FABRICATION AND CHARACTERIZATION OF POLY(AMIDE-IMIDES)/TiO₂ NANOCOMPOSITE GAS SEPARATION MEMBRANES

by

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Committee Chairman: Dr. Eva Marand

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(ABSTRACT)

Nanosized TiO₂ rich domains were generated in-situ within poly(amide-imide) (PAI) and 6F-poly(amide-imide) (6FPAI) by a sol-gel process. The composite films showed a high optical transparency. The morphology of the TiO₂ rich domains was observed by transmission electron microscopy (TEM). The TiO₂ rich domains were well dispersed within the poly(amide-imide) and 6F-poly(amide-imide) matrices and were 5 nm to 50 nm in size. Limited study was also carried out for the fabrication of the PAI/SiO₂ and PAI/TiO₂-SiO₂ composites. It was found that nanosized SiO₂ rich domains were difficult to form within the poly(amide-imide) matrix, although the SiO₂ could be bonded with the TiO₂, forming nanosized domains within the poly(amide-imide) matrix. The PAI/TiO₂ composites showed an increased glass transition temperature, and an increased rubbery plateau modulus, in comparison to the unfilled poly(amide-imide). Wide Angle X-ray Diffraction (WAXD) study and Differential Scanning Calorimetry (DSC) analysis suggest that the TiO₂ filled poly(amide-imide) have a lower crystallinity as compared to the unfilled poly(amide-imide). The dynamic mechanical properties in rubbery regions suggest that TiO₂ domains function as physical crosslinks, increasing the rubbery plateau modulus with increasing TiO₂ content. This behavior can be explained by the theory of rubbery elasticity. The actual formation of the nanosized TiO₂ and TiO₂-SiO₂ rich
domains was explained in terms of hydrogen bonding effects between the polymer, the solvent and the inorganic components.

The interactions between the TiO₂ and the poly(amide-imide) and 6F-poly(amide-imide) were studied by Fourier Transmission Infrared Spectroscopy (FTIR) and Attenuated Total Reflectance (ATR) spectroscopy. These studies suggest that the hydrogen bonding between the residual OH groups on the TiO₂ and the N-H groups in the poly(amide-imide) and 6F-poly(amide-imide) is responsible for the in-situ formation of the nanosized TiO₂ rich domains within the polymers.

The permeabilities of H₂, O₂, N₂, CH₄ and CO₂ gases were studied at temperatures of 35, 55, and 75 °C for the unfilled 6F-poly(amide-imide) and the 6F-poly(amide-imide)/TiO₂ nanocomposite with a TiO₂ content of 6.2 % by weight. The weight percentages were obtained by Thermal Gravimetric Analysis (TGA). Compared to the unfilled 6FPAI membrane, the TiO₂-filled 6F-poly(amide-imide) nanocomposite membrane showed an increase in the permselectivities of H₂/CH₄, H₂/CH₄, and CO₂/CH₄ gas pairs without appreciable loss in H₂ permeability. At 35 °C and 2 atmospheres, the permselectivity increased from 37.8 to 49.4 for H₂/CH₄, from 30.2 to 37.0 for H₂/N₂, and from 30.0 to 36.4 for CO₂/CH₄. However, at 75 °C and 2 atmospheres, no improved permselectivity of the TiO₂-filled 6F-poly(amide-imide) membrane over the unfilled 6F-poly(amide-imide) membrane was found for H₂/N₂ and CO₂/CH₄ gas pairs, except for H₂/CH₄, which showed an increase in the permselectivity from 30.0 (the unfilled membrane) to 34.8 (the filled membrane).

The permeability of the poly(amide-imide) was found to be too low to be of practical use. For example, the permeability of O₂ through the poly(amide-imide) membrane was found to be nearly 100 times lower than that through the 6F-poly(amide-
-imide) membrane. Accordingly, very limited permeability studies of the poly(amide-imide) were conducted but not included in this dissertation.
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Chapter 1

INTRODUCTION

1.1. Development of High Performance Gas Separation Membranes

Membrane separation is a fast-growing and competitive technology. The business of membrane separation technology in the United States has reached over one billion dollars annually. Microfiltration is the oldest but still most widely used process. All other membrane separation technologies have increasingly found industrial applications since the breakthrough development of polymer asymmetric membranes in the 1950s. As a consequence, significant achievements in ultrafiltration and reverse osmosis were made in the 1960s. During the last decade, polymeric membranes were also applied to gas separation. A number of industrial gas separation systems have been built in the United State since Monsanto introduced a polymer membrane separation process to recover hydrogen from ammonia purge gas in 1979. Due to the low cost, simplicity, and feasibility of the process, polymeric membrane-based gas separation has become a successful technology competing with traditional gas separation processes such as cryogenic distillation, absorption and pressure swing adsorption. Some typical applications for gas separations using polymeric membranes include [1-2]:

1. Hydrogen separations from industrial gas streams,

2. Oxygen and nitrogen enrichment from air,

3. Carbon dioxide recovery from natural gases,

4. Organic vapor separation,

5. Gas dehydration.
The fast-growing need for high performance polymeric membranes has been stimulating the exploration of new membrane materials. Ideally, a high performance polymeric membrane should have high permselectivity and high permeability, combined with good thermal stability and mechanical strength. Although these features in combination are generally difficult to achieve, two essential criteria for the molecular structure of a high performance polymeric membrane have been specified [3-4]. These include hindered segmental and subsegmental mobility, and inhibited segmental packing of molecular chains. The hindered segmental and sub-segmental mobility, which favors the permselectivity and the thermal stability, can be measured by increased glass transition or sub-glass transition temperature, respectively [5-6]. On the other hand, the inhibited packing, which favors permeability, particularly for glassy polymers, can be detected by an increase in the fractional free volume [5, 7]. Some typical polymers that have been chemically modified to meet these two criteria include polyimides [1, 8-9], polycarbonates [1,10-11], polysulphones [1, 10, 12], and poly(amide-imides) [13-14].

Although chemical structure has been used as an important tool to increase permselectivity and permeability, alternatively, the author of this dissertation postulates that segmental mobility and packing can also be controlled by the incorporation of nanosized metal oxide domains into a polymeric matrix. Specific molecular interactions between the two components (polymer and metal oxide) could also restrict segmental mobility and packing. Polymer/metal oxide nanocomposites exhibit an increase in the plateau modulus and glass transition temperature in comparison to their unfilled polymers, thus suggesting certain restrictions in molecular motion.

Thus, in order to enhance the interaction of the metal oxide and polymer components, a system capable of inter-molecular hydrogen bonding has been selected. Aromatic poly(amide-imides) were developed to take advantage of the high performance
and thermal stability of polyimides as well as the hydrogen bonding capabilities of polyamides [15]. The hydrogen bonding between the amide groups in the poly(amide-imide) and the OH groups on the metal oxide, which can arise from the sol-gel reactions of metal alkoxides, makes it possible to incorporate nanosized metal oxide domains within the poly(amide-imide) matrix.

This research is focused on the fabrication and the characterization of poly(amide-imide)/TiO₂ nanocomposite membranes to achieve improved permselectivity and thermal stability for gas separation applications. The study will provide a fundamental understanding not only for the gas transport properties of polymer/metal oxide nanocomposite membranes but also of the methodology of fabricating homogeneous composite materials using metal alkoxide and the polymer systems that contain either proton donors or proton acceptors, or both. In the long run, these composite materials can have potential applications not only in gas separations, but also in many other areas such as catalysts, electronic materials, optical materials and related applications.

1.2. Research Objectives

The overall objective of this research is to provide an understanding of the gas transport properties of polymer/ceramic nanocomposite membranes. However, the fabrication and characterization of such a type of membrane is clearly a prerequisite. This study will focus on two polymers, poly(amide-imide) (PAI), synthesized from 4,4’-oxy(phenyl trimellitimide)[OPTMI] and 4,4’-oxydianiline [ODA] using tert. butyl benzoic acid [t-BBA] as the monofunctional endcapper [15]; and 6F-poly(amide-imide) (6FPAI), synthesized from an imide-containing dicarboxylic acid (DAC) and hexafluoro-2,2-bis(4-amino-phenyl)-propane [13]. However, the emphasis of the studies of these two polymers will be different. The permeability of the PAI is much lower than the 6FPAI. Accordingly,
transport properties were focused on the 6FPAI due to its potential application in gas separation, while characterization studies were conducted on the PAI due to its availability in large quantities. The research objectives of this dissertation are itemized below:

1. In-situ formation of nanosized TiO$_2$ rich domains by a sol-gel process within the PAI and the 6FPAI, the desired size of the TiO$_2$ rich domains is below 10 nm,

2. Physical characterization of the morphology, and thermal and mechanical properties of the PAI/TiO$_2$ and 6FPAI/TiO$_2$ nanocomposites by a number of techniques such as DMTA, DSC, TGA and TEM,

3. FTIR and ATR studies of the molecular interactions between the PAI and TiO$_2$; and 6FPAI and TiO$_2$.

4. Studies of the transport properties of the unfilled 6FPAI and 6FPAI/TiO$_2$ nanocomposite using H$_2$, O$_2$, N$_2$, CO$_2$, and CH$_4$ gases.
Chapter 2

LITERATURE REVIEW

The background knowledge and the recent developments relevant to this research include the following four areas:

1. Membrane separation technology,
2. Sol-Gel chemistry of metal alkoxide,
3. In-Situ formation of metal oxide within polymeric matrices,

Clearly, a complete review of the work in these areas is beyond the scope of this study. However, specific important aspects, particularly those related to this research, will be covered.

2.1. Membrane Separation Technology

Readers interested in a thorough review of the membrane separation area may refer to cited references [2, 16-31]. The review given in this section will focus on polymeric membranes, while a brief review of other membrane processes will also be presented.

2.1.1. Overview of Membrane Separation Technology

The diversity of membrane materials existing in the separation technology makes it difficult to find an universal classification. Nevertheless, the pore size combined with a general transport mechanism of penetrant, as shown in Table 2.1, tends to categorize a variety of membranes.
Table 2.1. Membrane classification based on pore size and separation mechanism [19-24]

<table>
<thead>
<tr>
<th>Name</th>
<th>Liquid Membrane</th>
<th>Dense Membrane</th>
<th>Reverse Osmosis Membrane</th>
<th>Ultrafiltration Membrane</th>
<th>Microfiltration Membrane</th>
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<tr>
<td>Pore Size</td>
<td>-</td>
<td>Zero</td>
<td>2-30 Å</td>
<td>20-1000 Å</td>
<td>900 Å-10 μ</td>
</tr>
<tr>
<td>Separation Mechanism</td>
<td>Solution/</td>
<td>Solution/</td>
<td>Solution/</td>
<td>Knudsen Flow and Sieving</td>
<td>Sieving, or Poiseuille flow</td>
</tr>
<tr>
<td></td>
<td>Diffusion</td>
<td>Diffusion</td>
<td>Diffusion</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The pore size assigned to each class of the membrane in Table 2.1 may vary depending on the literature source. For example, a dense polymer membrane has free volume, and a polymer chemist cannot take the pore size as zero. Some literature also classifies inorganic liquids such as LiNO$_3$ and ZnCl$_2$ as dense membranes [25]. More than one separation mechanism may be involved, and the mechanism given in Table 2.1 corresponds only to the major applications of the membrane. In general, all membranes but the liquid membrane in Table 2.1 are solid membranes.

A liquid membrane is also called liquid pertration [19]. The separation system contains two homogeneous liquids separated by a third liquid that acts as a separation liquid membrane and is immiscible with the former two liquids. The solution containing the solute to be separated is referred to as the donor solution, while the solution on the other side of the separation membrane is referred to as the acceptor solution [19]. The difference in the chemical potentials of solute in two solutions makes the solute transfer from the donor solution, cross the separation liquid membrane, to the acceptor solution. The rate of the mass transfer increases with the difference in the chemical potentials.

The rate of molecular diffusion in liquid membranes can be several orders higher than that in solid membranes. The permselectivity of liquid membranes is also generally higher than that of polymeric membranes [19]. In addition, liquid pertration is considered to be one of the cheapest separation techniques. Thus, it is of no surprise that liquid membranes are used in a number of applications such as separations of hydrocarbons, pertration of metals, pertration of inorganic substance, pertration of organic substance, biotechnology and medicine, and gas, although few of these applications have reached industrial scale [19, 25].
Stable conditions of liquid pertrations are very difficult to achieve, particularly on an industrial scale. The liquid membrane is very sensitive to the pressure difference between two sides of the membrane and a very thin liquid film for increasing the flux is also generally unfeasible. All these factors restrict the commercial applications of liquid pertration.

Dense membranes include both organic and inorganic membranes. Organic membranes mainly involve polymeric membranes which will be reviewed more completely in section 2.1.2. Compared to the porous membrane, gas separation by a dense membrane follows a quite different mechanism in which the solubility and the diffusivity of penetrants must be simultaneously taken into account. Three steps are generally involved in the permeation of penetrants through a dense membrane: (1) adsorption or absorption on the upstream boundary, (2) diffusion through the membrane, and (3) dissolution or evaporation from the downstream boundary. In addition to the gas separation processes, other separation processes in which dense membranes are used include pervaporation (involving liquid phase in feed stream and vapor phase in permeate stream), vapor permeation, thermoosmosis, dialysis (osmosis), and electrodialysis [26-29]. The driving forces of these membrane processes are vapor pressure, temperature, concentration, and electric potential, respectively.

Typical representatives of the dense metal membranes are palladium and palladium alloys (with Ag, Ru, Ni, etc.) [25, 30-31]. A major application of these membranes is hydrogen separation because of the high solubility for hydrogen. Pure palladium tends to be brittle. The deposition of the palladium on porous glasses and ceramic supports can serve a large number of applications such as hydrogen separation and purification, dehydrogenation of isobutane, and aromatization of propane. The palladium deposition can be achieved by electroless plating, chemical vapor deposition (CVD), electrochemical
vapor deposition (EVD), sputtering, and spray pyrolysis, etc. [30]. Dense ceramic membranes such as ZrO₂, Bi₂O₃, and the composite membranes LiNO₃ and ZnO₂ supported on porous metals are principally impermeable to gas molecules [25, 30]. The separation mechanism of these membranes involves the transport of gas as gas ions at elevated temperatures, such as the transport of oxygen as oxygen ions and the hydrogen as protons at temperatures up to about 1000 °C [30]. The dense ceramic membranes are mainly used to separate the hydrogen and the oxygen from mixtures such as H₂/N₂, H₂/CO, H₂/CH₄, and O₂/N₂. [25, 30]. The palladium based membranes and the dense ceramic membranes are characterized by high thermal stability and anti-corrosion properties. The operating temperature can be as high as 1000 °C and even higher, which is uncompetitive with organic membranes. Accordingly, these membranes are also widely used as catalytic membrane reactors at elevated temperatures [30-31].

Industrial membranes for pervaporation and vapor permeation processes are generally of a composite type. A thin, dense layer of a permselective polymer is coated on a porous support. The typical application is the dehydration of ethanol. Other applications include the removal of organic vapor solvent from air, and organic-organic separations such as aromatics/non-aromatics, alcohols/alkanes and alcohols/ethers [27-28].

The thermoosmosis, dialysis (osmosis), and the electrodialysis follow a similar mechanism. The driving forces of these processes are the temperature gradient, the concentration gradient and the electropotential gradient, respectively [26]. A typical example of the electrodialysis process is the ion-exchange membrane. Small scale applications of these membrane processes include desalination of water, production of table water from seawater, recycling of water and metal ions from the rinse waters of the electroplating industry, concentration of reverse osmosis brines, production of ultrapure water and recovery of mineral acid from salt solutions [29].
The reverse osmosis membrane is a semipermeable membrane. Because of the very small pore size, the reverse osmosis membrane is also called a non-porous membrane [26]. This process is also called hyperfiltration [22]. A pressure greater than the osmotic pressure of feed solution must be exerted, allowing only the solvent to flow through the membrane [22].

The major application of reverse osmosis membranes is the desalination of water. The annual sale of desalination membranes is as high as $85 million in the United States [22]. The other applications such as metal finishing, pulp and paper, and textile industries are small. An evaluation of the membrane sale and the growth rate for the various industrial applications of reverse osmosis is given in reference [22]. The recent state of reverse osmosis is discussed in references [32-35].

The problems encountered in the industrial applications of reverse osmosis are the solute build-up at the surface of membrane, and the fouling of the surface of membrane by species from the feed stream. These two problems are responsible for the long-term decline in membrane flux [22].

Ultrafiltration and microfiltration membranes are porous membranes which can be either inorganic or organic. The microfiltration membrane functions only as a "sieving" element to retain colloidal particles with dimensions of several micrometers [20-21]. The ultrafiltration membrane is similar to the microfiltration membrane when working as a "sieving" element but can also separate gas penetrants based on their molecular weight when the pore size is smaller than the mean free path of the penetrant.

When ultrafiltration membranes are used in gas separation, the separation process follows the Knudsen mechanism and the separation factor is determined by the mean free path of gas and the pore radius, the mean free path is given by [36]:
\[ \lambda = \frac{3\eta \left( \frac{\pi RT}{2P} \right)^{1/2}} {2P} \]  

(2.1)

where \( \lambda \) is the mean free path of penetrant, \( \eta \) the viscosity, \( R \) the gas constant, \( T \) the absolute temperature, \( P \) the pressure and \( M \) the molecular weight. In the case that the pore radius is appreciably smaller than the free path of penetrant, the Knudsen flow is dominant and the flux for ideal gas is modeled by a capillary tube [36]:

\[ J_k = \left( \frac{8r^2RT}{9\pi M} \right)^{1/2} \frac{P_0 - P_I}{IRT} \]  

(2.2)

where \( J_k \) is the flux of Knudsen flow (in moles/sec-cm²); \( r \) is the pore radius; \( P_0 \) and \( P_I \) are the absolute pressures on two sides of the membrane, \( P_0 > P_I \); \( l \) is the pore length. The root square term is the Knudsen's diffusion coefficient \( (D_K) \) that is derived from a long capillary tube model [37], i.e.,

\[ D_K = \left( \frac{8r^2RT}{9\pi M} \right) \]  

(2.3)

In contrast, when the pore radius is appreciably larger than the free path of penetrant, the flux of Poiseuille flow is dominant and is given by Poiseuille's law [38]:

\[ J_p = \frac{r^4(P_0^2 - P_I^2)}{8\pi lRT} \]  

(2.4)

where \( J_p \) is the flux of Poiseuille's flow. The Knudsen flow is relevant to the molecular weight of penetrant as shown in Equations 2.1 and 2.3. The molecules with different molecular weights collide mainly with the pore wall and move independently at different velocities, which leads to the separation of these molecules [38]. The gas separation factor \( \alpha \) for the Knudsen flow is given by:
\[ \alpha = \left( \frac{M_2}{M_1} \right)^{1/2} \]  \hspace{1cm} (2.5)

It is also clear that almost no separation occurs in the Poiseuille region based on Equation 2.4. In general, the bulk flow is very small in a small porous tube (less than 1% [19]), and therefore the flow can be divided into two streams; one is the Knudsen flow and another one is the Poiseuille flow. The ratio of the pore radius to the mean free path of gases should be smaller than 0.25 to make the Knudsen flow larger than 90% [36]. Because the mean free path of most gases at atmospheric pressures ranges from 100-200 nm [36], a selective porous membrane for gases should have a pore radius smaller than 50 nm.

The diffusion of penetrants in porous membranes differs from that in the Knudsen's capillary tube model because the pores have a finite length and are randomly distributed [39]. A variable accounting for these effects was proposed and given by [40]:

\[ \zeta = \frac{D_k}{D_e} \varepsilon \]  \hspace{1cm} (2.6)

where \( \zeta \) is the tortuosity, which is the ratio of the actual distance to the shortest distance a molecule travels between two points and is generally assumed to be larger than 1 [41]; \( D_e \) is the effective diffusion coefficient; and \( \varepsilon \) is the porosity defined as the ratio of the volume of void space to total volume [41]. The physical significance of the tortuosity factor is the dimensionless diffusion path which should be larger than 1. The tortuosity factor defined by Equation 2.6 cannot provide a satisfactory explanation for the diffusion process through a porous membrane since the tortuosity factor can range from one to infinity, but in some cases it can be less than one [40, 42].

Shelekhin et al. applied the percolation theory to the diffusion process of porous membranes [42]. The tortuosity factor of Vycor glass membranes was calculated by a
Monte-Carlo simulation. Simulation results were found to be in agreement with the tortuosity factor defined by:

$$\xi = \frac{J_s}{J_i} \varepsilon$$ \hspace{1cm} (2.7)

where $J_s$ is the flux in a straight pore and $J_i$ the flux in an irregular porous structure.

In addition to the transport models for gas separation through porous membranes cited above, there exist also a number of other transport models for liquid separation. Fundamental principles in thermodynamics and statistical mechanics are generally used for establishing these models. A detailed review of these models can be referred to references [17, 43, 45].

The methods used to make microfiltration and ultrafiltration membranes are summarized below. A more detailed discussion of these methods can be found in references [20-21]

1. Membranes derived from microporous media:
   - Ceramics, Sintered metal, Sintered polymers, Wound wire or fiber;
2. Membranes derived from homogenous solid films:
   - Track etched membranes, Stretched polymers, Aluminum derivatives, Dense films (only for dialysis and gas separation membranes);
3. Membranes derived from heterogeneous solid films:
   - Leached glasses, Extracted polymers;
4. Symmetric membranes derived from solution:
   - Leached membranes, Thermally inverted solutions;
5. Asymmetric structures derived from solution:
   - Loeb-Sourirajan membranes;
6. Asymmetric composite structures:

Dynamic membranes, Thin film composites, Coated structures, Self assembled structures."

Applications for microfiltration still occupy the major market of membrane separation technology and the annual sale of the microfiltration membranes and equipment is as high as one billion dollars [20-21]. The major market for microfiltration is in pharmaceutical applications. Other applications include sterile filtration, wine, semiconductors, water and waste water [20-21].

Comparing ultrafiltration to microfiltration, one may simply state that the former is better than the latter. The reason for this is that the ultrafiltration membrane works better than the microfiltration membrane in retaining deformable particles and can separate soluble macromolecules from other soluble species [20-21]. In some cases, there is only a small fraction of pores that is smaller than the retained materials; therefore the microfiltration is probably considered an obvious choice, but ultrafiltration is still a correct choice. Accordingly ultrafiltration has found applications in electrocoat paint separation, textile sizing, oily waste water, juice, pulp and paper [20-21] and gas separation, etc. [46-51]. Porous membranes are attractive to applications involving high temperatures because of the thermal stability [30]. Porous membranes combined with inorganic or organic dense membranes are also attractive to the industrial gas separation, which will be reviewed in the next section.

The major problem encountered with the industrial applications of porous membranes is fouling, which may cause a dramatic loss in the flux and hamper their practical use. Most studies directed to reduce fouling are probably focused on the improvement of the boundary conditions between feed stream and membrane by the use of
techniques such as tangential flow, pulsated flow, vortex flow and, unstable flow [20-21, 26].

2.1.2. Gas Separation by Dense Polymeric Membranes

After a brief review of the membrane separation technology, the emphasis is shifted to polymeric membranes. Polymeric membranes can also be either porous or dense. The terminology "polymeric membrane" used throughout this chapter refers to the dense organic polymeric membrane unless otherwise stated. A general separation mechanism involving polymeric membranes is the same as that of any dense membrane that has been reviewed in the foregoing section. Because the gas transport property of the unfilled and TiO$_2$-filled poly(amide-imides) that are used in this study is directly related to the gas separation mechanism of polymeric membranes, the review given in this section will focus on the more detailed separation mechanism and the effect of various parameters in polymeric membrane processes. In the end of this section, some important applications of polymeric membranes in gas separations will be presented.

2.1.2.1 General Consideration of Polymeric Membrane Processes

Polymeric membranes generally include rubbery and glassy polymer membranes, depending on whether or not the temperature is above or below the glass temperature of the membrane [35]. One of the basic properties of membranes is the permeability, which is defined by [1, 10]:

$$P_A = \frac{N_A l}{\Delta P_A} = \frac{N_A j}{P_{A1} - P_{A2}}$$  \hspace{1cm} (2.8)

where $P_A$ is the permeability of the gas $A$ which is usually expressed in barrer. One barrer is equal to $10^{-10}$ cm$^3$(STP).cm/(cm$^2$.sec.cmHg); $N_A$ is the flux of penetrant in
\[ P_A = [S_A][D_A] \quad (2.9) \]

where \([S_A]\) is an effective solubility coefficient in \(\text{cm}^3(\text{STP})/\text{cm}^3 \text{polymer.cmHg}\), and it is the secant slope of the sorption isotherm if the downstream pressure equals zero [52]; \([D_A]\) is an average diffusion coefficient in \(\text{cm}^2/\text{sec}\) [52] or a concentration-averaged diffusivity [10]. Various factors that can influence the magnitude of the solubility coefficient and the diffusion coefficient will be discussed later. Another basic property is the separation factor. For a binary gas mixture, the separation factor for component \(A\) relative to \(B\) is defined as [1, 10]:

\[ \alpha_{AB}^* = \frac{y_A^2 / y_B^2}{y_A^1 / y_B^1} = \frac{N_A / N_B}{P_A^1 / P_B^1} \quad (2.10) \]

where \(\alpha_{AB}^*\) is the separation factor, \(y\) is the mole fraction, subscripts "2" and "1" refer to the downstream and upstream faces, respectively. From Equations 2.8, 2.9 and 2.10, the separation factor can be written in a more explicit form:

\[ \alpha_{AB}^* = \frac{[D_A]}{[D_B]} \times \frac{[S_A]}{[S_B]} \times \frac{\Delta P_A / P_A^1}{\Delta P_B / P_B^1} \quad (2.11) \]
The first term in Equation 2.11 is the mobility controlled selectivity, the second term is the solubility controlled selectivity. When the downstream pressure is negligible, \( \Delta p_A \approx p_{A1} \) and \( \Delta p_B \approx p_{B1} \), the separation factor obtained is called ideal selectivity or ideal permselectivity [53-54], \( \alpha_{AB} \), giving

\[
\alpha_{AB} = \frac{P_A}{P_B} = \frac{[D_A]}{[D_B]} \times \frac{[S_A]}{[S_B]}
\]  (2.12)

The ratio \([D_A]/[D_B]\) is called diffusivity selectivity and the ratio \([S_A]/[S_B]\) is called solubility selectivity. Most selectivity values reported in the literature are calculated from Equation 2.12 [54]. Equations 2.8 through 2.12 are the fundamental equations referring to the transport properties of a polymeric membrane. For the sake of simplicity, the review presented below refers to a pure penetrant. Therefore subscripts A and B are omitted. This should be sufficient for the understanding of the permeation behavior of polymeric membranes.

2.1.2.2 Rubbery Polymer Membranes

*Sorption process in rubbery polymers.* A rubbery polymer membrane lends itself to a relatively simple gas permeation mechanism. The sorption of ideal gases in a rubber membrane is generally assumed to follow Henry's law [10, 36]:

\[
C = Sp
\]  (2.13)

where \( C \) is the concentration of penetrant in the membrane in \( \text{cm}^3(\text{STP})/\text{cm}^3 \) polymer, \( S \) is the Henry's solubility constant for a polymer-penetrant system, and \( p \) is the pressure of penetrant in cmHg. For non-ideal gases, the pressure is replaced by fugacity.
Diffusion process in rubbery polymers. The diffusion of penetrants through the rubbery membrane due to the concentration gradient is normally described by Fick's first law [10, 36]:

\[ N = -D \left( \frac{dC}{dx} \right) \]  
\[ (2.14) \]

where \( N \) is the flux and \( x \) is the position coordinate. At steady state, \( N \) is a constant. Assuming that the diffusion coefficient \( D \) is independent of the concentration \( C \), combining Equations 2.13 and 2.14 [36] yields

\[ N = DS \frac{\Delta p}{l} = P \frac{\Delta p}{l} \]  
\[ (2.15) \]

If the diffusion coefficient is a constant, the permeability of a rubbery membrane at steady state can be found from Equations 2.8 and 2.15 to be

\[ P = DS \]  
\[ (2.16) \]

Experimental permeability methods on rubbery polymers. \( P \) and \( D \), and therefore \( S \) can be determined by a permeation experiment [36, 55-56]. As shown in Figure 2.1, the slope of the straight line in the steady state region is the steady state flux \( N \). In the case of constant \( D \), the steady state is reached after a period of about 3\( \theta \) where \( \theta \) is the time lag [36, 57-59]. The permeability, \( P \), can be determined from Equation 2.8 by measuring the membrane thickness and the upstream and downstream pressures. When the membrane is initially free of penetrant and the downstream is maintained at essentially zero concentration, the coefficient \( D \) can be estimated by equation [36, 55-56]:
Figure 2.1. Schematic of a permeation experiment.
\[ D = \frac{l^2}{6\theta} \]  

(2.17)

By knowing \( P \) and \( D \), the solubility is then determined from Equation 2.16. The diffusion coefficient, however, may not be a constant, which leads to the difficulty of achieving a true steady state. Furthermore, the determination of membrane thickness is often the least accurate part of the permeation experiment. On the other hand, the initial zero concentration of penetrant in the membrane and at the downstream is also difficult to achieve. All these factors can be the major source of error in the estimation of \( D \) by a permeation experiment [57]. The estimation of diffusion coefficient can also be achieved by fitting a theoretical model to all the permeation data [60-61].

A sorption experiment can also be used to directly determine \( D \), \( S \), and \( P \). The general techniques are the gravimetric or barometric methods, although the volumetric method and other techniques can also be used. More detailed description on the gravimetric and barometric techniques is given in references [56-58].

When a rubbery membrane does not undergo structural rearrangement in the presence of penetrants (gases), the diffusion of penetrants typically obeys Fick's first and second laws [62]. The diffusion coefficient is often a constant, particularly at low penetrant concentrations [62]. In this case, a single permeation experiment can be used to determine \( P \), \( D \), and \( S \). However, if the gas pressure is very high or if there exists a specific interaction between the penetrant and the polymer, the penetrant concentration may deviate from Henry's law and the diffusion coefficient may no longer be a constant [62]. This complicated case will be discussed in the following section.

2.1.2.3 Glassy Polymer Membranes

Glassy polymer membranes lend themselves to a relatively complicated gas permeation mechanism that can be well described by the dual mode sorption model [63-
The sorption isotherm (C vs. p curve) of a glassy polymer membrane shows the feature that C is a linear function of p at both low and high pressures, but nonlinear at moderate pressures. An example of this is the sorption of carbon dioxide in a polysulfone [10]. In general, the dual mode transport model postulates [58]:

1. Two modes, Henry's law sorption and Langmuir sorption, exist simultaneously;
2. The two modes are in equilibrium throughout the transport processes;
3. The mobility of penetrant in the Langmuir sorption sites is much smaller than that in the Henry's sorption sites;
4. The true diffusion coefficient is independent of the penetrant concentration and the position within the membrane.

The Henry's sorption occurs in the dense equilibrium structure of the polymer but the Langmuir sorption or hole-filling mode refers to the non-equilibrium excess volume of the glassy polymer [10]. The non-equilibrium excess volume as a function of temperature is illustrated in Figure 2.2. These four assumptions are the basis for understanding the sorption and diffusion processes of glassy polymer membranes.

**Sorption process in glassy polymers.** On the basis of assumption 1, the sorption equation in a glassy polymer membrane is given by [58, 63]:

\[
C = C_D + C_H = Sp + \frac{C_H'bp}{1+bp} \tag{2.18}
\]

where C is the total concentration of penetrant, \(C_D\) (\(C_D = Sp\)) is the Henry's mode penetrant concentration, \(C_H\) is the Langmuir mode penetrant concentration, \(S\) is the Henry's solubility constant, \(C_H'\) is the hole saturation constant or the Langmuir sorption capacity, and \(b\) is the Langmuir affinity parameter.
Figure 2.2. Schematic of the non-equilibrium excess volume in a glassy polymer.
Diffusion processes in glassy polymer. The flux equation for a glassy polymer is given by [36]

\[ N = -D_D \frac{dC_D}{dx} - D_H \frac{dC_H}{dx} \]  \hspace{1cm} (2.19)

where \( N \) is the total flux, and \( D_D \) and \( D_H \) are the true diffusion coefficients of the Henry's mode penetrant and the Langmuir mode penetrant. With assumption 4, the permeability \( P \) at steady state \( (N = \text{constant}) \) can be determined from Equations 2.8, 2.18 and 2.19 and is found to be [36]

\[ P = S D_D + \frac{C'_H b D_H}{P_1 - P_2} \left( \frac{P_1 - P_2}{1 + b p_1 - 1 - b p_2} \right) \]  \hspace{1cm} (2.20)

When the downstream pressure \( p_2 \) is equal to zero, Equation 2.20 reduces to

\[ P = S D_D + \frac{C'_H b D_H}{1 + b p_1} \]  \hspace{1cm} (2.21)

On the other hand, if \( p_2 \) is equal to zero and the upstream pressure is extremely high, Equation 2.20 can be further reduced to the form that is similar to Equation 2.16:

\[ P = S D_D \]  \hspace{1cm} (2.22)

Until now, assumptions 2 and 3 have not yet been used. The questions remain: how is the true diffusion coefficient measured and what is the relationship between the experimentally determined diffusion coefficient and the true diffusion coefficient? The answers can be found by combining Fick's second law with assumptions 2 and 3.

The assumption 3 mentioned above implies that the diffusion process takes place mainly in the Henry's mode. Assuming that the diffusion coefficient of the Langmuir mode
penetrant \( (D_H) \) is much smaller than that of the dissolved mode penetrant \( (D_D) \) (assumption 3) [63], and thereby is neglected, the flux equation is then reduced to [36].

\[
N = -D_D \left( \frac{dC_D}{dx} \right)
\]  
(2.23)

The equation of continuity for the penetrant gives

\[
\frac{dC}{dt} = \frac{d(C_D + C_H)}{dt} = -\frac{dN}{dx}
\]  
(2.24)

From assumption 2, a relationship between \( C_D \) and \( C_H \) can be achieved by equating the partial pressure \( p \) from Henry's law \( (C_D = Sp) \) and the pressure \( p \) from Langmuir isotherm \( (C_H = C'_Hbp / (1 + bp)) \) and is found to be

\[
C_H = \frac{(C'_Hbp / S)C_D}{1 + (b / S)C_D}
\]  
(2.25)

From Equations 2.23, 2.24 and 2.25 and noting that \( C_D = Sp \), one obtains

\[
D_D \frac{d^2C_D}{dx^2} = \frac{dC_D}{dt}
\]  
(2.26)

Equation 2.26 is the Fick's second law for a glassy polymer under assumptions 2 and 3 mentioned above. Therefore, the experimentally observed diffusion coefficient \( D \) is

\[
D = \frac{1}{C'_H(b / S)} \frac{D_D}{[1 + (b / S)C_D]^2}
\]  
(2.27)

Equation 2.27 states that the experimentally measured diffusion coefficient \( D \) is not constant. However, at very low pressures, \( C_D \ll 1 \), Equation 2.27 reduces to
\[ D = \frac{1}{1 + C_H^* (b / S)} D_D \] (2.28)

The experimentally measured diffusion coefficient \( D \) is a constant but is reduced by \( 1/(1 + C_H^* b / S) \) compared to the true diffusion coefficient. The physical significance of this reduction can be regarded as the delay required to reach the sorption equilibrium, which is caused by the immobilized penetrant. The term \( 1/(1 + C_H^* b / S) \) is therefore a measure of the amount of immobilized penetrants in microvoids relative to the amount normally dissolved in the glassy polymer membrane. On the other hand, at very high pressures, \( C_D \gg 1 \), Equation 2.27 reduces to

\[ D = D_D \] (2.29)

The experimentally measured diffusion coefficient \( D \) is again a constant and it is equal to the true diffusion coefficient. It should be also pointed out that the above derivations do not take the nonideal behavior of the gases into account. The effects of the nonideal behavior have been discussed in the foregoing section for the rubbery membrane.

Petropoulos proposed that the penetrant molecules sorbed in the Langmuir sites may not be necessarily completely immobilized [66]. Independent transport and NMR studies demonstrate that the penetrant molecules in these two distinct molecular environments have different inherent mobility [67-68]. These form the basis of the partial mobilization model [65]. The flux, for which no assumption is made in the partial mobilization model, obeys Equation 2.19. The partial mobilization model also assumes that there exists a local equilibrium between \( C_D \) and \( C_H^* \), and the relationship follows Equation 2.25. From Equations 2.19, 2.24 and 2.25, the \( D \) can be derived and is given by [63]:

25
\[ D = \left( \frac{1 + FK / (1 + bp)^2}{1 + K / (1 + bp)^2} \right) D_D \]  \hspace{1cm} (2.30)

where \( F = D_H / D_D \), and \( K = C_H b / S \). Equation 2.30 is later found to be in agreement with the experimental observations [69].

*Experimental permeability methods on glassy polymer membranes.* As mentioned in section 2.1.2.2, barometric or gravimetric techniques are the direct means to determine \( D \), \( S \), and \( P \) of a polymer-penetrant system, this includes rubbery as well as glass polymers. The permeation technique is also generally feasible for rubbery polymers, particularly in the low penetrant concentration. The glassy polymer, however, is involved in more complicated sorption and diffusion mechanisms in comparison to the rubbery polymer. Accordingly, the time lag of a glassy polymer may not be accurately obtained. It is also difficult to precisely calculate the time to reach the steady state of flow [58]. The diffusion coefficient typically depends on the penetrant concentration. However, it has been shown that a large class of functional dependencies of \( D \) on the penetrant concentration can be expressed by the inequality [57]:

\[ \frac{l^2}{6 \theta} \leq D \leq \frac{l^2}{2 \theta} \]  \hspace{1cm} (2.31)

Therefore, the diffusion coefficient estimated from Equation 2.17 may be smaller by a factor of 3. For some purposes, this order of accuracy may be sufficient. On the other hand, the ratio of the time reaching steady state to the time lag may not be 3 and it may vary from case to case. Therefore the time to reach steady state needs to be determined based on a permeation experiment for a specified system [58].
2.1.2.4 Free Volume Theory

As cited in the introduction, one of the criteria for a high performance polymer membrane is the large free volume. The effect of the free volume on the diffusion coefficient can be understood from the Doolittle expression [70]:

\[ D = D_0 \exp \left( -\frac{B}{V_f} \right) \]  \hspace{1cm} (2.32)

Where \( D_0 \) and \( B \) are constants relevant to a polymer-penetrant system; \( V_f \) is the fractional free volume, which is the fraction of the total polymer specific volume not occupied by polymer chains and is responsible for the transport of penetrant molecules [10]. Equation 2.32 demonstrates that the diffusion coefficient is a property related to both the penetrant and the polymer membrane. In fact, Fick's Laws, combined with a specified sorption model for the rubbery or the glass polymer membrane discussed in the previous section, provided only a phenomenological treatment for the transport processes of a penetrant through the dense membranes. The transport processes at a molecular level can be understood from free volume theories.

\( V_f \) is often estimated by [71]:

\[ V_f = \frac{V - V_0}{V} \]  \hspace{1cm} (2.33)

where \( V \) is the polymer specific volume, which is equal to the reciprocal of the polymer density; and \( V_0 \) is the occupied volume, which is a function of temperature and can be approximated from the van der waals volume \( V_w \) (\( V_0 \) is approximately equal to 1.3 \( V_w \)) [72]. \( V_w \) can be estimated from group contribution methods [72-73]. When \( V_w \) is used, Equation 2.33 can be rewritten as:
\[ V_f = \frac{V - 1.3V_w}{V} \]  

(2.34)

The basis of the free volume theory is that the penetrant molecule must have sufficient energy to overcome the attraction force between chains and moves only through the free volume in the polymer matrix [1, 10, 36, 74]. In order to model the transport process of a penetrant molecule, polymer chains are assumed to have a local semicrystalline chain packing [10, 36, 74]. These cylindrical bundles have a parallel packing and each bundle is generally assumed to have a coordination number of four. The movements of a penetrant molecule along these bundles are modeled by classical, quantum and statistical mechanics [10, 36, 74]. They include: (1) the “hole” or lattice vacancy theory, in which a certain amount of work must be done on a polymer matrix to expand a hole for the diffusion of the gas molecule to occur; (2) the activated complex theory, in which a penetrant molecule must be provided with sufficient energy to overcome a potential energy barrier when moving through the matrix; and (3) the fluctuation theory, where the thermal activation of density fluctuations provides the excess space to allow the movement of a penetrant molecule [1, 10, 36, 74]. These three approaches lead to final expressions of \( D \) and \( P \), which are similar to the empirical Arrhenius relations [36]. Accordingly, Arrhenius expressions for \( P \) and \( D \) and the van't Hoff relationship for \( S \) are widely used for the transport studies of polymeric membranes [1, 8, 10, 36, 74]:

\[ D = D_0 \exp\left(-\frac{E_d}{RT}\right) \]  

(2.35)

\[ S = S_0 \exp\left(-\frac{AH_s}{RT}\right) \]  

(2.36)

\[ P = P_0 \exp\left(-\frac{E_p}{RT}\right) \]  

(2.37)
where $D_0$, $P_0$, and $H_0$ are the pre-exponential factors, $E_d$ is the activation energy of diffusion, $E_p$ is the apparent activation energy of permeation, and $\Delta H_s$ is the enthalpy of sorption [75-76]. Other symbols have their usual significance. It is necessary to have a brief review of the solubility factor before using free volume theories for the description of the diffusion process of gas molecules in polymeric membranes.

The dissolution of a penetrant in a polymer matrix is viewed as a thermodynamic process which includes two steps: (1) condensing the gas penetrant to a condensed density, and (2) creating a molecular scale gap in the polymer to accommodate the penetrant molecule [10]. The enthalpy of sorption is accordingly written as:

$$\Delta H_s = \Delta H_{\text{cond}} + \Delta H_{\text{mix}}$$  \hspace{1cm} (2.38)

where $\Delta H_{\text{cond}}$ and $\Delta H_{\text{mix}}$ are the enthalpy changes associated with the first and second thermodynamic processes, respectively. The $\Delta H_{\text{mix}}$ depends on the intermolecular forces between the polymer and the penetrant. If either the London or the dipole-dipole attractions are involved, the $\Delta H_{\text{mix}}$ can be estimated by the Hildebrand equation [57]:

$$\Delta H_{\text{mix}} = \bar{g}(\delta_1 - \delta_2)^2 \phi_2^2$$  \hspace{1cm} (2.39)

where $\bar{g}$ is the partial molar volume of penetrant, $\delta_1$ and $\delta_2$ are the square roots of the cohesive energy densities of the penetrant and polymer, respectively, and $\phi_2$ is the volume fraction of polymer in the mixture. The temperature dependence of the solubility coefficient is therefore dependent upon the relative magnitude of $\Delta H_{\text{cond}}$ and $\Delta H_{\text{mix}}$. In general, the penetrant with a small molecular weight, such as H$_2$ and He, has a negligible condensation enthalpy $\Delta H_{\text{cond}}$ [75]. Accordingly $S$ increases with increasing temperature because of the positive value of $\Delta H_{\text{mix}}$. For more condensable gases (with higher critical temperature) and vapors, such as CO$_2$ and many organic vapors, the $\Delta H_{\text{cond}}$ makes a
large negative contribution and therefore the $\Delta H_s$ may be negative. As a result, $S$ decreases with increasing temperature [1, 75].

In the case of a highly condensable solvent vapors' separation, the solubility selectivity is a dominant contributor to the separation factor [69]. A high separation factor over 150 for $\text{H}_2\text{S}/\text{CH}_4$ gas pair has been reported by using a thermoplastic elastomer block copolymer as the membrane where the membrane contains ether and amide blocks [77-78]. However, membranes that are simply based on solubility selectivity are not attractive for the most applications of industrial gases [1]. The structure modifications for enhancing solubility selectivity can actually lead to excessive swelling of the membrane that causes deleterious losses in mobility selectivity, particularly in cases where glassy polymers are used [1].

The limitations involving the use of solubility selectivity have led to the studies focused on the improvement of mobility selectivity [1, 5]. The dependence of the diffusion coefficient $D$ on the free volume can be understood in a molecular level with the following equation [1, 5]:

$$D = \nu \lambda^2 / 6$$  \hspace{1cm} (2.40)

where $\nu$ is the jump frequency of penetrant molecule, $\lambda$ is the average jump length. As shown in Equation 2.1, for penetrants with a similar size such as $\text{O}_2$ and $\text{N}_2$, the jump length term is generally thought to be similar. However, a penetrant molecule moving through a polymer matrix having a large free volume has a high jump frequency and thereby a high diffusion coefficient [1]. An impressive feature of glassy polymers, which distinguishes them from rubbery polymers, is the well-controlled segmental motion and thereby the high dependence of the jump frequency on the penetrant size [1]. This feature makes it possible for glassy polymers to separate gases such as $\text{O}_2$ and $\text{N}_2$ whose kinetic
sieving diameters differ only by 0.18 Å [36]. Rubbery polymers are essentially unable to produce sufficiently subtle size selective transient gaps for the selective separation of such a gas pair because the large-scale segmental motions in rubbery polymers are not well controlled [1].

The $E_d$ is also equal to the energy to open a cylindrical path whose diameter and length are defined by the penetrant diameter $\sigma$ and the jump length $\lambda$, as suggested by the equation [79]:

$$E_d = \pi \lambda \sigma^2 \delta_2 / 4$$  \hspace{1cm} (2.41)

where $\delta_2$ is the square root of the cohesive energy of a polymer. A large $\delta_2$ corresponds to a great attractive force between the polymer chains, and accordingly a great energy is required to open a transient gap for the passage of a penetrant [1]. As shown in Equations 2.35 and 2.41, the exponential dependence of $D$ on the cohesive energy $\delta_2$ and the squared power of $\sigma$ makes diffusivity and diffusivity selectivity very sensitive to a small change in either parameter.

The transport of a penetrant through polycarbonates provides a good example in understanding the criterion cited above for a high performance glassy polymer membrane [1]. The carbonate linkage is regarded as a mobile "hinge". The rocking motion around this hinge produces a transient penetrant scale gap that allows the movement of a sorbed gas molecule. The conformation variations that increase the average distance between the nested backbones produce a more open and higher $V_f$ matrix. A large average aperture can be transiently opened with a smaller amplitude rocking motion of the surrounding segments in a more open matrix than in a less opened matrix, and accordingly enables the high jump frequency of both large and small penetrants. In the case that two polymers have the same segmental backbone stiffness or mobility, however, it is evident that the
transiently open gap tends to be larger in a more open matrix than in a less open matrix. Therefore, when an effort is made to increase the permeability by increasing the free volume, an effort should be made simultaneously to reduce the segmental backbone mobility to maintain the permselectivity. These strategies have been successfully used to tailor polycarbonates [1, 5, 80-82]. Different polycarbonates can be generalized based on the structure shown in Figure 2.3. PC (polycarbonate) corresponds to the structure in Figure 2.3 with C(CH$_3$)$_2$ in the Y position but nothing in the X position. Different substituents in X and Y positions bring about the appreciable changes for the permeation behavior of the O$_2$/N$_2$ gas pair [1]: (1) Substitution of the C(CH$_3$)$_2$ group with a higher free volume group, C(CF$_3$)$_2$, in the Y position (resulting polymer is called 6FPC (hexafluoro polycarbonate)), causes a four-fold increase in O$_2$ permeability due to increased $V'_f$ but a loss in the permselectivity of O$_2$/N$_2$ from 4.8 to 4.1, due to essentially no effect on the rocking motions around the mobile hinge composed of the carbonate linkage; (2) With maintaining C(CH$_3$)$_2$ unchanged in the Y position but attaching CH$_3$ in the X positions (resulting polymer is called TMPC (tetra methyl polycarbonate)), nearly four-fold increase in O$_2$ permeability but no loss in the permselectivity of O$_2$/N$_2$ can be attributed to the simultaneous increases in the $V'_f$ and the inhibition of rocking motions; (3) When the C(CH$_3$)$_2$ in the Y position is replaced by C(CF$_3$)$_2$ and the X positions are attached with CH$_3$ (resulting polymer is called TM6FPC (tetra methyl hexafluoro polycarbonate)), dramatic twenty-fold increases in the permeability are observed without appreciable loss in the permselectivity in comparison to PC. Important results that are believed to be sufficient for confirming the strategies cited above are summarized in Table 2.2. These strategies are also the most reliable guide in understanding the gas transport properties of polysulfones and polyimides [1].
Figure 2.3. Structure of polycarbonate. X and Y correspond to different substituents.
Table 2.2. Effect of the structure of polycarbonate on the transport properties [1]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>X and Y (See Fig. 4)</th>
<th>$T_a$ (°C)</th>
<th>$T_b$ (°C)</th>
<th>$V_r$ (25°C)</th>
<th>$P_{O_2}$</th>
<th>$P_{O_2}/P_{N_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>Y=C(CH$_3$)$_2$, X= nothing</td>
<td>150</td>
<td>-70</td>
<td>0.164</td>
<td>1.6</td>
<td>4.8</td>
</tr>
<tr>
<td>6FPC</td>
<td>Y=C(CF$_3$)$_2$, X= nothing</td>
<td>176</td>
<td>-71</td>
<td>0.195</td>
<td>6.9</td>
<td>4.1</td>
</tr>
<tr>
<td>TMPC</td>
<td>Y=C(CH$_3$)$_2$, X= CH$_1$</td>
<td>193</td>
<td>+111</td>
<td>0.180</td>
<td>5.6</td>
<td>5.1</td>
</tr>
<tr>
<td>TM6FPC</td>
<td>Y=C(CF$_3$)$_2$, X= CH$_3$</td>
<td>208</td>
<td>+107</td>
<td>0.220</td>
<td>32</td>
<td>4.1</td>
</tr>
</tbody>
</table>
As discussed in the introduction, a high performance polymer membrane (i.e., high permeability and high selectivity) should have inhibited segmental packing and inhibited segmental and subsegmental mobility [3-4]. The increased packing inhibition can be detected by an increase in the free volume fraction, \( V_f \) [5, 7]. The inhibition of the segmental and sub-segmental mobility can be measured by the increases in glass transition (\( T_\alpha \)) or sub-glass transition (\( T_\beta \)) temperatures [5-6]. As shown in Table 2.2, the sub-glass transition (\( T_\beta \)) temperature is a better indicator than the \( T_\alpha \) in reflecting the inhibition of the rocking motions. The problem is that as the motions become progressively inhibited, \( T_\beta \) becomes increasingly more difficult to detect [1]. Some computer models based on single chains have been developed for the estimate of the intrasegmental inhibition of motions [83-84].

The hindered segmental mobility that has been described on the molecular level must correspond to a greater relaxation time of the polymer. The hindered segmental packing has reverse effect on the relaxation time. The relaxation time is typically correlated with a shift factor [85]:

\[
\alpha_T = \frac{\tau(T)}{\tau(T_r)} = \frac{\eta(T)}{\eta(T_r)} \tag{2.42}
\]

where \( \alpha_T \) is the shift factor of the relaxation time \( \tau \) of a polymer at the temperature \( T \) with respect to that at the reference temperature \( T_r \), \( \eta \) is the viscosity of the polymer. Some important expressions for the shift factor or the relaxation time can be obtained from WLF equation [86], the free volume theory of Cohen and Turnbull [87], the statistical thermodynamic theory of Adam and Gibbs [88]. Many other theories such as Kohlrausch-Williams-Watts (KWW) equation [89-90] and the Phenomenological Model of Viscoelasticity [91] also provide the theoretical basis in studying the relaxation behavior of
polymers. A study of PVAc/silica nanocomposite shows that KWW equation is a good tool for the study of the distribution of relaxation times [92]. The free volume distributions of polystyrene and polyvinyl acetate probed by positron annihilation lifetime (PAL) spectra are found to be in agreement with the Cohen and Turnbull theory and the Simha-Somcynsky theory [93-94].

2.1.2.5 Effect of Penetrant Properties on Permeability and Permselectivity

**Penetrant Condensability.** The solubility can be estimated from Equations 2.36, 2.38 and 2.39. The temperature dependence of solubility has been discussed in the foregoing section. A penetrant that has a high critical temperature tends to have a large negative condensing enthalpy and thereby a high solubility in a polymer [62, 95]. The critical temperatures of some penetrants are listed in Table 2.3 [96]. A factor over 150 for H₂S/CH₄ gas pair by using a thermoplastic elastomer block copolymer that contains ether and amide blocks has been reported [77-78]. One can combine this separation factor with the values in Table 2.3 to estimate the possibility of separating a gas pair on the basis of solubility selectivity. Other parameters to measure the condensability are the normal boiling point and the Leonard-Jones force constant [62, 96].

**Penetrant Size and Shape.** In general, a penetrant that has large van der waals volume corresponds to a low diffusion coefficient [1, 10, 62]. The van der waals volume is defined as the volume enclosed by electron clouds of a molecule and can be calculated by purely geometrical method provided the covalent radius and the van der waals radius of each atom in the compound are available [72-73]. However, the van der waals volume does not take the shape of penetrants into account. The diffusion coefficient of a penetrant in polymer is also sensitive to the shape of penetrant [10]. The diffusion coefficient of CO₂ is typically larger than that of CH₄ [1, 97] although the van der waals volume of CO₂
<table>
<thead>
<tr>
<th>Penetrant</th>
<th>H$_2$S</th>
<th>CO$_2$</th>
<th>CH$_4$</th>
<th>O$_2$</th>
<th>N$_2$</th>
<th>H$_2$</th>
<th>He</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$ (°K)</td>
<td>373.2</td>
<td>304.2</td>
<td>190.6</td>
<td>154.6</td>
<td>126.2</td>
<td>33.2</td>
<td>5.19</td>
</tr>
</tbody>
</table>
(17.5 cm²/mole) is greater than that of CH₄ (17.2 cm²/mole) [98]. This is because, when the equivalent molecular volumes of two penetrants are same, the linear or oblong molecule like CO₂ tends to have a higher diffusivity than the spherical-like one like CH₄ [97]. To take these two factors into account, kinetic diameter [92, 98] or molecular sieving diameter [1] rather than van der waals radius, is often used to characterize the penetrant size [10, 98]. Kinetic diameter is the smallest diameter zeolite window which allows the penetrant to enter the zeolite cavity [98]. The kinetic diameters of some penetrants are listed in Table 2.4. For a given polymer and a gas pair, the difference in the kinetic diameters listed in Table 2.4 can be used to estimate the magnitude of the diffusivity selectivity. The O₂/N₂ selectivity has been reported to range from 3.5 to 5.5 for most glassy polymers [1, 10-11, 13] although the difference in kinetic diameters for this gas pair is only 0.18 Å. This example simply shows the significance for controlling the diffusivity selectivity in comparison to the solubility selectivity.

2.1.2.6 Effect of Membrane Structures on Permeability and Permselectivity

**Free Volume.** The dependence of the diffusion coefficient of the penetrant on the fractional free volume \( (V_f) \) of polymer has been discussed in section 2.1.2.4. \( V_f \) is generally estimated from Equation 2.34. Positron Annihilation Lifetime (PAL) spectroscopy is a good means of measuring the free volume of polymers [93-94]. Diffusivity of a penetrant may be also correlated to the packing density of polymers [100-101] and the \( d \)-spacing measured by wide angle X-ray diffraction (WAXD) [102-103].

**Chain Mobility.** Inhibition of the segmental and sub-segmental mobility can be measured by glass transition \( (T_g) \) or sub-glass transition \( (T_\beta) \) temperatures [5-6]. Polymer intrasegmental motion is particularly favorable for the transient molecular aperture to accommodate a penetrant molecule [1, 52, 100]. Therefore introduction of flexible
Table 2.4. Kinetic diameters of some penetrants [99]

<table>
<thead>
<tr>
<th>Penetrant</th>
<th>He</th>
<th>H₂</th>
<th>NO</th>
<th>CO₂</th>
<th>Ar</th>
<th>O₂</th>
<th>N₂</th>
<th>CO</th>
<th>CH₄</th>
<th>C₂H₄</th>
<th>C₃H₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic Diameter (Å)</td>
<td>2.6</td>
<td>2.89</td>
<td>3.17</td>
<td>3.3</td>
<td>3.4</td>
<td>3.46</td>
<td>3.64</td>
<td>3.76</td>
<td>3.8</td>
<td>3.9</td>
<td>4.3</td>
</tr>
</tbody>
</table>
linkages such as -O- and -CH₂- into a polymer backbone increases the tortional mobility and thereby the diffusion coefficient of penetrant [1, 100, 104]. However, diffusivity selectivity tends to decrease because of the low energetic barriers of these linkages to the intrasegmental bond rotation [105]. In contrast, introduction of rigid linkages such as aromatic groups decreases the tortional mobility and thereby the diffusion coefficient of penetrant but increases the mobility selectivity [1, 104]. In general, the flexible linkage and the rigid linkage tend to have opposite effect on the diffusivity selectivity of penetrant [1, 10, 105]. As mentioned earlier, the inhibition of the segmental and sub-segmental mobility is an important criterion for an ideal gas separation membrane. This accounts for why most commercial membranes such as polyimide, aromatic polysulfone and polycarbonate have aromatic groups in their backbones. The loss in diffusivity caused by the rigid linkages can be overcome by emphasizing another important parameter: the hindered segmental packing [1].

*Segmental Packing.* The strong dependence of the diffusion coefficient of penetrant on the fractional free volume ($V_f$) of polymer has been discussed in section 2.1.2.4. The $V_f$ of polymer increases typically with hindered segmental packing [5, 7]. The increase in chain irregularity [1, 10, 36] and the introduction of bulky side groups such as -CF₃, as compared to -CH₃ [1, 10, 13], favor the packing inhibition and therefore increase the diffusion coefficient. The chain irregularity can be inferred from the molecular structure of polymer. The effect of introducing various groups on the $V_f$ can be approximately evaluated by Equation 2.34. The bulky side groups may facilitate the inhibition of both segmental packing and the intrasegmental mobility [100, 106]. In this regard, the introduction of bulky side groups seems always favorable towards enhancing the gas transport properties of polymers. Unfortunately, exact nature of molecular motions that determine the gas diffusion is still unclear [10]. Bulky side groups increase the free
volume and thereby the diffusivity but simultaneously restrict the tortional mobility which results in the decrease in the diffusivity [100, 106]. These two opposite effects are usually difficult to predict for a specific gas separation. Therefore the free volume and the glass transition $T_\alpha$ or sub-glass transition $T_\beta$ serve primarily as the qualitative tools to evaluate the segmental packing efficiency and the segmental and the sub-segmental mobility [105].

**Polarity.** In general, polarity is the terminology related to the unevenness of the distribution of electrons about atoms, functional groups, and molecules [36]. The cohesive energy density, the $\delta_2$ as shown in Equation 2.39, is the attractive force holding a material together [96, 107-108] and perhaps the most useful measure expressing the polarity [36]. Three interactions are generally involved in the interactions between a polar polymer and a penetrant [96]. They are the interactions between a dipole and a quadrupole, a dipole and another dipole, as well as a dipole and an induced dipole. A polymer with high $\delta_2$ tends to have strong intermolecular interactions between the chains, thereby decreasing the diffusivity of penetrants [10, 36]. However, the solubility of a polar penetrant such as CO$_2$ within a high polarity polymer is enhanced because of the enhanced interaction between the polymer dipole and the quadruple of CO$_2$ [109]. On the other hand, the solubility of non-polar penetrants such as CH$_4$ is generally small. As a result, high polarity polymer membranes tend to increase the solubility of polar penetrants and increase the solubility selectivity of polar/nonpolar gas pairs [1]. A typical example is the separation of H$_2$S and CH$_4$ using a thermoplastic elastomer block polymer that contains ether and amide groups [77]. The permselectivity of this gas pair is reported to be as high as 150.

**Crosslinking.** Crosslinking can be regarded as a special mode of chain irregularity because crosslinks are randomly distributed over the volume of the specimen [110]. The additional constraint caused by introducing crosslinks significantly reduces the polymer segmental mobility [111-112]. Diffusion coefficient typically decreases with increasing
crosslink density [113]. A typical example for this is the natural rubber crosslinked by vulcanization [62].

**Crystallinity.** Polymer specific volume decreases with increasing crystallinity [114]. The highly ordered chain arrangement in crystalline regions precludes the solubility of penetrants, and the chain mobility in the amorphous region is also restricted by neighboring crystallites [82]. Lasoski and Cobs studied the effect of crystallinity on the solubility of water vapor in a partially crystallized poly(ethylene terephthalate) and nylon 6,10 [115]. They found the following relationship to be valid over a range of crystallinity from 0 to 40%.

\[
S = S_a \Phi
\]  

(2.43)

where \( S_a \) and \( \Phi \) are the solubility coefficient and the volume fraction for a totally amorphous material, respectively. The effect of crystallinity on the diffusion coefficient arises from the tortuosity and chain mobility. A correlation for this effect is given by [116]:

\[
D_c = \frac{D}{\xi \beta}
\]  

(2.44)

where \( D \) and \( D_c \) are the diffusion coefficients for completely amorphous and semi-crystalline materials, respectively, \( \beta \) is the parameter accounting for the effect of crosslinking, and \( \xi \) is the tortuosity, which may be related to \( \Phi \) by [116]:

\[
\xi = \Phi^{-n}
\]  

(2.45)

where \( n \) is a constant. The crystallization reduces both diffusivity and solubility of penetrants and therefore should be avoided in gas separation [10, 80].

**Interfacial Properties.** The interface considered here is focused on one that consists of a polymer and a ceramic. On the basis of dynamic and dielectric spectroscopy
studies of the local chain motion of PVAc/SiO$_2$ nanocomposite [92], there exists an interfacial region in the PVAc/SiO$_2$ nanocomposite where the PVAc interacts strongly with the silicate network, and the chain mobility is highly restricted due to these interactions. Because of the increased barriers to the relaxation mode at the glass transition temperature, the relaxation shifts to a higher temperature. Unfortunately, very little data is available to correlate such a type of interfacial properties with gas transport behaviors. The increased Tg or the reduced segmental mobility suggests that composite membranes may be favorably used in the gas separation for improving the permselectivity and the thermal stability, as compared to the unfilled polymer membranes. Based on a very recent study, where a polyimide was cast on silica-impregnated ceramic substrates, the intimate contact of polymer chains with the silica particles brought about a simultaneous increase in oxygen permeability and O$_2$/N$_2$ selectivity [117]. Although this intimate contact may be somewhat different from the interface within the PVAc/SiO$_2$ nanocomposite, this gas separation data has shown the application prospect of polymer/ceramic composite membranes.

**Molecular Weight.** One of ways of increasing the free volume of polymers is to increase the number of chain ends, which can be achieved by a decrease in the molecular weight [114]. Chain ends are more mobile and therefore the Tg typically decreases with increasing concentration of the chain ends [118-119]. Free volume generally increases with decreasing Tg [85]. As a result, the diffusivity decreases with increasing the molecular weight [120]. However the diffusivity of a given penetrant tends to be a constant as the molecular weight reaches a limit [10]. For example, O$_2$ diffusivity in a polystyrene at 25 °C is found to decrease with increasing the molecular weight from 1K to ~20K but stays approximately a constant from 20 K to 400 K [120].
2.1.2.7 Effects of Other Parameters on Permeability and Permselectivity

*Processing Parameters.* Membrane structure control is a key parameter for developing high performance membranes as described in the foregoing sections. However, because of the non-equilibrium character of glassy polymers, the processing conditions are also important for improving the gas transport properties of membranes.

A thin membrane has a high penetrant flux, which can be evaluated from Equation 2.15. However, the mechanical strength of thin films is generally poor, which may prohibit the use of thin membranes at high pressures. Casting a thin film on a porous inorganic substrate such as porous Vycor glass and polyacrylonitrile can overcome this limitation [44, 117]. The membranes prepared in this way are generally called polymer/ceramic composite membranes, but it should be pointed out that this kind of membranes are quite different from the polymer/ceramic nanocomposite membranes as mentioned in the preceding sections, where the ceramic component is actually dispersed within the polymer matrix.

Sub-Tg thermal annealing leads to the reduction of the free volume, which decreases the gas diffusivity and the solubility [121-122]. Heating at temperatures slightly above Tg and then fast cooling can be used to increase the free volume [85, 91, 123]. Aging drives glass polymers toward equilibrium and therefore reduces the free volume [47, 124].

Small amount of solvent in glassy polymers functions as plasticizer to increase the chain mobility [85]. Membranes fabricated using solvent having a large molecular volume show a high gas permeability in comparison to those using solvents having small molecular volumes [36, 125-126]. Previous exposure of a glassy polymer to highly soluble gases such as \( \text{CO}_2 \) or organic vapor tends to have the same effect as the plasticizers [127-128].
Operation Parameters. Primary operation parameters are pressure and temperature. The effect of the pressure on transport properties has been discussed in the foregoing sections, and can be realized from Equations 2.15, 2.18, 2.20 and 2.27. The diffusivity increases significantly at elevated temperatures which can be described by Equation 2.35. However, high temperatures also lead to a significant loss in the permselectivity [8, 129]. As a result, the temperature cannot be too high in order to maintain the purity of the gas separated by membranes. Polyimides are generally regarded as a highly thermally stable polymers, but their application temperature is still not high enough. The hydrogen separation from the ammonia synthesis off-gas of Monsanto and Ube Industries showed that the highest temperature was 150 °C for achieving the H$_2$ purity 95% with the recovery 90 % by using an asymmetric aromatic copolyimide membrane [9]. However, the highest temperature for achieving the H$_2$ purity of 99% with the recovery 84% sharply dropped to 25 °C.

2.1.2.8 Application of Polymeric Membranes in Gas Separations

A number of industrial gas separation systems have been built in the United States since Monsanto introduced a polymer membrane separation process to recover the hydrogen from the ammonia purge gas in 1979. The criteria for the design of commercial polymer membranes are the maximization of the surface area available to the contact with the gas, and the easy management. The majority of commercial membranes are either flat sheet, hollow fiber or spiral wound modules [2]. The flat sheet membranes are made in long rolls and assembled into plate-and-frame or spiral wound configurations. Hollow fibers are small tubes with outer diameters ranging from 50 to 500 micrometers. Feed gases are generally introduced to the outer shell and the permeate is collected from the core. The membrane module is the smallest unit that contains a set of membrane area and
any supporting structure. The modules are assembled into pressure vessels to form a large membrane unit. Some typical applications are briefly presented below.

*Hydrogen separation from industrial gas streams.* The hydrogen separation is one of the earliest commercial applications. As shown in Table 2.4, hydrogen is very permeable relative to most other gases like nitrogen (in ammonia purge stream), carbon monoxide (in syngas adjustments) and methane (in natural gas and refinery process). A selectivity of 200 for $\text{H}_2/\text{N}_2$ and $\text{H}_2/\text{CH}_4$ with the $\text{H}_2$ permeability of 8 barrers can be achieved by using polyamide or polyimide membranes [10]. This makes polymeric membranes particularly attractive for the hydrogen separation from the ammonia purge gas, the syngas ratio ($\text{H}_2/\text{CO}$) adjustment, and the hydrogen recovery from the refining process feed stream [1-2, 9, 10]. The purity of nitrogen produced generally ranges from 65-95%. Higher purity is possible but it accompanies the loss of recovery [2, 10]. These membrane processes have become a successful technology competing with cryogenic, catalytic and pressure swing adsorption. A detailed comparison among these processes, in terms of cost, management and feasibility, etc., can be found in references [2, 10].

*Oxygen and nitrogen enrichment from air.* Membrane-based air separation is relatively new but is growing rapidly, particularly for the applications requiring inert gas blanketing, such as the inert gas blanketing of fresh fruits and vegetables, and inflammable fluids [1-2,10]. The relatively low separation factor of $\text{O}_2/\text{N}_2$, generally 3.5-5.5 for most polymeric membranes [1, 10, 11, 13] makes production of the high purity oxygen difficult [10, 2]. One-stage separation produces the oxygen (permeate stream) with an upper purity limit of typically 30-45%. The purity of nitrogen (residue stream) can be as high as 99.5%, but the membranes are most efficient for the nitrogen purity ranging from 95-98% [2, 10]. The membrane-produced nitrogen showed a clear economic advantage. A powder metal company was using delivered liquid nitrogen with the total cost of $0.53$ per
hundred standard cubic feet (CSCF). For the delivery of same volume of 99% nitrogen gas produced by Monsanto Prism Alpha air separation membrane system, including all the costs such as the compressor power charge and the maintenance charge, the total cost was only $0.26 per CSCF, 50% saving over the delivered liquid nitrogen [2]. Nitrogen blanketing has benefits in the food industry as well. By providing an inert nitrogen-enriched environment for the storage of apples, the apples can be stored without spoiling for more than 28 weeks. This is markedly longer than 6 weeks when the conventional refrigeration is used [10].

Carbon dioxide recoveries from natural gases. Natural gas contains CO$_2$ and H$_2$S, which must be removed before the delivery to prevent the corrosion of pipelines. Both CO$_2$ and H$_2$S permeate much faster than CH$_4$. The ideal permselectivity of CO$_2$/CH$_4$ can be as high as 50 using polyimide and poly(amide-imide) membranes [8, 13]. Furthermore, natural gas from wells is already at high pressures, and therefore the methane (residue stream) purified by membrane is also at high pressures, which eliminates the recompression process [2]. Presently 70% of natural gases is treated by the conventional amine process in which the removal of CO$_2$ and H$_2$S from CH$_4$ is conducted by amine absorption [1-2, 10]. The amine plants are typically large and have a tall structure as compared to the membrane process. A comparison of the amine and the membrane processes for the treatment 10% CO$_2$ natural gas shows that the membrane process saves more than 20% in the processing cost over the amine process [2].

Organic vapor separation. Many industrial processes produce waste air streams which contain organic vapors such as hydrocarbons, naphtha and aromatics [2, 10]. In addition to the loss of these organic substances, it causes serious health, safety and environment problems. The membrane process can be used to clean the air by removing and recovering these vapors. The membranes used in these applications are permeable to
hydrocarbons with air being retained [2]. Although the accurate analysis for the economic advantages of these processes is not available so far, a rather low cost, in comparison to other processes such as condensation, incineration and carbon adsorption, can be expected. The requirements of the emission levels of these organic vapors play a key role in determining the economic advantages of the membrane process [2].

Gas dehydration. Water is much more permeable as compared to other gases, a selectivity over 400 for H₂O/CH₄ can be reached [2, 10]. The membrane process can be used to remove moisture very effectively from a pressurized air stream with a dew point as low as -35 °C [2]. The moisture-laden air exhausted from the dryer contains nearly 90% of energy in forms of latent heat. This heat is supplied to the air before it enters the dryer. The energy is lost when the hot air is vented to atmosphere. Bend Research used membranes to remove and concentrate the hot water vapor in a permeate stream from the exhausted air, making the energy contained in the hot water available to other processes [2]. The removal of carbon dioxide and hydrogen sulfide also accompanies the dehydration process. Natural gas is typically moisture-saturated [2]. The moisture causes corrosion problems if it is allowed to enter the delivery pipelines. Currently, the traditional glycol dehydration process still occupies the major market for the dehydration of natural gas [2]. However, the dehydration of natural gas by the membrane process can be expected to be another emerging application due to the environmental regulations against many organic vapors [1-2, 10, 130], although some technical problems remain in this field. The major problem is the performance constraint and thereby the cost of using the membrane process. The concentration of water in the high-pressure natural gas is generally lower than 0.2 % by mole. This concentration needs to be reduced to 0.014 % to meet the pipeline requirements [2]. Although the carbon dioxide in natural gas can act as the water carrier to bring the moisture cross membrane, and providing a dry air to sweep
the permeate side of membrane also helps to reduce the water concentration [2], too low driving force constrains the cost and performance of the membrane dehydration process [2].

2.2 Sol-Gel Chemistry of Metal Alkoxides

Sol-Gel chemistry of metal alkoxides plays a key role in developing polymer/ceramic nanocomposite materials. The review presented in this chapter will focus on some important fundamental principles, particularly those related to this research.

2.2.1 General Considerations of the Sol-Gel Reactions

Sol-Gel reactions of the precursor M(OR)\textsubscript{n}, where the M represents a metal such as Si, Ti, Zr, Al, and R is an alkyl group such as \(-\text{C}_2\text{H}_5\), are the key reactions in generating ceramic networks. The TEOS (tetraethoxysilane) has been extensively studied. The sol-gel reactions of the TEOS proceed by the hydrolysis, followed by the condensations:

\[ \text{Si} \text{--OR} + \text{H}_2\text{O} \rightarrow \text{Si} \text{--OH} + \text{ROH} \]  \hspace{1cm} (2.46)

\[ \text{Si} \text{--OH} + \text{HO} \text{--Si} \rightarrow \text{Si} \text{--O} \text{--Si} + \text{H}_2\text{O} \]  \hspace{1cm} (2.47)

\[ \text{Si} \text{--OH} + \text{RO} \text{--Si} \rightarrow \text{Si} \text{--O} \text{--Si} + \text{ROH} \]  \hspace{1cm} (2.48)

where R is \(-\text{C}_2\text{H}_5\). The hydrolysis reaction 2.46 can go to completion with the addition of sufficient water. The condensation reactions 2.47 and 2.48 are strongly influenced by the catalyst added. All these reactions are generally carried out in a solvent in which the
TEOS is soluble, with the addition of a certain amount of water and the desired catalyst such as HCl and NH₄OH. By-products ethanol and water must be removed from the system to achieve the three-dimensional silica network. The nature of the catalyst that is generally indicated by the pH of solution has significant effect on the network formed. In general, an acid catalyst tends to produce more extended and chain-like small size particles because of the fast hydrolysis and slow condensation rates. In contrast, a base catalyst tends to produce more compact and branched products due to the fast rate of the condensation reactions [131-134].

In the absence of a catalyst, the hydrolysis and condensation reactions both occur by the nucleophilic substitution mechanism as shown in Equations 2.49 through 2.51. They involve the nucleophilic addition (from a to b), followed by the proton transfer from the attacking molecule to an alkoxide (from b to c), and by the removal of the protonated species as either alcohol (alcoxolation) or water (oxolation) (from c to d) [135-137]:

hydrolysis

\[
\begin{align*}
\text{(a)} & \quad \text{(b)} & \quad \text{(c)} & \quad \text{(d)} \\
H-O + M-OR & \rightarrow & H-O-M-OR & \rightarrow & H-O-M-O-M & \rightarrow & R-O-M-OR & \rightarrow & R-O-M-OR+ROH
\end{align*}
\] (2.49)

alcoxolation

\[
\begin{align*}
\text{(a)} & \quad \text{(b)} & \quad \text{(c)} & \quad \text{(d)} \\
M-O + M-OR & \rightarrow & M-O-M-OR & \rightarrow & M-O-M-O-M & \rightarrow & R-O-M-O-M & \rightarrow & M-O-M+ROH
\end{align*}
\] (2.50)
oxolation

(2.51)

(a) (b) (c) (d)

The short arrow denotes the coordination bond. Equations 2.50 and 2.51 are condensation reactions. The effects of the catalyst along with the effects of the temperature and the alkyl group will be discussed later. The above mechanisms imply that the hydrolysis and condensation reactions are governed by the reactivity (i.e., the electrophilicity) of the metal, the strength of the entering nucleophile, and the partial charge and the stability of the leaving group. Among these, the reactivity of the metals is of the critical importance.

2.2.2. Reactivity of Transition Metals - Partial Charge Model

It can be seen in Equations 2.49 through 2.51 that the partial charge distribution in each species will strongly influence the rate of the hydrolysis and condensation reactions. Transition metals are very electropositive. Therefore, it can be seen from Equation 2.49 that, when the partial charge (denoted by \( \kappa \) in this dissertation) of the oxygen in water, \( \kappa(O) \), is negative, the nucleophilic attacking on the positively charged metal \( M \) is apparently favored. It is also evident that \( \kappa(ROH) > 0 \) in state c of Equation 2.50 favors the alcoxolation condensation, and \( \kappa(H_2O) > 0 \) in state c of Equation 2.51 favors the oxolation condensation. The partial charge distribution of any complex can be calculated by the Partial Charge Model [137].

The partial charge model can be stated as: charge transfer occurs when two or more atoms with different electronegativities combine, and it stops when the electron negativity of each atom equals the mean electronegativity of all the combined atoms [137].
An assumption of the partial charge model is that the electronegativity $\chi_i$ of an atom changes linearly with its charge [138]:

$$\chi_i = \chi_i^0 + w_i \kappa_i$$ (2.52)

where $\chi_i^0$ is the electronegativity of the neutral atom and $w_i$ is the "hardness" which is defined by [139]:

$$w_i = k\sqrt{\chi_i^0}$$ (2.53)

where $k$ is a constant that depends on the electronegativity scale ($k = 1.36$ for Pauling's scale). The mean electronegativity $\bar{\chi}$ is given by [140]

$$\bar{\chi} = \frac{\sum_i p_i \sqrt{\chi_i^0} + kZ}{\sum_i (p_i / \sqrt{\chi_i^0})}$$ (2.54)

where $p_i$ corresponds to the stoichiometry of the $i$th atom in the compound and $Z$ is the total charge of the ionic species ($Z = 0$ for neutral species). Let $\chi_i = \bar{\chi}$, combining Equations 2.52, 2.53, and 2.54 gives the partial charge $\kappa_i$ [137]:

$$\kappa_i = \frac{\bar{\chi} - \chi_i^0}{p_i \sqrt{\chi_i^0}}$$ (2.55)

The Partial Charge Model is derived on the basis of simple ideas and is easy to handle. However, its limitations in theoretical aspects are evident, namely [137]:

1. The Partial Charge Model given in Equation 2.55 does not consider the real structure of the chemical species;
2. The resonance effects and $\pi$ overlapping are not included;
3. The coordination variations that occur during the chemical process are difficult to account for.
On the other hand, the effects of the solvent and the additive such as catalyst are also not taken in account by the Partial Charge Model.

Nevertheless, the Partial Charge Model is found to be successful in describing the chemical reactions involved in the sol-gel process.

Application of the Partial Charge Model to calculate the partial charge on the metals for the precursors that are commonly used in the sol-gel process leads to the result that is given in Table 2.5 [137]. The result in Table 2.5 successfully explains why the hydrolysis and condensation kinetics of transition metals are much faster than those of the Si(OEt)$_4$. The hydrolysis rate constant for the Si(OEt)$_4$ varies from $k_h = 10^{-4}$ to $10^{-6}$ M$^{-1}$ s$^{-1}$ at pH = 3 [135, 141]. The $k_h$ value at pH = 7 can be estimated by extrapolation and found to be $5 \times 10^{-9}$ M$^{-1}$ s$^{-1}$[131]. A rough estimate of the minimum hydrolysis rate constant $k_h$ for the Ti(OEt)$_4$ [142-145] is $k_h = 10^{-3}$ M$^{-1}$ s$^{-1}$[146], that is five orders of magnitude higher! The condensation rate constant of the Ti(OEt)$_4$, $k_c = 30$ M$^{-1}$ s$^{-1}$ [145], is also roughly five orders of magnitude higher than that of the Si(OEt)$_4$, $k_c = 10^{-4}$ M$^{-1}$ s$^{-1}$ [147].

The calculation on the charge distribution within the transition state of a titania dimer (see reactions 2.50 and 2.51) indicates that the protonation of the -OEt group produces a more positively-charged leaving group ($\kappa$(EtOH) = +0.02) than the protonation of the OH ($\kappa$(H$_2$O) = -0.25) [137]. Thus alcoxolation should be the favored condensation reaction. However, the results from NMR investigations indicate that, although both the hydrolysis and the condensation kinetics of the Si(OEt)$_4$ are much slower than those of transition metals such as the Ti(OEt)$_4$, as predicted from the Partial Charge Model [137], the dominant condensation reaction is, however, the oxolation rather than the alcoxolation [141]. This may arise from the effects of solvents and catalysts, which are not accounted for by the Partial Charge Model [146].
Table 2.5. The partial charge on metal for some metal alkoxides [137]

<table>
<thead>
<tr>
<th>Alkoxide</th>
<th>Zr(OEt)$_4$</th>
<th>Ti(OEt)$_4$</th>
<th>Nb(OEt)$_4$</th>
<th>Ta(OEt)$_3$</th>
<th>VO(OEt)$_3$</th>
<th>W(OEt)$_4$</th>
<th>Si(OEt)$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\zeta$(M)</td>
<td>+0.65</td>
<td>+0.63</td>
<td>+0.53</td>
<td>+0.49</td>
<td>+0.46</td>
<td>+0.43</td>
<td>+0.32</td>
</tr>
</tbody>
</table>
2.2.3. Effect of Catalyst

Addition of catalysts has a significant effect on the hydrolysis, the condensation and the gel structure. Acid favors the protonation of the negatively-charged alkoxide group by the mechanism of electrophilic addition [148], increasing the hydrolysis rate by producing strong leaving group [146]:

\[ M\text{--OR} + H_3O^+ \rightarrow M^+ \text{--O} \quad + \text{H}_2\text{O} \]  \hspace{1cm} (2.56)

The protonation transfer within the transition state (see Equation 2.49) and the departure of the leaving group is no longer the rate limiting step [137]. As a result, all OR groups can be hydrolyzed with the addition of sufficient water. It tends to be a general conclusion that hydrolysis can always be improved by using an acid catalyst [135, 149]. More acidic conditions (close to \([H^+] = [Ti]\)) also strongly inhibit the condensation reactions [131]. Since the protonation of the hydroxy (OH) group becomes possible, mixed aquo-hydroxy species such as those encountered with inorganic precursors are formed [137]. On the other hand, the further growth of a condensed particle occurs by continuous addition of lower-molecular-weight species to the more highly-condensed species. In the case of silica, the solubility and the size and temperature dependencies of the solubility are greatly reduced when the silica particles reach 2-4 nm [132]. Thus at low pH, the rapid hydrolysis of the Si(OEt)\(_4\) produces a large number of nucleation sites, and small particles (2-4 nm) are formed [132]. Although these particles can further coagulate, particularly for silica particles, the further growth by condensation of these particles is negligible due to the slow condensation rate.
Base catalyst favors the hydrolysis by the mechanism of the nucleophilic addition [148]. Strong nucleophiles are produced in alkaline conditions via the deprotonation of hydroxo ligands [131]:

$$L-OH + B \rightarrow L-O^{-}BH^{+} \quad (2.57)$$

where $L = M$ or $H$, and $B = OH^{-}$ or $NH_{3}$. The solubility is large in alkaline conditions and is particularly high for small size particles, and furthermore it can be enhanced by increasing the temperature. Therefore the growth rate depends on the size distribution and the particle size depends mainly on the temperature. It is found that, for $Si(OEt)_{4}$, the hydrolysis is the highest at both strong acid and strong base conditions, and the lowest at pH 7 [150]. The silica particles of 1-2 nm in diameter are formed in a few minutes [131]. At pH 8-10, increase in the temperature from 80 to 350 °C leads to an increase in the silica size from 5 to 150 nm in diameter [132].

The mechanism of the electrophilic addition for the hydrolysis reaction in acid conditions implies that the decrease in the length of the alkyl group, $R$, helps to increase the negative partial charge of the $-OR$ group and thereby enhances the rate of hydrolysis [137]. The high-negative partial charge that an $-OR$ group with a short length alkyl group possesses, as compared to a long length alkyl group, can be determined from Equation 2.55. On the other hand, the increase in the length of $R$ also reduces the positive partial charge of the metal $M$, which hinders the hydrolysis reaction in base conditions that follows the mechanism of nucleophilic addition. In fact, the hindered hydrolysis reaction of a metal alkoxide with the long length alkyl group $R$ can also be interpreted in terms of the steric hindrance [146].

Increase in the length of alkyl groups also hinders the condensation reaction [142-143]. This effect can be discussed in the similar ways to that encountered in the hydrolysis
reaction when a long length alkyl group is used. The decreased condensation reaction can also be interpreted in terms of the steric hindrance that a lengthy alkyl group provides [146].

The two different modes of the hydrolysis by using acid and base catalysts also determine the pathways of the condensation. The charge distribution of groups, -OR or -OH, on the inorganic polymer chain can be estimated from the Partial Charge Model. The calculation on a partially-hydrolyzed titanium ethoxide polymer shows that, in acid conditions, the highest negatively-charged -OR groups tend to locate in the ends of the chains and are preferentially protonated. Thus the acid-catalyzed condensation tends to proceed in the ends rather than the middle of chains, producing more extended and less branched inorganic polymers [137]. This trend is found to be consistent with the observation that the combination of the acid catalyst and the low water/metal molar ratio produces monolithic gels [151-152]. In base conditions, the highest positively-charged titanium on the polymer tend to locate in the middle and are preferentially attacked by nucleophilies, as shown in Equation 2.57. Therefore, the base-catalyzed condensation should proceed in the middle rather than in the ends of the chains, resulting in more compact and highly branched products [137, 153].

2.2.4. Effect of Solvent

Sol-Gel reactions are carried out in a solvent. Solvents may be classified as polar and nonpolar, and as protic and aprotic (containing no removable proton) [131]. The parameters measuring the solvating power of a solvent includes polarity, dipole moment and the availability of labile (or removable) proton. The polarity can be judged from dielectric constant (a higher dielectric constant corresponds to a higher polarity). The dipole moment can be experimentally determined. However the availability of labile
protons must be found from the molecular structure of solvents. Although, in general, how well a metal alkoxide can dissolve in a solvent obeys the rule of "like dissolves like", which may be quantitatively judged by the cohesive solubility parameter or Hansen solubility sphere [154], this rule tends to fail when there exists a strong specific interaction between the solute and the solvent, such as hydrogen bonding. Therefore, special considerations need to be given for the effect of hydrogen bonding on the sol-gel reactions.

The hydrolysis of metal alkoxides is catalyzed by either hydronium ions (acid catalyst) or hydroxyl ions (base catalyst) as mentioned previously. Therefore, protic solvents, such as the water and the alcohol that have the labile proton hydrogen bonding to the hydroxyl or hydronium ions, tend to reduce the activity of both acid and base catalysts. On contrary, aprotic solvents such as DMAC (dimethyl acetamide) and THF (tetrahydrofuran) that do not hydrogen bond to the hydroxyl or hydronium ions, make the hydronium ions more electrophilic (acid catalysis) and hydroxyl ions more nucleophilic (base catalysis) [155], and accordingly increase the catalytic activity. For protic solvents with different dipole moments and dielectric constants, the solvents with the high dipole moment and the high dielectric constant tend to hydrogen bond strongly to hydroxyl or hydronium and reduce their catalytic activity to a greater extent [131].

As cited above, the condensation mechanism is also relevant to the pH of solvents, either protonated (acid catalysis) or deprotonated (base catalysis). Few data are available to determine the effect of the solvent type on the condensation kinetics [137]. Aprotic solvents can hydrogen bond to electrophilic protonated metal oxides (in acidic conditions) but cannot hydrogen bond to nucleophilic deprotonated metal oxides (in alkaline conditions). As a consequence, aprotic solvents should increase the base-catalyzed condensation rates but decrease the acid-catalyzed condensation rates [131]. On the other hand, protic solvents can hydrogen bond to nucleophilic deprotonated metal oxides but
hydrogen bond weakly to electrophilic protonated metal oxides. Thus, protic solvents should have the reverse effects \[131].

2.2.5. Effect of Water

The structure of condensed products is determined by the relative rates of four reactions: hydrolysis, oxolation, alcoxolation and olation \[146]. The oxolation and alcoxolation are the condensation processes that have been mentioned earlier and are shown in Equations 2.50 and 2.51. The olation is also a condensation process in which the hydroxyl bridge -OH- is formed between two metal centers \[156]. All these reactions strongly depend on the water amount added. Because of the fast kinetics of the hydrolysis and condensation reactions, little information is available regarding the structure evolution of transition metal systems \[144]. It is quite facile for the hydrolysis and the condensation of transition metal alkoxides to occur when the water/metal molar ratio, \( r \gg 2 \) \[157]. For low \( r \) values and carefully controlled hydrolysis conditions, the resulting product can be isolated as a single crystal and identified by X-ray crystallography \[146]. Four Models were proposed which can be referred to reference \[157]. On the basis of these models, TiO\(_2\) network from the sol-gel reactions of the Ti(OEt)\(_4\) can be expected to form with \( r \geq 2 \) \[146, 157].

Capillary pressure arising from the water in a pore of ceramic network is another problem encountered in the sol-gel process. Assuming the pore to be like a tube that has the height of \( h \) and the diameter of \( a \), the capillary pressure \( P_c \) can be expressed as \[158]:

\[
P_c = \frac{2\gamma_{LV} \cos(\theta)}{a}
\]

(2.58)

where \( \gamma_{LV} \) is the liquid-vapor surface tension, it is 72 dyn/cm for water; \( \theta \) is the contact angle, which is zero for most metal oxides such as TiO\(_2\) and SiO\(_2\) \[159]. Extremely high
capillary pressure $P_c$ can arise from the decrease in the diameter, $d$, during the drying process. For example, when $d = 3 \text{ nm} = 3 \times 10^{-7} \text{ cm}$, $\gamma_{LV} = 72 \text{ dyn/cm}$ and $\theta = 0$, the $P_c$ can be calculated to be $4.8 \times 10^8 \text{ dyn/cm}^2$ that is 474 atm! Such a high pressure often causes the cracking of the network. The cracking of the gels, especially those made from the alkoxides, poses a serious problem in making monolithic ceramics.

2.2.6. Effect of Temperature

The products of sol-gel reactions is not a pure metal oxide, which contains other groups such as water, unreacted alkyl groups, and hydroxyl groups. The amount of these groups on silica gels was studied and found to be strongly affected by temperature [160-163]. In general, majority of water evaporates below 200 °C [160]. Further increase in the temperature from 200 to 600 °C accompanies the decomposition of residual alkyl groups [160-162]. Hydroxyl groups can only be removed at temperatures above 800 °C [161, 163]. On the other hand, the metal oxide particles formed by sol-gel process are generally small. The network is therefore thermodynamically an unsteady system because of the large interfacial free energy [163]. Accordingly, an increase in temperature accompanies an irreversible densification process [163]. The densification can arise from the removal of the groups such as water, unreacted alkyl groups, and hydroxyl groups; the collapse of pores; and the crystallization [160-163]. The condensation reactions are enhanced with the removal of the alkyl groups and hydroxyl groups. The small pores (< 8 nm) collapse at relatively low temperatures of 400 to 500 °C and large pores collapse at higher temperatures of 700-900 °C [161]. Formation of the crack-free monolithic silica glass can be achieved by carefully heating the gel to 1070 °C [161]. However, no significant crystallization of silica gel was found with a heat treatment up to 1200 °C [160]. This may suggest that the crystallization of gels has little effect on the densification process.
2.2.7. Interaction among Metal Oxide Particles - DLVO Theory

One of the steps in making polymer/ceramic composites is the sol preparation. As mentioned earlier, the transition metal alkoxides such as the titanium ethoxide, Ti(OEt)$_4$, have rapid hydrolysis and condensation kinetics. The metal oxide particles may precipitate in sol preparation. Therefore reducing the particle size and maintaining the high dispersion of these particles before mixing them with the polymer are of importance. As discussed in the preceding sections, the metal oxide particles are generally larger than 1 nm. This size (1 nm) is generally recognized as the lower bound of the size of dense colloid particles. The dispersion/coagulation behavior of these particles can be described by the classical DLVO theory, which gives:

\[ E_I = E_d + E_e \]  \hspace{1cm} (2.59)

where, \( E_I \) is the total interaction energy; \( E_d \) the dispersion energy, which is always negative; and \( E_e \) the interaction energy of the electric double layers, which is positive for the same particles. The magnitude of \( E_d \) depends on the particle size, the minimum separation between two particles and the Hamaker constant of the material. The Hamaker constant is in the order of \( 10^{-19} \) J.

The dispersion/coagulation behaviors of particles are usually adjusted by changing the repulsive energy of the electric double layer. The \( E_e \) is related to the electric potential of the electric double layers, called zeta (\( \zeta \)) potential. The potential at slip plane or the plane of shear, as shown in Figure 2.4, is the \( \zeta \)-potential. In general, \( \zeta \)-potential should be 30-50 mV or higher to prevent the coagulation from taking place [164]. A high concentration of counter ions, and particularly a high valence of counter ions in solution can significantly reduce the \( \zeta \)-potential [165]. But at same solution conditions, a high PZC
Figure 2.4. Schematic of the structure of electric double layer. Surface charge on particles is assumed to be positive.
(Point of Zero Charge) helps to increase the $\zeta$-potential. For metal oxides, the PZC is the pH value at which point the surface charge of a metal oxide is equal to zero. In some solution conditions, the larger the difference between the pH of the solution and the PZC of the metal oxide, the greater is the $\zeta$-potential. The PZC values of some metal oxides are given in Table 2.6 [166-167].

The classical DLVO theory predicts the stability of colloid suspensions on the basis of the electrical repulsion and the dispersion attraction. However this theory is found to fail with very hydrophobic and very hydrophilic suspensions [168-178]. Therefore, an additional term, called structure force, needs to be added to the classical DLVO theory. The new model thus attained is called the Extended DLVO (ExDLVO) theory as described by van Oss et al. [168]. The studies on the hydrophilic materials such as rutile and silica [169-171], hematite [171] and mica [172] show that the structure force is a short-range repulsive force, for which the decay length is roughly from 0.5 to 1.5 nm. The hydrophobic materials such as coal [173-174] and nitrocellulose [175], however, display a long-range attractive (hydrophobic) force. The decay length of the hydrophobic force for the amine and octanol treated mica is found to be 6.8 nm [172]. A high ionic strength favors the hydrophilic structure repulsion [171], and a surfactant favors to disrupt the stability [172, 178].

Since metal oxides such as TiO$_2$ and SiO$_2$ are hydrophilic, addition of appropriate amount of water will favor the stability of the particles during the sol preparation.
Table 2.6. The Point of Zero Charge of some metal oxides [166-167]

<table>
<thead>
<tr>
<th>Oxide</th>
<th>ZrO$_2$</th>
<th>TiO$_2$</th>
<th>SiO$_2$</th>
<th>SnO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>Cr$_2$O$_3$</th>
<th>FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZC</td>
<td>pH 4</td>
<td>pH 6.0</td>
<td>pH 2.5</td>
<td>pH 4.5</td>
<td>pH 9.0</td>
<td>pH 8.6</td>
<td>pH 8.4</td>
<td>pH 6.7</td>
</tr>
</tbody>
</table>
2.3 Sol-Gel Approaches of In-Situ Formation of Inorganic Species within a Polymer Matrix

Polymer/Metal oxide nanocomposite materials have been developed in last ten years. The most outstanding feature of these materials that is different from the traditional composite materials is the nanosized domain; the physically constrained metal oxide domain can be reduced to several nanometers. Such kind of materials exhibit the new properties that the traditional materials do not possess and have found applications in optical materials [179-184], electronic materials [185-187], catalysts and adsorbents [188-190], and abrasive-resistant coatings [183, 191-194], etc. A brief review of these applications will be given at the end of this chapter. More interested readers can refer to the cited publications and find the earlier work.

In principle, the application of sol-gel techniques to form the organic/inorganic composite involve two approaches. The first approach is the incorporation of oligomeric polymers or small organic molecules into the inorganic network. The second approach is the in-situ formation of metal oxide within the polymer matrix. These two means involve similar mechanisms. The review presented below will be focused on the second approach since it is related to the research objectives outlined in chapter one. The in-situ formation of metal oxides within a polymer matrix was developed by Mark et al. in the 1980s [195-199]. A number of processes involved in this approach are outlined below.

2.3.1 Crosslinked Poly(dimethyilsiloxane)/Tetraethoxysilane Mixing System - Precipitation of silica within PDMS Elastomer

When an already cross-linked polymeric elastomer is swollen with the TEOS, the hydrolysis and the condensation of the TEOS are carried out within the organic polymer matrix, resulting in the precipitation of the silica filler in the matrix [195, 200]. The
polymer/ceramic composite, with very small and well dispersed metal oxide particles, usually a few hundred angstroms in diameter, can be obtained by this technique. The hydrogen bonding between the elastomer and the silica is an important driving force for the high compatibility. A phase-transfer catalyst favors the transportation of metal alkoxides and other active species into the elastomer matrix and enhances the miscibility. For example, the TEOS can easily transport into the PDMS network. However, the phase-transfer agent tetrabutylphosphonium bromide is found to be necessary for the easy transfer of the acetate ion (presumably the active species) into the PDMS network [195]. The incorporation of the silica network into poly(methylphenylsiloxane) (PMPS) that is cross-linked by benzoyl peroxide and polyisobutylene has also been obtained using this technique [200-201]. Other metal oxides such as titania [202] and alumina [198], and mixed metal oxides such as silica-titania, silica-zirconia and silica-alumina [199] have been also successfully generated in-situ within the PDMS matrix using the same technology. These composite materials display improved mechanical properties in comparison to their unfilled polymers.

2.3.2. Polymer/TEOS Mixing System - Incorporation By Hydrogen Bonding

Nanosized silica domains, which are generally smaller than 10 nm, can be generated in-situ within a polymeric matrix by codissolving the TEOS and polymers [153, 203]. The strong interaction between the silica domains and polymers is attributed to the hydrogen bonding between the residual silanols on the silica surface and the proton donors on the polymers [203]. This technique has found new uses for a number of glassy polymers. Some typical results are given in Table 2.7 [153, 203]. Table 2.7 presents the polymer names and their abbreviations as well as the functional groups capable of hydrogen bonding. This should be sufficient for the present discussions. The detailed
Table 2.7. Optical transparency of some polymer/silica composite films [153, 203]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Abbr.</th>
<th>Functional groups</th>
<th>Composite</th>
<th>Coating Temp (°C)</th>
<th>solvent</th>
<th>Film appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>PMMA</td>
<td>C=O</td>
<td>PMMA/TEOS 50/50 acid</td>
<td>≥ 30</td>
<td>THF</td>
<td>Transparent</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>PMMA</td>
<td>C=O</td>
<td>PMMA/TEOS 50/50 acid</td>
<td>~11</td>
<td>THF</td>
<td>Opaque</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>PMMA</td>
<td>C=O</td>
<td>PMMA/TEOS 50/50 base</td>
<td>≥ 30</td>
<td>THF</td>
<td>Opaque</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>PMMA</td>
<td>C=O</td>
<td>PMMA/TEOS 25/75 base</td>
<td>≥ 30</td>
<td>THF</td>
<td>Opaque</td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td>PVAc</td>
<td>C=O</td>
<td>PVAc/TEOS 50/50 acid</td>
<td>≥ 30</td>
<td>THF</td>
<td>Transparent</td>
</tr>
<tr>
<td>Bisphenol-A Polycarbonate</td>
<td>BPA-PC</td>
<td>C=O</td>
<td>BPA-PC/TEOS 50/50 acid</td>
<td>≥ 30</td>
<td>THF</td>
<td>Opaque</td>
</tr>
<tr>
<td>Poly(vinyl pyrrolidone)</td>
<td>PVP</td>
<td>C=O</td>
<td>PVP/TEOS 50/50 acid</td>
<td>≥ 30</td>
<td>EtOH</td>
<td>Transparent</td>
</tr>
<tr>
<td>Poly(acrylic acid)</td>
<td>PAA</td>
<td>C=O and O-H</td>
<td>PAA/TEOS 50/50 acid</td>
<td>≥ 30</td>
<td>EtOH</td>
<td>Opaque</td>
</tr>
<tr>
<td>P(MMA-co-MAA)</td>
<td>P(MMA-co-MAA)</td>
<td>C=O</td>
<td>P(MMA-co-MAA)/TEOS 50/50 acid</td>
<td>≥ 30</td>
<td>THF</td>
<td>Transparent</td>
</tr>
<tr>
<td>Poly(methyl methacrylate-co-methacrylic acid)</td>
<td>P(MMA-co-MAA)</td>
<td>C=O</td>
<td>P(MMA-co-MAA)/TEOS 50/50 base</td>
<td>≥ 30</td>
<td>THF</td>
<td>Opaque</td>
</tr>
<tr>
<td>Poly(N,N-dimethyl acrylamide)</td>
<td>PDMA</td>
<td>C=O</td>
<td>PDMA/TEOS 50/50 acid</td>
<td>≥ 30</td>
<td>DMF</td>
<td>Transparent</td>
</tr>
<tr>
<td>Nylon-Trogamid-T</td>
<td>Trogamid</td>
<td>C=O and N-H</td>
<td>Trogamid/TEOS 50/50 acid</td>
<td>≥ 30</td>
<td>DMF</td>
<td>Opaque</td>
</tr>
</tbody>
</table>
structures of these polymers can be found from the reference [203]. By using the optical transparency of composite films as the criterion of the high compatibility, the results in Table 2.7 can be summarized below:

1. Small silica domains (on the order of 10 nm) can be generated in-situ in the matrix of those polymers that contain only the proton acceptor C=O. These polymers are the PMMA, PVAc, PVP, and PDMA;

2. High compatibility cannot be obtained with those polymers that contain both proton acceptor and proton donor pair, such as C=O and O-H; and C=O and N-H. These polymers include the PAA and the Trogamid;

3. Copolymer P(MMA-co-MAA) is an exception. This polymer contains C=O/O-H pair, but the film appearance depends on the catalyst used. Acid catalyst leads to the transparent film, but base one results in the opaque film. The BPA-PC is another exception. The opaque film results although this polymer contains C=O group only.

The low compatibility of the Trogamid and the silica is believed to arise from the self-hydrogen bonding of the Trogamid (through the N-H and C=O groups), which weakens the interaction between these groups and the silica [203]. The poly(amide-imides) that will be used in this study also contain both proton acceptor and proton donor pair, C=O/N-H. Therefore, a careful analysis is needed to achieve the conditions that lead to the high compatibility of this polymer and metal oxides.

Fitzgerald et al. studied the local chain motions of the poly(vinyl acetate)/SiO$_2$ nanocomposite by DMTA, DETA and FTIR spectroscopies [92]. The poly(vinyl acetate), PVAc, has the C=O group on its backbone. FTIR result shows that the hydrogen-bonded C=O groups (centered at ~1710 cm$^{-1}$) increase with the SiO$_2$ content in the composite.
When the SiO₂ content changes from 5 to 60 % by weight, the weight fraction of hydrogen-bonded C=O groups was found to be from 30% to 80%. The hydrogen-bonded C=O groups in the vitrified composites decrease with increasing temperature of cure. This suggests that the hydrogen bonding between the polymer and the silica may be important in preventing macro-phase separation only before the vitrification stage. When dielectric data were fit by the KWW (Kohlrausch-Williams-Watts) equation, the distribution parameter β for the relaxation was found to decrease with increasing TEOS content, indicating a broadening of the relaxation times. However, on the basis of the DETA and DMTA results, high temperature cure leads to a narrow distribution of relaxation times. These results suggest that there exists an interfacial region in the composite where the PVAc interacts strongly with the silicate network, and the chain mobility is highly restricted due to these interactions. Because of increased barriers to the relaxation mode at the glass transition region, the relaxation shifts to higher temperatures [92, 153, 203].

2.3.3. Poly(dimethylsiloxane)/Tetraethoxysilane Mixing System - Endlinking by Covalent Bond

Hybrid networks can be formed by covalently linking the ceramic and inorganic components. Hydroxyl-Terminated poly(dimethylsiloxane) having a hydroxyl group chemically compatible with the hydroxyl group on the hydrolyzed TEOS makes it possible to end-link through a covalent bond the PDMS and the TEOS [197, 199, 204-205]. The silica precipitation occurs during the stage of cure. An excess TEOS ([-OC₂H₅]/[OH] molar ratio >>1, say, 100) and a long reaction time (say 3 days) were found to be necessary to enhance the end-linking reaction [197, 199]. The amount of the SiO₂ precipitated into the PDMS network increased with increasing [-OC₂H₅]/[OH] molar ratio. The resulting networks were extracted by solvents such as THF and toluene to get
rid of excess sols [197, 199]. The composite thus formed showed a maximum in ultimate strength. The toughness increases with the increase in the TEOS concentration [204]. The silica particles were found by electron microscopy to be unagglomerated, with the average domain size of ~200 Å in diameter [197]. This technique has also been applied to other polymer/metal-oxide systems such as poly(arylene ether phophine oxide)/titania composite [206], poly(arylene ether sulfone)/titania composite [107], poly(arylene ether ketone)/titania composite [207], poly(tetramethylene oxide)/alumina [208], the poly(tetramethylene oxide)/titania, and poly(tetramethylene oxide)/zirconia composites [209]. The polyurethane/silica composite is also obtained by the essentially same mechanism. The polyurethane is specially synthesized to provide an unsaturated pendant group along its backbone. The unsaturated polyurethane then reacts with the partially hydrolyzed tetramethoxysilane. The silica particles, with the domain size of 150-180 nm in diameter, as verified by TEM, were found to be highly dispersed throughout the polyurethane matrix [210].

2.3.4. Organic Monomer/Tetraethoxysilane Mixing System - Incorporation by "Site-isolation"

The TEOS can also react with a carboxylic acid, leading to the substitution of one or more alkoxide groups by carboxylate groups [131]. The reaction is found to be easy to carry out when the TEOS is mixed with the organic monomer (rather than polymer) that contains the carboxylic acid group [211-212]. This technique has been successfully employed to incorporate the nanosized silica network into the polyimides synthesized from ODA (4,4'-oxydianiline) and either PMDA (1,2,4,5-benzenetetracarboxylic acid dianhydride) or BTDA (3,3',4',4'-benzophenetetracarboxylic acid dianhydride) [211]. After the TEOS is bonded with the carboxylic acid, the synthesis of the polymer is carried
out in the normal procedure that follows the ring closure mechanism. The hydrolysis and the condensation reactions are believed to occur during the thermal curing step when the water is released from the ring closure reaction. The resulting silica particles remain site isolated after silica particles are formed because of the relative rigidity of the polyimide matrix. The "site isolation" strategy significantly prevents the agglomeration of silica particles and enables the formation of highly transparent composites. It is found that opaque composite forms when the polyimide (not the organic monomers) is mixed with the TEOS. The composite obtained by the "site-isolation" exhibited good mechanical properties. The domain size of silica particles is smaller than 1.5 nm on the basis of the TEM result. Other metal oxides such as TiO₂, Fe(O)OH and Cr₂O₃ were also generated in-situ within the same polyimides using the same technique [211-212].

2.3.5 Applications

The sol-gel technique makes it possible to develop organic/inorganic nanocomposite materials with a variety of properties such as hardness, optical properties and catalytic activity, depending on the reaction conditions and the primary materials used. As cited in section 2.2, the cracking of gels made from metal alkoxides is a serious problem in making monolithic ceramics. This can be greatly improved by adding some polymeric components [191-194, 213-215]. The polymer added also favors the adhesion between the coating and the polymer substrate. The optical loss of many inorganic glasses is generally lower than that of polymers. Organic glasses doped with the nanosized domain of inorganic compounds are therefore clearly superior to their unfilled glasses [179-184]. The organic/inorganic composite materials also provide a great opportunity to produce highly porous catalysts, porous supports and porous absorbents [13, 188-190]. The pores can be achieved by calcination of organic/inorganic composites at high temperatures,
generally 400-500 °C. The pore size can be adjusted by polymer concentration and structure. The polymer incorporated with nanosized ceramic domain should possess reduced chain mobility. This factor should undoubtedly affect the transport behavior of gases through such materials. It should be pointed out that commercial applications of these materials are not yet realized. However, their need in the market in the future has promise.

2.4. Hydrogen Bonding

As mentioned in the foregoing sections, strong hydrogen bonding is the major driving force for achieving the high compatibility between metal oxides and polymers when there is no chemical bond involved. In this section, the effect of some important molecular parameters on the hydrogen bonding will be reviewed. This will provide a theoretical guidance for achieving the high compatibility between metal oxides and polymers.

2.4.1. General Considerations of Hydrogen Bonding

A hydrogen bond can be expressed as:

\[ A-H \cdots B \]

where A and B are generally the atoms that have high electronegativity and small atomic radius, H is the hydrogen atom. A-H is called the proton donor and B the proton acceptor. The solid line is generally a covalent bond, the dashed line denotes the hydrogen bond. In most literature, the length of the hydrogen bond is defined as the distance from the center of A to the center of B [216]. The hydrogen bond is longer than the covalent radius but shorter than the van der waals radius [216-217]. The hydrogen bond energy ranges from 2-10 kcal/mole [218]. There is no universal definition for a hydrogen bond. The most basic
feature of a hydrogen bond is the electrostatic attraction between the naked proton and the lone electron pair in the acceptor B [216-217]. The naked proton results from the highly electronegative A that strongly attracts the electron of H. In general, there are four contributory effects for the formation of a hydrogen bond and they are all essentially electrostatic in character [216-221]:

1. Electrostatic interactions,
2. Delocalization effects,
3. Repulsive forces,
4. Dispersion forces.

(1) Electrostatic interactions, predominantly the Coulombic attraction, are the result of the attraction between the positively charged proton and the lone electron pair in the acceptor group; (2) Delocalization or charge transfer interactions arise from the mutual distortion of their negative-charge distributions when the proton donor A-H approaches the proton acceptor B, leading to a redistribution or a delocalization of the negative charge, and part of the negative charge residing at A or H; (3) Repulsive force arises from the overlapping of the electron clouds of atoms A, H and B in the case that too many electrons occupy a given volume, leading to the violation of the Pauli exclusion principle; (4) Dispersion interactions are attributed to the coordination motion of the electrons in the proton donor and the acceptor. This motion gives rise to the dispersion interactions between the fluctuating dipole in A-H and the fluctuating dipole in B induced by the dipole in A-H. It is clear that high electronegativity and small atomic size of both A and B favor the Coulombic attraction and the reduction of the repulsion. However, a large atomic size of the acceptor B should favor the delocalization interaction. The delocalization or charge transfer interactions have received the most attention [220]. A study of the hydrogen bonding energy on the –O–H···N and –O–H···O systems shows that, although the
acceptor O has a higher electronegativity and a smaller atomic size than the acceptor N [217], and therefore the Coulombic attraction should be high and the repulsion force caused by the electron overlapping should be low, the total hydrogen bonding energy of \(-\text{O}\cdots\text{H}\cdots\text{N}\) is nearly twice as that of \(-\text{O}\cdots\text{H}\cdots\text{O}\) [220]. An estimate indicates that the energy arising from the delocalization or charge transfer interactions for the \(-\text{O}\cdots\text{H}\cdots\text{N}\) is roughly ten times as that for the \(-\text{O}\cdots\text{H}\cdots\text{O}\) [220]. The large atomic dimension of both A and B should also favor the formation of fluctuating dipoles in A-H and B and thereby enhance the dispersion energy. However this may simultaneously reduce the Coulombic attraction and increase the repulsive force. These four contributions to the hydrogen bond in ice have been estimated by Colson [218] and are given below:

<table>
<thead>
<tr>
<th>Description</th>
<th>Energy (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrostatic (Coulombic)</td>
<td>-6.0</td>
</tr>
<tr>
<td>Delocalization (charge transfer)</td>
<td>-8.0</td>
</tr>
<tr>
<td>Repulsive overlap</td>
<td>+8.4</td>
</tr>
<tr>
<td>Dispersion</td>
<td>-3.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>-8.6 kcal/mole</strong></td>
</tr>
</tbody>
</table>

One half the experimental heat of sublimation of ice: -6.1 kcal/mole (at 0 °C) [220].

Above results simply show that none of the four individual interactions is small enough to be neglected.

2.4.2. Infrared Features of Hydrogen Bonding

An important parameter of a hydrogen bond is the bond length, which can be determined by X-ray and neutron diffraction studies [220, 222-223]. Many theoretical models are also developed for the calculation of hydrogen bonding energy. All these
models can be classified into three groups [224]: (1) molecular orbital theories, (2) valence bond theories, and (3) charge transfer theories. Since only hydrogen atom or hydrogen-like atoms can be accurately treated by the Schrödinger equation, all the quantum mechanical treatments of hydrogen bonds such as SCF model (Self-Consistent Field) and LCAO-MO model (Molecular Orbitals Built as Linear Combination of Atomic Orbitals) are unavoidably added with some approximations. Accordingly, the parameters such as the hydrogen bond length and energy for different systems can only be compared within the same model. An extensive review can be found from reference [225]. This section will focus on the IR spectroscopic feature of hydrogen bond systems.

2.4.2.1 General Features of IR Spectroscopy

A diatomic molecule P-Q where P and Q denote any two atoms is treated in vibrational spectroscopy as a spring connected with two small spheres P and Q. The fundamental motions are the stretching and the bending vibrations. The vibrational frequency and the intensity are the experimental parameters in IR vibrational spectroscopy. The vibrational frequency for the harmonic oscillator is given by the basic equation:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m_r}} \quad (2.62)$$

where $\nu$ is the vibrational frequency, $k$ is the force constant and $m_r$ is the reduced mass:

$$m_r = \frac{m_pm_Q}{m_p + m_Q} \quad (2.63)$$

The IR absorption is proportional to the rate of the change of the electrostatic dipole moment $\mu(P-Q)$. For a hydrogen bonded system A-H⋯B, the force constant $k$ of A-H is weakened by the hydrogen bonding, which shifts the A-H absorption to lower
frequencies. Furthermore, the electrostatic dipole moment \( \mu(A-H) \) becomes more sensitive to the IR radiation because of the increased polarity of molecules, which enhances the intensity of the absorption.

2.4.2.2 IR Shift and IR Absorption of Hydrogen Bonded Systems

For a complex A-H\(\cdots\)B, the IR feature can be summarized below [220, 226-227]:

1. A-H stretching vibrations (both fundamentals and overtones) are shifted to lower frequencies because of the weakening of the force constant of the A-H stretching mode. This shift ranges from about 30 cm\(^{-1}\) to several hundred cm\(^{-1}\);

2. A-H bending vibrations are shifted to higher frequencies due to the extra constraint added by the hydrogen bond to the bending mode. This shift is found to be appreciably smaller than that of A-H stretching vibrations;

3. The shifted absorption band of the A-H stretching mode is much broader and the integrated intensity of the fundamental A-H stretching band increases. The change in the half-band width \( \Delta v_{1/2} \) can vary from 30 cm\(^{-1}\) to 100 cm\(^{-1}\) and the integrated intensity can be up to ten times higher than that of free A-H modes. However, the integrated intensity of the corresponding overtones decreases slightly. This is believed to arise from the electrostatic character of hydrogen bonds that leads to a sensitive change of the IR active absorption to the rate of the change of electrostatic dipole moments;

4. The A-H bending modes do not show any appreciable band broadening or intensity change;

5. New H\(\cdots\)B stretching and bending vibrations can be found in far IR regions due to the weak force constant of the hydrogen bond;
6. Vibrations of the hydrogen bonded acceptor B are shifted to either lower or higher frequency but this shift is generally much smaller than that of hydrogen bonded A-H vibrations.

A-H stretching vibrations of hydrogen bonded systems have been widely investigated because the large IR shift can be easily measured [228-230]. The A-H bending vibrations may occur in 1700-1000 cm⁻¹ (in-phase deformation) and 1000-400 cm⁻¹ (out-phase deformation) [220]. However, a large number of other vibrational modes also occur in these two regions, which complicates the effect of the hydrogen bonding and therefore restricts its application. The H···B stretching and bending vibrations can be detected in the far IR region [231]. The far IR region, however, is very water sensitive. A good purge, preferably using dry nitrogen is needed for IR instrument, to rule out the effect of water. On the other hand, a large number of bands can also occur in far IR region, which could make the assignment of the H···B confusing [220]. The vibrations of the acceptor such as C=O stretch are widely studied for polymers [219, 229-230]. In general, the stretching vibrations of the C=O group are shifted to lower frequency upon hydrogen bonding. The change in the intensity can be the indication of hydrogen bonding [219-220, 229-230, 232]. However, a precaution must be taken for the effect of solvents, because even "inert" solvents can also cause a change in the absorption intensity [220].
Chapter 3

IN-SITU FORMATION OF NANOSIZED TiO₂ DOMAINS WITHIN POLY(AMIDE-IMIDE) BY A SOL-GEL PROCESS: MORPHOLOGY AND DYNAMIC MECHANICAL PROPERTIES

3.1 Abstract

Nanosized TiO₂ rich domains have been generated in-situ within a poly(amide-imide) (PAI) by a sol-gel process. The PAI/TiO₂ composite films showed a high optical transparency. The morphology of the TiO₂ rich domains was observed by transmission electron microscopy (TEM). The TiO₂ rich domains were well dispersed within the PAI matrix and the maximum size of the domains ranged from less than 5 nm to 50 nm and increased with the TiO₂ content (from 3.7% to 17.9 % by weight). In comparison to the unfilled PAI, the composites showed an increased glass transition temperature, an increased rubbery plateau modulus, and a decreased crystallinity. It was also found that nanosized SiO₂ rich domains were difficult to form within the PAI matrix. However, the SiO₂ could be bonded with the TiO₂ and formed nanosized domains within the PAI. The dynamic mechanical properties in rubbery regions suggest that TiO₂ domains function as physical crosslinks, increasing the rubbery plateau modulus with increasing TiO₂ content. This behavior can be explained by the theory of rubbery elasticity. The actual formation of the nanosized TiO₂ and TiO₂-SiO₂ rich domains was explained in terms of hydrogen bonding effects between the polymer, the solvent and the inorganic components.
3.2. Introduction

The aromatic poly(amide-imide) (PAI) brings together both the superior mechanical properties typically associated with polyamides and the high thermal stability characteristics of polyimides [13, 15]. A more important feature in the molecular structure of the PAI is the amide group in its backbone, which facilitates hydrogen bonding. This opens the possibility of incorporating nanosized metal oxides within the PAI by a sol-gel process. The resulting composites have potential applications in abrasive-resistant coatings, catalysts, electronic materials, and optical materials and absorbents.

Sol-Gel reactions of metal alkoxides, which can be generalized and divided into hydrolysis, alcoxolation, and oxolation [135-137], have been used extensively to form metal oxide networks within organic polymeric matrices. The sol-gel reactions of tetraethyltitanate (TET) can be expressed by

\[
\text{Hydrolysis: } \equiv \text{Ti(OEt)}_4 + \text{H}_2\text{O} \rightarrow \equiv \text{TiOH} + \text{EtOH} \\
\text{Alcoxolation: } \equiv \text{Ti-OH} + \text{EtO-Ti} \equiv \rightarrow \equiv \text{Ti-O-Ti} \equiv + \text{EtOH} \\
\text{Oxolation: } \equiv \text{Ti-OH} + \text{HO-Ti} \equiv \rightarrow \equiv \text{Ti-O-Ti} \equiv + \text{H}_2\text{O}
\]

The condensation products are the TiO\(_2\) rich network, not a pure TiO\(_2\) network, which may contain other residual groups, such as unreacted alkyl groups and hydroxyl groups.

Little success has been made in achieving nanosized metal oxide domains within glassy polymers that contain both the hydrogen acceptors and hydrogen donors, such as the PAI, although theoretically this can be achieved via the hydrogen bonding between the amide groups (either N-H or C=O, or both) in the PAI and the residual OH group on a metal oxide. This study is primarily focused on the PAI-TiO\(_2\) sol-gel system. The theory and the methodology involved will provide a fundamental understanding for the
fabrication of homogeneous nanocomposite materials using metal alkoxide and the polymer systems that contain either proton donors or proton acceptors, or both.

3.3. Experimental Methods

3.3.1. Materials

The structure of the PAI used throughout this study is shown in Figure 3.1. The polymer was synthesized in Professor McGrath's laboratory in the Department of Chemistry, Virginia Tech. The number average of molecular weight, Mn, of the PAI was determined by GPC to be 18.1 K with the dispersity ratio $M_w/M_n = 2.7$ where $M_w$ is the weight average of molecular weight. The glass transition temperature of the PAI is about 275 °C [15].

Tetraethyltitanate (TET) was obtained from Aldrich Chemical Company, the catalog number 24,457-9, based on 1992-1993 Aldrich Catalog Handbook of Fine Chemicals. The titanium content of received TET was ~20 %. The TET was used as received without further purification. The content of the Ti(OEt)$_4$ was calculated assuming that all the titanium existed in the form of Ti(OEt)$_4$.

Tetraethyl orthosilicate (TEOS) was also obtained from Aldrich Chemical Company, the catalog number 33,385-9, in 1992-1993 Aldrich Catalog Handbook of Fine Chemicals. The TEOS (Si(OEt)$_4$) content was 99.999% and was used as received without further purification.

3.3.2. Fabrication of Composite Films

The pyrex glass plate used to cast the solutions was treated by an aqueous solution containing 2% KOH by weight for 24 hours, and then washed by a sulfuric acid solution
Figure 3.1: Molecular structure of the poly(amide-imide) (PAl).
that contained \( \sim 5\% \) of \( \text{K}_2\text{Cr}_2\text{O}_7 \) and 1% of water by weight. The acid-washed plate was rinsed by tap water and treated again by the KOH aqueous solution for \( \sim 12 \) hours. The plate was finally rinsed by double-distilled water and dried in an oven at \( \sim 120 \, ^\circ\text{C} \) for 1-2 hours and then cooled down to room temperature. The plate was sprayed with acetone before the casting of solutions.

A DMAC solvent was used to dissolve the PAI. The incorporation of the TiO\(_2\) network or other metal oxides into the PAI was achieved by first dissolving the PAI of \( \sim 0.5 \) g in the DMAC solvent at the polymer concentration of \( \sim 7 \% \) by weight. The TET sol was prepared by adding the DMAC solvent, which contained a desired amount of HCl and double-distilled water, to TET under fast agitation. After being stirred for about 0.5-1 minute, the TET sol was added immediately to the PAI solution under continuous agitation. An orbital shaker was used to eliminate the bubble formation. The solution was then stirred at ambient temperature for 30-36 hours. The homogeneous transparent solution was then cast in a Teflon ring placed on the pre-treated pyrex glass plate at a controlled temperature. The drying rate was controlled by a heat lamp. The time of drying generally ranged from 12 to 48 hours, depending on the desired drying rate. The drying was carried out in a closed box with the dry nitrogen being purged. After drying, the free standing films automatically lifted off. The film thickness achieved was 15-70 \( \mu\text{m} \). The resulting films were then cured in a vacuum at 100 \( ^\circ\text{C} \) for 24 hours, 150 \( ^\circ\text{C} \) for 12 hours and 200 \( ^\circ\text{C} \) for another 12 hours. After curing, the residual DMAC and HCl in the film were extracted by immersing the film into \( \sim 300 \) ml methanol for 12-24 hours and cured again in a vacuum at room temperature for 24 hours, 150 \( ^\circ\text{C} \) for 24 hours and 220 \( ^\circ\text{C} \) for another 24 hours.

The incorporation of the TiO\(_2\)-SiO\(_2\) network into the PAI was carried out in a similar manner. The only difference was in the preparation of the TET/TEOS sol.
TET sol was added to partially hydrolyzed TEOS sol (the molar ratio of H₂O/Si = 1~1.5) under fast agitation. After the reaction of the TET and the TEOS proceeded for 30 minutes, the TET/TEOS sol was added to the PAI solution under agitation.

The preparation of the PAI/SiO₂ membrane was similar to that of the PAI/TiO₂ membranes.

3.3.3. Characterization

Thermal Gravimetric Analysis (TGA) was carried out with a TG/DTA 200 Seiko I instrument. The heating rate of 10 °C/minute was used for all experiments. Prior to the experiments, the sample of 5-10 mg was put in an aluminum pan and preheated at 100 °C in the TGA instrument for 5 minutes to get rid of the water absorbed from the atmosphere during the sample loading. The experiment was carried out in a N₂ atmosphere.

Dynamic Mechanical Thermal Analysis (DMTA) was carried out using a DMS210 Seiko II instrument. The samples were cut to be ~5 mm wide and ~35 mm long. The highest temperature employed was ~450 °C. The experiment was carried out in a N₂ atmosphere.

Differential Scanning Calorimetry (DSC) analysis was conducted with a DSC220C Seiko II instrument. The sample of 17 mg was placed in an aluminum pan and heated at a rate of 10 °C/minute in the DSC instrument from room temperature to ~290 °C, which is slightly above the Tg ~275 °C of the PAI, and then quenched using liquid nitrogen to ~70 °C. The quenched sample was then heated from ~70 °C to 450 °C at 10 °C/minute. The experiment was carried out in a N₂ atmosphere.

Wide Angle X-ray Diffraction (WAXD) analysis was carried out on a Nicolet diffractometer equipped with a STOE Bragg-Brentano type goniometer. CuKα radiation
of the wavelength 1.54 Å was used after monochromatization through a graphite monochromator. Data were collected from 50 to 500 with the increment 0.05 °.

Transmission Electron Microscopy (TEM) analysis was performed on thin cross-sections of 800-1200 Å using a Philips EM-420 scanning transmission electron microscope (STEM) operated at the transmission mode at 100 kV. The samples for the TEM analysis were microtomed at ambient temperature to obtain the cross-section through the thickness of samples.

3.4. Results and Discussions

3.4.1. Film appearance

Optical transparency can be used as an initial criterion for the homogeneous mixing of organic and inorganic components. When the inorganic domains and the polymer matrix have different refractive indices, it is possible that an optically opaque membrane will contain ceramic domains larger than 200 nm. This is generally the lower bound detected by the light scattering technique [233]. On the other hand, the scattering effect of light becomes negligible if the ceramic domains are appreciably smaller than 100 nm, giving rise to an optically transparent membrane [153]. The refractive index of metal oxides is generally different from that of polymers. For example, the refractive index of most polyimide-based polymers is 1.5-1.7 [234]. The refractive index of sol-gel derived TiO2 rich product may be compared with that of some crystalline forms of pure TiO2, which ranges from 2.49 to 2.90 [235]. Many experimental observations have shown that the optical appearance of a polymer/ceramic composite can be correlated with the ceramic domain size [92, 153, 203, 211-212]. The optical appearances of some typical composite films, along with the fabrication conditions, are given in Table 3.1.
Table 3.1. PAI/metal oxide membrane fabrication (use DMAC as solvent)

<table>
<thead>
<tr>
<th>No.</th>
<th>Membrane</th>
<th>Composite</th>
<th>MO$_2^a$ % by wt.</th>
<th>H$_2$O/M$_b$ Mol. Ratio</th>
<th>Optical appearance</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PAI/TET33/HCl(0.17)/CRm/FE</td>
<td>PAI/TiO$_2$</td>
<td>5.3</td>
<td>7</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>PAI/TET50/HCl(0.17)/CRm/FE</td>
<td>PAI/TiO$_2$</td>
<td>10.1</td>
<td>7</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PAI/TET50/HCl(0.17)/CRm/SD</td>
<td>PAI/TiO$_2$</td>
<td>10.1</td>
<td>7</td>
<td>Opaque</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PAI/TET50/HCl(0.11)/C70/FE</td>
<td>PAI/TiO$_2$</td>
<td>10.1</td>
<td>7</td>
<td>-</td>
<td>Gelled immediately</td>
</tr>
<tr>
<td>5</td>
<td>PAI/TET58/HCl(0.17)/CRm/FE</td>
<td>PAI/TiO$_2$</td>
<td>13.4</td>
<td>5</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>PAI/TET58/HCl(0.17)/CRm/MD</td>
<td>PAI/TiO$_2$</td>
<td>13.4</td>
<td>5</td>
<td>Opaque</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>PAI/TET66/HCl(0.21)/CRm/FE</td>
<td>PAI/TiO$_2$</td>
<td>17.9</td>
<td>6</td>
<td>Transparent</td>
<td>Brittle</td>
</tr>
<tr>
<td>8</td>
<td>PAI/TET36/TEOS36/</td>
<td>PAI/TiO$_2$-SiO$_2$</td>
<td>11.4/8.6</td>
<td>6</td>
<td>Transparent</td>
<td>Brittle</td>
</tr>
<tr>
<td>9</td>
<td>/HCl(0.19)/CRm/FE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>PAI/TEOS28/HCl(0.0022)/C25/FE</td>
<td>PAI/SiO$_2$</td>
<td>3.1</td>
<td>4</td>
<td>Opaque</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>PAI/TEOS46/HCl(0.0026)/C25/MD</td>
<td>PAI/SiO$_2$</td>
<td>6.7</td>
<td>4</td>
<td>Opaque</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>PAI/TEOS46/HCl(0.0026)/C70/FE</td>
<td>PAI/SiO$_2$</td>
<td>6.7</td>
<td>4</td>
<td>Opaque</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>PAI/TEOS50/HCl(0.21)/C25/FE</td>
<td>PAI/SiO$_2$</td>
<td>7.8</td>
<td>7</td>
<td>Opaque</td>
<td></td>
</tr>
</tbody>
</table>

*a* Assuming 100% conversion of metal alkoxides to metal oxides

*b* Water is based on 37% HCl (63 % water) and the water added, M=Ti, Si or both.
The nomenclature adopted to describe the fabrication conditions of each composite includes six parts. An example is PAI/TET50/HCl(0.17)/C70/FD, which includes the following information:

<table>
<thead>
<tr>
<th>PAI</th>
<th>TET(50)</th>
<th>HCl(0.17)</th>
<th>C70</th>
<th>FD</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
</tr>
</tbody>
</table>

(1) Polymer name, the PAI,
(2) Percentage of the metal alkoxide concentration by mole on the basis of amide-imide repeat unit in the PAI, TET(50) = 50% TET by mole,
(3) Catalyst concentration, HCl(0.17) = 0.17 mole HCl per liter of solvent,
(4) Coating temperature, C70 = 70 °C. CRm = room temperature (~25 °C - 35 °C);
All coating was done in an air atmosphere,
(5) Drying rate, SD = slow drying, ~90% of solvent is evaporated within 48 to 72 hours; FD = fast drying, ~90% of solvent is evaporated within 8 to 12 hours; MD = moderate drying, the ~90% of solvent is evaporated within 12 to 48 hours.

The optical appearances in Table 3.1 can be summarized below:

1. The PAI/SiO₂ composite films are generally opaque;
2. The PAI/TiO₂ and PAI/TiO₂-SiO₂ composite films are generally transparent if the fabrication conditions are correctly selected.

The optical transparency of the PAI/TiO₂ composites implies that the TiO₂ domain sizes are small and are well dispersed within the PAI in comparison to the opaque PAI/SiO₂ composites. This suggests that the sol-gel product TiO₂ has a stronger reactivity, presumably in hydrogen bonding, than the SiO₂. A more detailed discussion on the compatibility of the organic and inorganic components will be given in section 3.4.3.
In the fabrication conditions used in this investigation, the acid was selected as the catalyst and the H₂O/metal molar ratio was relatively high (5-7). The reason for this is that the acid catalyst generally always favors the formation of more extended and chain-like small size particles because of the relatively fast hydrolysis and slow condensation rates. On the other hand, a reasonably high water/metal molar ratio favors complete conversion from the metal alkoxide to the metal oxide, and it also favors the stability of the inorganic colloidal particles. The choice of these fabrication conditions can be justified by a number of experimental studies [92, 153, 161, 169-171, 211-212] and theories, such as the charge transfer model [137] and the ExDLVO theory [168], which can be referred to section 2.2. Thus, no further attempt will be made to discuss the effect of these factors. However, it is necessary to have some discussions about the dosage of the HCl and the cure process.

As shown in number 4 in Table 3.1, PAI-TET solution is gelled immediately at a low HCl concentration. The causes for this phenomenon are not very clear. One possibility is the attraction among the chain-like TiO₂ particles and the interaction between the TiO₂ and the PAI. It should be pointed out that the gelled solution still led to an optically transparent composite film after drying although many voids were visual. This suggests that the size of the condensation product TiO₂ in the solution is still small. It is known that the acid catalyst facilitates the formation of the chain-like small TiO₂ particles [131-134]. These particles interact strongly, presumably through the hydrogen bonding, with the PAI. On the other hand, the attraction among the TiO₂ particles is enhanced at low HCl concentrations as compared to high HCl concentrations because the pH value is closer to the PZC (Point of Zero Charge) of the TiO₂. As a consequence, the strong attraction among these TiO₂ particles connects together the PAI chains and reduces the flowability of whole system. This phenomenon is not expected to occur at relatively high HCl.
concentrations because the high repulsive forces among the TiO₂ particles will prevent the TiO₂ particles from approaching together.

Slow drying is another unfavorable condition for the fabrication of transparent composite films as shown in Table 3.1, numbers 3 and 6. The slow drying extends the time for the solution to maintain a relatively low viscosity, and hence the particles can move more freely in a long period of time as compared to the fast drying. This increases the possibility for the particles to collide with each other and continue to grow. The solvent at the top is always preferentially evaporated as compared to that at the bottom (or substrate). Therefore the particles at the bottom always have more time to aggregate due to the low viscosity, in comparison to those at the top. On the other hand, with the evaporation of the solvent at the top, the concentration of the TiO₂ particles on the top increases, forming a concentration gradient. This enables the diffusion of the particles toward the bottom, enhancing the aggregation aspect of the TiO₂ particles on the bottom. It is believed that further coagulation of the particles can be reduced if they already have formed hydrogen bonds with the PAI, due to the additional constraint on the movement of the particles. It is also clear that a reasonably fast drying favors a faster increase in the solution viscosity and thereby exerts sufficient drag forces to slow down the movement of the TiO₂ particles.

3.4.2. TGA study of the residual DMAC solvent and the TiO₂ content within the PAI

The DMAC solvent retained in samples must be removed because it functions as a plasticizer and complicates other properties of the matrix polymer, such as the glass transition and the crystallization. The DMAC solvent has a boiling temperature of 166 °C. Complete removal of this solvent needs a special treatment. The DMAC solvent trapped in the unfilled PAI and the PAI/TiO₂ (10.1%) composite films that were treated by different
processes was analyzed by TGA and the results are shown in Figure 3.2. Curve A in Figure 3.2 shows that at least ~6% of the DMAC solvent, based on the loss at 400 °C, remains in the unfilled PAI even after a cure at 220 °C. Further increase in the temperature of cure to 265 °C, which is close to the Tg ~275 °C, removes the solvent (curve B in Figure 3.2). However, it can be seen by comparing curve C with curve B that the same result can be achieved with the cure at 100 °C if a methanol extraction is used. The curve for the unfilled PAI that was cured at 220 °C after the methanol extraction almost completely coincides with the curve C (cured at 100 °C) and therefore is not shown in Figure 3.2. The methanol extraction is also an efficient way to remove the DMAC solvent in the PAI/TiO₂ (10.1%) composite as shown in Figure 3.2, curves D and E. Furthermore, methanol extraction may also act to wash out the residual HCl in the composites. The HCl may accelerate the degradation of polymers at high temperatures [236].

The actual content of the TiO₂ in the PAI/TiO₂ composites can also be determined using the TGA technique. This is based on the fact that most polymers are essentially burned off before reaching 700 °C in an air atmosphere but TiO₂ remains thermally stable over 1000 °C in an air atmosphere. Therefore the remaining residue reflects the TiO₂ content. The TiO₂ content of the PAI/TiO₂ composites was analyzed by TGA and presented in Table 3.2. All the samples were treated in the same way as indicated in Figure 3.2, curve E. The causes for the low percentage of incorporation of the PAI/TiO₂(5.3%) composite are unclear but the loss may arise when part of the incorporated TiO₂ particles get washed out during the methanol extraction process. It has been reported that the treatment with methanol completely washes out the palladium salt incorporated within the 12F-poly(amide-imide) [13]. Since majority of the TiO₂ was incorporated within the PAI,
Figure 3.2. Thermogram of the unfilled PAI and the PAI/TiO₂ composites at 10 °C/minute. (A) The unfilled PAI without methanol extraction. The PAI was cured in a vacuum at 100 °C for 24 hours, 150 °C for 24 hours and 220 °C for 24 hours; (B) The unfilled PAI without methanol extraction. In addition to A, the PAI was cured in a vacuum at 265 °C for another 24 hours; (C) The unfilled PAI with methanol extraction. The PAI was cured in a vacuum at 100 °C for 36 hours, then cured again in a vacuum at 100 °C for 24 hours after an extraction by sufficient methanol for 24 hours; (D) The PAI/TiO₂ (10.1%) composite without methanol extraction. The sample was cured in the way same as A; (E) The PAI/TiO₂ (10.1%) composite with methanol extraction. After the treatment same as A, the sample was extracted by sufficient methanol for 24 hours, and then cured again in a vacuum at 220 °C for 24 hours; (F) The PAI/TiO₂ (10.1%) composite with methanol extraction, treated in the way same as A. The number in the brackets is the TiO₂ content by weight based on 100% conversion from TET to TiO₂.
Table 3.2. The TiO$_2$ contents determined by TGA at 750 °C in an air atmosphere.

<table>
<thead>
<tr>
<th>No. in Table 3.1</th>
<th>-</th>
<th>1</th>
<th>2</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>PAI</td>
<td>PAI/TiO$_2$ (5.3%)</td>
<td>PAI/TiO$_2$ (10.1%)</td>
<td>PAI/TiO$_2$ (17.9%)</td>
</tr>
<tr>
<td>Theory (% by wt.)</td>
<td>0</td>
<td>5.3</td>
<td>10.1</td>
<td>17.9</td>
</tr>
<tr>
<td>Measured (% by wt.)</td>
<td>0</td>
<td>3.7</td>
<td>8.8</td>
<td>16.1</td>
</tr>
<tr>
<td>Loss of TiO$_2$</td>
<td>-</td>
<td>1.6</td>
<td>1.3</td>
<td>1.8</td>
</tr>
<tr>
<td>% Incorporated</td>
<td>-</td>
<td>69.8</td>
<td>87.1</td>
<td>88.8</td>
</tr>
</tbody>
</table>
this demonstrates the feasibility of the discussed methods for the fabrication of the composites.

3.4.3. Morphology of the unfilled PAI and the PAI/TiO₂ composites

With the aid of transmission electron microscopy, the subtle difference in the morphology of the composites can be observed. The morphologies of the PAI with varying TiO₂ contents are illustrated in Figure 3.3. The dark portions represent the TiO₂ rich phase. The phase contrast, as shown in Figures 3.2-A for the unfilled PAI, can be observed because the magnification is as high as 400,000.

Before the discussion of the morphologies of the PAI/TiO₂ composites, it is necessary to have a conceptual understanding of the domain. The term domain is widely used to describe a metal oxide rich phase [92, 153, 203, 206, 209] but an exact definition of domain seems difficult to find. Accordingly, the metal oxide (TiO₂, SiO₂, and TiO₂-SiO₂) domain used throughout this thesis is defined based on the TEM results. As shown in Figures 3.3 to 3.5, the metal oxide domain is understood as a collection of metal oxide particles. The particle is not a pure metal oxide, which may also contain other groups, such as the unreacted alkyl group -C₂H₅ and the hydroxyl group -OH. The interparticle forces are limited to van der waals forces and hydrogen bonding. Therefore, a aggregate can be regarded as a domain, but a single particle composed of covalently bonded atoms cannot be regarded as a domain.

Although the TiO₂ domains in the PAI/TiO₂ (5.3%) composite (Figure 3.3-B) are difficult to visualize, a careful comparison of the morphology with the unfilled PAI (Figure 3.3-A) reveals the difference. The aggregation of the TiO₂ particles in the PAI/TiO₂ (5.3%) composite is less pronounced and the maximum size of TiO₂ domains is less than
Figure 3.3. TEM of the unfilled PAI and the PAI/TiO$_2$ composites. (A) The unfilled PAI, (B) the PAI/TiO$_2$(5.3%), (C) the PAI/TiO$_2$(10.1%), and (D) the PAI/TiO$_2$(17.9%). The method for sample treatments are given in section 3.3.2. The number in the brackets is the TiO$_2$ content by weight based on 100% conversion from TET to TiO$_2$. 
5 nm. Increase in the TiO\textsubscript{2} content to 10.1\% and 17.9\%, as shown in Figures 3.3-C and 3.3-D, leads to the larger TiO\textsubscript{2} domains. For the PAI/TiO\textsubscript{2}(10.1\%) composite, the size of the majority of the TiO\textsubscript{2} domains, which are clearly aggregated from the individual TiO\textsubscript{2} particles, is estimated to be less than 30 nm. The TiO\textsubscript{2} domains in PAI/TiO\textsubscript{2}(17.9\%) composite as shown in Figure 3.3-D are distributed relatively less uniformly and the size is most probably less than 50 nm.

The morphology of the PAI/TiO\textsubscript{2}-SiO\textsubscript{2} (11.4/8.6\%) composite (number 8 in Table 3.1) is presented in Figure 3.4. The majority of the TiO\textsubscript{2}-SiO\textsubscript{2} mixture domains are less than 100 nm. Some white spots are due to the voids that may be generated during microtoming the samples.

The PAI/SiO\textsubscript{2} composites (number 12 and 13 in Table 3.1) are presented in Figure 3.5. The major difference between these two samples is the HCl dosage during the fabrication process. The HCl dosage for the PAI/SiO\textsubscript{2}(6.7\%) composite is 0.0022 mole per liter of the DMAC solvent, while for the PAI/SiO\textsubscript{2}(7.8\%) composite, it is 0.21 mole per liter of DMAC solvent. The SiO\textsubscript{2} domain size in these two composites is difficult to evaluate because of the irregular shape. Nevertheless, a rough estimate of the size distribution of these domains is from 200 nm to 2000 nm, in agreement with the opaque appearance of these two composites. However the size distribution of the SiO\textsubscript{2} domains in the PAI/SiO\textsubscript{2}(7.8\%) composite is much smaller but less uniform than that in the PAI/SiO\textsubscript{2}(6.7\%) composite. The PZC (The Point of Zero Charge) of the SiO\textsubscript{2} is pH=2.5 [166-167]. The SiO\textsubscript{2} surface is positively charged at pH values lower than 2.5. A high HCl concentration (but with a pH lower than 2.5) increases the electric charge or $\zeta$-potential on the SiO\textsubscript{2} surface because it shifts the pH of the solution away from the PZC. The surface charge, or high repulsive force on the SiO\textsubscript{2} surface, facilitates to prevent the
Figure 3.4. TEM of the PAI/TiO$_2$-SiO$_2$ (11.4/8.6 %) composite. The methods for sample treatments are given in section 3.3.2. The contents of the TiO$_2$ and SiO$_2$ within the composite are 11.4 and 8.6% by weight based on 100% conversion from the metal alkoxides to the metal oxides.
Figure 3.5. TEM of the PAI/SiO$_2$ composites. (A) The PAI/SiO$_2$ (7.8%); (B) the PAI/SiO$_2$ (6.7%). The HCl dosage in the fabrication of the composites is (A) 0.21 mole per liter of the DMAC solvent and (B) 0.0022 mole per liter of the DMAC solvent. The methods for sample treatments are given in section 3.3.2. The number in the brackets is the SiO$_2$ content by weight based on 100% conversion from TEOS to SiO$_2$. 
SiO₂ particles from aggregating. Accordingly, the smaller SiO₂ domains in the PAI/SiO₂(7.8%) composite can be interpreted in terms of the stronger repulsive forces among the SiO₂ particles at the high HCl concentration, as compared to the low HCl concentration for the PAI/SiO₂(6.7%) composite. Some large white spots are due to the voids generated from microtoming the samples.

The optical appearance of the composites presented in Table 3.1 and the TEM results shown in Figures 3.3-3.5 indicate that the inorganic domain size correlates strongly with the choice of metal oxide. The mechanism involved is presumed to be the hydrogen bonding between the metal oxides and the PAI. The evidence for the hydrogen bonding between the TiO₂ and the PAI will be discussed in the next chapter. Many studies have shown that, in cases of no chemical bond formation between a metal oxide and a polymer, strong hydrogen bonding becomes an indispensible condition to enhance the compatibility of two components [13, 92, 153, 203]. For example, nanosized silica [211] is difficult to form within polyimides, because there is no hydrogen bonding between these two components. No evidence has been shown that the imide C=O in the polyimide can form a hydrogen bond with a metal oxide. The incompatibility between the TiO₂ and a polyimide (Ultem 1000) was also observed in this study, mixing of the polyimide with the TET leading to an opaque solution that contains suspensions. The major structural difference between the poly(amide-imide) and the polyimide is that the PAI has N-H and amide C=O groups, which are capable of hydrogen bonding. Thus the hydrogen bonding between the TiO₂ domains and the PAI is presumed to be the major driving force for the compatibility of the two components.

As mentioned in section 2.4.1, there is no universal definition for a hydrogen bond and four contributory effects for the formation of hydrogen bonding arise from [216-221]:

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1. Electrostatic interactions,

2. Repulsive forces,

3. Delocalization effects,

4. Dispersion forces.

The hydrogen bond between the proton donor N-H in the PAI and the hydroxyl group OH (as a proton acceptor) on a metal oxide can be expressed as:

\[
\text{N-H} \cdots \text{O} \cdots \text{M} \\
\text{H}
\]

where M represents a metal such as Ti and Si, the dashed line denotes the hydrogen bond. On the basis of the theory of hydrogen bonding [216-221], it is believed that a metal with low electronegativity and a large size favors the four contributions to the hydrogen bond:

1. The low electronegativity of the metal atom, M, makes the electrons of M shift to the oxygen atom, O, and increases the negative partial charge of O. As a result, the Coulombic attractions between O and the proton donor N-H increase;

2. However, the increase in the negative partial charge in O also increases the possibility of the overlapping of the electron clouds in O and the electron clouds in N and thereby causes a stronger repulsive force;

3. A shift of the electrons of M to O due to the metal's low electronegativity and the large size reduces the electronegativity of O and makes these electrons move more freely. Accordingly, the delocalization, or charge transfer, interaction proceeds more favorably;

4. Because of the more freely electron motion around O, the fluctuating dipole in O is clearly more easily induced by the fluctuating dipole in N-H, giving rise to an increase in the dispersion force.
Whether or not the total hydrogen bonding energy can be increased depends on the relative contributions of the above four interactions. When the repulsive energy is too high, a decrease in the total hydrogen bonding energy could result. Transition metals such as Ti and Zr have a lower electronegativity and a larger atomic size than Si does. It is known that the reactivity of Ti and Zr is much higher than that of Si. The higher reactivity essentially results from the high degree of the charge transfer on the basis of Partial Charge Model [137] as is evidenced by the large amount of related experiments [135, 141, 145-147]. This suggests that the effect of attraction should be greater than that of repulsion as the electronegativity of metal decreases and the atomic size of metal increases. The electronegativity and atomic radius of some commonly used metals in the sol-gel process are given in Table 3.3. Thus the strength of the hydrogen bonding between the residual hydroxyl group on a metal oxide and the N-H group in the PAI should decrease in the following order:

\[ \text{Zr-OH} > \text{Ti-OH} > \text{Si-OH} \]  

(3.1)

On the other hand, the hydroxyl group on the metal oxide is also possible to function as a proton donor and hydrogen bond with the proton acceptor, amide C=O, in the PAI. This mode can be expressed by:

\[ \text{C=O} \cdots \text{H-OM} \]

In this mode, an increase in the electronegativity of metal M favors inclining the electrons in H towards O in the OM and enhances the interactions between the proton and the O atom in the acceptor C=O, and therefore strengthens the Coulombic attraction, delocalization or charge transfer interactions, and the dispersion forces. This also helps to reduce the repulsive overlapping. Thus the hydrogen bonding energy between the proton
Table 3.3. Electronegativity and covalent radius of some metals [237]

<table>
<thead>
<tr>
<th>Metal</th>
<th>Zr</th>
<th>Ti</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronegativity</td>
<td>1.4</td>
<td>1.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Covalent radius (Å)</td>
<td>1.45</td>
<td>1.32</td>
<td>1.17</td>
</tr>
</tbody>
</table>
donor OH on metal oxide and the proton acceptor amide C=O in the PAI should follow the reverse order, i.e., decrease in the following order:

\[ \text{Si-OH} > \text{Ti-OH} > \text{Zr-OH} \]  

The experimental observations did not show an appreciable evidence that the Si-OH hydrogen bonds with the amide C=O in the PAI. The small TiO₂ domains within the PAI/TiO₂ composites and the large SiO₂ domains within the PAI/SiO₂ composites as observed from the TEM and the optical appearances can only be interpreted by the order 3.1, rather than the order 3.2. This suggests that the Ti-OH is predominantly hydrogen bonded with the N-H group in the PAI. The evidence on this will be explored using FTIR and ATR and will be given in the next chapter.

The PAI/TiO₂-SiO₂ composite also shows a optical transparency and possesses small inorganic domains. Although some of the domains are slightly darker than others, as shown in Figure 3.4, a clear distinction between the individual TiO₂ and SiO₂ domains is difficult. This suggests that the TiO₂ and SiO₂ particles are most probably covalently bonded. This result shows the possibility that a mixture of metal oxides can be formed by combining a low reactivity metal oxide with a high reactivity metal oxide and thereby provides an improved compatibility with the PAI. The mechanism for the interaction between the inorganic and organic components has not been determined. However, since the reactivity of Si-OH in hydrogen bonding is affected by the incorporated TiO₂ domains, whether the PAI hydrogen bonds mainly with the Ti-OH or the Si-OH, or with both should be explored based on their relative tendency to form hydrogen bonds and their relative composition.

The increase in the TiO₂ domain size with the increase in the TiO₂ content as shown in Figure 3.3 suggests that, in addition to the reactivity of the metals in hydrogen
bonding, there exists at least one more important factor that has not been considered. Under the fabrication conditions used in this study, this factor is believed to be the number of the hydrogen bonds formed between the PAI and the Ti-OH. This can be explored from two aspects: (1) self-aggregation among TiO₂ particles and (2) the interaction between the PAI and the solvent. The DMAC is an aprotic solvent that contains the proton acceptor C=O but no proton donor capable of hydrogen bonding with the PAI. The concentration of the PAI in the DMAC used in the fabrication of the composites is ~7 % by weight. This concentration corresponds to a C=O(S)/N-H molar ratio of ~50 where C=O(S) denotes the C=O in the DMAC solvent. Such a large amount of solvent, not to mention the good solubility of the PAI in the solvent, makes the PAI chains have presumably a more extended conformation that enables the easy formation of the hydrogen bond between the C=O groups in the DMAC and the N-H groups in the PAI. Thus, the N-H groups in the PAI can be assumed to have hydrogen bonded with the C=O groups in the DMAC solvent before introducing the Ti-OH into the system. Accordingly, after introducing the TET sol, the formation of the hydrogen bond 

\[ \text{C}=\text{O(S)\ldotsH-N + HO-Ti} \overset{\text{N-H\ldotsO \sim Ti + C=O(S)}}{\rightleftharpoons} \text{H} \]

As mentioned above, C=O(S) is the C=O in the DMAC solvent which is distinguished from the amide C=O in the PAI. The HO-Ti denotes the residual group on the surface of the TiO₂ particles. The hydrogen bonding energies between the N-H and C=O and between the N-H and OH are generally in the order of 5 kcal/mole [219]. However, as mentioned earlier, the high reactivity metal, Ti, favors the formation of strong hydrogen bonds. Thus, although the equilibrium constant of Equation 3.3 is not available, the strong interaction between the PAI and the TiO₂ suggests that the strength of the hydrogen bonding interaction is greater on the right than on the left. The initial concentration of the

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HO-Ti can be reasonably assumed to increase with increasing the TiO₂ content. One can presume from Equilibrium 3.3 that the concentration of the actual HO-Ti and hence the concentration of the free TiO₂ particles also increases with increasing the TiO₂ content. As consequences, these free TiO₂ particles aggregate either with themselves or with those TiO₂ particles that already have hydrogen bonded with the PAI, leading to the formation of large TiO₂ domains. Accordingly, it is clear that the TiO₂ domain size should increase with increasing TiO₂ content and these aggregated domains should have a relatively loose structure, as compared to a particle, because they result from the weak van der waals attraction. The loose structures can be observed from the TEM results for the PAI/TiO₂(10.1%) and the PAI/TiO₂(17.9%) composites shown in Figures 3.3-C and 3.3-D.

Thus, under the fabrication condition of acid catalysis, two dominant parameters that determine the size of metal oxide domains are: (1) the metal's reactivity in hydrogen bonding and (2) the concentration of the hydrogen bonds between the metal oxide and the PAI. The second parameter is determined by the magnitude of hydrogen bonding energy between the PAI and the solvent, and between the PAI and the metal oxide.

### 3.4.4. The effect of TiO₂ domains on the dynamic mechanical properties of the PAI

The TEM results presented in Figure 3.3 show that even the largest TiO₂ domain in the PAI/TiO₂(17.9%) composite is less than 50 nm. The small TiO₂ domains create a large specific interface area and thereby a large number of interfacial interactions between the TiO₂ and the PAI. These interfacial interactions must bring about the change in the thermal and mechanical properties of the PAI. Results of DMTA studies will be discussed in this section.
The PAI/TiO₂(17.9%) composite was too brittle and no attempt was made to study this composite by DMTA. The DMTA results of the composites with the TiO₂ content of 5.3 % and 10.1 % along with the unfilled PAI are given in Figure 3.6. The storage moduli before the glass transition (~275 °C) are essentially the same for all the samples. For the unfilled PAI, as shown in curve A in Figure 3.6, the storage modulus drops from ~2x10⁹ Pa at 270 °C in the glass region to ~2x10⁸ Pa at 330 °C in the rubbery region, a drop of only one decade which is far less than the three decades for a typical amorphous glassy polymer. A DSC study conducted at the heating rate of 10 °C/minute and WAXD studies of this polymer (but the molecular weight may differ) showed a significant crystallinity after the sample was annealed at 325 °C for 3 minutes [15]. Therefore, at the slow heating rate of 2 °C/minute, the modulus drop around 310-330 °C must accompany a crystallization process. The crystallites induced in this process cause the modulus increase, as shown in the region from ~330 to ~390 °C. Although the drop in the modulus after ~390 °C may be interpreted in terms of the viscous flow of the amorphous PAI and the melting process of the crystallites, precaution needs to be taken because the PAI also decomposes at ~ 420 °C [15]. Whether or not there exist crystallites in the PAI before the glass transition needs further study which will be given in the next section with the aid of DSC and WAXD experiments.

As shown in Figure 3.6, the wells of the moduli at ~330 °C decrease with increasing the TiO₂ content. This suggests that the incorporated TiO₂ domains reduce the segmental mobility and thereby make the crystallization process of the PAI more difficult. More evidence can be found from the response of the rubbery plateau modulus. As shown in Figure 3.6, the rubbery plateau modulus increases with increasing the TiO₂ content. The modulus in the rubbery region for the PAI/TiO₂(10.1%) composite levels off after
Figure 3.6. The DMTA of the unfilled PAI and the PAI/TiO₂ composites. Experiments were carried out at 1 Hz with a heating rate of 2 °C/minute. The samples were cured in a vacuum at 100 °C for 24 hours, 150 °C for 24 hours and then after extracted by sufficient methanol for 24 hours, cured again in a vacuum at room temperature for 24 hours, 100 °C for 24 hours and 150 °C for another 24 hours. The number in the brackets is the TiO₂ content by weight based on 100% conversion from TET to TiO₂.
~350 °C which is typically a response of a crosslinked elastomer. It should be emphasized
that there are no chemical crosslinking agents in these composites. Therefore the TiO₂
domains function as the crosslinking agent. The interfacial interactions between the TiO₂
domain and the PAI are responsible for the reduced segmental mobility and thereby the
delayed relaxation temperature and the disrupted crystallinity. The shift in the glass
transition temperature can be estimated from the loss peak in Figure 3.6 from ~300 °C for
the unfilled PAI to ~312 °C for the PAI/TiO₂(5.3%) composite, or to ~318 °C (the
maximum value) for the PAI/TiO₂(10.1%) composite.

The heterogeneity of the molecular motion of the PAI chains can be analyzed from
the loss peak at the glass transition region. With increasing the TiO₂ content, the peak of
the Tanδ for the composites as shown in Figure 3.6 decreases and broadens. Although
the actual TiO₂ content for the PAI/TiO₂(5.3%) composite is only 3.7 % by weight as
shown in Table 3.2, a decrease in the height and an increase in the breadth of the Tanδ
peak can also be observed. This indicates that the molecular motions of at least part of the
PAI chains are restricted by the interfacial interactions adjacent to TiO₂ networks. For the
PAI/TiO₂(10.1%) composite, the Tanδ peak distinctly decreases and broadens. The actual
TiO₂ content for the PAI/TiO₂(10.1%) composite is 8.8% by weight, much higher than
that for the PAI/TiO₂(5.3%) composite. As observed directly from the TEM shown in
Figure 3.3, a high TiO₂ content leads to a more pronounced aggregation. Large
aggregates could cause an increase in the segmental mobility. One typical example is the
poly(methyl methacrylate)/SiO₂ composite; a decreased glass transition temperature of the
poly(methyl methacrylate) was observed and attributed to the large SiO₂ aggregate fillers
[153]. Each aggregate is composed of a certain number of the individual TiO₂ particles.
The interactions between these individual particles are generally weak, because they result
from the weak van der waals attraction. Thus, the PAI chains adjacent to a TiO₂
aggregate can be assumed to be more perturbed than that of the chains adjacent to an individual TiO$_2$ particle or a denser TiO$_2$ domain. The aggregates have different sizes and the strength of the interactions among the individual TiO$_2$ particles within each aggregate may differ from one aggregate to another aggregate. Different local environments of the PAI chains compose the diversity of the segmental mobility, giving rise to the distinct change for the loss peak at the glass transition region as compared to the unfilled PAI.

Cure at a high temperature also leads to a change in the dynamic mechanical properties, particularly for the PAI/TiO$_2$(10.1 %) composite. The samples shown in Figure 3.7 were subjected to additional cure at 220 °C in a vacuum for 24 hours after the sample treatment given in Figure 3.6. As mentioned earlier, the residual DMTA solvent trapped in the sample can seriously complicate the measurement of the dynamic mechanical properties. The TGA results presented in Figure 3.2 have shown that a DMAC-free sample can be obtained by methanol extraction and a cure in a vacuum at 100 °C. Compared Figure 3.6 to Figure 3.7, there is essentially no difference between the unfilled PAI with and without the additional high temperature cure, suggesting that the DMAC solvent was effectively removed with both treatments. Emphasis on this is necessary, because all the comparisons between the results shown in Figures 3.6 and 3.7 can be made without the effect of the DMAC solvent being involved.

On the other hand, as shown in Figure 3.7, there is also a crystallization process at ~325 °C. However, as compared to the crystallization behavior at ~325 °C shown in Figure 3.6, no evident difference can be observed for both the PAI/TiO$_2$(5.3 %) composite and the unfilled PAI. For the PAI/TiO$_2$(10.1 %) composite, the increase in the slope of the modulus in the rubbery region, as compared to the slope shown in Figure 3.6, also cannot be simply interpreted in terms of the enhanced crystallinity. It is believed that, after
Figure 3.7. The DMTA of the unfilled PAI and the PAI/TiO\textsubscript{2} composites. Experiments were carried out at 1 Hz with a heating rate of 2 \textdegree C/minute. The samples were subjected to additional cure at 220 \textdegree C in a vacuum for 24 hours after the sample treatment given in Figure 3.6. The number in the brackets is the TiO\textsubscript{2} content by weight based on 100\% conversion from TET to TiO\textsubscript{2}.
additional cure at 220 °C, the appreciable change in the modulus in the rubbery region arises mainly from the enhanced interfacial interactions between the PAI chains and TiO₂. Emphasis on this is also necessary, because all the comparisons between the results shown in Figures 3.6 and 3.7 can be focused on the interfacial interactions between the organic and inorganic components.

As shown in Figures 3.6 and 3.7, the cure at 220 °C causes an increase in the rubbery modulus of the PAI/TiO₂(5.3 %) composite. It is believed that the interfacial area between the PAI and the TiO₂, the structure of the TiO₂ domain (loose or dense) and the interfacial interaction energy between the TiO₂ and the PAI are the important parameters for the dynamic mechanical properties of the composites. It has been reported that some monomeric water molecules and hydrogen-bonded water molecules have a strong affinity to the TiO₂ particles [238]. The monomeric water is of significance for the dynamic mechanical properties since it is tightly bonded with the TiO₂ and cannot be completely removed even at 200 °C [238]. On the other hand, the OH groups that are chemically bonded with the TiO₂ decrease with increasing temperature on the basis of the near IR study of the silica gel prepared from an acid-catalyzed TEOS [239]. The loss of these chemically bonded OH groups can be explained in terms of the oxolation. The loss of the OH groups and the monomeric water at elevated temperatures unavoidably accompanies a contraction of the TiO₂ domains, particularly for the aggregated TiO₂ domains. Since PAI chains can penetrate into the aggregated TiO₂ domains, it is clear that the contraction of these domains facilitates to reduce the segmental mobility of the PAI. For the PAI/TiO₂(5.3 %) composite as shown in Figure 3.3-B, there is no distinct aggregation for the TiO₂ particles, and thereby no distinct changes in both the interfacial area and the structure of the TiO₂ domains are expected. Therefore, with the additional cure at 220
°C, the enhanced interfacial interactions, in comparison to the cure at 150 °C, are believed to be responsible for the increased rubbery modulus.

For the PAI/TiO$_2$(10.1%) composite, however, a distinct change in the rubbery modulus and the loss Tan δ peak can be observed in Figures 3.6 and 3.7. For sake of clarity, the PAI/TiO$_2$(10.1%-150 °C) is used to denote the composite given in Figure 3.6 and the PAI/TiO$_2$(10.1%-220 °C) is for the composite given in Figure 3.7. The only difference between them is the cure temperature shown in the brackets. As mentioned in the foregoing section, the PAI chains adjacent to a dense TiO$_2$ domain should have more hindered mobility than those adjacent to a loose TiO$_2$ domain. It can be seen in Figure 3.3-C that the TiO$_2$ domains within the PAI/TiO$_2$(10.1%) composite indeed have a relatively loose structure as compared to those within the PAI/TiO$_2$(5.3%) composite as shown in Figure 3.3-B. It is believed that the oxolation and the removal of the monomeric water occur not only on the TiO$_2$ surface but also among the individual TiO$_2$ particles. This suggests that at an elevated temperature a certain degree of the inter-particle micro-contraction could occur and thereby densify the TiO$_2$ domains. The loose structure also increases the possibility of the PAI chains penetrating into these TiO$_2$ domains. If the chains of the PAI and the "hole" in the TiO$_2$ domains have a close dimension, it is clear that the contraction of these holes will reduce the segmental mobility of the PAI. Therefore, on the one hand, the contraction process at the elevated temperature reduces the interfacial area of the TiO$_2$ domains and thereby the adjacent interactions with the PAI, which should lead to a decrease in the rubbery plateau modulus. On the other hand, the densifying process and the enhanced interfacial diffusion at elevated temperatures reduce the mobility of the PAI chains adjacent to or inside these TiO$_2$ domains, which should give rise to an increase in the rubbery plateau modulus. As shown in Figures 3.7 and 3.6, the PAI/TiO$_2$(10.1%-220 °C) composite indeed has a better defined loss Tan δ
peak than the PAI/TiO₂(10.1%-150°C) composite, indicating that the contraction of the TiO₂ domains reduces the heterogeneity in the segmental mobility of the PAI. Initially, the rubbery modulus of the PAI/TiO₂(10.1%-220°C) composite is distinctly lower than that of the PAI/TiO₂(10.1%-150°C) composite. At this stage, the effect from the decrease in the interfacial area between the PAI and the TiO₂ domains may be stronger. On the other hand, because the PAI/TiO₂(10.1%-150°C) composite was not subjected to a long time cure for 24 hours at 220°C, the contraction process of the TiO₂ domains within this composite is therefore relatively weak, in comparison to the PAI/TiO₂(10.1%-220°C) composite. But at a very high temperature a rapid contraction could occur during a short period of time. Accordingly, the two composites should show a similar behavior in the molecular motion of the PAI chains. This accounts for why the increase in temperature reduces the difference in the modulus of the PAI/TiO₂ (10.1%-220°C) and the PAI/TiO₂(10.1%-150°C) composites. The difference finally disappears at ~440°C. It also needs to be emphasized that the increase in the slope of the modulus in the rubbery region for the PAI/TiO₂(10.1%-220°C) composite, as compared to that for PAI/TiO₂(10.1%-150°C) composite, cannot be simply interpreted in terms of the increase in the number of pseudo crosslinks.

3.4.5. The effect of the TiO₂ domains on the crystallization of the PAI

It can be seen from Figures 3.6 and 3.7 that a fast crystallization process occurs at ~325°C. A solvent and inappropriate cure process can also induce crystallinity [240-241]. Whether or not there exists any crystallinity during the fabrication processes of the unfilled and filled PAI will be explored in this section by using WAXD and DSC techniques.

The WAXD patterns of the PAI/TiO₂ composites along with the unfilled PAI are
shown in Figure 3.8. The highest cure temperature for all the samples is 220 °C, much lower than the glass transition temperature of ~275 °C and the crystallization temperature of ~325 °C for the unfilled PAI. Some crystalline forms of the pure TiO₂ are the anatase and the rutile [242-243]. The anatase has the d-spacing of 3.5 Å and a sharp peak at 2θ = 25.4° when Cu Kα X-ray (λ=1.54Å) is used. The rutile has two d-spacings. One of them is 3.2 Å and corresponds to a sharp peak at 2θ = 27.8°. Another one is 2.4 Å and has a sharp peak at 2θ = 37.4°. All of these sharp peaks cannot be found in Figure 3.8, indicating that these crystalline TiO₂ products are negligible within the PAI matrix.

The WAXD patterns of the PAI/TiO₂ composites, as shown in curves B and C in Figure 3.8, reveal essentially an amorphous halo. The amorphous halos are principally the results of scattering from the PAI, with a small contribution from the TiO₂. These results are identical in shape to the WAXD patterns of the amorphous PAI [15]. Thus these patterns also provide the information in evaluating the crystallinity of the unfilled PAI.

For the unfilled PAI as shown in Figure 3.8, a careful examination on crystallinity is needed. Since the WAXD patterns of the composites represent essentially the amorphous PAI, the difference of the patterns of the filled and unfilled PAI implies the possibility that some crystallinity exists in the unfilled PAI. Sekharipuram studied the crystallization behavior of the unfilled PAI (with the same molecular structure but the molecular weight may differ) [15]. Their result shows that a significant crystallinity develops after an original amorphous PAI was annealed at 325 °C for only 3 minutes. An examination of the annealed sample revealed a sharp peak in the WAXD pattern. The peak that starts from 2θ = ~16° and ends at 2θ = ~23° with the maximum intensity at ~20°. Although the peak identified by Sekharipuram is much more narrow than the one observed in this study as shown in Figure 3.8, curve A, which ranges from ~2θ = ~8° to 2θ = ~33°
Figure 3.8. WAXD patterns for the unfilled PAI and the PAI/TiO$_2$ composites. The methods for sample treatments are given in section 3.3.2. The number in the brackets is the TiO$_2$ content by weight based on 100% conversion from TET to TiO$_2$. 
with the maximum intensity at ~19°, both scattering angles of the maximum intensities are very close. On the other hand, the patterns of the unfilled PAI cannot be normalized to achieve the shape of the patterns of the PAI/TiO_2(5.3%) and PAI/TiO_2(10.1%) composites as demonstrated in curves B and C in Figure 3.8. All these facts suggest that the unfilled PAI develops some crystallinity during the fabrication process and that the presence of even a small amount of TiO_2 domains disrupts the crystallinity of the PAI.

Further examination of the crystallinity for the filled and unfilled PAI was conducted with the aid of DSC analysis. As shown in Figure 3.9, the exotherms at ~325 °C represent the crystallization process. Although the exotherm of the unfilled PAI is expected to be stronger than that of the PAI/TiO_2 composites, the observed exotherm of the unfilled PAI at ~325 °C is actually distinctly weaker than those of the composites. This suggests that, as shown in curve A in Figure 3.8, some crystallinity is indeed present in the unfilled PAI before the glass transition. The presence of the crystallites makes the crystallization at ~325 °C less pronounced, as compared to crystallization process of the PAI/TiO_2 composites.

For the PAI/TiO_2 composites, it suggests that the crystallization at ~325 °C decreases with an increase in the TiO_2 content. Since little crystallinity develops during the fabrication process of the composite films, as indicated by the amorphous halos shown in Figure 3.8, the decrease in the crystallization with increasing TiO_2 content at ~325 °C indicates that the incorporated TiO_2 domains also facilitate to depress the crystallization of the PAI above the glass transition.
Figure 3.9. DSC results of the second heat for the unfilled PAI and the PAI/TiO₂ composites. The heating rate of experiments was 10 °C/minute. The methods for sample treatments are given in section 3.3.2. The procedures for the first heat are given in section 3.3.3. The number in the brackets is the TiO₂ content by weight based on 100% conversion from TET to TiO₂.
3.5. Summary and Conclusions

This study opens the possibility of incorporating nanosized metal oxide rich domains within high-Tg poly(amide-imides) by a sol-gel process. Although the poly(amide-imide), synthesized from 4,4'-oxy(phenyl trimellitimide)[OPTMI] and 4,4'-oxydianiline [ODA] using tert. butyl benzoic acid [t-BBA] as the monofunctional endcapper [15], self-hydrogen bonds, a high compatibility of the poly(amide-imide) and the metal oxide can be achieved by using the metal alkoxide in which the metal has a high reactivity, or by adjusting the reactivity of the metal oxide. The interaction between the metal oxide and the poly(amide-imide) is presumably attributed to the hydrogen bonding. The direct evidence of the hydrogen bonding will be presented in the next chapter. Under the condition of a sufficient low pH value at which the enhanced hydrolysis and the hindered condensation kinetics of the metal alkoxide predominate, and the sufficiently strong repulsive forces among the metal oxide particles are ensured, two interactions are believed to be critical for achieving nanosized metal oxide rich domains: the first one is the strong hydrogen bonding interaction between the metal oxide and the polymer; the second one is that the hydrogen bonding interaction between the solvent and the polymer should be sufficiently weak but the solvent should be strong enough to provide good solubility for all the species involved. Compared to the unfilled poly(amide-imide), the poly(amide-imide)/TiO₂ composites showed increased glass transition temperatures, increased rubbery plateau moduli, and hindered crystallizations for which the interfacial interactions between the PAI and the TiO₂ are believed to be responsible. On the basis of this study, the following results are thought to be important:

1. Nanosized TiO₂ and TiO₂-SiO₂ rich domains can be formed in-situ within the poly(amide-imide) by using dimethylacetamide as the solvent;
2. Incorporated nanosized TiO$_2$ rich domains reduce the segmental mobility of the poly(amide-imide), which leads to an increase in the glass transition temperature and the rubbery plateau modulus;

3. Some crystallinity is found to be induced in the preparation of the unfilled poly(amide-imide) film and a significant crystallization of the unfilled poly(amide-imide) occurs at $\sim$325 $^\circ$C. These two crystallization processes are depressed by the presence of the nanosized TiO$_2$ rich domains.

The following conclusions can be made:

1. The reduced poly(amide-imide) segmental mobility for the poly(amide-imide)/TiO$_2$ composites is attributed to the interfacial interactions between the poly(amide-imide) and the TiO$_2$.

2. The nanosized TiO$_2$ rich domains and the large SiO$_2$ rich domains within the poly(amide-imide) arise from the high reactivity of Ti and the low reactivity of Si in hydrogen bonding.

3. Poly(amide-imides) can be filled with highly dispersed and nanosized metal oxides by using a sol-gel process to achieve reduced segmental mobility and packing. Such a type of material should be favorably used for gas separations and other related applications.
Chapter 4

IN-SITU FORMATION OF NANOSIZED TiO₂ DOMAINS WITHIN
POLY(AMIDE-IMIDE): FTIR AND ATR STUDIES OF THE INTERACTIONS
BETWEEN POLY(AMIDE-IMIDE) AND TiO₂

4.1 Abstract

The poly(amide-imide)/TiO₂ composites prepared by a sol-gel process were studied by FTIR (Fourier Transform Infrared spectroscopy) and ATR (Attenuated Total Reflectance). An intensity and frequency change in the N-H band was attributed to hydrogen bonding. Specifically, the spectral changes were interpreted in terms of the hydrogen bonding between the H-N groups in the PAI and the residual OH on the TiO₂. It was found that the PAI-TiO₂-DMAC (dimethyl acetamide) sol-gel system involved competition for the proton donor functional groups in the PAI. The hydrogen bonding between the N-H groups in the PAI and the C=O groups in the DMAC solvent was found to be the unfavorable interaction for the hydrogen bonding between the Ti-OH and the PAI. This study, in combination with the summary given in chapter three, provides a conceptual understanding for the in-situ formation of the nonasized metal oxide domains within the polymers that contain either proton donors or proton acceptors, or both.

4.2 Introduction

In chapter three, it was assumed that the compatibility of the PAI and the TiO₂ was attributed to the hydrogen bonding. The author of this dissertation also pointed out that the hydrogen bonding between the N-H group (rather than the amide C=O) in the PAI and the OH groups on the TiO₂ was the favorable interaction responsible for the formation of the nanosized TiO₂ domains within the PAI. Direct evidence for hydrogen
bonding can be obtained from infrared spectroscopic studies. For the polymers that contain only the proton acceptor such as C=O in the poly(methyl methacrylate), poly(vinyl pyrrolidone) and poly(vinyl acetate), the hydrogen bonding has been found to occur primarily between the polymers and the metal oxides, such as SiO₂ domains, generated in-situ within the polymer matrices [153, 203]. Furthermore, the self-hydrogen bonding within these polymers is negligible because there is no proton donor within these polymers capable of hydrogen bonding with the proton acceptor C=O. On the other hand, the hydrogen bonding between these polymers and the solvent is also negligible because the aprotic solvent THF is used in these sol-gel systems [153, 203]. However for the PAI-TiO₂-DMAC sol-gel system, the following hydrogen bonding interactions are possible:

1. Self-hydrogen bonding between the N-H and the amide C=O in the PAI,
2. Hydrogen bonding between the N-H in the PAI and the C=O in the DMAC,
3. The hydrogen bonding between the N-H in the PAI and the Ti-OH where the Ti-OH acts as a proton acceptor,
4. Hydrogen bonding between the amide C=O in the PAI and the Ti-OH when the Ti-OH acts as a proton donor,
5. Hydrogen bonding between the C=O in the DMAC and the Ti-OH when the Ti-OH acts as a proton donor.

Each hydrogen bond relates two characteristic bands. For example, self-hydrogen bonding between the N-H and amide C=O in the PAI has two bands, the hydrogen-bonded N-H and amide C=O. Therefore, ten characteristic bands related to these five different types of hydrogen bonding interactions are likely to occur. On the other hand, the effect of water and methanol on the hydrogen bonding interactions also needs to be taken into account.
Methanol extraction in combination with the cure at low temperature (say 100 °C) is a feasible way to get rid of the effect of DMAC solvent, but methanol extraction could bring about additional changes to the PAI, such as crystallization [240-241], and therefore complicates the analysis of the interaction responsible for the in-situ formation of the nanosized TiO₂ domains within the PAI. In this chapter, FTIR study was performed on the films cast on KBr without methanol extraction, but the ATR study was for the free standing films that were subjected to a methanol extraction.

4.3. Experimental methods

ATR and transmission FTIR spectra were obtained using a BIO-RAD FTS-40A spectrometer. The resolution for the spectra was 4 cm⁻¹. Samples for the FTIR studies were prepared by directly casting the solution onto KBr discs at room temperature (~25 °C). The methods involved in the solution preparation can be found in chapter three. The cast solution was heated under a heat lamp for ~10 minutes to drive off the majority of DMAC solvent. Subsequent treatments will be outlined since they varied. The sample temperature was controlled with a CN2011 Programmable Temperature Controller manufactured by Omega Technologies. The temperature sensor was a J-type iron vs. copper-nickel thermal couple, and the maximum error was ± 2 °C.

The ATR study was carried out on free standing films, the unfilled PAI and the PAI/TiO₂(17.9% by weight) composite. The methods for the film preparation can be found in chapter three. However it must be pointed out that the highest temperature for the cure of the films was 100 °C. After the films were dried and solidified under a heat lamp, the unfilled and the TiO₂-filled transparent films were cured in a vacuum at 100 °C for 36 hours, and then cured again at the same conditions after the films were subjected to a methanol extraction for 24 hours to remove the DMAC solvent. ATR spectra were
collected employing an IRE crystal, zinc selenide hemisphere with the refractive index 2.42. The crystal was obtained from Harrick Scientific Corporation. A small piece of rubber was used to enhance the contact between the film and the crystal. The incident angle was selected to be 55° because it maximized the intensity of spectra.

4.4. Results and Discussions

4.4.1. The general FTIR features of the unfilled PAI and the PAI/TiO$_2$ composite

The FTIR spectra of the unfilled PAI and the composites with different TiO$_2$ contents at 100 °C are shown in Figure 4.1. The spectra in Figure 4.1, and all the spectra throughout this chapter, have been normalized based on the intensity of the imide C=O stretch near 1780 cm$^{-1}$ since the change in the intensity of this band due to molecular interactions is insignificant.

TiO$_2$ has a broad and strong absorption band from ~800 to 450 cm$^{-1}$ [242, 244-246]. Accordingly, as shown in Figure 4.1, the increase in the intensity at ~800 to 450 cm$^{-1}$ with increasing TiO$_2$ content is attributed to the broad characteristic band of the Ti-O-Ti linkage [242, 244-246] overlapping with the bands of the PAI in this region. In principle, the deconvoluted and integrated intensity of the broad underlying band can be related to the TiO$_2$ content. The actual TiO$_2$ contents in these samples have been analyzed by TAG and found to be 3.7%, 8.8% and 16.1% by weight, corresponding to the composites PAI/TiO$_2$(5.3%), PAI/TiO$_2$(10.1%) and PAI/TiO$_2$(17.9%), respectively. The TGA analysis is summarized in Table 3.2. The discussion presented below will be focused on the N-H and the amide C=O regions since these two regions contain the most important information on the interactions between the TiO$_2$ and the PAI. Before the discussion, it is necessary to introduce special terminology to distinguish between two
Figure 4.1. FTIR spectra of the unfilled PAI and the PAI/TiO$_2$ composites at 100 °C. (A) The unfilled PAI, (B) the PAI/TiO$_2$(5.3%), (C) the PAI/TiO$_2$(10.1%), (D) the PAI/TiO$_2$(17.9%). Samples were cured in a vacuum at 100 °C for 24 hours before experiments. The number in the brackets is the TiO$_2$ content by weight based on 100% conversion from TET to TiO$_2$. 
carbonyl groups to avoid confusion:

Amide C=O denotes the amide C=O group in the PAI,
DMAC C=O denotes the C=O group in the DMAC solvent.

4.4.2. FTIR features of the unfilled PAI in the N-H and amide C=O regions

The spectra for the unfilled PAI in the N-H and the amide C=O regions at different temperatures are shown in Figure 4.2. The bands near 3558 and 3324 cm\(^{-1}\) will be discussed in section 4.4.3. Increase in the temperature from 100 to 200 °C leads to an increase in the intensity around 3368 cm\(^{-1}\), which is due presumably to the free N-H groups in the PAI. This can be satisfactorily interpreted in terms of the break up of hydrogen bonding at elevated temperatures. However, further increase in the temperature from 200 to 260 °C gives rise to a reverse effect. Compared to the spectrum at 200 °C as shown in curve C in Figure 4.2, the intensity around 3368 cm\(^{-1}\) at 260 °C decreases rather than increases. In addition, the intensity of the hydrogen-bonded amide C=O stretch also increases at 260 °C, which will be discussed later. This shows that the N-H groups in the PAI may hydrogen bond predominantly with different components at 200 and 260 °C. The N-H groups hydrogen bond with either the amide C=O groups or the DMAC C=O groups as only the DMAC solvent was used in the preparation of the unfilled PAI sample. Furthermore, the DMAC solvent is significantly removed at 260 °C based on the TGA analysis as shown in Figure 3.2. Thus the dominant hydrogen bonding should arise from the interaction between the N-H and the amide C=O at 260 °C, while, at or below 200 °C, the major contributor to the hydrogen bonding should be the interaction between the N-H groups and the DMAC C=O.
Figure 4.2. FTIR spectra of the unfilled PAI at varying temperatures. (A) 100 °C, (B) 150 °C, (C) 200 °C, (D) 260 °C and (E) 35 °C. Spectrum E was obtained after spectrum D was taken at 260 °C and then the sample was cooled down to 35 °C. Samples were cured in a vacuum at 100 °C for 24 hours before experiments.
That the N-H is predominantly hydrogen bonded with the amide C=O at 260 °C but with the DMAC C=O below 200 °C can be further justified from the change in the spectrum around 3321 cm⁻¹, which is due presumably to the hydrogen-bonded N-H stretch. Although the peak around 3321 cm⁻¹ at 100 °C, as shown in curve A, disappears with increasing temperature, an increase in the intensity at this frequency with increasing temperature can be clearly observed. This is obviously impossible if the N-H groups hydrogen bond with only one other group, either the amide C=O or the DMAC C=O. For the intensity of a hydrogen bond should decrease with increasing temperature. However, this can be explained if a new hydrogen bond that has a different hydrogen bonding energy forms during the course of temperature change. As mentioned in chapter three, during the fabrication process, a large amount of DMAC solvent and the good solubility of the PAI in the solvent enable the majority of PAI chains to bond with the DMAC solvent through the hydrogen bonding between the N-H groups in the PAI and the C=O groups in the DMAC. Accordingly, the residual DMAC solvent after the curing process remains hydrogen bonded with PAI. On the basis of TGA analysis as shown in Figure 3.2, the DMAC solvent higher than ~6 % by weight remains in the PAI even if the sample is cured in a vacuum at 220 °C. The 6 % by weight corresponds to a molar ratio DMAC/AI of roughly 0.5:1 where AI denotes the amide-imide repeat unit. The PAI sample for this FTIR study was only subjected to a vacuum cure at 100 °C. Thus one may expect that the residual DMAC solvent remaining in the PAI is much higher than 6 %. Thus one can reasonably assume that the N-H groups are predominantly hydrogen bonded with the DMAC C=O groups at 100 °C. More evidence on this will be given later in the discussion of the spectra in the amide C=O region. The increase in the temperature removes the solvent from the PAI and accelerates the break up of the hydrogen bonds between the N-H and the DMAC C=O, but it simultaneously creates the more free N-H groups. These
new-generated free N-H groups can, in turn, self-hydrogen bond with the amide C=O, leading to an increase in the intensity at 3321 cm\(^{-1}\). The much higher intensity around 3321 cm\(^{-1}\) at 260 °C than at 100 °C suggests that the absorptivity of the amide C=O bonded N-H is much higher than that of the DMAC C=O bonded N-H. The appreciable increase in the intensity at 260 °C as compared to that at 200 °C can be interpreted in terms of the appreciable loss of the DMAC at 260 °C which makes a large number of the free N-H groups available for the formation of the self-hydrogen bonds between the N-H and the amide C=O.

The temperature dependence of the amide C=O that is also shown in Figure 4.2 provides more evidence in support of the analysis for the N-H region. For a DMAC solvent, there is a well-defined peak at 1646 cm\(^{-1}\) due to the free C=O stretch [229-230]. Although this band cannot be observed from the PAI spectra shown in Figure 4.2, an additional band can be visualized at a lower frequency 1630 cm\(^{-1}\) in the spectrum at 100 °C. This additional band can be explained only by the fact that the DMAC C=O groups are hydrogen bonded with the N-H groups in the PAI. The absence of the free C=O of the DMAC suggests that at 100 °C the majority of the DMAC C=O groups are indeed hydrogen bonded with the N-H groups. With the temperature increasing from 100 °C to 150 °C, the band around 1630 cm\(^{-1}\) disappears, suggesting a removal of a certain amount of DMAC solvent. No appreciable change in the amide C=O region is observed when the temperature increases from 150 to 200 °C. However, further increase in the temperature to 260 °C gives rise to two well-defined peaks. The first one is located at 1677 cm\(^{-1}\) due to the free amide C=O and the second one is at 1653 cm\(^{-1}\) arising from the hydrogen-bonded amide C=O. This evident change is consistent with the distinct change in the N-H region. It is also clear that the increase in the intensity for the hydrogen-bonded amide C=O accompanies the decrease in the intensity for the free amide.
C=O as shown in curves C and D in Figure 4.2. All these facts indicate again that at 100 °C the N-H groups are predominantly hydrogen bonded with the DMAC C=O groups; the majority of the amide C=O exists in the form of free components. The increase in temperature reduces the number of the N-H groups hydrogen-bonded to DMAC C=O but increases the number of the N-H groups hydrogen-bonded to amide C=O in the PAI, leading to an increase in the intensity at 3321 cm⁻¹.

Until now, the characteristic frequencies that were assigned to the free N-H and amide C=O, and the self-hydrogen-bonded N-H and amide C=O groups have not been determined. This can be achieved from the spectra that are free of the DMAC solvent. The spectrum shown in Figure 4.2, curve E, was taken after the spectrum D was obtained, and then the PAI was cooled down from 260 °C to 35 °C. As mentioned in the foregoing section, the PAI is free of the solvent at 260 °C and thereby the hydrogen bond arises only from the interaction between the N-H and the amide C=O. It is clear, as shown in curves D and E in Figure 4.2, that a decrease in the temperature from 260 to 35 °C causes an increase in the intensities for both hydrogen-bonded N-H and the amide C=O. The frequency shift for the free N-H at ~3368 cm⁻¹ is not appreciable. The frequency shifts of the free amide C=O at ~1677 cm⁻¹ and hydrogen-bonded amide C=O at ~1653 cm⁻¹ are also not evident. However, the peak for the hydrogen-bonded N-H distinctly shifts from ~3321 to ~3295 cm⁻¹. For the hydrogen-bonded N-H bending mode, the band near ~1528 cm⁻¹ also clearly becomes stronger and shifts to a higher frequency as the temperature is lowered. This band results from the combined mode for the N-H bending and the C-N stretch that occurs at 1600-1500 cm⁻¹ [228, 224].
4.4.3. Interaction between the PAI and the TiO$_2$ - hydrogen bonding

After the characteristic bands for the N-H and the amide C=O are identified, the emphasis is shifted to the interaction between the PAI and the TiO$_2$. For sake of clarity, the N-H and the amide C=O regions at 100 °C in Figure 4.1 are replotted. The replotted spectra, along with the spectra at 150, 200 and 260 °C, are presented in Figures 4.3 to 4.6.

As shown in Figure 4.3, upon loading the PAI with the TiO$_2$, the band at 1600 cm$^{-1}$, due to the O-H bending of monomeric water [228, 238], becomes clearly visible. Although the O-H bending mode of the monomeric water at 1600 cm$^{-1}$ overlaps with the characteristic band of the benzene ring [228, 247], the higher intensity for the PAI/TiO$_2$ composite, in comparison to the unfilled PAI that contains no water, clearly shows the existence of this component. It is also quite possible for the monomeric water to hydrogen bond with the HO-Ti. The water is therefore called the hydrogen-bonded water, which has a bending frequency at 1620-1630 cm$^{-1}$ [228, 238, 247]. Because the intensity at ~1630 cm$^{-1}$ is higher for the composites than for the unfilled PAI, it may suggest the existence of the hydrogen-bonded water. The monomeric water is tightly bonded on the TiO$_2$ surface and cannot be completely removed even at 200 °C [238]. The OH groups in the monomeric water could be similar, in terms of hydrogen bonding, to the OH groups that are chemically bonded with the TiO$_2$, and act as the functional group to hydrogen bond with the PAI. As shown in Figures 4.3 to 4.6, an increase in the temperature from 100 °C to 260 °C leads to a monotonic decrease in the monomeric water within the composites. At 260 °C, it can be seen from Figure 4.6 that the bands near ~1600 cm$^{-1}$ become essentially identical for all the unfilled and filled PAI, indicating a negligible effect of the monomeric water at 260 °C.
Figure 4.3. FTIR spectra of the unfilled PAI and the PAI/TiO₂ composites at 100 °C. (A) The unfilled PAI, (B) the PAI/TiO₂(5.3%), (C) the PAI/TiO₂(10.1%), (D) the PAI/TiO₂(17.9%). Samples were cured in a vacuum at 100 °C for 24 hours before experiments. The number in the brackets is the TiO₂ content by weight based on 100% conversion from TET to TiO₂.
Figure 4.4. FTIR spectra of the unfilled PAI and the PAI/TiO$_2$ composites at 150 °C. (A) The unfilled PAI, (B) the PAI/TiO$_2$(5.3%), (C) the PAI/TiO$_2$(10.1%), (D) the PAI/TiO$_2$(17.9%). Samples were cured in a vacuum at 100 °C for 24 hours before experiments. The number in the brackets is the TiO$_2$ content by weight based on 100% conversion from TET to TiO$_2$. 
Figure 4.5. FTIR spectra of the unfilled PAI and the PAI/TiO₂ composites at 200 °C. (A) The unfilled PAI, (B) the PAI/TiO₂(5.3%), (C) the PAI/TiO₂(10.1%), (D) the PAI/TiO₂(17.9%). Samples were cured in a vacuum at 100 °C for 24 hours before experiments. The number in the brackets is the TiO₂ content by weight based on 100% conversion from TET to TiO₂.
Figure 4.6. FTIR spectra of the unfilled PAI and the PAI/TiO$_2$ composites at 260 °C. (A) The unfilled PAI, (B) the PAI/TiO$_2$(5.3%), (C) the PAI/TiO$_2$(10.1%), (D) the PAI/TiO$_2$(17.9%). Samples were cured in a vacuum at 100 °C for 24 hours before experiments. The number in the brackets is the TiO$_2$ content by weight based on 100% conversion from TET to TiO$_2$. 
The free TiO-H stretch can be compared with the free SiO-H stretch that is near 3600 cm\(^{-1}\), based on a study of the in-situ formation of the SiO\(_2\) within poly(vinyl acetate) [92]. It can be seen from curve D in Figure 4.3 that, when the TiO\(_2\) content increases to 17.9 % by weight, the intensity at 3558 cm\(^{-1}\) becomes appreciably strong. Although this band also emerges in the spectrum of the unfilled PAI, the stronger intensity and the weak temperature dependence as shown in Figures 4.3 to 4.6 suggest that this band includes the contribution of the free TiO-H stretch. Accompanying the medium band at 3558 cm\(^{-1}\), another medium band for the PAI/TiO\(_2\)(17.9%) composite emerges at 3224 cm\(^{-1}\), which is believed to be due to the hydrogen-bonded TiO-H stretch. As shown in curve D in Figure 4.3, an increase in temperature lowers the intensity and the band shifts to lower frequency.

The high intensity at 3558 cm\(^{-1}\) indicates that there exist appreciable Ti-OH groups on the TiO\(_2\) surface. As expected, this brings about a distinct change to the spectra in the N-H region. As shown in Figure 4.3, although there is no appreciable change in N-H bands with the TiO\(_2\) content lower than 10.1%, further increase in the TiO\(_2\) content to 17.9% causes the N-H stretch to split evidently into two bands. One is the free N-H at 3368 cm\(^{-1}\) and another is the hydrogen boned N-H at 3321 cm\(^{-1}\). The intensity of the hydrogen-bonded N-H at 3321 cm\(^{-1}\) also increases clearly with the increase in the TiO\(_2\) content. The strong dependence of the hydrogen-bonded N-H groups on the TiO\(_2\) contents and thereby on the number of the Ti-OH groups suggests that there is a hydrogen bonding interaction between the N-H and the Ti-OH. On the other hand, there is adequate DMAC solvent in the composite at 100 °C on the basis of TGA study as shown in Figure 3.2. As discussed in the foregoing section, the DMAC C=O can also hydrogen bond with the N-H. Unfortunately, the hydrogen bonds between the N-H and the Ti-OH, and between the N-H and the DMAC C=O are indistinguishable in terms of the N-H vibration. As discussed earlier, the effect of the DMAC solvent and the monomeric water is
negligible at 260 °C. However, adequate Ti-OH groups, as indicated by the strong intensity at 3558 cm⁻¹, remain on the TiO₂ surface at 260 °C. On the other hand, the self-hydrogen bonding between the N-H and the amide C=O are also relatively small which can be justified from the spectrum in the amide C=O region and will be discussed in the subsequent section. Accordingly, the Ti-OH groups are believed to be the major contributor to the strong intensity of the shoulder at 3321 cm⁻¹ at 260 °C, as shown in curve D in Figure 4.6. This band represents the hydrogen bonding interaction between the N-H and the Ti-OH. Recall that the self-hydrogen bond between the N-H and amide C=O is also near ~3321 cm⁻¹. This suggests that the characteristic bands for the hydrogen bond between the N-H and the Ti-OH, and for the self-hydrogen bond between the N-H and the amide C=O are also indistinguishable.

On the other hand, the changes brought about by the TiO₂ domains to the free amide C=O near 1677 cm⁻¹ and the hydrogen-bonded amide C=O near 1653 cm⁻¹ are not appreciable. All the spectra for the PAI/TiO₂ composites as shown in curves B, C and D in Figures 4.3 to 4.6 do not show the evidence for the hydrogen-bonded amide C=O as indicated by the band near 1653 cm⁻¹. All the spectra are essentially similar at the temperature range from 100 to 260 °C. The evident splitting of the free and the hydrogen-bonded amide C=O at 260 °C as observed for the unfilled PAI (curve D in Figure 4.2) does not occur either. It is clear that the residual OH groups on the TiO₂ are predominantly hydrogen bonded with the N-H groups. This suggests that the TiO₂ domains act as physical crosslinks, as discussed in chapter three, and hinder the formation of the self-hydrogen bond between the N-H and the amide C=O.

It has been shown that, as compared to the unfilled PAI, the most evident change occurs in the PAI/TiO₂(17.9%) composite. The spectra of this composite shown in Figures 4.3 to 4.6 are replotted in Figure 4.7. The replotted spectra, along with the
Figure 4.7. FTIR spectra of the PAI/TiO₂(17.9%) composite at varying temperatures. (A) 100 °C, (B) 150 °C, (C) 200 °C, (D) 260 °C and (E) 35 °C. Spectrum E was obtained after spectrum D was taken at 260 °C and then the sample was cooled down to 35 °C. Samples were cured in a vacuum at 100 °C for 24 hours before experiments. The number in the brackets is the TiO₂ content by weight based on 100% conversion from TET to TiO₂.
spectrum at 35 °C demonstrate the temperature dependence. From 100 to 200 °C, the intensity near 3321 cm⁻¹ for the hydrogen-bonded N-H stretch increases but there is essentially no change in the intensity near 3368 cm⁻¹ for the free N-H stretch. This suggests that the free N-H groups released from the break up of the DMAC-bonded N-H groups participate in the interaction of the hydrogen bonding with the Ti-OH during the course of increasing temperature. However, further increase in the temperature to 260 °C lowers the intensities for both free and hydrogen-bonded N-H groups. This may be interpreted in terms of the loss of hydrogen-bonded water (for example, the monomeric water hydrogen-bonded on the TiO₂ surface) at 260 °C since a broad band of the hydrogen-bonded water also occurs in this region [245-246]. Because the DMAC solvent was removed at 260 °C, the temperature dependence of the hydrogen bonds in the PAI/TiO₂(17.9%) composite without the effect of the DMAC solvent involved can be observed from curves D and E in Figure 4.7. As the temperature decreases from 260 to 35 °C, the band at 3321 cm⁻¹ in the N-H region becomes broad and the shoulder for the hydrogen-bonded N-H is difficult to identify. This is a result of more hydrogen-bonded N-H groups formed at 35 °C. In the amide C=O region, no evident change occurs because the majority of the amide C=O groups are not hydrogen bonded with the either N-H or Ti-OH.

All the results presented so far have the effect of the solvent involved in the interaction with the N-H groups in the PAI. It can be concluded from these results that the hydrogen bonding between the N-H and the residual OH groups on the TiO₂ is responsible for the mixing interaction between the PAI and the TiO₂, and thereby for the formation of the nanosized TiO₂ domains within the PAI. As soon as the films are cured at an elevated temperature (say 150 °C in a vacuum), little change in the size of the TiO₂ domains is expected in the subsequent treatment, such as the methanol extraction. As
discussed in chapter three, the methanol extraction process is the effective means for the removal of the DMAC solvent in the unfilled and filled PAI. However, it was observed that this process accompanied a process of softening and contracting once the samples were immersed in the methanol. Therefore, the methanol extraction could bring about some new changes to the PAI/TiO₂ composites and the unfilled PAI. Although these changes are not responsible for the formation of the nanosized TiO₂ domains within the PAI, they could affect the segmental mobility of the PAI and thereby the other properties, such as mechanical and thermal properties, and transport properties.

The spectroscopic study of the free standing films that were subjected to the methanol extraction and thereby are free of the DMAC solvent can be carried out with the aid of the ATR technique. The results for the unfilled PAI and the PAI/TiO₂ (17.9 %) composite are shown in Figure 4.8. For the unfilled PAI, it is clear that the self-hydrogen bonding within the PAI is enhanced after methanol extraction. This can be justified from the broad band in the amide C=O region and the strong intensity of the hydrogen-bonded amide C=O at ~1650 cm⁻¹, as compared to the unfilled PAI that was not treated by methanol as shown in Figure 4.2. In the N-H region, the change is also evident. The broad band at ~3348 cm⁻¹ must arise from the overlapping of the free and hydrogen-bonded N-H.

For the PAI/TiO₂ (17.9 %) composite as shown in Figure 4.8, the intensity of the hydrogen-bonded N-H at ~3289 cm⁻¹ is clearly much stronger than for the unfilled PAI. This again demonstrates that there must exist a hydrogen bonding interaction between the N-H in the PAI and the Ti-OH on the TiO₂. In the amide C=O region, the intensity near 1650 cm⁻¹ for the hydrogen-bonded amide C=O in the composite is clearly stronger than that in the unfilled PAI. This strong band was not observed for the same composite which
Figure 4.8. ATR spectra of the unfilled PAI and the PAI/TiO$_2$ (17.9%) composite at 35 °C. (A) The unfilled PAI, (B) the PAI/TiO$_2$(17.9%). Samples were pre-cured in a vacuum at 100 °C for 36 hours, then cured again in a vacuum for 36 hours after extracted by sufficient methanol for 24 hours. The number in the brackets is the TiO$_2$ content by weight based on 100% conversion from TET to TiO$_2$. 
was not subjected to the methanol extraction. As mentioned above, the methanol extraction enhances the self-hydrogen bonding within the PAI, which gives rise to an increase in the intensity of the hydrogen-bonded amide C=O. However, as discussed in chapter three, the incorporated nanosized TiO₂ domains act as the crosslinks and thereby result in a reduced segmental mobility of the PAI, which should disrupt the self-hydrogen bonding. These two opposite effects should have made the intensity at 1650 cm⁻¹ weaker, rather than stronger for the composite than for the unfilled PAI. The stronger intensity of the 1650 cm⁻¹ band for the composite than for the unfilled PAI suggests that the methanol extraction enhances the hydrogen bonding between the amide C=O and the Ti-OH, although this hydrogen bonding interaction is weak during the in-situ formation of the nanosized TiO₂ domains within the PAI.

4.5. Summary and Conclusions

The PAI-TiO₂-DMAC sol gel system involves many hydrogen bonding interactions. In addition to the hydrogen bonding between the PAI and the TiO₂, there also exist many side interactions such as the hydrogen bonding between the N-H in the PAI and the C=O in the DMAC, and the self-hydrogen bonding within the PAI. The N-H in the PAI can hydrogen bond with either the Ti-OH, the amide C=O in the PAI or the C=O in the DMAC. The characteristic bands for these hydrogen bonds are difficult to identify in both N-H and amide C=O regions. Both FTIR and ATR studies lead to one conclusion:

There is a hydrogen bonding interaction between the N-H groups in the poly(amide-imide) and the residual OH groups on the TiO₂. This interaction, in combination with other physical forces, could be responsible for the in-situ formation of the nanosized TiO₂ rich domains within the poly(amide-imide).
Chapter 5

FABRICATION AND CHARACTERIZATION OF 6F-POLY(AMIDE-IMIDE)/TiO₂
NANOCOMPOSITE GAS SEPARATION MEMBRANES

5.1 Abstract

The permeabilities of H₂, O₂, N₂, CO₂ and CH₄ gases were studied at temperatures of 35, 55, and 75 °C for the unfilled 6F-poly(amide-imide) (6FPAI) and the 6FPAI/TiO₂ nanocomposite with the TiO₂ content of 7.3 % by weight, assuming 100% conversion from tetraethyltitmate (TET) to TiO₂ and 100% incorporation of the TiO₂, or 6.2% by weight based on Thermal Gravimetric Analysis (TGA). The 6FPAI/TiO₂ composites with different TiO₂ contents were fabricated by a sol-gel process. The composite membranes showed a high optical transparency. The TiO₂ domains were well dispersed within the 6FPAI matrix and found by transmission electron microscopy (TEM) to be less than 5 nm in size. Compared to the unfilled 6FPAI membrane, the 6FPAI/TiO₂ (7.3%) composite membrane showed an increase in the permselectivities of gas pairs H₂/CH₄, H₂/N₂ and CO₂/CH₄. This study evaluates the potential of polymer/ceramic nanocomposite membranes in gas separations.

5.2 Introduction

It has been shown in chapters three and four that nanosized TiO₂ domains can be generated in-situ within a poly(amide-imide) as a result of hydrogen bonding. This technology can be favorably used in gas separations. As mentioned in section 1.1, a high performance polymeric membrane should have molecular structural features of hindered segmental and subsegmental mobility and inhibited segmental packing [3-4]. If nanosized metal oxide domains can be formed in a highly dispersed manner within a polymer, the
hindered segmental and subsegmental mobility is expected through the organic/inorganic interfacial interactions [92, 153, 203]. In chapter three, it has been shown that the nanosized TiO₂ domains indeed reduce the segmental mobility of the PAI.

Pd-filled fluorinated poly(amide-imides) have shown a promising application as catalytic membranes in gas separations [13]. Hybrid materials obtained by covalently bonding a functional polymer and a metal oxide are also favorably used in gas separations [248]. Recent work by Schrotter et al. [248] suggests that a polyimide/SiO₂ hybrid membrane falls above the upper bond for H₂/CO₂ separation. However, it needs to point out that work by Kita et al. suggests that polyimide/SiO₂ hybrid membranes have no improvement for H₂/CO₂, H₂/CH₄, H₂/N₂ and O₂/N₂ separations [249]. The polymer/ceramic nanocomposite membranes presented in this chapter are not hybrid materials. As shown in chapters three and four, these membranes are fabricated through essentially a hydrogen bonding interaction between the organic and inorganic components. In this chapter, the similar route employed in the fabrication of the PAI/TiO₂ nanocomposites will be followed for the fabrication of the 6FPAI/TiO₂ nanocomposite membranes. The morphological features, the glass transition behavior, and the gas transport property of resulting membranes will be studied.

5.3 Experimental Methods

The experimental methods are essentially the same as those presented in chapters three and four. In this chapter, additional details and variations are presented.

5.3.1 Materials

The 6FPAI used throughout this study was provided by Dr. D. Fritsch at GKSS Research Center, Geesthacht, Germany. The structure of the 6FPAI is shown in Figure
5.1. The number average of molecular weight, Mn, of the 6FPAI was determined by GPC to be 18.3 K with the dispersity ratio Mw/Mn = 1.54 where Mw is the weight average of molecular weight.

5.3.2  Characterization

Differential Scanning Calorimetry (DSC) analysis was conducted with a DSC220C Seiko II instrument. A sample of 21 mg was placed in an aluminum pan and heated at a rate of 10 °C/minute in the DSC instrument from room temperature to 260 °C and then quenched using liquid nitrogen to 70-100 °C. The quenched sample was then heated from ~ 70 °C to 450 °C at 10 °C/minute. The experiment was carried out in a N2 atmosphere.

5.3.3  Permeation Experiments

Permeation experiments were carried out using a constant volume permeation technique. The permeation set-up is shown in Figure 5.2 [250]. The gases employed in permeation experiments were H2, O2, N2, CH4 and CO2. The membrane was pretreated in a vacuum at ~ 200 °C for ~24 hours, and afterwards the membrane was cooled down to room temperature and then immediately transferred to a membrane cell and degassed for at least 24 hours. After degassing, pressure as low as 0.01 mmHg at the two sides of the membrane was maintained for 10 hours. To minimize the effect of plasticization by CO2 on the transport properties of other gases, CO2 was run after all the other gases were finished. The permeation data was collected from zero to a time ranging from 15 to 50 times the time lag, depending on the specific membrane/gas system. The permeability was evaluated from the pressures at the feed stream and the permeate stream, the thickness of membrane, and the slope of Q vs. t curve where Q is the amount of gas passing through the membrane and t is the time.
Figure 5.1. Molecular structure of the 6F-poly(amide-imide) (6FPAI)
Figure 5.2. Schematic of the permeation set-up. PT1 and PT2 are the pressure transducers for feed stream and permeate stream, respectively. A, B, C, D and E are pneumatic valves.
5.4. Results and Discussions

5.4.1 Membrane appearance

The optical appearances of some typical composite membranes, along with the fabrication conditions, are given in Table 5.1. The descriptions for the correlation of the optical transparency with the homogeneous mixing of organic and inorganic components and for the nomenclature adopted to describe the fabrication conditions of the membranes are presented in chapter three.

It can be seen from Table 5.1 that the solvent has an extremely important effect on the membrane appearance; use of DMAC (dimethylacetamide) generally leads to a phase-separated membrane but the THF (tetrahydrofuran) favors the formation of the optically transparent membranes. In chapter three, it has been pointed out that the hydrogen bonding between the solvent and the polymer should be sufficiently weak but the solvent should be strong enough to provide the good solubility for all the species involved. This is evident from the obvious dependence of the membrane appearance in Table 5.1 on the choice of solvents. Since DMAC is more polar than THF, the interaction of the 6FPAI with DMAC is presumed to be stronger than that with THF. As a consequence, the strong interaction between 6FPAI and DMAC hinders the interaction between 6FPAI and TiO₂, leading to a phase-separated 6FPAI/TiO₂ membrane. In comparison, the weak hydrogen bonding, yet polar interaction between THF and 6FPAI favors the interaction between 6FPAI and TiO₂, enabling good compatibility of the 6FPAI/TiO₂ system.

As shown in Table 5.1, an opaque solution (number 3) occurs when the HCl concentration is low. This can be explained by the electric double layer theory. The PZC (The Point of Zero Charge) of the pure TiO₂ is pH=6 [166-167]. The TiO₂ surface is
Table 5.1. 6FPAI/TiO₂ membrane fabrication

<table>
<thead>
<tr>
<th>No.</th>
<th>Membrane</th>
<th>Composite %</th>
<th>TiO₂&lt;sup&gt;a&lt;/sup&gt; by wt</th>
<th>H₂O/Ti&lt;sup&gt;b&lt;/sup&gt; Mol. Ratio</th>
<th>Solvent</th>
<th>Optical appearance</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6FPAI/TET39/HCl(0.22)/CRm/FD/N₂&lt;sup&gt;c&lt;/sup&gt;</td>
<td>6FPAI/TiO₂</td>
<td>6</td>
<td>9</td>
<td>DMAC</td>
<td>Partially white</td>
<td>Phase separated</td>
</tr>
<tr>
<td>2</td>
<td>6FPAI/TET55/HCl(0.22)/CRm/FD/N₂</td>
<td>6FPAI/TiO₂</td>
<td>11</td>
<td>7</td>
<td>DMAC</td>
<td>Partially white</td>
<td>Phase separated</td>
</tr>
<tr>
<td>3</td>
<td>6FPAI/TET44/HCl(0.15)/CRm/FD/Air</td>
<td>6FPAI/TiO₂</td>
<td>7.3</td>
<td>7</td>
<td>THF</td>
<td>-</td>
<td>Opaque solution</td>
</tr>
<tr>
<td>4</td>
<td>6FPAI/TET44/HCl(0.22)/CRm/FD/Air</td>
<td>6FPAI/TiO₂</td>
<td>7.3</td>
<td>10</td>
<td>THF</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6FPAI/TET61/HCl(0.24)/CRm/FD/Air</td>
<td>6FPAI/TiO₂</td>
<td>13.4</td>
<td>10</td>
<td>THF</td>
<td>Transparent</td>
<td>Brittle</td>
</tr>
<tr>
<td>6</td>
<td>6FPAI/TET66/HCl(0.20)/CRm/FD/Air</td>
<td>6FPAI/TiO₂</td>
<td>16.3</td>
<td>8.7</td>
<td>THF</td>
<td>Transparent</td>
<td>Brittle</td>
</tr>
<tr>
<td>7</td>
<td>6FPAI/TET75/HCl(0.21)/CRm/FD/Air</td>
<td>6FPAI/TiO₂</td>
<td>22.5</td>
<td>9.3</td>
<td>THF</td>
<td>Transparent</td>
<td>Brittle</td>
</tr>
</tbody>
</table>

<sup>a</sup> Assuming 100% conversion of TET to the TiO₂

<sup>b</sup> Water is based on 37% HCl (63 % water) and the water added

<sup>c</sup> The N₂ or Air is the purge gas during the drying of membranes
positively charged at pH values lower than 6. Accordingly, the low HCl concentration (but with a pH lower than 6) reduces the electric charge on the TiO₂ surface because it shifts the pH of the solution closer to PZC. The decrease in the surface charge reduces, in turn, the ζ-potential that is a direct indicator for the repulsive force among the TiO₂ particles. Therefore, the occurrence of the suspension that makes the solution opaque is believed to arise from the weak repulsive forces among the TiO₂ particles. This phenomenon is not expected to occur at relatively high HCl concentrations because the high repulsive forces among the TiO₂ particles will prevent the TiO₂ particles from approaching together.

5.4.2. The analysis of TiO₂ content within the 6FPAI

The TiO₂ content analyzed by TGA is presented in Table 5.2. The high percentage of the incorporation shows the feasibility of the fabrication conditions given in Table 5.1. Some loss of the TiO₂ may arise from the methanol extraction process.

5.4.3. Morphology of the unfilled PAI and the 6FPAI/TiO₂ composites

The morphologies of the 6FPAI with varying TiO₂ content are illustrated in Figure 5.3. The dark portions represent the TiO₂ rich phase. Despite the phase contrast as shown in Figure 5.3-A for the unfilled 6FPAI, a careful comparison of the unfilled 6FPAI with other three composites reveals a difference. Although the size of TiO₂ domains increases typically with an increase in the TiO₂ content, as shown clearly in Figure 3.3, the maximum size of the TiO₂ domains in the 6FPAI/TiO₂(22.5%) is less than 5 nm.

It has been observed that the TiO₂ domain size within the 6FPAI is much smaller than that within the PAI, as shown in Figures 3.3 and 5.3. This difference is believed to arise from the choice of the solvents, as THF was used for the fabrication of the
Table 5.2. The TiO$_2$ contents determined by TGA at 750 °C in an air atmosphere

<table>
<thead>
<tr>
<th>No. in Table 5.1</th>
<th>Membrane</th>
<th>6FPAI</th>
<th>6FPAI/TiO$_2$ (7.3%)</th>
<th>6FPAI/TiO$_2$ (16.3%)</th>
<th>6FPAI/TiO$_2$ (22.5%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory (% by wt.)</td>
<td>0</td>
<td>7.3</td>
<td>16.3</td>
<td>22.5</td>
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</tr>
<tr>
<td>Measured (% by wt.)</td>
<td>0</td>
<td>6.2</td>
<td>14.3</td>
<td>20.8</td>
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<tr>
<td>Loss of TiO$_2$</td>
<td>-</td>
<td>1.1</td>
<td>2.0</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>% Incorporated</td>
<td>-</td>
<td>84.9</td>
<td>87.7</td>
<td>92.4</td>
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</tbody>
</table>
Figure 5.3. TEM of the unfilled 6FPAI and the 6FPAI/TiO$_2$ composites. (A) The unfilled 6FPAI, (B) the 6FPAI/TiO$_2$(7.3%), (C) the 6FPAI/TiO$_2$(16.3%), and (D) the 6FPAI/TiO$_2$(22.5%). The method for sample treatments are given in section 3.3.2. The number in the brackets is the TiO$_2$ content by weight based on 100% conversion from TET to TiO$_2$. 
6FPAI/TiO₂ composites shown in Figure 5.3, but the DMAC was used for the fabrication of the PAI/TiO₂ composites. However, when the DMAC solvent is also used for the fabrication of the 6FPAI/TiO₂ composites, as shown in numbers 1 and 2 in Table 5.1, a poor compatibility between the 6FPAI and the TiO₂ results. This demonstrates that the interaction between the 6FPAI and the TiO₂ may be actually weaker than that between the PAI and the TiO₂. Thus, besides the sol-gel chemistry of a metal alkoxide, the interactions between the polymer and the metal oxide and between the polymer and the solvent must be simultaneously taken into account in controlling the domain size.

5.4.4. Effect of TiO₂ on the crystallization and the glass transition of the 6FPAI

The WAXD patterns of the 6FPAI/TiO₂ composites and the unfilled 6FPAI are shown in Figure 5.4. The highest cure for all the samples is 220 °C, lower than the glass transition temperature of the unfilled 6FPAI that is reported to be higher than 250 °C [13]. All the sharp peaks for the crystalline forms of pure TiO₂, which have been cited in section 3.4.5, cannot be found in Figure 5.4, indicating that the TiO₂ domains also exist in an amorphous state within the 6FPAI matrix.

Based on the results shown in Figure 5.4, the crystallization behavior of the 6FPAI seems to be unaffected by the presence of the TiO₂ domains. Although the scattering intensity of the filled 6FPAI is lower than that of the unfilled 6FPAI, this can be due to the X-ray absorption by the TiO₂ component. As shown in Figure 5.5, the pattern of the 6FPAI/TiO₂(7.3%) can be normalized and the normalized pattern almost completely coincides with the pattern of the unfilled 6FPAI. The scattering intensity for the 6FPAI/TiO₂(16.3%) composite is too low and the normalization is therefore of no significance.
Figure 5.4. WAXD patterns for the unfilled 6FPAI and the 6FPAI/TiO$_2$ composites. The methods for sample treatments are given in section 3.3.2. The number in the brackets is the TiO$_2$ content by weight based on 100% conversion from TET to TiO$_2$. 
Figure 5.5. Normalized WAXD patterns of the unfilled 6FPAI and the 6FPAI/TiO$_2$(7.3\%) composite. The patterns were normalized based on the peak height at $\sim$14 $^\circ$. The methods for sample treatments are given in section 3.3.2. The number in the brackets is the TiO$_2$ content by weight based on 100\% conversion from TET to TiO$_2$. 
The DSC analysis provides more detailed information about the crystallization behavior of the 6FPAI. As shown in Figure 5.6, a significant crystallization for the unfilled and filled 6FPAI occurs at temperatures from ~275 to ~420 °C. The unfilled 6FPAI has only one broad crystallization exotherm, but all the composites have two crystallization exotherms, which will be discussed below.

For the unfilled 6FPAI, as shown in curve A in Figure 5.6, the crystallization exotherm is much smaller than that of the composites. This may suggest that the 6FPAI already has developed some crystallites during the membrane fabrication. The process of the membrane fabrication is given in section 3.3.2. The presence of these crystallites decreases the subsequent crystallization of the amorphous 6FPAI at temperatures above ~275 °C.

All the 6FPAI/TiO₂ composites have two crystallization peaks as shown in curves B, C, and D in Figure 5.6. The exotherm at ~320 °C increases with an increase in the TiO₂ content. Since the crystallization arises from the amorphous 6FPAI, this may suggest that the incorporated TiO₂ domains depress the crystallization of the 6FPAI during the membrane fabrication. However, no distinct difference in the crystallizations at 320 °C for the 6FPAI/TiO₂(7.3%) composite and the unfilled 6FPAI can be observed. This is consistent with the normalized WAXD patterns shown in Figure 5.5. This suggests, on the other hand, that the incorporated TiO₂ domains have no effect on the crystallization process during the membrane fabrication processes, at least for the 6FPAI/TiO₂(7.3%) composite. These facts suggest that it is difficult to justify, based on present results, the effect of the incorporated TiO₂ domains on the crystallization of the 6FPAI during the membrane fabrication processes.
Figure 5.6. DSC results of the second heat for the unfilled 6FPAI and 6FPAI/TiO$_2$ composites. The heating rate of experiments was 10 °C/minute. The methods for sample treatments are given in section 3.3.2. The procedures for the first heat are given in section 5.3.2. The number in the brackets is the TiO$_2$ content by weight based on 100% conversion from TET to TiO$_2$. 
The second crystallization exotherm of the 6FPAI/TiO$_2$ composites occurs at temperatures from ~375 to 410 °C, depending on the TiO$_2$ content. The dependence of the magnitude and the temperature maximum of the exotherms on the TiO$_2$ content suggests that there exists a heterogeneous crystallization process. As mentioned in chapter three, the size of the TiO$_2$ domains within the PAI/TiO$_2$ composites increases with the increase in the TiO$_2$ content. A careful examination of the TiO$_2$ domain size within the 6FPAI/TiO$_2$ composites as shown in Figure 5.3 also reveals an increase in the size of the TiO$_2$ domains with increasing the TiO$_2$ content, although the difference is not appreciable. Therefore, the crystallization temperature of the second exotherm shown in Figure 5.6 may correlate essentially with the size of the TiO$_2$ domains. Although the mechanism governing this correlation is not clear, a fact with certainty is that the highly dispersed TiO$_2$ domains enhance the crystallization above the glass transition.

The presence of appreciable crystallites within the unfilled and filled 6FPAI complicates the evaluation of the glass transition of the 6FPAI. For the unfilled 6FPAI, the molecular motion of the amorphous chains neighboring the crystallite is more restricted than that of those far from the crystallite. For the filled 6FPAI, on the other hand, there also exists the interaction between the 6FPAI and the TiO$_2$ domains. Different local environments of the 6FPAI chains constitute the complexity of the segmental mobility. As a consequence, as shown in Figure 5.6, no distinct glass transition can be observed.

5.4.5. Interaction of the 6FPAI and the TiO$_2$ - FTIR and ATR studies

FTIR spectra of the unfilled and filled 6FPAI are shown in Figure 5.7. The regions that do not show IR absorption are omitted. The bands in the region from ~800 to 450 cm$^{-1}$ increase with increasing the TiO$_2$ content. As mentioned in chapter three, this is due
Figure 5.7. FTIR spectra of the unfilled 6FPAI and the 6FPAI/TiO$_2$ composites at 35 °C. (A) The unfilled 6FPAI, (B) the 6FPAI/TiO$_2$(7.3%), (C) the PAI/TiO$_2$(22.5%). Samples were cured in a vacuum at 100 °C for 24 hours before experiments. The number in the brackets is the TiO$_2$ content by weight based on 100% conversion from TET to TiO$_2$. 
to the broad characteristic band of the Ti-O-Ti linkage [242, 244] overlapping with the bands of the 6FPAI in this region. Figure 5.7 presents the general features of the spectra of the unfilled 6FPAI and the 6FPAI/TiO$_2$ composites. Here, the discussion is again focused on the N-H and amide C=O regions since these two regions contain the most information on the interaction between the 6FPAI and the TiO$_2$.

For the sake of clarity, the spectra in the N-H and amide C=O regions shown in Figure 5.7 are replotted and shown in Figure 5.8. The boiling temperature of the THF is 66 °C. All the samples shown in Figure 5.8 were subjected to a vacuum cure at 100 °C, and it is believed that all of the THF solvent was removed because the polymer films were less than 5 μm thick. The characteristic band at 1600 cm$^{-1}$ arises from the benzene ring [247] and a contribution from the O-H bending of monomeric water [238, 242]. Since the unfilled 6FPAI contains no water, the fact that the bands near ~1600 cm$^{-1}$ for all the unfilled and filled 6FPAI are essentially identical indicate a negligible amount of the monomeric water. However, an additional band for the composites at ~1630 cm$^{-1}$ can be observed as shown in Figure 5.8. A careful examination reveals that the intensity, although it is very weak, increases with an increase in the TiO$_2$ content. This suggests that all the residual monomeric water is hydrogen bonded within the composites.

On the basis of the assignment of the free amide C=O in the PAI as discussed in chapter four, the band at 1690 cm$^{-1}$ is due presumably to the free amide C=O in the 6FPAI. The shoulder at 1666 cm$^{-1}$ for the unfilled 6FPAI is therefore believed to arise from the amide C=O hydrogen-bonded to the N-H in the polymer (self-hydrogen bonding). Although the intensity of this shoulder is weak, an increase in the TiO$_2$ content makes this shoulder clearly disappear. This suggests that the incorporated TiO$_2$ domains disrupt the self-hydrogen bonding to some extent. The important information which can be
Figure 5.8. FTIR spectra of the unfilled 6FPAI and the 6FPAI/TiO$_2$ composites at 35 °C. (A) The unfilled 6FPAI, (B) the 6FPAI/TiO$_2$(7.3%), (C) the 6FPAI/TiO$_2$(22.5%). Samples were cured in a vacuum at 100 °C for 24 hours before experiments. The number in the brackets is the TiO$_2$ content by weight based on 100% conversion from TET to TiO$_2$. 
obtained in the amide C=O region shown in Figure 5.8 is that there exists no evidence for the hydrogen-bonded amide C=O in both composites. This proves again that, as observed in the PAI/TiO₂ composites, the OH groups on the TiO₂ are not hydrogen bonded with the amide C=O in the 6FPAI/TiO₂ composites.

As shown in the N-H region in Figure 5.8, the frequency shift of the hydrogen-bonded N-H in the 6FPAI/TiO₂ composites cannot be observed clearly as compared to that in the unfilled 6FPAI. The cause for this lies in the difficulty in distinguishing the characteristic frequency of the hydrogen bonded N-H groups in the 6FPAI with the OH on the TiO₂ from the characteristic frequency of the hydrogen bonded N-H groups with the amide C=O in the 6FPAI.

However, if the N-H groups hydrogen bond with the OH groups on the TiO₂ in the 6FPAI/TiO₂ composite, the intensity of the hydrogen-bonded N-H should increase with an increase in the TiO₂ content. As shown in Figure 5.8, the intensity at 3275 cm⁻¹, due presumably to the hydrogen-bonded N-H stretch, indeed increases with increasing TiO₂ content. Increase in the TiO₂ content to 22.5%, as shown in curve C in Figure 5.8, makes the shoulder at ~3275 cm⁻¹ become visible. Although the intensity is not as significant as that observed for the PAI/TiO₂ composite system as discussed in chapter four, compared to the unfilled 6FPAI, this shoulder can only be interpreted by the hydrogen bonding between the N-H in the 6FPAI and the residual OH on the TiO₂.

ATR spectra of the unfilled 6FPAI and the 6FPAI/TiO₂(22.5%) composite, as shown in Figure 5.9, are employed to further study the interaction between the 6FPAI and the TiO₂. The samples in Figure 5.9 were extracted with sufficient methanol for 24 hours. In chapter three, it has been shown that the methanol extraction completely removes the
Figure 5.9. ATR spectra of the unfilled 6FPAI and the 6FPAI/TiO$_2$(22.5%) composite at 35 °C. (A) The unfilled 6FPAI, (B) the 6FPAI/TiO$_2$(22.5%). Samples were pre-cured in a vacuum at 100 °C for 36 hours, then cured again in a vacuum for 24 hours after extracted by sufficient methanol for 24 hours. The number in the brackets is the TiO$_2$ content by weight based on 100% conversion from TET to TiO$_2$. 
DMAC solvent trapped in the unfilled and filled PAI matrix. Thus the unfilled and filled 6FPAI shown in Figure 5.9 can be presumed to be solvent free. By drawing a horizontal baseline passing the intensity at 1850 cm\(^{-1}\) in Figures 5.9 and 5.8, the ratios of the intensity of hydrogen-bonded amide C=O at 1666 cm\(^{-1}\) to that of free amide C=O at \(~1688\) cm\(^{-1}\) with and without the methanol extraction can be achieved and are tabulated in Table 5.3. It can be seen from Table 5.3 that the methanol extraction does not affect the self-hydrogen bonding within the unfilled 6FPAI. However, the intensity of the hydrogen-bonded amide C=O in the 6FPAI/TiO\(_2\) (22.5\%) composite is clearly stronger than that in the unfilled 6FPAI (the ratio changes from 0.55 to 0.70). This can also be justified directly by the decrease in the intensity of the free amide C=O at 1688 cm\(^{-1}\). As mentioned earlier, the TiO\(_2\) domains disrupt, rather than enhance, the self-hydrogen bonding. Thus the increase in the intensity of the hydrogen-bonded amide C=O suggests that the methanol extraction enhances the hydrogen bonding between the OH on the TiO\(_2\) and the amide C=O in the 6FPAI. Compared Figure 5.9 with Figure 5.8, on the other hand, it can be seen that the band at \(~1630\) cm\(^{-1}\) due to the hydrogen-bonded monomeric water disappears after the methanol extraction. Accompanying the removal of the monomeric water, the shoulder at 3275 cm\(^{-1}\) for the hydrogen-bonded N-H becomes less pronounced although the intensity is still stronger than that of the unfilled 6FPAI. This suggests that the hydrogen bonding between the N-H in the 6FPAI and the monomeric water that is tightly bonded with the TiO\(_2\) may be also responsible for the in-situ formation of the nanosized TiO\(_2\) domains within the 6FPAI.
Table 5.3. Intensity ratio of the hydrogen bonded amide C=O to the free amide C=O

<table>
<thead>
<tr>
<th>Membrane</th>
<th>6FPAI</th>
<th>6FPAI/TiO₂ (22.5%)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{I_{1666 \text{ cm}^{-1}}}{I_{1690 \text{ cm}^{-1}}}$</td>
<td>0.63</td>
<td>0.55</td>
<td>Without methanol extraction</td>
</tr>
<tr>
<td>$\frac{I_{1666 \text{ cm}^{-1}}}{I_{1688 \text{ cm}^{-1}}}$</td>
<td>0.60</td>
<td>0.70</td>
<td>With methanol extraction</td>
</tr>
</tbody>
</table>
5.4.6 Permeation experiment

All the data so far have suggested that there exist interfacial interactions between the 6FPAI and the TiO₂. Although the attempt to evaluate the segmental mobility of the 6FPAI by DSC and DMTA failed due to the crystallization at temperatures above the glass transition, one can, based on the DMTA study of the PAI/TiO₂ composites presented in chapter three, presume that the incorporated TiO₂ domains reduce the segmental mobility of the 6FPAI. The 6FPAI has a much higher permeability than the PAI. It was found that the permeability of O₂ through the PAI was nearly 190 times lower than that through the 6FPAI (at 35 °C the permeability of O₂ was found to be ~0.09 barrers for the PAI and 10.6 barrers for the 6FPAI). This arises from the -CF₃ groups providing a high fractional free volume, and the side groups -CH₃ providing an inhibited rocking motion of the carbonyl linkage. As a result, the permeability significantly increases without appreciable loss in the permselectivity. Since the permeability of the PAI is too low to be of practical use and the permeability measurement for the PAI also unavoidably accompanies a large error (as will be shown later), the discussion presented in the following sections is focused on the unfilled and filled 6FPAI membranes. The most direct response of the reduced segmental mobility in gas transport properties is the increase in the permselectivity. In this section, the permeation properties of the unfilled 6FPAI and 6FPAI/TiO₂(7.3%) composite membranes will be studied. All other composite membranes, with higher TiO₂ contents, were too brittle to be subjected to a permeation experiment.

The permeation experiments were carried out at 35, and 55, 75 °C. The analysis for the temperature dependence of the permeability and permselectivity is focused on the data at 2 atmospheres, since the low pressure helps to minimize the effect of the non-ideal behavior of gases. The logarithm of the permeability as a function of the reciprocal
temperature for the 6FPAI and 6FPAI/TiO$_2$(7.3%) membranes at feed pressure of 2 atmospheres is shown in Figure 5.10. All the permeability data at different pressures, including the diffusivity data estimated from the time lag method, are tabulated in the appendix of this chapter. The linear relationship of Log $P$ vs. 1/$T$ where $P$ is the permeability and $T$ is the temperature indicates that the permeability obeys the Arrhenius expression:

$$P = P_0 \exp\left(-\frac{E_p}{RT}\right)$$  \hspace{1cm} (5.1)

where $P_0$ is the pre-exponential factor, $E_p$ the apparent activation energy of permeation. Equation 5.1 will be discussed later. The permselectivities for gas pairs O$_2$/N$_2$, H$_2$/CH$_4$, H$_2$/N$_2$ and CO$_2$/CH$_4$ at 2 atmospheres are presented in Figure 5.11. The error bars shown in Figure 5.11 will be discussed below.

For the permselectivity of gas pair O$_2$/N$_2$, an error analysis is necessary because the permselectivities for the unfilled and filled membranes are very close. The permeability data of three repeated experiments for O$_2$ and N$_2$ at 35 °C and 2 atmospheres are shown in Figure 5.10. The relative statistical deviation for O$_2$ is 1% for both membranes. The relative statistical deviation for N$_2$ is 2.4% for the unfilled 6FPAI membrane and 2.7% for the TiO$_2$-filled 6FPAI composite membrane. Therefore, the maximum relative statistical deviation can be considered to be less than 3%. A highly permeable gas tends to have a lower error than a low permeable gas. The ideal permselectivity of any two gases A and B is defined by:

$$\alpha_{A/B} = \frac{P_A}{P_B}$$  \hspace{1cm} (5.2)
Figure 5.10. The logarithms of the permeabilities as a function of the reciprocal temperature at 2 atmospheres. (○) The unfilled 6FPAI, (●) the 6FPAI/TiO₂(7.3%). The solid lines are the results of the linear regression. The methods for sample treatments are given in section 3.3.2. The number in the brackets is the TiO₂ content by weight based on 100% conversion from TET to TiO₂.
Figure 5.11. The logarithms of the permselectivities as a function of the reciprocal temperature at 2 atmospheres. (○) The unfilled 6FPAI, (●) the 6FPAI/TiO₂(7.3%). The solid lines are the results of the linear regression. The error bars of the O₂/N₂ permselectivity are based on the error of 2.6% for the unfilled 6FPAI and 2.9% for the 6FPAI/TiO₂(7.3%). All other error bars are based on the maximum error 4.2%. The methods for sample treatments are given in section 3.3.2. The number in the brackets is the TiO₂ content by weight based on 100% conversion from TET to TiO₂.
where $P_A$ and $P_B$ are the permeability of gases A and B, respectively. The relative standard deviation in $\alpha_{A/B}$ is given by [251]:

$$\frac{\sigma_{\alpha}}{\alpha_{A/B}} = \pm \sqrt{\left(\frac{\Delta P_A}{P_A}\right)^2 + \left(\frac{\Delta P_B}{P_B}\right)^2}$$ (5.3)

where $\sigma_{\alpha}$ is the standard deviation in the permselectivity $\alpha_{A/B}$, the $\Delta P_A$ or $\Delta P_B$ is the statistical deviation which is defined by:

$$\Delta P_j = \sqrt{\sum_{i} \left(\frac{P_{ij} - \bar{P}_j}{n-1}\right)}$$

where $j$ denotes a gas (A or B) and $n$ is the number of repeated experiments, $\bar{P}_j$ is the arithmetic average of $n$ experiments for gas $j$. Therefore, the relative standard deviation in the permselectivity for gas pair $O_2/N_2$ at 35 °C and 2 atmospheres can be calculated based on Equation 5.3 to be $\pm 2.6 \%$ for the unfilled 6FPAI membrane and $\pm 2.9 \%$ for the 6FPAI/TiO$_2$(7.3\%) composite membrane. Assuming that the relative standard deviation in the permeability at other temperatures are also $\pm 2.6 \%$ for the unfilled 6FPAI membrane and $\pm 2.9 \%$ for the 6FPAI/TiO$_2$(7.3\%) composite membrane, as shown in Figure 5.11, the permselectivities between the filled and unfilled membranes at 2 atmospheres for $O_2/N_2$ gas pair become indistinguishable.

However, even assuming the relative statistical deviation in the permeability to be $3 \%$ for all the gases, the maximum relative standard deviation in the permselectivity of any gas pair is still only $\pm 4.2 \%$ based on Equation 5.3. Plotting the error bars of $\pm 4.2\%$ for gas pairs $H_2/CH_4$, $H_2/N_2$ and $CO_2/CH_4$, in Figure 5.11, one can still see the improvement of the permselectivity for the TiO$_2$-filled 6FPAI membrane, in comparison to the unfilled 6FPAI membrane.
As shown in Figures 5.10, the 6FPAI/TiO₂(7.3%) composite membrane always has the lower permeability for all the gases than the unfilled 6FPAI membrane. This indicates that the interfacial interaction between the 6FPAI and the TiO₂ gives rise to a less open matrix. By using the least square analysis for the data shown in Figure 5.10, the linear regression of Equation 5.1 leads to the apparent activation energy of permeation, \( E_p \), and the pre-exponential factor, \( P_0 \), and the results are tabulated in Table 5.4. The Except for CO₂ and H₂, which will be discussed later, all other gases have a higher \( E_p \) for the 6FPAI/TiO₂(7.3%) membrane than for the unfilled 6FPAI membrane. Increase in the apparent activation energy of permeation suggests that the 6FPAI/TiO₂(7.3%) membrane has a more hindered segmental mobility than the unfilled 6FPAI membrane.

A comparison of the permeability and the apparent activation energy of permeation with other polymers is presented in Table 5.5. The TMHFPC, TMPC and PC have been defined in section 2.1.2.4. The 6FDA-6FmDA denotes Hexafluoro Dianhydride 3, 3'-Hexafluoro Diamine and the 6FDA-6FpDA denotes Hexafluoro Dianhydride 4, 4'-Hexafluoro Diamine [8]. As shown in Table 5.5, although a decrease in permeability generally accompanies an increase in the apparent activation energy of permeation, this does hold for all the membranes. The typical examples are the 6FPAI and TMHFPC. Although the apparent activation energy of permeation of CO₂ and O₂, N₂ and CH₄ gases for both membranes are very close, the permeabilities of these gases for TMHFPC are apparently higher than those for 6FPAI. It must be pointed out that the higher permeabilities of the TMHFPC membrane accompany no significant loss in the permselectivity. The CO₂/CH₄ permselectivity for the TMHFPC membrane is even higher than that for the 6FPAI membrane. This example demonstrates that the correlation between the apparent activation energy of permeation and the segmental mobility may be
Table 5.4. Apparent activation energy of permeation and the pre-exponential factor based on a linear regression using Equation 5.1.

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<td>2.2</td>
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<tr>
<td>$N_2$ (3.64 Å)</td>
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<td>3.4</td>
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<tr>
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<tr>
<td>$CO_2$ (3.3 Å)</td>
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<td>0.33</td>
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<tr>
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<th>6FPAI/TiO$_2$(7.3%)</th>
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<td>302</td>
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</tr>
<tr>
<td>$N_2$ (3.64 Å)</td>
<td>426</td>
<td>459</td>
<td></td>
</tr>
<tr>
<td>$CH_4$ (3.8 Å)</td>
<td>768</td>
<td>904</td>
<td></td>
</tr>
<tr>
<td>$CO_2$ (3.3 Å)</td>
<td>189</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>$H_2$ (2.89Å)</td>
<td>3337</td>
<td>1829</td>
<td></td>
</tr>
</tbody>
</table>

* The numbers in the brackets are the kinetic diameters of gases.
Table 5.5  Comparison of permeability, \( P \), and apparent activation energy of permeation, \( E_p \), for various polymers and penetrants

<table>
<thead>
<tr>
<th>Penetrant</th>
<th>6FPAI&lt;sup&gt;a&lt;/sup&gt;</th>
<th>6FPAI/TiO&lt;sub&gt;2&lt;/sub&gt;(7.3%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>6FDA-6FmDA&lt;sup&gt;b&lt;/sup&gt;</th>
<th>6FDA-6FpDA&lt;sup&gt;b&lt;/sup&gt;</th>
<th>TMHFPC&lt;sup&gt;c&lt;/sup&gt;</th>
<th>TMPC&lt;sup&gt;c&lt;/sup&gt;</th>
<th>PC&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( P^* )</td>
<td>( E_p^{**} )</td>
<td>( P )</td>
<td>( E_p )</td>
<td>( P )</td>
<td>( E_p )</td>
<td>( P )</td>
</tr>
<tr>
<td>He</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>54.3</td>
<td>2.6</td>
<td>129</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>67.0</td>
<td>2.4</td>
<td>66.2</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>53.1</td>
<td>0.78</td>
<td>48.7</td>
<td>0.33</td>
<td>5.8</td>
<td>2.2</td>
<td>64.7</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>10.6</td>
<td>1.9</td>
<td>8.99</td>
<td>2.2</td>
<td>2.0</td>
<td>3.1</td>
<td>16.0</td>
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<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.22</td>
<td>3.2</td>
<td>1.79</td>
<td>3.4</td>
<td>0.26</td>
<td>5.4</td>
<td>3.1</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.77</td>
<td>3.7</td>
<td>1.34</td>
<td>4.0</td>
<td>0.08</td>
<td>7.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

a. Data from this study
b. Data from reference [8]
c. Data from reference [11]

* \( P \) in Barrer

** \( E_p \) in kcal/mole
of significance only by comparing a same series of polymer, since a subtle difference in the molecular structure can cause a significant change in the gas transport properties [1].

The apparent activation energy of permeation, $E_p$, is the sum of the activation energy of diffusion, $E_d$, and the enthalpy of sorption, $\Delta H_s$:

$$E_p = E_d + \Delta H_s$$  \hspace{1cm} (5.4)

As shown in Table 5.4, of the three non-polar gases, O$_2$, N$_2$, and CH$_4$, O$_2$ has the smallest kinetic diameter and CH$_4$ has the largest kinetic diameter. The permeability of a glassy polymer is generally controlled by diffusivity, particularly for the permeability of non-polar gases [1, 5]. Since the activation energy of diffusion increases with increasing the kinetic diameter as shown in Equation 2.41, this accounts for why the apparent activation energies of permeation for non-polar gases O$_2$, N$_2$, and CH$_4$ increase with their kinetic diameter. Accordingly, the activation energy of diffusion should be responsible for the increase in the apparent activation energy of permeation. The increase in the activation energy of diffusion should lead to a decrease in the diffusivity. The data indeed show an appreciable loss in diffusivity but a distinct increase in diffusivity selectivity upon the incorporation of the TiO$_2$ domains within the 6FPAI. This trend is clearly shown in the data presented in the appendix although the accurate activation energy of diffusion was not available. On the other hand, a large difference in the kinetic diameters corresponds to a large permselectivity. This may also accounts for the largest improvement in the H$_2$/CH$_4$ permselectivity for the TiO$_2$-filled 6FPAI over the unfilled 6FPAI, as shown in Figure 5.11 or Table 5A-2.

As shown in Table 5.5, CO$_2$ has a lower $E_p$ for the TiO$_2$-filled 6FPAI than for the unfilled 6FPAI and other polymers. This suggests that the TiO$_2$ domains increase the negative contribution of the enthalpy of sorption. CO$_2$ is a polar gas. The residual OH
groups on the TiO₂ are also polar. Accordingly, the interaction between the CO₂ and the OH makes the enthalpy of sorption greater in the 6FPAI/TiO₂(7.3%) membrane than in the unfilled 6FPAI membrane. As shown in Equation 5.4, the apparent activation energy of permeation is the sum of the activation energy of diffusion and the enthalpy of sorption. Although the activation energy of diffusion for the composite membrane is higher than that for the unfilled 6FPAI membrane, which can be qualitatively justified by the diffusivity data presented in Table 5A-1, the larger negative contribution of the enthalpy of sorption for the composite membrane causes the apparent activation energy of permeation decrease.

H₂ also shows a decrease in $E_p$ for the TiO₂-filled 6FPAI than for the unfilled 6FPAI as shown in Table 5.4 or 5.5. Although H₂ is a non-polar gas, the H₂ shows a certain solubility in dense ceramic membranes such as ZrO₂, Bi₂O₃, [25, 30]. The separation mechanism of these membranes involves the transport of gas as gas ions [30]. Accordingly, the lower apparent activation energy of permeation of H₂ in the TiO₂-filled 6FPAI than in the unfilled 6FPAI also suggests that the TiO₂ domains increase the enthalpy of sorption of H₂. Although the pertinent solubility and diffusivity data are not available, the permeability data of H₂ shown in Table 5A-1 provides some evidence. An increase in the enthalpy of sorption will increase the temperature dependence of solubility. As shown in Table 5A-1, the increase in temperature gives rise to a less pronounced increase in the H₂ permeability for the TiO₂-filled 6FPAI membrane than for the unfilled 6FPAI membrane. One can reasonably assume that the activation energy of diffusion of H₂ is also higher for the TiO₂-filled 6FPAI membrane than for the unfilled 6FPAI membrane. Thus the only explanation for the less pronounced increase in the H₂ permeability for the TiO₂-filled 6FPAI membrane is the faster decrease in the solubility with increasing temperature, as compared to the unfilled 6FPAI membrane. Accordingly, the faster
decrease in the solubility results from the larger negative contribution of the enthalpy of sorption.

The data presented in Table 5.4 provides the information about the temperature dependence of the permeability and the permselectivity. The temperature dependence of the permeability has been shown by the solid lines in Figure 5.10, which can be achieved by directly substituting the data in Table 5.4 into Equation 5.1. The temperature dependence of the permselectivity can be obtained from Equation 5.2 and is given by:

\[
\alpha_{A/B} = \frac{P_0(A)}{P_0(A)} \exp \left( -\frac{\Delta E_{p,A/B}}{RT} \right)
\]  (5.5)

where the \( A \) and \( B \) denote any gas pair, \( \Delta E_{p,A/B} = \Delta E_{p,A} - \Delta E_{p,B} \). By substituting the data in Table 5.4 into Equation 5.5, ratio of the \( P_0(A)/P_0(B) \) and the \( \Delta E_{p,A/B} \) are tabulated in Table 5.6. Equation 5.5 shows that the permselectivities of the unfilled and filled 6FPAI decrease monotonically with an increase in temperature. The permeability of gas pair \( O_2/N_2 \) is not sensitive to the presence of the TiO\(_2\). However, the permselectivities for gas pairs \( H_2/CH_4, H_2/N_2 \) and \( CO_2/CH_4 \) show a similar trend. The data in Table 5.6 show that the \( \Delta E_{p,A/B} \) for the composite membrane is greater than that for the unfilled membrane. Accordingly, an increase in the temperature will lead to a more pronounced decrease in the permselectivity of the 6FPAI/TiO\(_2\) membrane than that of the unfilled 6FPAI. This suggests that, at low temperatures, the permselectivity is higher for the composite membrane than for the unfilled membrane. However, there will exist a critical temperature at which the distinction in the permselectivity for both membranes disappears. At temperatures above the critical temperature, the permselectivity of the composite membrane becomes lower than the unfilled membrane. As mentioned earlier, the TiO\(_2\)
Table 5.6. Ratio of pre-exponential factor and difference in the apparent activation energy of permeation of two gases

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{p, A/B}$ (kcal/mole)</th>
<th>6FPAI</th>
<th>6FPAI/TiO$_2$(7.3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2/\text{N}_2$</td>
<td>1.3</td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>$\text{H}_2/\text{CH}_4$</td>
<td>1.3</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>$\text{H}_2/\text{N}_2$</td>
<td>0.8</td>
<td></td>
<td>1.4</td>
</tr>
<tr>
<td>$\text{CO}_2/\text{CH}_4$</td>
<td>2.9</td>
<td></td>
<td>3.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$P_{\alpha}(A)/P_{\alpha}(B)$ (Barerrer)</th>
<th>6FPAI</th>
<th>6FPAI/TiO$_2$(7.3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2/\text{N}_2$</td>
<td>0.61</td>
<td></td>
<td>0.66</td>
</tr>
<tr>
<td>$\text{H}_2/\text{CH}_4$</td>
<td>4.4</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>$\text{H}_2/\text{N}_2$</td>
<td>7.8</td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>$\text{CO}_2/\text{CH}_4$</td>
<td>0.25</td>
<td></td>
<td>0.09</td>
</tr>
</tbody>
</table>
domain increases the negative contribution of the enthalpy of sorption for both CO₂ and H₂. This accounts for why the permselectivities of gas pairs H₂/CH₄, H₂/N₂ and CO₂/CH₄ for the TiO₂-filled 6FPAI decrease faster than those for the unfilled 6FPAI. However, it needs to be emphasized that, at a certain temperature range, the observed increases in the permselectivities of gas pairs H₂/CH₄, H₂/N₂ accompany inappreciable loss in the H₂ permeability. This suggests that the 6FPAI/TiO₂ composite membrane is superior to the unfilled 6FPAI membrane, at least for the H₂/CH₄ and H₂/N₂ separations.

Although incorporation of the TiO₂ domains within the 6FPAI increases the permselectivities of gas pairs H₂/CH₄ and H₂/N₂ without the appreciable loss in the H₂ permeability, the overall performance of the composite membrane is still moderately under the upper bound [10, 252]. For example, the upper bound of the permselectivity of CO₂/CH₄ is ~50 at the CO₂ permeability of 50 barrers [10]. The permselectivity of CO₂/CH₄ for the PAI/TiO(7.3%) composite membrane is only 36.4 at the CO₂ permeability 48.7 barrers, as shown in Table 5A-1 and 5A-2. For the gas pair H₂/CO₂, the upper bound of the permselectivity is ~ 4 at the H₂ permeability of 100 barrers [252]. However, the permselectivity of H₂/CO₂ for the PAI/TiO(7.3%) composite membrane is only 1.9 at the H₂ permeability 100 barrers based on the permeability data at 75 °C as shown in Table 5A-1. Thus a simple, but important fact is that the correct choice of both metal oxides and polymers are of equal importance in the development of high performance composite membranes.

After the discussion of the temperature dependence of the permeability and the permselectivity, a brief discussion is given to the pressure dependence of the permeability. The permeability of gases O₂, N₂, CO₂ and CH₄ as a function of pressure at 35 °C is shown in Figure 5.12. Except for O₂ permeating in the unfilled 6FPAI and CO₂ in the
Figure 5.12. The permeabilities as a function of feed stream pressure at 35 °C. (○) The unfilled 6FPAI, (●) the 6FPAI/TiO₂ (7.3%). The solid lines were drawn manually. The methods for sample treatments are given in section 3.3.2. The number in the brackets is the TiO₂ content by weight based on 100% conversion from TET to TiO₂.
6FPAI/TiO$_2$(7.3%) composite, all other permeabilities tend to be independent of pressure over the pressure range employed. The causes for the distinctly higher permeability of O$_2$ through the unfilled membrane at 6 atmospheres are not clear. More permeability data at other pressures may be needed for a meaningful statement.

The CO$_2$ permeability through the TiO$_2$-filled 6FPAI, as shown in Figure 5.12, follows the dual mode sorption model. But the CO$_2$ permeability through the unfilled 6FPAI does not show this feature at the pressure range employed. This can be explained in terms of the enhanced CO$_2$ sorption in the Langmuir sites, which enables the saturation sorption of CO$_2$ in the TiO$_2$-filled 6FPAI to occur at a relatively lower pressure, as compared to the sorption within the unfilled 6FPAI. As a consequence, with increasing pressure, the solubility $S$ of CO$_2$ decreases faster in the TiO$_2$-filled 6FPAI than in the unfilled 6FPAI. Accordingly, the faster decrease in CO$_2$ permeability in the TiO$_2$-filled 6FPAI than in the unfilled 6FPAI is attributed to the faster decrease in the CO$_2$ solubility with increasing pressure.

5.5 Summary and Conclusions

The success in incorporating nanosized TiO$_2$ rich domains within the high Tg and high permeable 6F-poly(amide-imide) provides a potential application of inorganic/organic nanocomposite membranes in gas separations. The observed increases in the permselectivities of gas pairs H$_2$/CH$_4$, H$_2$/N$_2$ without the appreciable loss in the H$_2$ permeability suggest that the 6FPAI/TiO$_2$(7.3%) composite membrane is superior to the unfilled 6FPAI membrane. The solvent for the membrane fabrication is of particular importance. A strong solvent hinders the interaction between the polymer and the metal oxide, and thereby leads to a phase-separated membrane. Although the hydrogen bonding between the residual OH on the TiO$_2$ and the N-H in the 6FPAI is presumed to be
responsible for the in-situ formation of the nanosized TiO$_2$ rich domains within the 6FPAI, only a weak evidence of this was found. The following results are clear on the basis of this study:

1. Nanosized TiO$_2$ rich domains smaller than 5 nm can be generated in-situ within the 6FPAI by using tetrahydrofuran (THF) as the solvent;
2. The incorporated nanosized TiO$_2$ rich domains enhance the crystallization above the glass transition;
3. In a certain temperature range, the 6FPAI can be filled with nanosized TiO$_2$ rich domains to achieve increased permselectivities for gas pairs H$_2$/CH$_4$, H$_2$/N$_2$ and CO$_2$/CH$_4$;
4. Although the 6FPAI/TiO$_2$(7.3%) composite membrane is superior to the unfilled 6FPAI membrane, the upper bound analysis for H$_2$/CO$_2$ separation shows that the overall performance of the 6FPAI/TiO$_2$(7.3%) composite membrane still falls below the upper bound.

The following conclusions can be made based on this study:

1. As compared to the unfilled 6FPAI, increased permselectivities of H$_2$/CH$_4$, H$_2$/N$_2$ and CO$_2$/CH$_4$ gas pairs result from the highly dispersed TiO$_2$ domains within the 6FPAI matrix.
2. A high TiO$_2$ content, combined with the nanosized distribution of TiO$_2$ rich domains is critical for the significant improvement of gas transport properties. However, such membranes are too brittle to be of practical use. Use of porous support is essential to overcome the brittleness problem of the composite membranes and to find the industrial application in gas separations.
5.6. Appendix

By knowing the permeability and the time lag from a permeation experiment, the diffusivity and solubility data presented in Table 5A-1 to 5A-6 are estimated by the following equations:

\[
D = \frac{l^2}{6\theta} \quad (5A-1)
\]

\[
S = \frac{76P}{D} \quad (5A-2)
\]

where: \( P = \text{permeability in barrer} \), (1 barrer equals \( 10^{-10} \) cc(STP)-cm/(cm\(^2\)-sec-cmHg),

\( D = \text{diffusivity in cm}^2/\text{s} \);

\( S = \text{solubility in cm}^3\text{(STP)}/(\text{cm}^3 \text{ polymer} \cdot \text{ atm}) \);

\( l = \text{thickness of membrane in cm} \);

\( \theta = \text{time lag in second} \).
Table 5A-1. Permeabilities, diffusivities and solubilities of the 6FPAI and 6FPAI/TiO$_2$(7.3%) at 2 atmospheres.

<table>
<thead>
<tr>
<th>Ideal permeability, barrer</th>
<th>6FPAI</th>
<th>6FPAI/TiO$_2$(7.3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35 °C</td>
<td>55 °C</td>
</tr>
<tr>
<td>$P_{O_2}$</td>
<td>10.6</td>
<td>12.8</td>
</tr>
<tr>
<td>$P_{N_2}$</td>
<td>2.22</td>
<td>3.04</td>
</tr>
<tr>
<td>$P_{CO_2}$</td>
<td>53.1</td>
<td>57.9</td>
</tr>
<tr>
<td>$P_{CH_4}$</td>
<td>1.77</td>
<td>2.60</td>
</tr>
<tr>
<td>$P_{H_2}$</td>
<td>67.0</td>
<td>87.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Diffusivity x10$^8$, cm$^2$/second</th>
<th>6FPAI</th>
<th>6FPAI/TiO$_2$(7.3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35 °C</td>
<td>55 °C</td>
</tr>
<tr>
<td>$D_{O_2}$</td>
<td>8.88</td>
<td>21.0</td>
</tr>
<tr>
<td>$D_{N_2}$</td>
<td>2.51</td>
<td>5.58</td>
</tr>
<tr>
<td>$D_{CO_2}$</td>
<td>2.81</td>
<td>5.72</td>
</tr>
<tr>
<td>$D_{CH_4}$</td>
<td>0.54</td>
<td>1.06</td>
</tr>
<tr>
<td>$D_{H_2}$*</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solubility, cm$^3$(STP)/ [cm$^3$(polymer).atm]</th>
<th>6FPAI</th>
<th>6FPAI/TiO$_2$(7.3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35 °C</td>
<td>55 °C</td>
</tr>
<tr>
<td>$S_{O_2}$</td>
<td>0.90</td>
<td>0.46</td>
</tr>
<tr>
<td>$S_{N_2}$</td>
<td>0.67</td>
<td>0.42</td>
</tr>
<tr>
<td>$S_{CO_2}$</td>
<td>14.4</td>
<td>7.68</td>
</tr>
<tr>
<td>$S_{CH_4}$</td>
<td>2.48</td>
<td>1.87</td>
</tr>
<tr>
<td>$S_{H_2}$*</td>
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<td>-</td>
</tr>
</tbody>
</table>

* No data available due to the time lag being too fast.
Table 5A-2. Permselectivities, diffusivity selectivities and solubility selectivity of the 6FPAI and 6FPAI/TiO/TiO2 (7.3%) at 2 atmospheres.

<table>
<thead>
<tr>
<th></th>
<th>Ideal permselectivity</th>
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<tbody>
<tr>
<td></td>
<td>6FPAI</td>
<td>6FPAI/TiO2(7.3%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35 °C</td>
<td>55 °C</td>
<td>75 °C</td>
<td>35 °C</td>
<td>55 °C</td>
<td>75 °C</td>
<td></td>
</tr>
<tr>
<td>$P_{O_2}/P_{N_2}$</td>
<td>4.76</td>
<td>4.21</td>
<td>3.86</td>
<td>5.02</td>
<td>4.43</td>
<td>4.02</td>
<td></td>
</tr>
<tr>
<td>$P_{CO_2}/P_{CH_4}$</td>
<td>30.0</td>
<td>22.3</td>
<td>17.1</td>
<td>36.4</td>
<td>25.6</td>
<td>18.1</td>
<td></td>
</tr>
<tr>
<td>$P_{H_2}/P_{N_2}$</td>
<td>30.2</td>
<td>28.8</td>
<td>27.2</td>
<td>37.0</td>
<td>33.0</td>
<td>29.9</td>
<td></td>
</tr>
<tr>
<td>$P_{H_2}/P_{CH_4}$</td>
<td>37.8</td>
<td>33.6</td>
<td>30.0</td>
<td>49.4</td>
<td>41.1</td>
<td>34.8</td>
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<table>
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<tr>
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<tbody>
<tr>
<td></td>
<td>6FPAI</td>
<td>6FPAI/TiO2(7.3%)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>35 °C</td>
<td>55 °C</td>
<td>75 °C</td>
<td>35 °C</td>
<td>55 °C</td>
<td>75 °C</td>
<td></td>
</tr>
<tr>
<td>$D_{O_2}/D_{N_2}$</td>
<td>3.53</td>
<td>3.76</td>
<td>3.75</td>
<td>5.69</td>
<td>3.86</td>
<td>4.61</td>
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<tr>
<td>$D_{CO_2}/D_{CH_4}$</td>
<td>5.16</td>
<td>5.41</td>
<td>4.45</td>
<td>7.25</td>
<td>5.56</td>
<td>3.69</td>
<td></td>
</tr>
<tr>
<td>$D_{H_2}/D_{N_2}$*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$D_{H_2}/D_{CH_4}$*</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<th>Solubility selectivity</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>6FPAI</td>
<td>6FPAI/TiO2(7.3%)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35 °C</td>
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<td>75 °C</td>
<td>35 °C</td>
<td>55 °C</td>
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</tr>
<tr>
<td>$S_{O_2}/S_{N_2}$</td>
<td>1.35</td>
<td>1.12</td>
<td>1.03</td>
<td>0.88</td>
<td>1.15</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>$S_{CO_2}/S_{CH_4}$</td>
<td>5.80</td>
<td>4.12</td>
<td>3.84</td>
<td>5.01</td>
<td>4.61</td>
<td>4.90</td>
<td></td>
</tr>
<tr>
<td>$S_{CO_2}/S_{CH_4}$*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$S_{CO_2}/S_{CH_4}$*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

* No data available due to the time lag being too fast.
Table 5A-3. Permeabilities, diffusivities and solubilities of the 6FPAI and 6FPAI/TiO\(_2\) (7.3\%) at 4 atmospheres.

<table>
<thead>
<tr>
<th></th>
<th>6FPAI</th>
<th>6FPAI/TiO(_2) (7.3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ideal permeability, barrer</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(P_{O_2})</td>
<td>10.7</td>
<td>9.21</td>
</tr>
<tr>
<td>(P_{N_2})</td>
<td>2.34</td>
<td>1.84</td>
</tr>
<tr>
<td>(P_{CO_2})</td>
<td>53.3</td>
<td>43.8</td>
</tr>
<tr>
<td>(P_{CH_4})</td>
<td>1.83</td>
<td>1.35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Diffusivity x10(^8), cm(^2)/second</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>35 °C</td>
</tr>
<tr>
<td>(D_{O_2})</td>
</tr>
<tr>
<td>(D_{N_2})</td>
</tr>
<tr>
<td>(D_{CO_2})</td>
</tr>
<tr>
<td>(D_{CH_4})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Solubility, cm(^3)(STP)/[cm(^3)(polymer).atm]</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>35 °C</td>
</tr>
<tr>
<td>(S_{O_2})</td>
</tr>
<tr>
<td>(S_{N_2})</td>
</tr>
<tr>
<td>(S_{CO_2})</td>
</tr>
<tr>
<td>(S_{CH_4})</td>
</tr>
</tbody>
</table>
Table 5A-4. Permselectivities, diffusivity selectivities and solubility selectivity of the 6FPAI and 6FPAI/TiO/TiO₂ (7.3%) at 4 atmospheres.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( P_{O_2}/P_{N_2} )</th>
<th>( P_{CO_2}/P_{CH_4} )</th>
<th>( D_{O_2}/D_{N_2} )</th>
<th>( D_{CO_2}/D_{CH_4} )</th>
<th>( S_{O_2}/S_{N_2} )</th>
<th>( S_{CO_2}/S_{CH_4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 °C</td>
<td>4.57</td>
<td>29.2</td>
<td>3.93</td>
<td>4.56</td>
<td>1.6</td>
<td>6.40</td>
</tr>
<tr>
<td>55 °C</td>
<td>4.20</td>
<td>21.2</td>
<td>3.57</td>
<td>5.48</td>
<td>1.18</td>
<td>3.87</td>
</tr>
<tr>
<td>75 °C</td>
<td>3.96</td>
<td>18.0</td>
<td>3.75</td>
<td>4.45</td>
<td>1.03</td>
<td>3.84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( P_{O_2}/P_{N_2} )</th>
<th>( P_{CO_2}/P_{CH_4} )</th>
<th>( D_{O_2}/D_{N_2} )</th>
<th>( D_{CO_2}/D_{CH_4} )</th>
<th>( S_{O_2}/S_{N_2} )</th>
<th>( S_{CO_2}/S_{CH_4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 °C</td>
<td>5.02</td>
<td>32.5</td>
<td>4.09</td>
<td>8.46</td>
<td>1.23</td>
<td>3.83</td>
</tr>
<tr>
<td>55 °C</td>
<td>4.44</td>
<td>23.6</td>
<td>3.88</td>
<td>6.15</td>
<td>1.14</td>
<td>3.83</td>
</tr>
<tr>
<td>75 °C</td>
<td>4.02</td>
<td>18.08</td>
<td>4.61</td>
<td>3.69</td>
<td>0.87</td>
<td>4.90</td>
</tr>
</tbody>
</table>
Table 5A-5. Permeabilities, diffusivities and solubilities of the 6FPAI and 6FPAI/TiO/TiO$_2$ (7.3%) at 6 atmospheres.

<table>
<thead>
<tr>
<th>Ideal permeability, barrier</th>
<th>6FPAI</th>
<th>6FPAI/TiO$_2$ (7.3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35 °C 55 °C 75 °C</td>
<td>35 °C 55 °C 75 °C</td>
</tr>
<tr>
<td>$P_{O_2}$</td>
<td>12.3  14.6  18.2</td>
<td>9.29  11.5  14.2</td>
</tr>
<tr>
<td>$P_{N_2}$</td>
<td>2.27   3.39   4.68</td>
<td>1.83  2.59  3.51</td>
</tr>
<tr>
<td>$P_{CO_2}$</td>
<td>51.7   54.5   64.6</td>
<td>41.5  47.7  48.0</td>
</tr>
<tr>
<td>$P_{CH_4}$</td>
<td>1.80   2.53   3.64</td>
<td>1.34  1.98  2.92</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Diffusivity x10$^8$, cm$^2$/second</th>
<th>6FPAI</th>
<th>6FPAI/TiO$_2$ (7.3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35 °C 55 °C 75 °C</td>
<td>35 °C 55 °C 75 °C</td>
</tr>
<tr>
<td>$D_{O_2}$</td>
<td>9.52  22.3  44.2</td>
<td>7.09  13.0  19.8</td>
</tr>
<tr>
<td>$D_{N_2}$</td>
<td>2.04   5.76   10.5</td>
<td>1.87  3.61  5.20</td>
</tr>
<tr>
<td>$D_{CO_2}$</td>
<td>3.04   8.33   10.6</td>
<td>3.28  4.83  7.29</td>
</tr>
<tr>
<td>$D_{CH_4}$</td>
<td>1.00   1.59   2.65</td>
<td>0.36  0.81  1.67</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solubility, cm$^3$(STP)/[cm$^3$(polymer) atm]</th>
<th>6FPAI</th>
<th>6FPAI/TiO$_2$ (7.3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35 °C 55 °C 75 °C</td>
<td>35 °C 55 °C 75 °C</td>
</tr>
<tr>
<td>$S_{O_2}$</td>
<td>0.98  0.50  0.31</td>
<td>1.00  0.68  0.54</td>
</tr>
<tr>
<td>$S_{N_2}$</td>
<td>0.85  0.45  0.34</td>
<td>0.75  0.55  0.51</td>
</tr>
<tr>
<td>$S_{CO_2}$</td>
<td>12.9  4.97  4.63</td>
<td>9.61  7.20  5.00</td>
</tr>
<tr>
<td>$S_{CH_4}$</td>
<td>1.37  1.21  1.05</td>
<td>2.85  1.87  1.33</td>
</tr>
</tbody>
</table>
Table 5A-6. Permselectivities, diffusivity selectivities and solubility selectivity of the 6FPAI and 6FPAI/TiO/TiO₂ (7.3%) at 6 atmospheres.

<table>
<thead>
<tr>
<th></th>
<th>Ideal permselectivity</th>
<th></th>
<th>Diffusivity selectivity</th>
<th></th>
<th>Solubility selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6FPAI</td>
<td>6FPAI/TiO₂(7.3%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35 °C  55 °C  75 °C</td>
<td>35 °C  55 °C  75 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(P_{O_2}/P_{N_2})</td>
<td>5.42  4.29  3.90</td>
<td>5.06  4.45  4.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(P_{CO_2}/P_{CH_4})</td>
<td>28.7  21.5  17.8</td>
<td>30.9  23.0  16.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6FPAI</td>
<td>6FPAI/TiO₂(7.3%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35 °C  55 °C  75 °C</td>
<td>35 °C  55 °C  75 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(D_{O_2}/D_{N_2})</td>
<td>4.68  3.87  4.21</td>
<td>3.79  3.60  3.81</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(D_{CO_2}/D_{CH_4})</td>
<td>3.06  5.24  4.00</td>
<td>9.18  5.98  4.37</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CONCLUDING REMARKS

Organic/Inorganic composites based on the high Tg poly(amide-imides) (the poly(amide-imide) and the 6F-poly(amide-imide)) and metal oxides were fabricated. The poly(amide-imide) (PAI) was synthesized from 4,4’-oxy(phenyl trimellitimide)[OPTMI] and 4,4’-oxydianiline [ODA] using tert. butyl benzoic acid [t-BBA] as the monofunctional endcapper [15], and 6F-poly(amide-imide) (6FPAl) was synthesized from an imide-containing dicarboxylic acid (DAC) and hexafluoro-2,2-bis(4-amo-no-phenyl)-propane [13]. Nanosized TiO$_2$ rich domains were incorporated within both the poly(amide-imide) and the 6F-poly(amide-imide). The poly(amide-imide)/SiO$_2$ systems showed considerably larger SiO$_2$ rich domains. However, the SiO$_2$ could be bonded with the TiO$_2$, forming nanosized domains within the poly(amide-imide) matrix. There are several parameters which control the final morphology of the system. In addition to the sol-gel chemistry of metal alkoxides, two parameters are important; one important factor is the hydrogen bonding energy between the polymer and the metal oxide, and the second factor is the interaction between the polymer and the solvent. Strong hydrogen bonding interaction between the polymer and the metal oxide and a weak interaction between the polymer and the solvent serve to reduce the domain size of the metal oxide. In the case that the metal oxide provides a proton acceptor, as the author of this dissertation pointed out in chapter three, the metal oxide in which the metal has a high electronegativity and a large atomic size will form the strongest hydrogen bond with the proton donor in the poly(amide-imides). Although direct data of the pertinent hydrogen bonding energies were not obtained, the proof of this hypothesis is evident on the basis of the optical appearances of composite films, the TEM results, DMTA study, and FTIR and ATR studies.
The incorporated nanosized TiO$_2$ rich domains reduce the segmental mobility of the poly(amide-imide) and shift the glass transition to higher temperatures. The dynamic mechanical properties in rubbery regions can be interpreted by the theory of rubbery elasticity. For the 6F-poly(amide-imide), the attempts to obtain these properties by DMTA and DSC failed due to the fast crystallization of the polymer above the glass transition. The nanosized TiO$_2$ rich domains also disrupt the crystallinity of the poly(amide-imide) during the fabrication processes of the composites and above the glass transition. However, an enhanced crystallization of the 6F-poly(amide-imide) around the TiO$_2$ domains is found above the glass transition.

The permeation experiments for H$_2$, O$_2$, N$_2$, CH$_4$ and CO$_2$ gases show that, below a certain temperature, the 6F-poly(amide-imide)/TiO$_2$ composite membrane, with the TiO$_2$ content of 6.2% based on Thermal Gravimetric Analysis (TGA), or 7.3% by weight assuming 100% conversion from TET to TiO$_2$, has higher permselectivities for gas pairs H$_2$/CH$_4$, H$_2$/CH$_4$, and CO$_2$/CH$_4$ than the unfilled 6F-poly(amide-imide). Compared to the permeabilities of the unfilled 6F-poly(amide-imide) membrane, some losses in the permeabilities of the 6F-poly(amide-imide)/TiO$_2$ composite membrane for gases O$_2$, N$_2$, CH$_4$ and CO$_2$ were found, but the loss in the permeability of the composite membrane for H$_2$ was minimum. For the gas pair O$_2$/N$_2$, improvement in the permselectivity of the filled 6F-poly(amide-imide) over the unfilled 6F-poly(amide-imide) was not observed. Unfortunately, the composite membrane with higher TiO$_2$ content (higher than 16.3 % by weight) was too brittle to be used in a permeation experiment. To overcome the limitation of the brittleness of the composite membrane, an attempt was made to fabricate a bilayer membrane (the 6F-poly(amide-imide)/TiO$_2$ composite films supported on a porous TiO$_2$ membrane). Unfortunately, the bilayer films fabricated had pinholes, presumably due to the fast shrinkage of the composite films during the fast evaporation of solvent evaporation.
Although the 6F-poly(amide-imide)/TiO₂ composite membrane is superior to the unfilled 6F-poly(amide-imide) membrane for H₂/CH₄ and H₂/N₂ separations, the overall performance of the composite membrane is still below the upper bound. However, this technique has provided a method of fabricating the composite membrane based on polymers and metal oxides. Correct choice of the primary polymers and the metal oxides is critical for the resulting composite membranes falling above upper bounds. An asymmetric membrane (the polymer/ceramic nanocomposite membrane on a porous support) could overcome the brittleness problem of the composite membrane; the success in this technology could provide a prospect for the industrial application in gas separations.
FUTURE WORK

Organic/Inorganic composite membranes constitute a new area in the separation technology. There are many challenges facing the future and many questions which still need to be answered. Future studies can address some of the issues outlined below.

1. Fabrication of the PAI/ZrO₂, 6FPAI/ZrO₂, and other composite membranes via hydrogen bonding.

The author of this dissertation pointed out in chapter three that the hydrogen-bonding energy between the residual hydroxyl group on metal oxide and the proton donor in a polymer should decrease in the following order:

\[ \text{Zr-OH} > \text{Ti-OH} > \text{Si-OH} \]

This order has been partially proved by the differences in the compatibility of the PAI and 6FPAI with the TiO₂ and SiO₂. Whether or not this theory is correct can be further confirmed by studying the compatibility of the same polymers and the ZrO₂.

The author of this dissertation also pointed out that the hydrogen-bonding energy between the residual hydroxyl group on the metal oxide and the proton acceptor in a polymer should decrease in the following order:

\[ \text{Si-OH} > \text{Ti-OH} > \text{Zr-OH} \]

To prove this theory, the information can be obtained by studying the compatibility between these metal oxides and the polymers that contain only the proton donor such as PC and PMMA.

Use of the mixtures of metal oxides, such as TiO₂-SiO₂ and ZrO₂-SiO₂, as the fillers is also an exiting research area. It is believed that the hydrogen bonding strength of
a metal oxide is affected by another metal oxide. The success in fabricating an optically transparent PAI/TiO$_2$-SiO$_2$ composite, as presented in chapter three, shows the feasibility of this strategy. This strategy may be particularly useful for fabricating an organic/inorganic composite that requires specific metal oxides as the filler and a specific polymer as the matrix for a specific application.

It should be pointed out that the application of these high-Tg polymer/metal oxide nanocomposites is not limited to gas separations. Other potential applications can also be found in optical materials, abrasive-resistant coatings, electronic materials, catalysts, and absorbents.

2. Fabrication of Bilayer Membranes

Fabrication of bilayer membranes is challenging. Increase in the metal oxide content is essential for the significant improvement of permselectivity and thermal stability. Composite membranes with high metal oxide contents are generally brittle and must be fabricated on porous supports to enhance the mechanical strength. Future attempts should focus on the control of the evaporation rate of solvents during the coating process and the correct selection of porous supports. These suggestions are based on the following observations:

(1) A fast evaporation of the solvent caused defects and local cracking of composite membranes. This may be due to the uneven stress created by the fast evaporation of the solvent;

(2) The results of AFM (Atomic Force Microscopy) showed many sharp sites on the bilayer membrane (the 6FPAI/TiO$_2$ film coated on a porous TiO$_2$ support). These sharp sites have an appearance which is distinctly different from the rest of the films. The average thickness of the film was estimated to be $\sim 3 \, \mu$m. However, the thicknesses of the
film on these sharp sites may be much smaller than ~3 μm. On the other hand, the film is believed to have a higher local stress at these sites than at the rest of the sites and therefore cracks immediately after an external pressure is exerted. Other organic porous supports such as porous nylon and porous polyvinylidene (PVDF) may be better than porous TiO₂.

3. Fabrication of organic/inorganic membranes by other strategies

Hydrogen bonding is only one of the approaches used to incorporate nanosized metal oxides within glassy polymers. Other approaches, such as direct covalent bonding of the organic and inorganic components and the "site-isolation" method as cited in chapter two, can also be used. The feasibility of such approaches is beyond doubt. The pertinent references may be obtained in section 2.3. Incorporation of metal oxides within polyimides by the "site-isolation" method is an exiting research area although it may involve a complicated process. An important feature of the "site-isolation" method is that the synthesis of the polyimide and the formation of the metal oxide need to be carried out simultaneously. One of the problems is that, because the SiO₂ is covalently bonded with the amic acid during the polymerization step, one may not get complete ring closure and thereby the product may not be a polyimide. However, since the metal oxide particles interact directly with the monomers that are used to synthesize the polyimides, very small inorganic particles are expected to form within the polyimides. Since polyimides are generally superior in overall gas transport properties to other polymers, success in making polyimide/ceramic nanocomposite membranes could provide a new prospect in the gas separation technology.

Covalent bonding between a functional polymer or oligomer and a metal oxide leads to a hybrid material. Because of the covalent bonding, the interfacial interaction
between the organic and inorganic components could significantly reduce the segmental mobility of the polymer and thereby increase the permselectivity and thermal stability of the membrane. Fluorinated polyimides should be of particular interest because of the high free volume or high permeability. Fluorinated polyimides can be synthesized containing reactive end groups, such as amine and nadimide [253]. The amine and nadimide terminated polyimides can be covalently bonded with the SiO$_2$ network [253]. Fluorinated poly(hydroxyl-imides) are also of interest [253-254]. The possibility of using coupling agents, such as diisocyanate and bisphenol-A [255-256], to permit covalent bonding between the hydroxyl-containing polyimides with metal oxide network should be explored. Another possible candidate for a membrane may be a PDMS/SiO$_2$ hybrid material which has been extensively characterized. It is known that PDMS has extremely high permeability but low permselectivity. A PDMS/SiO$_2$ hybrid material is expected to have a significant increase in permselectivity. The methodology for synthesizing the PDMS/metal oxide hybrid materials has been well developed and the pertinent references may be found in section 2.3.3.
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VITA

Qingchun Hu was born in P.R. China on March 19, 1959. He received his B. S. degree in mineral engineering and science in Kunming Institute of Technology in 1982. After working in Changsha Gold Company for two years and in Changsha Metallurgy Institute for one year, he was enrolled in graduate program in Department of Mineral Engineering, Central South University of Technology in 1985. Two and half years later, he obtained his first M. S. degree. His work in surface electrochemistry of sulfides was published in International Journal of Mineral Processing. In 1989, he was accepted by Department of Mineral Engineering in The Pennsylvania State University. Three years later, he received his second M. S. degree in environmental pollution control. In 1992, he come to Department of Mineral Engineering in Virginia Tech. and worked for his Ph. D. degree in the area of ZnS surface electrochemistry. His work in this area was also published in International Journal of Mineral Processing. One year later, he changed his interest and joined polymer material program in Department of Chemical Engineering, Virginia Tech. His dissertation research is the fabrication and characterization of poly(amide-imide)/ceramic nonaccomposite gas separation membranes. Three years later, he completed his Ph. D. degree in chemical engineering. His current interests include membrane materials, abrasive-resistant coatings, catalysts, electronic materials, optical materials and absorbents. He now works as materials research engineer in World Minerals Inc. His first assignment is to improve the current filtration materials.

[Signature]