INVESTIGATION OF DITHIOLENES FOR PROPYLENE/PROPANE MEMBRANE SEPARATIONS

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INVESTIGATION OF DITHIOLENES FOR PROPYLENE/PROPANE MEMBRANE SEPARATIONS

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LIST OF SYMBOLS AND ABBREVIATIONS

6FDA	4,4'-(hexafluorisopropylidene) dipthalic anhydride
6FpDA	4,4' (hexafluoro-isopropylidene) dianiline
DAM	diaminomesitylene
Ni[tfd]$_2$	Ni[$S_2C_2(CF_3)_2$]$_2$
PCHE	Polycyclohexylethylene
FFV	Fractional Free Volume

SUMMARY

Ethylene and propylene are among the most important chemical feedstocks of the petrochemical industry. In 2004, the United States produced 146 and 82 billion pounds of ethylene and propylene, respectively. A significant amount of these olefins are found in petrochemical product streams and must be separated. Due to their relatively low volatilities and similar boiling points to their paraffin analogs, the separation is carried out by cryogenic distillation, which is highly energy and capital intensive. The necessary columns are normally 300 feet tall and contain over 200 trays. The capital cost of such a unit exceeds $50 million, providing the incentive for a less expensive alternative such as membrane separation. Studies have shown that several polymeric membranes offer promising potential, but separation selectivity needs to be improved. Specifically, glassy polyimides, and polyimide-co-polypyrrolones have received considerable research.

Polyimides based on 4,4'-(hexafluorisopropylidene)dipthalic anhydride (6FDA) have exhibited the best performance. The selectivities of these polyimides are in the range of 16-27. Recently, in order to surpass current olefin/paraffin membranes, poly(pyrrolone-imide) materials have been investigated. Such materials are extremely rigid, and because of their sieve-like behavior, may offer a high degree of size selectivity. Other attempts for superior selectivity involve facilitated transport membranes containing silver ions. These membranes are highly selective, but are subject to poisoning by small amounts of petrochemical by-products such as sulfur. Silver ions also form a silver acetylide salt if reacted with acetylene which is typically present as an impurity in

practical feed streams. It is the goal of this project to investigate a carrier other than silver that will push olefin/paraffin selectivity over 30 and be susceptible to poisoning.

Historically, attempts at separating olefins and paraffins via non-distillation methods have involved using metal complexing agents. As early as 1827, it was reported that olefins reversibly react with transition metals such as Cu(I) and Ag(I) to form a complex. Since then, there have been many attempts to perform separations based on reversible chemical complexation.

Recently, dithiolenes have sparked interest as a complexing agent for olefin/paraffin separation. It was been reported that the dithiolene, $Ni[S_2C_2(CF_3)_2]_2$, reacted reversibly with olefins such as ethylene and propylene via an electron-switch mechanism. Furthermore, the dithiolene was not poisoned when exposed to H_2, CO, C_2H_2, or H_2S. When exposed to an argon environment, the intermediate is returned to the original dithiolene, suggesting reversibility.

In this work we investigated the result of incorporating this dithiolene in a polymeric membrane via a preliminary screening test. Permeation and sorption experiments were conducted for pure polyimide and polycycloolefin films and films blended with 10% $Ni[S_2C_2(CF_3)_2]_2$.

The dithiolene, $Ni[S_2C_2(CF_3)_2]_2$ was not proven to be a suitable carrier for separating propylene from propane via a facilitated transport mechanism. Although, there is evidence of some solubility enhancement, overall permeability selectivity is not enhanced upon addition of $Ni[S_2C_2(CF_3)_2]_2$ to a polymer film; which is due to a decrease in the diffusivity of both propylene and propane. This effect is common for all gases measured in both polyimide and polycycloolefin films. Reduction in permeability and solubility suggest an antiplasticization response which is accompanied by a reduction in the glass transition temperature and an increase in polymer stiffness. This phenomenon is supported by the results of Dynamic Mechanical Analysis. Experiments involving polymers known as polycycloolefins supported observations made in polyimide films but provided a contrasting view in certain areas. Specifically, these experiments suggested that in addition to antiplasticization there is evidence of polymer-dithiolene interactions and simple compaction/rigidification which may be responsible for reductions in gas transport in the presence of $Ni[S_2C_2(CF_3)_2]_2$.

CHAPTER 1

INTRODUCTION

1.1 REFINING TECHNOLOGY OVERVIEW

Petroleum, or crude oil, may simultaneously be the most important energy source and the most important chemical feedstock in the world. Of the five major sources of energy, oil accounts for 37% of the world's energy; 10% higher than the next highest source, natural gas [1].

The modern petroleum industry began in 1859 in Titusville, Pennsylvania. In 1859, the U.S. produced 2000 barrels of crude oil and by the year 1874, 420 million barrels of oil were produced. By 1945, Middle Eastern countries discovered large reserves and have now become major producers in the industry. In 2004 over 80 million barrels of oil were produced in the world per day [1-3] (1 barrel= 42 US Gallons).

Petroleum is defined as a "naturally occurring mixture of hydrocarbons, generally in a liquid state, which may also include compounds of sulfur, nitrogen, oxygen, metals and other elements [2]." The compounds can be separated via distillation based on their boiling points (Table 1.1), but the proportion of the different components differs from region to region. Common descriptors of crude oil from around the world are light, heavy, sweet, and sour. Characteristically, light and heavy refer to the proportion of high molecular weight, high carbon compounds, in the crude. Whereas, crude oil containing large amounts of sulfur are known as sour, and those with little or no sulfur are sweet.

Middle Eastern oil, known as light oil, is inexpensive to produce using standard practices. Russia and parts of North America contain large amounts of heavy oil which are more expensive to produce, but methods are being developed to refine these crudes and replenish the world's useful oil reserves [4].

Knowing the compositions and properties of the crude oil determines the methods of refining it into more valuable and salable products. The major refinery products are liquefied petroleum gas (LPG), gasoline, jet fuel, solvents, kerosene, middle distillates (*gasoil*), residual fuel oil, and asphalt. In its simplest form, the refining process involves taking the heavy, or high carbon, crude oil and breaking it down to lighter, low carbon, products through thermal and catalytic processes [2].

Table 1.1 Distillation Fractions of Petroleum[2, 3]

Fraction	Boiling Range (°C)	(°F)
Light naphtha	-1 - 150	30 - 300
Gasoline	-1 - 180	30 - 355
Heavy Napththa	150 - 205	300 - 400
Kerosene	205 - 260	400 - 500
Stove Oil	205 - 290	400 - 550
Light gas oil	260 - 315	400 - 600
Heavy gas oli	315 - 425	600 - 800
Lubricating gas oil	>400	>750
Vacuum gas oil	425 - 600	800 - 1100
Residuum	>600	>1100

Refining can be divided into three basic steps: separation, conversion, and finishing. Figure 1.1 provides an overview of the processes involved in each step. During separation, the crude oil is divided into various fractions via distillation. Conversion processes change the number of carbon atoms within a molecule (cracking), change the hydrogen-to-carbon ratio, or change the molecular structure without altering the number of carbons (reforming, isomerization). Finishing processes purify product streams through distillation or washing [2, 3].

Both catalytic and thermal cracking thermally decompose higher boiling fractions to lower boiling products, but catalytic cracking produce higher octane gasoline and more olefins. Hydroprocessing is also incorporated to improve catalytic products. The presence of hydrogen during thermal reactions reduces the amount of coke formed and increases the yield of gasoline and other fuels. Reforming and isomerization processes also increase the octane of gasoline.

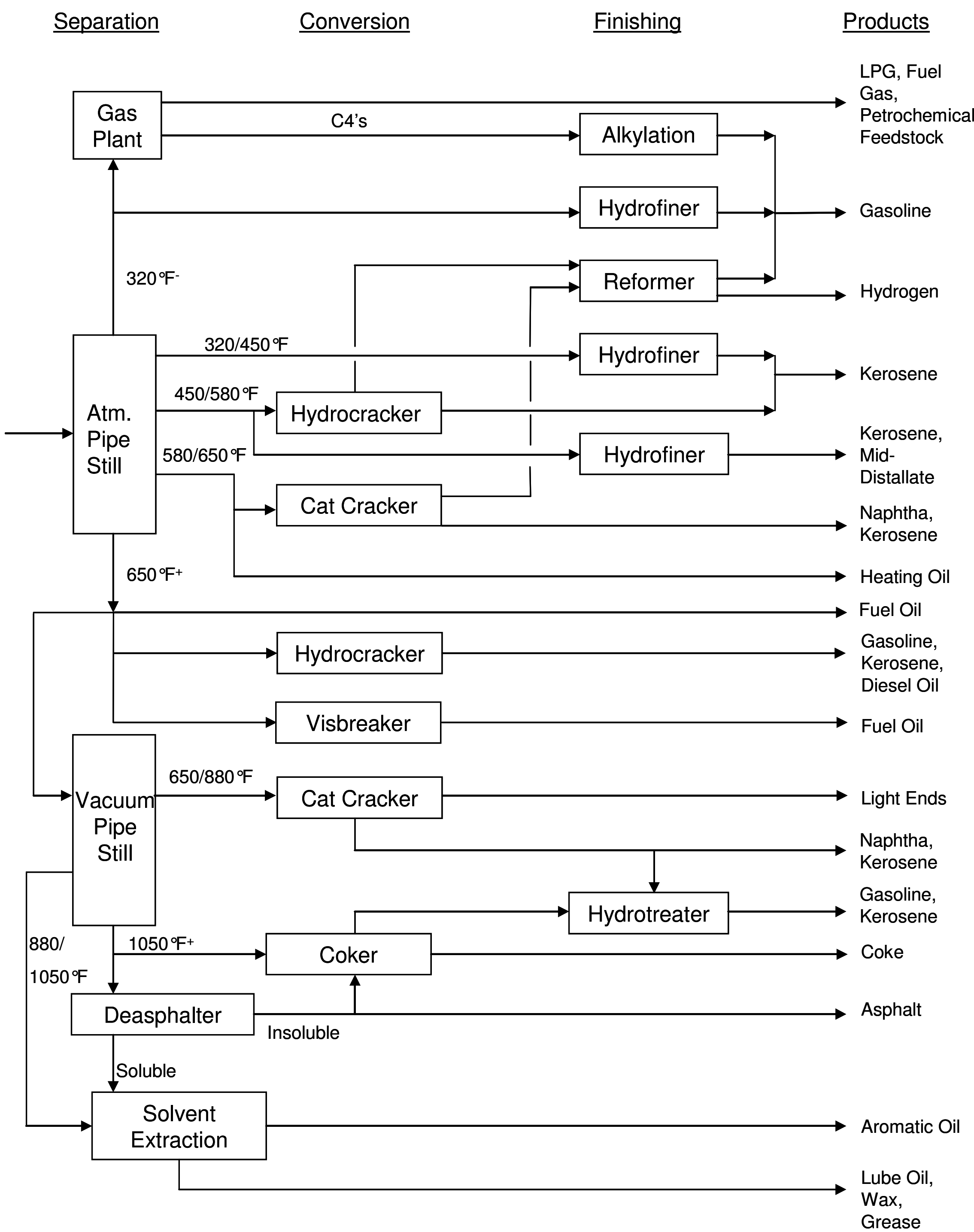

Figure 1.1. Typical Refinery. Adapted from Speight 2001

1.2 OLEFIN PRODUCTION OVERVIEW

Two of the most important petrochemicals are the olefins ethylene and propylene. In 2004, 146 and 82 billion pounds of ethylene and propylene, respectively, were produced worldwide [5]. Both are feedstocks for many other important chemical products; the most important being polyethylene and polypropylene. Worldwide, 72 billion pounds of polyethylene and 42 billion pounds of polypropylene were produced in 2004. Figure 1.2 outlines the many products derived from ethylene and propylene.

Propylene and propane are found in the low and middle fractions of the distillation process albeit in small amounts. Large amounts are formed when gasoline is made by cracking or reforming. Other olefins and paraffins can be found throughout the refining process. Ethane and propane is found in natural gas. Additional propane is formed during catalytic reforming, and ethylene and propylene in the cracking processes.

Besides being a refining byproduct, 60-70% of the U.S.'s ethylene is produced through steam cracking with propylene as a byproduct [6]. Whereas, 50% of propylene produced is from refinery gas streams. Ethylene can also be produced through hydrogenation of ethane; and propylene from propane. By-products such as butadiene, butylenes, and aromatics are also formed during propane hydrogenation. If hydrogenation is not selective, the dienes and acetylenes are converted to ethane and/or propane. The propylene/propane stream is finally sent to a C3 splitter to separate propane (which is recycled to the reactors) and propylene product.

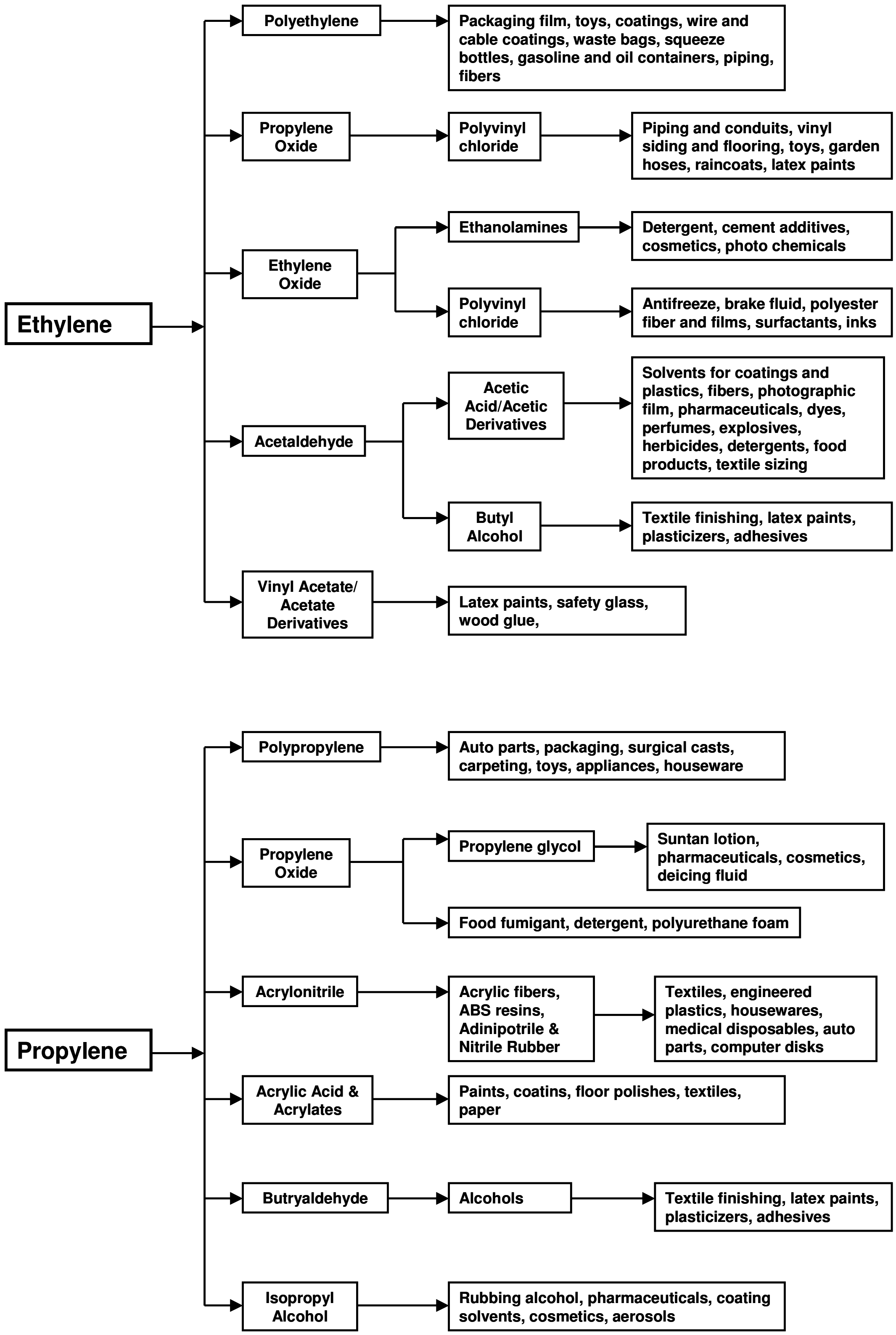

Figure 1.2. a) Ethylene product chain b) Propylene product chain. Adapted from John L. Pelligrino, U.S. Dept. of Energy, 2000

1.3 OLEFIN / PARAFFIN SEPARATION TECHNOLOGY

The processes discussed above usually do not produce olefin of sufficient purity for industrial use. The propylene produced from an ethylene steam cracker does not require further purification, but refinery grade propylene contains 30-40% propane. The most common method of achieving desired purity levels is cryogenic distillation. It is

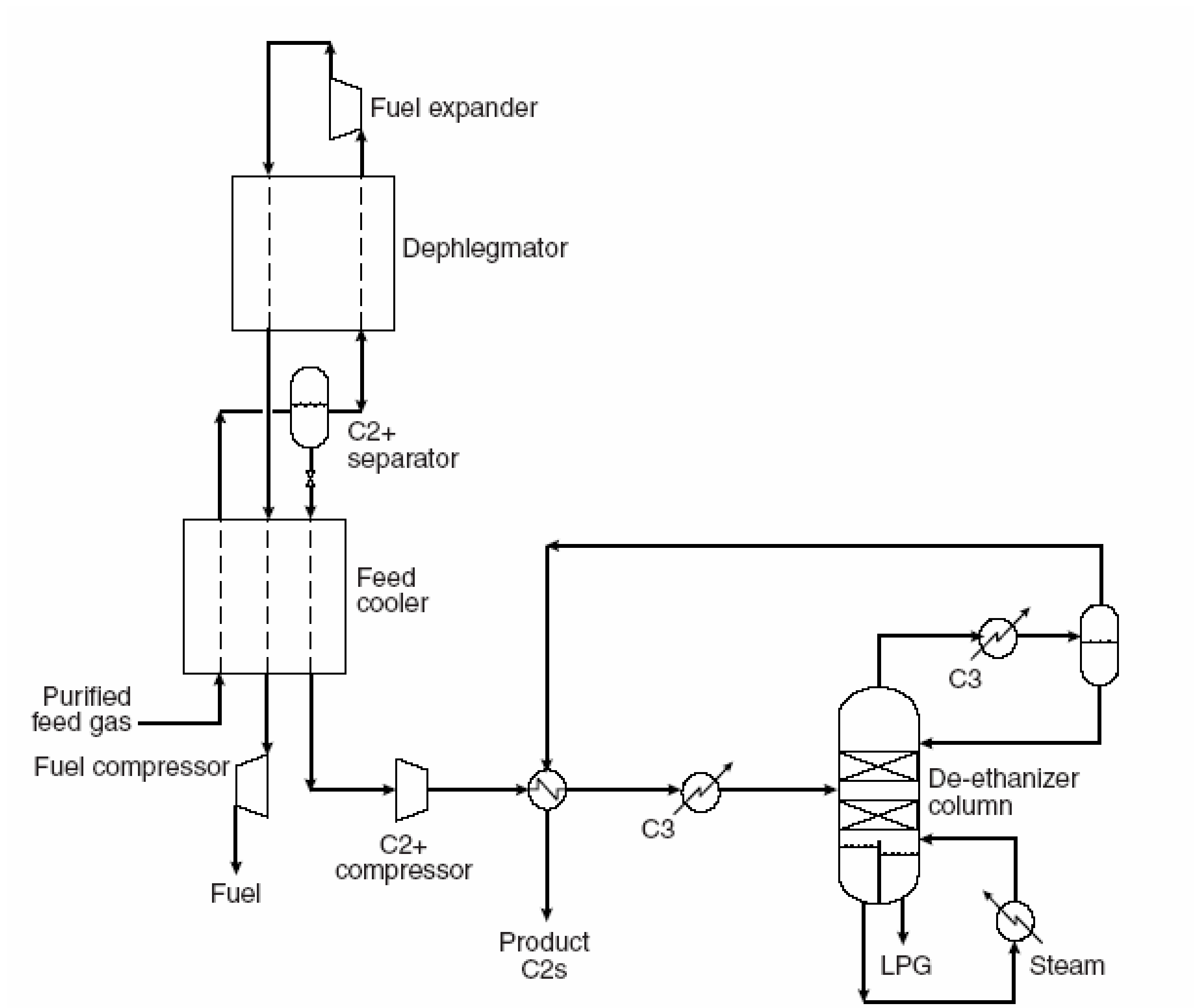

Figure 1.3 FCC offgas ethane/ethylene recovery process. Agrawal 2003

common to adapt a hydrogen purification unit to recover light olefins and LPG streams. The streams are pretreated then cooled to an appropriate temperature for propylene and ethylene recovery. Further cooling is necessary to recover methane and other hydrocarbons before the resulting streams are each flashed to a low pressure. They are then revaporized and warmed with the produced hydrogen and recovered via refrigeration [7].

Another cryogenic separation method incorporates the use of dephlegmators, or fractionating condensers, to recover ethane/ethylene from fluid catalytic cracking (FCC) off-gas (Figure 1.3). Dephlegmators are specially designed heat exchangers which use condensed liquid in counter-current flow resulting in mass transfer between the liquid and the vapor. The feed gas is cooled to approximately 230 K requiring refrigeration which is provided by revaporizing and warming liquid C2+ streams and then expanding the light gases. The separated product can be further purified in a de-ethanizer column. This process also requires refrigeration.

The energy requirements of cryogenic distillation are quite high as well as the capital cost of the equipment. It is estimated that such separations account for 40% of the petroleum industry's energy usage (approximately 1.2×10^{14} BTUs of energy per year) [8]. The aforementioned processes require towers 300 or more feet tall and require capital investments in excess of $50 million. For these reasons, alternative separation methods are desired.

Alternative olefin/paraffin separation technologies include extractive distillation, physical and chemical adsorption, and membrane separation [8]. Membrane separation has become an attractive alternative due to its relative ease of use and low capital and energy costs [8-15]. It is estimated that membrane separation can lead to energy savings of 27 – 105 trillion BTUs per year [16-18]. Although membranes can lead to extensive energy and cost savings, many researchers envision membrane separation units fitted in-line with current separation systems rather than completely replacing them. Figures 1.4 and 1.5 show examples of how membrane units can be used with current olefin/paraffin separation systems.

Polyimide membranes based on 4,4'-(hexafluorisopropylidene)dipthalic anhydride (6FDA) have exhibited the best performance in propylene/propane separation. The selectivities of these polyimides are in the range of 16-27 [9-15]. Recently, in order to surpass current olefin/paraffin membranes, Burns investigated poly(pyrrolone-imide) materials [14]. Such materials are extremely rigid, and because of their sieve-like behavior, may offer a high degree of size selectivity. Other attempts for superior selectivity involve facilitated transport membranes containing silver ions [19-24]. These membranes are highly selective, but are subject to poisoning by small amounts of by-products such as sulfur. Silver ions also form a silver acetylide salt if reacted with acetylene which is typically present as an impurity in practical feed streams. It was the goal of this project to investigate a carrier other than silver that would push olefin/paraffin selectivity over 30 and not undergo poisoning.

Wang and Stiefel investigated a reversible reaction of olefins with a compound known commonly as a "dithiolene [25]." The dithiolene was dissolved in a solvent and shown to react with light olefins such as ethylene and propylene. A complex was formed, then the dithiolene and olefin were returned to their original form by bubbling an inert gas through the solution. Wang and Stiefel suggested this reaction would be useful for olefin/paraffin separation since the dithiolene was not poisoned by hydrogen, acetylide and others compounds known to react adversely with silver ions.

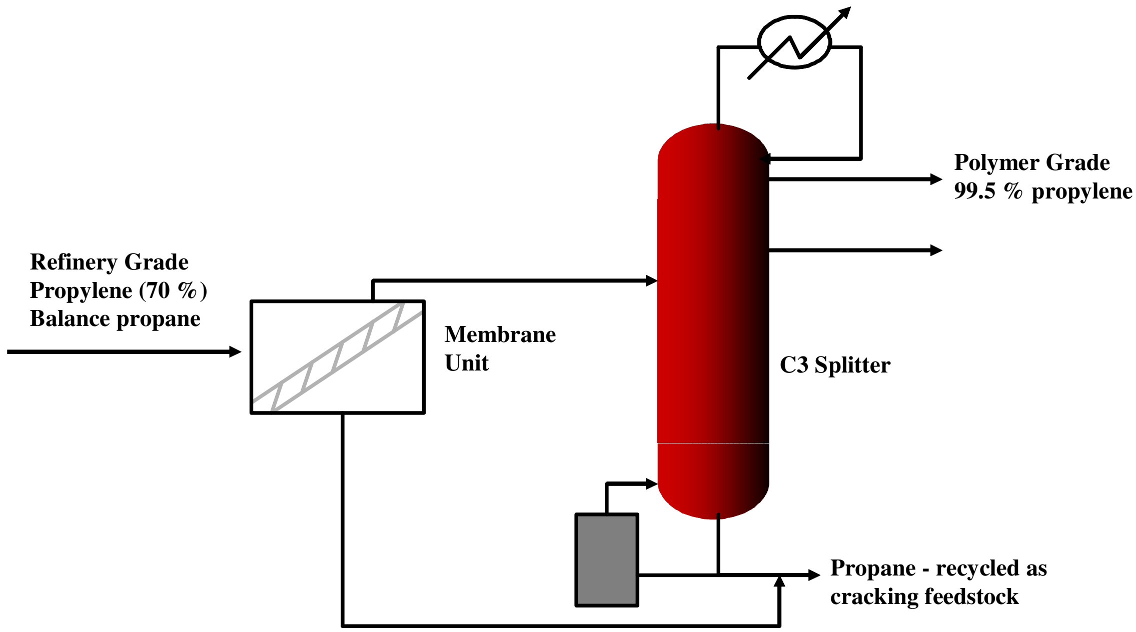

Figure 1.4. In-line membrane with refinery distillation column. Courtesy of Ryan Burns

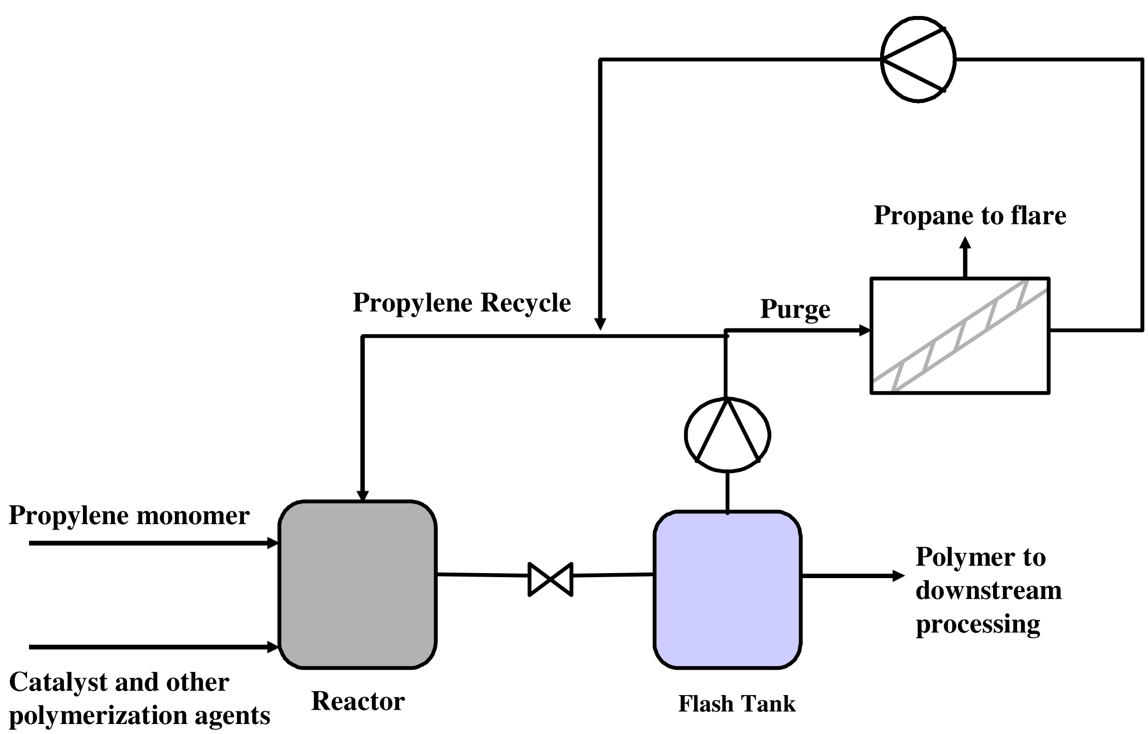

Figure 1.5. Possible placement of membrane unit in polymer production unit. Courtesy of Ryan Burns

In order to utilize this reversible reaction with olefins, Burns incorporated dithiolenes in a membrane as a preliminary study [26]. The results were intriguing and suggested that strong interactions occurred with dithiolenes as facilitated transport carriers, and were worthy of more in depth analysis. The study indicated that low loadings of dithiolene reduced the permeability of the propylene and capacity coefficient, C'_H of both propane and propylene. These observations suggested a reduction in the free volume of the polymer matrix. It was hypothesized that the reduced C_3H_6 permeation was due to a "sticky diffusion" whereby the dithiolene inhibits mobility of the C_3H_6 due to a stronger interaction than originally expected. The apparent reduction in free volume was believed to be due to a phenomenon known as antiplasticization. An antiplasticization response is usually marked by reductions in permeability due to reductions in the free volume of the polymer. The goal of this project was to investigate the dithiolenes for olefin/paraffin separations and understand these phenomena. Specific research objectives to fully understand the effects of dithiolenes are outlined in the following section.

1.4 RESEARCH OBJECTIVES

1. Measure the transport properties at ambient conditions as well as elevated temperatures and pressures to investigate the performance of the dithiolenes under extreme conditions.

As noted above, our recent experiments have investigated the dithiolene-membrane performance. These experiments were conducted at 35˚C and 2 atm as these are the most common conditions reported in the literature. It is important to continue to operate at these conditions to understand the transport properties of these materials. Additionally, the industrial practice is to operate membrane systems at 90˚C and 400psi. We, therefore, investigated membrane performance as a function of increasing pressure and temperature.

2. Measure the effects of increasing dithiolene content on the C_3H_6/C_3H_8 transport properties.

An important parameter to consider is the weight % loading of dithiolene. We will incorporate higher loadings of dithiolene in the membranes to find an appropriate load that will maximize the performance of our membranes. Marisato saw a decrease in both ethylene and ethane permeability coefficients with an increase in silver salt concentration [27]. We hypothesize that there will be an optimum concentration of dithiolene for significant olefin/paraffin separation. Dithiolene loadings of 10, 25, and 50 weight percent were considered; however the amount of dithiolene that could be loaded was limited by solubility limits to approximately 15%.

3. Investigate and explain the reduction in permeability observed with incorporation of the dithiolene in a polymeric membrane.

Preliminary results indicated a reduction in the permeability of both propane and propylene as the loading of dissolved dithiolene is increased. This suggested that the dithiolene was acting as an antiplasticizer, and a further objective of this research was to determine the cause of such an unexpected response.

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2.1 GAS TRANSPORT AND SORPTION

2.1.1 Permeation

Transport of gases through membranes occurs by a solution-diffusion mechanism [1]. In the absence of bulk flow, diffusion is governed by Fick's First Law:

$$N = -D\nabla C \tag{2.1}$$

where N is the diffusive flux and D is the diffusion coefficient, and C is the local penetrant concentration. Diffusion for a gas penetrant, A, in a flat one-dimensional membrane is then given simply by:

$$N_A = -D_A \frac{\partial C_A}{\partial x} \tag{2.2}$$

The permeability coefficient, P_A, is defined as:

$$P_A = \frac{N_A}{\Delta p / l} \tag{2.3}$$

where Δp is the pressure difference across the membrane and l is the membrane thickness. In most cases, the downstream pressure at x = l is much less than the upstream value and in this study will be effectively zero.

According to Henry's law, a linear relationship exists between the external penetrant pressure, p_A, and the equilibrium concentration, C_A, within the membrane, so the following holds true:

$$C_A = S_A p_A \tag{2.4}$$

where, S_A, is the sorption coefficient. It then follows that the permeability coefficient, P_A, of a penetrant, A, is the product of a kinetic parameter, D_A, and a thermodynamic parameter, S_A [2].

$$P_A = \frac{N_A}{\Delta p / l} = -\frac{D_A(\partial C_A / \partial x)}{\Delta p / l} = \frac{D_A(C_2 - C_1)}{\Delta p} = D_A S_A \tag{2.5}$$

For a given gas pair, the selectivity, α_{AB}, of the membrane can be written as the ratio of the mole fractions of the two components, A and B, in the downstream and upstream, y_i, and x_i, respectively .

$$\alpha_{AB} = \frac{(y_A / y_B)}{(x_A / x_B)} \tag{2.6}$$

When the downstream pressure is negligible compared to the upstream pressure, the selectivity is known as the "ideal" selectivity, $\alpha^*_{AB,}$ and eqn. (2.6) can be written as

$$\alpha^*_{AB} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B}\right)\left(\frac{S_A}{S_B}\right) \tag{2.7}$$

Qualitatively, eqn. (2.7) can be interpreted as the product of the mobility selectivity and the solubility selectivity.

2.1.2 Sorption

Sorption in *glassy* polymers, such as those studied here, is said to follow a dual-mode model which accounts for penetrants in the normally densified and so-called "microvoid" (packing defect) regions of the polymer matrix. The sorption in densified regions is visualized to be similar to the sorption concentration in rubbery polymers and is represented by C_D; the Henry's Law concentration [1]. The Langmuir concentration, C_H, describes sorption in the molecular scale "microvoids" or "holes" throughout the matrix, which are believed to be associated with packing defects in the non-equilibrium glassy matrix. Thus sorption in glassy polymers is given as

$$C_A = C_{D_A} + C_{H_A} \tag{2.8}$$

The pressure relationship is then

$$C_A = k_{D_A} p_A + \frac{C'_{H_A} b_A p_A}{1 + b_A p_A} \tag{2.9}$$

where k_D is the Henry's Law coefficient which is a measure of inherent polymer-penetrant interaction [1]. The Langmuir sorption capacity is represented by C'_H and is a measure of the saturation of all "macrovoids" or "holes" in the polymer matrix. The Langmuir affinity constant, *b,* is a measure of the tendency of the gas to saturate the Langmur capacity. From eqn. (2.4) the sorption coefficient is then

$$S_A = \frac{C_A}{p_A} = k_{D_A} + \frac{C'_{H_A} b_A}{1 + b_A p_A} \tag{2.10}$$

2.1.3 Diffusion

The dual-mode model can be extended to describe the local diffusive jumps in and out of the Henry's and Langmuir regions of the polymer [1]. Thus, eqn. 2.2 can then be written as:

$$N_A = -D_{D_A} \frac{\partial C_{D_A}}{\partial x} - D_{H_A} \frac{\partial C_{H_A}}{\partial x} \tag{2.11}$$

Here D_D and D_H reflect the mobility of the penetrants in the respective domains. An effective diffusion coefficient dependent on local concentration is then:

$$N_A = -D_{eff}(C) \frac{\partial C_A}{\partial x} \tag{2.12}$$

Based on the dual-mode model [1, 3], an expression for D_{eff} is:

$$D_{eff}(C) = D_D \left[\frac{1 + FK/(1 + \alpha C_D)^2}{1 + K/(1 + \alpha C_D)^2} \right] \tag{2.13}$$

where $F = D_H/D_D$, $K = C'_H b/k_D$, and $\alpha = b/k_D$.

This model can then be extended to describe permeability in the Henry's law and Langmuir domains [1] for the case of p_A upstream, with a vacuum downstream.

$$P_A = k_{D_A} D_{D_A} + \frac{C'_{H_A} D_{H_A} b_A p_A}{1 + b_A p_A} \tag{2.14}$$

2.1.4 Plasticization and Antiplasticization responses

Glassy polymers are known to "plasticize" at high feed pressures with strongly sorbing components like propane and propylene. As the sorption uptake in the dissolved mode, C_D, increases, the matrix swells significantly. Such swelling, or dilation, also causes an increase in the fractional free volume (FFV) of the polymer. This phenomenon usually involves significant increases in segmental mobility reflected by an upswing in the permeability isotherm. The pressure at which this upswing occurs depends heavily on the condensability of the penetrant gas, since this tends to determine the amount of component sorbed at a given partial pressure of the component. As the membrane plasticizes, a decrease in selectivity usually accompanies the increase in permeability. The membrane becomes less size selective as the polymer matrix expands and can no longer differentiate one penetrant from another with equivalent capability to that in the original polymer matrix. Plasticization, therefore, is thought of as an increase in polymer flexibility brought upon by the presence of a gas penetrant.

Figure 2.1 depicts another permeability response known as "antiplasticization." It has been observed that, when compared to a neat polymer, an antiplasticized polymer exhibits a reduced permeability and an increase in the plasticization pressure[4]. The term "antiplasticization" reflects the fact that the material, tested over very short time scales, tends to display a higher modulus and a *lower* glass transition temperature (T_g).

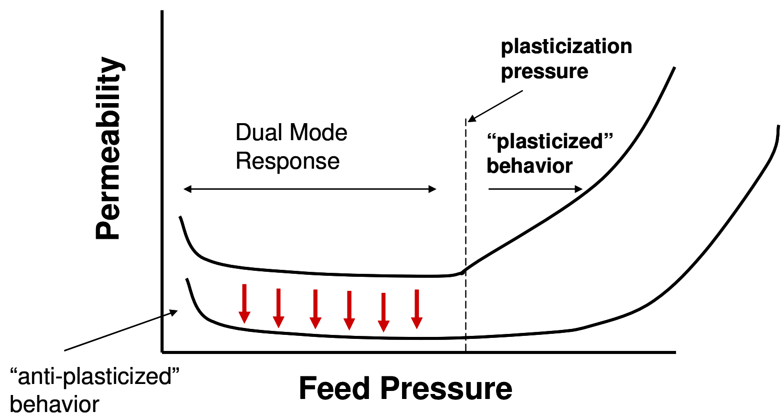


Figure 2.1. Plasticization and antiplasticization responses of glassy polymers.

The causes of antilplasticization are best interpreted from the effects of an additive on chain mobility and free volume of a polymer. Jackson and Caldwell described in detail the mechanical properties attributed to antiplasticization; increases in "short time testing" tensile module and tensile strength and decreases in elongation and impact strength [5-7] . Robeson has shown that this behavior is due to partial elimination of the secondary transitions, small local motion required for ductility, within the polymer matrix [8, 9]. The secondary transitions and modulus are readily measured using dynamic mechanically analysis and will be discussed in Chapter 6. Furthermore, Robeson has shown that antiplasticizers at low concentrations have a *non-additive effect* on the volume suggesting that they tend to fill the polymer free volume. Due to the filling of polymer volume and elimination of secondary transitions it is easily inferred that a subsequent reduction in diffusion will occur. Upon heating toward the pure polymer T_g, however, the excess sorbent is "oversaturated" in the free volume of the matrix and tends to act as an actual promoter of segmental motion, thereby lowering the T_g as probed by DSC or other temperature scanning methods.

Robeson as well as Maeda and Paul measured the density, and subsequent specific volume, of polymer mixtures with increasing amount of an additive. Additives with the strongest antiplasticization effect tended to cause a decrease in the specific volume and hence filling up the free volume and restricting the motions responsible for low temperature transitions at sub-T_g conditions [6, 7]. It is readily understood that an impediment of chain mobility could result in loss of ductility and increased stiffness, but it is not as easily understood why there is a decrease in T_g associated with antiplasticization. The preceding qualitative explanation helps to understand this, at first, surprising observation. A quantitative description of this phenomenon is best understood through an interpretation of the effects of an additive on the specific volume as shown in Figures 2.2 and 2.3.

Both plasticizers and antiplasticizers tend to decrease the T_g of a polymer because they typically have a much lower T_g than the polymer. Common antiplasticizers possess glass transition temperatures as low as -40°C. The T_g of these substances are usually measured from the quench. Simply, on a weighted average, the polymer mixture containing an antiplasticizer or plasticizer will have a lower T_g than the neat polymer as shown in Equation 2.14.

$$T_{gm} = \phi_p T_{gp} + \phi_d T_{gd} \qquad (2.14)$$

where the polymer and additive are denoted by p and d, respectively. The weight percent is denoted by ϕ in the same manner. The effect of the additive on the free volume coupled with the decrease in temperature determines if it will cause plasticization or antiplasticization.

Based on work down by Maeda and Paul Madden developed an interpretation of plasticization and antiplasticization effects using a volume-temperature plot [4, 10-13]. Using Figures 2.2 and 2.3, Madden explained that when a penetrant with concentration $c_A > 0$ is added to a polymer, the polymer/penetrant mixture has a higher specific volume in the rubbery state than the pure polymer. The resulting penetrant/polymer mixture has a lower glass transition temperature. It is then possible for the specific volume of penetrant/polymer $V_g\,(c_{A1},T)$ mixture in the glassy state to be less than the specific volume of the pure polymer in the glassy state $V_g\,(c_{A0},T\,)$, at a given temperature. This condition results in an antiplasticization response. Plasticization occurs at high penetrant concentration when the specific volume of the *polymer sorbate mixture* in the glassy state $V_g\,(c_{A2},\,T)$ is significantly greater than that of the pure polymer in glassy state, $V_g\,(c_{A0},T)$.

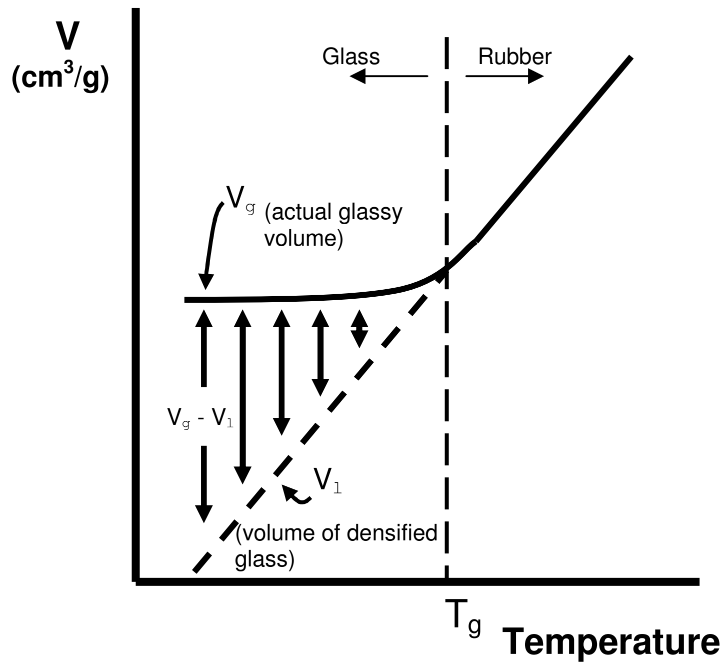


Figure 2.2. Specific volume schematic representation.

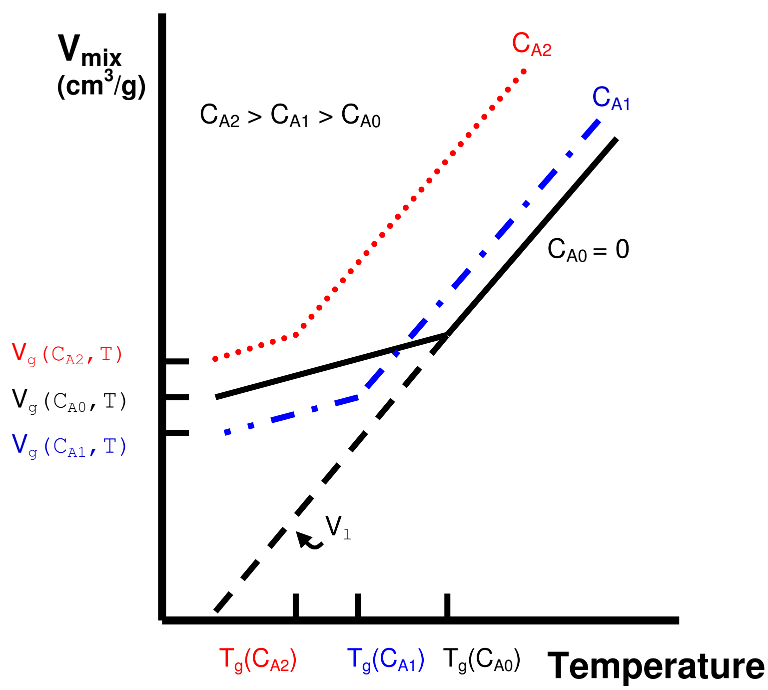


Figure 2.3. Specific volume interpretation of plasticization and antiplasticization of a polymer mixture [10]. C_{A2}, C_{A1}, C_{A0} are the concentrations of the plasticized, antiplasticized and pure mixtures, respectively

2.2 TEMPERATURE DEPENDENCE OF GAS TRANSPORT AND SORPTION

An Arrhenius relationship represents the temperature dependence of permeability [14]

$$P = P_o \exp\left[\frac{-E_p}{RT}\right] \tag{2.15}$$

where P_o is the pre-exponential factor, E_p is the apparent activation energy for permeation, R is the universal gas constant, and T is the permeation temperature. The temperature dependence of diffusion is also represented by an Arrhenius relationship [14].

$$D = D_o \exp\left[\frac{-E_d}{RT}\right] \tag{2.16}$$

As above, D_o is the pre-exponential factor, and E_d is the apparent activation energy for diffusion which represents the energy required for a gas penetrant to "jump" within the equilibrium sites of the polymer matrix. The temperature dependence of sorption is represented by the van't Hoff equation [14]

$$S = S_o \exp\left[\frac{-H_S}{RT}\right] \tag{2.17}$$

where S_o is the pre-exponential factor, and H_s is the apparent heat of sorption combining the temperature dependence in both the Henry's law and Langmuir regions. As such, H_S can show a significant concentration dependence not seen in simple rubbery polymers. The temperature dependence of the sorption parameters, k_D and b, can also be represented by individual van't Hoff relationships [15].

$$k_D = k_{Do} \exp\left[\frac{-H_D}{RT}\right] \quad (2.18)$$

$$b = b_o \exp\left[\frac{-H_H}{RT}\right] \quad (2.19)$$

2.3 FACILITATED TRANSPORT

Facilitated transport is a term used to describe membranes that function by means of a solution-diffusion mechanism *as well as* a chemical reaction or complexation [16]. As the solution-mechanism model is well understood, multiple models of facilitated transport exist [16-19]. In its simplest form, a carrier selectively reacts with a solute and "facilitates" the permeation of one solute, or gas, over another leading to higher selectivity. Carriers can be mobile or fixed within a membrane. Mobile carriers are typically found in liquid membranes. In this case, the carrier reacts with the solute on one side of the membrane to form a complex. The complex diffuses through membrane to the other interface where the solute is released and carrier is returned to its initial form. Fixed-site carriers are either covalently bonded to the membrane material or have limited mobility. The solute then jumps from carrier to carrier until it diffuses through the membrane. These carriers are usually found in solid state polymeric membranes. The important key to both mobile and fixed-site carriers is the ability to *reversibly* interact to enable the release of the gas.

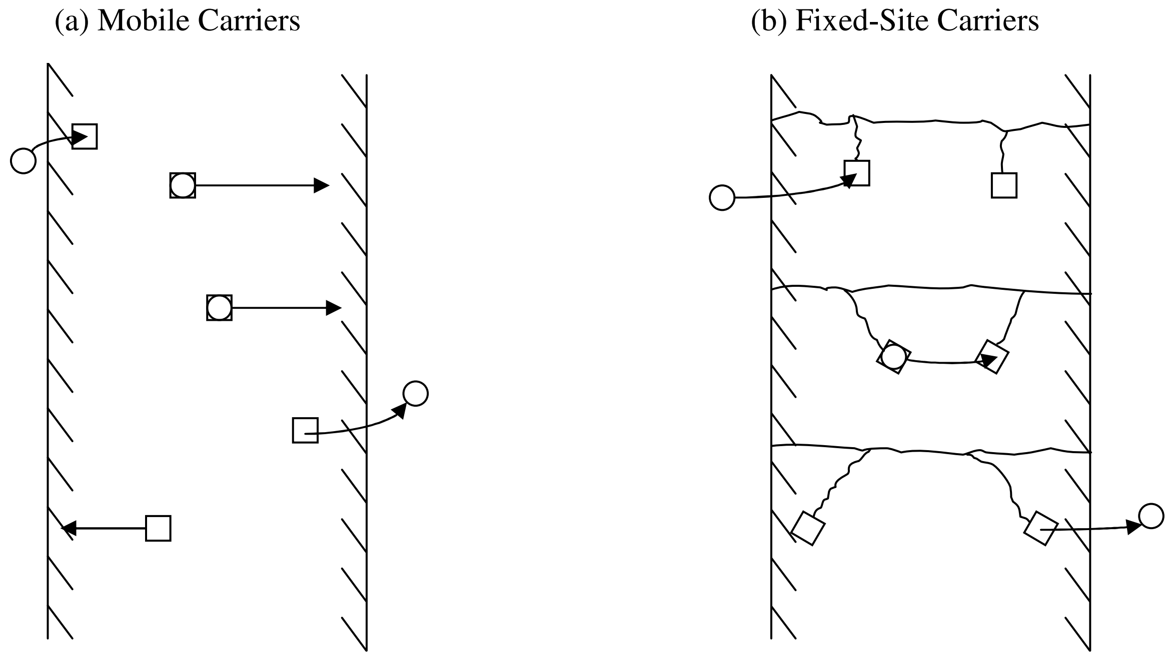


Figure 2.4. Mobile vs. Fixed-Site Carriers. Adapted from Cussler 1989

Such a simplistic model exists because the reactions that undergo within the membrane are not always fully understood. Thus, criteria based on experimental observation have been adopted to identify facilitated transport membranes [16]:

1. The solute's flux is larger and more selective than expected
2. The flux varies linearly with solute concentration difference at low solute concentration, but reaches a limiting value-"saturates"-at high solute concentration
3. The flux of one solute can be easily poisoned or may be strongly influenced by the gradient of a second solute.

There have also been attempts to derive mathematical models to describe facilitated transport [16-18]. Noble derived an effective diffusion coefficient for the solute-carrier complex and the resulting model is similar to the well-known dual-mode model [18].

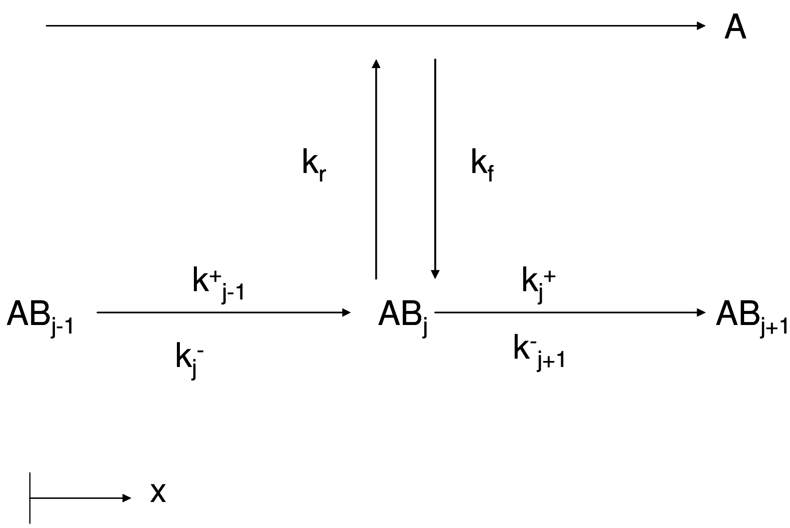


Figure 2.5. Schematic of interactions between solute and three adjacent fixed sites. Adapted from Noble 1990.

The model developed by Noble is based on the schematic in Figure 2.5. The concentration of the solute-carrier complex is denoted by C_{ABj} at a location j in the membrane. The rate of migration between sites is given by k_j^+ and k_j^- in the respective direction; the kinetic rate constants for interactions between the permeate and fixed carrier site are k_f and k_r. The carrier is assumed to be in excess and the concentration of unreacted permeated (C_B) is assumed to be constant.

A balance on AB at j yields:

$$\frac{dC_{AB_j}}{dt} = -C_{AB_j}(k_j^+ + k_j^-) + C_{AB_{j+1}} k_{j+1}^- + C_{AB_{j-1}} k_{j-1}^+ + k_f C_A - k_r C_{AB_j} \qquad (2.20)$$

This allows the following definitions:

$$\bar{k}_j = \frac{1}{2}\left(k_j^+ + k_j^-\right)$$

$$\delta k_j = \left(k_j^+ - k_j^-\right)\mathrm{j}$$

$$\bar{k}_{j+\frac{1}{2}} = \frac{1}{2}\left(k_j^+ + k_{j+1}^-\right)_j$$

$$\delta k_{j+\frac{1}{2}} = k_j^+ - k_{j+1}^-$$

where $\bar{k}_j$ = average mobility at location *j* and $\bar{k}_{j+\frac{1}{2}}$ = average mobility between locations *j* and *j*+1. δk_j = degree of directional preference at location *j* and δ_{kj+1} = degree of directional preference between locations *j* and *j*+1. The most important term is $\bar{k}_{j+\frac{1}{2}}$ for it defines mobility between carrier sites.

The net flux due to mobility between *j* and *j*+1 is:

$$J_{j+\frac{1}{2}} = k_j^+ C_{AB} - k_{j+1}^- C_{AB_{j+1}} \qquad (2.21)$$

With algebraic arrangement and defining D_{AB}, Noble then shows that

$$-J_{j+\frac{1}{2}} + J_{j-\frac{1}{2}} = D_{AB}\frac{\partial^2 C_{AB}}{\partial x^2} \qquad (2.22)$$

And

$$0 = D_{AB}\frac{\partial^2 C_{AB}}{\partial x^2} + k_f C_A - k_r C_{AB} \qquad (2.23)$$

Solving the differential equations yields

$$F = 1 + \frac{\alpha K}{1 + K} \qquad (2.24)$$

which is mathematically equivalent to the dual mode sorption model where

F = facilitation factor (solute flux with carrier/solute diffusional flux)
K = dimensionless reaction equilibrium constant ($k_f C_A)/k_r$)
α = ratio of mobility of carrier to mobility of solute ($D_{AB}C_T/D_A C_{AO}$)
D_A = solute diffusion coeffiecient

C_T = total concentration of carrier

The above derivation is presented in brief to show that models of facilitated transport do indeed exist, but numerous literature regarding the subject do not apply this or any model to reported data. Instead, literature on facilitated transport assume a classical dual-mode model and facilitation is implied by observed effects on selectivity when compared to a membrane without a carrier. Thus, it is noted, that this work does not attempt to fit reported data to any facilitated transport model. Following the lead of current reported work, membrane separation properties of membranes with a carrier are compared those in the absence of said carrier.

2.4 POLYMERIC MEMBRANE OLEFIN / PARAFFIN SEPARATION

Robeson [20], in 1991, defined the upper-bound of polymeric membranes for gas pairs such as O_2/N_2, CO_2/CH_4, H_2/CH_4, and others. Since then, Burns and Koros [21] have identified the upper bound for C_3H_6/C_3H_8 separation (Figure 2.3). The upper bound is currently defined by the 6FDA-based polymers prepared from the diamines TrMPD (also known as DAM) and DDBT. The ideal selectivity of these polymers are 11 and 27, respectively at 35˚C [21, 22]. Staudt-Bickel and Koros [23] also reported an ideal selectivity of 16 for the polyimide 6FDA-6FpDA. The report showed an increase in selectivity with a decrease of temperature from 308K to 298K. Strong plasticization effects were seen at 4 atm for propylene. In 50:50 propane/propylene mixed gas experiments, the selectivity decreased with increasing feed pressure by as much as 50% from ideal selectivity.

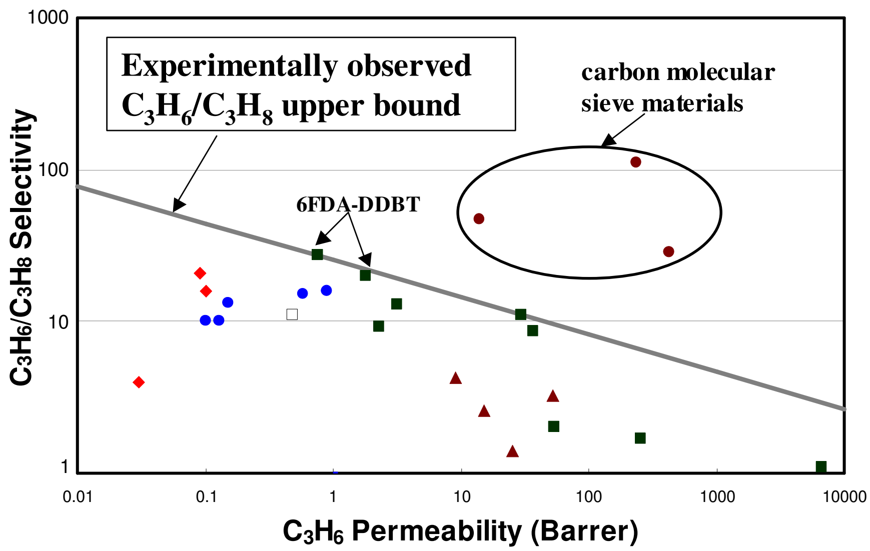


Figure 2.6. Burns' C_3H_6/C_3H_8 tradeoff curve [10].
C_3H_6/C_3H_8 experimental upper bound based on pure gas permeation data over the range 1 – 4 atm feed pressure. □ = 100°C, ■ = 50°C, ● = 35°C, ▲ = 30°C, ◆ = 26°C.

Shimazu et al and Tanaka et al investigated the influence of chemical structure on the permeability of 6FDA-based polyimides [22, 24]. The study showed that with a decrease in unrelaxed volume and corresponding increase in glass transition temperature (T_g), the permeability of the polyimides decreased. In mixed gas experiments, polyimides with large unrelaxed volume exhibited increased propylene permeability and decreased selectivity. An increase in propylene permeability was also accompanied by an increase in solubility. Controlling the solubility of propylene proved to be an important factor in increasing the selectivity of 6FDA-based polyimides according to the researchers.

Work by Burns proved that the propylene/propane selectivity of 6FDA-TrMPD (6FDA-DAM) could be increased by using rigid sieve-like polymeric materials known as polypyrrolones[25]. The monomer 1,2,4,5-tetraaminobenzine (TAB) was added to create a poly(pyrrolone-imide) material. This monomer is flat, packable, and rigid. The bulky CF_3 groups of 6FDA and the methyl groups of DAM act as molecular spacers, and when combined with TAB, created a polymer that packed into molecular sieve regions. Burns created a family of copolymers with varying amounts of TAB. Surprisingly, as the DAM/TAB ratio was increased, a selectivity maximum was observed for propylene/propane.

2.5 OLEFIN / PARAFFIN SEPARATION VIA FACILITATED TRANSPORT

Historically, attempts at separating olefins and paraffins via non-distillation methods have involved using metal complexing agents. As early as 1827, it was reported that olefins reversibly react with transition metals such as Cu(I) and Ag(I) to form a complex. Since then, there have been many attempts to perform separations based on reversible chemical complexation. The Dewar-Chatt Model suggests a π-bond complexation. The s and d orbitals of the metal overlapped with both the antibonding and bonding π orbitals of the olefin [26].

Most facilitated transport systems involving silver are in an aqueous state. Silver nitrate is the most common aqueous system for olefin/paraffin separations. In concentrated solutions of silver nitrate, Ag^+ and NO_3^- self-complex to restrict the formation of a silver ion-olefin complex. The activity of silver anions also decreases with increasing silver concentration.

There have also been attempts at facilitated transport by using silver ions in a solid state by blending or grafting the ions in the polymer membranes [27-33]. Yang et al synthesized complex membranes grafted with silver ions [31]. The complex membrane of poly[(trimethylsilyl)-1-propyne]-graft-poly(acrylic acid)-Ag^+ showed low selectivity of 7.7 and 7.3 for isobutene/isobutane and trans-2-butene/n-butane, respectively. The membrane was also only stable at low pressures [32]. Yang et al also synthesized a silicon rubber (SR) grafted copolymer, SR-graft-poly(acrylic acid). The selectivity and permeability coefficients of these membranes decreased with an increase in the percentage of acrylic acid grafted. The selectivity of this complex was only 2.9 and 4.0 for isobutene/isobutane and trans-2-butene/n-butane, respectively.

Pinnau and Toy have investigated solid polymer electrolyte composite membranes for olefin/paraffin separation [28]. Solid polymer electrolytes do not require the presence of a solvent or plasticizer to allow ionic motions within the membranes. These composite membranes were made by making solutions of poly(ethylene oxide) and silver tetrafluoroborate ($AgBF_4$) then casting using a dip-coating process. Membranes containing 80 wt% $AgBF_4$ had a mixed gas ethylene/ethane selectivity of 120 at 23˚C and 100 psig. These membranes were mechanically stable, but the silver ions were very chemically unstable. The Ag^+ ions degraded in the presence of hydrogen sulfide and formed explosive silver acetylide when reacted with acetylene that is usually found in industrial feed streams. Another solid polymer electrolyte membrane, nylon-12/tetramethylene oxide block copolymer (PA12-PTMO/$AgBF_4$) showed a decrease in both ethylene and ethane fluxes as the silver salt concentration was increased from 0 to 70 wt% [27].

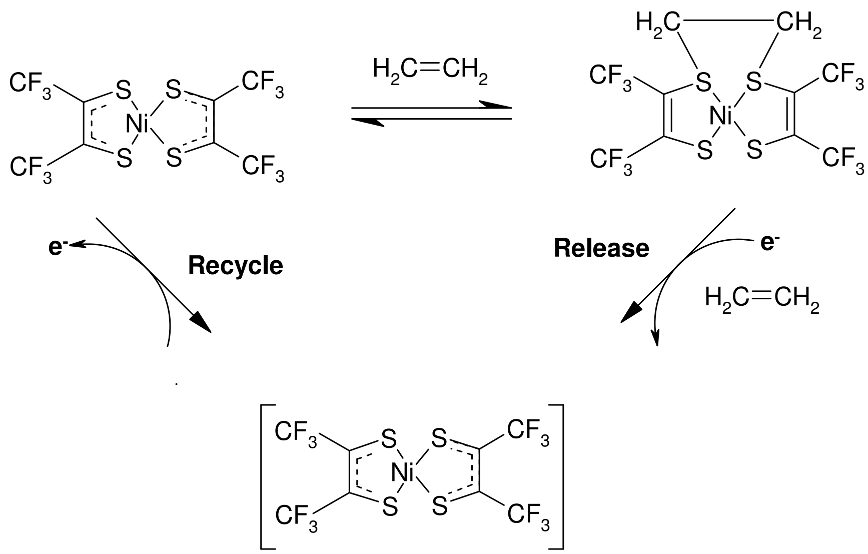
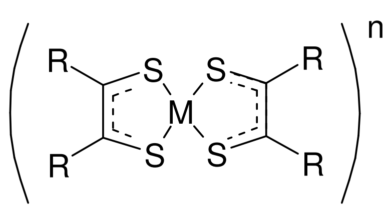


Figure 2.7. Proposed Reaction Mechanism for C_3H_6 and $Ni[S_2C_2(CF_3)_2]_2$

Recently, dithiolenes have sparked interest as a complexing agent for olefin/paraffin separation [34-45]. Wang and Stiefel [37], reported that the dithiolene, $Ni[S_2C_2(CF_3)_2]_2$, reacted reversibly with olefins such as ethylene and propylene via an electron-switch mechanism (Figure 3). Deep purple solutions of the dithiolene turned yellow when reacted with olefins. Furthermore, the dithiolene was not poisoned when exposed to H_2, CO, C_2H_2, or H_2S. When exposed to an argon environment, the intermediate is returned to the original dithiolene, suggesting reversibility.

The reaction of dithiolene complexes and olefins was first reported in 1964 by Schrauzer et al [46]. The general structure of dithiolene complexes was discovered to be:



where the R-group can be CN, CF_3, or C_6H_5. The charge, n, is either 0, -1, or -2. Early studies by Davison et al [47] indicated that the neutral compound with $–CF_3$ groups was "extremely soluble" in nonpolar solvents such as cyclohexane, benzene, and dichloromethane to give intense purple solutions. Brown-green solutions were formed when the compound was dissolved in "more basic solvents" such as ketones, amides, nitriles, amines, and DMSO [47]. Davison also observed that this compound is a strong π-acid (electron acceptor) rendering it highly useful in electron-transfer reactions.

In 1964, Schrauzer et al [46] reported dithiolene reactions with olefins. The Ni, Pd, and Pt complexes combined with dienes in a simple 1:1 addition reaction. Ni-substituted complexes were found to be more labile, indicating reversibility. Most importantly, Schrauzer suggested that the adducts formed were not complexing with the metal center but with the ligands. Because the adducts formed were so labile, the olefins had to be joined by weak C-S bonds.

Ryan Burns investigated the result of incorporating this dithiolene in a polymeric membrane in a preliminary screening test [25]. Permeation and sorption experiments were conducted for pure 6FDA/6FpDA films and films blended with 11% $Ni[S_2C_2(CF_3)_2]_2$. Within the dithiolene film, Burns observed an increase in the affinity constant, b, and the Henry's law constant, k_D, for C_3H_6, compared to the pure polymer film. Additionally, the C'_H parameter (eqn. 9) decreased for both C_3H_6 and C_3H_8 suggesting a decrease in the free volume of the polymer matrix. Burns hypothesized that the dithiolene acted as a plasticizer, decreasing the glass transition temperature of the polyimide.

Table 2.1. Dual Mode Parameters for C_3H_6/C_3H_8 in 6FDA-6FpDA and 6FDA-6FpDA/$Ni[S_2C_2(CF_3)_2]_2$-11% as reported by Burns

Membrane Material	Gas	k_D cc (STP) / cc polymer - psia	C'_H cc (STP) / cc polymer	b psia^{-1}
6FDA-6FpDA	C_3H_6	0.32	26.4	0.14
6FDA-6FpDA / $Ni[S_2C_2(CF_3)_2]_2$	C_3H_6	0.40	17.2	0.70
6FDA-6FpDA	C_3H_8	0.36	14.6	-
6FDA-6FpDA / $Ni[S_2C_2(CF_3)_2]_2$	C_3H_8	0.34	9.9	0.37

As expected, the solubility selectivity of the 6FDA-6FpDA/ $Ni[S_2C_2(CF_3)_2]_2$ was higher than that of 6FDA-6FpDA for all pressure ranges as shown in Figure 2.8.

However, there was not a corresponding increase in the permeability with the addition of the dithiolene. Table 2.2 shows that at a feed pressure of 2 atm, the pure C_3H_6 permeability decreased and because the pure C_3H_8 permeability stayed approximately the same selectivity decreased. On the other hand, at low feed pressures, mixed gas

Table 2.2. Permeation results for 6FDA-6FpDA obtained by Ryan Burns

	P_{C3H6}	Selectivity
6FDA-6FpDA[a]	0.89	16
6FDA-6FpDA/$Ni[S_2C_2(CF_3)_2]_2$-11%[b]	0.25	4.9

[a] Staudt-Bickel and Koros, JMS, 2000
[b] Burns, PhD Dissertation, 2002

C_3H_6/C_3H_8 permeation resulted in a selectivity of approximately 11 due to a decrease in both the C_3H_6 and C_3H_8 permeability coefficients. The mixed gas C_3H_6 permeability was the same as in the pure gas experiment. Burns suspected that the mixed gas results were caused by competitive sorption. The presence of a second gas hindered the ability of C_3H_8 to sorb into the polymer matrix. It was an important objective of the work in this study to probe the detailed phenomena responsible for these complex results.

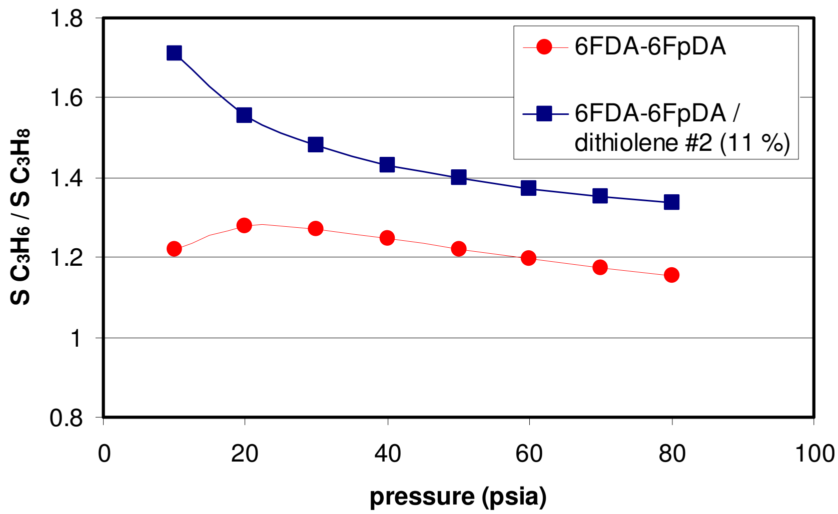


Figure 2.8. Effect of dithiolene on the selectivity of 6FDA-6FpDA [20].

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CHAPTER 3

MATERIALS AND EXPERIMENTAL PROCEDURE

3.1 MATERIALS STUDIED

3.1.1 Polymeric Materials

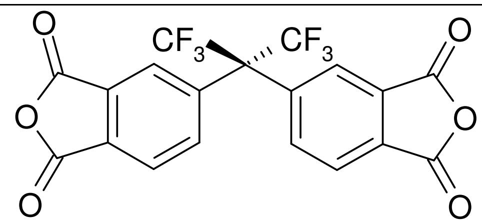
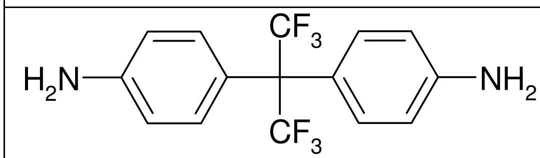
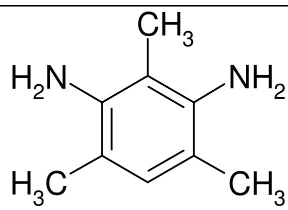
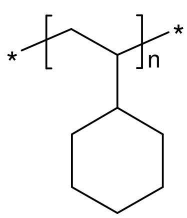
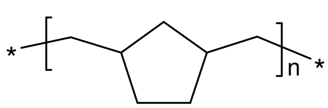
Two of the polymers studied were polyimides based on the dianhydride 4,4'-(hexafluoroisopropylidene) diphthalic anhydride(6FDA). Some of the polymers based on 6FDA lie on the upper bound for C_3H_6/C_3H_8 defined by Burns and Koros and have previously been studied in this group[1].

Extensive work has been done with the diamines trimethylphenylinediamine (TrMPD), or diaminomesitylene (DAM) and 4,4' (hexafluoro-isopropylidene) dianiline (6FpDA), or 2-bis(4-aminophenyl)hexafluoropropane (BAAF). Both DAM and 6FDpA have been used to provide molecular spacers within the polymer matrix in addition to the $–CF_3$ groups of 6FDA. The polymers formed with these monomers are known as 6FDA-DAM and 6FDA-6FpDA.

Additionally, hydrogenated polystyrene or poly(cyclohexylethylene) (PCHE) and a norbornene derivative known commercially as Zeonex® were studied. These polymers were chosen for their non-aromatic character and to serve as a contrast to the polyimides. Both are known for their optical properties as they have been developed for use in DVDs. The structures of the monomers and polymers studied are shown in Table 3.1.

Samples of PCHE were provided by Dr. Frank Bates of the University of Minnesota. Zeonex® is provided by ZeonChemicals of Louisville, Kentucky. The specific grade investigated in this study is Zeonex 480®. The polyimide 6FDA-6FpDA was provided by Hoechst-Celanese Corporation and 6FDA-DAM was synthesized via chemical imidization as has been reported previously [2, 3].

Table 3.1 Monomers and Polymers Studied

Structure	**Abbreviation**	**Chemical Name**
	6FDA	4,4'-(hexafluoroisopropylidene) diphthalic anhydride
	6FpDA (BAAF)	4,4'-(hexafluoro-isopropylidene) dianiline
	TrMPD (DAM)	trimethylphenylinediamine
	PCHE	Poly(cyclohexylethylene)
	Zeonex®	

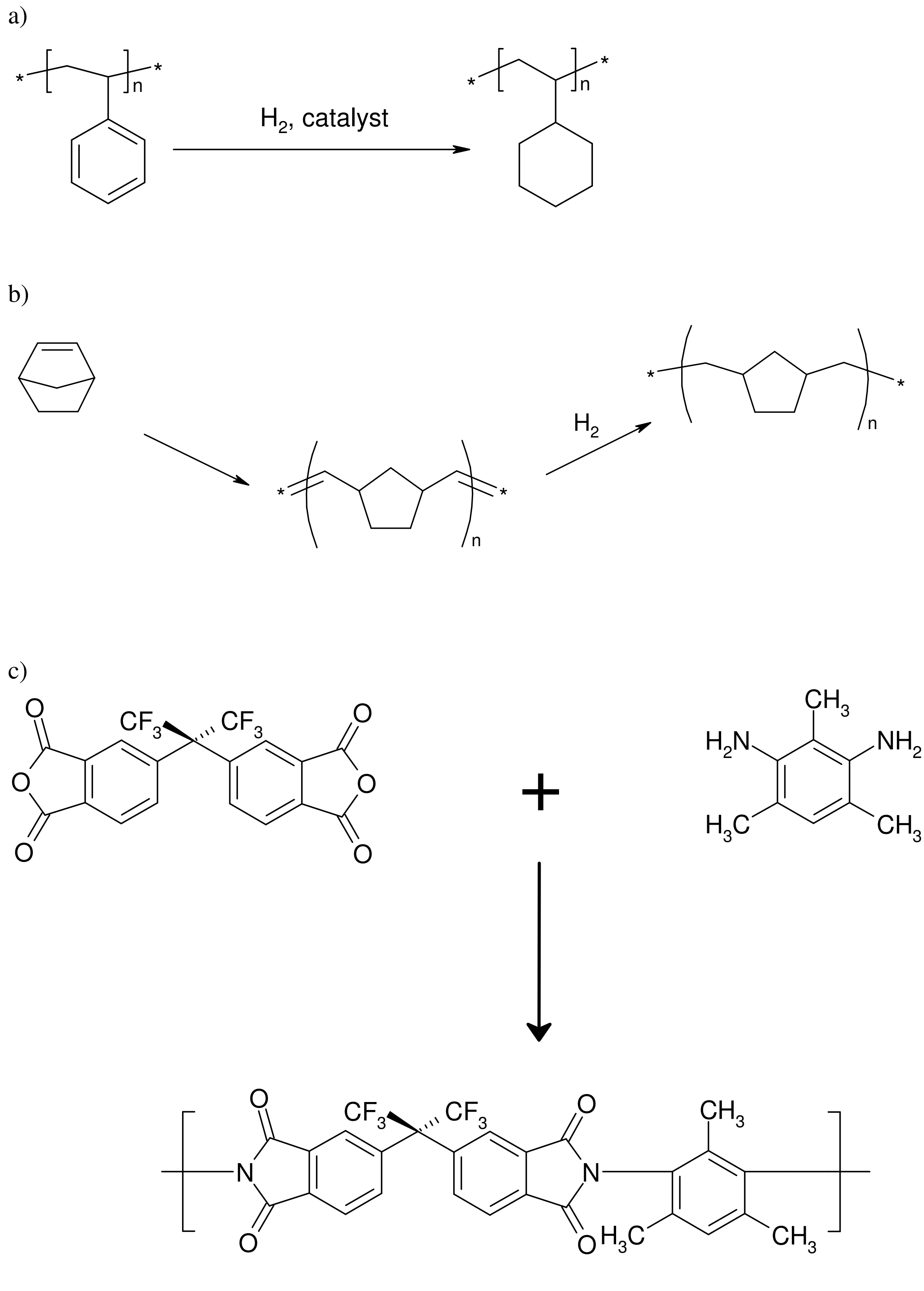


Figure 3.1 Polymer synthesis mechanisms. a) PCHE [4], b) Zeonex® [5], c) 6FDA-DAM

3.1.3 Nickel Dithiolenes

Dithiolene samples in a dark purple powder form were provided by Dr. Joel Miller of the University of Utah. As discussed in Chapter 2, Burns determined that the dithiolene, $Ni[S_2C_2(CF_3)_2]_2$ was the most suitable for incorporating into a 6FDA-6FpDA due its $–CF_3$ groups [1]. Other dithiolenes were attempted in this study, but they were not miscible with 6FDA-6FpDA supporting the preliminary results of Burns.

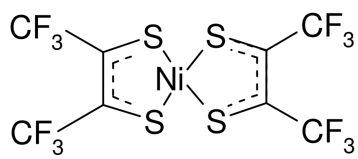


Figure 3.2 Structure of $Ni[S_2C_2(CF_3)_2]_2$

The general form of a dithiolene is shown in figure 3.3. Dithiolenes have a somewhat ambiguous oxidation state. The metal center is either 0, II, or IV [6, 7]. The overall charge of the complex is either 0,-1,-2. It has been accepted that the dithiolene exists in a resonance hybrid of structures shown in Figure 3.3.

The term dithiolene refers to the S-S linkage and those containing a metal center are known as metal-dithiolenes. The above dithiolene is also known as a homoleptic bis(dithiolene); bis because there are two ligands attached to the metal center and homoleptic because the ligands are identical [7]. The ligand in this particular dithiolene, $[S_2C_2(CF_3)_2]$, or bis(trifluoromethyl)-1,2, dithiete [8]. For simplicity, it is commonly abbreviated as -tfd. For the remainder of the dissertation, the dithiolene studied will be abbreviated $Ni[tfd]_2$.

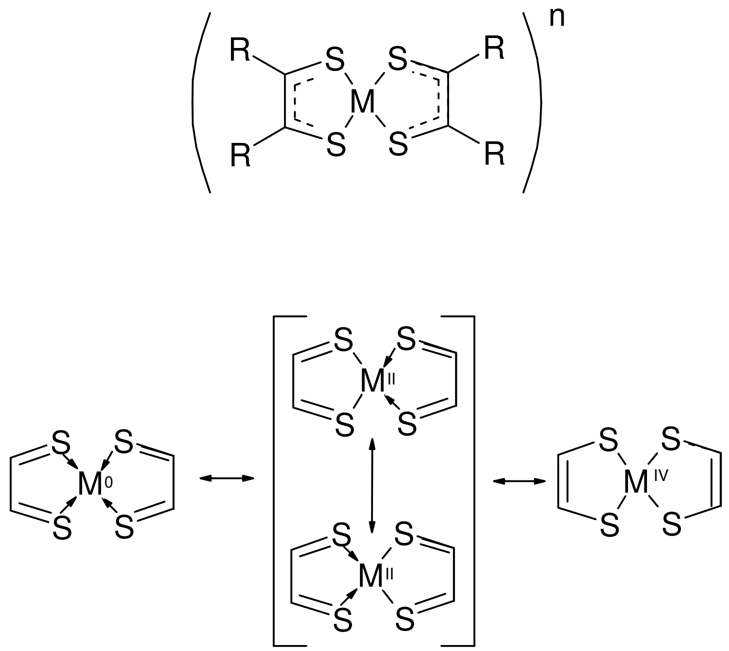


Figure 3.3 General structure of a bis-dithiolene and its resonance structures.

3.2 SAMPLE PREPARATION

Polyimide films were prepared by dissolving the polymer in methylene chloride and shaking (or rolling) the solution for at least an hour. The solution is then filtered through a 0.2 micron Teflon® syringe filter onto a circular Teflon® dish. Polyimide-dithiolene solutions were prepared by dissolving the appropriate amount of dithiolene with the polyimide in methylene chloride to form a dark purple solution. The films were cast in the same manner. Cast films were then dried in a vacuum oven at 110ºC for 12 or more hours.

Solutions of PCHE and Zeonex® were prepared similarly, but toluene was used as a solvent due to the insolubility of the polymers in methylene chloride. Also, films were cast in steel rings onto a glass plate. PCHE and Zeonex® were repelled by the Teflon®

surface and would not form a film. Instead, the polymers “beaded up.” Due to the low boiling point of toluene and the low degradation temperature of these polymers, the films were dried at 50ºC rather than 110℃.

3.3 PERMEATION

Gas permeabilities were measured using a constant volume method in a temperature controlled atmosphere. Gas is allowed to permeate through a membrane and then collected in a downstream ballast of known volume. The increase in pressure of the ballast is recorded and a permeability coefficient in Barrers, is calculated using eqn. 3.1

$$P_A = \frac{2.939x10^4 \bullet \left(\frac{dp}{dt}\right) \bullet V \bullet l}{T \bullet A \bullet \Delta p_A} \qquad (3.1)$$

For a given gas A, (dp/dt) in torr/min, is measured using a Baraton® transducer. The permeation rate is adjusted for leaks by subtracting out a measured leak rate. The volume, V in cm^3 is the volume of the downstream ballast and the driving force, Δp_A, is simply the upstream pressure (psia) since the downstream volume is originally under vacuum. The thickness (mils) is measured using a micrometer and the area (cm^2) is measured using the software package ScionImage®. The temperature (℃) is held constant. In addition to propylene and propane, oxygen, nitrogen, carbon dioxide, and methane permeabilities were also measured. The temperatures and upstream pressures ranged from 35-90℃ and 30-700 psia, respectively. Figure 3.4 shows a diagram of the permeation system.

A permeation cell is shown in Figure 3.5 and the masking technique used is shown in Figure 3.6. This masking technique was developed by Cathy Zimmerman and Zen Mogri, and discussed in detailed by Ryan Burns [1].

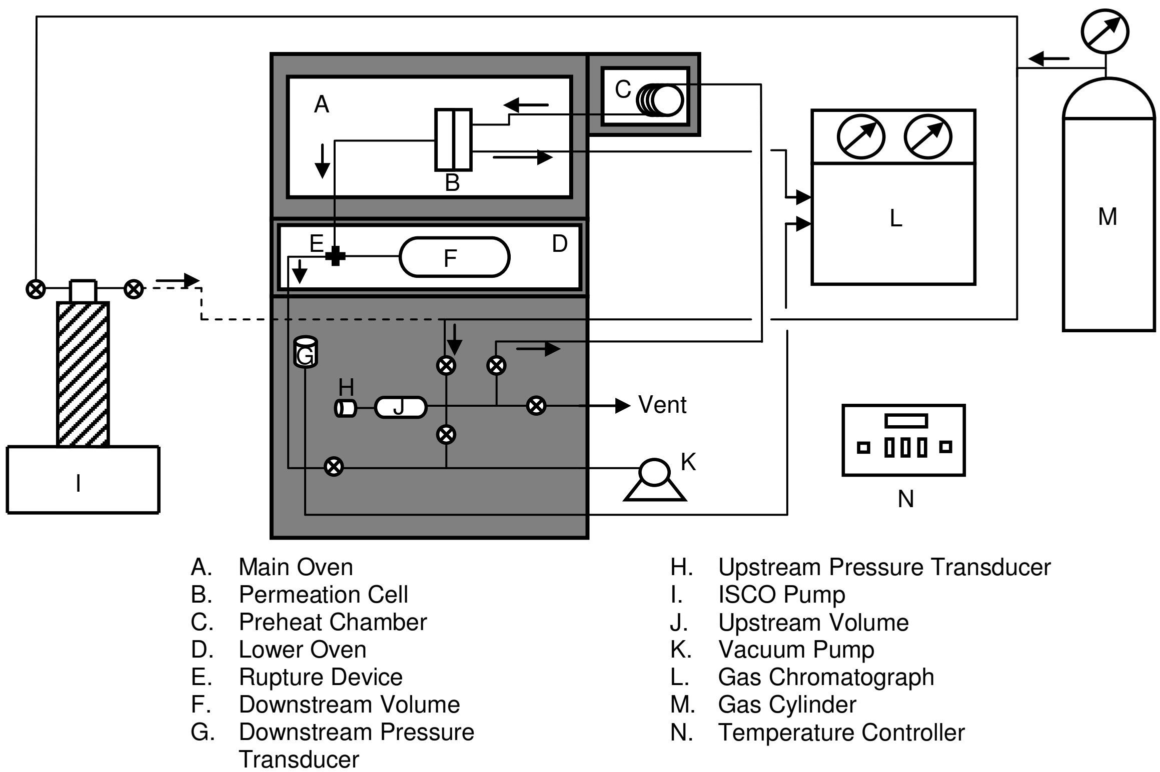


Figure 3.4. Diagram of the high temperature/pressure permeation system

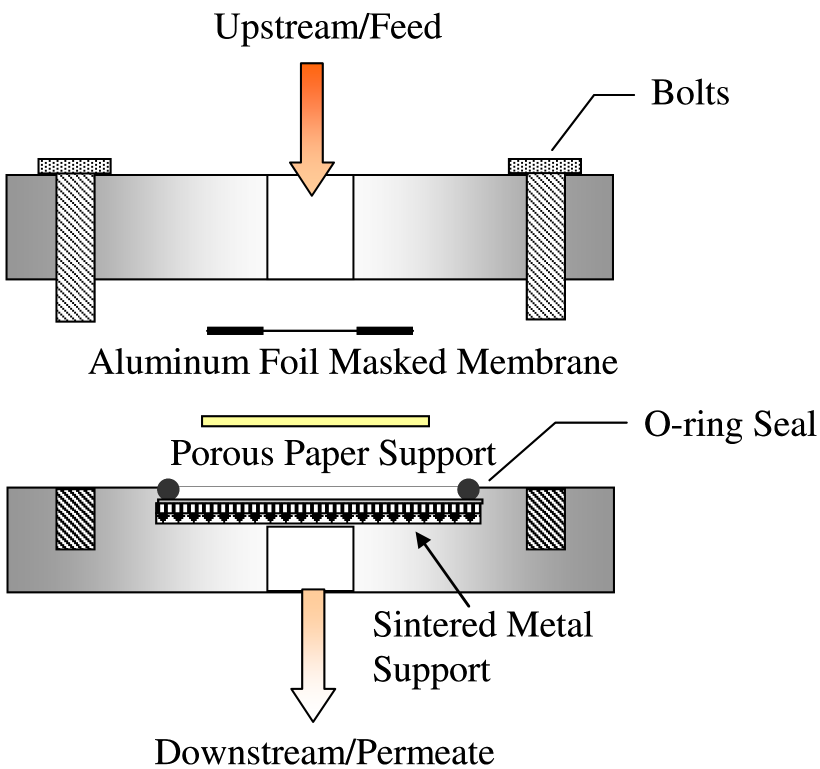


Figure 3.5. Permeation cell. Courtesy of Dr. Ryan Burns.

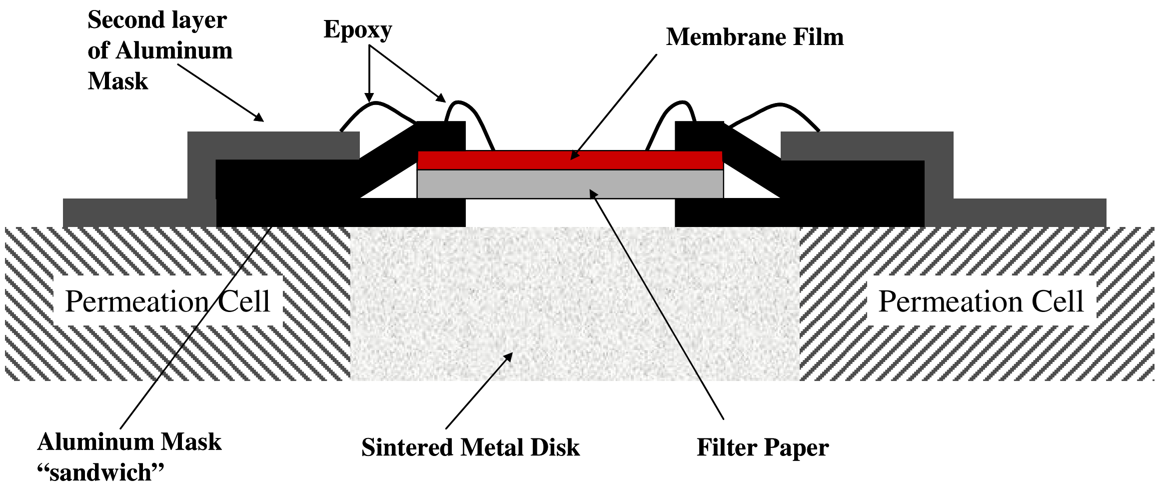


Figure 3.6. Masking technique for rigid materials. Courtesy of Dr. Ryan Burns.

3.4 SORPTION

Sorption is measured using a pressure decay method that has previously been described in detail [9, 10]. The procedure allows measurement of moles of gas sorbed by a polymer sample. The sorption experimental apparatus is shown in Figure 3.7. The apparatus consists of a reservoir and a cell. Both sit in a temperature controlled bath. Gas is introduced into the reservoir and the pressure is monitored using an AMETEK® transducer. Once the reservoir is allowed to reach thermal equilibrium with the bath, the control valve between the reservoir and the cell is opened briefly. The cell contains the polymer and the pressure drop in the cell is measured as the gas sorbs into the polymer film. Upon reaching equilibrium, a mole balance relating the pressure drop in the cell to the moles sorbed by the polymer is then conducted. The concentration of gas in the polymer can then be calculated.

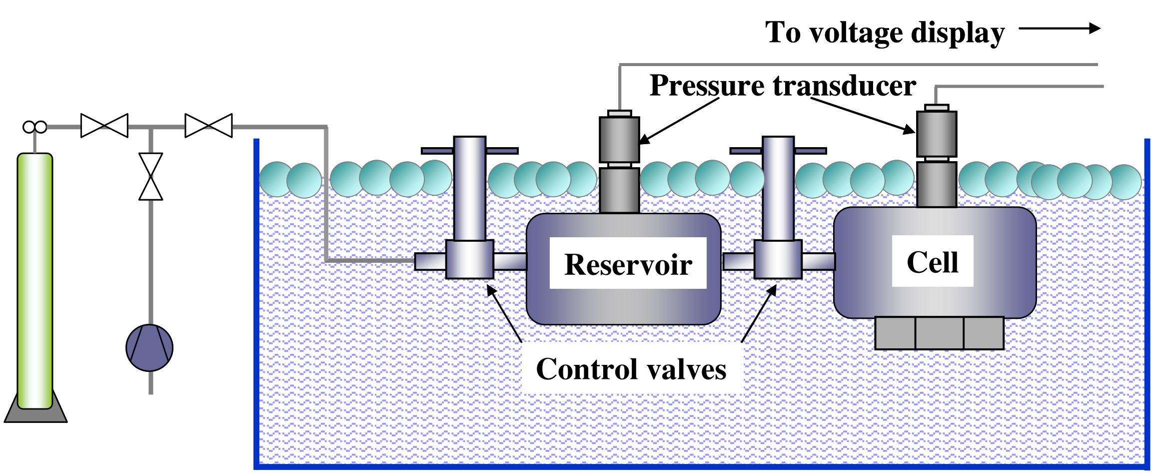


Figure 3.7. Sorption Apparatus. Courtesy of Ryan Burns

3.5 PHYSICAL PROPERTIES

3.5.1 Density

The densities of the polyimide films with and without dithiolene were measured using a TECHNE® density gradient column in a calcium nitrate solution. Glass beads of known density were submerged in the column along with the films. The positions were noted and a linear calibration curve was generated to determine the density of the films. The glass beads and films were allowed to float in the column for 12-24 hours before their respective heights were recorded.

The reported densities of PCHE and Zeonex® are 0.94 and 1.01, respectively, so a calcium nitrate solution was not suitable. Thus, the densities of PCHE and Zeonex® films were measured using a similar technique to that employed by Zimmerman using mixtures of diethylene chloride and isopropanol [11]. The films floated in diethylene glycol ($\rho = 1.114$ g/cm^3) and sank in isopropanol ($\rho = 0.785$ g/cm^3). A film was placed in a bottle then filled with a known amount of diethylene chloride. Isopropanol was incrementally added. The solution was shaken to ensure proper mixing and the volumes at which the films floated were noted. Similarly, diethylene chloride was added to a beaker of isopropanol until the film began to sink.

3.5.2 DSC Measurements

Differential Scanning Calorimetry (DSC) measurements were conducted on a TA Instruments DSC Q100. The heat rate was 10℃/min. Polyimide films were heated to 400℃ and the cycloolefins to 200℃.

3.5.3 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was employed to measure the T_g, sub-T_g, and modulus of the polymer films. DMA works by supplying an oscillatory force to a polymer sample, causing a sinusoidal stress to be applied. If the sample stays within its elastic limits it responds in a sinusoidal strain. Measuring the amplitude of this response and the phase lag between the stress and strain waves allows the calculation of the modulus and viscosity of the sample as well as other properties [12].
Experiments were conducted at a heating rate of 5°C/min and a frequency of 1Hz on a Rheometrics RSA III dynamic mechanical analyzer. These experiments were run by Sudhakar Jagannathan of the Dr. Kumar's lab in PTFE.

3.5.4 Solid-State Infrared Spectroscopy

Infrared spectroscopy was used to further investigate if polymer-dithiolene interactions were occurring between the polyimide backbone and the dithiolene, $Ni[tfd]_2$. Films were prepared as outlined above and the IR spectra measured on a Bruker IFS 66 V/S spectrometer in transmission mode under a N_2 purge. Use of this instrument was provided by Dr. Christopher Jones' research group.

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CHAPTER 4

C_3H_6/C_3H_8 TRANSPORT IN POLYIMIDE MEMBRANES

4.1. INTRODUCTION

As has been discussed in chapters 2 and 3, the polyimides 6FDA-6FpDA and 6FDA-DAM were blended with the dithiolene, $Ni[S_2C_2(CF_3)_2]_2$ to investigate C_3H_6/C_3H_8 membrane separation. Wang and Stiefel indicated that light olefins reversibly complex with $Ni[tfd]_2$ and may be suitable for industrial olefin separation practices since they are not poisoned by components in refinery streams [1]. These two polyimides were selected as the base resins, since they had relatively attractive intrinsic permeabilities and selectivities, as a starting point. This work by Wang and Stiefel is the basis for incorporating $Ni[tfd]_2$ in a polymeric membrane to serve as a complexing moiety which enhances solubility selectivity [2, 3].

4.2 PERMEABILITY AND PERMSELECTIVITY

The C_3H_6/C_3H_8 permeation results of the two polyimides 6FDA-6FpDA and 6FDA-DAM blended with 10 weight percent of $Ni[tfd]_2$ are listed in Table 4.1. The addition of the dithiolene *significantly* reduced the permeability of both propylene and propane and there was no apparent enhancement in selectivity within the experimental uncertainty. While a reduction in propylene permeability is not a desired result, it is further intriguing that a similar reduction in propane permeability is observed. Such an effect would not be anticipated as a result of adding a component that simply increased the relative solubility selectivity of propylene versus propane. The observed phenomenon suggests that unforeseen interactions may be occurring between the dithiolene and propane and/or the polymer membrane.

Preliminary work by Burns suggested that the dithiolene only affected propylene permeability [3]; however, this early work was not as extensive as the current study. Burns reported a 70% decrease in the permeability of propylene in 6FDA-6FpDA

Table 4.1. Permeability Coefficients and Permselectivities of 6FDA-6FpDA and 6FDA-DAM at 35°C and 2atm

Polymer	P_{C3H6} [a]	P_{C3H8} [a]	P_{C3H6}/P_{C3H8}
6FDA-6FpDA	0.92	0.06	16.4
6FDA-DAM	25.7	2.1	12.0
6FDA-6FpDA / Ni[tfd]2 -10%	0.16	0.01	16.1
6FDA-DAM / NI[tfd]2 - 10%	6.13	0.51	12.0

[a] Barrers [=] 1 Barrer = $1x10^{-10} \frac{cc(STP)cm}{cm^2\, s\, cmHg}$

containing 11 wt% of $Ni[tfd]_2$ compared to the pure polymer, which is on the same order of magnitude as seen in the current study (~ 82%). On the other hand, in this earlier study, the permselectivity decreased by the same amount due to that fact that there was no decrease in the propane permeability. It was believed that this was due to the attraction between the dithiolene and the olefin and was described as a so-called "sticky diffusion" phenomenon by which propylene is sorbed strongly by interactions with the dithiolene and not readily released. That phenomenon <u>was not observed</u> in this study as shown in Table 4.1. In my work, propylene and propane permeability is suppressed to a similar extent so the permselectivity of 6FDA-6FpDA does not drop significantly, but rather, there is little or no change.

It is important to note, that the majority of this work was conducted with a different batch of dithiolene than used by Burns. Due to limited quantities of the previous batch, Tom Richmond and Joel Miller of the University of Utah, Department of Chemistry, kindly synthesized a new batch of dithiolene for use. As reported in literature, the dithiolene powder was a deep dark purple [4]. The dithiolene sample used by Burns was instead dark green. Davison et al [4] reported that solutions of $Ni[tfd]_2$ with basics solvents were brown-green so it was speculated that overexposure to air moisture may have caused the difference in color since this batch was several years old. Nonetheless, experiments with both batches of dithiolene had similar results. For these reasons, the work presented here only include experiments using the second batch of $Ni[tfd]_2$. Comparisons between experiments containing the two batches of dithiolene can be found in Appendix A.

Experiments with 6FDA-6FpDA were also repeated with another polyimide, 6FDA-DAM. The reasons for doing so were two-fold. 6FDA-DAM possesses a higher fractional free volume (FFV) than 6FDA-6FpDA so its gas permeability is higher (Table 4.2). Since the addition of dithiolene caused significant decrease in the permeability of the polymer, a polymer with high permeability would have an acceptable flux for practical application. Secondly, 6FDA-DAM was used to determine if the effects were transferable. Even so, similar results were observed in this second polymer as well. As noted above, the decrease in propane permeability was unexpected as no interaction between propane should occur. Also as, discussed in Chapter 2, the dithiolene operates via the same π-complex mechanism that governs silver-based facilitated transport and thus was not expected to interact with propane. These surprising results led us to investigate the causes of reduced propylene and propane permeation in the polyimide films to try to discover a strategy to overcome them.

Table 4.2. Polyimide Properties

Polymer	T_g (℃)	FFV
6FDA-6FpDA	320	0.186
6FDA-DAM	377	0.188

The reduction in permeability was first addressed by increasing the temperature and feed pressure, since it was expected that the strength of any specific penetrant-sorbate interactions would be reduced relative to the average thermal motion motivating diffusion. The pressure dependent permeability of 6FDA-6FpDA and 6FDA-DAM are shown below (Figures 4.1- 4.4).

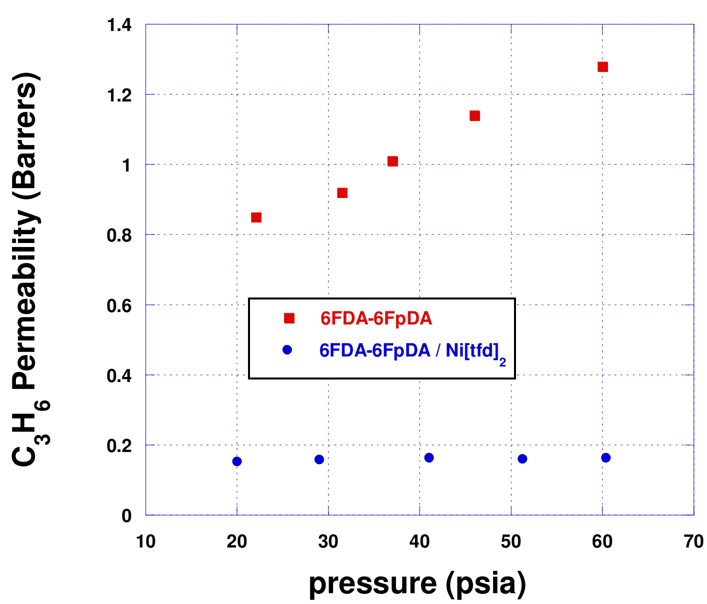


Figure 4.1. Pressure dependent C_3H_6 permeability in 6FDA-6FpDA.

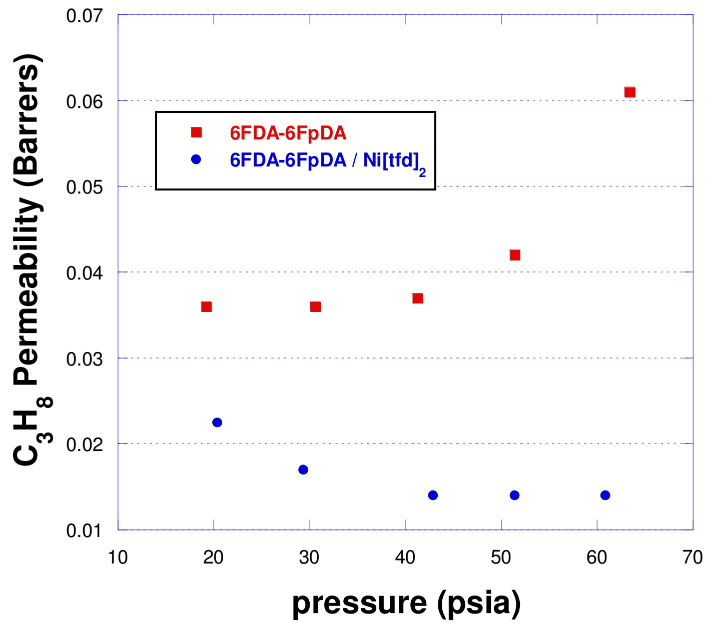


Figure 4.2. Pressure dependent C_3H_8 permeability in 6FDA-6FpDA

There is significant upturn in the propylene permeability isotherm for 6FDA-6FpDA at about 2 atm. Staudt-Bickel observed an upturn after reaching roughly 4 atm [5], but others in the same lab have also observed plasticization at 2 atm. There is a plasticization response for propane in 6FDA-6FpDA as well. High sorbing gases such as propane and propylene are known to cause plasticization in polyimide films, and Tanaka reported plasticization at 5 atm for both propylene and propane at 50℃, in 6FDA-DAM [6]. This effect is expected in 6FDA-DAM material, since sorption levels are higher than in 6FDA-6FpDA [3, 6, 7]. Burns measured the pressure dependence of 6FDA-DAM at 75℃ between 20 and 100 psia but observed no plasticization [3]. Due to reduced sorption at higher temperatures it is expected that plasticization effects would be reduced, which explains the difference in plasticization pressures.

The importance of figures 4.1- 4.4 is primarily in the permeability response of polyimide films containing $Ni[tfd]_2$. The permeability of propylene and propane was reduced with the addition of the dithiolene in both polyimides at all pressures and *the plasticization response is suppressed*. Again, the reduction in propane permeability suggests that the idea of "sticky diffusion" in the case of propylene is not applicable. As discussed, the observations of Burns are still not understood, and since the same batch of dithiolene used in this study was also used in some of the preliminary studies in this work, the results are truly perplexing. Again, comparisons between the batches will be discussed in Appendix A.

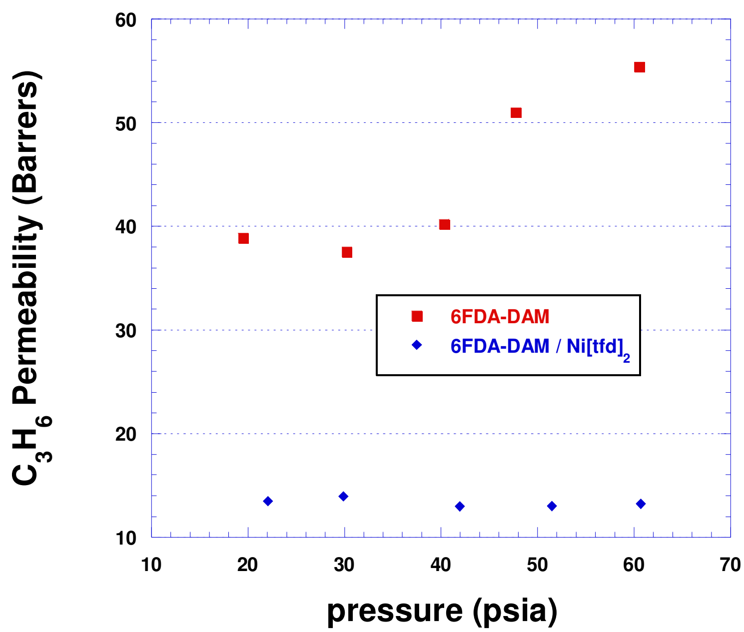


Figure 4.3. Pressure dependent C_3H_6 permeability in 6FDA-DAM

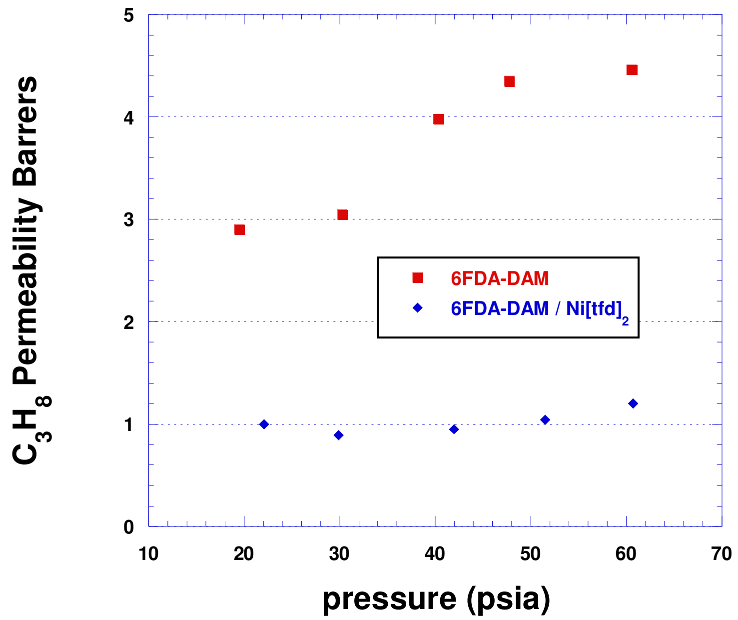


Figure 4.4. Pressure dependent C_3H_8 permeability in 6FDA-DAM

The results found in this study tend to support an antiplasticization response rather than traditional "facilitated transport." Antiplasticization has been investigated in depth by Maeda and Paul [8-11] in the context of O_2/N_2, CO_2/CH_4, and He/CH_4 systems. As discussed in Chapter 2, antiplasticization is characterized by a reduction in the permeability of gases in a polymer and an increase in the "plasticization pressure," at which the permeability shows an upward inflection. Maeda and Paul reported a reduction in poly(phenylene oxide) (PPO) and polysulfone (PSF) permeability to CO_2 with increasing amounts of low molecular diluents. Diluents such as tricresyl phosphate (TCP) and Kronitex 50 were mixed with PPO, and at 10% loading CO_2 permeability at 35°C decreased by about 65% [8-11].

Although, the reduction in permeability observed in the 6FDA-based polyimides of this work was not desired, it is not uncommon when additives are mixed with polymers. Literature regarding olefin/paraffin separation via facilitated transport [12-25] suggest that similar results have been observed even though they were not identified by the researchers as such. Yang and Hsiue incorporated silver ion into silicon rubber grafted copolymer but reported reduced permeability and selectivity in C_4 olefin/paraffin gas pairs [26]. Morisato developed solid polymer electrolytes based on PA12-PTMO containing silver tetrafluroborate ($AgBF_4$) [21]. The membranes also exhibited reduced permeability of both ethylene and ethane with increasing concentration of $AgBF_4$. In those cases, however, an actual permselectivity increase was observed.

Hess *et al.* produced crosslinked copolyimides membranes based on 6FDA containing silver ions for propylene/propane separations [13]. Benzoic acid was used as a monomer to provide a crosslinkable group and 15-crown-5-ether diamine added facilitated transport sites. The membranes were then impregnated with the silver salts $AgBF_4$ and $AgNO_3$. The silver ions complexed with the crown ether by bonding within its cavity. The resulting membrane was considered "dry" because it required no carrier medium. Mixed gas permeation experiments were conducted at 35℃ with different types of pure copolyimide membranes and those containing the silver ions. For all types of membranes, the total permeability dropped when the silver salts were incorporated. In one case, the permeability dropped from 4 Barrers to 0.5 and was attributed to a loss in free volume. In this case, there was, in fact, an improvement in the selectivity, but after 24 hours the selectivity was shown to decrease. For an ethylene glycol crosslinked membrane containing silver ions, the selectivity decreased to that of the pure polymer. Hess *et al.* believed this was due to chemical reduction of the silver ions. The authors did not indicate what the reducing agent may be.

In many cases it is apparent that incorporating silver or other diluents into polymers tends to reduce the free volume causing a reduction in the permeability. If the intended purpose is to create facilitated transport, analysis of the solubility would provide further insight into the level at which facilitation is indeed occurring. Presently, in can be inferred that facilitation does not occur since there is no enhancement in the permselectivity in neither 6FDA-6FpDA nor 6FpDA-DAM. The following section discusses the effects of the dithiolene on the solubility and solubility selectivity of the polyimides to further explore the effects seen in permselectivity.

4.3 SORPTION ISOTHERMS AND SOLUBILITY SELECTIVITY

Pure gas C_3H_6/C_3H_8 sorption experiments were conducted using the pressure decay method described in Chapter 3. The data was then fit to the dual mode sorption model. Table 4.3 lists the sorption coefficients and solubility selectivities of pure polyimide films and films containing 10% $Ni[tfd]_2$ at 35°C. It is apparent that there is a decrease in the sorption coefficients, but an increase in the solubility selectivity is observed. For 6FDA-6FpDA addition of $Ni[tfd]_2$ reduced propylene sorption by approximately 15% and propane sorption by over 60%. The result is a 45% increase in the sorption selectivity suggesting that the dithiolene, although reducing the amount sorbed, has preferentially sorbed more propylene than propane.

Table 4.3. Sorption coefficients and solubility selectivities of 6FDA-6FpDA and 6FDA-DAM at 35℃ and 2atm

Membrane	S_{C3H6}	S_{C3H8}	S_{C3H6}/S_{C3H8}
6FDA-6FpDA	0.94	0.84	1.12
6FDA-6FpDA/ Ni[tfd]$_2$	0.82	0.50	1.63
6FDA-DAM	1.69	1.37	1.23
6FDA-DAM / Ni[tfd]$_2$	1.47	1.15	1.28

S [=] cc(STP) / cc polymer - psia

The sorption isotherms of 6FDA-6FpDA and 6FDA-DAM are shown in figures 4.5-4.8. For both polyimides, the addition of Ni[tfd]$_2$, reduces sorption of both propylene and propane at all pressures up to 60 psia. Reductions in sorption levels by additives was first reported by Maeda and Paul [8, 9]. In both polysulfone and poly(phenylene oxide) (PPO), carbon dioxide sorption was decreased with increasing amounts of tricresyl phosphate and other diluents.

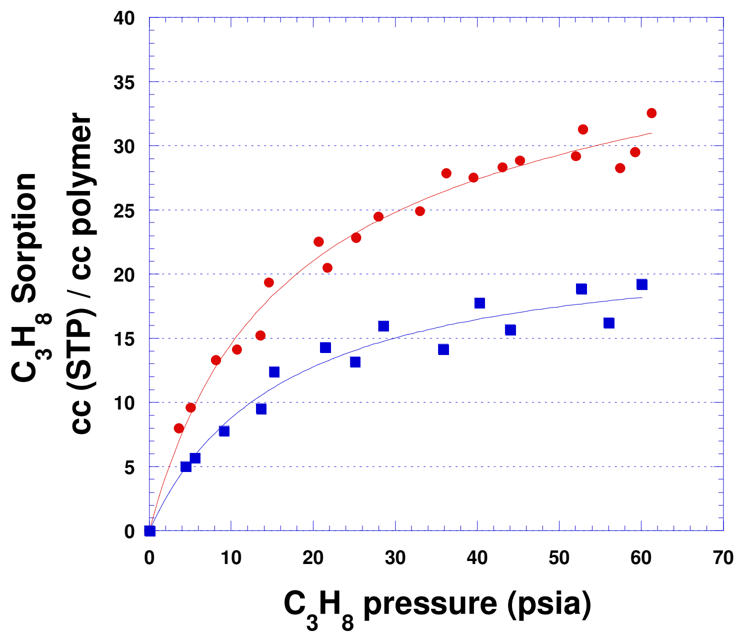


Figure 4.5 C_3H_8 sorption isotherms at 35℃. ● 6FDA-6FpDA; ■ 6FDA-6FpDA/Ni[tfd]$_2$

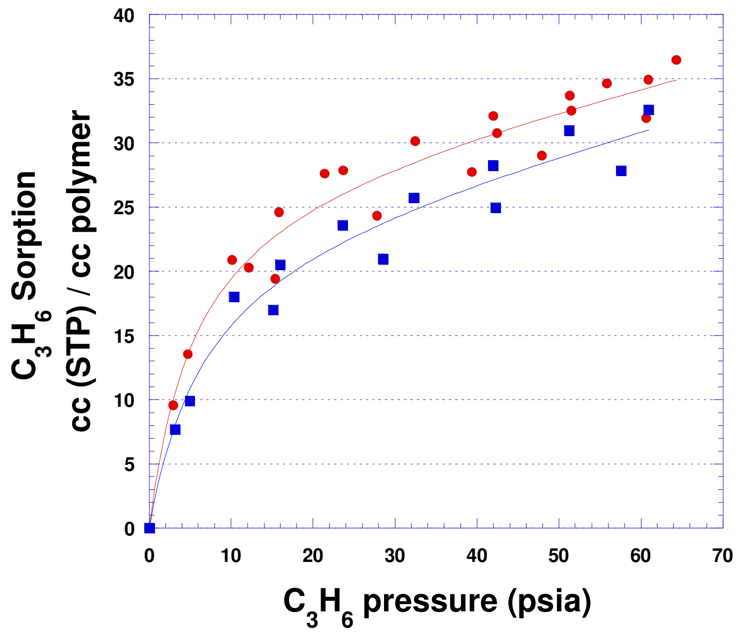


Figure 4.6 C_3H_6 sorption isotherms at 35℃. ● 6FDA-6FpDA; ■ 6FDA-6FpDA/Ni[tfd]$_2$

Loracca and Pessan later observed similar results in polyetherimide (Ultem® 1000) containing crystalline additives [27]. It was hypothesized that reduced sorption is indicative of antiplasticization as the additives reduce the free volume of the host polymer. It is apparent that a similar response is observed in these polyimide samples. Propane sorption in 6FDA-6FpDA is most greatly reduced. This may be due to less available sorption sites due to the presence of the dithiolene. Although propylene sorption is also affected by the reduced number of sorption sites, the dithiolene's preferential affinity for propylene allows for less of a reduction in the amount sorbed.

Comparatively, addition of dithiolene affects 6FDA-6FpDA more so than 6FDA-DAM. The solubility is not affected equally although there is roughly an 80% reduction in permeability in both 6FDA-based polyimides. It appears the effects of the dithiolene are not completely transferable. As previously mentioned, 6FDA-DAM was chosen because, in spite of the permeation-reducing property of the dithiolene, it would still possess a relatively high permeability. Shimazu et al. has attributed increased permeability in 6FDA-DAM over 6FDA-6FpDA to an increase in FFV, albeit a small change [7, 28]. 6FpDA-6FDA contains two additional -CF_3 which are bulkier than the –CH_3 groups of 6FDA-DAM so higher FFV is expected.

In addition to a higher FFV, increased stiffness as evidenced by a higher T_g, is suggested as reason for increases in permeability and in the dual mode sorption parameters [7, 28]. Shimizu cites theory by Hensema suggesting that a flexible polymer tends to have an efficiently packed polymer matrix which can limit segmental motion, while a rigid, but packing-disrupted polymer may have a large free volume. This large free volume can enable high diffusion coefficients, despite the chain rigidity (29). Hensema explains that polymer flexibility is not the only criterion for increased permeability as evidenced by polymers with high glass transition temperatures having higher permeabilities than those with lower glass transition temperatures; as in the case here. Instead, in the glassy state below T_g, segmental motion is significantly reduced compared to the rubbery state. According to Koros and Chern gas transport occurs through a series jumps within the "holes" (Langmuir) and "dissolved" (Henry) regions of the polymer matrix [30]. Thus a gas molecule must "find its way" from within these regions to allow transport through minor segmental motion [29]. The ease at which this occurs depends on the concentrations of holes and accessibility of dissolved regions. Conceivably, polymers with a large free volume would allow easy accommodation of gas molecules within the extra room available. This can increase sorption levels while still allowing for the small scale volume perturbations needed to accommodate movement of said molecule. In the case of an efficiently packed polymer, the space needed to open is hindered and both sorption and diffusion is hindered.

Tables 4.4 and 4.5 list the C_3H_6/C_3H_8 dual mode parameters for the 6FDA-6FpDA and 6FDA-DAM. In addition to reduced sorption levels, Maeda and Larocco observed reduction in the dual mode Langmuir capacity coefficient (C'_H) [8-10, 27] with addition of additives polysulfalone and PPO. Koros and Hellums have shown that C'_H is related to the free volume of a glassy polymer and thus reductions in C'_H are caused by a reduction in the free volume of the polymer [31]. There is a decrease in C'_H for propylene and propane with the addition of Ni[tfd]$_2$ in both polymers. Preliminary studies by Burns also showed a decrease in C'_H with the addition of the dithiolene.

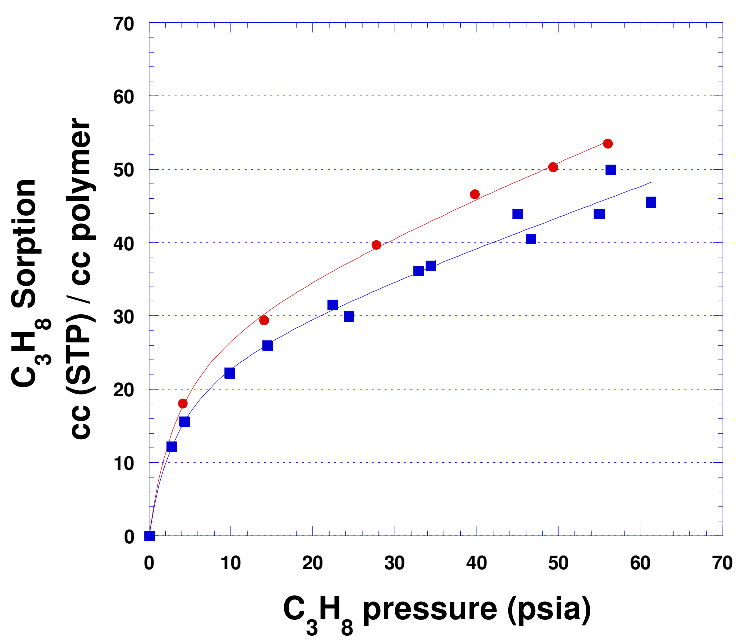


Figure 4.7 C_3H_8 sorption isotherms at 35°C. ● 6FDA-DAM; ■ 6FDA-DAM/Ni[tfd]$_2$

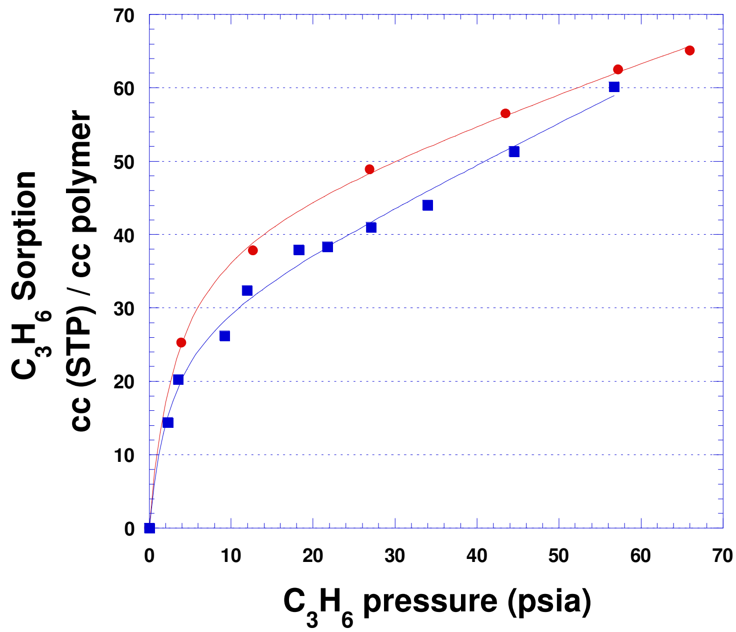


Figure 4.8 C_3H_6 sorption isotherms at 35℃. ● 6FDA-DAM; ■ 6FDA-DAM/Ni[tfd]$_2$

This understanding of gas transport could aid in explaining the differing effects of the dithiolene on gas transport in 6FDA-6FpDA and 6FDA-DAM. I believe that the overall effect of the dithiolene is antiplasticization which impedes segmental motion and slows the permeation of gas molecules through a polymer membrane. The apparent reduction of the free volume does not seem to greatly influence solubility in 6FDA-DAM although there is a significant change in the permeability. Based on the above theory for gas transport, the inefficient packing of 6FDA-6FpDA should aid in enhancing its permeability, but instead it is significantly lower than 6FDA-DAM. Since the difference in FFV is rather small, the presence of the –CF_3 groups plays the largest role in determining gas transport in 6FDA-6FpDA, and perhaps the distribution of free volume as well as its total amount contributes to the effective diffusion coefficients in the two different matrices. In comparison, 6FDA-6pDA has a limited amount of “space” for gas transport, so the presence of less bulky side groups in 6FDA-DAM can "afford" the space-filling behavior of Ni[tfd]$_2$ more readily.

Table 4.4. Dual Mode Parameters for 6FDA-6FpDA at 35°C

Membrane	**Gas**	**k_D[a]**	**C'_H[b]**	**b[c]**
6FDA-6FpDA	C_3H_6	0.14 ± 0.05	27.9 ± 3.9	0.18 ± 0.06
6FDA-6FpDA / Ni[tfd]$_2$	C_3H_6	0.16 ± 0.08	23.9 ± 5.5	0.15 ± 0.07
6FDA-6FpDA	C_3H_8	0.04 ± 0.07	35.1 ± 6.8	0.07 ± 0.02
6FDA-6FpDA / Ni[tfd]2	C_3H_8	-0.01 ± 0.10	23.7 ± 9.5	0.06 ± 0.03

[a]cc (STP) / cc polymer -psia [b]cc (STP) / cc polymer [c]psia^{-1}

Table 4.4 shows that Henry's constant, k_D, is negative for propane in this 6FDA-6FpDA. Although, that doesn't make physical sense, the error calculated by the least squares fit would allow a low positive or effectively zero value of k_D, thereby suggesting that sorption is primarily occurring in the Langmuir mode in this case. The affinity constant, b, in 6FDA-6FpDA shows little effect within experimental error, but there are marked changes of these parameters in 6FDA-DAM. There is an increase in the affinity constant of propylene in the pure polymer compared to 6FDA-DAM/Ni[tfd]$_2$. There is no increase in the affinity constant of propane suggesting that the dithiolene has increased the affinity of the polymer for propylene as expected. Additionally, there is an increase in k_D for propylene and a decrease for propane. It can be interpretated that dithiolene moieties dispersed in the dissolved and "macrovoid" (holes) region are in fact interacting to increase propylene sorption by serving as complexation sites, but reducing the available sites for propane to sorb and retarding segmental motion.

Table 4.5. Dual Mode Parameters for 6FDA-DAM at 35°C

Membrane	Gas	k_D [a]	C'_H [b]	b [c]
6FDA-DAM	C_3H_6	0.38 ± 0.03	42.7 ± 1.9	0.31 ± 0.04
6FDA-DAM/ Ni[tfd]$_2$	C_3H_6	0.54 ± 0.05	29.6 ± 2.4	0.40 ± 0.10
6FDA-DAM	C_3H_8	0.46 ± 0.04	30.2 ± 2.3	0.27 ± 0.05
6FDA-DAM / Ni[tfd]$_2$	C_3H_8	0.39 ± 0.06	25.6 ± 3.4	0.27 ± 0.10

[a] cc (STP) / cc polymer -psia   [b] cc (STP) / cc polymer   [c] $psia^{-1}$

The sorption selectivity of 6FDA-6pDA is shown in Figure 4.9. The selectivity of the dithiolene containing film is over 30% higher than the pure film.

The observed upturn in the sorption selectivity of 6FDA-6FpDA/Ni[tfd]$_2$ is due to the flattening of its propane isotherm at high pressures shown in Figure 4.5. Enhancement of C_3H_6/C_3H_8 sorption selectivity in 6FDA-DAM is also observed but is not as significant as in 6FDA-6FpDA, but becomes larger as the pressure is increased (Figure 4.8). Further examination of Figures 4.7 and 4.8 indicate that sorption of propylene and propane is affected relatively equally in 6FDA-DAM with the addition of dithiolene, initially. As pressure increases, propane sorption in the 6FDA-DAM/Ni[tfd]$_2$ deviates more from that of the pure film. Whereas, propylene sorption in 6FDA-DAM/Ni[tfd]$_2$ begins to approach the levels of pure 6FDA-DAM. The increase in the C_3H_6 affinity constant, b, allows for a maintained increase in solubility selectivity in 6FDA-DAM/Ni[tfd]$_2$.

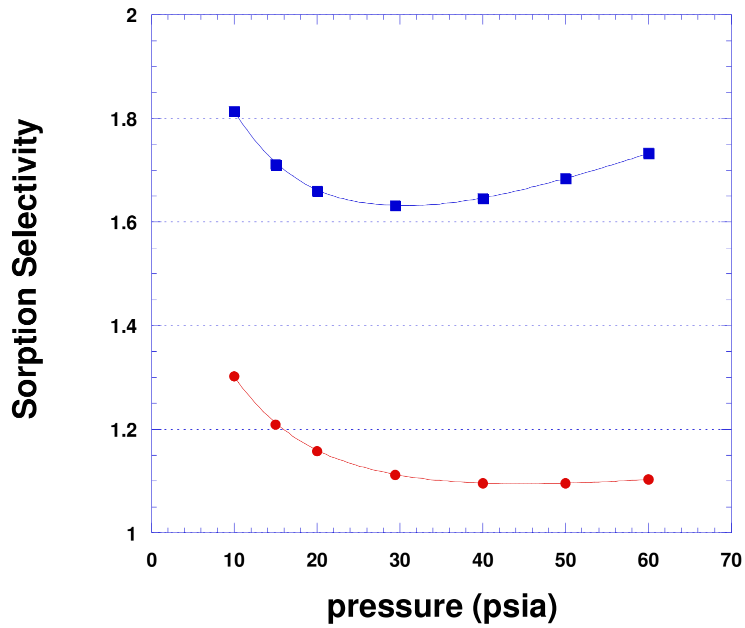


Figure 4.9 C_3H_6/C_3H_8 solubility selectivity at 35ºC. ● 6FDA-6FpDA; ■ 6FDA-6FpDA/Ni[tfd]$_2$

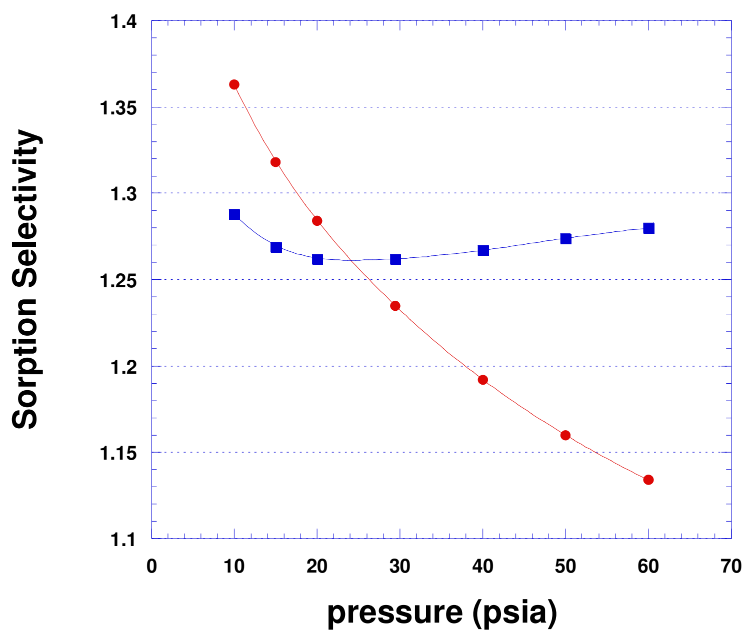


Figure 4.10 C_3H_6/C_3H_8 solubility selectivity at 35ºC. ● 6FDA-DAM; ■ 6FDA-DAM/Ni[tfd]$_2$

4.4 TEMPERATURE DEPENDENT TRANSPORT

The temperature dependence of propylene/propane transport was investigated to better understand the effects of Ni[tfd]$_2$. Permeation and sorption measurements were made from 35℃ to 90℃. In some cases, 75℃ was the highest temperature. As discussed in Section 4.2, increasing the temperature was expected to overcome penetrant-sorbate interactions through increased thermal energy. In figures 4.11 and 4.12 are the temperature dependent permeation and the corresponding Arrhenius plot, respectively for 6FDA-6FpDA. As expected, permeability of both propane and propylene increases with increasing temperature and follows a classical linear Arrhenius relationship in both pure and dithiolene films. Increasing the temperature does not increase the permeability of either propylene or propane in the dithiolene films to the level of the pure films.

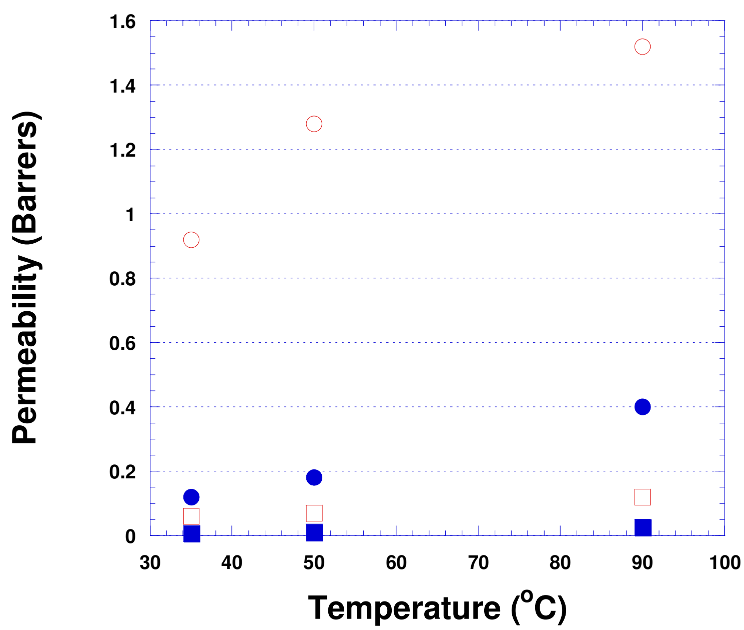


Figure 4.11. Temperature dependant permeation for 6FDA-6FpDA. ○C_3H_6 in 6FDA-6FpDA; □C_3H_8 in 6FDA-6FpDA; ● C_3H_6 in 6FDA-6FpDA/Ni[tfd]$_2$; ■ C_3H_8 in 6FDA-6FpDA/Ni[tfd]$_2$

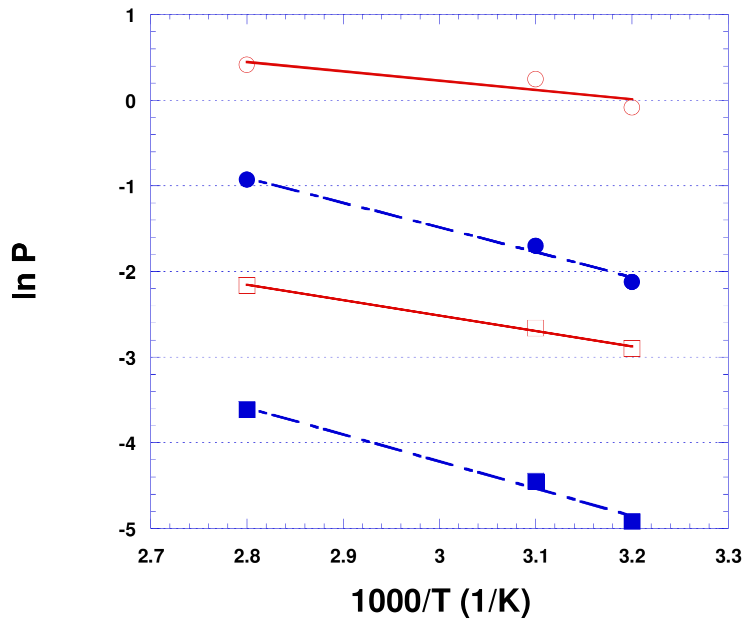


Figure 4.12. Arrhenius plots for 6FDA-6FpDA. ○C_3H_6 in 6FDA-6FpDA; □C_3H_8 in 6FDA-6FpDA; ● C_3H_6 in 6FDA-6FpDA/Ni[tfd]$_2$; ■ C_3H_8 in 6FDA-6FpDA/Ni[tfd]$_2$

Table 4.6. Activation energies and pre-exponential factors for 6FDA-6FpDA

Membrane	Gas	E_p kcal/mol	P_o (Barrers)	E_d kcal/mol	D_o (cm^2/s)
6FDA-6FpDA	C_3H_6	2.2	33	6.5	1.7×10^{-5}
6FDA-6FpDA / Ni[tfd]$_2$	C_3H_6	5.7	1300	10.5	168×10^{-5}
6FDA-6FpDA	C_3H_8	3.6	18	8.4	2.5×10^{-5}
6FDA-6FpDA / Ni[tfd]$_2$	C_3H_8	6.3	185	10.3	11×10^{-5}

The activation energies for permeation and diffusion are shown in Table 4.6. For 6FDA-6FpDA, the activation energy for diffusion, E_d, which is usually dependent on the penetrant size and shape of the polymer, increases for both propylene and propane in the presence of the dithiolene. Similarly, the activation energy for permeation, E_p increases indicating that a significant change occurs to the polymer matrix with the addition of the dithiolene. Since E_p is the sum of the activation energies for diffusion, E_d, and the heat of sorption, H_s, this result indicates that thermodynamic changes as well diffusional mobility changes occur. Both E_d and D_o increase which results in a significant reduction in the apparent diffusion coefficient of both components.

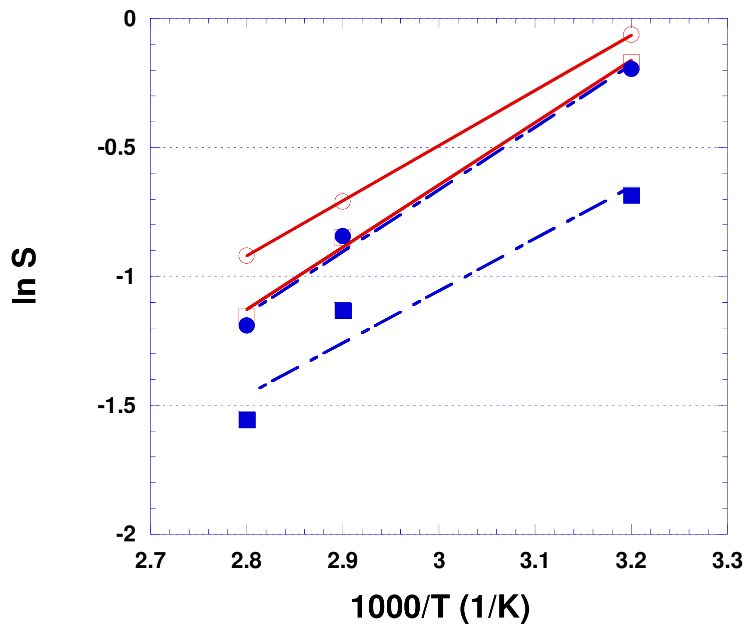


Figure 4.13. van't Hoff plot for 6FDA-6FpDA. ○C_3H_6 in 6FDA-6FpDA; □C_3H_8 in 6FDA-6FpDA; ● C_3H_6 in 6FDA-6FpDA/Ni[tfd]$_2$; ■ C_3H_8 in 6FDA-6FpDA/Ni[tfd]$_2$

The van't Hoff plot for C_3H_6/C_3H_8 sorption in 6FDA-6FpDA is shown in Figure 4.13. Table 4.7 shows the heats of sorption and pre-exponential factors. Intriguingly, the heat of sorption for propylene in 6FDA-6FpDA/Ni[tfd]$_2$ is a larger negative than the pure film, but that is not the case for propane. The sorption of gaseous penetrants into a polymer matrix is associated with a negative average enthalpy and hence high sorbing penetrants show a larger negative contribution [32, 33]. The trends, which show a more negative sorption enthalpy for propylene and a less negative sorption enthalpy for propane in the presence of Ni[tfd]$_2$ is consistent with some complexation occurring between Ni[tfd]$_2$ and propylene, and not propane.

Table 4.7. Heats of sorption and pre-exponential factors for 6FDA-6FpDA

Membrane	Gas	H_s (kcal/mol)	S_o ($cm^3(STP)/cm^3$-psia)
6FDA-6FpDA	C_3H_6	-4.3	10×10^{-4}
6FDA-6FpDA / $Ni[tfd]_2$	C_3H_6	-4.7	4.0×10^{-4}
6FDA-6FpDA	C_3H_8	-4.8	3.7×10^{-4}
6FDA-6FpDA / $Ni[tfd]_2$	C_3H_8	-4.0	8.5×10^{-4}

Temperature dependant permeation and Arrhenius plots for 6FDA-DAM are shown in Figure 4.14. Compared to 6FDA-6FpDA, the effect of temperature is small for 6FDA-DAM, but still follows a classic linear Arrhenius relationship. Again, the effect of $Ni[tfd]_2$ on 6FDA-DAM is different from that of 6FDA-6FpDA. The activation energy for permeation of both propylene and propane increases with the addition of dithiolene. Also, the activation energy for diffusion increases for *both* gases, but the heat of sorption of propylene becomes a larger negative with the addition of $Ni[tfd]_2$, indicating a greater affinity in the dithiolene film.

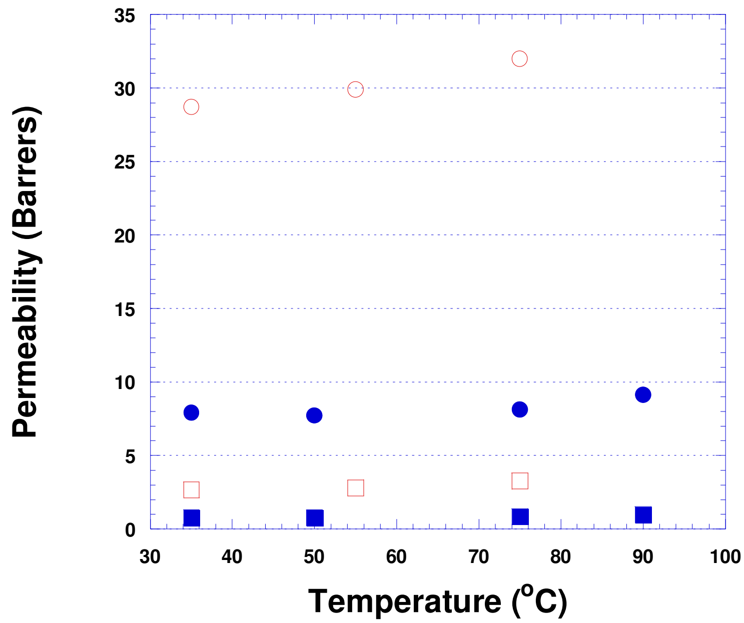


Figure 4.14. Temperature dependant permeation for 6FDA-DAM. ○C_3H_6 in 6FDA-DAM; □C_3H_8 in 6FDA-DAM; ● C_3H_6 in 6FDA-6DAM/Ni[tfd]$_2$; ■ C_3H_8 in 6FDA-DAM/Ni[tfd]$_2$. 6FDA-DAM plots adapted from data reported by Ryan Burns.

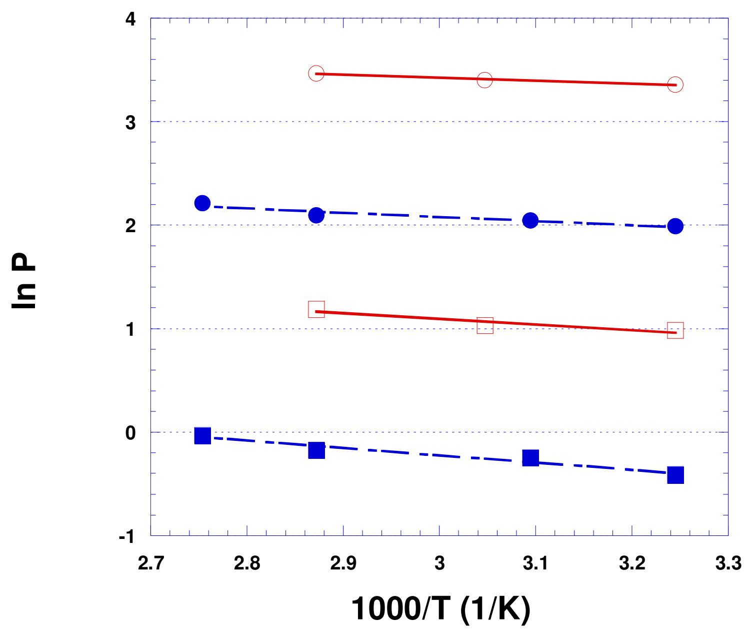


Figure 4.15. Arrhenius plot for 6FDA-DAM. ○C_3H_6 in 6FDA-DAM; □C_3H_8 in 6FDA-DAM; ● C_3H_6 in 6FDA-6DAM/Ni[tfd]$_2$; ■ C_3H_8 in 6FDA-DAM/Ni[tfd]$_2$. 6FDA-DAM plots adapted from data reported by Ryan Burns.

Table 4.8. Activation energies and pre-exponential factors for 6FDA-DAM

Membrane	Gas	E_p kcal/mol	P_o (Barrers)	E_d kcal/mol	D_o (cm^2/s)
6FDA-DAM	C_3H_6	0.6	73	3.6	3.0×10^{-6}
6FDA-DAM / Ni[tfd]$_2$	C_3H_6	0.8	27	4.2	2.5×10^{-6}
6FDA-DAM	C_3H_8	1.1	15	4.5	1.3×10^{-6}
6FDA-DAM / Ni[tfd]$_2$	C_3H_8	1.4	6.7	6.3	8.5×10^{-6}

Also, the activation energy for diffusion increases for *both* gases, but the heats of sorption of both gases become a larger negative with the addition of Ni[tfd]$_2$ indicating a greater affinity of penetrants in the dithiolene film. The effect on the activation energy of diffusion indicates a hindrance of gas mobility which supports an antiplasticization response.

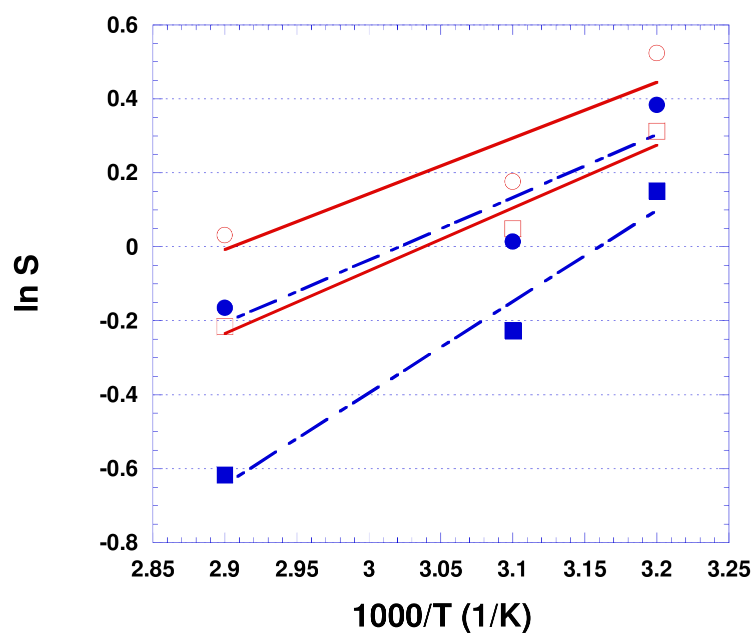


Figure 4.16. van't Hoff plot for 6FDA-DAM. ○C_3H_6 in 6FDA-6FDAM; □C_3H_8 in 6FDA-6FDAM; ● C_3H_6 in 6FDA-6FDAM/Ni[tfd]$_2$; ■ C_3H_8 in 6FDA-6FDAM/Ni[tfd]$_2$

Table 4.9. Heats of sorption and pre-exponential factors for 6FDA-DAM

Membrane	**Gas**	**H_s (kcal/mol)**	**S_o ($cm^3(STP)/cm^3$-psia)**
6FDA-DAM	C_3H_6	-3.0	125×10^{-4}
6FDA-DAM / $Ni[tfd]_2$	C_3H_6	-3.4	57×10^{-4}
6FDA-DAM	C_3H_8	-3.4	60×10^{-4}
6FDA-DAM / $Ni[tfd]_2$	C_3H_8	-4.9	4.1×10^{-4}

Below in Figures 4.17 to 4.20 are the sorption isotherms at varying temperature for 6FDA-6FpDA and 6FDA-DAM. As expected, the level of sorption decreases with increasing temperature. Temperature affects 6FDA-6FpDA most strongly as a 40-50% drop in sorption is seen in all cases. It is perhaps more important to analyze the changes in the dual mode parameters and the overall effect of the dithiolene of sorption selectivity. Tables 4.10 and 4.11 show the dual mode parameters of 6FDA-6FpDA and 6FDA-6FpDA/$Ni[tfd]_2$. Each parameter decreases with increasing temperature and the error in measuring C'_H is largest of the three parameters.

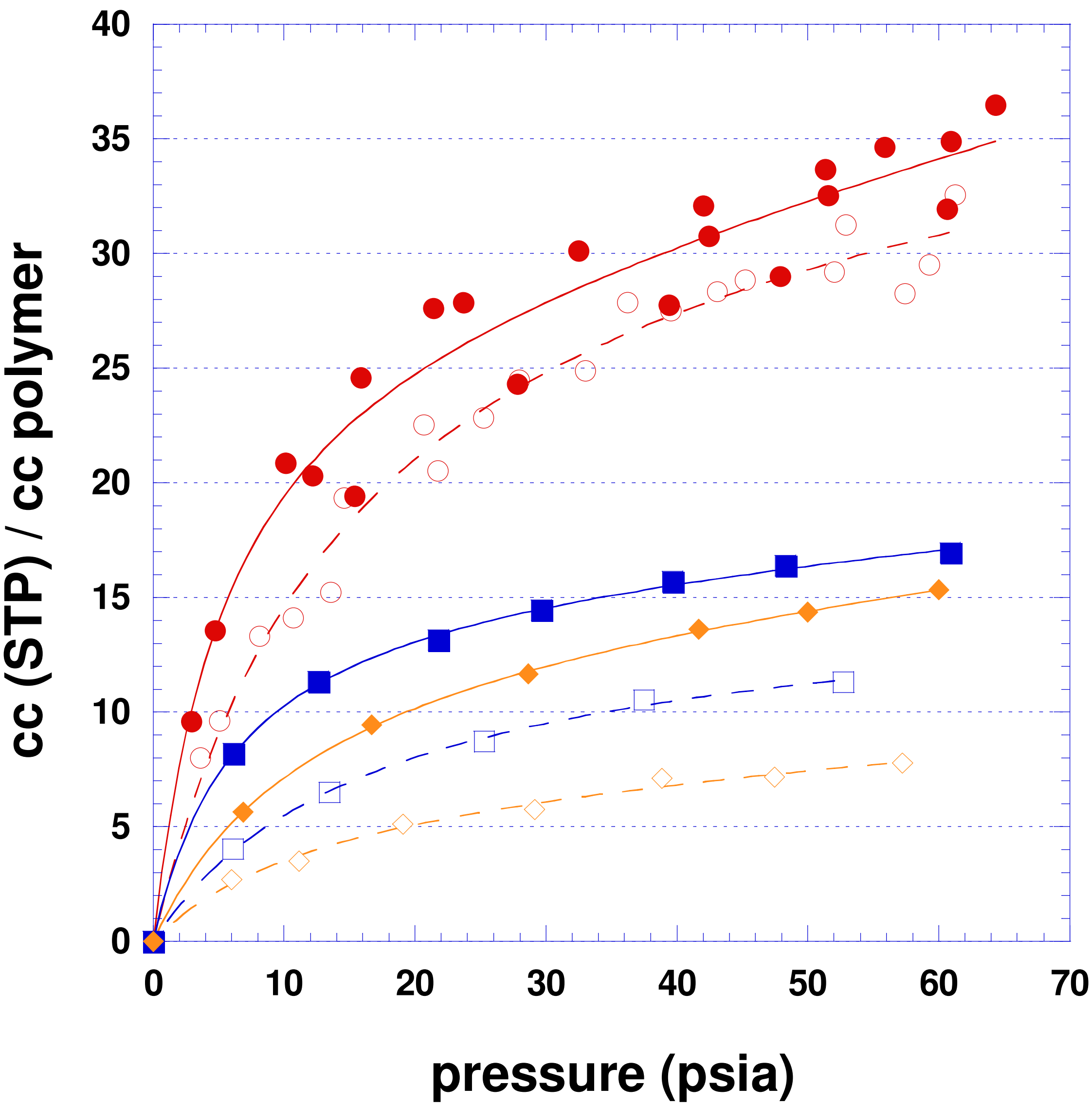


Figure 4.17. Sorption Isotherms for 6FDA-6FpDA.
C_3H_6 (solid symbols) C_3H_8 (open symbols). 35ºC (●,○), 75ºC (■,□), 90ºC (♦,◊).

Table 4.10. Temperature Dependent Dual Mode Parameters for 6FDA-6FpDA

	35°C		75°C		90°C	
	C_3H_6	C_3H_8	C_3H_6	C_3H_8	C_3H_6	C_3H_8
k_D	0.14 ± 0.05	0.04 ± 0.07	0.04 ± 0.01	0.06 ± 0.04	0.05 ± 0.01	0.06 ± 0.03
C'_H	27.9 ± 3.9	35.1 ± 6.8	16.1 ± 0.75	15.5 ± 3.5	14.6 ± 0.7	10.4 ± 2.2
b	0.18 ± 0.06	0.07 ± 0.02	0.16 ± 0.02	0.08 ± 0.03	0.08 ± 0.01	0.08 ± 0.03

[a] cc (STP) / cc polymer -psia [b] cc (STP) / cc polymer [c] $psia^{-1}$

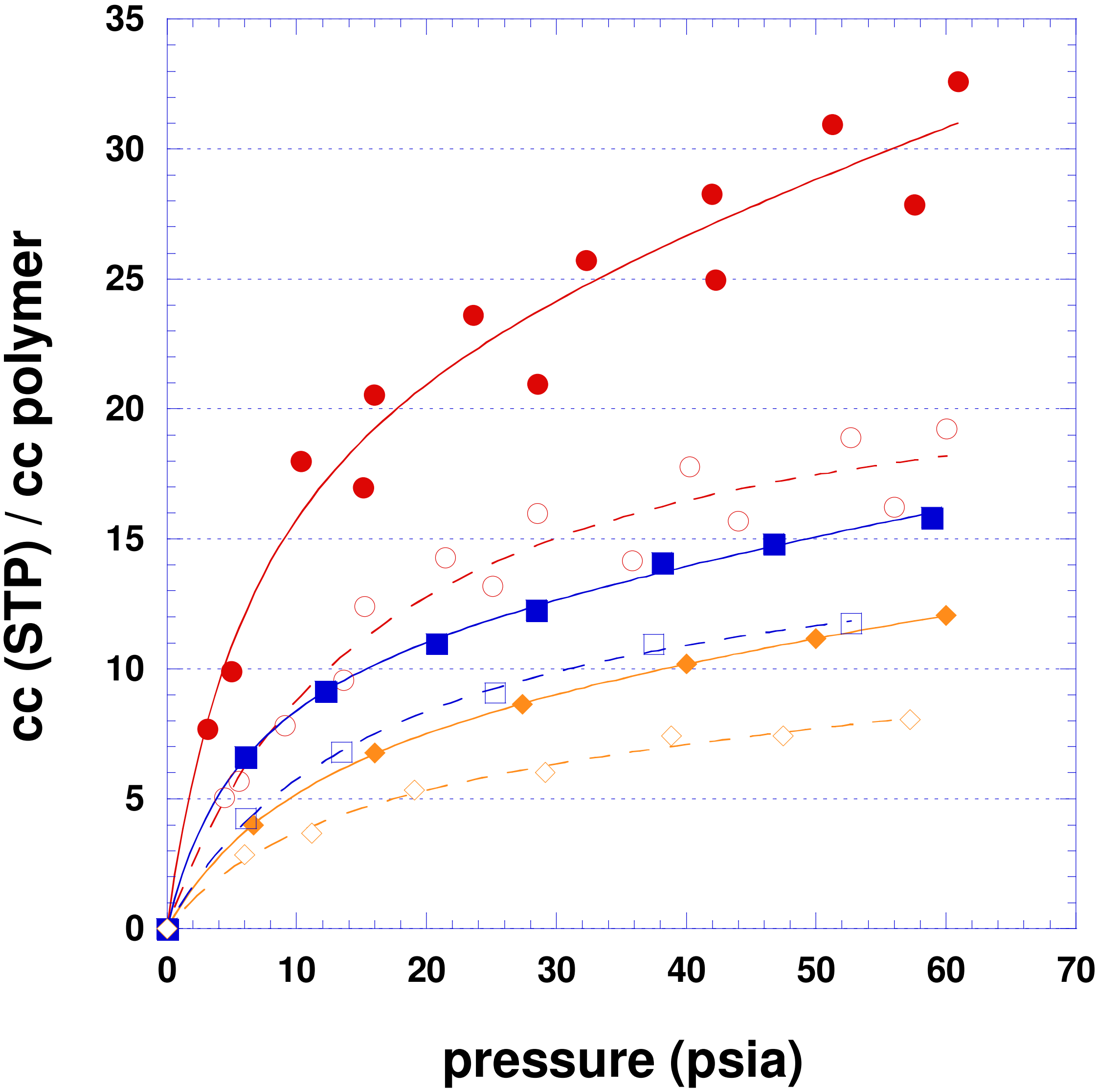


Figure 4.18. Sorption Isotherms for 6FDA-6FpDA/Ni[tfd]$_2$.
C_3H_6 (solid symbols) C_3H_8 (open symbols). 35ºC (●,○), 75ºC (■,□), 90ºC (♦,◊).

Table 4.11. Temperature Dependent Dual Mode Parameters for 6FDA-6FpDA/Ni[tfd]$_2$

	35°C		75°C		90°C	
	C_3H_6	C_3H_8	C_3H_6	C_3H_8	C_3H_6	C_3H_8
k_D	0.16 ± 0.08	-0.01 ± 0.10	0.09 ± 0.01	0.01 ± 0.03	0.06 ± 0.00	0.03 ± 0.03
C'_H	23.9 ± 5.5	23.7 ± 9.5	12.1 ± 0.9	14.4 ± 2.7	10.0 ± 0.2	7.6 ± 2.3
b	0.15 ± 0.07	0.06 ± 0.03	0.2 ± 0.03	0.06 ± 0.02	0.08 ± 0.00	0.08 ± 0.04

[a]cc (STP) / cc polymer -psia [b]cc (STP) / cc polymer [c]psia^{-1}

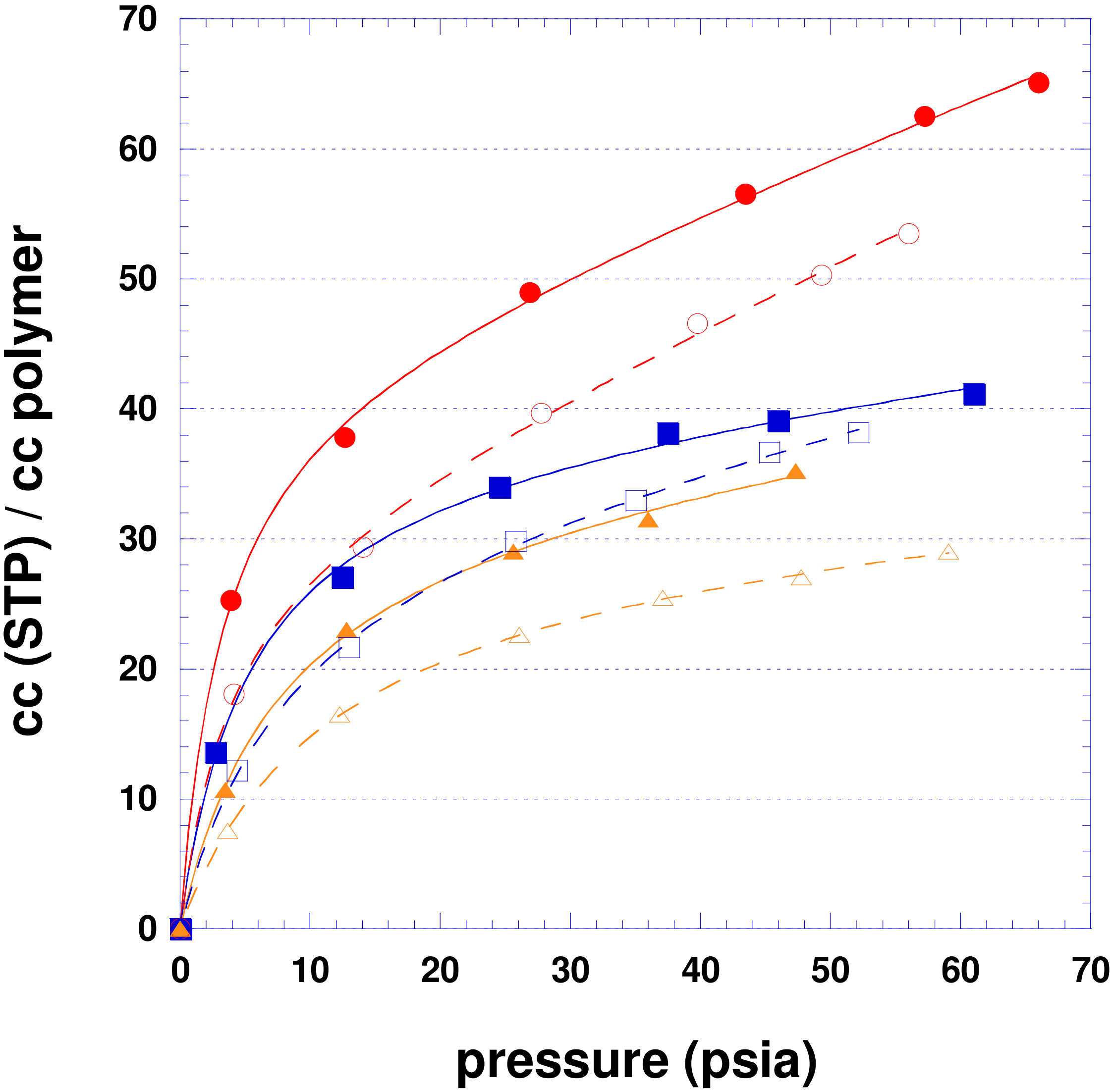


Figure 4.19. Sorption Isotherms for 6FDA-DAM.
C_3H_6 (solid symbols) C_3H_8 (open symbols). 35ºC (●,○), 75ºC (■,□), 90ºC (♦,◊).

Table 4.12. Temperature Dependent Dual Mode Parameters for 6FDA-DAM

	35°C		**50°C**		**75°C**	
	C_3H_6	C_3H_8	C_3H_6	C_3H_8	C_3H_6	C_3H_8
k_D	0.38 ± 0.03	0.46 ± 0.04	0.11 ± 0.04	0.21 ± 0.03	0.13 ± 0.05	0.07 ± 0.01
C'_H	42.7 ± 1.9	30.2 ± 2.3	37.5 ± 2.4	31.7 ± 2.3	33.0 ± 3.2	29.8 ± 1.1
b	0.31 ± 0.04	0.27 ± 0.05	0.19 ± 0.03	0.12 ± 0.02	0.14 ± 0.04	0.09 ± 0.01

[a]cc (STP) / cc polymer -psia [b]cc (STP) / cc polymer [c]$psia^{-1}$

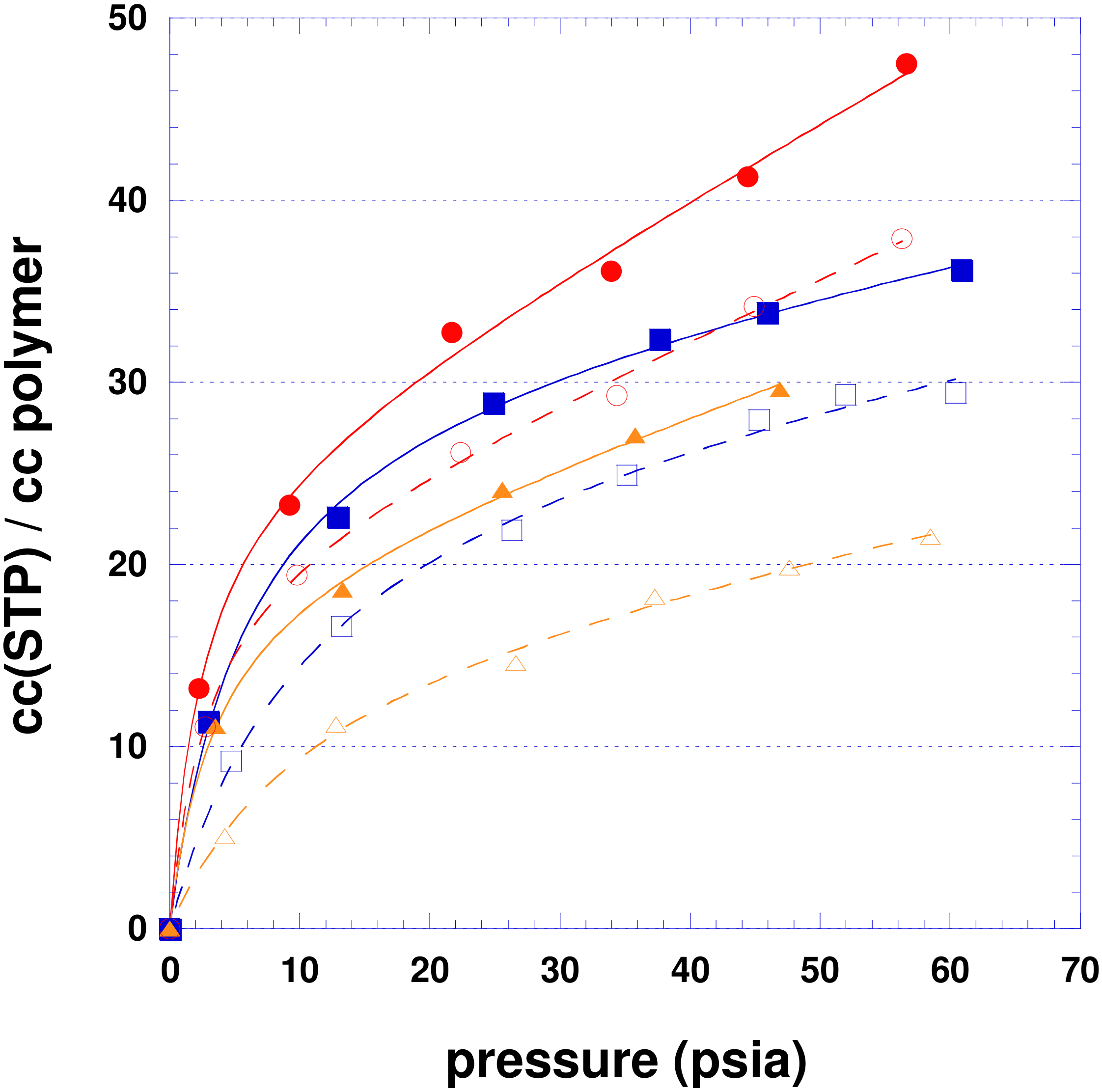


Figure 4.20. Sorption Isotherms for 6FDA-DAM/Ni[tfd]$_2$.
C_3H_6 (solid symbols) C_3H_8 (open symbols). 35ºC (●,○), 75ºC (■,□), 90ºC (♦,◊).

Table 4.13. Temperature Dependent Dual Mode Parameters for 6FDA-DAM/Ni[tfd]$_2$

	35°C		**50°C**		**75°C**	
	C_3H_6	C_3H_8	C_3H_6	C_3H_8	C_3H_6	C_3H_8
k_D	0.54 ± 0.05	0.39 ± 0.06	0.12 ± 0.05	0.12 ± 0.05	0.24 ± 0.03	0.13 ± 0.04
C'_H	29.6 ± 2.4	25.6 ± 4.1	31.2 ± 1.7	26.7 ± 3.8	19.9 ± 1.4	16.6 ± 3.5
b	0.40 ± 0.10	0.27 ± 0.10	0.17 ± 0.02	0.10 ± 0.02	0.30 ± 0.05	0.09 ± 0.03

[a]cc (STP) / cc polymer -psia [b]cc (STP) / cc polymer [c]psia^{-1}

At this time, I introduce an enhancement factor, ξ, to elucidate more clearly the increase in solubility selectivity.

$$\alpha_{C_3H_6/C_3H_8} = \frac{D^0_{C_3H_6}}{D^0_{C_3H_8}} \cdot \left(\frac{S^0_{C_3H_6}}{S^0_{C_3H_8}} \bullet \xi \right) = \left(\frac{P^0_{C_3H_6}}{P^0_{C_3H_8}} \right) \bullet \xi \qquad (4.1)$$

$$\xi = \frac{\alpha_s^{dit+pol}}{\alpha_S^0} = enhancement\ \ factor \qquad (4.2)$$

The enhancement factor is simply the ratio of the selectivity of the dithiolene film divided by the selectivity of the pure film. In theory, by enhancing the solubility selectivity, in turn, the overall selectivity is also increased barring any changes in the mobility selectivity. In this instance, the enhancement factor only refers to increases in solubility selectivity and is shown in Figure 4.21 for 6FDA-6FpDA and 4.22 for 6FDA-DAM. In 6FDA-6FpDA, with increasing temperature, the enhancement factor decreases, but increases with pressure. The enhancement due to the dithiolene has diminished in 6FDA-6FpDA, but not in 6FDA-DAM. Based solely on the 6FDA-6FpDA it would appear that the dithiolene may have been deactivated by temperature, but the results with 6FDA-DAM counter this hypothesis.

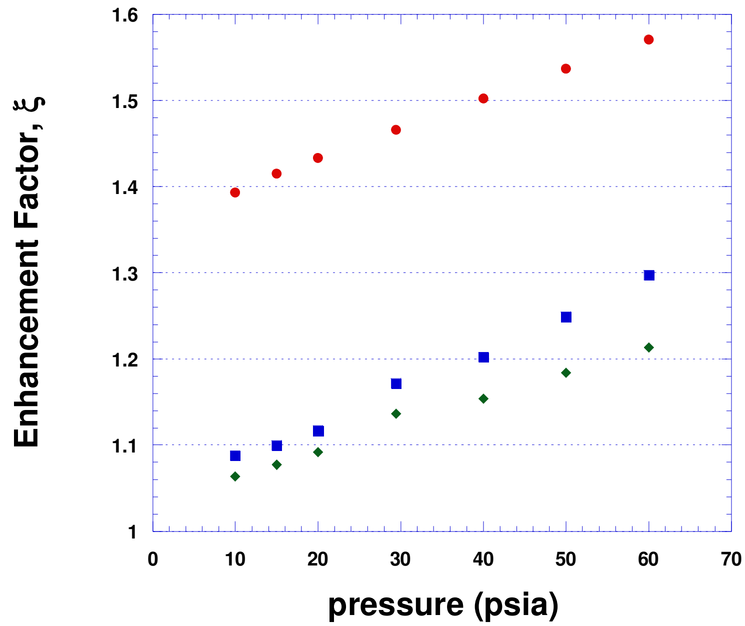


Figure 4.21. Enhancement factor of 6FDA-6FpDA/Ni[tfd]$_2$ to 6FDA-6FpDA. ●35°C ■75°C ♦90°C.

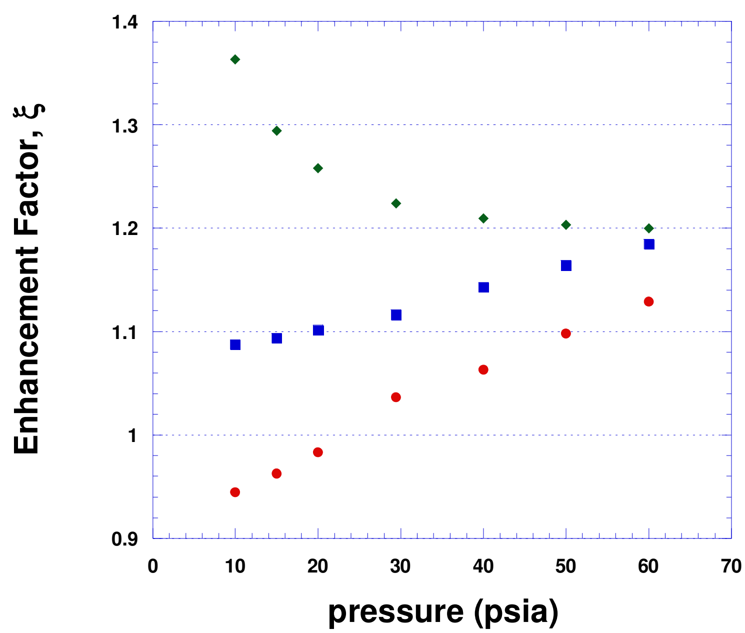


Figure 4.22. Enhancement factor of 6FDA-DAM/Ni[tfd]$_2$ to 6FDA-DAM. ●35°C ■50°C ♦75°C.

4.5 THE EFFECT OF DITHIOLENE CONCENTRATION AND POSSIBLE POLYMER-DITHIOLENE INTERACTIONS

The differing responses of these two polyimides lead to the hypothesis that specific polymer-complexer interactions are a key in developing suitable facilitated transport membranes. In preliminary studies, Ryan Burns attempted to blend $Ni[tfd]_2$ with Matrimid®, a commercial polyimide. He observed that the dithiolene and Matrimid were not sufficiently miscible as the dithiolene would leach out along the edges of the polymer [3]. He then chose 6FDA-6FpDA as a better candidate with the belief that the presence of more $–CF_3$ groups would increase solubility of the dithiolene in the polymer. The work by Burns is noted because Ryu and Kim have stated that the polymer choice with an appropriate functional group would be an important factor in determining the performance of a particular membrane [12, 25, 34, 35]. They studied three interactions within the realm of facilitated olefin transport using silver ions: silver salt/polymer, silver salt/olefin, olefin/silver/salt polymer interactions. The polymer/silver salt system studied was dry cellulose acetate (CA) complexed with $AgBF_4$. Investigation of IR spectra of the $AgBF_4$/CA system indicated that carbonyl groups coordinated with the silver ions and the degree of shift of the carbonyl absorption group increased with increasing molar ratio of $AgBF_4$/CA. It is believe then that at a higher molar ratio of $AgBF_4$/CA, carbonyl groups have more chances to interact with silver ions.

In an attempt to further investigate the effect of dithiolene concentration on transport properties, the weight percent of $Ni[tfd]_2$ was increased over 10%. Unfortunately, 10-20% was the solubility limit of dithiolene in the polyimide as brittle membranes with visible crystals were formed with dithiolene content over 20%. Figure

4.23 is a photograph of a 6FDA-6FpDA film containing 25% dithiolene. The crystals are evident. This film and others like it were not suitable for testing because they would break at pressures as low as 30 psi. On the other hand, SEM photographs of a 6FDA-6FpDA film with 10% dithiolene showed a homogeneous film (Figure 4.24).

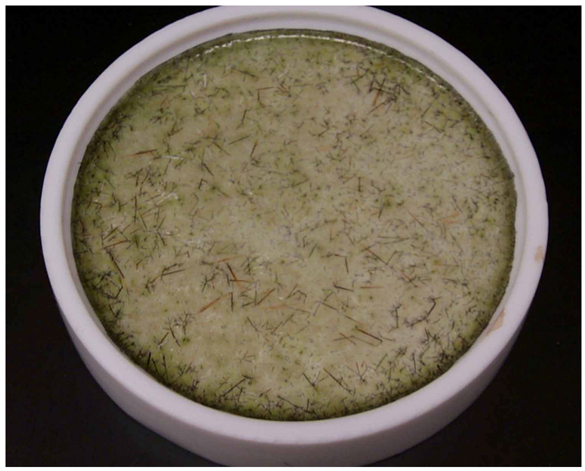


Figure 4.23. Photograph of 6FDA-6pDA film with 25% Ni[tfd]$_2$.

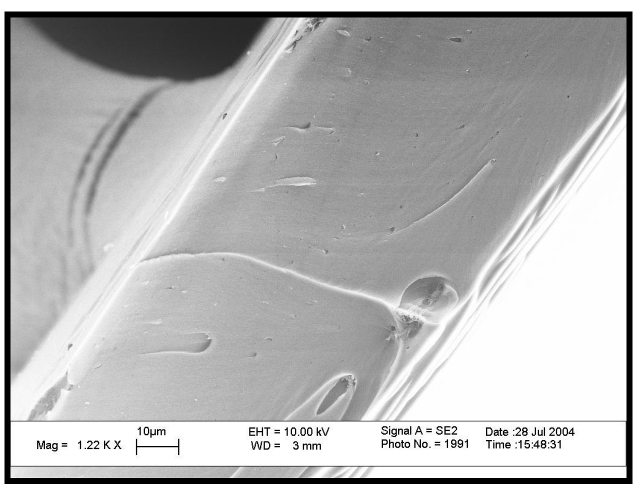


Figure 4.24. SEM photograph of 6FDA-6FpDA film with 10% Ni[tfd]$_2$

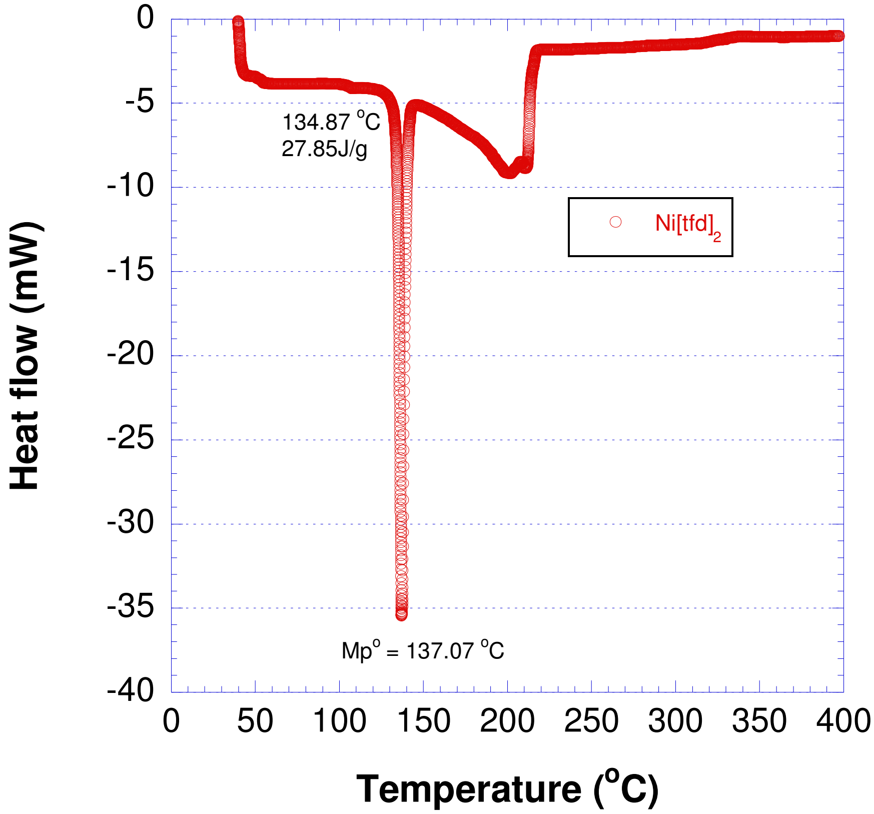
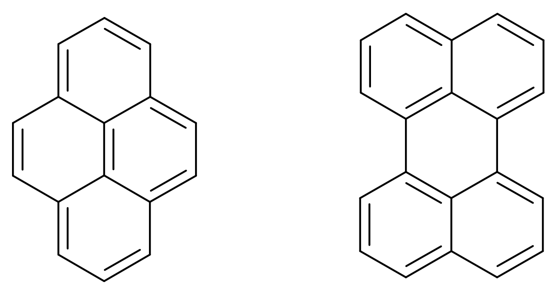


Figure 4.25. DSC plot of pure $Ni[tfd]_2$.

In addition to SEM photograph, the melting point of the pure dithiolene was also measured (Figure 4.25). By noting the melting point peak, we would be able to determine crystallinity in our films if a DSC plot of dithiolene-polymer contained a similar peak. The DSC plots of the films in this study are presented in Chapter 6. No film contained a melting point peak, thus the dithiolene was not in crystal form in films containing 10% dithiolene.

In a 1969 study, Schmitt et al. reported the formation of 1:1 complexes between $Ni[tfd]_2$ and highly conjugated aromatics [36]. Schmitt showed that the aromatics, perylene and pyrene, formed a donor-acceptor complex. The complexes formed via charge transfer involving the corresponding π-orbitals. The complexes are considered weak because the extent of the charge transfer is small, but an interaction was observed nonetheless. These results are intriguing since the choice of polymers to study in this work did not take into consideration possible interactions between the polymer and Ni[tfd]$_2$. It is believed that the interactions observed with pyrene and perylene could also be occurring along the aromatic backbone of the polyimides. The gas transport responses reported previously could be affected by such interactions and could be working in conjuction with the antiplasticization effects.



Pyrene Perylene

Figure 4.26. Structures of Pyrene and Perylene

In order to decouple aromatic-dithiolene interactions or prove the existence of one and not the other, nonaromatic polymers were also studied. The results of permeation and sorption experiments with nonaromatic polymer membranes are discussed in Chapter 5. Infrared spectroscopy was also used to investigate the extent of interactions in the polyimide membranes with Ni[tfd]$_2$. These results are discussed in Chapter 6.

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CHAPTER 5

GAS TRANSPORT IN NON-AROMATIC POLYMERS

5.1 INTRODUCTION

To better characterize the effect of a nickel dithiolene on polymeric gas membrane separation, gas transport in non-aromatic polymers was studied. In Chapter 4 it was hyptothesized that the aromatic nature of the polyimides enabled attractive interactions with the dithiolene additive, which may reduce gas permeation properties by suppressing segmental motions. Since dithiolenes are known to interact with complex aromatics, such interactions may hinder desirable complexation with propylene molecules [1]. The non-aromatic polymers chosen were polycyclohexylethylene (PCHE) and a commercial polymer, Zeonex® (480 grade). These polymers are sometimes referred to as polyolefins or poly(cycoolefins). To date, the gas transport properties of PCHE and Zeonex® have not been measured.

PCHE, which is synthesized by hydrogenating polystyrene (PS), possesses a higher glass transition temperature and a lower density compared to PS. PCHE was developed by Dow Chemical Company for the production of DVDs, but was never commercialized. Despite its excellent optical properties, PCHE is an extremely brittle polymer [2-9]. Since the pendant cyclohexyl group impedes packing and thus leads to a high entanglement molecular weight [2-9]. The brittleness of PCHE also caused difficulty in casting suitable films for permeation experiments.

Zeonex® is an amorphous polymer manufactured by Zeon Chemicals Corporation. It is used in the lenses of laser printers and the optical parts of cameras [10]. Zeonex® is synthesized by ring-opening methathesis polymerization (ROMP) of norbornene followed by complete hydrogenation [11]. The gas separation properties of polynorbornene (PNB) have been studied previously[12-25]. The presence and size of pendant side groups have been correlated to transport properties of PNB [12-14, 18, 19, 24]. Marked differences have been observed in polynorbornene synthesized via different mechanisms. A major difference is that PNB synthesized by addition polymerization retains norbornene's bicyclic conformation while those of ROMP are cyclolinear [20].

Characteristics of PCHE, Zeonex® and their precursors are shown in Table 5.1. PCHE and Zeonex® both possess a higher density and glass transition temperature (T_g) than their precursors. The fractional free volume (FFV) of PCHE and Zeonex® was calculated using the group contribution method of van Krevelen [26]. The FFV for PS and PNB was obtained from literature. Note that PCHE has a higher FFV than PS, but Zeonex® has a lower FFV than PNB. The low T_g value of PNB indicates that it is in the rubbery state during transport experiments which are usually conducted at 35ºC.

Table 5.1. Characteristics of poly(cycloolefins) studied and their respective precursors

Polymer	**T_g (ºC)**	**Density (g/cm^3)**	**FFV**	**ref**
PCHE	147	0.94	0.181[a]	this work, 2
PS	102	1.05	0.177	19
Zeonex®	138	1.01	0.134[a]	this work, 10
PNB	31	0.98	0.156	25

[a]Calculated by group contribution method

5.2 PERMEABILITY AND PERMSELECTIVITY

The transport properties of PCHE and Zeonex® are not exceptional but they still provide valuable ways to better understand the impact of Ni[tfd]$_2$. As discussed above, these polymers were chosen to observe the general effect of the dithiolene, Ni[tfd]$_2$, on gas separation properties of a non-aromatic polymer, and to compare to 6FDA-6FpDA and 6FDA-DAM.

5.2.1 Selected permeability of polyolefins and their respective precursors

There are limited data available for hydrocarbon transport data in polycycloolefins such as polynorbornene and polystyrene, but some insight to how the transport properties of PCHE and Zeonex® compare to PS and PNB, respectively, can be gained from information available for other non-hydrocarbon gases.

Table 5.2. Permeability Coefficients and Permselectivities of polycycloolefins studied and their precursors at 35°C and 2 atm, unless otherwise noted.

Polymer	P_{O2} [a]	P_{CO2} [a]	P_{O2}/P_{N2}	P_{CO2}/P_{CH4}	ref
PCHE	4.3	15	4.8	10	this work
PS [b]	2.9	12.4	5.5	15.8	19
Zeonex®	2.6	9.8	5.0	11.2	this work
PNB [c]	2.8	15.4	1.9	6.3	25

[a] Barrers [=] 1 Barrer = 1x 10^{-10} cm^3(STP)/cm^2-s-cmHg
[b] at 1 atm
[c] at <1 atm

As seen in Table 5.2, hydrogenation led to differing properties for polystyrene and polynorbornene. The permeability of PCHE is higher than its precursor, whereas Zeonex® has a lower permeability than PNB. Since PNB is above its T_g at the temperature of measurement, 35℃, care must be taken when comparing the properties of these two polymers. However, a general understanding can still be gained. Although both polymers respond similarly in terms of permeability, there is an opposite effect on the permselectivity. The increase in permeability seen in PCHE may be attributed to an increase in FFV, but the decrease in selectivity indicates a difference in the free volume distribution as discussed in previous work [19, 27-29]. The differences between Zeonex® and PNB are more complicated since this involves comparing rubbery and glassy polymers.

5.2.2 Effect of dithiolene on C_3H_6/C_3H_8 permeability in PCHE and Zeonex®

Polyolefins such as polyethylene have previously been investigated for C_3H_6/C_3H_8 separations, but offered no desirable properties. Henley and Santos reported preferential permeability of propane over propylene and ethane over ethylene in polyethylene films [30]. Li and Henley also investigated the strong plasticization effects of ethane and propane [31]. Robeson studied polyethylene for ethane-butane separation [32] and reported a permeability of 10 Barrers for ethane and 58 Barrers for butane at 30ºC. Yampolskii et al have reported ethane permeability of 1.4 Barrers and diffusivity of 1.6 x 10^{-6} cm^2/s in polynorbornene [21].

The propylene and propane permeability coefficients of PCHE and Zeonex® are listed in Table 5.3. The permeability of each polymer blended with 10% of $Ni[tfd]_2$ is also shown.

Table 5.3. Permeability Coefficients and Permselectivities of PCHE and Zeonex® at 35°C and 2atm.

Polymer	P_{C3H6} [a]	P_{C3H8} [a]	P_{C3H6}/P_{C3H8}
PCHE	0.78	0.25	3.1
PCHE / $Ni[tfd]_2$	0.36	0.12	3.0
Zeonex®	0.47	0.08	6.0
Zeonex® / $Ni[tfd]_2$	0.16	0.03	5.7

[a] Barrers [=] 1 Barrer = 1x 10^{-10} cm^3(STP)/cm^2-s-cmHg

As exhibited in the polyimides, incorporation of $Ni[tfd]_2$ did not enhance the permselectivity of PCHE nor Zeonex®. In fact, the permeability of both propylene and propane decreased similarly to the polyimides, again suggesting an antiplasticizing effect of the $Ni[tfd]_2$. Propylene and propane permeability was reduced by 46 and 48%, respectively in PCHE. In Zeonex®, propylene permeability decreased 37%, for propane, 34%. Just as in the polyimides, the effect of the dithiolene is not the same in both polyolefins. Although gas permeability of both gases decreased, PCHE was more greatly affected. As discussed previously, this suggests that the choice in polymer is important since the dithiolene does not affect all the polymers in the same manner.

Previous groups have studied facilitated transport of polyolefin films [33-38]. Kim et al investigated polystyrene and polystyrene-butadiene copolymers containing silver salts for olefin/paraffin separations [33, 37, 38]. Using $AgBF_4$ in polystyrene, Kim et al observed enhancement of propylene permeance from 0.14 to 11.4 GPU; enhancement using $AgCF_3SO_3$ only enhanced propylene permeance to 4.5 GPU. The enhancement in permeance was not seen until the silver mole fraction was at least 0.14. Propane permeance below 0.1 GPU was not detectable by the bubble flow meter used by these researchers.

Additionally, mixed gas propylene/propane selectivity increased from 1.0 for neat PS to 60 for PS/$AgBF_4$ membranes. The enhancement is attributed to coordination between the π-electrons of the aromatic C=C bonds in PS and the silver ions. Kim et al explain that such coordination form "transient crosslinks" between the polymer chains and cause contraction and rigidification [35, 38]. It is argued that the rigidification and facilitated olefin transport occur simultaneously, but at low concentrations, rigidification dominates which would explain why enhancement was not seen below a mole fraction of 0.14 of the silver salt. Also, propane permeance initially decreases sharply and then slowly decreases with increasing amount of silver salt. It is foreseen that a similar response could have been observed in the 6FDA-based polyimides studied herein if a larger fraction of dithiolene could be successfully blended with the polymer samples; however, the solubility limits of the dithiolene prevented this from being pursued.

Using poly(2-ethyl-2-oxazoline) (POZ) and poly(*N*-vinyl pyrrolidone) (PVP), Kim observed similar results as above. Neither POZ nor PVP contain phenyl rings but both contain a carbonyl group. There was no enhancement in propylene in either polymer until the silver ion mole ratio was at least 0.34. Propane permeance also sharply dropped and coordination interaction between silver ions and the carbonyl oxygens was hypothesized to cause rigidification and densification, which lead to reduction in propane permeance.

In any case, the work by Kim et al supports the notion that polymer-additive interaction can have strong effects on the transport properties of facilitated transport membranes. We could suggest that interactions between dithiolenes and the aromatic backbone of the polyimides have a similar effect, but the permeability response of PCHE and Zeonex® indicate that more than this effect may be at play. The following will consider this issue in more detail.

5.3 EFFECT OF DITHIOLENE ON C_3H_6/C_3H_8 SORPTION AND SORPTION SELECTIVITY

Pure gas C_3H_6/C_3H_8 sorption experiments were conducted for PCHE and Zeonex® films at 35ºC using the pressure decay method. The data was then fit to the dual mode sorption model. Table 5.4 lists the sorption coefficients for propylene and propane along with the sorption selectivity for pure PCHE and Zeonex® films and films containing 10% $Ni[tfd]_2$ at 2 atm. The addition of $Ni[tfd]_2$ had varying effects on PCHE and Zeonex® sorption. Propylene sorption in PCHE decreased 6% while propane sorption decreased 21%, resulting in an enhancement of the neat PCHE propylene/propane solubility selectivity by 13%. The response was similar in Zeonex®. There was a slight decrease in propane sorption but an increase in propylene sorption, so sorption selectivity was increased by 20%. Sorption in Zeonex® was preferential to propane over propylene, but such a result has been seen in other polyolefins such as polyethylene [30]. It appears that the dithiolene has rendered propylene sorption in Zeonex® more favorable, offsetting the otherwise unfavorable sorption selectivity, but still effectively reducing permeability. The overall effect, therefore is quite complex.

Table 5.4. C_3H_6/C_3H_8 Sorption and diffusion properties for PCHE and Zeonex® films with and without 10% $Ni[tfd]_2$ at 35°C and 2 atm.

Membrane	S_{C3H6}	S_{C3H8}	D_{C3H6}	D_{C3H8}	S_{C3H6}/S_{C3H8}	D_{C3H6}/D_{C3H8}
PCHE	0.33	0.29	12.3	4.5	1.13	2.75
PCHE / $Ni[tfd]_2$	0.31	0.24	6.0	2.6	1.28	2.34
Zeonex®	0.27	0.33	9.0	1.3	0.80	7.18
Zeonex® / $Ni[tfd]_2$	0.29	0.29	2.9	0.5	1.00	5.33

S [=] cc(STP) / cc polymer - psia
D [=] 1×10^{-10} cm^2/s

Since the permeability of propylene and propane both decreased, these results indicate that there is a significant decrease in the diffusivity, calculated from P=DS, of both gases as well as the diffusivity selectivity as outlined in Table 5.4. The diffusivity of propylene in Zeonex®/$Ni[tfd]_2$ is then 68% lower than the neat film, and propane diffusivity decreased over 61%. Thus, the diffusivity selectivity is about 16% lower because of the greater change in propylene diffusivity. The diffusivity selectivity of PCHE decreased also, but not as greatly as Zeonex®.

Figures 5.1 – 5.4 show propylene and propane sorption isotherms in PCHE and Zeonex®. The effect of $Ni[tfd]_2$ is similar in both polymers. Propylene sorption in PCHE/$Ni[tfd]_2$ and Zeonex®/$Ni[tfd]_2$ is not reduced compared to the neat polymer, and at higher pressures, propylene sorption in Zeonex®/$Ni[tfd]_2$, slightly surpassed that of the neat polymer. The sustained propylene sorption despite a reduction in propane sorption suggests that the dithiolene may facilitate propylene sorption while simultaneously offsetting the mobility suppression induced by the presence of $Ni[tfd]_2$.

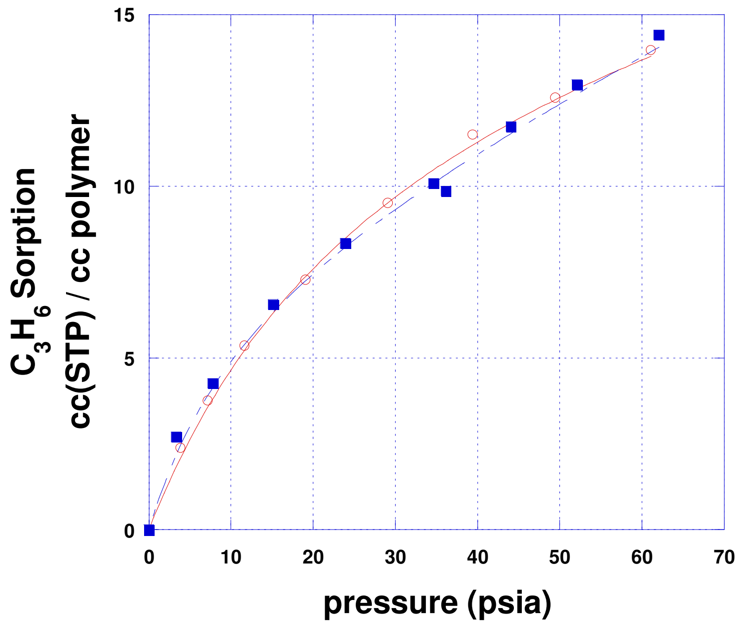

Figure 5.1. C_3H_6 sorption isotherms at 35℃. ○ PCHE; ■ PCHE/Ni[tfd]$_2$

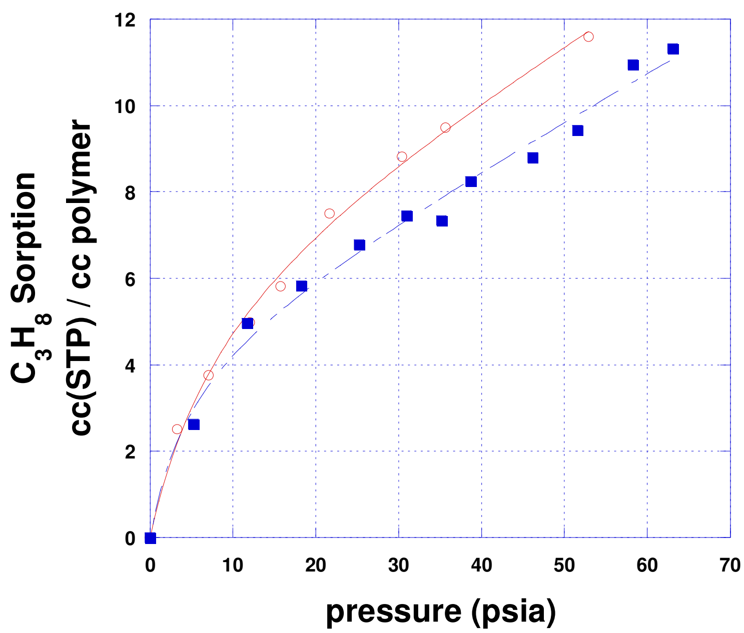

Figure 5.2. C_3H_8 sorption isotherms at 35°C. ○ PCHE; ■ PCHE/Ni[tfd]$_2$

Tables 5.5 and 5.6 show a reduction in the Langmuir capacity coefficient, C'_H, of propylene and propane in PCHE and Zeonex upon addition of Ni[tfd]$_2$. Although Figures 5.1 and 5.3 show similar propylene isotherms in pure films versus dithiolene containing films, the shape of the isotherms at higher pressures differ and dictate the estimate of C'_H. Sorption at higher pressures would be needed to more accurately delineate the differences. Nonetheless, it can be inferred, within the limits of the error in the fit, that there is a reduction of C'_H with the addition of Ni[tfd]$_2$ to PCHE and Zeonex® and this may reflect reductions in the fractional free volume (FFV) in the polymer.

Table 5.5. Dual Mode Parameters for PCHE at 35ºC and 2 atm.

Membrane	**Gas**	**k_D[a]**	**C'_H[b]**	**b[c]**
PCHE	C_3H_6	0.07 ± 0.02	13.2 ± 2.1	0.05 ± 0.01
PCHE / Ni[tfd]$_2$	C_3H_6	0.15 ± 0.01	5.7 ± 0.6	0.18 ± 0.05
PCHE	C_3H_8	0.11 ± 0.02	6.8 ± 1.3	0.11 ± 0.04
PCHE / Ni[tfd]$_2$	C_3H_8	0.11 ± 0.01	4.7 ± 0.9	0.2 ± 0.11

[a]cc (STP) / cc polymer -psia [b]cc (STP) / cc polymer [c]psia^{-1}

Table 5.6. Dual Mode Parameters for Zeonex® at 35ºC and 2 atm.

Membrane	**Gas**	**k_D[a]**	**C'_H[b]**	**b[c]**
Zeonex®	C_3H_6	0.20 ± 0.02	6.7 ± 1.0	0.2 ± 0.1
Zeonex® / Ni[tfd]$_2$	C_3H_6	0.20 ± 0.02	1.9 ± 0.7	1.5 ± 4.3
Zeonex®	C_3H_8	0.14 ± 0.04	7.7 ± 3.0	0.098 ± 0.06
Zeonex® / Ni[tfd]$_2$	C_3H_8	0.17 ± 0.03	5.2 ± 3.1	0.06 ± 0.05

[a]cc (STP) / cc polymer -psia [b]cc (STP) / cc polymer [c]psia^{-1}

Although, Ni[tfd]$_2$ has shown enhancement in sorption and sorption selectivity in PCHE and Zeonex®, it still causes significant reduction in permeability and diffusivity. This effect seems to not be limited to polyimide films and suggests that the absence of aromaticity aided in curtailing reductions in solubility while still enhancing solubility selectivity. These effects are similar to that observed by Kim et al, which were attributed to simultaneous rigidification and facilitation [34-37]. As shown above, large reductions in permeability yet smaller, or zero, changes in solubility indicate a marked reduction in diffusivity. While sorption levels are not greatly affected, the results suggest, that diffusion through the polymer matrix is slowed by reduced molecular motion as we have discussed in Chapter 4. Also, the effects on diffusivity selectivity could be a result of a change in the distribution of FFV; this could be probed using X-ray diffraction in future work. However, the relative change in rigidity can be measured by Dynamic Mechanical Analysis (DMA). The results of these tests are discussed in the following chapter.

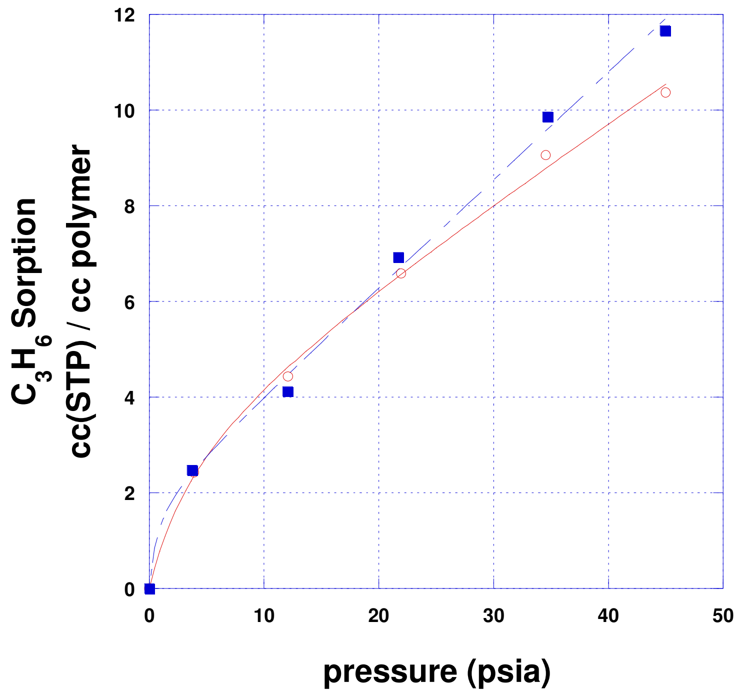

Figure 5.3 C_3H_6 sorption isotherms at 35℃. ○ Zeonex®; ■ Zeonex®/Ni[tfd]$_2$

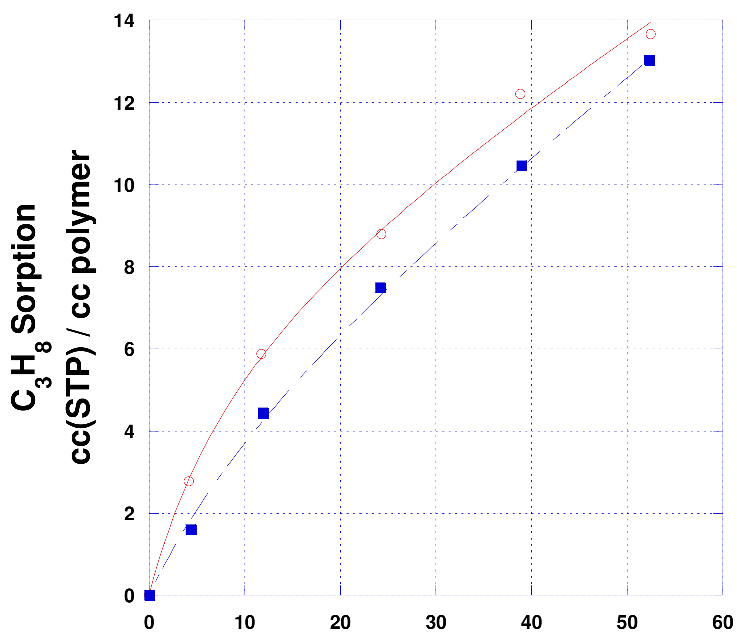

Figure 5.4 C_3H_8 sorption isotherms at 35℃. ○Zeonex®; ■ Zeonex®/Ni[tfd]$_2$

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CHAPTER 6

EXPLANATION OF OBSERVED EFFECT OF DITHIOLENES ON GAS TRANSPORT AND SORPTION

6.1. INTRODUCTION

As discussed in Chapters 4 and 5, adding just 10% of the dithiolene, Ni[tfd]$_2$, to polyimides and polyolefins reduced the permeability and solubility coefficients of propylene *and* propane. This effect is similar to the antiplasticization response that has been observed by Maeda and Paul for CO_2 in polysulfone and poly(phenylene oxide) [1-3]. The same effect has been seen by other researchers investigating facilitated transport using silver ions. In some instances, these responses were not termed "antiplasticization" but instead attributed to silver-polymer coordination interactions which lead to compaction and rigidification [4-9]. Since the films studied showed an increase in T_g with an increase of silver content, antiplasticization was not claimed by the authors.

The various results presented previously in this work, have shown evidence of antiplasticization and limited facilitation. Polyolefins were studied to determine if the presence of aromatic structures played a part in reducing the transport of propane and propylene in the presence of a nickel dithiolene. Permeability of propylene and propane in the polyolefins was reduced while the effect on sorption of these gases differed. The following sections will investigate the transport of other gases in both polyolefins and polyimides to further understand these responses. Analytical measures have also been taken to examine possible changes to the polymer matrix upon addition of Ni[tfd]$_2$.

6.2 EFFECT OF DITHIOLENE ON CO_2/CH_4 AND O_2/N_2 TRANSPORT AND SORPTON

6.2.1 Permeability response of 6FDA-6FpDA and 6FDA-DAM

Table 6.1 lists the permeability and selectivity of CO_2/CH_4 and O_2/N_2 gas pairs in 6FDA-6FpDA and 6FDA-DAM. As observed for propylene and propane, the permeability of all gases was reduced in films containing 10% dithiolene. Although there is a decrease in the permeability there is an increase in the selectivity for both gas pairs. A larger increase in selectivity is seen for CO_2/CH_4 than for O_2/N_2 in both 6FDA-6FpDA and 6FDA-DAM.

Table 6.1. Permeability and Permeability Selectivity in 6FDA-6FpDA and 6FDA-DAM at 35℃ and 2 atm

Membrane	P_{CO2}	P_{CH4}	P_{O2}	P_{N2}	P_{CO2}/P_{CH4}	P_{O2}/P_{N2}
6FDA-6FpDA	111	2.5	23	5.1	45	4.5
6FDA-6FpDA/ Ni[tfd]$_2$	42	0.6	6.7	1.3	69	5.1
6FDA-DAM	496	23	103	29	21	3.6
6FDA-DAM / Ni[tfd]$_2$	165	5.3	68	16	31	4.3

Maeda and Paul observed a comparable response when studying the effects of antiplasticization on overall selectivity [10]. The permeability of helium, carbon dioxide, and methane was measured in polysulfone containing increasing amounts of an antiplasticizer. In all cases, the permeability of each gas decreased upon adding the antiplasticizer. There were varying effects on the selectivity, though. For the pairs He/CO_2 and He/CH_4, the selectivity increased with the amount of antiplasticizer. For the pair CO_2/CH_4, the selectivity initially increased at 10% antiplasticizer then decreased slightly at 20% or higher. Maeda and Paul indicated that the enhancement is the largest for gas pairs with the largest difference in molecular diameter as is the case for He/CO_2 or He/CH_4. In comparison, of the two gas pairs studied in this work, the molecular diameters of O_2/N_2 are more similar than CO_2/CH_4. The difference in diameters would account for the significant increase in CO_2/CH_4 selectivity versus O_2/N_2 (see Table 6.2).

Table 6.2 Kinetic diameters of molecular gases determined by Lennard-Jones Interaction Parameters [11].

Gas	Kinetic Diameter (Å)
CO_2	3.3
CH_4	3.8
O_2	3.46
N_2	3.64

The differing effect on selectivity based on molecular diameters of the gas pairs can be attributed to a change in the distribution of free volume of the transiently appealing intersegmental gaps that enable diffusive jumps [12]. As a polymer's free volume distribution narrows, the ratio of high FFV areas to low FFV areas has been hypothesized to lessen, and the polymer becomes more size selective and the permeability selectivity, barring a substantial change in the solubility selectivity, increases. Gases with a larger difference in size are more easily differentiated and in turn the diffusivity selectivity of the polymer increases.

The pressure dependant CO_2 permeabiliity for 6FDA-6FpDA and 6FDA-DAM films are shown in Figures 6.1 and 6.2. The overall permeability of CO_2 decreases, as mentioned above, throughout the pressure range. Also, the plasticization response is significantly suppressed. The upturn in 6FDA-6FpDA permeability is about 100 Barrers from 200-500 psia. In the same range, the CO_2 permeability upturn in 6FDA-6FpDA/Ni[tfd]$_2$ is 25 Barrers. In 6FDA-DAM, the upturn is 250 Barrers from 200-500 psia, and in 6FDA-DAM/Ni[tfd]$_2$ it is only 125 Barrers. Such a response was not reported by Maeda and Paul in their investigation of the implications of antiplasticization on gas transport properties, but the polymers from their study did not plasticize under the operating conditions. Nonetheless, this tends to agree with the physical picture of antiplasticization as a generalized rigidification of the matrix.

Plasticization is understood to be caused by dilation ("swelling") of a polymer matrix due to highly sorbing gases. Another accepted cause which may occur simultaneously, is an increase in the polymer flexibility due to added free volume contributed by sorbed penetrants. This notion of plasticization provides a framework for understanding the suppressed plasticization response in 6FDA-6FpDA and 6FDA-DAM. If plasticization is caused by swelling and/or increases in polymer flexibility, suppressed plasticization suggests impeded polymer motion and retarded dilation. This is consistent with the physical picture of antiplasticization provided by others [1-3, 12-19]. By impeding polymer motion and dilation, antiplasticization tends to reduce the effects of classical plasticization and hence the pressure at which plasticization occurs is higher.

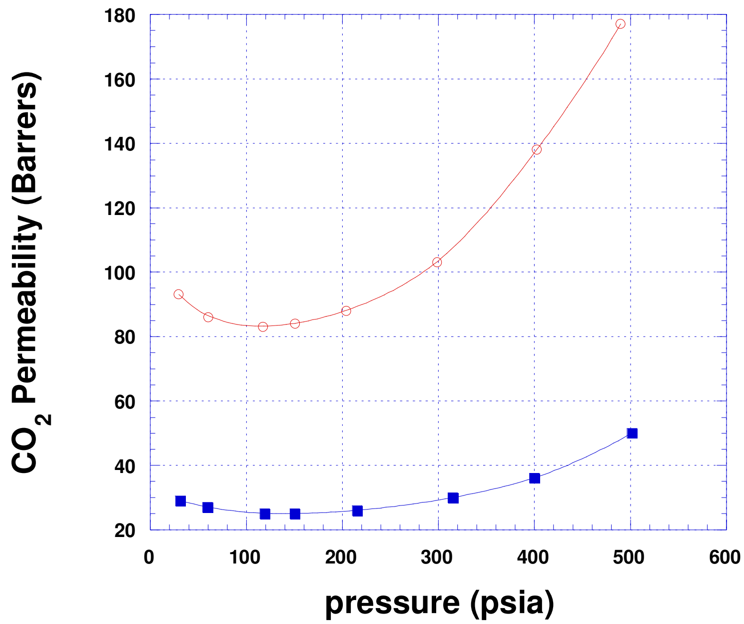

Figure 6.1. CO_2 Permeability at 35℃ in ○6FDA-6FpDA and ■6FDA-6FpDA/Ni[tfd]$_2$

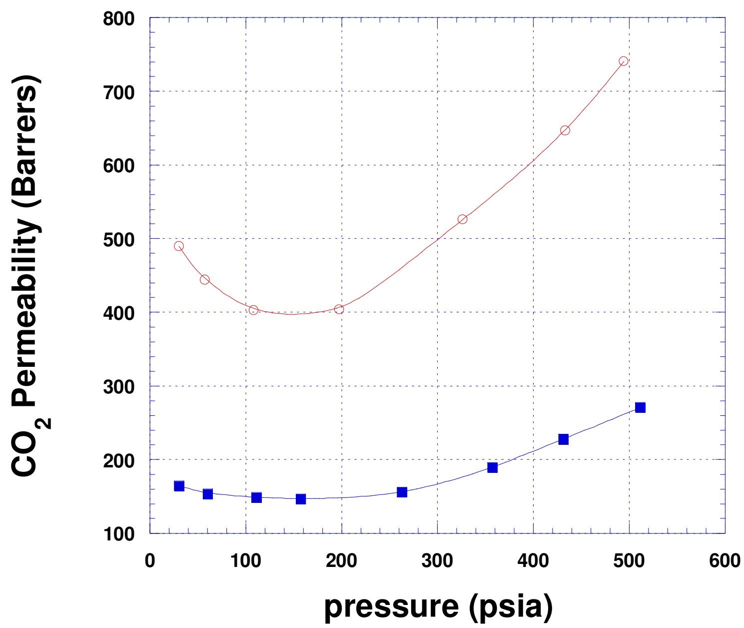

Figure 6.2. CO_2 Permeability at 35℃ in ○6FDA-DAM and ■6FDA-DAM/Ni[tfd]$_2$

6.2.2. Solubility response of 6FDA-6FpDA and 6FDA-DAM

Table 6.3. Sorption and diffusion properties of 6FDA-6FpDA and 6FDA-DAM at 35°C and 2 atm

Membrane	S_{CO2}	S_{CH4}	S_{O2}	S_{N2}	S_{CO2}/ S_{CH4}	S_{O2}/ S_{N2}
6FDA-6FpDA	0.83	0.18	0.09	0.09	4.6	1.0
6FDA-6FpDA/ Ni[tfd]$_2$	0.62	0.15	0.09	0.07	4.2	1.3
6FDA-DAM	1.24	0.29	0.12	0.10	4.2	1.2
6FDA-DAM / Ni[tfd]$_2$	0.94	0.23	0.10	0.08	4.0	1.3

S [=] cc(STP) / cc polymer - psia

The solubilities of oxygen, nitrogen, carbon dioxide and methane in 6FDA-6FpDA and 6FDA-DAM films were also studied. The results are summarized in Table 6.2. The addition of 10% Ni[tfd]$_2$ to 6FDA-6FpDA and 6FDA-DAM has the same effect on these gases as seen previously for propylene and propane. Sorption of all gases was reduced approximately by 20% except for oxygen in 6FDA-6FpDA. Due to the low solubility of oxygen it is sometimes difficult to accurately measure its concentration in a polymer film. This may also be attributed to the large error in fitting the Langmuir capacity coefficient, C'_H, for oxygen in 6FDA-6FpDA. Since the dual mode parameters are used when calculating the solubility coefficient at a specific pressure, an inaccurate value for C'_H can lead to an inaccurate value of the sorption coefficient. The method for calculating the sorption coefficient from the dual mode parameters was illustrated in Chapter 3. Nonetheless, it is apparent that in all other cases, the solubility coefficient is reduced with the addition of Ni[tfd]$_2$. Furthermore, Tables 6.4 and 6.5 show a reduction in C'_H for all gases (except the aforementioned) in dithiolene-containing films compared to the neat polymer. This correlates to data reported by Maeda and Paul for CO_2 sorption.

Table 6.4. Effect of Ni[tfd]$_2$ on Dual Mode Parameters of 6FDA-6FpDA at 35°C

Membrane	**Gas**	k_D[a]	C'_H[b]	b[c]
6FDA-6FpDA	CO_2	0.10 ± 0.03	67.6 ± 15.1	0.016 ± 0.006
6FDA-6FpDA / Ni[tfd]$_2$	CO_2	0.010 ± 0.03	42.7 ± 14.5	0.019 ± 0.011
6FDA-6FpDA	CH_4	-0.005 ± 0.01	53.5 ± 12.2	0.004 ± 0.001
6FDA-6FpDA / Ni[tfd]$_2$	CH_4	0.004 ± 0.004	25.5 ± 3.9	0.007 ± 0.001
6FDA-6FpDA	O_2	0.06 ± 0.06	5.1 ± 26.5	0.01 ± 0.03
6FDA-6FpDA / Ni[tfd]$_2$	O_2	0.027 ± 0.002	4.9 ± 0.5	0.021 ± 0.002
6FDA-6FpDA	N_2	0.017 ± 0.004	14.8 ± 3.3	0.005 ± 0.001
6FDA-6FpDA / Ni[tfd]$_2$	N_2	0.027 ± 0.003	5.2 ± 1.5	0.011 ± 0.004

Table 6.5 Effect of Ni[tfd]$_2$ on Dual Mode Parameters of 6FDA-DAM at 35°C

Membrane	**Gas**	k_D[a]	C'_H[b]	b[c]
6FDA-DAM	CO_2	0.10 ± 0.01	92.0 ± 8.9	0.019 ± 0.004
6FDA-DAM/ Ni[tfd]$_2$	CO_2	0.12 ± 0.01	59.1 ± 4.7	0.023 ± 0.004
6FDA-DAM	CH_4	0.010 ± 0.004	41.5 ± 2.7	0.009± 0.001
6FDA-DAM / Ni[tfd]$_2$	CH_4	0.008 ± 0.005	32.1 ± 4.0	0.009 ± 0.002
6FDA-DAM	O_2	0.06 ± 0.01	7.0 ± 1.1	0.13 ± 0.01
6FDA-DAM/ Ni[tfd]$_2$	O_2	0.05 ± 0.01	5.1 ± 4.3	0.13 ± 0.01
6FDA-DAM	N_2	0.02 ± 0.01	16.1 ± 7.0	0.006 ± 0.003
6FDA-DAM / Ni[tfd]$_2$	N_2	0.02 ± 0.01	12.2 ± 5.0	0.005 ± 0.002

[a]cc (STP) / cc polymer -psia [b]cc (STP) / cc polymer [c]$psia^{-1}$

Maeda and Paul note that the decrease in sorption with addition of a diluent, or additive, is similar to the effect of raising the measurement temperature [3]. They then extend this explanation by relating C'_H to the excess volume using the following relationship:

$$C_H' = \frac{22{,}414(\alpha_l - \alpha_g)(T_g - T)}{\tilde{V}_{CO2}}$$

where $(\alpha_l - \alpha_g)$ is the difference in the thermal expansion coefficients between the liquid and glassy states of the polymer, $(T_g - T)$ is the difference between the polymer T_g and the measurement temperature, and $\tilde{V}_{CO2}$ is the molar volume of CO_2 in the liquid-like state. A plot of C'_H versus $(T_g$-$T)$ increased linearly as the quantity, $(T_g$-$T)$, for both pure samples and additive containing samples diluent increased. Based on this result, Maeda and Paul conclude that the effect of antiplasticization on the Langmuir capacity coefficient is due to an accompanying reduction in T_g. The effect of the dithiolene on T_g is investigated in section 6.3.

Maeda and Paul also correlated k_D using the Flory-Huggins theory to show strong polymer-diluent interactions. It would be useful to repeat a similar experiment for the polymer-dithiolene systems studied within, but such an analysis requires varying amounts of additive to make a strong correlation. At 10 wt%, the change in k_D for CO_2 and other gases upon addition of dithiolene varies (Tables 6.4 and 6.5). The largest change is seen in CO_2 and O_2 sorption in 6FDA-6FpDA. Since the effect is not consistent for every gas nor is it consistent in 6FDA-6FpDA and 6FDA-DAM, no conclusions about the effect of antiplasticization on k_D can be made at this time.

Nonetheless, it is apparent that addition of Ni[tfd]$_2$ to both 6FDA-6FpDA and 6FDA-DAM reduced the sorption level of all gases. This effect is further illustrated by the sorption isotherms in Figures 6.3 through 6.6 for CO_2/CH_4 and O_2/N_2 in 6FDA-6FpDA and 6FDA-DAM. For all gases, sorption is reduced with the addition of Ni[tfd]$_2$. The difference is sustained and is more apparent at higher pressures.

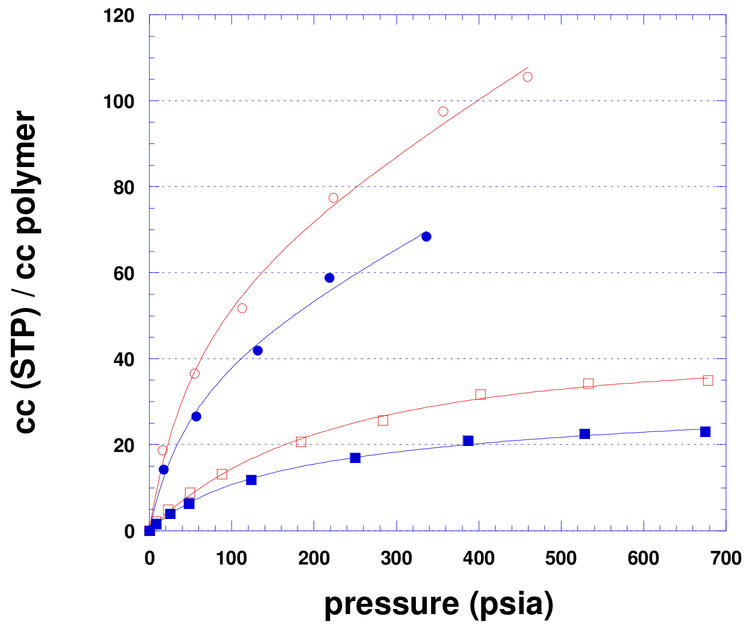

Figure 6.3. CO_2/CH_4 Sorption in 6FDA-6FpDA at 35℃. ○CO_2 in 6FDA-6FpDA. ●CO_2 in 6FDA-6FpDA/ Ni[tfd]$_2$ □CH_4 in 6FDA-6FpDA. ■CH_4 in 6FDA-6FpDA / Ni[tfd]$_2$.

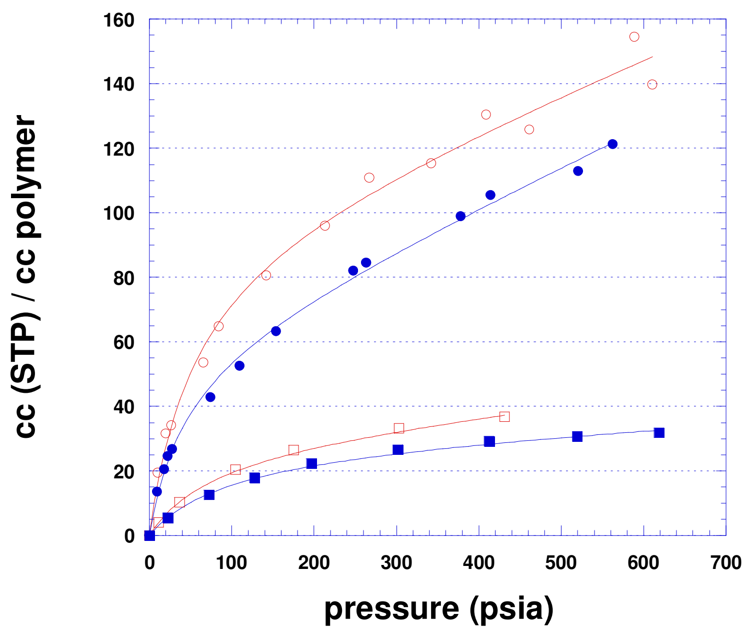

Figure 6.4. CO_2/CH_4 Sorption in 6FDA-DAM at 35℃. ○CO_2 in 6FDA-DAM. ●CO_2 in 6FDA-DAM/ Ni[tfd]$_2$ □CH_4 in 6FDA-DAM. ■CH_4 in 6FDA-DAM / Ni[tfd]$_2$.

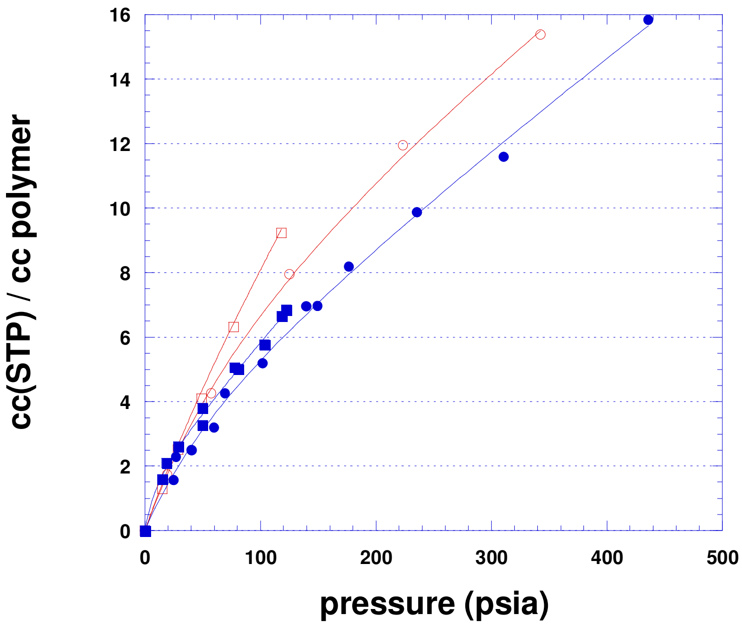

Figure 6.5. O_2/N_2 Sorption in 6FDA-6FpDA at 35℃. □O_2 in 6FDA-6FpDA. ■O_2 in 6FDA-6FpDA / Ni[tfd]$_2$. ○N_2 in 6FDA-6FpDA. ●N_2 in 6FDA-6FpDA/ Ni[tfd]$_2$

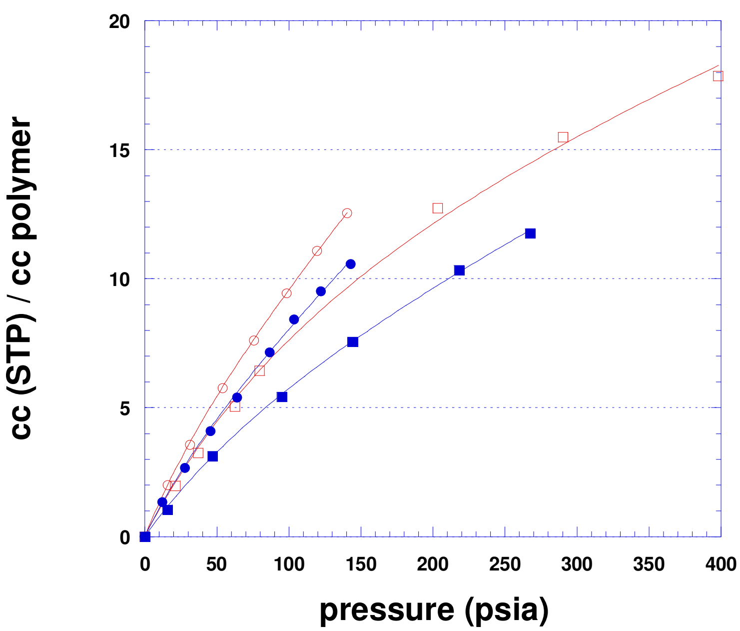

Figure 6.6. O_2/N_2 Sorption in 6FDA-DAM at 35℃. ○O_2 in 6FDA-DAM. ●O_2 in 6FDA-DAM/ Ni[tfd]$_2$ □N_2 in 6FDA-DAM. ■N_2 in 6FDA-DAM / Ni[tfd]$_2$.

6.2.3 Permeability response of PCHE and Zeonex®

The permeabilities and associated selectivities of CO_2, CH_4 and O_2, N_2 in PCHE and Zeonex were measured. The permeability coefficients at 35°C and 2 atm are shown below in Table 6.6. The permeability of CO_2, CH_4, and O_2 decreases in both PCHE and Zeonex® with addition of Ni[tfd]$_2$. There is a slight increase of N_2 permeability in PCHE/Ni[tfd]$_2$ compared to the pure polymer. Similarly, there is minimal or no change in CO_2/CH_4 and O_2/N_2 selectivity. The lower O_2/N_2 permeability selectivity in PCHE/Ni[tfd]$_2$ compared to PCHE was due to the increase in N_2 permeability. The effect of Ni[tfd]$_2$ on the permeability of non-aromatic polymers PCHE and Zeonex® is not as strong as seen in polyimides 6FDA-6FpDA and 6FDA-DAM. This suggests that the aromatic nature of the polyimides may play a role in the reduced transport. The fact that the permeability of all gases did decrease in both aromatic and non-aromatic films containing Ni[tfd]$_2$ supports an antiplasticization effect, but due to the differing extent of reduction, I propose that there exists a combination of effects which cause reduction in gas transport properties. The CO_2 sorption properties presented in the following section supports this interpretation also.

Table 6.6. Permeation in PCHE and Zeonex® at 35°C and 2 atm

Membrane	P_{CO2}	P_{CH4}	P_{O2}	P_{N2}	P_{CO2}/P_{CH4}	P_{O2}/P_{N2}
PCHE	15	1.5	4.3	0.9	10	4.8
PCHE/ Ni[tfd]$_2$	12	1.2	4.1	1.0	10	4.1
Zeonex®	9.8	0.9	2.6	0.5	11	5.2
Zeonex®/ Ni[tfd]$_2$	8.2	0.7	2.3	0.4	12	5.2

6.2.4. CO_2 Solubility Response of PCHE and Zeonex®

The sorption coefficient and dual mode parameters for CO_2 sorption in PCHE and Zeonex® are shown in Table 6.7. As indicated, the addition of Ni[tfd]$_2$ did not reduce sorption of CO_2 in PCHE. The dual mode parameters also were not affected greatly. The recorded change in the Langmuir capacity coefficient is within the error of the experimental fit so is not considered to be significant. Similar results are observed in Zeonex®. We report a small difference in C'_H between the neat polymer and the dithiolene-containing polymer, but it is within experimental error. Furthermore, Figures 6.7 and 6.8 illustrate that the sorption isotherms for both films are practically identical. Unlike the polyimide films, the addition of Ni[tfd]$_2$ does not effectively alter the sorption of CO_2 in the polyolefin films. It is suspected that a similar response would be observed for other gases as well.

Table 6.7. Sorption Properties for CO_2 in PCHE and Zeonex®

Membrane	S	k_D[a]	C'_H[b]	b[c]
PCHE	0.091	0.015 ± 0.004	15.1 ± 3.9	0.006 ± 0.002
PCHE / Ni[tfd]$_2$	0.092	0.01 ± 0.001	16.9 ± 5.6	0.006 ± 0.002
Zeonex®	0.082	0.002 ± 0.007	25.5 ± 8.4	0.003 ± 0.001
Zeonex®/ Ni[tfd]$_2$	0.089	0.008 ± 0.005	19.4 ± 5.6	0.005 ± 0.002

S [=] cc(STP) / cc polymer - psia
[a]cc (STP) / cc polymer -psia
[b]cc (STP) / cc polymer
[c]$psia^{-1}$

Merkel et al. reported similar findings suggesting the stiffness of the polymer plays a primary role in the effect of an additive [20]. The addition of fumed silica to poly[2,2-bis(trifluormethyl)-4,5-difluoro-1,3-dioxole-*co*-tetrafluoroethanylene (AF2400) did not alter the glass transition temperature and sorption of n-butane also did not change. Merkel suggests that the primary impact of the filler, or additive, is on chain packing and not on chain stiffness or mobility. Lipatov and Fabulyak also argue that the effect of filler-surface interaction on chain mobility may not be detectable in rigid polymers [21]. Thus, the rigidity of PCHE and Zeonex may be a reason for the less effect of antiplasticization compared to the polyimide films. And based on our findings, in the case of rigid PCHE and Zeonex®, the dithiolene reduces permeability by affecting the diffusivity of the carbon dioxide since minimal change in solubility is observed.

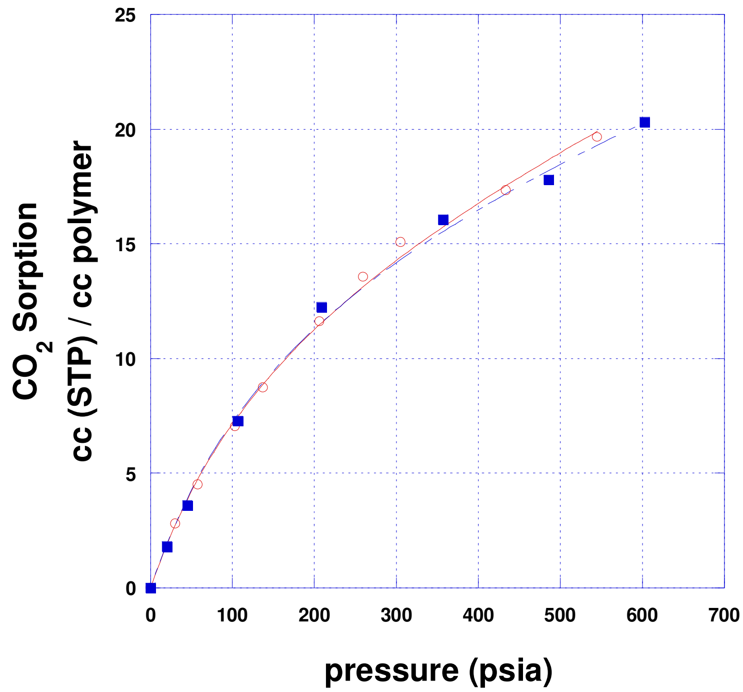

Figure 6.7. CO_2 Sorption at 35 ℃ in ○PCHE and ■PCHE/Ni[tfd]$_2$

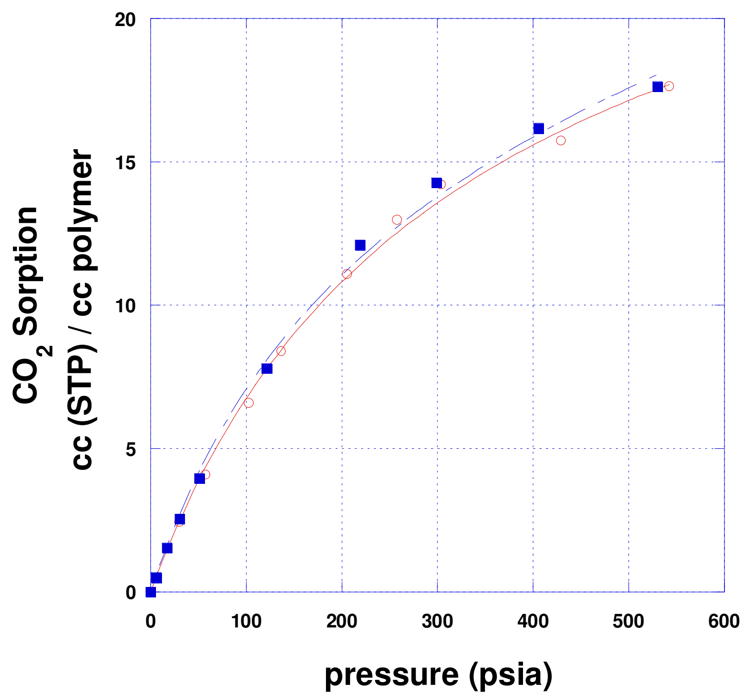

Figure 6.8. CO_2 Sorption at 35 ℃ in ○Zeonex® and ■Zeonex®/Ni[tfd]$_2$

6.2.5 Comparative analysis of overall effect of dithiolene on permeability

In Chapters 4 and 5, the effects of Ni[tfd]$_2$ on C_3H_6/C_3H_8 in polymides and polyolefins was discussed. In this chapter we discussed the permeability of CO_2/CH_4 and O_2/N_2. Below, in Tables 6.8 and 6.9, are comparison of the percent changed in permeation and selectivity, respectively, for all polymers and gases studied upon adding 10 wt% Ni[tfd]$_2$. The change in C_3H_6/C_3H_8 permeability is over 50% for all gases, while a larger reduction is seen in the polyimide films compared to the polyolefins. Interestingly, the decrease in O_2, N_2, CO_2, and CH_4 permeabilities are significantly larger in the polyimide films than in PCHE and Zeonex®. This again shows that there is a marked difference in the effect of Ni[tfd]2 on the polymer films. This difference may be due to the rigidity of the polyolefins as discussed earlier or may point towards the absence of aromatic rings as being the cause.

Table 6.8. Percent change in permeability with addition of Ni[tfd]$_2$

	6FDA-6FpDA	**6FDA-DAM**	**PCHE**	**Zeonex 480**
C_3H_6	83%	76%	54%	67%
C_3H_8	82%	76%	52%	67%
O_2	72%	34%	4%	13%
N_2	74%	46%	-8%	17%
CO_2	62%	67%	17%	16%
CH_4	76%	77%	19%	20%

Note: Increase (+); Decrease (-)

Table 6.9. Percent change in permeability selectivity with addition of $Ni[tfd]_2$

	6FDA-6FpDA	**6FDA-DAM**	**PCHE**	**Zeonex 480**
P_{C3H6}/P_{C3H8}	3%	0%	4%	0%
P_{O2}/P_{N2}	-9%	-22%	11%	-5%
P_{CO2}/P_{CH4}	-55%	-42%	-3%	-5%

Note: Increase (+); Decrease (-)

6.3 DYNAMIC MECHANICAL ANALYSIS

It has been shown that the addition of low molecular weight diluents to polymeric materials leads to an increase in the stiffness accompanied by decreases in the elongation to break and impact strength. Experimental results have shown this to be due a retardation on segmental motion [1-3, 10, 14, 16-19, 22]. The increase in stiffness also correlates well with observed reduction in the gas transport properties of these materials [1-3, 10]. Typically, the addition of low molecular weight diluents is marked by a decrease in the glass transition temperature (T_g), and an increase in the storage modulus (E') as well as the sub-T_g transition temperature (T_γ) [23]. Increases in the storage modulus and sub-T_g transition temperature are expected as the former is an indication of the increased stiffness of the materials and the latter indicates the retardation of segmental motion.

In the case of antiplasticization, the glass transition temperature of polymeric materials decreases. Numerous papers have indicated that such a phenomenon is due to a decrease in the fractional free volume (FFV) of the material [1-3, 10, 14, 19, 22]. It is believed that known “antiplasticizers” occupy the previously “unoccupied” areas of the polymer matrix. Dynamic Mechanical Analysis (DMA) was employed to study changes in the polymer properties with the addition of Ni[tfd]$_2$.

Figure 6.9 below shows the tan δ plots of pure 6FDA-6FpDA and 6FDA-6FpDA containing 10 wt% dithiolene. The plot for 6FDA-6FpDA is similar to that reported by Coleman who reported a T_g of 318℃ compared to 314℃ shown here [24]. The plot of 6FDA-6FpDA/Ni[tfd]$_2$ shows that it possesses a lower T_g which is a sign of antiplasticization as expected. Additionally, the tan δ peak is lower in 6FDA-

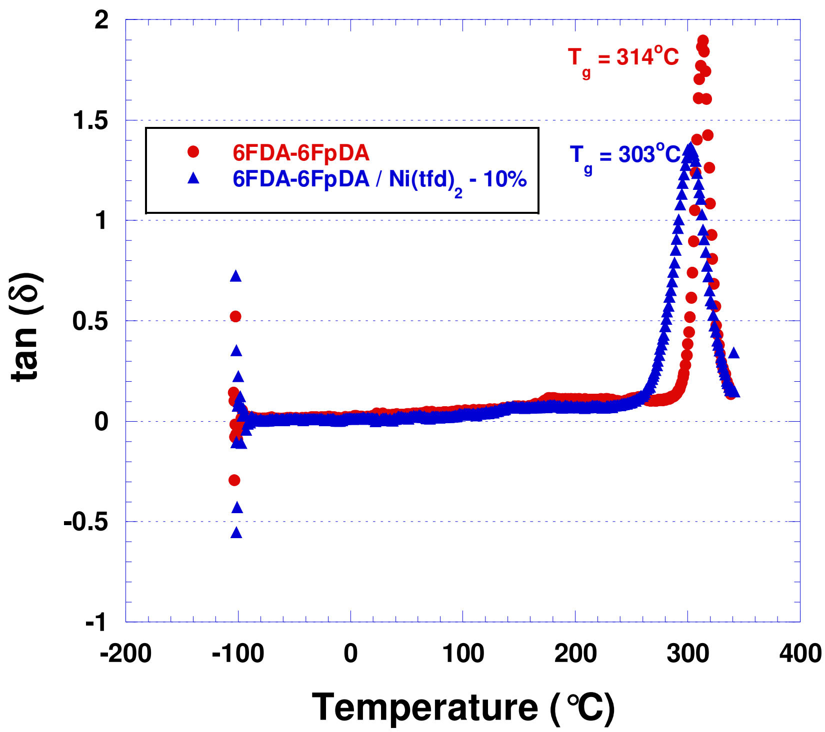

Figure 6.9. Tan δ for 6FDA-6FpDA and 6FDA-6FpDA/Ni[tfd]$_2$.

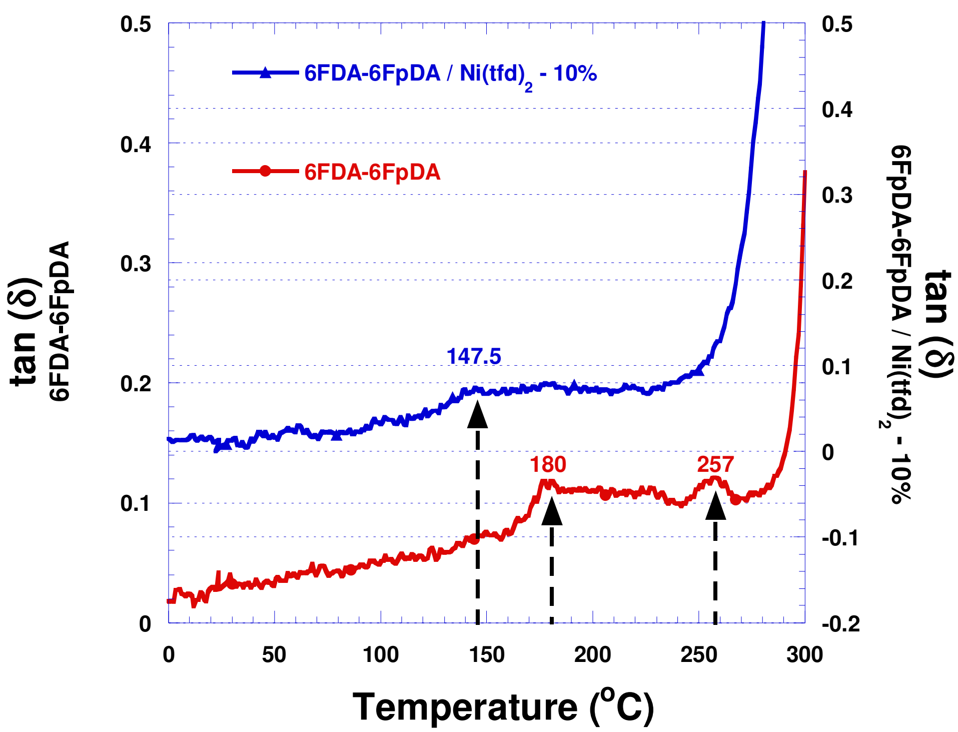

Figure 6.10. Sub-T_g transition of 6FDA-6FpDA and 6FDA-6FpDA/Ni[tfd]$_2$

6FpDA/Ni[tfd]2. Menard has attributed this response to a hardening or stiffening of the polymer sample [25].

Robeson and others have shown, with various polymers such as polysulfone and polyvinyl chloride, elimination of secondary transitions with the addition of additives. These transitions have been observed for 6FDA-6FpDA by Coleman and in this current work [24]. A closer view of the sub-T_g transitions is shown in Figure 6.10. The transitions in 6FDA-6FpDA at 180℃ and 257℃ are eliminated with addition of Ni[tfd]$_2$. In 6FDA-6FpDA/Ni[tfd]$_2$ a new, but weaker, peak appears at 147.5℃. The elimination of the peaks in 6FDA-6FpDA correlate well with the results of Robeson with polysulfone containing Arochlor 5442 (42% chlorinated terphenyl). As the amount of the additive increased, the peak of the polysulfone sub-T_g peak decreased. Maeda and Paul observed similar results but also reported the appearance of a new peak with addition of a diluent, or additive. New, but weaker peaks were observed when di-2-ethylhexylphthalate (DOP) and Kronitex 50 were added to PPO and become more prominent as the content increased. Others observed similar results, and Maeda and Paul argued that the size and location of these peaks are dependent on the nature of the diluent since the peaks are not always present in all antiplasticization systems [2].

Figure 6.11 below shows that the storage module of 6FDA-6FpDA increases with the addition of 10% Ni[tfd]$_2$. In addition to a reduction in T_g, an increase in the storage modulus due to an increased stiffness is attributed to antiplasticization.

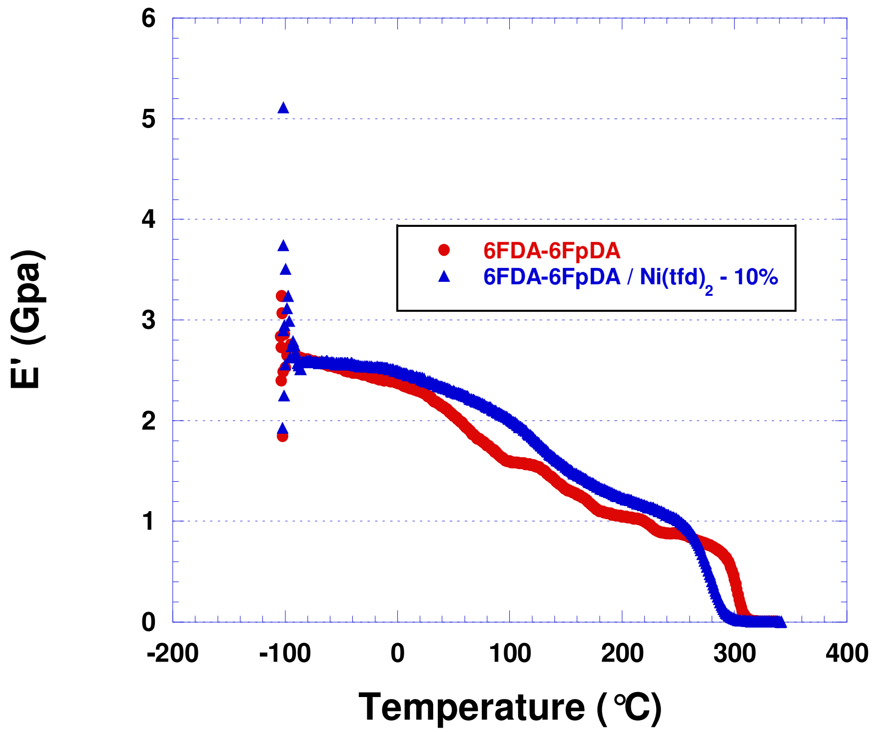

Figure 6.11. Storage modulus for 6FDA-6FpDA and 6FDA-6FpDA/Ni$[tfd]_2$

The DMA scans for PCHE and Zeonex® are shown in Figures 6.12-6.15. It was not possible to obtain a tan δ peak for neither the neat polymer nor the corresponding dithiolene-containing films. The samples could not withstand the conditions of the DMA experiment. At the onset of the tan δ peak, the films would break and the experiment could not be continued. According to ZeonChemicals company literature, the deformation temperature of Zeonex® is 123ºC which is close to the temperature at which the film breaks. It is possible that PCHE films break for a similar reason. The deformation temperature for PCHE was not found, though.

Despite the inability to measure the tan δ peak, there is evidence of increased stiffness in Figures 6.13 and 6.15. For both PCHE and Zeonex®, the pure film has a lower modulus than the dithiolene film. Also, the tan δ plots for PCHE and Zeonex® do not display secondary transitions. This response may suggest that the extent of antiplasticization is not great in PCHE and Zeonex®. Researchers have illustrated that antiplasticization is weak in polystyrene and other brittle polymers with no or very small secondary transition temperatures. So, by this tenet PCHE and Zeonex® do not antiplasticize to a great extent.

The onset of the E' drop is located at a similar temperature for both the pure film and the dithiolene film in PCHE and Zeonex® also. This would suggest that there is little or minimal change in the T_g with the addition of $Ni[tfd]_2$, but DSC plots suggest that there is a change in the T_g. Figures 6.16 and 6.17 are DSC plots of PCHE and Zeonex®. They show that with addition of 10% dithiolene, the T_g of both PCHE and Zeonex® decreases. At the moment, it is not understood why there is a difference in T_g via the various methods of measurement.

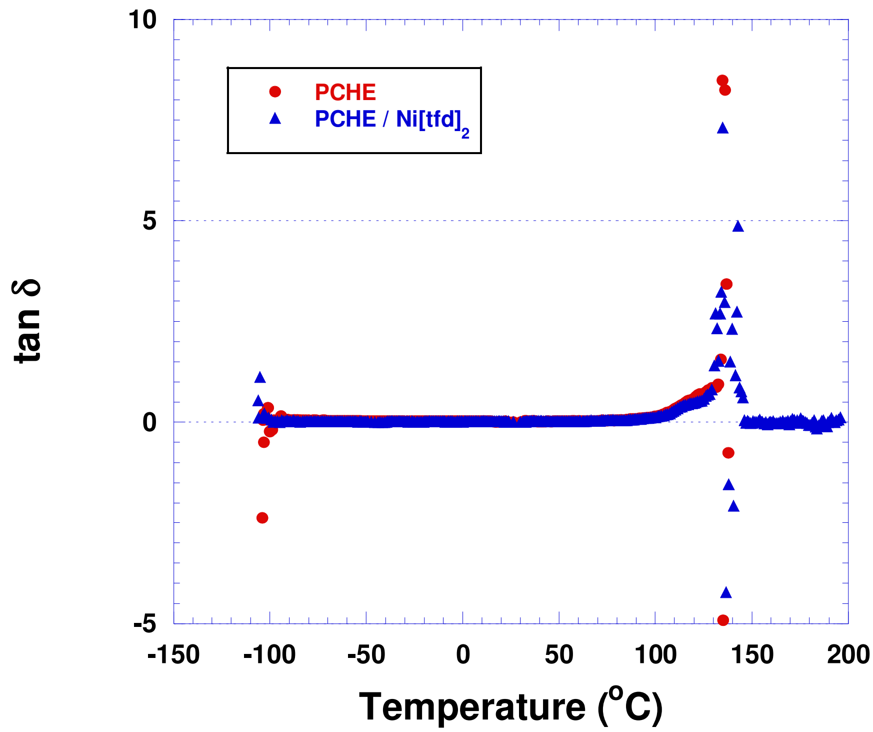

Figure 6.12. Tan δ for PCHE and PCHE/Ni[tfd]$_2$

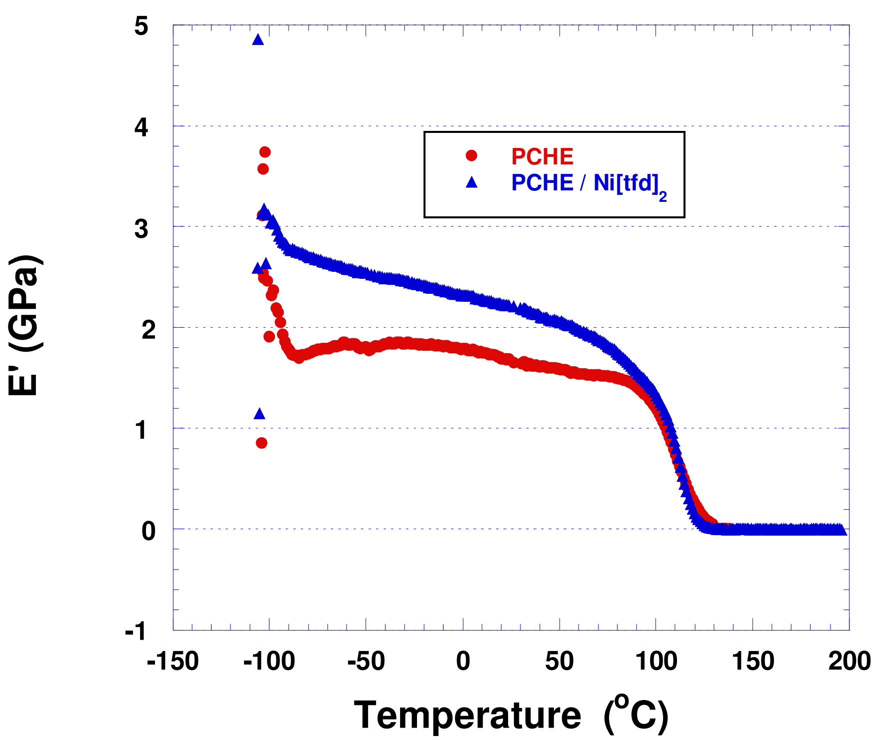

Figure 6.13. Storage modulus for PCHE and PCHE/Ni[tfd]$_2$

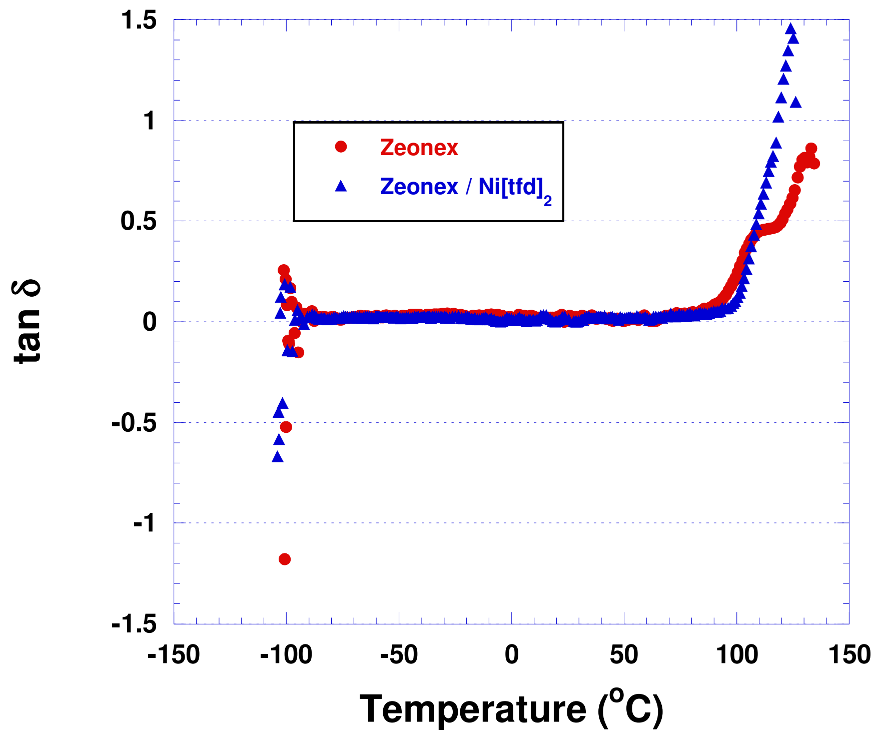

Figure 6.14. Tan δ for Zeonex® and Zeonex®/Ni[tfd]$_2$

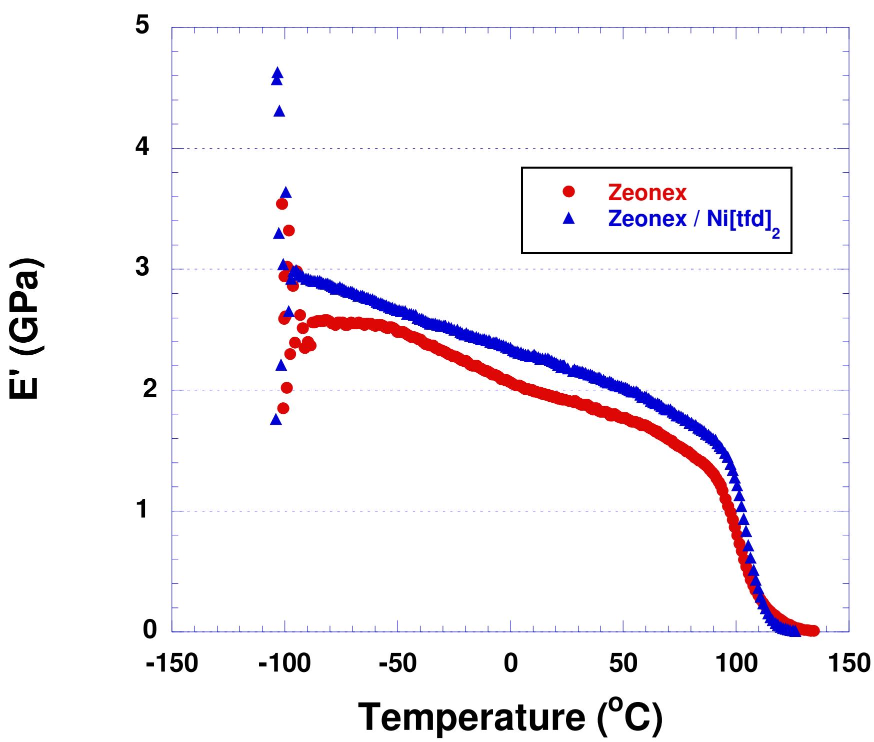

Figure 6.15. Storage modulus for Zeonex® and Zeonex®/Ni[tfd]$_2$

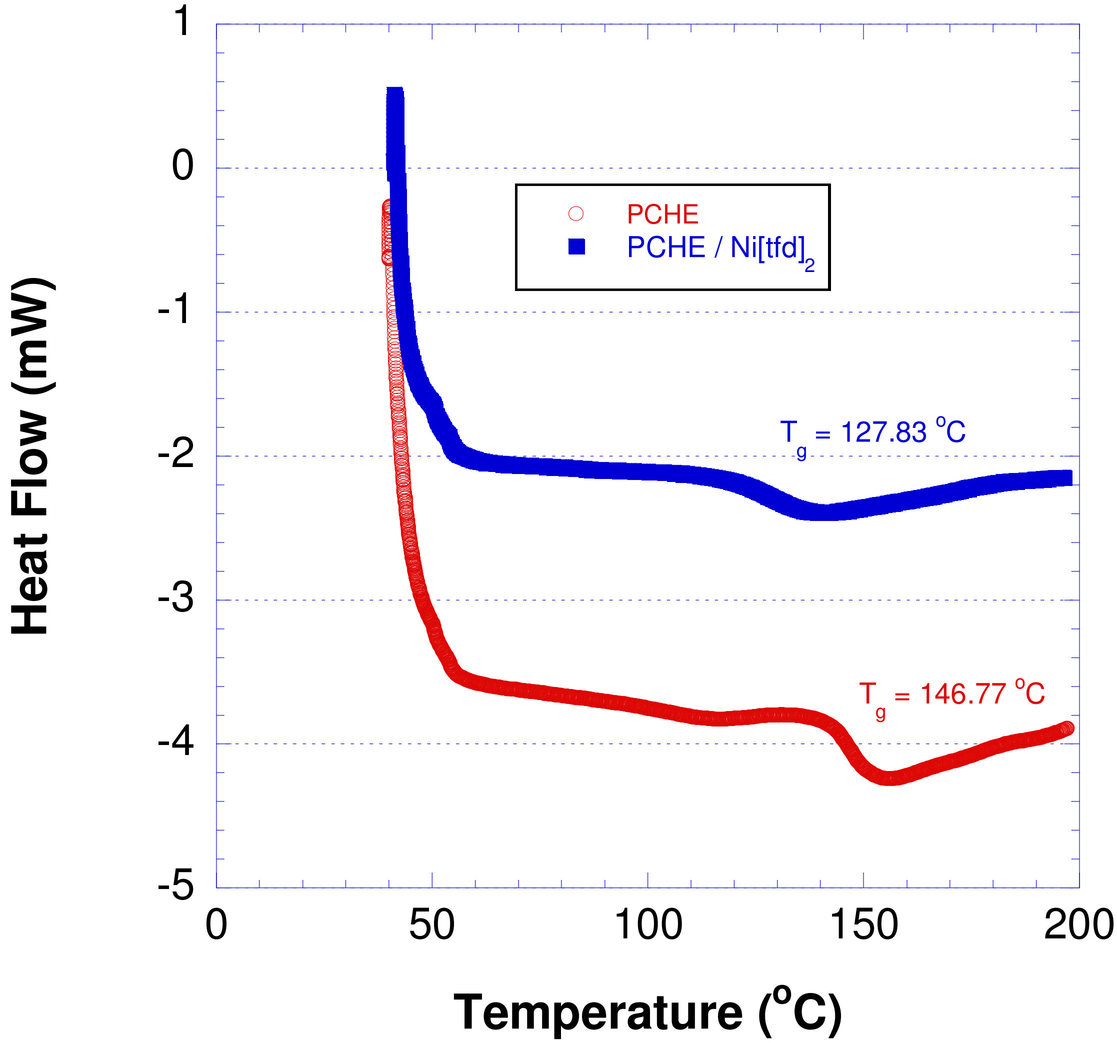

Figure 6.16. Glass transition temperature of pure PCHE and PCHE/Ni[tfd]$_2$ as measured by DSC.

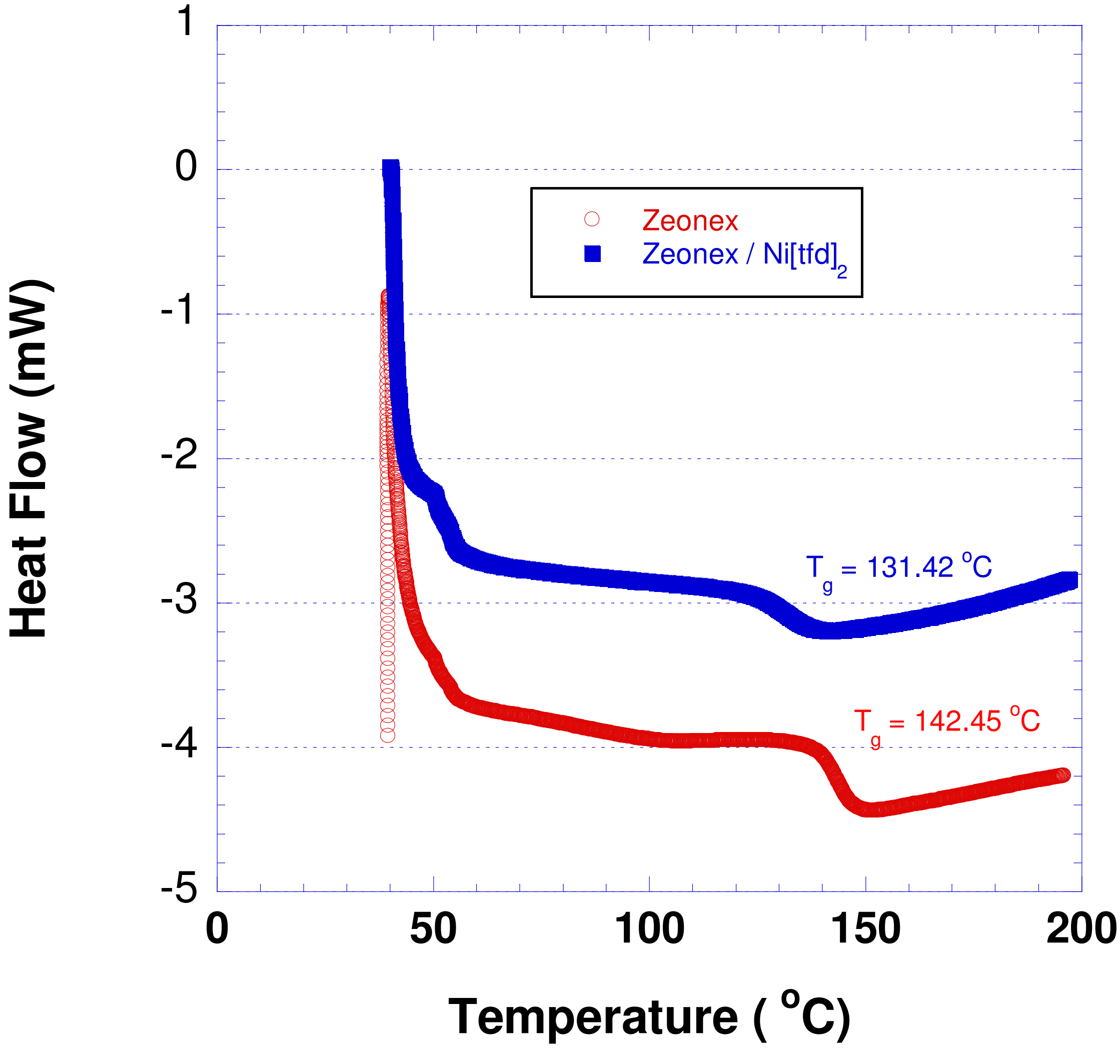

Figure 6.17. Glass transition temperature of pure Zeonex® and Zeonex®/Ni[tfd]$_2$ as measured by DSC.

6.4 MODEL FOR CALCULATING FRACTIONAL FREE VOLUME of DITHIOLENE-CONTAINING FILMS

As discussed previously, it has been shown that the addition of low molecular weight diluents leads to an increase in the stiffness of polymeric materials by retarding their segmental motion [1-3, 10, 12, 16, 17, 26-29]. The increase in stiffness correlates well with observed reduction in the gas transport properties of these materials. Typically, the addition of low molecular weight diluents is marked by a decrease in the glass transition temperature (T_g), and an increase in the storage modulus (E') as well as the sub-T_g transition temperature (T_γ) [1-3, 10, 19]. Increases in the storage modulus and sub-T_g transition temperature are expected as the former is an indication of the increased stiffness of the materials and the latter indicates the retardation of segmental motion.

In the case of antiplasticization, the glass transition temperature of polymeric materials decreases. It is believed that known "antiplasticizers" occupy the previously "unoccupied" areas of the polymer matrix. In the previous section, DSC results showed that the addition of the dithiolene to polymer films decreases the T_g. Maeda and Paul has attributed the drop in T_g to a decrease in FFV [1-3, 10]. It is usually difficult to quantify the FFV of a polymer-additive mixture because the FFV of the additive is not known. Ruiz-Trevino and Paul have attempted to do so by developing a model to estimate the specific volume of polymer-additive systems [19, 30]. Madden combined the theory of Maeda and Paul with that of Ruiz-Trevino to form a model that estimated the FFV of a polymer-additive mixture [31].

The FFV of a polymer-additive mixture can be written as [1, 31]:

$$FFV_{mix} = \frac{V_{mix}^{g} - (V_0)_{mix}}{V_{mix}^{g}} \tag{6.1}$$

where V_{mix}^{g} is the specific volume of the mixture in the glassy state and $(V_0)_{mix}$ is the occupied specific volume. $(V_0)_{mix}$ is given as [1, 31]

$$(V_0)_{mix} = 1.3\left[w_d \sum_{j=1}^{J} (V_w)_j + w_p \sum_{k=1}^{K} (V_w)_k \right]$$

The terms w_d and w_p are the weight percent of the diluent and polymer, respectively, and V_w is the van der Waals volume of the respective groups in the polymer repeat unit.

Assuming a linear volume-temperature relationship and that volume additivity applies in the liquid state, specific volume of the mixture in the glassy state, V_{mix}^{g}, can be measured using the following proposed by Ruiz-Trevino and Paul [30]:

$$V_{mix}^{g}(T) = w_d V_{dl}(T) + w_p V_{pl}(T) + \left(\frac{dV_{ml}}{dT} - \frac{dV_{mg}}{dT} \right)(T_{gm} - T) \tag{6.2}$$

where V_{dl} and V_{pl} are the equilibrium specific volumes of the diluent (additive) and polymer in the liquid state, respectively. They are not directly calculated but can be calculated from:

$$V_{il} = V_{ig}(T) + \left(\frac{dV_{ml}}{dT} - \frac{dV_{mg}}{dT} \right)(T_{gm} - T) \tag{6.3}$$

The quantity: $\left(\frac{dV_{ml}}{dT}-\frac{dV_{mg}}{dT}\right)$ represents the thermal expansion coefficients of the mixture in the liquid and glassy state, respectively. Ruiz-Trevino and Paul have approximated this to be equivalent to the thermal expansion coefficients of the pure polymer [30, 31]:

$$\left(\frac{dV_{ml}}{dT}-\frac{dV_{mg}}{dT}\right)\approx\left(\frac{dV_{pl}}{dT}-\frac{dV_{pg}}{dT}\right) \tag{6.4}$$

The polymer thermal expansion coefficients are estimated as:

$$\frac{dV_{pl}}{dT}=1x10^{-3}\frac{V_w}{MW} \tag{6.5}$$

and

$$\frac{dV_{pg}}{dT}=0.45x10^{-3}\frac{V_w}{MW} \tag{6.6}$$

The glass transition temperature of the mixture, T_{gm}, is given in the form of the Gordon-Taylor equation as [30]:

$$T_{gm}=\frac{w_d T_{gd}+Kw_p T_{gp}}{w_d+Kw_p} \tag{6.7}$$

where K is an adjustable parameter. Values of K are found by fitting experimental data.

Using this fit, the fractional free volume the polymer-dithiolene mixture could be calculated. Unfortunately, the van der Waals volume of the dithiolene was not calculated because the group contribution values are not available in the current literature. Group contribution values could be calculated via methods developed my Bondi, but is beyond the scope of this work. Nevertheless the model presented can be used for predicting the affect of an additive on a polymer sample. An experimental fit to determine the parameter, K is shown in Appendix B.

6.5 INFRARED SPECTROSCOPY

In order to investigate the possible interactions of the dithiolene and the polymer matrix, FTIR experiments were conducted. Figure 6.18 shows the spectra for 6FDA-DAM and 6FDA-DAM/Ni[tfd]$_2$. The spectra are similar except for the broadening of the peak at 3500 cm^{-1} and the appearance of a peak at 2300 cm^{-1}. According to Schlapfer and Nakamoto, the characteristic peaks of Ni[tfd]$_2$ are at low frequency (Figure 6.19) [32]. Due to the noise at low frequency, which is probably due to the presence of water, it is not possible to discern the peaks attributed to the dithiolene.

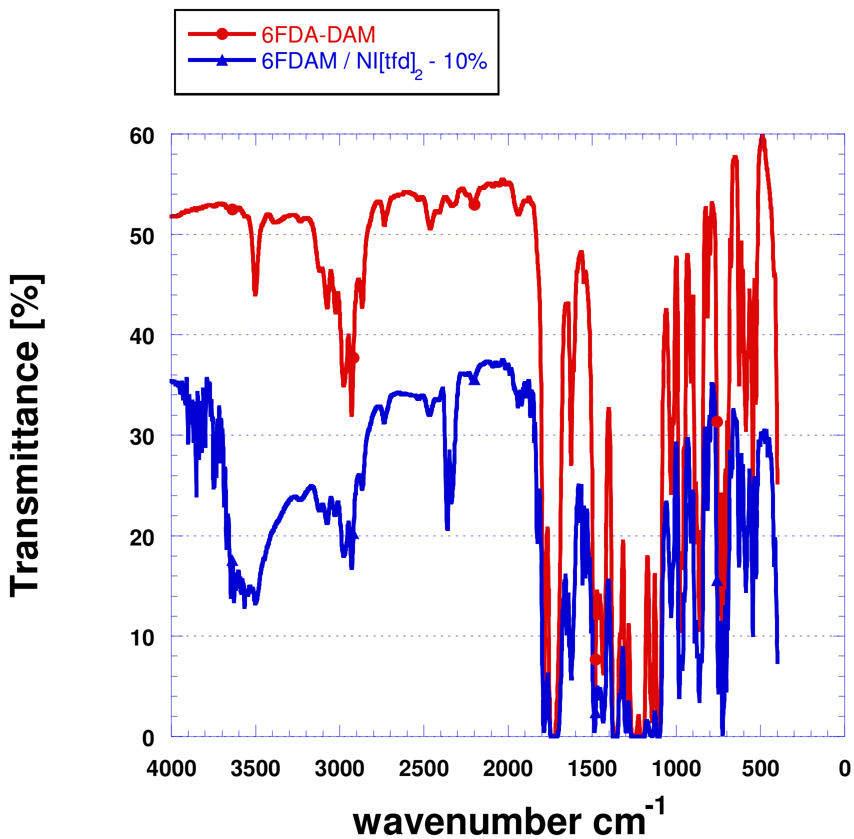

Figure 6.18. IR Spectra for 6FDA-DAM and 6FDA-DAM/Ni[tfd]$_2$

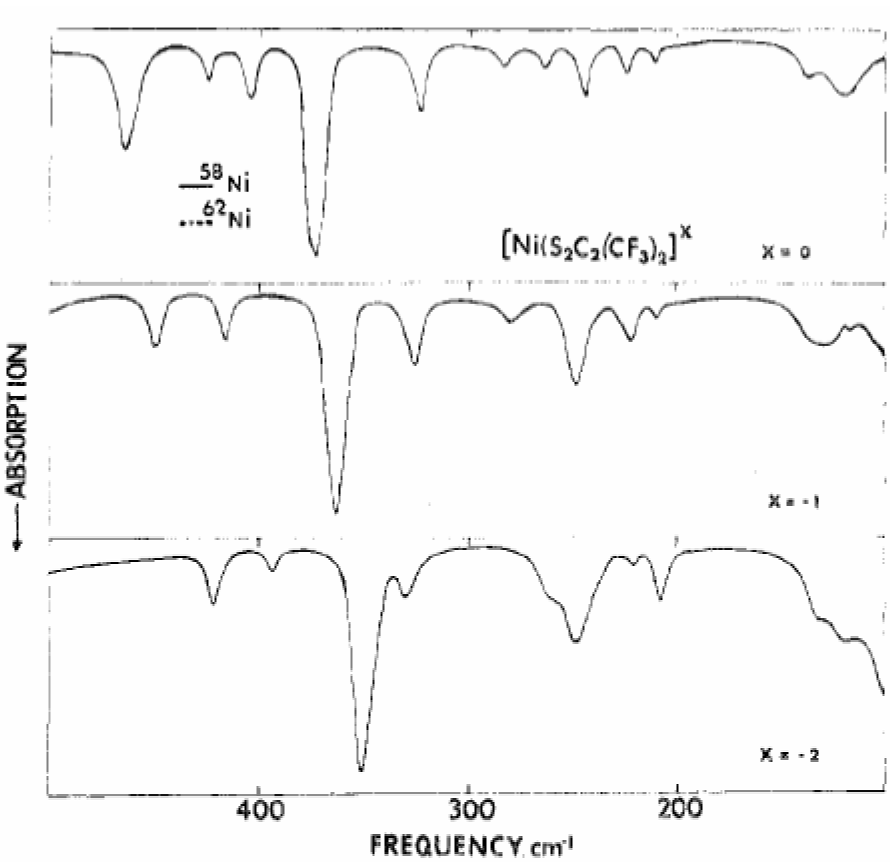

Figure 4. Low-frequency infrared spectra of $[Ni(S_2C_2(CF_3)_2)_2]^x$.

Figure 6.19. IR Spectra of $Ni[tfd]_2$.

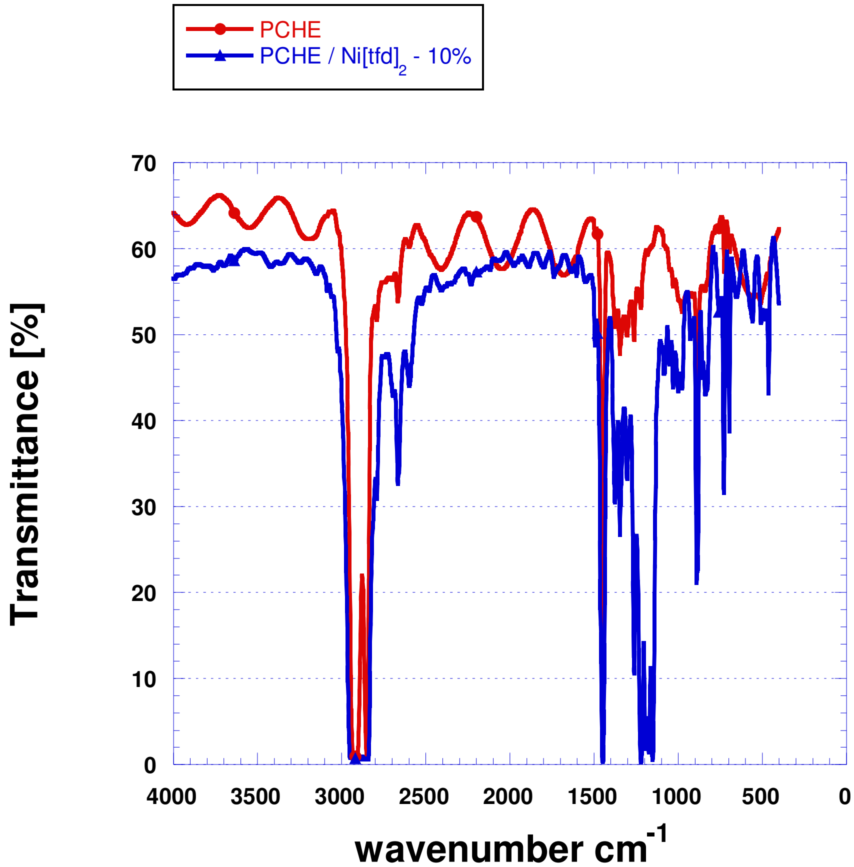

Figure 6.20. IR Spectra for PCHE and PCHE/Ni[tfd]$_2$

The IR spectra for the non-aromatic polymer, PCHE is shown in Figure 6.20. The peaks are similar in both the pure and dithiolene film. There appear to be no signs of complexation of coordination in these films. At the moment, it is not quite understood why, the spectra for pure PCHE is wavy in manner.

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CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 SUMMARY AND CONCLUSIONS

As detailed in Chapter 1, the purpose of this work was to research three main objectives:

> **1. Measure the transport properties at ambient conditions as well as elevated temperatures and pressures to investigate the performance of the dithiolenes under extreme conditions.**
>
> **2. Measure the effects of increasing dithiolene content on the C_3H_6/C_3H_8 transport properties.**
>
> **3. Investigate and explain the reduction in permeability observed with incorporation of the dithiolene in a polymeric membrane.**

In Chapter 4, the transport properties of the polyimides 6FDA-6FpDA and 6FDA-DAM were studied by measuring permeation and sorption of pure propylene and propane in both neat samples and those containing small amounts of the dithiolene, $Ni[S_2C_2(CF_3)_2]_2$. This dithiolene was chosen to investigate its ability to serve as a facilitator and increase the solubility selectivity of the chosen polyimides. Enhancement in solubility selectivity was observed, but the permeability selectivity was decreased due to reductions in the permeability of both propylene and propane. The effects were not overcome by increasing temperature or pressure. In fact, the plasticization response of the polyimides seemed to be reduced in the presence of $Ni[tfd]_2$.

As per our second objective, the effect of increasing dithiolene content was investigated. Unfortunately, the solubility of dithiolene in the polymer samples was limited to 12 wt% dithiolene. Subsequent studies were conducted at 10 wt% dithiolene.

The purpose of Objective 3 was to investigate and explain the apparent reduction in permeability and solubility upon addition of $Ni[tfd]_2$. The literature suggested that $Ni[S_2C_2(CF_3)_2]_2$ is known for having strong interactions with complex aromatics [1]. We hypothesized that similar interactions could be occurring in polyimide-dithiolene films and interfering with the complexation properties between the dithiolene and propylene gas. Such interactions may have explained the hindrance of propane permeation also. To test this hypothesis, the non-aromatic polymers polycyclohexylene and a polynorbornene derivative trademarked Zeonex® were also studied. Nonetheless, the observed reduction in permeability and solubility was also observed in these non-aromatic polymers as outlined in Chapter 5.

Investigation of other gases such as oxygen, nitrogen, carbon dioxide and methane further supported what is known as an antiplasticization effect. Antiplasticization is marked by reductions in permeability and solubility consequently to decreases in chain mobility and fractional free volume of the polymer with addition of an additive or diluent [2-5]. A reduction in fractional free volume has been correlated to a reduction in the Langmuir capacity coefficient, $C'_{H,}$ which was observed in this work [4]. Additionally, the results with other gas pairs suggest a change in the free volume distribution with the addition of dithiolene. In the polyimides, the selectivity of CO_2/CH_4 is reduced to a greater amount than O_2/N_2 selectivity when compared to the pure polymer samples.

Studies with the polyaromatics also indicated that the overall reduction of permeation and sorption differed from that of the polyimides. Propylene and propane permeability is reduced 20-30% less in the polycycloolefins compared to the polyimides. Carbon dioxide, methane, oxygen, and nitrogen permeation was reduced to a lesser amount with addition of $Ni[tfd]_2$ in PCHE and Zeonex® compared to propylene and propane. Furthermore the effect of sorption differs in PCHE and Zeonex® differs from the polyimides also. Upon addition of $Ni[tfd]_2$, propylene sorption is not reduced in PCHE and Zeonex® and propane sorption is reduced by a relatively low level resulting in sorption selectivity enhancement. Carbon dioxide sorption was not reduced in either PCHE or Zeonex® also. Authors have indicated that such a response is due to an additive's affect on chain packing rather then chain mobility in some rigid polymers.

Dynamic Mechanical Analysis indicate increases in stiffness and reductions in the glass transition temperature with the addition of 10% $Ni[tfd]_2$ supporting an antiplasticization response. Despite these responses, the whole of the research indicate a more complex picture than simply antiplasticization. It appears that various factors play a role in the observed results that include, but are not limited to, choice of polymer, choice of dithiolene, and solubility limits.

The dithiolene, $Ni[S_2C_2(CF_3)_2]_2$ was not proven to be a suitable carrier for separating propylene from propane via a facilitated transport mechanism. Although, there is evidence of some solubility enhancement, overall permeability selectivity is not enhanced upon addition of $Ni[tfd]_2$ to a polymer film; which is due to a decrease in the diffusivity of both propylene and propane. This effect is common for all gases measured in both polyimide and polycycloolefin films. Reduction in permeability and solubility suggest an antiplasticization response which is accompanied by a reduction in the glass transition temperature and an increase in polymer stiffness. This phenomenon is supported by the results of Dynamic Mechanical Analysis. Experiments involving polymers known as polycycloolefins supported observations made in polyimide films but provided a contrasting view in certain areas. Specifically, these experiments suggested that in addition to antiplasticization there is evidence of polymer-dithiolene interactions and simple compaction/rigidification which may be responsible for reductions in gas transport in the presence of $Ni[S_2C_2(CF_3)_2]_2$. In the following section, recommendations for improving the performance of propylene/propane gas separation membrane.

7.2 RECOMMENDATIONS

The initial goal of this work was to enhance the overall permeability selectivity for a propylene/propane system via facilitated transport. We envisioned the ability to enhance solubility selectivity in the absence of adverse affects on the mobility selectivity. As this was not achieved, the following recommendations are provided to achieve this goal and to further understand the observations made in this work.

- Many research groups have attempted to use silver ions as a facilitator for olefin/paraffin separation. Nickel dithiolenes seemed to be promising because they did not undergo poisoning common to silver ions [6]. Wang and Steifel showed that nickel dithiolenes are capable of selectively and reversibly complexing with propylene in solution form but only a small group of dithiolenes were investigated. It may be possible to follow on the work by previous groups [1, 7, 8] and synthesize more suitable dithiolenes for membrane applications. It may alo be possible to take better advantage of dithiolene properties by physically binding it to the polymer backbone via crosslinking. This does not promise favorable effects but would aid in better understanding the mechanism at which dithiolenes interact with the polymer matrix and olefin gases. Wang et al successfully produced poycarbonates and polyurethanes with bis(dithiolenes) in the main chain [9]. These polymers were electroactive and showed unique opto-electronic properties. It may be useful to study these polymers for their gas separation properties.

- Our work suggests that the $Ni[tfd]_2$ may narrow the free volume distribution of polymers. This hypothesis could be further investigated through x-ray diffraction. X-ray diffraction would also provide insight on the changes to the relative size of the un-relaxed regions of the polymer matrix sometimes referred to as "holes."
- Kim et al studied interactions in polymer-metal systems using FT-IR and UV spectroscopy [10]. Specifically, they studied polymer-metal, metal-olefin, polymer-metal-olefin interactions in a controlled environment. They were able to isolate the specific interactions that are responsible for the facilitated transport. In the present work, it was not possible to study all three interactions in a controlled environment, but would be valuable in learning more about polymer-dithiolene-olefin interactions.
- The latest research in the gas separation membranes is in the area of mixed matrix membranes which are specifically tuned for the gas pair in question. Although it may be difficult, with the advances in the field thus far, it is feasible to believe membranes incorporating intricately designed zeolites can be capable of achieving highly selective separation of propylene from propane.
- Earlier work with nickel dithiolenes indicated differing responses based on the solvent used to put them into solution. For this work, we chose a suitable solvent for the polymer in question and kept it consistent to minimize variables. Research with various solvents would be valuable in determining the proper solvent polymer pair that would unlock the

potential of nickel dithiolenes in a facilitated transport environment. Although, this would not be feasible for an industrial application, it would still provide insightful academic research.

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APPENDIX A

COMPARISON OF DITHIOLENE SAMPLE BATCHES

A.1 PERMEABILITY AND SOLUBILITY COMPARISONS

In Chapter 4, it was mentioned that two batches of Ni[tfd]$_2$ were used in the early stages of this research. For consistency, only the the second and newer batch was used for the majority of the work. There was a significant difference in appearance between the two batches. The older batch was dark green in color while the newer batch was deep purple. Davison et al [1] reported that solutions of Ni[tfd]$_2$ with basics solvents were brown-green so is speculated that overexposure to air moisture may have caused the difference in color since this batch was several years old. Nonetheless, experiments with both batches of dithiolene had similar results. Gas permeability was decreased with addition of the old batch of dithiolene, but in some cases the absolute values of permeability differed. As shown in Table A.1 there appears to be a differenc in permeability between the 6FDA-6FpDA samples with the different dithiolene batches. At this time, the reason for the discrepancy is not known. Furthermore, the effect on sorption is not that same as in permeabtion. In figures A.1 and A.2 are the sorption isotherms in 6FDA-DAM/Ni[tfd]2 for propane and propylene, respectively. There is no apparent difference between the isotherms for the different batches of dithiolene. It was because of this inconsistency that it was decided to use the newer batch of dithiolenes to ensure further variability was not introduced into the experiments.

Table A.1. Permeability of 6FDA-6FpDA containing different batches of $Ni[tfd]_2$ at 35℃ and 2 atm

	P_{O2}	P_{N2}	P_{CO2}	P_{CH4}	P_{O2}/P_{N2}	P_{CO2}/P_{CH4}
New Batch	6.7	1.3	64	0.6	5.1	69
Old Batch	9.3	1.6	42	1.0	5.9	41

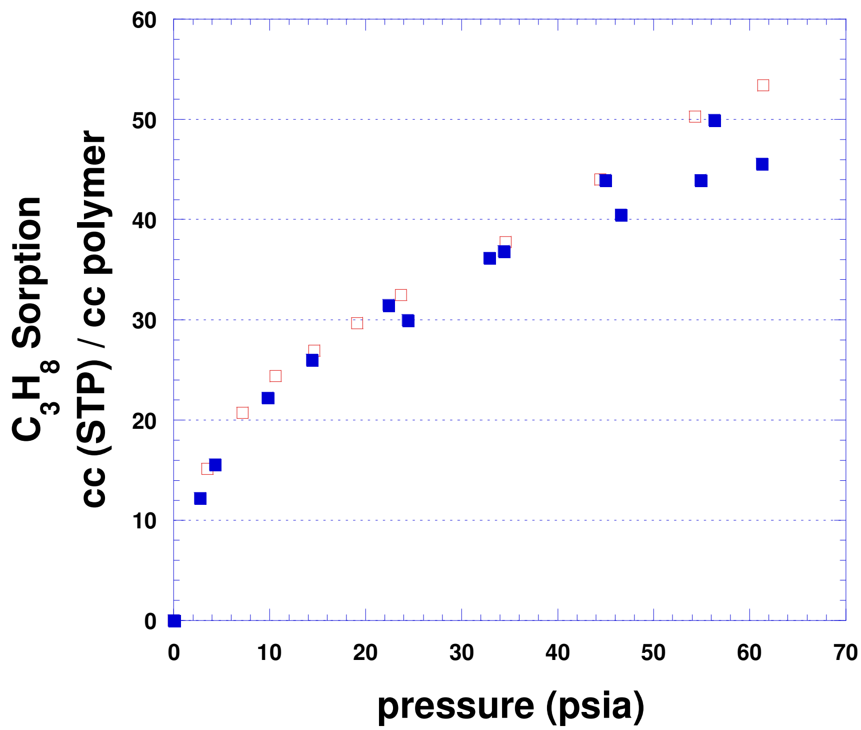

Figure A.1. C_3H_8 Sorption Isotherm for 6FDA-DAM at 35℃ containing different batches of $Ni[tfd]_2$. □ Old Batch ■ New Batch

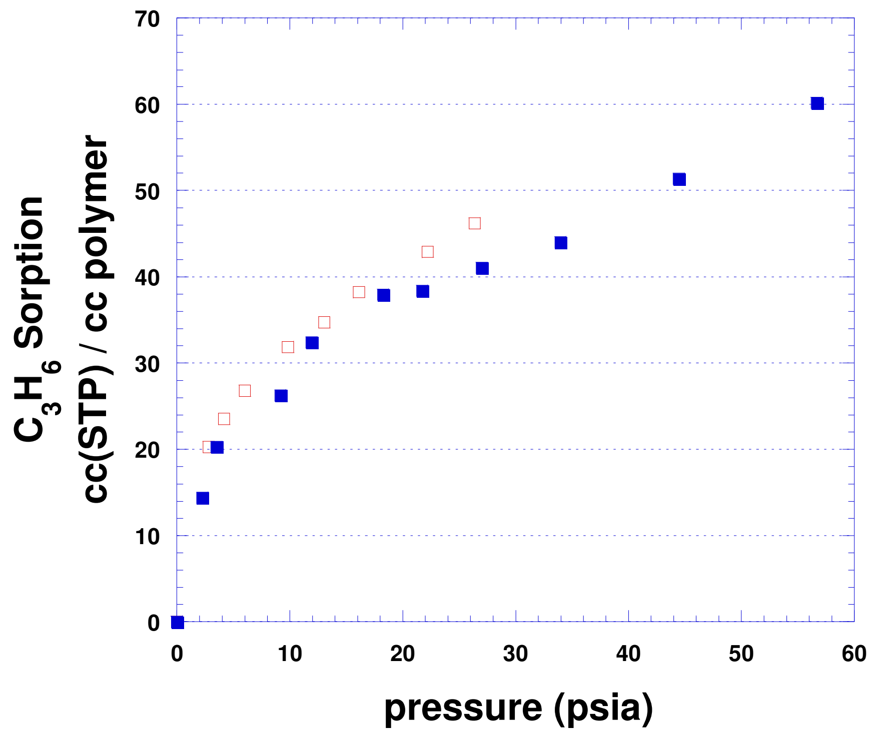

Figure A.2. C_3H_6 Sorption Isotherm for 6FDA-DAM at 35℃ containing different batches of Ni[tfd]$_2$. □ Old Batch ■ New Batch

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APPENDIX B

ESTIMATING FRACTIONAL FREE VOLUME OF POLYMER FILMS

B.1 FFV OF PURE POLYMER SAMPLES

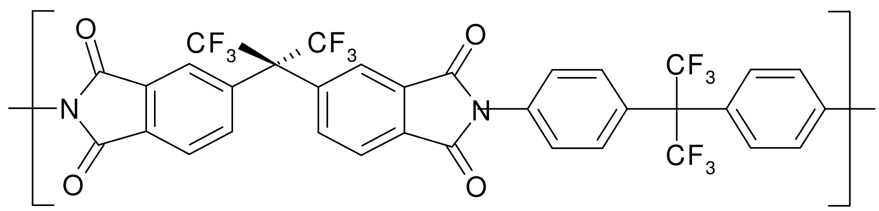
Fractional free volume (FFV) describes the relative packing of polymer chains, taking into account the specific and occupied volumes of the polymer matrix. FFV is the ratio of the specific free volume to the specific volume. The specific free volume calculation, developed by Lee [1], uses the group contribution method of Van Krevelen [2] and is defined as the difference between the experimentally measure specific volume, V, and the occupied volume, V_0.

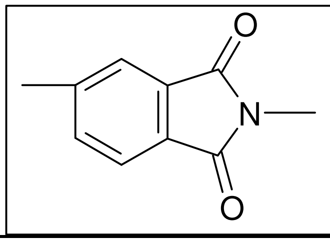
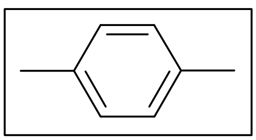
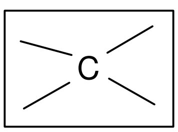
$$FFV = \frac{V - V_o}{V} \qquad \text{(B.1)}$$

Bondi [3] approximates V_0 as $1.3V_w$, where V_w, is the Van der Waals volume obtained from group contribution calculations.

In general, increases in FFV lead to higher permeation rates as a result of an increased diffusion coefficient. Although studies have shown that membrane transport properties can be tuned using various functional groups that increase and decrease the FFV [4], the distribution of FFV also plays a role in transport properties [5].

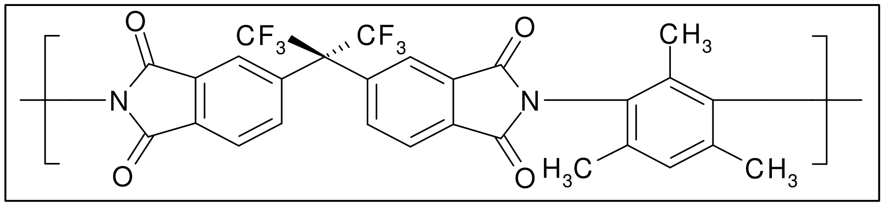
B.1.1 FFV Calculation for 6FDA-6FpDA

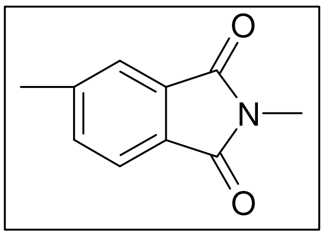
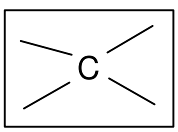
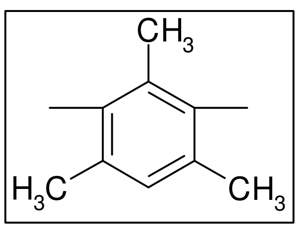


Group	Vw	No.	Total
	69.4	2	138.8
$-CF_3$	21.3	4	85.2
	43.3	2	86.6
	3.3	2	6.6

Vw(cm3/mol	317.2
Vw(cm3/g)	0.42722
Vo	0.55538
MW	742.477
density	1.466
V	0.68213
FFV	**0.186**

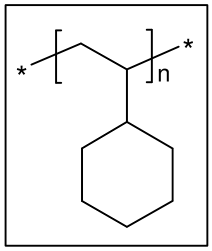
B.1.2 FFV Calculation for 6FDA-DAM

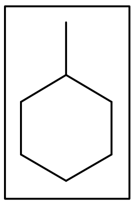
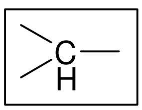
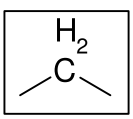


Group	Vw	No.	Total
	69.4	2	138.8
$-CF_3$	21.3	2	42.6
	3.3	1	3.3
	76.75	1	76.75

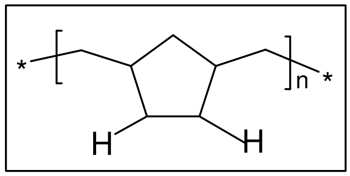
Vw(cm3/mol	261.45
Vw(cm3/g)	0.46988
Vo	0.61084
MW	556.421
density	1.33
V	0.75188
FFV	**0.188**

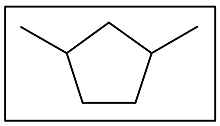
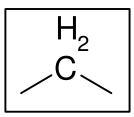
B.1.3 FFV Calculation for PCHE



Group	Vw	No.	Total
	56.8	1	56.8
	6.8	1	6.8
	10.23	1	10.23
		Vw(cm3/mol	73.83
		Vw(cm3/g)	0.669968809
		Vo	0.870959452
		MW	110.19916
		density	0.94
		V	1.063829787
		FFV	**0.181**

B.1.4 FFV Calculation for ZEONEX®



Group	Vw	No.	Total
	43	1	43
	10.23	2	20.46

Vw(cm3/mol	63.46
Vw(cm3/g)	0.65986
Vo	0.85781
MW	96.1723
density	1.01
V	0.9901
FFV	**0.134**

B.2 FFV OF DITHIOLENE-CONTAINING POLYMER SAMPLES

In Chapter 6 a model was proposed for calculating the fractional free volume of dithiolene films. Due to the inability to calculate or measure van der Waals volume of $Ni[tfd]_2$, a complete calculation of fractional free volume of dithiolene containing films could not be conducted. If one is to calculate the effect of an additive on the fractional free volume, experimental data of polymer-additive mixture glass transition temperatures at varying amounts of additive is necessary. Table B.1 lists the T_g of PCHE-dithiolene films at increasing amounts of $Ni[tfd]_2$. The data is plotted and fit to equation B.1. From the fit, the T_g of the dithiolene is 138.9 °C and the adjustable parameter, K, is 0.779.

$$T_{gm} = \frac{w_d T_{gd} + K w_p T_{gp}}{w_d + K w_p} \qquad \text{(B.2)}$$

Table B.1. Effect of Dithiolene on T_g of PCHE

Wt % Dithiolene	T_g (°C)
0	145.6
2	134.7
5	127
10	122.9

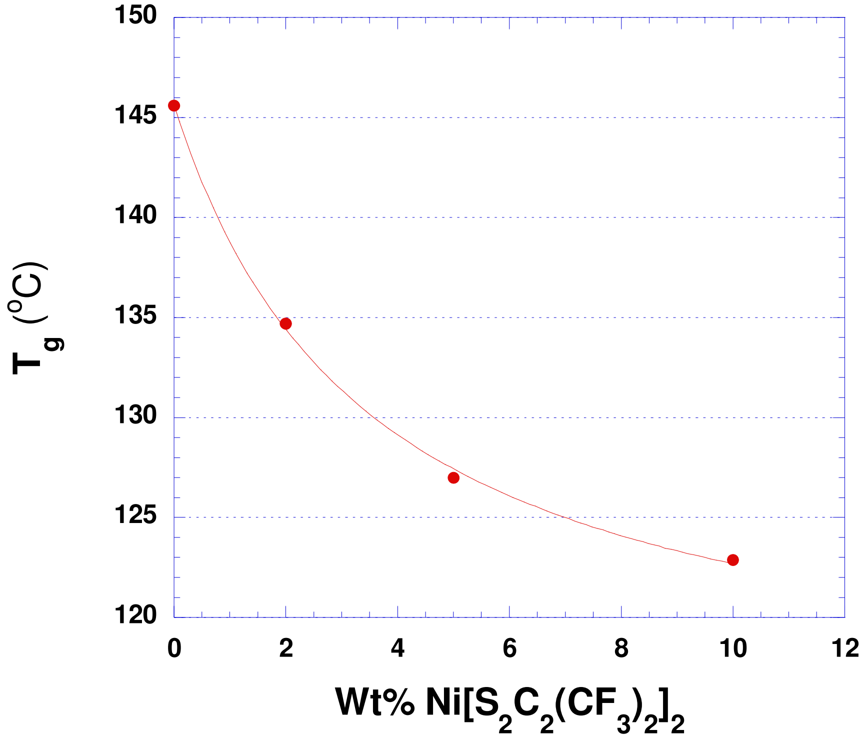


Figure B.1. Plot of T_g vs. Dithiolene weight percent for PCHE

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APPENDIX C

COMPRESSIBILITY FACTOR EQUATIONS

The following pressure and temperature dependent compressibility factor equations were used in determining solubility coefficients. The equations were constructed from a least squares fit of factors calculated by software programs provided by the National Institute of Standards and Technology (NIST). The SUPERTRAPP program was used to calculate C_3H_6 and C_3H_8 factors. Compressibility factors for O_2, N_2, CO_2 and CH_4 were calculated using the program, NIST12: Thermodynamic and Transport Properties of Pure Fluids.

C.1 PROPYLENE

p [=] psia

35°C: $Z = 1 - 8.8605 \times 10^{-4}p - 3.0317 \times 10^{-7}p^2 - 3.1067 \times 10^{-9}p^3$

50°C: $Z = 1 - 7.8376 \times 10^{-4}p + 3.8075 \times 10^{-7}p^2 - 2.4345 \times 10^{-9}p^3$

75°C: $Z = 1 - 5.9822 \times 10^{-4}p - 1.8682 \times 10^{-7}p^2 - 6.1378 \times 10^{-9}p^3$

90°C: $Z = 1 - 5.2037 \times 10^{-4}p - 1.6990 \times 10^{-7}p^2 - 2.8334 \times 10^{-9}p^3$

C.2 PROPANE

p [=] psia

35℃: $Z = 1 - 9.9332 \times 10^{-4}p - 4.9576 \times 10^{-7}p^2 - 4.1269 \times 10^{-9}p^3$

50℃: $Z = 1 - 8.7278 \times 10^{-4}p - 1.1763 \times 10^{-7}p^2 - 3.2142 \times 10^{-9}p^3$

75℃: $Z = 1 - 7.3496 \times 10^{-4}p + 2.9189 \times 10^{-7}p^2 - 2.1026 \times 10^{-9}p^3$

90℃: $Z = 1 - 5.8240 \times 10^{-4}p - 2.4459 \times 10^{-7}p^2 - 3.4518 \times 10^{-10}p^3$

C.3 OXYGEN

p [=] psia

35℃: $Z = 1 - 3.7203 \times 10^{-5}p + 5.3077 \times 10^{-9}p^2 + 1.1150 \times 10^{-12}p^3$

50℃: $Z = 1 - 2.8350 \times 10^{-5}p + 5.0495 \times 10^{-9}p^2 + 8.2219 \times 10^{-13}p^3$

75℃: $Z = 1 - 1.6770 \times 10^{-5}p + 4.4797 \times 10^{-9}p^2 + 5.0418 \times 10^{-13}p^3$

90℃: $Z = 1 - 1.1295 \times 10^{-5}p + 4.1183 \times 10^{-9}p^2 + 3.7994 \times 10^{-13}p^3$

C.4 NITROGEN

p [=] psia

35℃: $Z = 1 - 8.2039 \times 10^{-6}p + 1.0069 \times 10^{-8}p^2 + 2.3085 \times 10^{-13}p^3$

50℃: $Z = 1 - 1.2821 \times 10^{-6}p + 9.0150 \times 10^{-9}p^2 + 5.2346 \times 10^{-14}p^3$

75℃: $Z = 1 + 7.5703 \times 10^{-6}p + 7.4811 \times 10^{-9}p^2 - 1.1169 \times 10^{-13}p^3$

90℃: $Z = 1 - 1.1646 \times 10^{-5}p + 6.6925 \times 10^{-9}p^2 - 1.6242 \times 10^{-13}p^3$

C.5 CARBON DIOXIDE

p [=] psia

35℃: $Z = 1 - 2.8695 \times 10^{-4}p - 1.7967 \times 10^{-7}p^2 + 2.2140 \times 10^{-10}p^3 - 1.9322 \times 10^{-13}p^4$

50℃: $Z = 1 - 2.6719 \times 10^{-4}p + 1.9176 \times 10^{-8}p^2 - 4.0255 \times 10^{-11}p^3$

75℃: $Z = 1 - 2.0350 \times 10^{-4}p - 1.9555 \times 10^{-8}p^2 - 4.7571 \times 10^{-12}p^3$

90℃: $Z = 1 - 1.7570 \times 10^{-4}p - 1.3231 \times 10^{-8}p^2 - 3.2585 \times 10^{-13}p^3$

C.4 METHANE

p [=] psia

35℃: $Z = 1 - 1.0547 \times 10^{-4}p + 5.4787 \times 10^{-9}p^2 + 3.9748 \times 10^{-12}p^3$

50℃: $Z = 1 - 8.7927 \times 10^{-5}p + 7.2789 \times 10^{-9}p^2 + 2.2684 \times 10^{-12}p^3$

75℃: $Z = 1 - 6.4521 \times 10^{-5}p + 7.7587 \times 10^{-9}p^2 + 1.5777 \times 10^{-12}p^3$

90℃: $Z = 1 - 5.3304 \times 10^{-5}p + 7.6618 \times 10^{-9}p^2 + 3.2585 \times 10^{-12}p^3$

APPENDIX D

RAW DATA

The following include the raw data for the figures and tables found throughout this dissertation. It is clearly identified where multiple film samples were used. Also, in for some sorption experiments, multiple film samples were used. These plots are reproduced below with error bars included to show the variability of the data.

D.1. PERMEABILITY DATA

Table D.1. Permeability Data at 35°C - 6FDA-6FpDA cast in Dichloromethane.

	C3H6		C3H8		O2		N2	
	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)
Film 1	22.1	0.85	19.2	0.046	28.5	23.6	30.1	5.04
	31.5	0.92	30.6	0.055	29.3	23	29.3	5.06
	37	1.01	41.2	0.057				
	46	1.14	51.4	0.064				
	60	1.28	63.4	0.069				
Film 2	30.3	0.92	31.3	0.046				
Film 3	-	-	3.13	0.056				

Table D.2. Permeability Data at 35°C - 6FDA-6FpDA/Ni[tfd]$_2$ cast in Dichloromethane.

	C3H6		C3H8		O2		N2	
	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)
Film 1	33.1	0.14	30.2	0.01	29.2	6.65	30.2	1.3
	33.2	0.15	3.2	0.01	29.2	6.65	30.2	1.3
Film 2	27.6	0.17	27.9	0.01				
	30	0.17	30.5	0.008				
Film 3	29	0.15	-	-				
	29	0.16	-	-				
Film 4	27.8	0.14	30	0.008				
	27.2	0.15	-	-				

Table D.3. CO_2/CH_4 Permeability Data at 35C
for: a) 6FDA-6FpDA
Both cast in dichloromethane

a) 6FDA-6FpDA

	CO2		CH4	
	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)
Film 1	28.6	110.9	28.7	2.51
	29.5	109.19	28.7	2.51
Film 2	29.9	92.1		
	29.6	92.9		
	60.4	85.2		
	60.3	86.1		
	117.6	80.9		
	117.4	84.5		
	150.9	82.9		
	150.9	84.2		
	204.2	83.2		
	204.2	86.3		
	204.1	88.8		
	299.0	88.8		
	299.1	99.9		
	299.0	106.7		
	402.7	124.6		
	402.6	136.8		
	402.6	139.4		
	489.7	162.7		
	489.7	175.3		
	489.7	178.6		

b) 6FDA-6FpDA/Ni[tfd]$_2$- 10%

	CO2		CH4	
	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)
Film 1	29	42	29.2	0.61
	28.9	42	29	0.6
Film 2	31.4	28.7		
	31.3	28.8		
	59.8	26.8		
	59.7	27.0		
	59.7	27.0		
	119.3	25.1		
	119.4	25.5		
	119.3	25.6		
	150.6	25.1		
	150.6	25.5		
	150.5	25.7		
	215.6	24.9		
	215.6	25.8		
	215.6	26.1		
	314.9	26.6		
	314.9	30.0		
	314.8	31.9		
	400.0	32.8		
	400.0	36.7		
	399.8	39.7		
	501.4	43.9		
	501.4	49.9		
	501.2	54.7		

Table D.4. Permeability Data at 35℃ - 6FDA-DAM cast in Dichloromethane.

	C3H6		C3H8		O2		N2	
	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)
Film 1	19.5	38.83	19.5	2.90	28.3	101.77	28.3	28.9
	29.4	38.61	31.1	3.05	28.4	104.01	29.6	28.3
	39	41.59	41.7	3.98				
	45	49.3	50.5	4.35				
	49.3	53.99	50.5	4.17				
	60.3	55.6	60.8	4.46				
Film 2	27.1	25.66	28.9	2				
	27.9	23.48	-	-				
	29	28.42	-	-				

Table D.5. Permeability Data at 35℃ - 6FDA-DAM/Ni[tfd]$_2$ cast in Dichloromethane.

	C3H6		C3H8		O2		N2	
	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)
Film 1	28.4	7.45	30.9	0.76	29.9	66.27	28.8	15.96
	28.4	8.38	30.9	0.76	29.7	67.04	28.8	15.96
Film 2	30.5	6.13	29.6	0.51				

Table D.6. CO_2/CH_4 Permeabi°lity Data at 35°C
for: a) 6FDA-DAM

b) 6FDA-DAM/Ni[tfd]$_2$- 10%

Both cast in dichloromethane

a) 6FDA-DAM

	CO2 press (psia)	CO2 Perm (Barrers)	CH4 press (psia)	CH4 Perm (Barrers)
Film 1	28.4	466.79	28	23.5
	28.6	525.77	29.3	23.08
Film 2	31.1	485.3		
	30.0	495.2		
	57.6	441.8		
	57.5	446.4		
	108.6	396.7		
	108.5	409.6		
	197.6	389.5		
	197.6	418.0		
	326.0	423.7		
	326.5	526.3		
	431.8	558.2		
	433.3	643.2		
	433.3	638.3		
	433.1	658.9		
	492.4	704.1		
	494.1	730.8		
	494.2	751.6		
	494.1	739.4		
	572.0	721.4		
	570.9	746.9		
	571.0	729.6		

b) 6FDA-DAM/Ni[tfd]$_2$- 10%

	CO2 press (psia)	CO2 Perm (Barrers)	CH4 press (psia)	CH4 Perm (Barrers)
Film 1	30.7	164	30.2	5.42
	307	164.9	30.2	5.29
Film 2	30.7	164.0		
	30.6	165.5		
	60.6	153.2		
	60.5	154.9		
	111.4	148.3		
	111.0	149.9		
	157.6	145.7		
	157.5	147.6		
	262.9	150.4		
	262.9	162.1		
	357.1	184.2		
	357.1	187.7		
	357.0	194.4		
	430.4	193.5		
	431.7	227.6		
	431.6	229.2		
	509.0	240.3		
	512.1	265.3		
	512.0	275.8		

Table D.7. Permeability Data at 35°C – PCHE cast in Toluene

	C3H6		C3H8		O2		N2		CO2		CH4	
	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)
Film 1	29.7	0.78	30.1	0.25	28.8	4.21	31.1	0.88	29.7	16.23	29.7	1.51
	29.5	0.77	30.2	0.25	28.8	4.32	31	0.9	30.5	15.8	29.7	1.49
Film 2									34.3	14.96		
									34.3	15.86		
									34.3	15.56		
									62.4	15.15		
									62.4	15.2		
									111.4	14.73		
									110.9	14.95		
									169.1	14.52		
									246.4	14.1		
									359.3	13.99		
									511.1	13.75		
									525.3	13.97		
									693.2	13.38		
									692	13.72		

Table D.8: Permeability Data at 35°C – PCHE/Ni[tfd]$_2$ cast in Toluene

	C3H6		C3H8		O2		N2		CO2		CH4	
	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)	press (psia)	Perm (Barrers)
Film 1	28.4	0.36	30	0.12	29.1	4.11	28.6	1.63	30.5	12.34	29.9	1.21
	28.1	0.39	30	0.13	28.6	4.13	28.6	1.63	30.5	12.44	29.8	1.23
Film 2									32.2	124.9		
									32.1	120.8		
									32.1	119.7		
									60.1	109.9		
									60.1	104.2		
									60.1	103.0		
									101.7	84.1		
									101.6	74.5		
									101.6	72.0		
									154.5	55.8		
									154.4	48.0		
									154.2	43.9		
									213.3	34.4		
									213.3	30.2		
									213.3	29.0		
									299	20.1		
									299	17.5		
									298.5	16.7		

Table D.9. Permeability Data at 35℃ - Zeonex cast in Toluene

	C_3H_6		C_3H_8		O_2		N_2		CO_2		CH_4	
	press (psia)	**Perm (Barrers)**	**press (psia)**	**Perm (Barrers)**	**press (psia)**	**Perm (Barrers)**	**press (psia)**	**Perm (Barrers)**	**press (psia)**	**Perm (Barrers)**	**press (psia)**	**Perm (Barrers)**
Film 1	29.6	0.47	29.6	0.08	28.8	2.59	28.4	0.51	32	9.47	31.8	0.87
	29.6	0.49	29.6	0.09	28.8	2.59	28.4	0.52	32	9.98	31.8	0.87
Film 2									63	9.49		
									133.6	9.31		
									133.6	9.37		
									213.6	9.08		
									213.2	9.26		
									340	8.95		
									339.6	9.13		
									478.8	8.9		
									478.6	9.13		

Table D.10. Permeability Data at 35℃ - Zeonex/Ni[tfd]$_2$ cast in Toluene

	C_3H_6		C_3H_8		O_2		N_2		CO_2		CH_4	
	press (psia)	**Perm (Barrers)**	**press (psia)**	**Perm (Barrers)**	**press (psia)**	**Perm (Barrers)**	**press (psia)**	**Perm (Barrers)**	**press (psia)**	**Perm (Barrers)**	**press (psia)**	**Perm (Barrers)**
Film 1	30	0.15	28.6	0.03	29.6	2.29	30.6	0.43	31.7	8.04	30.2	0.72
	31	0.17	28.6	0.03	29.6	2.33	30.5	0.44	31.4	8	30.2	0.71
Film 2									64.7	8.2		
									64.9	8.4		
									141.4	8.3		
									140.2	8.4		
									229.1	8.2		
									228.2	8.4		
									346.2	8.2		
									343.3	8.2		
									509.1	7.8		
									505.8	8.2		

D.2. SORPTION DATA

Table D.11. Sorption Data for 6FDA-6FpDA; Pure and Dithiolene Samples

	Pure				**Dithiolene**			
	C3H6		**C3H8**		**C3H6**		**C3H8**	
	Press(psia)	**Conc.**	**Press(psia)**	**Conc.**	**Press(psia)**	**Conc.**	**Press(psia)**	**Conc.**
Film 1	0	0	0	0	0	0	0	0
	12.178	20.304	10.692	14.119	4.9612	9.9028	4.4356	5.0437
	21.375	27.621	21.731	20.517	10.298	18.001	9.094	7.8066
	42.473	30.744	32.996	24.905	15.952	20.544	15.221	12.404
	51.551	32.53	43.09	28.328	23.6	23.599	21.471	14.276
	55.86	34.638	52.879	31.265	32.273	25.716	28.559	15.97
	64.308	36.471	61.266	32.555	41.951	28.277	40.255	17.764
					51.244	30.96	52.672	18.898
					60.941	32.596	60.022	19.232
Film 2	0	0	0	0	0	0	0	0
	4.707	13.547	3.597	7.995	3.1393	7.6925	5.5358	5.683
	10.146	20.862	8.13	13.3	15.099	16.975	13.629	9.5516
	15.868	24.606	14.602	19.353	28.518	20.963	25.111	13.172
	23.704	27.86	20.675	22.526	42.253	24.974	35.856	14.153
	32.465	30.119	27.981	24.493	57.567	27.861	43.984	15.691
	42.033	32.092	39.544	27.515			56.021	16.222
	51.364	33.676	52.024	29.185				
	60.931	34.896	59.275	29.513				
Film 3	0	0	0	0				
	2.932	9.576	5.0654	9.6071				
	15.345	19.421	13.569	15.232				
	27.814	24.315	25.236	22.831				
	39.367	27.746	36.251	27.85				
	47.921	29.017	45.224	28.848				
	60.629	31.943	57.406	28.257				

Table D.12. Sorption Data for 6FDA-6FpDA; Pure and Dithiolene Samples, cont'd

	Pure				**Dithiolene**			
	CO2		**CH4**		**CO2**		**CH4**	
	Press	**Conc**	**Press**	**Conc**	**Press**	**Conc**	**Press**	**Conc**
Film 1	0	0	0	0	0	0	0	0
	16.735	18.679	8.379	2.148	17.701	14.212	8.499	1.618
	55.311	36.5	22.67	4.876	56.977	26.569	25.24	3.946
	113.03	51.692	49.258	8.873	131.73	41.876	47.687	6.373
	223.79	77.356	87.869	13.122	218.74	58.747	123.73	11.846
	357.06	97.477	184.49	20.726	336.24	68.375	249.63	16.951
	459.36	105.44	283.2	25.678			386.66	20.956
			401.9	31.737			528.04	22.549
			532.79	34.247			674.8	23.037
			678.2	34.918				

	Pure				**Dithiolene**			
	O2		**N2**		**O2**		**N2**	
	Press	**Conc**	**Press**	**Conc**	**Press**	**Conc**	**Press**	**Conc**
Film 1	0	0	0	0	0	0	0	0
	14.978	1.3	19.042	1.746	15.062	1.586	26.998	2.283
	28.606	2.508	57.24	4.258	28.792	2.609	69.031	4.259
	49.158	4.093	125.19	7.951	49.59	3.807	149.34	6.967
	76.903	6.311	223.37	11.949	77.524	5.051	24.536	1.5686
	118.19	9.225	342.43	15.38	118.43	6.643	40.236	2.4975
					18.552	2.1021	59.676	3.195
					49.842	3.272	101.92	5.1942
					80.972	5.012	139.72	6.9549
					103.47	5.769	176.62	8.1834
					122.24	6.8435	235.54	9.8784
							310.5	11.594
							435.97	15.842

Table D.13. Sorption Data for 6FDA-DAM; Pure and Dithiolene Samples

	Pure				**Dithiolene**			
	C3H6		**C3H8**		**C3H6**		**C3H8**	
	press	**conc**	**press**	**conc**	**press**	**conc**	**press**	**conc**
Film 1	0	0	0	0	0	0	0	0
	25.263	2.656	4.159	18.059	2.256	14.4	2.705	12.212
	37.819	12.474	14.067	29.347	9.187	26.228	9.791	22.243
	48.933	24.569	27.741	39.667	21.709	38.368	22.368	31.504
	56.546	37.494	39.779	46.575	33.954	44.013	34.379	36.845
	62.511	45.971	49.288	50.259	44.482	51.385	44.9	43.943
	65.112	61.01	56.003	53.5	56.688	60.171	56.288	49.964
Film 2					0	0	0	0
					3.53	20.257	4.301	15.579
					11.914	32.407	14.406	25.989
					18.245	37.95	24.351	29.967
					27.011	41.019	32.891	36.18
							46.574	40.5
							54.874	43.931
							61.273	45.553

Table D.14. Sorption Data for 6FDA-DAM; Pure and Dithiolene Samples, cont'd

	Pure				Dithiolene			
	CO2		CH4		CO2		CH4	
	Press	Conc	Press	Conc	Press	Conc	Press	Conc
Film 1	0	0	0	0	0	0	0	0
	20.098	31.581	11.235	4.009	9.129	13.604	22.373	5.448
	84.406	64.759	36.324	10.29	17.932	20.567	71.831	12.573
	213.51	95.892	104.82	20.367	27.946	26.69	127.61	17.875
	342.1	115.31	174.88	26.514	73.801	42.915	196.57	22.281
	461.44	125.7	302.65	33.157	153.58	63.252	301.26	26.575
	610.83	139.63	431.47	36.813	247.63	82.069	412.45	29.237
					378.09	98.923	519.49	30.747
					562.7	121.26	618.22	31.806
Film 2	0	0			0	0		
	10.299	19.439			22.593	24.58		
	26.708	34.031			109.72	52.548		
	65.643	53.499			262.98	84.482		
	142.19	80.58			414.43	105.56		
	266.8	110.85			520.36	112.95		
	408.85	130.39						
	588.53	154.36						

	Pure				Dithiolene			
	O2		N2		O2		N2	
	Press	Conc	Press	Conc	Press	Conc	Press	Conc
Film 1	0	0	0	0	0	0	0	0
	16.238	1.988	36.997	3.251	12.162	1.343	15.765	1.038
	31.363	3.564	79.597	6.436	27.819	2.651	46.953	3.123
	54.219	5.753	203.41	12.73	45.563	4.08	95.012	5.43
	75.934	7.605	290.3	15.483	64.129	5.384	144.04	7.544
	98.594	9.426	398.07	17.86	86.827	7.147	218.11	10.331
	119.78	11.074	21.129	1.97	103.65	8.416	267.57	11.751
	140.62	12.529	62.594	5.043	122.13	9.5		
					143	10.569		

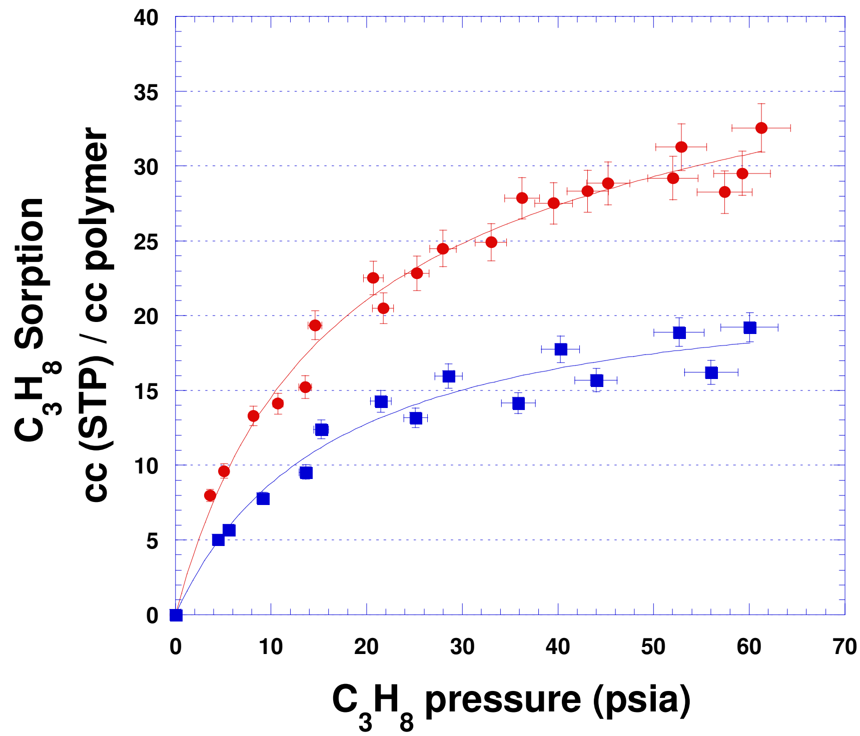
Table D.15. Sorption Data for PCHE; Pure and Dithiolene Samples

	Pure				Dithiolene					Pure		Dithiolene	
	C3H6		C3H8		C3H6		C3H8			CO2		CO2	
	Press	Conc	Press	Conc	Press	Conc	Press	Conc		Press	Conc	Press	Conc
Film 1	0	0	0	0	0	0	0	0	Film 1	0	0	0	0
	3.862	2.395	3.258	2.508	3.306	2.71	5.225	2.627		30.178	2.793	20.192	1.81
	7.141	3.768	7.052	3.751	7.728	4.263	11.672	4.968		57.774	4.5	45.017	3.598
	11.647	5.353	12.027	4.98	15.098	6.573	18.239	5.832		103.11	7.038	106.65	7.28
	19.046	7.276	15.779	5.811	23.85	8.341	25.234	6.789		137.24	8.729	208.69	12.238
	29.075	9.522	21.623	7.5	34.604	10.089	30.92	7.453		206.3	11.611	357.05	16.067
	39.401	11.503	30.372	8.816	44.042	11.739	38.665	8.249		259.13	13.559	485.49	17.791
	49.44	12.577			52.061	12.963	46.143	8.792		305.47	15.067	602.6	20.315
	61.04	13.962			62.05	14.406	51.531	9.432		433.46	17.331		
							58.232	10.948		545.3	19.655		
							63.071	11.325					
Film 2			0	0	0	0	0	0					
			35.654	9.487	36.143	9.864	35.132	7.347					
			52.879	11.589									

Table D.16. Sorption Data for Zeonex®; Pure and Dithiolene Samples

	Pure				Dithiolene				Pure		Dithiolene	
	C3H6		C3H8		C3H6		C3H8		CO2		CO2	
	Press	Conc	Press	Conc	Press	Conc	Press	Conc	Press	Conc	Press	Conc
Film 1	0	0	0	0	0	0	0	0	0	0	0	0
	3.885	2.43	4.155	2.777	3.731	2.474	4.392	1.606	30.131	2.426	5.973	0.509
	12.102	4.439	11.764	5.876	12.061	4.126	11.931	4.447	57.715	4.09	17.258	1.54
	21.935	6.585	24.305	8.79	21.697	6.922	24.196	7.487	102.74	6.586	30.328	2.542
	34.548	9.056	38.841	12.204	34.689	9.861	38.944	10.459	136.86	8.393	51.508	3.967
	45.007	10.369	52.448	13.662	44.942	11.667	52.282	13.026	205.49	11.088	121.37	7.799
									258.08	12.976	218.85	12.106
									303.68	14.21	299.06	14.275
									429.18	15.746	405.64	16.184
									542.53	17.644	530.14	17.641

a)



b)

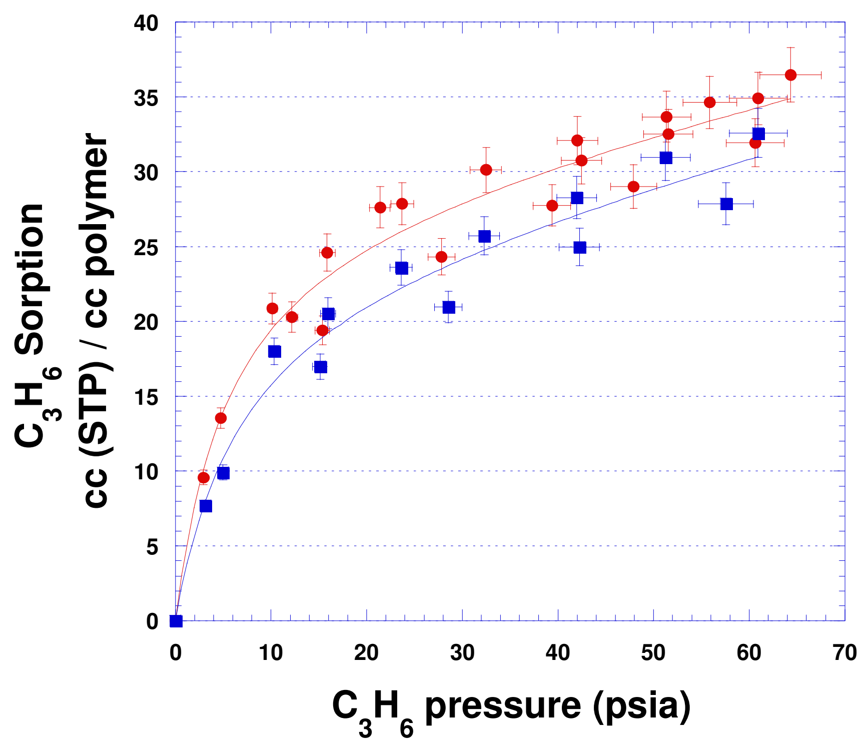
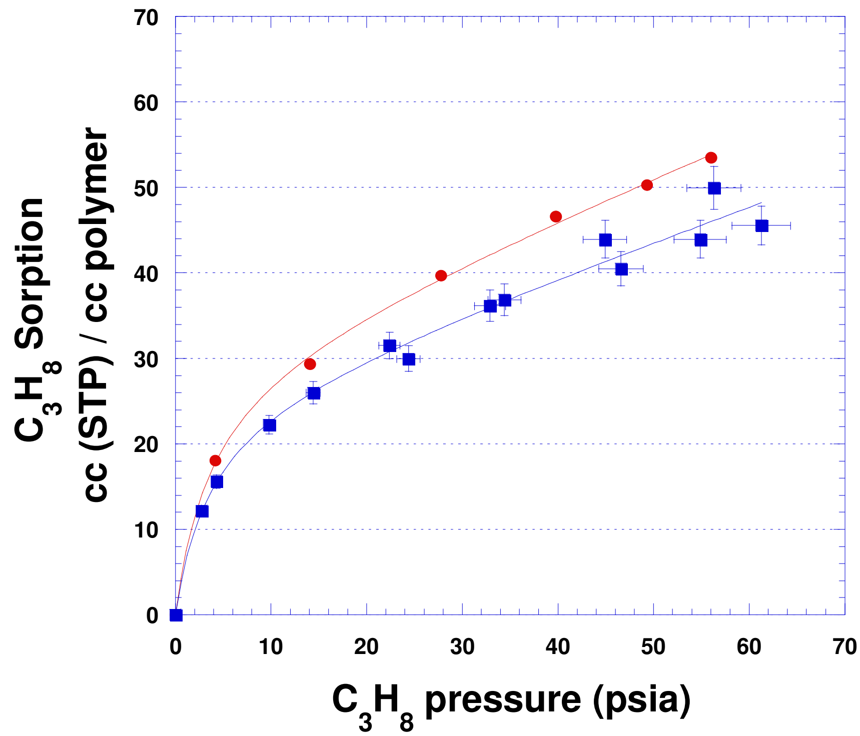


Figure D.1. (a) Propane and (b) Propylene Sorption Plot for 6FDA-6FpDA. ● 6FDA-6FpDA; ■ 6FDA-6FpDA/Ni[tfd]$_2$

a)



b)

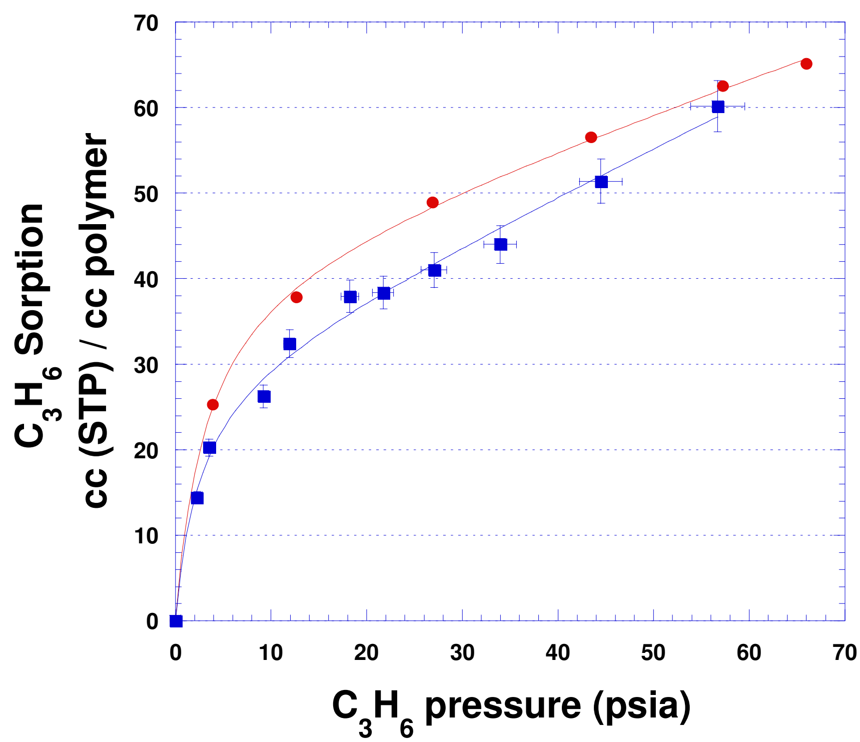


Figure D.2. (a) Propane and (b) Propylene Sorption Plot for 6FDA-DAM. ● 6FDA-DAM; ■ 6FDA-DAM/Ni[tfd]$_2$

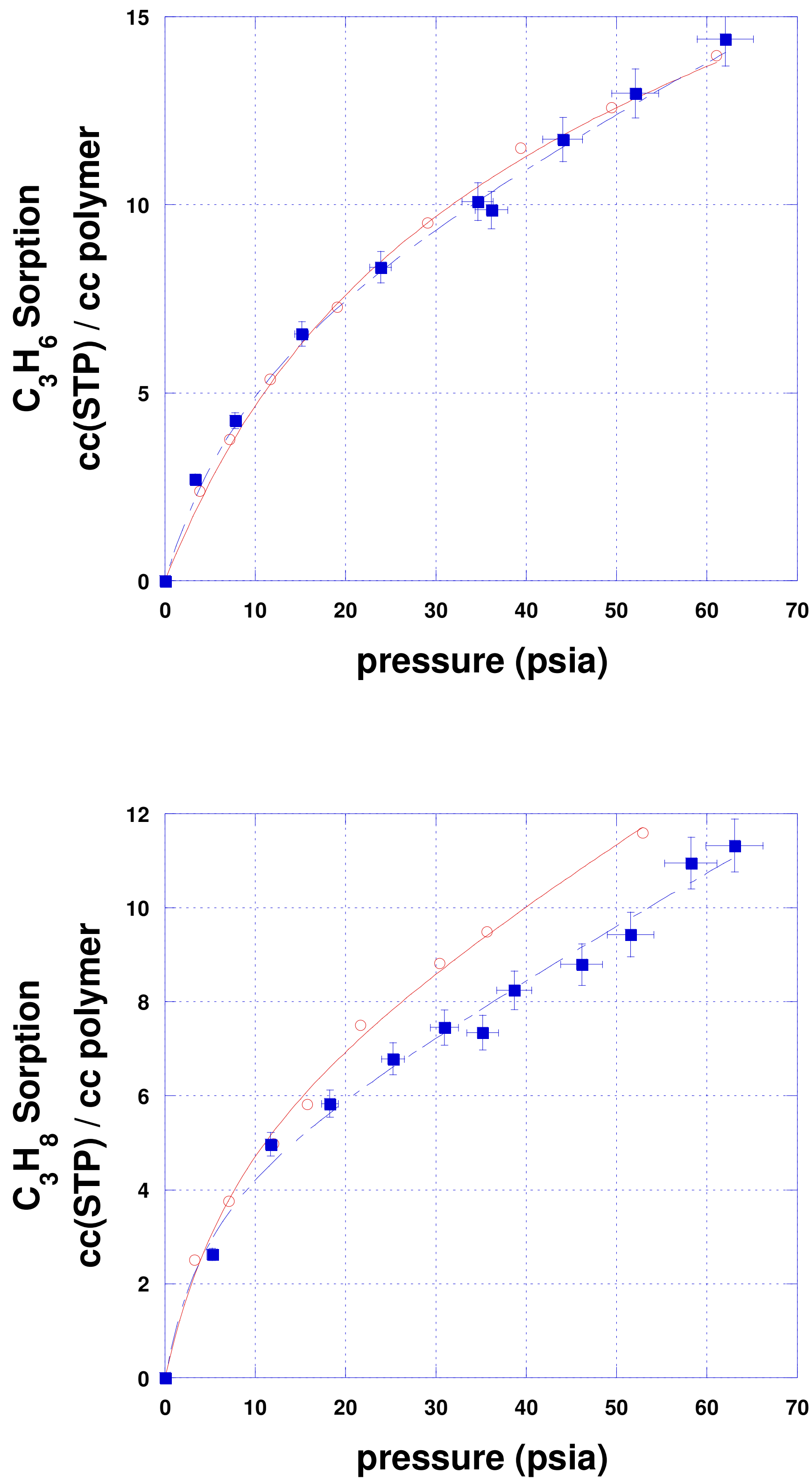


Figure D.3. (a) Propane and (b) Propylene Sorption Plot for PCHE. ● PCHE; ■ PCHE/Ni[tfd]$_2$

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