in background, it is difficult to compare ion dose from different ion and energies because the energy deposited in the material is not proportional to the dose. Therefore, following a brief comparison of irradiation effect in terms of ion dose, a detailed discussion based on total energy per square centimeter. The total energy and energy for each mechanism were calculated using the method describe in the experimental section.

7.3.1 Dissolution

The samples irradiated with H$^+$ were less crosslinked than the samples irradiated with nitrogen or fluorine. This was true even at high dose H$^+$ irradiation. The larger ions generally impact greater energies at similar doses than does H$^+$ which is more likely to result in crosslinking [10, 11, 117].

7.3.2 FTIR

As mentioned earlier, comparing the effect of irradiation of different ions by ion dose is not as effective as other means. However, using ion dose as base of comparision provides insight into how different ions cause damage and the amount of damage done by various ions at given conditions. Figures 7.14 – 15 shows the relative area for all the CF$_3$ and asymmetric C=O peaks, respectively, for each of the three ions as a function of ion. Two important trends are demonstrated in these figures and are consistent for all
Figure 7.14. FTIR of the C=O group at 1778 cm$^{-1}$ for H$^+$ irradiation (○), N$^+$ irradiation (■) and F$^+$ irradiation (▲).

Figure 7.15. FTIR of the CF$_3$ bend for H$^+$ irradiation (○), N$^+$ irradiation (■) and F$^+$ irradiation (▲).
functional groups. The first trend is that H⁺ irradiation at higher ion doses than N⁺ or F⁺ resulted in significantly less damage than the other ions. The second trend is that N⁺ and F⁺ irradiation resulted in very similar decreases, and typically F⁺ decreased slightly more than N⁺.

7.3.3 Ion impact based on energy comparison

In the section of this chapter, the FTIR and dissolution results were examined for each ion type in terms of ion dose. Using ion dose is useful only when comparing results from the same ion at similar energies. Because total energy transfer is crucial to determine the extent of modification, this section will focus on structural data in terms of energy transfer. Total energy transfer includes two mechanisms to transfer energy, electronic and nuclear. For the ions used in this studied, (H⁺, N⁺ and F⁺), the primary mechanism was electronic energy, however, the relative nuclear transfer contribution differed considerable with ion choice. The total energy transfer and transfer by each mechanism were estimated for each irradiated sample. N⁺ and F⁺ irradiation results in very similar energy transfer for both nuclear and electrical energy loss.

7.3.4 Dissolution

The dissolution as a function of electric energy transfer and nuclear transfer energy transfer is shown in Tables 7.7 and 8, respectively. At similar electronic energy losses, irradiation with H⁺ maintain complete dissolution with partial dissolution for N⁺ or no noticeable dissolution for F⁺. Note that the nuclear energy transfer was much lower for H⁺ irradiation, than other ions used. In this case, the H⁺ irradiated samples exhibited negligible dissolution at lower relative nuclear energy than other ions. Therefore a combination of electronic and nuclear mechanism were important in crosslink formation.
Table 7.7 Dissolution results with electronic energy transfer

<table>
<thead>
<tr>
<th>Result</th>
<th>$H^+$ (eV/Å)</th>
<th>$N^+$ (eV/Å)</th>
<th>$F^+$ (eV/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete Dissolution</td>
<td>Virgin $- 3.30 \times 10^{14}$</td>
<td>Virgin</td>
<td>Virgin</td>
</tr>
<tr>
<td>Partial Dissolution</td>
<td>$6.60 \times 10^{14}$</td>
<td>$1.38 \times 10^{14}$ - $2.76 \times 10^{14}$</td>
<td>$1.09 \times 10^{14}$ - $1.36 \times 10^{14}$</td>
</tr>
<tr>
<td>No Dissolution</td>
<td>$3.95 \times 10^{15}$ and greater</td>
<td>$1.10 \times 10^{15}$ and greater</td>
<td>$2.72 \times 10^{14}$ and greater</td>
</tr>
</tbody>
</table>

Table 7.8 Dissolution results with nuclear energy transfer

<table>
<thead>
<tr>
<th>Result</th>
<th>$H^+$ (eV/Å)</th>
<th>$N^+$ (eV/Å)</th>
<th>$F^+$ (eV/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete Dissolution</td>
<td>Virgin $- 2.20 \times 10^{11}$</td>
<td>Virgin</td>
<td>Virgin</td>
</tr>
<tr>
<td>Partial Dissolution</td>
<td>$4.40 \times 10^{11}$</td>
<td>$2.49 \times 10^{12}$ - $4.99 \times 10^{12}$</td>
<td>$4.20 \times 10^{12}$ - $5.35 \times 10^{12}$</td>
</tr>
<tr>
<td>No Dissolution</td>
<td>$2.64 \times 10^{12}$ and greater</td>
<td>$1.99 \times 10^{13}$ and greater</td>
<td>$1.07 \times 10^{13}$ and greater</td>
</tr>
</tbody>
</table>

7.3.5 FTIR

Since, for the ions in this study, electronic energy is primary component of total energy transfer, the results will be discussed in terms of electronic energy. Figures 7.16 and 17 shows the relative area for the two peaks discussed earlier as a function of electrical energy transfer. Even though $H^+$ irradiation had a significantly higher ion dose and total electronic energy transfer, the nuclear energy transfer is towards the lower values from $N^+$ and $F^+$ irradiation. With the shift in position, the $H^+$ irradiation falls into similar trend, for the most part as $N^+$ and $F^+$ irradiation. The normalized area for the specific peaks discussed earlier in terms of dose for each ion and is plotted as a function of total nuclear energy transfer in Figure 7.18 and 19. For all of the functional groups, the $H^+$ irradiated samples at comparable total deposited nuclear energy resulted in the least decrease in relative area. The C=O bonds, CF$_3$ bending, CFs and CNC relative area shows that $H^+$ resulted in significantly less modification, specifically in the higher nuclear energy region. However, even though this trend continues for the C-H out of plane stretch, $H^+$ irradiation caused significant reduction in the relative area and was most effected by $H^+$ irradiation. The amount of electronic energy transfer is over a comparable
Figure 7.16. FTIR of the C=O at 1778 cm\(^{-1}\) for H\(^+\) irradiation (○), N\(^+\) irradiation (■) and F\(^+\) irradiation (▲) as a function of electronic energy transfer.

Figure 7.17. FTIR of the CFs stretches for H\(^+\) irradiation (○), N\(^+\) irradiation (■) and F\(^+\) irradiation (▲) as a function of electronic energy transfer.
range for the various ions used, however, the amount of nuclear energy transfer is considerable less for H\(^+\) irradiation.

The general trends for each energy loss for loss of functional groups will be discussed in terms of C=O at 1778 cm\(^{-1}\) and CF\(_3\). The carbonyl groups at 1778 and 1725 cm\(^{-1}\) shows very similar trends with regards to electronic and nuclear energy loss. First of all, as mentioned earlier, comparing peak area for electronic energy mechanism show that even though the hydrogen irradiated samples had a comparable amount of electronic and total energy transfer, the nitrogen and fluorine irradiated samples showed significantly greater peak reduction at similar electronic energy transfer. The primary difference is larger nuclear energy loss for the larger ions. In addition, while nuclear energy transfer mechanism does more damage at same energy levels, with enough electrical energy transfer, significant damage can be done to structure.

Much like the results for the C=O groups, the two CF group showed that nuclear energy transfer was more effective in destroying this peak than electrical energy. At the highest electrical energy transfer for H\(^+\) irradiation, the CF\(_3\) group was \(~ 67\%\) of the original, while the highest N\(^+\) sample is less then 15\% of the original. When these two samples are compared, the N\(^+\) sample received over a magnitude greater amount of nuclear energy with similar electronic loss. The difference for the CFs was significantly less the difference for the CF\(_3\) group. Similar trends are seen for the CNC and the para connect C-H stretch.

7.3.6 Microstructure and Chemical Structure

The modification of the polyimide structure by ion irradiation should result in evolution in microstructure, specifically packing defects and chain rigidity. This section
Figure 7.18. FTIR of the C=O at 1778 cm$^{-1}$ for H$^+$ irradiation (○), N$^+$ irradiation (■) and F$^+$ irradiation (▲) as a function of nuclear energy transfer.

Figure 7.19. FTIR of the CF$_3$ bend for H$^+$ irradiation (○), N$^+$ irradiation (■) and F$^+$ irradiation (▲) as a function of nuclear energy transfer.
describes a proposed evolution in the microstructure packing of materials based on knowledge of virgin microstructure and chemical structure evolution based on FTIR results. These results will be discussed in terms of a cartoon of dynamic free volume versus occurrence as shown in Figure 7.20. The expected impact on gas transport properties will also be discussed.

Virgin Material

The polyimide, 6FDA-6FpDA was been very well characterized in regard to microstructure [19] as discussed in detail in Chapter 6. The solid line in Figures 7.21 (a-c) represents a sample of distribution of dynamic free volume for virgin polymer. The dynamic free volume results from a combination of average chain spacing, molecular scale packing defects and polymer chain mobility. For example, a high Tg polymer with bulky side groups would be expected to have high inherent steric hendrence due to packing inhibition. At the same time rigidity could tend to reduce formation of diffusion gaps and narrow distribution. On the x-axis, represent a specific volume of openness, while the y-axis represents the number of each specific volume. 6FDA-6FpDA would expect regions of high free volume in combination with dense packed area due to rigid bulky nature.

Low Dose (1 X 10^{14} H^+/cm^2 and below, 1.83 X 10^{12} N^+/cm^2 and below, 8.33 X 10^{11} F^+/cm^2 and below)

At low dose irradiation (1 X 10^{14} H^+/cm^2 and below, 1.83 X 10^{12} N^+/cm^2 and below, 8.33 X 10^{11} F^+/cm^2 and below), a small amount of function groups (ie. CF_3) is removed and minimal crosslinking occurs. The removal of a small amount of fluorines or CF_3 groups would result in an increase in the free volume and therefore increases in
permeance. Since there is only a small reduction in FTIR area for the CF groups, the impact of functional groups on the free volume and free volume distribution will be fairly small at this point. Note, that in addition, the 6FDA-6FpDA is a fairly rigid high free volume polymer with a large percentage of free volume in form of packing defects. Also, these materials are prone to physical aging which results in loss of some of these packing defect with losses in free volume [116]. This will tend to result in shifting of the free volume distribution to smaller sizes and some narrowing of the distribution. The aging is typical of thin films [116]. In addition, the transfer of energy from ions to polymer chains may cause some rearrangement of polymer chains with an effect that is similar to aging. Figure 7.21(a) shows a drawing of the microstructure would be expected to change following low dose irradiation, with the irradiated microstructure as the dashed line and the virgin material as the solid line. The net result would be small changes in free volume due to combination of physical aging (lower free volume), and removal of bulky groups (higher free volume). Therefore, slight shift of FFV to lower values is expected with corresponding loss in permeance.

Medium Dose ($6 \times 10^{14} - 2 \times 10^{15}$ $H^+/cm^2$, $6.66 \times 10^{12}$ $N^+/cm^2$, $1.83 \times 10^{12} - 6.66 \times 10^{12}$ $F^+/cm^2$)

Based on structural evolution studies at medium dose ($6 \times 10^{14} - 2 \times 10^{15}$ $H^+/cm^2$, $6.66 \times 10^{12}$ $N^+/cm^2$, $1.83 \times 10^{12} - 6.66 \times 10^{12}$ $F^+/cm^2$) of 6FDA-6FpDA there is considerable loss of function groups and formation of crosslinks. However, there is still sufficient CF$_3$ groups present to provide steric hindrance and hold the polymer matrix open. Crosslinking would cause the polymer matrix to be more rigid and thus limit the amount of dynamic free volume resulting from chain mobility. When both crosslinking
and the removal of fluorines and CF$_3$ occur the free volume can changes dramatically. However, since this polymer is inherently rigid, the additional free volume would be expected to dominate in this region. Figure 7.21 (b) shows a cartoon of potential shift in dynamic free volume at the intermediate irradiation range based on considerable crosslinking and loss of function groups. This shift to high free volume would be expected to increase the large molecule permeances. Therefore the selectivities may decrease for several gas pairs.

*High Dose (greater than 2 \times 10^{15} \text{H}^+/\text{cm}^2, 1.83 \times 10^{13} \text{N}^+/\text{cm}^2, \text{and} 1.83 \times 10^{13} \text{F}^+/\text{cm}^2)*

FTIR was not performed at very high doses for H$^+$ because samples were broken during irradiation, however, data was recorded for both N$^+$ and F$^+$ irradiation. Based on trends for lower doses, it is expected that there were be gradual loss of CF$_3$ and other groups from H$^+$ irradiation. In addition, the polymer matrix was insoluble which indicates considerable crosslinking occurred for all samples. At very high irradiation doses, there was little CF$_3$/CF groups present in the polymer matrix. The loss of these bulky groups, which provides resistance to chain packing, could result in a collapse of the polymer matrix and loss of free volume. Also, with the reduced mobility caused by increased crosslinking, the dynamic free volume may be further reduced following irradiation at higher fluences. Figure 7.21 (c) shows a schematic of the change in free volume distribution following high dose irradiation. The collapse of microstructure at high dose could result in formation of numerous smaller size defects, which are not accessible to larger gases (i.e. nitrogen and methane). The permeance of the larger gases, such as, methane and nitrogen, could decrease significantly, while small molecules would
Figure 7.21  Schematic of the free volume distribution of three regions of irradiation of 6FDA-6FpDA, low (a), medium (b) and high (c). The irradiation polymer matrix (---) is compared to the virgin material (—).
be expected to increase or show smaller decreases. This results in a large increase in selectivity for some gas pairs at high doses.

7.3.7 Crosslinking

Potential crosslinking mechanisms for H+ irradiation of 6FDA-6FpDA were discussed in detail with the most likely crosslink mechanism occurring between two CF3 bonds in Chapter 6. The mechanism occurs when energy breaks the bond between a CF3 and the backbone along with the removal of a fluorine from a CF3 group. The two free radicals form a bond and a crosslink of CF2 is formed. A cartoon of this mechanism is shown in Figure 7.22 (a). The FTIR analysis for N+ irradiation supports a similar mechanism, however, at lower doses, the mechanism is not supported for F+ irradiation. This is because, at the lowest F+ irradiation, there is no decrease in the relative peak area for CF3. This could be due to the fact that additional fluorines from the irradiation source are replacing the targeted fluorines. There is a slight decrease in the relative area for both of the C=O peaks. A potential mechanism would be formation of a crosslink at C=O groups as shown in Figure 6.34 (b). This could be accomplished by breaking one of the double bonds from two groups on neighboring polymer chains and two C-O-C groups would be formed. This mechanism is not supported by FTIR because there is no peak growth in the area of C-O-C bonds.

7.4 Conclusions

The choice of ion plays an important role in determining the effect of irradiation on structure evolution through variations in the total energy and energy loss mechanisms. For example, in dissolution studies, N+ and F+ irradiation resulted in significant crosslinking at lower ion doses than H+ irradiation. Based on FTIR studies, more damage
Figure 7.22. Potential crosslinking for 6FDA-6FpDA. Crosslinking occurs at the CF₃ bonds between polymer chains (a) is more likely than a crosslink at the C=O (b).
is down with larger ions such as $N^+$ and $F^+$ as compared to $H^+$. When comparing the results of relative area based on electrical and nuclear energy transfer, it shows that the ion with high nuclear transfer energy are much more damaging than electrical energy transfer. For example, significant shift of $H^+$ irradiation dose and energy transfer total to achieve similar damage as was seen for $N^+$ and $F^+$ irradiation. $H^+$ which has a small mass has a smaller nuclear loss component. For $N^+$ irradiation and at higher ion doses for $F^+$ irradiation, the crosslinking mechanism is similar to that of $H^+$ irradiation induced crosslinking in that it occurs at the CF$_3$ functional groups. However, FTIR does not support the mechanism at lower $F^+$ doses, but this could be due source $F^+$ replacing fluorines from the polymer.
Chapter 8:  6FDA-6FpDA Permeation Evolution after Ion Irradiation by H\(^+\), N\(^+\) or F\(^+\) Ions

8.1 Introduction

The effect of ion type and energy transfer mechanism on the structure and microstructure evolution of 6FDA-6FpDA was discussed in Chapter 7. In general, samples that were irradiated with H\(^+\) exhibited less modification at similar ion doses and total energy transferred than the larger ions. While the majority of energy transfer occurs through electronic mechanism for all ions used, the nuclear loss is largest for larger ions. Therefore, the greater damage to the polymer from N\(^+\) and F\(^+\) irradiation can be attributed to nuclear energy mechanism. In all cases, there was considerable evolution in chemical structure with loss of functional groups both along the polymer backbone and pendent groups. The CF\(_3\) group exhibited the largest degradation with irradiation, and the C=O group being the most stable in presence of ion irradiation. There was considerable evidence of crosslink formation with the polymer following irradiation at intermediate and higher ion doses. The evolution in chemical structure would be expected to result in corresponding evolution in microstructure.

This chapter examines the impact of ion size and energy transfer mechanism on permeation properties of 6FDA-6FpDA composite membranes. The results for 15 6FDA-6FpDA composite membranes irradiated with H\(^+\), N\(^+\) or F\(^+\) are compared to virgin properties. The bulk properties for 6FDA-6FpDA are given in Table 8.1. The results
will be discussed in terms of impact of irradiation on chemical structure and microstructure of 6FDA-6FpDA. Table 8.2 shows the irradiation conditions used for different ions and membranes.

**Table 8.1** Bulk Properties of 6FDA-6FpDA [19]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T_g (ºC)</th>
<th>Density (g/cm³)</th>
<th>( \overline{P}_{O_2} )</th>
<th>( \overline{P}_{CO_2} )</th>
<th>( \overline{P}_{He} )</th>
<th>( \alpha_{O_2/N_2} )</th>
<th>( \alpha_{CO_2/CH_4} )</th>
<th>( \alpha_{He/CH_4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6FDA-6FpDA</td>
<td>320</td>
<td>1.466</td>
<td>16.3</td>
<td>63.9</td>
<td>137</td>
<td>4.7</td>
<td>40</td>
<td>85.6</td>
</tr>
</tbody>
</table>

\( a = 1 \text{Barra} = 10^{-10} \text{ cm}^3 \text{cmHg} \cdot \text{cm} \cdot \text{s} \cdot \text{cm}^2 \)

*Table 8.2. Irradiation Conditions*

<table>
<thead>
<tr>
<th>Ion Type</th>
<th>Energy (KeV)</th>
<th>Range of ion Dose (ions/cm²)</th>
<th>Number of Membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>180</td>
<td>1 X 10¹⁴ to 1 X 10¹⁶</td>
<td>5</td>
</tr>
<tr>
<td>N⁺</td>
<td>400</td>
<td>2 X 10¹³ to 1 X 10¹⁵</td>
<td>6</td>
</tr>
<tr>
<td>F⁻</td>
<td>2400</td>
<td>2 X 10¹⁵ to 1 X 10¹⁶</td>
<td>4</td>
</tr>
</tbody>
</table>

**8.2 Results**

The pure gas permeances were measured for the composite 6FDA-6FpDA membranes prior to and following irradiation. Each membrane had an O₂/N₂ selectivity that was at least 78% of the bulk value prior to irradiation and was therefore considered defect free. The selective layer thickness was estimated using virgin oxygen permeance and bulk polymer permeability reported in literature[19]. The selective layer thicknesses were between 0.5 and 0.9 µm for H⁺, 0.4 and 1.3 µm for N⁺ and 1.2 and 2.1 µm for F⁻ irradiation. The virgin permeances and permselectivities for all 15 membranes, along with the estimated thickness of the selective layer are given in Table 8.3. The permeance and permselectivities at 35 °C for irradiated membranes are reported in Table 8.4.
Table 8.3 Virgin Permeance and Estimated Thickness of Selective layer

<table>
<thead>
<tr>
<th>Film ID (Ion)</th>
<th>( \frac{P}{T} ) (<em>{O_2} ) ( \frac{P}{T} ) (</em>{CO_2} ) ( \frac{P}{T} ) (_{He} )</th>
<th>( \alpha_{O_2}/N_2 )</th>
<th>( \alpha_{CO_2}/CH_4 )</th>
<th>( \alpha_{He}/CH_4 )</th>
<th>Estimated Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>32.8</td>
<td>114.1</td>
<td>204.6</td>
<td>4.5</td>
<td>49.7</td>
</tr>
<tr>
<td>B</td>
<td>24.3</td>
<td>106.8</td>
<td>179.8</td>
<td>4.2</td>
<td>51.9</td>
</tr>
<tr>
<td>C</td>
<td>17.7</td>
<td>73.4</td>
<td>139.2</td>
<td>4.1</td>
<td>61.8</td>
</tr>
<tr>
<td>D</td>
<td>17.3</td>
<td>73.3</td>
<td>136.2</td>
<td>4.2</td>
<td>59.5</td>
</tr>
<tr>
<td>E</td>
<td>16.0</td>
<td>69.8</td>
<td>130.2</td>
<td>4.2</td>
<td>63.8</td>
</tr>
<tr>
<td>F</td>
<td>33.8</td>
<td>140.9</td>
<td>225.3</td>
<td>4.5</td>
<td>56.1</td>
</tr>
<tr>
<td>G</td>
<td>19.2</td>
<td>110.2</td>
<td>168.2</td>
<td>4.0</td>
<td>55.4</td>
</tr>
<tr>
<td>H</td>
<td>32.8</td>
<td>143.2</td>
<td>216.8</td>
<td>4.4</td>
<td>54.2</td>
</tr>
<tr>
<td>I</td>
<td>12.4</td>
<td>46.7</td>
<td>119.3</td>
<td>3.6</td>
<td>38.2</td>
</tr>
<tr>
<td>J</td>
<td>16.1</td>
<td>65.4</td>
<td>127.6</td>
<td>4.9</td>
<td>56.3</td>
</tr>
<tr>
<td>K</td>
<td>44.3</td>
<td>160.3</td>
<td>270.4</td>
<td>4.8</td>
<td>47.2</td>
</tr>
<tr>
<td>L</td>
<td>7.8</td>
<td>33.2</td>
<td>52.1</td>
<td>3.8</td>
<td>45.4</td>
</tr>
<tr>
<td>M</td>
<td>11.8</td>
<td>48.6</td>
<td>90.3</td>
<td>4.6</td>
<td>61.9</td>
</tr>
<tr>
<td>N</td>
<td>13.3</td>
<td>48.6</td>
<td>91.8</td>
<td>4.7</td>
<td>35.6</td>
</tr>
<tr>
<td>O</td>
<td>11.4</td>
<td>46.6</td>
<td>87.7</td>
<td>4.5</td>
<td>40.9</td>
</tr>
</tbody>
</table>

8.2.1. Impact of H\(^+\) irradiation

The results of H\(^+\) irradiation of 6FDA-6FpDA composite membranes were discussed in detailed in Chapter 6 and will be reviewed briefly here. Irradiated membranes exhibited similar trends for each gas studied with an initial decrease in permeance at low fluences, followed by an increase in the intermediate range and a decrease at high fluences. However, the maximum increase in permeance occurred at slightly different fluences for each gas, which resulted in significant variation in selectivity. Normalized permeances and permselectivities are reported to account for any differences in properties of virgin membranes and to allow for comparison between
### Table 8.4 Permeance and permselectivity for irradiated samples

<table>
<thead>
<tr>
<th>Film ID (ion type)</th>
<th>Film Modification (ions/cm²)</th>
<th>( \frac{P}{T} ) ( O_2 ) ( a )</th>
<th>( \frac{P}{T} ) ( CO_2 ) ( a )</th>
<th>( \frac{P}{T} ) ( He ) ( a )</th>
<th>( \alpha_{O_2/\text{N}_2} )</th>
<th>( \alpha_{CO_2/\text{CH}_4} )</th>
<th>( \alpha_{He/\text{CH}_4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1 x 10¹⁴</td>
<td>15.1</td>
<td>69.6</td>
<td>114.4</td>
<td>4.3</td>
<td>61.5</td>
<td>101.0</td>
</tr>
<tr>
<td>B</td>
<td>1 x 10¹⁵</td>
<td>36.0</td>
<td>181.6</td>
<td>259.1</td>
<td>4.6</td>
<td>44.9</td>
<td>64.0</td>
</tr>
<tr>
<td>C</td>
<td>2 x 10¹⁵</td>
<td>27.8</td>
<td>119.1</td>
<td>191.2</td>
<td>6.3</td>
<td>83.8</td>
<td>134.4</td>
</tr>
<tr>
<td>D</td>
<td>5 x 10¹⁶</td>
<td>11.8</td>
<td>65.1</td>
<td>292.8</td>
<td>5.6</td>
<td>86.3</td>
<td>388.0</td>
</tr>
<tr>
<td>E</td>
<td>1 x 10¹⁶</td>
<td>7.2</td>
<td>46.2</td>
<td>264.7</td>
<td>6.0</td>
<td>157.8</td>
<td>904.3</td>
</tr>
<tr>
<td>F</td>
<td>2 x 10¹³</td>
<td>13.9</td>
<td>74.9</td>
<td>152.8</td>
<td>4.3</td>
<td>61.6</td>
<td>125.5</td>
</tr>
<tr>
<td>G</td>
<td>8 X 10¹³</td>
<td>19.4</td>
<td>101.2</td>
<td>178.2</td>
<td>6.1</td>
<td>30.2</td>
<td>53.1</td>
</tr>
<tr>
<td>H</td>
<td>2 X 10¹⁴</td>
<td>26.7</td>
<td>132.8</td>
<td>335.7</td>
<td>5.8</td>
<td>93.9</td>
<td>237.3</td>
</tr>
<tr>
<td>I</td>
<td>4 X 10¹⁴</td>
<td>18.6</td>
<td>76.7</td>
<td>208.2</td>
<td>5.3</td>
<td>50.1</td>
<td>136.1</td>
</tr>
<tr>
<td>J</td>
<td>8 X 10¹⁴</td>
<td>3.9</td>
<td>45.9</td>
<td>175.2</td>
<td>2.4</td>
<td>41.7</td>
<td>159.4</td>
</tr>
<tr>
<td>K</td>
<td>1 X 10¹⁵</td>
<td>4.6</td>
<td>26.3</td>
<td>198.7</td>
<td>3.2</td>
<td>60.5</td>
<td>457.3</td>
</tr>
<tr>
<td>L</td>
<td>2 X 10¹⁴</td>
<td>2.8</td>
<td>14.6</td>
<td>23.1</td>
<td>4.0</td>
<td>53.3</td>
<td>84.5</td>
</tr>
<tr>
<td>M</td>
<td>4 X 10¹⁴</td>
<td>27.3</td>
<td>40.6</td>
<td>80.8</td>
<td>11.4</td>
<td>63.9</td>
<td>127.1</td>
</tr>
<tr>
<td>N</td>
<td>8 X 10¹⁴</td>
<td>1.6</td>
<td>17.2</td>
<td>35.8</td>
<td>2.2</td>
<td>53.1</td>
<td>110.3</td>
</tr>
<tr>
<td>O</td>
<td>1 X 10¹⁵</td>
<td>0.68</td>
<td>20.7</td>
<td>6.5</td>
<td>1.1</td>
<td>62.5</td>
<td>19.6</td>
</tr>
</tbody>
</table>

\( \alpha = \frac{\text{GPU}}{10^n \cdot \frac{cm^3(57P)}{cm^2 \cdot s \cdot cmHg}} \)

Irradiated samples. The normalized properties are defined as the ratio of the properties of the irradiated membrane to the virgin membrane property. Figure 8.1 shows the normalized permeance plotted against increasing ion fluence for all five gases studied. All of the gases showed a significant decrease in permeance at the lowest fluence, followed by an increase in the intermediate range. At the highest doses, helium continued to increase in relative permeance while all of the other gases exhibit a significant decrease relative to virgin membrane. The largest gases, methane and nitrogen, exhibited the largest drop in relative permeance at high ion dose. For example, helium had a normalized permeance of 2.0 at \( 1 \times 10^{16} \) H\(^+\)/cm\(^2\), while, methane had a normalized permeance of 0.26 at the same fluences. This leads to a large increase in selectivities at higher fluences.
The normalized permselectivities and relative permselectivities for \( \text{O}_2/N_2 \) as a function of ion dose is shown in Figure 8.1. The relative permselectivities compared to bulk materials is calculated as the ratio of actual selectivity to the reported bulk value for the 6FDA-6FpDA and is plotted to show membrane changes compared to the bulk material. As shown in Figure 8.2, oxygen exhibited a maximum relative permeance of \( \sim 1.6 \) at \( 2 \times 10^{15} \text{ H}^+/\text{cm}^2 \). While nitrogen exhibited a permeance increase at the same fluence, the increase was less than for oxygen. This corresponds to minimal change to normalized permselectivity at the lowest doses, but an increase of around 1.4 times the virgin selectivity for doses at or above \( 2 \times 10^{15} \text{ H}^+/\text{cm}^2 \). At \( 2 \times 10^{15} \text{ H}^+/\text{cm}^2 \), there was a
significant combined increase of permeance and permselectivity where the $O_2/N_2$ irradiated selectivity was 6.3.

As discussed earlier, the relative permeance of helium decreased to 50% of virgin values following low fluence irradiation followed by a steady increase with increasing doses (Figure 8.1). The methane permeance also decreased at low doses and increased at intermediate doses with a maximum at $1 \times 10^{15}$ H$^+$/cm$^2$. As fluences were increased further, the relative permeance of methane decreased sharply. As shown in Figure 8.3, the relative He/CH$_4$ relative and normalized permselectivities exhibited small changes at the lowest fluences, followed by a sharp increase to over 7.5 times the virgin selectivity.
at the highest dose. At the highest dose, there was significant increase in both the He permeance and permselectivity where the ideal selectivity of irradiated membranes was ~900. The virgin membranes had He/CH$_4$ permselectivity that were a bit higher than the bulk material and resulted in a normalized selectivity of over 10 for He/CH$_4$.

8.2.2. Impact of N$^+$ Irradiation

The relative permeance for six 6FDA-6FpDA composite membranes irradiated with N$^+$ at 400 KeV over a range of $2.0 \times 10^{13}$ to $1.0 \times 10^{15}$ N$^+$/cm$^2$ is shown in Table 8.4. The relative permanence for all of the gases (Figure 8.4), except methane, shows a similar trend to those following hydrogen irradiation, in that there is an initial decrease with increasing ion dose followed by a maximum at intermediate doses and a sharp decrease. The maximum relative permeance for all of the gases, except methane,
occurred at 4.0 \times 10^{14} \text{N}^+/\text{cm}^2$. Helium had the largest relative permeance at 1.8 times higher than the virgin membrane at its maximum at 4 \times 10^{14} \text{N}^+/\text{cm}^2$. Nitrogen exhibited the lowest maximum relative permeance that is just slightly higher then the virgin material at 4 \times 10^{14} \text{N}^+/\text{cm}^2$. Unlike H\(^+\) irradiation, helium’s permeance reached a maximum at 4 \times 10^{14} \text{N}^+/\text{cm}^2 and started to decline following N\(^+\) irradiation at higher doses. Methane’s relative permeance exhibited a maximum relative permeance at 8 \times 10^{13} \text{N}^+/\text{cm}^2. A sharp decrease and then an increase follow this spike for methane.

The relative and normalized permeances for O\(_2\)/N\(_2\) as a function of ion dose is shown in Figure 8.5. The permselectivities for O\(_2\)/N\(_2\) showed a slight decrease initially, a moderate increase and then a significant drop-off at the highest dose. The membranes with the best overall result for this gas pairs are those irradiated at 8 \times 10^{13} or 4 \times 10^{14} \text{N}^+/\text{cm}^2. At 8 \times 10^{13} \text{N}^+/\text{cm}^2, there was minimal change in oxygen permeance, but the
O₂/N₂ relative permselectivity is 1.55, with an ideal permselectivity of 6.1. At $4 \times 10^{14}$ N⁺/cm², the oxygen permeance increased by approximately by 1.5 folds and the relative permselectivity is 1.45, or with an ideal permselectivity of 5.32.

The He/CH₄ selectivity, shown in Figure 8.6, fluctuates more significantly than the O₂/N₂ selectivity, due to in large part, to the fluctuation in the methane’s permeance. The He/CH₄ selectivity improves when compared to the virgin membranes and bulk material at every ion dose except where methane permeance had the large spike, at $8 \times 10^{13}$ N⁺/cm². The highest selectivity for He/CH₄ occurred at $1 \times 10^{15}$ N⁺/cm², where the relative permselectivity was nearly 6 and an ideal permselectivity of approximately 460. There were several membranes that exhibited large increases in He/CH₄ permselectivity.
following N\(^+\) irradiation. For example, at 2 X 10\(^{14}\) N\(^+\)/cm\(^2\), the relative permeance is approximately 1.5 time greater than that of the virgin membrane, while the selectivity is almost 3 folds higher or an ideal permselectivity of 237.

8.2.3. Impact of F\(^+\) Irradiation

Figure 8.7 shows the relative permeance for four 6FDA-6FpDA composite membranes irradiated with F\(^+\) at 2400 KeV over the ion dose range of 2.0 X 10\(^{14}\) to 1.0 X 10\(^{15}\) F\(^+\)/cm\(^2\). Overall, F\(^+\) irradiated 6FDA-6FpDA membranes resulted in a reduction in permeance, except for oxygen permeance at 4 X 10\(^{14}\) F\(^+\)/cm\(^2\). At 4 X 10\(^{14}\) F\(^+\)/cm\(^2\), the oxygen permeance was 2.3 times greater than that of the virgin permeance. While all of the permeances, for all of the samples exhibited a reduction in value, the trend of a maximum at intermediate ion dose. The relative and normalized permselectivity for
O₂/N₂ gas pair is shown in Figure 8.8. While the O₂/N₂ relative permselectivity at the lowest dose exhibited minimal change, at higher F⁺ doses, there was a significant increase to ~ 2.5 times greater than the virgin permselectivity for a value of 11.4. The permselectivity for He/CH₄, in Figure 8.9, show a slight to modest increase at the lowest three doses, but a sharp decrease at the highest F⁺ dose with a relative permselectivity of 0.25 or an actual selectivity of 19.6.

8.2.4 Impact of Ion Dose

As discussed in Chapter 7, comparing the effect of different ions at similar irradiation doses was useful to demonstrate important trends, but not effective for direct
Figure 8.8. The permselectivity for O$_2$/N$_2$ as compared to the virgin value (○) and the bulk value (■) as a function of increasing F$^+$ dose.

Figure 8.9. The permselectivity for He/CH$_4$ as compared to the virgin value (○) and the bulk value (■) as a function of increasing F$^+$ dose.
comparison. The relative permeance for helium for all ions as a function of all ion dose is shown in Figures 8.10. For most irradiated membranes, there was an initial decrease in permeance, followed by an increase with maximum permeance at intermediate doses and decreases at higher doses. This is not true for helium permeance from $H^+$, where the maximum is reached at higher ion doses with no decrease in relative permeance at higher doses. The $H^+$ doses at maximum relative permeance for most gases studied were greater than for $N^+$ or $F^+$ irradiation. At the highest ion doses, of the membranes irradiated with $N^+$ and $F^+$ exhibited larger reduction in permeance. Finally, in general, the relative permeance for $N^+$ irradiation were greater than that of $F^+$ irradiation samples.

Figure 8.10. The relative permeance of He as a function of ion dose for $H^+$ irradiation (○), $N^+$ irradiation (■) and $F^+$ irradiation (▲).
8.2.5 Energy Transfer

Since ion dose is effective for demonstrating relative trends but not for describing impact of ions on material properties, the permeation results will be discussed in terms of electrical and nuclear energy. Since the thickness varied from membrane to membrane, the total energy transfer to a particular membrane was not proportional to the dose. The thickness of the selective layer were estimated from the oxygen permeance. Therefore, in some cases the energy transfer for a sample irradiated at high dose could be lower than that of a lower dose irradiation. Table 8.5 shows that the electrical energy transfer range is comparable from one ion to another, however, the nuclear energy transfer range is considerable lower for H\(^+\) irradiation than N\(^+\) or F\(^+\).

Table 8.5. Electronic and Nuclear energy transfer for each membrane

<table>
<thead>
<tr>
<th>Film ID (Ion)</th>
<th>Ion Dose (Ion/cm(^2))</th>
<th>Electronic Energy (eV/Å)</th>
<th>Nuclear Energy (eV/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1 x 10(^{14})</td>
<td>8.98E+14</td>
<td>9.04E+11</td>
</tr>
<tr>
<td>B</td>
<td>1 x 10(^{15})</td>
<td>9.11E+15</td>
<td>9.62E+12</td>
</tr>
<tr>
<td>C</td>
<td>2 x 10(^{15})</td>
<td>1.85E+16</td>
<td>2.00E+13</td>
</tr>
<tr>
<td>D</td>
<td>5 x 10(^{15})</td>
<td>4.63E+16</td>
<td>5.03E+13</td>
</tr>
<tr>
<td>E</td>
<td>1 x 10(^{16})</td>
<td>9.29E+16</td>
<td>1.02E+14</td>
</tr>
<tr>
<td>N(^+)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>2 x 10(^{13})</td>
<td>8.61E+14</td>
<td>4.72E+13</td>
</tr>
<tr>
<td>G</td>
<td>8 X 10(^{13})</td>
<td>3.00E+15</td>
<td>2.90E+14</td>
</tr>
<tr>
<td>H</td>
<td>2 X 10(^{14})</td>
<td>8.58E+15</td>
<td>4.76E+14</td>
</tr>
<tr>
<td>I</td>
<td>4 X 10(^{14})</td>
<td>1.19E+16</td>
<td>1.69E+15</td>
</tr>
<tr>
<td>J</td>
<td>8 X 10(^{14})</td>
<td>2.61E+16</td>
<td>3.64E+15</td>
</tr>
<tr>
<td>K</td>
<td>1 X10(^{15})</td>
<td>4.45E+16</td>
<td>2.19E+15</td>
</tr>
<tr>
<td>F(^+)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>2 X 10(^{14})</td>
<td>1.82E+16</td>
<td>3.43E+14</td>
</tr>
<tr>
<td>M</td>
<td>4 X 10(^{14})</td>
<td>4.20E+16</td>
<td>5.25E+14</td>
</tr>
<tr>
<td>N</td>
<td>8 X 10(^{14})</td>
<td>8.62E+16</td>
<td>1.01E+15</td>
</tr>
<tr>
<td>O</td>
<td>1 X 10(^{15})</td>
<td>1.03E+17</td>
<td>1.34E+15</td>
</tr>
</tbody>
</table>

Figures 8.11 show the relative permeance for helium as a function of electrical energy transfer for all ions. With the exception of helium, the relative permeance for each ion followed very similar trends. At lower energy transfer, electronic energy correlates well for the helium permeance for N\(^+\) and H\(^+\). No samples were available for
F⁻ at low energies. However, the helium permeance in membranes irradiated with H⁺ at high energies continued to increase, while for other ions there was a trend of decrease relative permeance. In addition, at high energy transfer, all relative permeance following H⁺ irradiation were greater than those following N⁺ and F⁺ irradiation for similar energies. Therefore, the electronic energy cannot solely account for impact of different ions on permeance.

Since electronic energy does not correlate well with relative permeance at higher energies, therefore, the impact of nuclear energy will be used to compare results for different ions. The relative permeance for helium, as a function of nuclear energy transfer, for all ions is shown in Figures 8.12. From this figures several trends are shown with one of the most important being that the maximum amount of nuclear energy transfer from H⁺ irradiation is near the minimum for the other two ions. In addition, for all gases except helium for H⁺ irradiation, resulted in a maximum and significant decrease well before the other two ions.

8.3 Discussion

Since ion dose does not accurately reflect relative impact of ions on permeance of 6FDA-6FpDA, results will be discussed in terms of electronic and nuclear energy transfer. This section will focus on discussion of impact of different ion on permeance of 6FDA-6FpDA composite membranes. The first section will provide a comparison of the impact of H⁺ and N⁺ irradiation on permeance and permselectivity. These ions were used to provide very different energy transfer mechanisms. For example, the much larger N⁺ ion has a greater nuclear transfer contribution than H⁺ at similar total energy transfer.
Figure 8.11. The relative permeance of He as a function of electronic energy transfer for H\(^+\) irradiation (○), N\(^+\) irradiation (■) and F\(^+\) irradiation (▲).

Figure 8.12. The relative permeance of He as a function nuclear energy transfer for H\(^+\) irradiation (○), N\(^+\) irradiation (■), and F\(^+\) irradiation (▲).
The second section focuses on N⁺ and F⁺ irradiation, which have similar masses and energy transfer mechanism.

8.3.1 H⁺ and N⁺

The SRIM simulation of energy transfer versus depth for 180 KeV H⁺ irradiation and 400 KeV N⁺, are shown in Figure 8.13 and 14, respectively. The Monte Carlo SRIM simulation for H⁺ and N⁺ irradiation showed significant differences. The first difference is that in H⁺ irradiation, the amount of energy transfer is significantly lower for both electronic and nuclear mechanisms than N⁺ irradiation. For electronic mechanism, the difference is several times greater for N⁺ irradiation, while for nuclear mechanism there is several orders of magnitude difference. The depth of modification is greater for the H⁺ ions. Also, the shape of the profiles is different. For H⁺ irradiation, the electronic energy profile is very horizontal with a sharp decrease at the end, while for N⁺ irradiation; the decrease is spread out evenly over the entire depth of modification. This leads to a more uniform energy transfer from N⁺ ion to polymer than for H⁺ irradiation. The depth of modification is similar for both ions at their energy.

As shown in Figure 8.11, the relative permeance of N⁺ and H⁺ are similar following low energy transfer for each gas studied. However, there was a greater decreases in permeance following N⁺ than H⁺ for similar electronic energy loss levels following irradiation above intermediate range. This give N⁺ irradiated samples a narrower peak for relative permeance than was seen for H⁺ irradiation. At similar total energy transfer, N⁺ irradiation resulted in significantly greater nuclear energy transfer. Therefore, while the range of electronic energy transfer is similar for H⁺ and N⁺ irradiation, the nuclear energy transfer is significantly higher for N⁺. As discussed in
Figure 8.13. The Monte Carlo simulation of 450 KeV H\(^+\) irradiation of 6FDA-6FpDA. The electronic energy transfer (○) and nuclear energy transfer (●) are both shown.

Figure 8.14. The Monte Carlo simulation of 400 KeV N\(^+\) irradiation of 6FDA-6FpDA. The electronic energy transfer (○) and nuclear energy transfer (●) are both shown.
Chapter 7, the greater damage to chemical structure by N⁺ irradiation was attributed to larger nuclear contribution. So, the larger decrease in permeance for N⁺ irradiation maybe also is due to the increase in the amount of nuclear energy transfer that caused a significant change in chemical structure along with microstructure.

As discussed in Chapter 7, with increasing irradiation, the polymer matrix loss more functional groups following irradiation, and there was significantly more damage with N⁺ irradiation then there was with H⁺ irradiation. At high dose irradiation FTIR could not be used to analyze structure evolution because the freestanding dense films could not withstand the damage in this region. However, if the trend continues for the loss of functional groups, is expected that at high doses there will be a point at which insufficient bulky groups (ie CF₃) are present and the microstructure will collapse. Therefore, it is possible that for N⁺ irradiation, the large nuclear energy transfer resulted in dramatic change in microstructure to another microstructure region. The microstructure may changes from an open structure of virgin polymer (Figure 8.15), to a more densely packed structured (Figure 8.16) with larger concentration of smaller voids. This would result in large decreases in permeance for larger molecules. This change in microstructure occurred between 1. X 10¹⁶ and 2. X 10¹⁶. The difference in the nuclear energy transfer required for this damage to the microstructure is significantly larger than H⁺ energies used in this study. Therefore, H⁺ irradiated samples do not display this change in microstructure. The larger damage from nuclear energy transfer is expected, since the ion displaces the target atom in this mechanism followed by subsequent damage from displaced atoms. With these displacements of the target atoms, the microstructure
would collapse, and based on permeation data the point is between $1 \times 10^{16}$ and $2 \times 10^{16} \text{ eV/Å}$.

8.3.2 F$^+$ and N$^+$

The SRIM simulation for 2400 KeV F$^+$ is shown in Figure 8.17. The F$^+$ irradiation has a higher energy transfer for both electronic and nuclear mechanism than N$^+$ irradiation. The electronic energy profile for F$^+$ is steeper than that of 400 KeV N$^+$. The other main difference is that the depth of modification is almost three times greater.
with 2400 KeV F⁺. When comparing N⁺ and F⁺ irradiation relative to electronic energy loss (Figure 8.11) and nuclear energy loss (Figure 8.12) there are several similarities. For example F⁺ irradiation follows a similar trend to N⁺ irradiation. With initial decreases in relative permeance followed by a peak at intermediate energies and a drop at higher energy transfer. Also, just like N⁺ irradiation compared to H⁺, F⁺ resulted in a sharper relative permeance distribution. The last similarity is that F⁺ sharp drop in permeance between 5. X 10^{15} and 1 X 10^{16} eV/Å. However, unlike the sample following N⁺ irradiation, the helium permeance decreases significantly following F⁺ at high energy. Also the F⁺ irradiated samples exhibited larger decreases in permeance that N⁺ samples. This corresponds to a significant decrease in free volume even at small void sizes from F⁺.
irradiation, including the smaller regions where \( \text{N}^+ \) irradiation did not affect. The proposed shift in dynamic free volume distribution is shown in Figure 8.18.

![Free Volume Distribution](image)

Figure 8.18 Schematic of the free volume distribution after the change in microstructure for \( \text{F}^+ \) of the irradiation of sample (---) compared to the virgin material (—).

### 8.4 Conclusion

As discussed in Chapter 7 the choice of ion and irradiation doses has a significant impact on evolution in structure and microstructure of 6FDA-6FpDA. In addition, the amount of energy transferred along with transfer mechanism (ie. nuclear or electronic) was critical in determining structural evolution. For example, \( \text{H}^+ \) irradiation is almost exclusively electronic energy, while \( \text{N}^+ \) and \( \text{F}^+ \) irradiation has a much higher nuclear energy contribution.

Similar results were seen for the evolution in permeance of composite membranes following irradiation over wide range of fluences. For example there was a large decrease in permeance for \( \text{N}^+ \) and \( \text{F}^+ \) irradiated samples relative to \( \text{H}^+ \) at higher irradiation energies. In addition, there is a general narrowing of the relative permeance distribution from \( \text{H}^+ \) to \( \text{N}^+ \) to \( \text{F}^+ \) irradiation. The electronic energy loss is similar for all of the ions; therefore the large decrease for \( \text{N}^+ \) and \( \text{F}^+ \) compared to \( \text{H}^+ \) and narrowing of permeance with increasing fluence is due to the larger nuclear energy transfer for these
ions. The other trend is that for both N\(^+\) irradiation and F\(^+\), there is a sharp decrease in relative permeance between two membranes.
Chapter 9: Permeability and Trade-Off Curves of Irradiated 6FDA-6FpDA Membranes.

9.1 Introduction

The results reported in previous chapters were in terms of absolute or relative permeance of the membrane instead of permeability. While relative permeance were the measured values for the irradiated membranes, the permeability is useful in comparing the bulk properties. The difference between permeance and permeability is that permeance is a membrane property and permeability is a property of the polymer. In addition, the trade-off curve between permeability and permselectivity are useful approach to compare potential membrane materials. As discussed in background, commercial membrane materials must have a combination of high permeability and permselectivity for a given gas pair. Therefore, this chapter will focus on comparison of trade-off curve for several gas pairs of commercial interest, including O₂/N₂ and He/CH₄.

The permeability can be estimated from measured values of permeance based on the following two assumption. (I) The thickness of the selective layer is estimated using O₂ permeance. This is a reasonable assumption for defect free membranes, but will underestimate actual thickness for membranes that are not. (II) The thickness of the selective layer does not change during irradiation. This assumption is reasonable at low ion doses where minimal damage is done to the membrane [4]. However, with increase ion dose the thickness could decrease more, due to the loss of functional groups and compaction. Xu et al., reported that boron irradiation of polyimide films resulted in minimal shrinkage at lower ion doses, but up to 50% reduction in thickness at higher ion dose.
dose. However, in a comparable ion dose range, the maximum shrinkage reported was less the 20% of the original value [4]. Therefore, the permeability may be higher than the are actually.

The permeability for irradiated membrane was calculated by multiplying the permeance of the irradiated sample by the estimated thickness of the virgin membrane based on oxygen permeance. As mentioned earlier, there are two assumptions for calculating the permeability of irradiated membranes: 1) the estimated thickness based on oxygen is accurate and 2) the thickness of the membrane does not change with irradiation. The first assumption should be accurate if the membranes are defect-free or nearly defect free. All 6FDA-6FpDA membranes used in this study were nearly defect free. If the membrane were defective, the estimated thickness would be to low relative to actual values due to increase nonselective flow in defects. The second assumption that the thickness of the membranes does not change with ion irradiation should be true at low and moderate ion doses. At higher doses, the membrane thickness may decrease relative to virgin membrane due to loss of functional groups and compaction. If the thickness of the irradiated membranes decreased relative to the estimated permeabilities would be greater than the actual permeabilities.

9.2 Results

9.2.1 H⁺ Irradiation

The estimated permeability for the hydrogen-irradiated membranes along with the estimated thickness based on oxygen permeance of the virgin membrane and the virgin O₂/N₂ selectivity are given in Table 9.1. Figure 9.1 shows the permeability of H⁺ irradiated membranes as a function of increasing ion dose. For the four slowest gases
there is a maximum in permeability followed by a decrease with increasing irradiation. Helium showed no maximum at increasing doses following $H^+$ irradiation. Therefore, the permeabilities of helium and the other gases, specifically, methane and nitrogen, were diverging at higher doses. This resulted in an increase in the He/CH$_4$ and He/N$_2$ selectivities.

Table 9.1 The estimated permeability for $H^+$ irradiation

<table>
<thead>
<tr>
<th>Film ID</th>
<th>$P_{O_2}^d$</th>
<th>$P_{CO_2}^d$</th>
<th>$P_{He}^d$</th>
<th>$P_{N_2}^d$</th>
<th>$P_{CH_4}^d$</th>
<th>$\alpha_{O_2/N_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>● Bulk</td>
<td>16.3</td>
<td>63.9</td>
<td>137.0</td>
<td>3.47</td>
<td>0.625</td>
<td>4.7</td>
</tr>
<tr>
<td>A 1 x $10^{14}$</td>
<td>7.5</td>
<td>34.5</td>
<td>56.8</td>
<td>1.7</td>
<td>0.56</td>
<td>4.5</td>
</tr>
<tr>
<td>B 1 x $10^{15}$</td>
<td>24.1</td>
<td>121.6</td>
<td>173.6</td>
<td>5.3</td>
<td>2.7</td>
<td>4.2</td>
</tr>
<tr>
<td>C 2 x $10^{15}$</td>
<td>25.7</td>
<td>110.1</td>
<td>176.7</td>
<td>4.1</td>
<td>1.3</td>
<td>4.1</td>
</tr>
<tr>
<td>D 5 x $10^{15}$</td>
<td>11.1</td>
<td>61.3</td>
<td>275.8</td>
<td>2.0</td>
<td>0.71</td>
<td>4.2</td>
</tr>
<tr>
<td>E 1 x $10^{16}$</td>
<td>7.4</td>
<td>47.1</td>
<td>269.6</td>
<td>1.2</td>
<td>0.30</td>
<td>4.2</td>
</tr>
</tbody>
</table>

$^a = 1$Barrer = $10^{-10}$ cm$^3$(STP)$\cdot$cm/$cm^2 \cdot s \cdot cmHg$

While this plot demonstrate the change in the properties of the membranes relative to the virgin material, it is important to compare it to other materials. A good comparison is the well-known trade-off curve of permeability and permselectivity for polymeric membranes [34, 35]. Figure 9.2 and 9.3 shows the trade off curve, with the typical upper bound as the dotted diagonal line identified by Robeson et al., for the gas pairs O$_2$/N$_2$ and He/CH$_4$, respectively. For both graphs, the x-axis is the permeability, the y-axis is the selectivity. The virgin polymer bulk properties are designated by a solid circle. Each of the individual irradiated samples is designated by a letters and is referenced in Table 8.1. The designations of letters are in order of increasing ion dose. For the gas pair of O$_2$/N$_2$ there are several doses from $H^+$ irradiation that approach the upper bound, and one that surpasses it. The letters, starting with A at 1 X $10^{14}$ H$^+$/cm$^2$ and increasing in dose until a maximum at E at 1 X $10^{16}$ H$^+$/cm$^2$ shows the O$_2$ permeability decrease initially, and increases with addition irradiation until point C,
Figure 9.1. The calculated permeability for the H\(^+\) irradiation for oxygen (○), CO\(_2\) (●), He (▲), N\(_2\) (■) and CH\(_4\) (X).

Figure 9.2 H\(^+\) Irradiation of 6FDA-6FpDA tradeoff curve for O\(_2\)/N\(_2\) with A-E referring film ID in Table 9.1.
followed by a decrease. The permselectivity shows an initial increase, followed by minimal change from the bulk values, then an increase and finally a steady decline until below the bulk value. The optimum O$_2$/N$_2$ separation characterization occur at intermediate range where O$_2$ had maximum permeability and N$_2$ beginning to decrease relative to ion dose.

However, for the gas pair He/CH$_4$, three samples surpass the upper bound, including one sample that is significantly beyond this line. The difference in behavior for this gas pair is probably due to large size difference for He/CH$_4$. Since the kinetic diameter of oxygen and nitrogen being very similar, subtle changes in free volume distribution would affect both molecules similarly, unless there was a sharp decrease in
the distribution of free volume range between them. However, the kinetic diameter of helium and methane is significantly different, therefore, a change in free volume distribution could more easily affect helium and methane differently. For the gas pair He/CH$_4$, there was a distinct trend with increasing irradiation with H$^+$. The trend, starting with point B, shows a slight increase in permeability, with significant improvement in selectivity, which is due to the significant decrease in the permeability of methane at higher H$^+$ doses.

9.2.2 N$^+$ Irradiation

Table 9.2 shows the calculated permeability for the nitrogen-irradiated membranes along with the estimated thickness based on oxygen permeance of the virgin membrane and the virgin O$_2$/N$_2$ selectivity. The absolute permeability of N$^+$ irradiated membranes as a function of increasing ion dose is given in Figure 9.4. The trends of nitrogen irradiation are similar to those of hydrogen irradiation where there is an initial increase in the permeability with ion dose, followed by a decrease at higher ion doses. However, there are several differences, such as, methane sees a spike at 8 $\times$ 10$^{13}$ N$^+$/$\text{cm}^2$, so that methane has a higher permeability than nitrogen. Another difference is that for nitrogen irradiation, there was a decrease in helium permeance at higher ion doses. For nitrogen irradiation, the maximum occurred at 4 $\times$ 10$^{14}$ N$^+$/cm$^2$. At the highest ion dose methane and carbon dioxide exhibited the largest decreases in permeability, while helium and oxygen had the smaller decreases. These results are discussed in detail in terms of permeance in Chapter 8.
Table 9.2 The estimated permeability for N$^+$ irradiation

<table>
<thead>
<tr>
<th>Film ID</th>
<th>$P_{O_2}$</th>
<th>$P_{CO_2}$</th>
<th>$P_{He}$</th>
<th>$P_{N_2}$</th>
<th>$P_{CH_4}$</th>
<th>$\alpha_{O_2}/N_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>●</td>
<td>16.3</td>
<td>63.9</td>
<td>137.0</td>
<td>3.47</td>
<td>0.625</td>
<td>4.7</td>
</tr>
<tr>
<td>F</td>
<td>6.7</td>
<td>36.1</td>
<td>73.6</td>
<td>1.5</td>
<td>0.6</td>
<td>4.5</td>
</tr>
<tr>
<td>G</td>
<td>8 X 10$^{13}$</td>
<td>16.5</td>
<td>86.0</td>
<td>151.5</td>
<td>2.7</td>
<td>2.8</td>
</tr>
<tr>
<td>H</td>
<td>2 X 10$^{14}$</td>
<td>13.3</td>
<td>66.0</td>
<td>166.9</td>
<td>2.3</td>
<td>0.70</td>
</tr>
<tr>
<td>I</td>
<td>4 X 10$^{14}$</td>
<td>24.6</td>
<td>101.1</td>
<td>274.5</td>
<td>4.6</td>
<td>2.0</td>
</tr>
<tr>
<td>J</td>
<td>8 X 10$^{14}$</td>
<td>4.1</td>
<td>49.3</td>
<td>188.1</td>
<td>1.8</td>
<td>1.2</td>
</tr>
<tr>
<td>K</td>
<td>1 X 10$^{15}$</td>
<td>1.7</td>
<td>9.7</td>
<td>73.1</td>
<td>0.5</td>
<td>0.16</td>
</tr>
</tbody>
</table>

$^a$ = 1 Barrer = 10$^{-10}$ cm$^3$(STP)$\cdot$cm$^{-1}\cdot$s$\cdot$cmHg

The trade off curve for 6FDA-6FpDA nitrogen-irradiated membranes for the gas pairs O$_2$/N$_2$ is shown in Figure 9.5. The letters corresponds to the N$^+$ irradiation dose starting with F at 2 X 10$^{13}$ N$^+$/cm$^2$ and increasing until K at 1 X 10$^{15}$ N$^+$/cm$^2$. Three irradiated samples are beyond the upper bound curve for O$_2$/N$_2$, and three N$^+$ irradiated membranes exhibited properties below those of bulk 6FDA-6FpDA. When comparing the effect of ion dose on properties, samples in the middle range of the selected N$^+$ irradiated doses benefited the most and all were above the trade-off curve. The sample that was below this range (F) had a moderate decrease in permeability, and a minimal decrease in selectivity. The samples above the positive range (K and J) had significant decreases in both permeability and permselectivity.

The tradeoff for He/CH$_4$ is given Figure 9.6 with four irradiated samples above the trade-off curve. Much like hydrogen irradiation, there are more samples above upper bound for the He/CH$_4$ than there are for O$_2$/N$_2$ which is likely due to the fact that He/CH$_4$ have much greater size difference. The lowest and highest level of N$^+$ irradiation (F and K, respectively) resulted in an increase in the permeability of He, but a moderate loss of He/CH$_4$ selectivity. All of the other samples (G – J) resulted in a slight or moderated increases in permeability and general increases in selectivity. Much as was see for H$^+$.
Figure 9.4. The calculated permeability for N⁺ irradiation for oxygen (o), CO₂ (●), He (▲), N₂ (■) and CH₄ (X).

Figure 9.5. N⁺ Irradiation of 6FDA-6FpDA tradeoff curve for O₂/N₂ with F-J referring film ID in Table 9.3.
irradiation, the largest selectivities were exhibited at high fluence were CH$_4$ saw large drops in permeability.

9.2.3 F$^+$ Irradiation

The estimated permeability for the fluorine-irradiated membranes along with the estimated thickness based on oxygen permeance of the virgin membranes are give in Table 9.3. Figure 9.7 shows the absolute permeability of F$^+$ irradiated membranes plotted against increasing ion dose. The trends for fluorine irradiation are similar to those of hydrogen and nitrogen irradiation in that there is an initial upward slope in the permeability followed by a decrease. However, there are several unique differences with
fluorine irradiation compared to the other ions. For example, at $4 \times 10^{14}$ F$^+$/cm$^2$, the permeability for oxygen is extremely high and is comparable to the permeability of carbon dioxide and helium. Also, at the highest ion dose, $1.0 \times 10^{15}$ F$^+$/cm$^2$, the permeability are considerably lower than bulk material. The large increase in oxygen permeability at $4 \times 10^{14}$ F$^+$/cm$^2$ leads to a significant increase in selectivity for the gas pair O$_2$/N$_2$. Interestingly, the permeability for carbon dioxide at this ion dose was greater than that of helium. Additionally, oxygen and nitrogen were greatly reduced and similar in value.

Table 9.3: The estimated permeability for F$^+$ irradiation

<table>
<thead>
<tr>
<th>Film ID</th>
<th>$P_{O_2}$</th>
<th>$P_{CO_2}$</th>
<th>$P_{He}$</th>
<th>$P_{N_2}$</th>
<th>$P_{CH_4}$</th>
<th>$\alpha_{O_2/N_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Bulk</td>
<td>16.3</td>
<td>63.9</td>
<td>137.0</td>
<td>3.47</td>
<td>0.625</td>
<td>4.7</td>
</tr>
<tr>
<td>L 2 X $10^{14}$</td>
<td>5.9</td>
<td>30.3</td>
<td>48.0</td>
<td>1.4</td>
<td>0.57</td>
<td>3.8</td>
</tr>
<tr>
<td>M 4 X $10^{14}$</td>
<td>37.6</td>
<td>55.9</td>
<td>111.3</td>
<td>3.3</td>
<td>0.88</td>
<td>4.6</td>
</tr>
<tr>
<td>N 8 X $10^{14}$</td>
<td>2.0</td>
<td>21.2</td>
<td>43.9</td>
<td>0.9</td>
<td>0.40</td>
<td>4.7</td>
</tr>
<tr>
<td>O 1 X $10^{15}$</td>
<td>0.96</td>
<td>29.5</td>
<td>9.3</td>
<td>0.9</td>
<td>0.47</td>
<td></td>
</tr>
</tbody>
</table>

$P_{gas} = 10^{-10} \frac{cm^3(STP) \cdot cm}{cm^2 \cdot s \cdot cmHg}$

The trade off curve for fluorine-irradiated 6FDA-6FpDA membranes for O$_2$/N$_2$ is shown in Figure 9.8. The letters L – O corresponds to a F$^+$ irradiation dose from $2 \times 10^{14}$ to $1 \times 10^{15}$ F$^+$/cm$^2$. There is one membrane that is significantly above the trade-off curve, while the rest of the membranes are below the trade-off curve for O$_2$/N$_2$, with a couple of the membranes being significantly below the line. This is because only one irradiated samples exhibited increases in O$_2$ permeability. All of the other samples saw
Figure 9.7. The calculated permeability for the F⁺ irradiation for oxygen (○), CO₂ (●), He (▲), N₂ (■) and CH₄ (X).

Figure 9.8 F⁺ Irradiation of 6FDA-6FpDA tradeoff curve for O₂/N₂ with L-O referring film ID in Table 9.31.
decrease in both oxygen permeability and O₂/N₂ permselectivity, relative to bulk properties.

The He/CH₄ curve for fluorine irradiated samples are shown in Figure 8.10. As was seen for O₂/N₂, only one irradiated sample is above the upper bound curve, while the other three samples are well below it. While no sample saw an increase in the He permeability, several membranes resulted in a slight increase in the He/CH₄ permselectivities. At high ion dose, one membrane saw a significant decrease in both He permeability and He/CH₄ permselectivity.
Figure 9.10 Irradiated 6FDA-6FpDA membranes that surpass the $O_2/N_2$ upper bound.

Figure 9.11 Irradiated 6FDA-6FpDA membranes that surpass the $He/CH_4$ upper bound.
9.2.4 Overall Results

The trade-off curves for all of the irradiated samples that exceeded the upper bound curve for the gas pairs O$_2$/N$_2$ and He/CH$_4$ are shown in Figures 10.10 and 10.11. The O$_2$/N$_2$ trade-off curve shown in Figure 8.10 shows the five irradiated membranes are above the upper bound curve. As mention earlier, the fluorine-irradiated sample is well above the upper bond curve, while the other membranes are only slightly above it. Figure 8.11 shows the upper bound curve for He/CH$_4$ with all of the irradiated membranes that fall above the line. Eight irradiated membranes fell above this limit, with several membranes seeing significant improvement and therefore, with the proper selection of conditions, significant improvement can be achieved for this separation.

9.3 Conclusions

While these results are interesting and demonstrate potential of irradiation to modify membrane properties, considerable work in need to fully qualify irradiation effects. The calculated permeability was based on two assumptions. The assumptions were the estimated thickness of the virgin membrane is accurate, and that the thickness does not change with irradiation. The permeability for each ion showed a general trend of an increase followed by a decrease after a maximum. Also, the data was plotted on a trade-off curve and showed that there were several membranes above the upper bound, including several that were significantly higher. Therefore, the results showed that ion irradiation can change the permeability significantly and under the proper irradiation conditions, can provide a significant improvement, when compared to the upper limit of the current trade-off curves.
Chapter 10 Conclusions

In this study, ion irradiation of two very different polymers (Polysulfone and polyimide, 6FDA-6FpDA) was performed with several different ions over a wide range of ion doses. While the results for both polymers showed a significant evolution in chemical structure, microstructure and permeation properties, the overall results were very different for each material and ion.

The effects of H+ irradiation on structure and transport properties of bulk PSF were studied. In addition, effect of irradiation on the properties of asymmetric PSF membranes was investigated. H+ irradiation resulted in a significant change in chemical structure, microstructure and permeation of bulk PSF. There was a general decrease in permeance with increase ion dose. The effects of H+ and C- irradiation on the porous substructure and transport properties of asymmetric PSF membranes were also studied. The porous support for asymmetric membranes irradiated at or above 4 X 10^{14} H+/cm^2 resulted in a collapse that resulted in a significant decrease in permeance and Knudsen like selectivity. Irradiation of non-selective asymmetric PSF membrane blanks with C\(^-\) resulted in similar losses in permeance. Therefore, a process, such as, plasma immersion ion irradiation, which uses lower energies and low penetration depth, could be used to avoid the modification of the porous substructure and only modify the selective layer.

6FDA-6FpDA freestanding films and composite membranes were irradiated with several different ions (H\(^+\), N\(^+\) and F\(^+\)) to investigate effect on chemical structure,
microstructure and permeation properties. In all cases, there was considerable evolution in structure and properties. While ion dose is useful in comparing the effect of ion irradiation for one ion, energy transfer is a better indicator of effect of different ion on 6FDA-6FpDA. When larger mass ions were used, there was a higher relative nuclear energy transfer and greater loss of functional groups. This resulted in a larger change in microstructure and more significant change in permeation properties at higher ion doses for N+ and F+ irradiation than H+ samples.

With ion irradiation, there were significant changes in the permeation properties for 6FDA-6FpDA compared to the virgin material and bulk properties of the polymer. Another good comparison approach is to compare results with other polymer membrane material. In several cases irradiated of typical polymer membranes surpassed the upper bound for several gas pairs. However, several membranes exhibited significant loss in both permeability and permselectivity, compared to bulk properties, especially those following high dose F+ irradiation.

In conclusion, with proper selection of irradiation conditions (ion type, dose and energy), 6FDA-6FpDA membranes can be irradiated to produce positive changes in permeation properties for several important gas pairs. However, more research is required to be able to optimize ion variable conditions.
Chapter 11 Recommendations

Ion irradiation of polymeric materials has shown that there are many variables that effect the results, such as, virgin polymer structure, ion type, ion energy and ion dose. A comprehensive examination of many polymers would not be practical because of time and money and therefore a more practical procedure is needed to answer several interesting questions and expand the results.

1. Add several additional techniques to aid in studying the evolution of the polymer’s chemical structure, microstructure and permeation properties.

While a wide range of techniques was used to study the evolution of polymer, several additional techniques would add a large amount of addition data. For example, by adding a GC-MS to the outlet of the irradiation chamber, the off-gas could be studied, and a better understanding of chemical structure would be obtained. Another technique would be sorption studies of the material to gain a better understanding of the permeation process through the membranes. Other techniques that could be helpful include Ramen spectroscopy, XPS, TGA and DMA.

2. Study several additional polymers that have similar properties to 6FDA-6FpDA, both physically and transport properties.

From the work done in this group, not all polymer react favorably to ion irradiation. Therefore, polymers that has similar characteristics to 6FDA- 6FpDA, which yielded positive results. For example, 6FDA-6FpDA exhibited such characteristic, as good
inherent transport properties, openness of the matrix and rigidity of the polymer chains, and polymers that exhibit such properties should be studied. On the other hand, PSF did not respond to ion irradiation as well as 6FDA-6FpDA and could be contributed to the lack of open structure and high chain mobility. Therefore, a material the contained bulky groups, such as CF$_3$, within a rigid polymer chain that has inherently good transport properties should be used.

3. *Evaluate membrane performance in non-ideal situations, such as mix-gas environment and elevated temperature.*

All of the gas permeation studies in this work were performed with pure gases and with temperatures at 35°C. While pure gas studies provide very useful information, the membranes can behave differently with mixed gases and other harsh conditions. Mix gas studies shows the behavior of the membrane accurately because of the streams that would be separated in commercial applications. Other studies include testing membranes at elevated temperatures, with corrosive gases, and gases at highly soluble concentrations.

4. *Work towards commercialization of irradiated membranes through plasma immersion ion irradiation.*

While ion irradiation is a practical method to modify flat sheet membranes, it cannot be used for hollow fibers because ion irradiation works on a line of sight principal and cannot easily modify shapes. Plasma immersion ion irradiation (PIII) can be used to modify shapes, such as hollow fibers, which are used in commercial applications. Another positive about PIII is that it can be used at low energies, so that only the selective layer is
modified. However, the first step would be to do PIII on flat sheet asymmetric membranes, prior to hollow fiber membranes to ensure positive results.
### Table 12.1: Permeation Properties of Virgin PSF Composite Membranes

<table>
<thead>
<tr>
<th>Film ID</th>
<th>((P/T)_{O_2})</th>
<th>((P/T)_{CO_2})</th>
<th>((P/T)_{He})</th>
<th>(\alpha_{O_2}/N_2)</th>
<th>(\alpha_{CO_2}/CH_4)</th>
<th>(\alpha_{He}/CH_4)</th>
<th>Estimated Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>0.34</td>
<td>1.7</td>
<td>2.8</td>
<td>4.7</td>
<td>19.3</td>
<td>32.0</td>
<td>4.1</td>
</tr>
<tr>
<td>H</td>
<td>0.32</td>
<td>1.6</td>
<td>2.6</td>
<td>3.8</td>
<td>15.2</td>
<td>24.0</td>
<td>3.6</td>
</tr>
<tr>
<td>I</td>
<td>0.25</td>
<td>1.1</td>
<td>1.9</td>
<td>3.5</td>
<td>11.0</td>
<td>18.4</td>
<td>5.7</td>
</tr>
<tr>
<td>J</td>
<td>0.32</td>
<td>1.5</td>
<td>2.5</td>
<td>3.6</td>
<td>8.9</td>
<td>14.8</td>
<td>4.3</td>
</tr>
</tbody>
</table>

\(a = 1 \text{GPU} = 10^{-6} \frac{\text{cm}^3 (STP)}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}\)

### Table 12.2: Permeation Properties of Irradiated PSF Composite Membranes

| Film ID | Film Modification (H'/cm²) | \((P/T)_{O_2}\) | \((P/T)_{CO_2}\) | \((P/T)_{He}\) | \(\alpha_{O_2}/N_2\) | \(\alpha_{CO_2}/CH_4\) | \(\alpha_{He}/CH_4\) |
|---------|-----------------|----------------|----------------|---------------|-----------------|-----------------|-----------------|-----------------|
| G       | 1x10^{13}       | 0.364          | 1.50           | 2.73          | 4.50            | 14.9            | 27.4            |                 |
| H       | 1x10^{14}       | 0.316          | 1.30           | 2.58          | 2.80            | 10.2            | 20.0            |                 |
| I       | 4x10^{14}       | 0.361          | 1.50           | 3.11          | 4.60            | 12.2            | 25.4            |                 |
| J       | 4x10^{15}       | 0.311          | 1.02           | 2.33          | 2.50            | 6.4             | 14.7            |                 |

\(a = 1 \text{GPU} = 10^{-6} \frac{\text{cm}^3 (STP)}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}\)
Table 12.3: Permeation Properties of Virgin PSF Asymmetric Membranes used for H⁺ irradiation

<table>
<thead>
<tr>
<th>Film ID</th>
<th>Film Thickness (µm)</th>
<th>Estimated Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20.5</td>
<td>0.068</td>
</tr>
<tr>
<td>B</td>
<td>22.7</td>
<td>0.062</td>
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<tr>
<td>C</td>
<td>25.6</td>
<td>0.057</td>
</tr>
<tr>
<td>D</td>
<td>24.7</td>
<td>0.057</td>
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<tr>
<td>E</td>
<td>25.6</td>
<td>0.058</td>
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<tr>
<td>F</td>
<td>24.1</td>
<td>0.058</td>
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\[ a = 1GPU = 10^{-6} \frac{cm^3 (STP)}{cm^2 \cdot s \cdot cmHg} \]

Table 12.4: Permeation Properties of Virgin PSF Asymmetric Membranes used for C⁻ irradiation

<table>
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<tr>
<th>Film ID</th>
<th>Film Thickness (µm)</th>
<th>Estimated Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
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</tr>
<tr>
<td>J</td>
<td>8.1</td>
<td>0.17</td>
</tr>
<tr>
<td>L</td>
<td>6.9</td>
<td>0.20</td>
</tr>
<tr>
<td>M</td>
<td>7.4</td>
<td>0.19</td>
</tr>
<tr>
<td>N</td>
<td>5.2</td>
<td>0.27</td>
</tr>
<tr>
<td>O</td>
<td>4.6</td>
<td>0.30</td>
</tr>
<tr>
<td>P</td>
<td>4.6</td>
<td>0.30</td>
</tr>
<tr>
<td>Q</td>
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<tr>
<td>R</td>
<td>149.8</td>
<td>N/A</td>
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\[ a = 1GPU = 10^{-6} \frac{cm^3 (STP)}{cm^2 \cdot s \cdot cmHg} \]
Table 12.5: Permeation Properties of Irradiated H⁺ PSF Asymmetric Membranes

<table>
<thead>
<tr>
<th>Film ID</th>
<th>Film Modification (H⁺/cm²)</th>
<th>($P_{O_2}^a/ T$)</th>
<th>($P_{CO_2}^a/ T$)</th>
<th>($P_{He}^a/ T$)</th>
<th>$\alpha_{O_2}/ N_2$</th>
<th>$\alpha_{CO_2}/ CH_4$</th>
<th>$\alpha_{He}/ CH_4$</th>
</tr>
</thead>
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<td>23.0</td>
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<td>39.8</td>
</tr>
<tr>
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<td>1x10^{14}</td>
<td>26.3</td>
<td>102</td>
<td>212</td>
<td>3.29</td>
<td>12.0</td>
<td>25.0</td>
</tr>
<tr>
<td>C</td>
<td>4x10^{14}</td>
<td>3.9</td>
<td>15.2</td>
<td>54.4</td>
<td>3.07</td>
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<td>68.4</td>
</tr>
<tr>
<td>D</td>
<td>8x10^{14}</td>
<td>2.8</td>
<td>10.3</td>
<td>52.1</td>
<td>1.90</td>
<td>9.67</td>
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<td>1x10^{15}</td>
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<td>70.0</td>
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<td>33.0</td>
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$a = 1\text{GPU} = 10^{-6} \frac{cm^3\text{(STP)}}{cm^2 \cdot s \cdot cmHg}$

Table 12.6: Permeation Properties of Irradiated PSF Asymmetric Membranes used for C⁻ irradiation

<table>
<thead>
<tr>
<th>Film ID</th>
<th>Film Modification (C⁻/cm²)</th>
<th>($P_{O_2}^a/ T$)</th>
<th>($P_{CO_2}^a/ T$)</th>
<th>($P_{He}^a/ T$)</th>
<th>$\alpha_{O_2}/ N_2$</th>
<th>$\alpha_{CO_2}/ CH_4$</th>
<th>$\alpha_{He}/ CH_4$</th>
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<td>5.0</td>
<td>40.3</td>
<td>133.3</td>
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<tr>
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<td>4.9</td>
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<td>1.1</td>
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<td>NA</td>
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$a = 1\text{GPU} = 10^{-6} \frac{cm^3\text{(STP)}}{cm^2 \cdot s \cdot cmHg}$
<table>
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<tr>
<th>Film ID (Ion)</th>
<th>(\frac{P^d}{P^1_{O_2}})</th>
<th>(\frac{P^d}{P^1_{CO_2}})</th>
<th>(\frac{P^d}{P^1_{He}})</th>
<th>(\alpha_{O_2}/N_2)</th>
<th>(\alpha_{CO_2}/CH_4)</th>
<th>(\alpha_{He}/CH_4)</th>
<th>Estimated Thickness ((\mu m))</th>
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<tr>
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</tr>
<tr>
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<td>33.8</td>
<td>140.9</td>
<td>225.3</td>
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<td>56.1</td>
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<tr>
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<td>168.2</td>
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Table 12.8 Permeance and permselectivity for irradiated samples for 6FDA-6FpDA composite Membranes

<table>
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<tr>
<th>Film ID (ion type)</th>
<th>Film Modification (ions/cm²)</th>
<th>$\left( \frac{P^a}{l} \right)_{O_2}$</th>
<th>$\left( \frac{P^a}{l} \right)_{CO_2}$</th>
<th>$\left( \frac{P^a}{l} \right)_{He}$</th>
<th>$\alpha_{O_2}/N_2$</th>
<th>$\alpha_{CO_2}/CH_4$</th>
<th>$\alpha_{He}/CH_4$</th>
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<tbody>
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<td>A</td>
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<td>101.0</td>
</tr>
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<td>259.1</td>
<td>4.6</td>
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<td>64.0</td>
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<tr>
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<td>$2 \times 10^{15}$</td>
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<td>119.1</td>
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<td>6.5</td>
<td>1.1</td>
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<td>19.6</td>
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</tbody>
</table>

$a = \text{GPU} = 10^{-6} \text{cm}^3 \text{(STP)} \text{cm}^{-2} \text{s} \text{cmHg}$
Chapter 13 References


102. Langsam, M., *Fluorinated polymeric membranes for gas separation processes*: US.


