INFRARED SPECTROSCOPIC STUDY OF
CROSS-LINKED POLYAMINES FOR CO₂ SEPARATION

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of the Requirements for the Degree
Master of Science

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ABSTRACT

CO₂ emission is considered one of the major causes of climate change. The control of CO₂ emission is of prime importance. In this thesis, the current researches and progress on the CO₂ capture and CO₂ capturing materials are reviewed.

Polyethylenimine (PEI) has been used as an active species for the preparation of CO₂ capture materials. CO₂ has a maximum adsorption rate on PEI at 75°C due to the mass transfer limitation through liquid layers. In-situ Fourier Transform Infrared Spectroscopy (FTIR) could be applied to characterize the interactions between CO₂ and amines, and to understand the diffusion process of CO₂ in the CO₂ capture materials. This technique was used to probe the CO₂ diffusion process in PEI layers of different thicknesses and in PEI cross-linked with 1,6-hexanediol diacrylate (PEI/HDDA). Preliminary results show a diffusion limitation of CO₂ on ~500μm-thick layer of PEI and low CO₂ capture capacity on PEI/HDDA. The cross-linking reaction of PEI and HDDA was evaluated with FTIR by monitoring the consumption of the C=O band at 1635 cm⁻¹.

This technique was extended to study the effect of pH on the precipitation of silica from sodium silicate solutions. Near infrared spectroscopy results were used to correlate the water content on the silica precipitated at different pH values. PEI and PEI/HDDA will be incorporated with sodium silicate to create hybrid amine/silica networks with enhanced mechanical strength and CO₂ transport properties.
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CHAPTER I

INTRODUCTION

Polyethylenimine (PEI) has been used as an active species for the preparation of CO₂ capture materials. However, due to the chain entanglement of the large molecular size, PEI does not exhibit as high CO₂ capture capacity as small molecular amines. Meanwhile, the mechanical strength of PEI is poor.

In this thesis, it is hypothesized that long-chain cross-linking agents such as 1,6-hexanodial diacrylate (HDDA) could enhance the CO₂ capture capacity of PEI by expanding the cross-linked network.

The scope and organization of this thesis is shown in Figure 1. In this thesis, first, literature review on amines and polyamines for CO₂ capture will be presented in Chapter II. Second, the experiments on the cross-linking reaction of PEI and its CO₂ capture properties will be introduced and discussed in Chapter III and Chapter IV. Third, the conclusions and the proposed future work are included in Chapter V.

While preparing this thesis, the author also worked on the literature survey and preparation of substrates to support the polyamines. These will be presented in the appendices, including the IR spectroscopic study of water on PVA substrate, NIR study of silica precipitated from sodium silicate and acetic acid, literature survey on preparation of porous
polyethylene films, and using phase inversion method to prepare porous PVA or polysul-
fone.

Figure 1. Scope and organization of this thesis.
CHAPTER II

LITERATURE REVIEW

2.1 CO₂ Emissions

![Graph showing CO₂ emissions by country from 1990 to 2009.](image)

Figure 2. Carbon Dioxide Emissions by Country, 1990-2009. (From Ref.¹)

CO₂ is considered as the predominant cause of the global warming. The CO₂ emission is now one of the most important topics in the energy industrial and environmental engineering. Since the Industrial Revolution in the 1700’s, human activities, such as the burning of oil, coal and gas, and deforestation, have increased CO₂ concentrations in the
atmosphere. In 2005, global atmospheric concentrations of CO$_2$ were 35% higher than they were before the Industrial Revolution$^2$. According to the Energy Information Administration, human beings have emitted a huge amount of CO$_2$ when producing the industrial products. And more CO$_2$ is predicted to be emitted per year in the next two decades (Figure 2). The report from U.S. Environmental Protection Agency$^2$ says, “The largest source of CO$_2$ emissions is the combustion of fossil fuels such as coal, oil and gas in power plants, automobiles, industrial facilities and other sources. A number of specialized industrial production processes and product uses such as mineral production, metal production and the use of petroleum-based products can also lead to CO$_2$ emissions.”

In 1896, Svante August Arrhenius, who received the Nobel Prize for Chemistry in 1903, was the first scientist to speculate that changes in the levels of CO$_2$ in the atmosphere could substantially alter the surface temperature through the greenhouse effect$^3$. Then many scientists came into the field of greenhouse effect study and developed a systematic theory about how CO$_2$ and some other greenhouse gases led to the global warming.

2.2 CO$_2$ Separation and Capturing Materials

As CO$_2$ has a known impact on the climate, the controlling of CO$_2$ emission, separation and capturing of CO$_2$ and its utilization are of prime importance. With more and more concerns on the CO$_2$ emissions reduction from the people and the governments, a number of researches have been funded to find out an economical way to capture the CO$_2$ and make good use of it. The development of CO$_2$ separation and capturing materials are among the most important researches in this field.
Currently, there are three major types of CO\textsubscript{2} separation and capturing materials: solid phase sorbents, liquid phase sorbents and gas separation membranes. Membranes are highly efficient mass-separating materials, especially when the species that are to pass through the membrane are present in a large concentration\textsuperscript{4}. Liquid phase sorbents were widely studied in the past decade. The liquid sorbents usually contain amine species to facilitate the adsorption and transportaion of CO\textsubscript{2} molecules. Materials containing amine sites (e.g., monoethanol amine and diethanolamine) have been developed for chemical adsorption of CO\textsubscript{2}. Solid particles and pellets are well-known CO\textsubscript{2} adsorption medias. Some of the effective species are supported by porous solid structure, which contritube to an effective adsorption of CO\textsubscript{2}. Both the liquid sorbents and solid sorbents are applicable for the exausted flue gases from the coal-fuel power plants. So they are widely used as post-combustion sorbents.

In this thesis, the literature reviews will be focused on the amine contained CO\textsubscript{2} capturing materials.

2.2.1 CO\textsubscript{2} Separation Membranes

A number of membranes have been developed to meet the demands of separating the CO\textsubscript{2} from the mixed gas. Membranes are usually used to filter the gases before their applications. For example, the need of high purity hydrogen as the main fuel is critical to fuel cells\textsuperscript{5}. CO\textsubscript{2}-selective membranes have the potential to obtain high purity H\textsubscript{2} by separating CO\textsubscript{2} from the mixed gas.

Figure 3 presents a schematic of the CO\textsubscript{2} transport mechanism in the membranes. This mechanism consists of four main steps\textsuperscript{6}:
(a) reactive dissolution of CO₂ from the high-pressure feed side by reacting with the carrier molecules present in the membrane to forms complexes,

(b) diffusion of the CO₂-carrier complexes across the membrane,

(c) CO₂ is released from the CO₂-carrier complexes to the gas phase at the low-pressure sweep side, and the carrier molecules are restored to their original forms, and

(d) the carriers diffuse back to the feed side to repeat the process.

Figure 3. Schematic representation of CO₂ transport mechanism in the membranes. (from Ref. 7)

The gases can diffuse through the membrane in two ways: physical solution-diffusion and facilitated transport by the carrier. Since H₂, N₂ and some other gases do not react with the carrier in the membrane, the diffusion of CO₂ is faster than the diffusion of other gases. In other words, the flux of CO₂ is enhanced by the CO₂ specific carrier. This is the principle of the gas separation membrane.
Researchers have done a lot of work on developing CO₂ separation membranes.

Huang et al.⁸ reported a CO₂-selective hallow-fiber type membrane in 2008. In their study, the membrane contained poly(allylamine) and AIBA-K as the amine carriers and was supported by a cross-linked PVA network. Formaldehyde and a certain amount of KOH were added into the PVA solution to get a cross-linked network. Poly(allylamine) and 2-Aminoisobutyric acid (AIBA) potassium salt (AIBA-K) were added to the cross-linked product and finally they got a composition of 50 wt% PVA (60 mol% crosslinking), 10 wt% AIBA-K, 20 wt% KOH, and 20 wt% poly(allylamine). The membrane was tested using a gas mixture that contained 20% CO₂. A good CO₂ permeability and CO₂/N₂ selectivity was observed up to 170 °C. The highest CO₂/N₂ selectivity of 493 and the highest CO₂ permeability of 6196 Barrers (1 Barrer = 10⁻¹⁰ cm³/(cm² s cmHg)) were observed at 110 °C. Zou et al.⁷ reported a membrane with a similar composition. In their work, a CO₂/H₂ selectivity of 450 and the CO₂ permeability of 8200 Barrers were observed at 120 °C.

Xing and Winston Ho⁹ developed a cross-linked poly(vinyl alcohol)–polysiloxane/fumed silica mixed matrix membrane for CO₂/H₂ separation. Both fixed and mobile amine carriers were contained in the membrane. The fixed amine carriers were AIBA-K and KHCO₃-K₂CO₃, and the fixed carriers were poly(allyl amine) and aminosilica. FS nanoparticles were applied as fillers in order to promote the physical contact between silica and the polymer matrix. The highest CO₂ permeability of 1296 Barrers and a CO₂/H₂ selectivity of 87 were obtained in their study. They believed that the FS nanoparticles had a significant effect on the gas separation performance.
Matsuyama et al.\textsuperscript{10} developed a functional cation-exchange membrane and applied it to the facilitated transport of CO\textsubscript{2}. Ethylenediamine (EDA) was used as a CO\textsubscript{2} carrier in their work. EDA A square porous polyethylene substrate was used and treated by glow-discharge plasma for the grafting polymerization with acrylic acid. Then the membrane was soaked in aqueous EDA solution. The obtained membrane was found to have remarkably high CO\textsubscript{2} permeability and selectivity of CO\textsubscript{2} over N\textsubscript{2}. At a CO\textsubscript{2} partial pressure of 0.047, the selectivity was 4700. They believed that the new functional cation-exchange membrane had much higher efficiency than conventional polymeric membranes for CO\textsubscript{2} separation.

Table 1. Some CO\textsubscript{2} Separation Membranes and Their Performances\textsuperscript{11}

<table>
<thead>
<tr>
<th>Material</th>
<th>Facilitator</th>
<th>CO\textsubscript{2} Permeability</th>
<th>Selectivity (CO\textsubscript{2}/N\textsubscript{2})</th>
<th>Selectivity (CO\textsubscript{2}/H\textsubscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>EDA (50 wt%)</td>
<td>161</td>
<td>/</td>
<td>26.1</td>
</tr>
<tr>
<td>PVA</td>
<td>AIC+-EDA (50 wt%)</td>
<td>67</td>
<td>/</td>
<td>14.3</td>
</tr>
<tr>
<td>Vinyl alcohol/acrylate</td>
<td>2M K\textsubscript{2}CO\textsubscript{3}</td>
<td>6100</td>
<td>317</td>
<td>/</td>
</tr>
<tr>
<td>Vinyl alcohol/acrylate</td>
<td>2M K\textsubscript{2}CO\textsubscript{3} and 0.05M 18-crown-6</td>
<td>740</td>
<td>670</td>
<td>/</td>
</tr>
<tr>
<td>Vinyl alcohol/acrylate</td>
<td>2M K\textsubscript{2}CO\textsubscript{3} and 0.05M EDTA</td>
<td>2400</td>
<td>1417</td>
<td>/</td>
</tr>
<tr>
<td>PVA</td>
<td>Glycine (50 wt%)-PEI (25 wt%)</td>
<td>194</td>
<td>/</td>
<td>28</td>
</tr>
<tr>
<td>PVA (cross-linked)</td>
<td>Glycine (50 wt%)-PEI (25 wt%)</td>
<td>186</td>
<td>/</td>
<td>31</td>
</tr>
<tr>
<td>PVA (cross-linked)</td>
<td>DMG (23.6 wt%)-PEI (23.6 wt%)</td>
<td>/</td>
<td>/</td>
<td>602</td>
</tr>
<tr>
<td>PVA (cross-linked)</td>
<td>DMG (27.2 wt%)-PAA (10.1 wt%)-KOH (16.8 wt%)</td>
<td>6196</td>
<td>/</td>
<td>262</td>
</tr>
<tr>
<td>PVA (cross-linked)</td>
<td>DMG (19.6 wt%)-PAA (9.8 wt%)-KOH (18.1 wt%)</td>
<td>8278</td>
<td>/</td>
<td>170</td>
</tr>
</tbody>
</table>

Note: a) PVA = poly(vinyl alcohol); b) EDA = Ethylene Diamine; c) AIC = Aminoisobutyric Acid; d) PEI = Polyethyleneimine; e) DMG = Dimethylglycine.

Scholes et al.\textsuperscript{11} summarized a number of recently developed polymeric membranes for CO\textsubscript{2} separation. shows the performances of some of the developed membranes.
Table 2. Cross-link Effect on The Tensile Properties of The PVA Membranes

<table>
<thead>
<tr>
<th></th>
<th>PVA (g)</th>
<th>Formaldehyde (ml)</th>
<th>Ultimate stress (N)</th>
<th>Elongation (mm)</th>
<th>Young's modulus (N)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30</td>
<td>5</td>
<td>4.23</td>
<td>3.401</td>
<td>0.882</td>
<td>34.011</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
<td>10</td>
<td>6.409</td>
<td>5.479</td>
<td>1.485</td>
<td>54.79</td>
</tr>
<tr>
<td>C</td>
<td>30</td>
<td>15</td>
<td>9.935</td>
<td>17.493</td>
<td>3.688</td>
<td>174.933</td>
</tr>
<tr>
<td>D</td>
<td>30</td>
<td>20</td>
<td>7.498</td>
<td>14.39</td>
<td>0.724</td>
<td>144.903</td>
</tr>
</tbody>
</table>

It is believed and discovered by many scientists that cross-linking can enhance the mechanical strength of membranes. Alves et al.\textsuperscript{13} reported a cross-linked ulvan membrane. The cross-linking of ulvan increased the tensile modulus from 580.0 kPa to 1760.0 kPa; and the tensile strength was increased by 203\%, from 4.7 kPa to 44.0 kPa. But the ductility of the membrane was decreased as demonstrated by the tensile strain dropping from 26.4\% to 15.2\%. Dong et al.’s research\textsuperscript{12} suggested that the mechanical properties of the PVA-based polymeric membranes could be artificially controlled through the adjustment of the cross-linking degree. They prepared four membranes with different degree of cross-linking. Each membrane contains 30 g of PVA and 5 ml, 10 ml, 15 ml, and 20 ml of formaldehyde, respectively. The mechanical properties of these membranes are listed in Table 2. Their study illustrated that the ultimate stress, Young’s modulus increased with the amount of formaldehyde or the degree of cross-linking. Thus, the mechanical strength of the membranes was enhanced. However, when continuing adding cross-linking agent, a drop of the elongation and Young’s modulus was observed. It suggested that the degree of cross-linking had a significant impact on the mechanical strength of the membranes and there might be an optimum point of the degree of cross-linking which resulted in the best mechanical strength.
2.2.2 Polymeric sorbents for CO$_2$ capture

Inorganic and organic materials can both be applicable to CO$_2$ adsorption. Inorganic sorbents, like zeolites, activated carbons, metal oxides (MgO, Li$_2$ZrO$_3$, K$_2$CO$_3$, etc.), hydrotalcite, etc., have been proved to be effective for the CO$_2$ capture. However, the high costs of the inorganic sorbents have limited their wide application. In contrast, organic sorbents, including polymeric sorbents, are much cheaper than inorganic ones. The most commonly applied organic sorbents are amine-contained or amine-grafted materials. Amines such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and tetraethylpentamine (TEPA) are being studied as effective components of the CO$_2$ capturing materials by many scientists. The exploring of polymers such as polyethyleneimine (PEI) is also a hot spot in the research field of CO$_2$ sorbents in the present.

![Chemical structures of branched PEI and linear PEI.](image)

Figure 4. Chemical structures of branched PEI and linear PEI.

PEI contains a huge number of amine sites that is effective for CO$_2$ capture. PEI contains primary amines, secondary amines and tertiary amines. Branched PEI and linear
PEI are two types of PEI available in the market. Their chemical structures are shown in Figure 4.

P.Y. Li et al.\textsuperscript{14} developed a polyethyleneimine-modified fibrous sorbent. They coated PEI on the glass fiber matrix through a wet impregnation method and used epichlorohydrin (ECH) as cross-linking agent. The sorbents showed a maximum adsorption capacity of 4.12 mmol CO\textsubscript{2} / g sorbent and 13.56 mmol CO\textsubscript{2} / g PEI at 1 atm and 30 °C. The researchers found that the sorbents had a low regeneration temperature of 120 °C and a high thermal stability (about 250 °C). The PEI-modified sorbent was stable in the presence of moisture, which is welcomed by most power plants.

Heydari-Gorji and Sayari\textsuperscript{15} investigated the CO\textsubscript{2} capture property on PEI-impregnated hydrophobic mesoporous silica. PEI was impregnated to pore-expanded MCM-41. MCM-41 is a type of mesoporous silica. MCM-41 was synthesized at 80 °C using cetyltrimethylammonium bromide (CTAB) and a 25% solution of tetramethylammonium hydroxide (TMAOH) in water for pH adjustment. Pore expansion was achieved via hydrothermal treatment of as-synthesized MCM-41 at 120 °C for 72 hours using DMDA as swelling agent. PEI was impregnated into the mesoporous silica by wet impregnation method. The well-dispersed PEI inside the MCM-41 support exhibited a CO\textsubscript{2} adsorption capacity as high as 206 mg CO\textsubscript{2} / g sorbent for 55 wt\% PEI loading at 75 °C. It was also reported that at 25 °C, the CO\textsubscript{2} uptake increased with PEI loading up to 30 wt\% and then decreased due to strong diffusion limitation at higher amine loading. On the contrary, at 75 °C, the CO\textsubscript{2} capacity increased with PEI loading.

Li\textsuperscript{16} and Jiang et al.\textsuperscript{17} reported a solid sorbent prepared by layer-by-layer nanoassembly technique via alternate deposition of a CO\textsubscript{2}-adsorbing amine polymer (e.g. PEI) and
an oppositely-charged polymer (e.g. polystyrene sulfonate). They used the by layer-by-layer nanoassembly chamber to spread the PEI and PSS nano-layers alternatively on the porous polymethylmethacrylate (PMMA) micro-particles, which had a specific surface area of 470 m²/g. PEI solution was positively charged and PSS solution was negatively charged. Thus, these two solutions could be stacked layer by layer at a nano scale. They also prepared a PEI-impregnated PMMA sorbent without PSS layers. The result was that PEI/PSS multi-layered solid sorbents showed substantially faster CO₂ desorption rates during sorbent regeneration and relatively faster CO₂ adsorption rates during adsorption cycles than PEI-impregnated PMMA sorbents. And, with the increasing number of layers, the CO₂ capture capacity increased. Their explanation was that the amine sites on the PEI chains in the multi-layered sorbents were partially neutralized by PSS, thereby these sites might bind acidic CO₂ more weakly than uncomplexed PEI. In this study, the reported CO₂ capture capacity was 0.8 mmol CO₂ / g sorbent for 5-layer PEI/PSS sorbent, which was as much as the CO₂ capture capacity of the PEI-impregnated PMMA, and 1.7 mmol CO₂ / g sorbent for 10-layer PEI/PSS sorbent.

A lot of work has been done by the researchers to achieve a relatively high CO₂ capture capacity as long as a reduced cost since cost-effectiveness is one of the most important factors which influence the applications of the developed materials. Some of the recently developed sorbents for CO₂ capture and their performance were reviewed by C.W. Jones et al.⁴ They organized a table to compare the different amine species and supports. The data is shown in Table 3.
Table 3. CO₂ capture performances of some reported amine contained sorbents

<table>
<thead>
<tr>
<th>Amine</th>
<th>Support</th>
<th>T (K)</th>
<th>pCO₂ (bar)</th>
<th>Dry q[a]</th>
<th>Dry Eff.[b]</th>
<th>Humid q[a]</th>
<th>Humid Eff.[b]</th>
</tr>
</thead>
<tbody>
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</table>

Note: [a] q is the reported CO₂ capture capacity, mmol CO₂ / g sorbent; [b] The amine efficiency, mol CO₂ / mol N.

2.3 Cross-linking of PEI

Some studies on the cross-linking of PEI have been reported by researchers. Golander and Eriksson³⁷ reported that they cross-linked PEI with glutaraldehyde and found that the cross-linked PEI is more hydrophobic than noncross-linked PEI. Xia et al³⁸ also
used glutaraldehyde as a cross-link agent to cross-link PEI. They pointed out that the glutaraldehyde is popular for biochemical materials with amine sites. Shum et al.\textsuperscript{39} used 1,6-hexanediol diacrylate (HDDA) as a cross-link agent to react with PEI. The diacrylate groups on HDDA were found reacting with both primary and secondary amines on the PEI chain. A similar cross-link agent, 2,4-pentanediol diacrylate (PDDA), was used in the work of Peng et al.\textsuperscript{40}. The PDDA cross-linked PEI was reported in their work to be a biodegradable material. They presented the degradation pathway of the cross-linked PEI at different pH values by real-time $^1$H-NMR spectroscopy and Monte Carlo simulation.
3.1 Preparation of Chemicals

In this study, polyethyleneimine (PEI, 50 wt% aqueous solution, purchased from Sigma Aldrich, $M_n = 750,000$, $M_w = 600,000$) and 1,6-hexanediol diacrylate (HDDA, Tech., 80%, purchased from Sigma Aldrich) were used. PEI was dissolved in the deionized water to prepare 10 wt% solution and 0.5 wt% solution. The solutions were prepared in sealed bottles, which were kept 90 °C in the oven. The solutions were then cooled down to room temperature. HDDA was dissolved in ethanol and well mixed to prepare the 20% solution.

3.2 Instrumentations

A flow gas system (Figure 5) and a DRIFT-IR spectrometer were used. This system consisted of a four-port valve, two three-way valves, three bi-pass valves and some gas lines. The four-port valve was used to switch between the purging gas and CO$_2$/air. The gases flew into the DRIFT unit and went to the outlet. A bypass line was included in the system to make the gases skip flowing into the DRIFT unit to control the gas composition and atmosphere in the DRIFT unit.
Figure 5. Flow gas system used in this study. The gas lines transport the mixed gas into the DRIFT-IR unit.

A ThermoScientific Nicolet 6700 diffuse reflectance infrared Fourier transform spectrometer (DRIFT-FTIR) was used to characterize the samples and their CO$_2$ capture properties. The picture of the DRIFT reactor unit is shown in Figure 6. In order to control the atmosphere of the reactor, a dome was used to cover the reactor. The dome had three ZnSe optical windows, allowing the penetration of infrared beams and the real-time observation. The reactor was a homemade metal cup, which was made of stainless steel. The samples were placed and spread on top of the metal cup. A heating rod was placed
under the reactor in the DRIFT unit and a thermocouple was used to detect the temperature of the metal cup.

![Diagram of DRIFT reactor](image)

Figure 6. Schematic drawing and photo of the atmosphere-controlled DRIFT reactor. The metal cup is placed on a heating unit and was covered by the dome. IR beam pass through the ZnSe window on the right, hit the sample which is spread on the metal cup, penetrate the ZnSe window on the other side and is finally received by the IR detector.

3.3 FTIR Calibration and Quantification of CO$_2$ via Methane Injection

In order to use the FTIR to simply quantify the CO$_2$ amount in the CO$_2$ capture study, a calibration and quantification method was developed. The front ZnSe windows was replaced by a rubber piece to allow gas injection. Before starting the experiment, the system was checked to make sure that no leaking existed. Then 0.20 mL of methane was injected into the dome on the DRIFT unit and then 0.10 mL, 0.20 mL, 0.30 mL, … , 0.70 mL and 0.80 mL of CO$_2$ was injected into the dome with a gas syringe. The whole process was recorded by the FTIR spectrometer.
3.4 PEI Thickness Effect on CO\textsubscript{2} Capture

In this series of experiments, 2 µL, 40 µL and 100 µL of 0.5wt% PEI solution were spread homogeneously on the metal cup reactor with a microliter syringe, respectively. The metal cup had a temperature of 75 °C to evaporate the water in the solution. For 40 µL and 100 µL samples, this procedure was separated to several steps. 20 µL of PEI solution was spread and allowed time for the contented water to evaporate in each step. In other words, the layers were stacked one by one.

\textit{In-situ} IR observation was included in this study. During the IR observation experiments, the metal cup surface was kept 75 °C as this was considered the best temperature for CO\textsubscript{2} adsorption on PEI layers according to the previous work. Before covering the metal cup with the dome, water in the PEI thin layers was allowed to evaporate until no obvious water absorbance signals were detected by IR spectrometer. The samples were purged by argon at the beginning of the experiments and the CO\textsubscript{2} (20%) and air gas mixture was flowed into the dome for 10 minutes. Then the samples were purged by argon for 10 minutes again. After that, the metal cup was heated up to 110°C to observe the desorption process of CO\textsubscript{2}.

3.5 PEI Cross-linking Study

10wt% PEI aqueous solution was prepared and a batch of the solution was treated by pure CO\textsubscript{2} at 75°C for 12 hours. 5 grams of HDDA was dissolved in 14 grams of ethanol to a 26wt% solution.

The CO\textsubscript{2} treated PEI was cross-linked at 80°C with HDDA at a weight ratio of 1:2. The reaction took place in an aluminum weighing disk and the aluminum disk was placed on the hot plate. The CO\textsubscript{2}-free PEI solution was cross-linked at 80°C with HDDA at a
weight ratio of 1:2 and 1:1. The same condition and method were applied as the CO₂ treated PEI.

3.6 TPD Study

TPD is the abbreviation for Temperature Programmed Desorption. TPD is a process to investigate the CO₂ desorption property of the sorbents. In this study, a thermal controller was used to perform the TPD process. The sample was heated to 130 °C at the rate of 10 °C / min. When the temperature reached the set point, the thermal controller started keep that temperature for 5 minutes. Then, the sample was cooled down to room temperature.
CHAPTER IV
RESULT AND DISCUSSION

4.1 FTIR Quantification and Calibration

FTIR is the major characterization method applied in this study. In order to quickly obtain the CO₂ capture capacity and compare between different experiments, the quantification and calibration of CO₂ amount came off ground. The basic theory of IR quantitative analysis is the Beer’s Law. It explains the relationship between the infrared absorbance and the concentration of the samples. The quantitative IR technique has been widely applied in the food industry, medicine analysis, biological characterization, etc. In the research of CO₂ capture, TGA and Mass Spectroscopy are the two most commonly used technique to investigate the CO₂ capture capacity. Since IR is being used for an in-situ study, it is good to use IR directly analyze the CO₂ capture capacity to get an initial and rough result.

CO₂ injection of different amounts can provide a calibration plot for the quantification of CO₂ amount in other experiments. As introduced in the experiment section, the IR quantitative analysis of CO₂ amount involves the injection of methane. Methane does not adsorb on the PEI layer and the methane peak on the IR spectra does not overlap on other useful peaks. The methane is injected to get a reference peak for the CO₂ peak. Another important reason to introduce methane in the quantification and calibration is
that it can reduce or eliminate fluctuation of IR signal at different experimental conditions. Since the MCT (Mercury Cadmium Telluride) detector in the IR instrument, which is one of the main components for the detection of received IR beams, can only work at extremely cold environment, the liquid nitrogen is used to provide such an environment for the MCT detector. The level of liquid nitrogen affects the IR signal. So under different experimental conditions, the intensities of IR spectra are different, which makes it difficult apply one calibration result to other experiments.

As is mentioned in Chapter II, in each cycle of calibration, a certain amount of CO$_2$ was injected into the purged DRIFT reactor and the gas was allowed about 5 minutes for diffusion. The IR intensities of each injection are shown in Figure 7.

This calibration method compares the absorbance ratio of CO$_2$ and methane to the concentration of CO$_2$. This will help reduce the influence of experimental conditions on the quantification because the same concentration of CO$_2$ and methane gives a fixed ratio of the absorbance ratio under various experimental conditions. The calibration curve is shown in Figure 8.

In order to get this calibration curve, the ratio of the peak areas between (2421 cm$^{-1}$, 2253 cm$^{-1}$) and (3184 cm$^{-1}$, 2855 cm$^{-1}$) and the ratio of the peak height at 2360 cm$^{-1}$ and 3014 cm$^{-1}$ are both calculated and plotted. Two linear curves are obtained, which satisfies the Beer’s Law. The calibration results from the two calibration equations are close. But the results cannot be used as CO$_2$ capture capacity since the IR spectrometer comes blinded when the CO$_2$ concentration is very low due to the extinction coefficient. Nevertheless, the calibration curves are useful to compare qualitatively the CO$_2$ amount during the desorption process.
Figure 7. IR intensity profile of the calibration process.
4.2 PEI Thickness Effect on CO₂ Adsorption

The thickness of PEI affects the CO₂ adsorption. In this study, the thickness of PEI layer could not be precisely measured since the water content in the PEI solution was evaporated on the metal disk before starting the IR observation and CO₂ adsorption, which made it difficult to measure the thickness of the sample. So the volume of the PEI solution used for each sample will be used to explain the observations.

The infrared absorbance spectra of the samples prepared with 2µL, 40µL and 100µL of 0.5wt% PEI solution are shown in Figure 9, Figure 10 and Figure 11, respectively. The PEI samples were all evaporated and contained little water compared to the standard spectrum of water-free PEI. The primary amine, secondary amine and CO₂ show their absorbance peak at around 3357 cm⁻¹, 3290 cm⁻¹, and 2360 cm⁻¹. To compare the CO₂ adsorption property, the peak height of 2360 cm⁻¹, peak area between 3500 cm⁻¹ and 3100 cm⁻¹
cm\(^{-1}\) and ratio of peak height at 3357 cm\(^{-1}\) and 3290 cm\(^{-1}\) are calculated as a function of time and plotted, which are shown in Figure 12.

![Figure 9. IR absorbance spectra of water-evaporated 2µL PEI layer](image)

From Figure 9, Figure 10 and Figure 11, it can be explored that when CO\(_2\) is being flowed into the dome, the secondary amine absorbance peak (3290 cm\(^{-1}\)) changes little while the primary amine peak (3357 cm\(^{-1}\)) is observed to be decreasing. And when the sample is being purged by argon after adsorption, the primary amine peak (3357 cm\(^{-1}\)) is increased. Figure 12c can illustrate these changes more clearly. The ratio of primary amine peak intensity and secondary amine peak intensity decreases when adsorbing CO\(_2\) and increases when desorbing CO\(_2\). It indicates that the main species which interact with CO\(_2\) during its adsorption process is the primary amine groups.
Figure 10. IR absorbance spectra of water-evaporated 40µL PEI layer

Figure 12b shows that higher thickness leads to a faster decreasing in the amine peak area as thick layers have more amine groups to interact with CO₂. But this does not necessarily mean that the thick PEI layers adsorb CO₂ faster.
In Figure 12c, both 2µL and 40µL PEI layers show a sharp drop in the primary amine and secondary amine peak ratio as soon as CO₂ was flowed onto the samples, while 100µL PEI layer only shows a gradual decrement. A possible explanation is that the mobility of molecular chains of water-free PEI is quite poor and the PEI chains are entangled in a compact arrangement. The PEI used in the experiments has highly branched chains and high molecular weight. When CO₂ molecules come to the surface of the PEI layer, they can only diffuse into the PEI layer for a very short distance at the beginning (but they can diffuse farther when longer time is allowed). Therefore, for the 100µL layer, the PEI molecules and amine groups which are relatively far away from the
surface even do not have the opportunity to react with CO$_2$ molecules due to the low mobility and strong entanglement. While for thinner layers, a larger proportion of primary amine groups can be reacted as soon as CO$_2$ come to the surface. Thus, the drop at the beginning of CO$_2$ flowing appears when the PEI thickness is relatively small.

From **Figure 12c**, it is also known that the CO$_2$ adsorption on PEI is very weak though chemical reaction takes place during the CO$_2$ adsorption. Most CO$_2$ was desorbed during the argon purging without heating.

This study suggests an investigation on the water effect on the CO$_2$ adsorption on PEI layers as water may increase the mobility of PEI chains and allows more space for CO$_2$ diffusion. Also, linear PEI, porous PEI, lower molecular weight may also increase the rate of CO$_2$ adsorption on PEI layers.

These observations suggest that there is an optimum thickness of PEI which contributes to the fastest adsorption and largest capture capacity.
Figure 12. The IR profiles obtained from the experiments of PEI thickness effect. a) The peak intensity at 2360 cm$^{-1}$ as a function of time. b) The peak area between 3500 cm$^{-1}$ and 3100 cm$^{-1}$. c) The peak height ratio of 3357 cm$^{-1}$ and 3290 cm$^{-1}$.
4.3 Cross-linking Study of PEI with HDDA

The cross-linking study of PEI with HDDA involves both the cross-linking reaction of CO$_2$ treated PEI solution and fresh PEI solution. The purpose of CO$_2$ treatment is to occupy some of the amine sites and avoid the reaction between these amine sites and HDDA. After cross-linking, the CO$_2$-occupied amine sites can be regenerated by heating the sorbent up. Thus, the CO$_2$ capture capacity won’t decrease much after cross-linking.

The photos of the cross-linked products are shown in Figure 13. Comparing Figure 13a with Figure 13b, it is observed that with more cross-linking agent, the product is more opaque. When the PEI is treated by CO$_2$, the solution gets yellow. The cross-linking product of CO$_2$ treated PEI gives two different phases: a yellow part and a white part. The yellow part has very different property compared to the white part and the cross-linking products of pure PEI with HDDA. The yellow part has much higher rigidity than the others when the product is heated up and cooled to room temperature, while
the products shown in Figure 13a and Figure 13b are very brittle. These products are characterized by FTIR spectroscopy. The IR spectra are shown in Figure 14.

![Figure 14. The IR spectra of the cross-linked products of PEI and HDDA. 10wt% PEI aqueous solution was prepared and a batch of the solution was treated by pure CO2 at 75°C for 12 hours. 5 grams of HDDA was dissolved in 14 grams of ethanol to a 26wt% solution. The CO2 treated PEI was cross-linked at 80°C with HDDA at a weight ratio of 1:2 (spectrum a indicates the CO2 affected part of the cross-linked product and spectrum b is the IR spectrum of rest part of the product). The CO2-free PEI solution was cross-linked at 80°C with HDDA at a weight ratio of 1:2 and 1:1 (shown as spectrum c and spectrum d).](image-url)
Figure 15. IR spectra of the cross-linking process of PEI and HDDA. The spectrum of the cross-linked PEI is shown at the bottom. a, b and c are three groups of spectra. a) 4 µL of HDDA solution was added to the initial cross-linked PEI; b) Another 4 µL of HDDA solution was added to the product shown as group a; c) 4 µL of PEI solution was added to the product shown as group b.
From the IR spectra, the functional groups on the products of CO₂-treated cannot be observed clearly since the IR absorbance is quite large in most ranges of wavenumbers, which is quite different from the other samples. Infrared inspection shows that the white part of the product shown in Figure 13c has similar composition as the samples shown in Figure 13a and Figure 13b. In order to make the cross-linking reaction clear, an in-situ IR study has been done. The IR spectra are shown in Figure 15.
To clearly illustrate the changes in the labeled peaks in Figure 15, an IR profile has been plotted and shown in Figure 16. The peak between 3393 cm\(^{-1}\) and 3152 cm\(^{-1}\) is assigned to the N-H stretching vibration from the amine species on PEI. The peak between 1662 cm\(^{-1}\) to 1546 cm\(^{-1}\) is the reflection of the C=O bonds from the HDDA. From Figure 15 and Figure 16, it is clear that the amine species are reacted when the cross-linking agent is added and the C=O bonds show a decreasing peak as well. This can prove the reaction equation between PEI and HDDA, which is shown in Figure 17.

![Reaction between PEI and HDDA](image)

Figure 17. Reaction between PEI and HDDA. Both primary amines and secondary amines can react with HDDA.

4.4 CO\(_2\) Capture on PEI

The CO\(_2\) capture process was monitored by the \textit{in-situ} IR. The spectra of the adsorption and desorption processes on PEI layers are shown in Figure 18 and Figure 19. Using the calibration and quantification method introduced in Chapter 3.1, the CO\(_2\) capture capacity of the 4 µL PEI layer was about 4.29 mmol CO\(_2\) / g sorbent. This value is higher than the reported CO\(_2\) capture capacity in Chapter 1. A possible explanation is that the tested PEI layer was in liquid phase.
The CO$_2$ capture process of the HDDA cross-linked PEI was also studied by in-situ FTIR technique. The FTIR spectra during the TPD process of HDDA/PEI, the CO$_2$ peak area around 2360 cm$^{-1}$, the C=O peak area at around 1670 cm$^{-1}$ are shown in Figure 20.

During the TPD process, the cross-linked PEI released a very small amount of CO$_2$. The growth of C=O band at 1672 cm$^{-1}$ indicates the bond breaking during the TPD process.

The low CO$_2$ capture capacity is expected for the cross-linked PEI because in the cross-linking reaction of HDDA and PEI, the amine sites, which are considered the active sites for CO$_2$ capture, have been reacted and eliminated (Figure 17). The remaining
amine sites in the cross-linked PEI are very limited. Thus, the CO$_2$ capture capacity significantly decreased after the cross-linking reaction.

Figure 19. IR spectra of the CO$_2$ desorption process on 4 µL PEI layer.
Figure 20. IR spectra of the CO$_2$ desorption process on 4 µL PEI layer.
CHAPTER V

CONCLUSION AND FUTURE WORK

In this thesis, the recent work on CO₂ capture and CO₂ sorbents were reviewed. An IR quantification and calibration method for the estimation of CO₂ amount during the CO₂ desorption process was developed and introduced. The thickness of the PEI layers was proved to influence the performance of CO₂ adsorption and desorption. The experiments indicated the existence of an optimum thickness for the PEI layer to obtain both high adsorption rate and CO₂ capture capacity. The cross-linking reaction of PEI and HDDA was evaluated with FTIR by monitoring the consumption of the C=O band at 1635 cm⁻¹. A diffusion limitation of CO₂ on ~500µm-thick layer of PEI and low CO₂ capture capacity on PEI/HDDA were observed due to the reduced / reacted active amine sites for CO₂ capture.

The study of water spectra on different substrates and the precipitation of sodium silicate and acetic acid is included in the appendices. Band shift of water was observed on the PVA substrate. NIR technique was used to identify water in the SS/AA precipitation and the removal of water under different pH conditions. Preliminary results show that water is more tightly “locked” in the precipitated silica at high pH value.

As for the future work, (1) amine sites will be impregnated or grafted onto the cross-linked PEI to make up the reduction of amine sites in the cross-link reaction; (2) the ef-
fect of molecular weight of PEI on the CO$_2$ capture capacity will be investigated; (3) the degree of cross-link will be studied; (4) the comparison between different cross-link agents will be performed; (5) the cross-linked PEI will be used to prepare polyamines / silica hybrids.
REFERENCES


APPENDICES
APPENDIX A

IR SPECTRA OF WATER ON DIFFERENT SUBSTRATES

IR spectroscopy is very sensitive to water. The broad -OH band between 4000 cm\(^{-1}\) and 3000 cm\(^{-1}\) covers some other important features, e.g., -NH\(_2\) and -NH bands. However, different amounts of water or different thicknesses of water layer on different substrates do exhibit some fine distinctions.

Figure 21. Simple set-up for the spectroscopy study of water between two ZnSe windows. The edges of one ZnSe window were wrapped with PTFE tape to increase the space between the two windows.
Figure 22. IR spectra of water between two ZnSe windows.

A.1 IR Spectra of Water Layer between ZnSe Windows

In this experiment, water of 1µL, 2µL, 3µL, 4µL and 5µL were injected between two ZnSe windows. The edges of one of the ZnSe windows were wrapped with a layer of PTFE tape to increase the space between the two windows (Figure 21). The IR spectra were obtained by Thermo Nicolet 6700 FTIR spectrometer with a DRIFT accessory. The spectra were shown in Figure 22. With the increasing amount of water, the band of -OH between 3700 cm⁻¹ and 3000 cm⁻¹ becomes a little broader.

A.2 IR Spectra of Water Layer on Poly(vinyl alcohol) Thin Film

In this experiment, a thin film was prepared from 10% poly(vinyl alcohol) (PVA) solution on an aluminum substrate. 20 µL of water was spread on the dried PVA film. Wa-
ter was allowed evaporating for 15 minutes and the evaporation process was monitored by *in-situ* FTIR technique.

![FTIR spectra of water on PVA thin film during the process of water evaporation for 15 minutes.](image)

Figure 23. FTIR spectra of water on PVA thin film during the process of water evaporation for 15 minutes.

The IR spectra during the water evaporation are shown in Figure 23. An interesting result is that during the evaporation of water (decreasing content of water), the broad band of water (between 3700 cm\(^{-1}\) to 3000 cm\(^{-1}\)) shifts to the higher wavenumber. Two dashed paralleled lines are marked on the figure tracing the shifting of the water band. This provides a potential way to identify the content of water on / inside a polymer film.
APPENDIX B

NIR STUDY OF SODIUM SILICATE / ACETIC ACID PRECIPITATION

This appendix shows some preliminary results of the near infrared (NIR) study on sodium silicate / acetic acid (SS/AA) precipitation. The purpose of this study is to find out an optimum recipe to prepare silica and impregnate polyamines onto / into the silica to enhance the mechanical strength of the cross-linked polyamines and their CO₂ capture capacity.

B.1 NIR Setup for Thermo Nicolet 6700 FTIR Spectrometer

Thermo Nicolet 6700 FTIR Spectrometer is equipped with a KBr beamsplitter and an MCT detector or a DTGS detector. It is typically used for mid IR range. However, the combination of the ETC IR source, KBr beamsplitter and the either of the two detectors has the capability of looking into a combined range of mid IR and near IR. The IR spectral coverages of different combinations of beamsplitter and detector are listed in Table 4. Spectral Range can be extended to up to 11700 cm⁻¹ when the combination of CaF₂ and white light source is used. The spectral coverage of the ETC IR source is 7400 cm⁻¹ – 50 cm⁻¹.

To set up the NIR spectral range, the recommended range (4000 cm⁻¹ to 400 cm⁻¹) should be ignored in OMNIC software – Experiment Setup. The parameter “Max range
“limit” can be set to 7800 cm\(^{-1}\) (Figure 24) for the typical IR source with KBr beamsplitter and MCT-A detector.

Table 4. IR spectral ranges of different combinations of beamsplitter and detector

<table>
<thead>
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<th>Beamsplitter</th>
<th>Detector</th>
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<td>CaF(_2)</td>
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<tr>
<td></td>
<td>MCT-B</td>
<td>7400 - 1111</td>
</tr>
<tr>
<td></td>
<td>MCT-A</td>
<td>7400 - 600</td>
</tr>
<tr>
<td>KBr</td>
<td>MCT-B</td>
<td>7400 - 400</td>
</tr>
<tr>
<td></td>
<td>DTGS-KBr</td>
<td>7400 - 350</td>
</tr>
</tbody>
</table>

Figure 24. Parameters in OMNIC Experiment Setup for NIR spectra coverage.
B.2 Preparation of SS/AA Precipitation Gradient

A microchannel reactor was designed for the study of SS/AA precipitation gradient. Two ZnSe crystals were stacked together with two thin rubber strips along the edges of the ZnSe windows, leaving a very small channel between the two windows. An outlet was designed for balancing the pressure during the injection of reactants. The schematic drawing of the reactor is shown in Figure 25 and its photo is shown in Figure 26.

Inject Sodium Silicate

Outlet

Inject Acetic Acid

Figure 25. Schematics of the microchannel reactor for SS/AA precipitation.

Figure 26. Photo of the microchannel reactor.
Sodium silicate and acetic acid were injected from the two ends of the microchannel reactor and the two reactants met in the center of the reactor, forming a concentration gradient of the precipitated product. This gradient was characterized by FTIR spectroscopy. Four spectra taken near the sodium silicate side are shown in Figure 27. An obvious variation of the peak height of Si-O bond vibration at around 1100 cm$^{-1}$ can be observed, indicating the composition change of the precipitation gradient. The significance of this reactor and this study is that it provides a means of combinatory study and makes it much easier to find the optimum composition point in the gradient.

![Figure 27. IR spectra of SS/AA precipitation gradient near the sodium silicate side.](image)

B.3 Effect of pH on the Water Removal from Precipitated SS/AA

The pH value of the SS/AA precipitation was controlled by adding excessive amount of acetic acid. Water was removed by heating the samples to 130 °C with a temperature
controller. NIR spectroscopy was used to probe the water content in the sample. The IR spectra of the samples with pH values of 9 and 11 before heating and after heating are shown in Figure 28. The peak at 5250 cm\(^{-1}\) is correlated to the combination of -OH. It indicates the existence and amount of water in the sample. The broad band between 4000 cm\(^{-1}\) to 3000 cm\(^{-1}\) is usually contributed by water and other -OH functional groups. However, in this case, water does not contribute much to that peak as is revealed by the NIR spectra, the broad band does not change much after water is removed. Thus, the water peak in the near infrared range at 5250 cm\(^{-1}\) can provide better identities for water in some experiments.

![NIR spectra of precipitated SS/AA with pH values of 9 and 11.](image)

Figure 28. NIR spectra of precipitated SS/AA with pH values of 9 and 11.
By monitoring the water peak at 5250 cm\(^{-1}\) with \textit{in-situ} FTIR technique, profiles of the peak height change \textit{vs.} time (Figure 29) in the spectra of precipitated SS/AA with pH values of 5, 7, 9 and 11 were obtained during the water removal. From Figure 29, it can be concluded that water is more difficult to be removed in a more basic condition. A possible explanation is that SS/AA precipitation is more likely to form a dense structure at low pH environment. Thus water may accumulate on the surface instead of being buried inside the bulk. So water can be easily removed when the pH value is low.

Figure 29. Peak height at 5250 cm\(^{-1}\) \textit{vs.} time during the removal of water from SS/AA precipitation.
C.1 Introduction

Polyethylene (PE) is one of the most commonly used commercial plastics depending on its crystallinity. It is flexible at low density and rigid at high density, which makes PE be for a variety of applications. PE exhibits resistance to most of chemicals and thus, they are not easy to be bonded. This leads to wide utilizations in the packaging and environmental materials. Low cost of PE is another main advantage for its wide applications. The motivation of this study is to take advantage of this low-cost, highly processible and chemically resistant material to develop economical porous films for various application, creating added value for this commonly used cheap material.

C.2 Preparation of Porous PE Films

C.2.1 Uniaxial Stretching Method

A commonly used dry method usually involves three steps: extrusion, annealing and uniaxial stretching\textsuperscript{41}. The schematic of the set-up for extrusion processes is shown in Figure 30.\textsuperscript{42} In the extrusion step, the raw material is molten and extruded to form a uniaxial films with the help of air blowing and nip rolls. Morphology and orientation of the films can be adjusted by the parameters such as temperature and stress of extrusion,
quench height, air blowing rate and pressure as well as the intrinsic characteristics of extruded polymers. In the second step, the oriented polymer films are annealed which result in a better crystalline phase. In the last step, the uniaxial stretching step, a stretching machine is typically used. The annealed or unannealed polymer films are stretched in the machine direction (MD). Normally, there are two different processes involved in this step: cold stretch and a hot stretch. The cold stretch is a fast process that polymer films are stretched along the MD at a relatively low temperature with a high speed to form micro pores. This process is followed by a hot stretch process which is performed to expand the size of the pores at a higher temperature.

Figure 31 shows a TEM picture of a uniaxially oriented polyethylene thin film and an SEM picture of it after uniaxial stretching. The alignment of the extruded PE film and the pores on it are clearly shown in the micrographs.

Figure 30. Schematic of the set-up for the tubular film process (Ref 42)
This dry method is easy to perform and has an advantage of low cost compared to other processes because no additional materials and chemicals are needed. Also, the pore size can be easily adjusted to a desired value as long as the stretching machine locks in good accuracy. Many commercial porous PE thin films are fabricated by this method.

![Figure 31](image)

**Figure 31.** a) TEM image of a uniaxially oriented PE film. b) SEM image of the stretched PE porous thin film. (Ref 41)

**C.2.2 Cocontinuous Blending Method**

This method is newly developed and patented to prepare porous PE films. The main idea of this method is to mix two polymers which have different solubility in a solvent (e.g., water) to generate a cocontinuous blend and, then after the films are formed, they are immersed to a solvent to dissolve the soluble part of the cocontinuous blended films, and obtain the porous structure. A cocontinuous blend is defined by the coexistence of at least two three-dimensionally continuous network structures within the same volume.
This method is reported by Christopher W. Macosko and his research group in University of Minnesota.\textsuperscript{45-48} Zhou et al\textsuperscript{49} also reported similar methods of preparing porous polymeric thin films from bicontinuous microemulsion. In the study reported by Trifkovic et al,\textsuperscript{45} they melted PE and poly(ethylene oxide) (PEO) at an elevated temperature (150 °C) and mixed these two polymer melts with a batch microcompounder and a recirculating conical twin-screw extruder.\textsuperscript{50} The configuration of the screws can affect the structure of the weight ratio of PE : PEO is 55 : 45. The blend was then rapidly quenched in liquid nitrogen. This is an essential step to freeze the morphology of the polymer blend formed in the melt because the cocontinuous morphology is a nonequilibrium state and if the polymer blend is not quenched at extremely low temperature, i.e., the morphology of the cocontinuous blend is not frozen, coarsening and retraction can happen.\textsuperscript{44, 45} After the polymer blend was quenched in liquid nitrogen, small pieces of the blend were heated and pressed to form films. These films were then annealed at 150 °C and cooled to room temperature with cold water. In order to obtain a porous structure, the PE/PEO film was immersed in water for 24 hours to extract the PEO phase. Using this method, the researchers successfully prepared microporous PE films as supporting layers for gas separation membranes. The SEM micrograph and the laser scanning confocal microscopy image (Figure 32) clearly exhibit the porous structure of the film they fabricated.

This method is beneficial to control the pore size and porosity. By adjusting the screw configuration in the extruder, the rotor speed, as well as the composition of the cocontinuous polymer blend, the pore size is under tight control\textsuperscript{44, 45, 47}. Those researchers also reported enhanced mechanical strength and wettability of these newly developed PE
films. This method can also be applied to the preparation of some other porous polymeric films, for example, PP microporous membranes. Though PEO parts in this wet process contribute to additional cost of membrane preparation compared to the dry process like uniaxial stretching method, the cocontinuous method is compatible with the current manufacturing methods and a competitive cost to win itself a future of application.

Figure 32. a) Computer rendered laser scanning confocal microscopy image. B) SEM micrograph of the PE/PEO blend. (Ref. 45)

C.2.3 Diblock-copolymer Templating Method

This method is also a wet process. One principle similar to the method of cocontinuous blend is to remove one phase from the bulk. The key idea of this method is using a diblock-copolymer as a template and remove one block of it to form porous structure. Uehara et al 51-53 reported this method in 2009 to prepare a separate membrane for glucose sensors. Peinemann et al 54 and Chen et al 55 also used similar methods to prepare the porous polymer films. In Uehara et al’s studies, 51-53 a PE/polystyrene diblock copol-
ymer (PE-b-PS) was used as a template. The PE-b-PS sample was dissolved in $p$-xylene at its boiling point for 10 minutes and then cast and dried in vacuum at room temperature. The cast films with a thickness of 15 to 30 µm were melted at an elevated temperature and isothermally crystallized in vacuum for 3 days at 90 °C. A so-called “etching” process of the films was performed with fuming nitric acid (FNA) at room temperature for different times (5 to 60 minutes). This process is targeted to remove the amorphous parts, i.e., the PS blocks, in the polymer film. This is the key step for forming the pore structure by extracting one of the blocks of the copolymer. Finally, the films were immersed and washed by distilled water and ethanol to remove the excess FNA followed by drying at room temperature. The prepared thin films were characterized by scanning electronic microscopy (SEM). The SEM micrographs of low and high magnifications are shown in Figure 33.

Figure 33. SEM micrographs of the nanoporous membranes etched for 30 minutes at room temperature. a) low-magnification micrograph. b) high-magnification micrograph. (Ref.51)
By controlling the time of etching, its pore size could be adjusted as desired. However, the pore size remained at the nano scale due to the molecular phase separation of the copolymer itself. Thus, PE films prepared by this method has limited diffusion capacity and permeability. Furthermore, due to the nature of nanoporous PE, it shows a high hydrophobicity, which limits its applications such as in battery separator.

C.2.4 Thermally Induced Phase Separation Method

Thermally induced phase separation (TIPS) is widely applied when preparing porous films, including polyolefins, copolymers and polymer blends. This method can also be adopted to prepare porous PE films. TIPS, as implied by its name, is caused by a temperature change rather than driven by a compositional change which is usually involved in phase inversion process. Typically, TIPS process consists of the following four steps:

1) A polymer melt is mixed with a low molecular weight liquid at an elevated temperature and a homogeneous solution is formed. The small molecules are referred as the diluent.

2) The hot solution is cast onto a cold surface to form the desired shape, e.g., films.

3) The cast solution is then cooled to induce phase separation and solidification of the polymer.

4) The diluent is removed (typically by solvent extraction) to produce a microporous structure.

TIPS is more powerful than the phase inversion process because many polymers such as PE and other semi-crystalline polymers cannot be easily dissolved at room temperature, which is an obstacle for the application of phase inversion process. TIPS method provides
a solution to mix the insoluble polymer with a diluent to form a homogeneous mixture and thus, contributes to the preparation of asymmetric and symmetric membranes from polymers with poor solubility for various application. TIPS process is beneficial to the controllability of pore size and the overall porosity. Compared to conventional phase inversion process, as the TIPS process is caused by the temperature change rather than the composition change or solvent-(non-solvent) exchange, fewer variables are needed to be controlled in the phase separation which makes it easier and more flexible.

C.2.4.1 Two-Component TIPS Process

In the review paper of Yoneda et al., 58 typical procedures of preparing microporous PE films were summarized.

First, a certain amount of PE and dibutyl phthalate (DBP) as a solvent (diluent), which had a high boiling point of 340 °C, were mixed with a batch-type kneader or extruder at a raised temperature. The temperature was high enough to melt the polymer. Second, the resulting mixture was pressurized to obtain a film and cooled down to room temperature to induce the phase separation process. Third, the mixture film was immersed into an excess amount of methylene chloride to extract the diluent. A microporous PE film was then obtained. The average pore diameter varied from 0.9 µm to 3.8 µm.

In order to tightly control the pore size, a phase diagram is needed. For a two-component polymer-diluent system, usually it is transparent at an elevated temperature, the phase diagram can thus be determined optically by measuring the cloud point of the mixture.
Some other parameters including the compatibility of the solvent with PE, the cooling rate and the molecular weight of PE can all affect the pore size of the resulting film. They observed that increasing the cooling rate during the phase separation decreases the pore diameter and a higher molecular weight of PE resulted in a smaller pore size.

C.2.4.2 Three-Component TIPS Process

![3 component and 2 component SEM micrographs](image)

Figure 34. SEM micrographs of the thin films prepared via three-component TIPS process and two-component TIPS process. (Ref 58)

As concluded by Yoneda et al.\textsuperscript{58}, three-component TIPS process have rarely been reported. In the published works, researcher introduced inorganic powders like silica to the mixture. The procedures were similar to the two-component TIPS process. One step that is different was the small molecules extraction. The silica involved three-component film was immersed in an excessive aqueous solution of caustic soda and washed with water. Their results showed that the addition of silica powder led to the reduction of phase separation temperature. By comparing the resulting porous thin film prepared by two-
component system and three-component system, they discovered that the two-component one resulted in larger pore sizes and thus, a loosened structure (Figure 34).

C.2.4.3 Hydrophilic Porous PE Membrane via TIPS

The TIPS method has already been widely applied in the preparation of many commercially available products. However, those products typically have poor hydrophilicity and wettability which retarded its applications in some fields.

To improve the hydrophilicity of PE membranes prepared by TIPS method, Zhang et al. modified the surface of PE membrane with PEO by introducing the PE/PEO block copolymer to the mixture in the TIPS. In their experiments, PE and PE/PEO block-copolymer were melted at a raised temperature above their melting points and mixed with diphenyl ether (DPE) as a diluent. The mixture was quenched into the liquid nitrogen to freeze the morphology. A piece of sample was placed in the press molder to form the film. The press molder had a heating element in the bottom, as shown in Figure 35.

The sample was heated to an elevated temperature higher than the melting points of PE and PE/PEO block-copolymer. The thickness of the membrane was controlled by the pressure applied. The resulting film was quickly quenched in a water bath of 25 °C for 10 minutes. This film was then immersed in ethanol to extract and remove the excessive DPE and finally generated pores on the membrane.

The introduction of PE/PEO significantly improved the hydrophilicity and wettability of the surface of PE film and thus, made it possible be applied as battery separators and in the biomedical practices. However, the hydrophilicity is not the only benefit:
1) The further functionalization is made possible by performing the PEGylation chemistry. Amine groups and many other functional groups can be added to the surface to create the value of these low cost PE materials.

2) This method provides inspiration for preparation of other functional porous PE films by changing the type of the polyethylene copolymer.

![Figure 35. The process of preparing hydrophilic PE membrane (Ref 59).](image)

### C.2.5 Other Methods

Some other methods of preparing porous PE films have also been reported:

#### C.2.5.1 Gel-Spinning

**Pennings et al** 69 and **Zhang et al** 70 used gel-spinning to prepare ultra-high-molecular-weight PE (UHMWPE) and porous films. In the work of Pennings et al, the UHMWPE was dissolved in paraffin oil at a concentration of 5 wt% and a temperature of 150 °C for 48 hours. The sample was then slowly cooled down to room temperature. The resulting gel was cut into cylinders and placed in a piston-cylinder apparatus equipped with a conical die and a winder. The spinning experiments were then performed and the extrudate was quenched in air, forming a gel-filament. The paraffin oil was extracted.
with n-hexane and the hot drawing was carried out after the fiber was dried. An SEM image of the extracted PE filament is shown in Figure 36.

![SEM micrograph of gel-spun PE filament exhibiting crazes. The further biaxial stretching can expand the size of pores. (Ref. 69)](image)

Figure 36. SEM micrograph of gel-spun PE filament exhibiting crazes. The further biaxial stretching can expand the size of pores. (Ref. 69)

C.2.5.2 Electrospinning

The work exhibited by Givens et al.\textsuperscript{71} provides the possibility of preparing porous PE films from the electrospun fiber. The standard electrospinning experimental setup was used in their study, as shown in Figure 37. The p-xylene solution of PE consisted of 2-5 wt% of linear low-density PE and 0.2 wt% of tetrabutylammonium bromide (to enhance the solution conductivity). The obtained PE fibers has a diameter of around 4.7µm. By collecting a number of fibers in a short time on the grounded aluminum foil sheet, a PE fiber network can be formed and further modified to obtain a microporous PE film.

Larrondo and Manley also reported a series of work\textsuperscript{72-74} using electrospinning technique to generate fine PE fibers.
C.2.6 Summary

Some of the literature results of preparation of porous PE films are tabulated in Table 5. This table shows that films prepared by copolymer templating method have the smallest pore diameters due to the nature of the molecular size while cocontinuous phase approach results in largest pores. The pore size can be even larger if the PEO composition in the mixture is richer. The TIPS method usually gives a pore size around 1 to 10 µm. The annealing temperature and time also affect the pore sizes and porosity. Among the published work, the films are mostly prepared through solution or melt casting and pressing. The thickness of the films are limited by the casting equipment or pressure applied.
<table>
<thead>
<tr>
<th>Method</th>
<th>Material</th>
<th>Diluent</th>
<th>Extractor / Solvent</th>
<th>Die Temp. (°C)</th>
<th>Annealing Temp. (°C)</th>
<th>Quench Cond. (°C)</th>
<th>Thickness (µm)</th>
<th>Pore diameter (µm)</th>
<th>Porosity Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry - Stretching</td>
<td>/</td>
<td>N/A</td>
<td>N/A</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>0.5</td>
<td>/</td>
<td>75</td>
</tr>
<tr>
<td>Dry - Stretching</td>
<td>85 wt% HDPE</td>
<td>15 wt% alumnia</td>
<td>/</td>
<td>160</td>
<td>120</td>
<td>/</td>
<td>20</td>
<td>0.897</td>
<td>76</td>
</tr>
<tr>
<td>Dry - Stretching</td>
<td>86 wt% HDPE</td>
<td>16 wt% alumnia</td>
<td>/</td>
<td>160</td>
<td>23</td>
<td>/</td>
<td>20</td>
<td>4.050</td>
<td>76</td>
</tr>
<tr>
<td>Dry - Stretching</td>
<td>PE</td>
<td>N/A</td>
<td>N/A</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>12</td>
<td>0.1 - 1</td>
<td>~40-50%</td>
</tr>
<tr>
<td>Wet – Block copolymer</td>
<td>LEL 14-28-14</td>
<td>/</td>
<td>NaOH</td>
<td>N/A</td>
<td>160</td>
<td>/</td>
<td>150</td>
<td>0.024</td>
<td>78</td>
</tr>
<tr>
<td>Wet – Block copolymer</td>
<td>LEL 37-28-27</td>
<td>/</td>
<td>NaOH</td>
<td>N/A</td>
<td>160</td>
<td>/</td>
<td>150</td>
<td>0.038</td>
<td>78</td>
</tr>
<tr>
<td>Wet – Block copolymer</td>
<td>PS-b-PE</td>
<td>p-xylene</td>
<td>Fuming nitric acid</td>
<td>180</td>
<td>/</td>
<td>30</td>
<td>0.030</td>
<td>/</td>
<td>53</td>
</tr>
<tr>
<td>Wet – Block copolymer</td>
<td>HDPE, PE-b-PEG</td>
<td>Diphenyl ether</td>
<td>Ethanol</td>
<td>200</td>
<td>50</td>
<td>Liq. N₂</td>
<td>100</td>
<td>2.25</td>
<td>-</td>
</tr>
<tr>
<td>Wet – Cocontinuous Phase</td>
<td>LDPE, PEO</td>
<td>/</td>
<td>Water</td>
<td>150</td>
<td>150</td>
<td>Liq. N₂</td>
<td>100</td>
<td>10</td>
<td>50%</td>
</tr>
<tr>
<td>Wet - TIPS</td>
<td>UHMWPE</td>
<td>Liq. paraffin</td>
<td>Ethanol</td>
<td>160</td>
<td>116</td>
<td>Liq. N₂</td>
<td>100</td>
<td>3 - 5</td>
<td>79</td>
</tr>
<tr>
<td>Wet - TIPS</td>
<td>UHMWPE</td>
<td>Liq. paraffin</td>
<td>Ethanol</td>
<td>160</td>
<td>111</td>
<td>Liq. N₂</td>
<td>100</td>
<td>1 - 2</td>
<td>79</td>
</tr>
<tr>
<td>Wet - TIPS</td>
<td>19 wt% HDPE</td>
<td>Mineral Oil</td>
<td>1,1,1-trichloroethane</td>
<td>175</td>
<td>/</td>
<td>30 °C</td>
<td>1</td>
<td>/</td>
<td>56</td>
</tr>
<tr>
<td>Wet - TIPS</td>
<td>34 wt% HDPE</td>
<td>Mineral Oil</td>
<td>1,1,1-trichloroethane</td>
<td>175</td>
<td>/</td>
<td>30 °C</td>
<td>&lt;1</td>
<td>/</td>
<td>56</td>
</tr>
<tr>
<td>Wet - TIPS &amp; Extension</td>
<td>HDPE</td>
<td>Liq. paraffin</td>
<td>Methylene chloride</td>
<td>230</td>
<td>/</td>
<td>/</td>
<td>73</td>
<td>0.3</td>
<td>58</td>
</tr>
</tbody>
</table>
C.3. Cost Analysis

Low cost of raw material and ease of fabrication are two of the most important factors why PE is so widely applied. The prices of some common polymeric raw materials and commercially available porous membranes are summarized in Table 6 and Table 7, respectively. From these two tables, it can be concluded that the price of PE raw material is among the cheapest of the common resins. Comparing the price of commercial porous films, $450 for 1 lb, the price of porous PE, is still among the most affordable in the listed products, though the price is several times higher than the raw material. This also shows the great added value of porous PE films, i.e., “Turn ash into gold”. As mentioned previously, the fabrication process does not cost much since all of the process can be used for mass production to lower the unit cost. The methods of preparing porous PE films are almost compatible with the current industrial approaches. Thus, the research on the preparation and functionalization of porous PE film is very meaningful, both scientifically and economically.

C.4. Applications

Thanks to its relatively low cost and easy fabrication, porous PE films are widely applied in all aspects of modern life:

1) Environmental Applications. In 2008, Sekine and his colleagues developed a highly sensitive passive sampler \(^\text{80}\) for NO\(_2\) where porous PE membrane filter was used as turbulence limiting diffuser, a key component of the sampler. Wang et al \(^\text{81}\) coated porous PE films on their electrodes as a support for amperometric oxygen gas sensor. Tanigaki et al \(^\text{82}\), Sawada et al \(^\text{83, 84}\) and Hashizume et al \(^\text{85}\) utilized the porous PE membranes for water purification. Specifically, they successfully removed mutagens and en-
dotoxin molecules from the drinking water. Li et al.\textsuperscript{86} used microporous PE hollow fiber membranes for desalination. The work of Hedegaard et al.\textsuperscript{46} demonstrated their utilization of porous PE film prepared from cocontinuous polymer blend for gas separation.

Table 6. Prices of polymeric raw materials

<table>
<thead>
<tr>
<th>Product (Grade)</th>
<th>Price\textsuperscript{a,b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET (Bottle Resin)</td>
<td>94-96</td>
</tr>
<tr>
<td>LLDPE (Extrusion liner film)</td>
<td>95-98</td>
</tr>
<tr>
<td>HDPE (Drums)</td>
<td>95-98</td>
</tr>
<tr>
<td>PP (Extrusion Film)</td>
<td>97-98</td>
</tr>
<tr>
<td>PVC (Dispersion Resin Homopolymer)</td>
<td>100-104</td>
</tr>
<tr>
<td>LDPE (Extrusion Clarity film)</td>
<td>99-102</td>
</tr>
<tr>
<td>ABS (Injection Medium Impact)</td>
<td>119-120</td>
</tr>
<tr>
<td>PS (Crystal High Heat)</td>
<td>124-125</td>
</tr>
<tr>
<td>Acrylic</td>
<td>125-130</td>
</tr>
<tr>
<td>Polyarylate</td>
<td>176-210</td>
</tr>
<tr>
<td>Nylon 6/6</td>
<td>198-209</td>
</tr>
<tr>
<td>Polyurethane (Injection)</td>
<td>213-222</td>
</tr>
<tr>
<td>PC (Blow Molding)</td>
<td>225-235</td>
</tr>
<tr>
<td>Polysulfone (Injection)</td>
<td>450-650</td>
</tr>
<tr>
<td>PTFE</td>
<td>670-765</td>
</tr>
<tr>
<td>PVDF</td>
<td>720-760</td>
</tr>
<tr>
<td>Polyetherimide (Injection)</td>
<td>880</td>
</tr>
<tr>
<td>Polyamide/imide</td>
<td>1800-2600</td>
</tr>
<tr>
<td>Polyetherketone</td>
<td>4500</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Price collected from PlasticNews.com on Nov. 26\textsuperscript{th}, 2012. \\
\textsuperscript{b} Prices are in U.S. cents per pound.
Table 7. Prices and specifications of some commercial porous membranes

<table>
<thead>
<tr>
<th>Product</th>
<th>Thickness (µm)</th>
<th>Pore diameter</th>
<th>Porosity</th>
<th>Specification</th>
<th>Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pall® HT Tuffryn 200 Membrane Disc Filters</td>
<td>/</td>
<td>0.2 - 0.45µm</td>
<td>/</td>
<td>ϕ25mm, 100/pkg</td>
<td>$100</td>
</tr>
<tr>
<td>Whatman® GD/X syringe filters</td>
<td>/</td>
<td>0.45µm</td>
<td>/</td>
<td>ϕ 25mm, 50/pkg</td>
<td>$543</td>
</tr>
<tr>
<td>PTFE porous membrane</td>
<td>/</td>
<td>12.5µm</td>
<td>98%</td>
<td>90×150mm</td>
<td>$390</td>
</tr>
<tr>
<td>PTFE porous membrane</td>
<td>/</td>
<td>0.45µm</td>
<td>84%</td>
<td>200×300mm</td>
<td>$475</td>
</tr>
<tr>
<td>Nylon Membrane Filter</td>
<td>/</td>
<td>0.45µm</td>
<td>/</td>
<td>ϕ25mm, 400/pkg</td>
<td>$206</td>
</tr>
<tr>
<td>CA Membrane Filter</td>
<td>/</td>
<td>0.45µm</td>
<td>/</td>
<td>ϕ25mm, 400/pkg</td>
<td>$206</td>
</tr>
<tr>
<td>Celgard Separator Film (PE)</td>
<td>25</td>
<td>0.03µm</td>
<td>36% - 44%</td>
<td>1 lb</td>
<td>$450</td>
</tr>
<tr>
<td>Celgard PP 2075 (PP)</td>
<td>20</td>
<td>/</td>
<td>High</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>SUNMAP LC-T (UHMWPE)</td>
<td>500</td>
<td>17µm</td>
<td>26%</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>GE Cellulose Acetate</td>
<td>/</td>
<td>20000 MWCO</td>
<td>/</td>
<td>12×12in</td>
<td>$86</td>
</tr>
<tr>
<td>GE Polysulfone</td>
<td>/</td>
<td>30000 MWCO</td>
<td>/</td>
<td>12×12in</td>
<td>$86</td>
</tr>
<tr>
<td>GE Composite polyamide</td>
<td>/</td>
<td>1000 MWCO</td>
<td>/</td>
<td>12×12in</td>
<td>$86</td>
</tr>
</tbody>
</table>

Note:

a) Price and specification are not available for many commercial porous films, thus they are not listed.

b) MWCO is the abbreviation of Molecular Weight Cut Off.
2) **Battery Separator and Electrolyte.** Clean energy is becoming more and more popular and important which has flourished the researches on the battery separators. Among these battery separators, those for lithium ion batteries are most commonly reported.\(^{58,87}\) Porous PE films are also used to support polymer electrolytes. **Yang et al.**\(^ {88}\) used porous PE membrane to support their composite gel polymer electrolyte.

3) **Biomedical Applications.** Films are frequently utilized in the biomedical practices. **Fu et al.**\(^ {89-91}\) applied the porous PE film for the adsorption of bovine serum albumin and observed good interactions between the serum proteins and PE film. **Kumar et al.**\(^ {92}\) inoculated microporous PE membrane biofilm reactor with *pseudomonas putida strain To1 1A* for gaseous toluene removal. **D’Britto et al.**\(^ {93}\) developed porous PE scaffolds for antibacteria purpose.

4) **Other Applications.** Porous PE films were utilized as a support for a novel liquid crystalline photo-actuator,\(^ {77}\) which showed advantaged of high deformation ability and relatively low cost of fabrication.
APPENDIX D

PREPARATION OF POROUS PVA/PSF USING PHASE INVERSION METHOD

Preparation of Porous PVA Films

Poly(vinyl alcohol) (M$_w$ ~ 96,000, purchased from chemistrystore.com) and polyethylene glycol (M$_w$ ~ 10,000, Alfa Aesar) were used to prepare the casting solution. Commercial polyethylene terephthalate (PET) fabric with one hydrophilic side and one hydrophobic side was applied as the substrate of the membranes.

PVA powders and PEG powders were mixed with deionized water at a concentration of 10 wt% and 1 wt%, respectively, to prepare the aqueous casting solution. The mixture was kept in the oven at 95 °C for 30 minutes for faster and better dissolution. The air bubbles inside the casting solution were removed by the sonicator in a 30-min process after that at 30 °C. A piece of PET fabric where the membrane would be cast was wet and cleaned with ethanol and Kimwipes. Any pooled liquid and fibers from the Kimwipes were removed. Then the solution was cast on the PET fabric (hydrophilic side) using a casting knife which had limitator of different thickness on each side. In this experiment, the 200 μm limitator was applied. The freshly cast membrane was immediately immersed into pure acetone precipitation bath which acted as a coagulant and initiated the phase inversion process. The membrane was allowed 30 minutes in the acetone precipitation bath. After that it could be either taken out for post treatment or stored in the acetone.
General Procedures of Preparing Phase Inversion Membrane

1. Prepare the casting solution with the desired polymer solute ($p$) and solvent ($s$). Three common combinations of solute, solvent and non-solvent are listed in Table 8.

2. Remove the air bubbles inside the casting solution with the sonicator.

3. Prepare a clean glass plate or PET sheet for membrane casting.
   - Wet and clean the glass plate surface or PET sheet surface with solvent;
   - Any pooled solvent or liquid should be removed and cleaned before casting;
   - Use Kimwipes® or other cloth / paper that do not leave fiber or residue on the glass or PET surface;
   - If using PET sheet, tape it onto the countertop or glass plate.

4. Cast membranes with the casting knife homogeneously on the glass or PET surface.
   - When using PET sheet, check with a piece of tape whether the side is hydrophilic or hydrophobic and cast the membranes on the hydrophilic side;
   - Fixed the two ends of the membranes onto the substrate to make sure they would not shrink or collapse in the following process (need to verify).

5. Immediately immerse the freshly cast membranes into a non-solvent ($ns$) precipitation bath.

6. Allow some time for the polymer solute to precipitate in the non-solvent ($ns$).

7. Take the membranes out for post treatment or keep them in the non-solvent for storage.

Table 8. Commonly Reported Phase Inversion Membranes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Non-solvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>water</td>
<td>acetone</td>
<td>94</td>
</tr>
<tr>
<td>Polysulfone (support)</td>
<td>DMF</td>
<td>water</td>
<td>95, 96</td>
</tr>
<tr>
<td>Polysulfone (support)</td>
<td>NMP</td>
<td>water</td>
<td>96</td>
</tr>
</tbody>
</table>