Block Copolymer Pervaporation Membranes for Biofuel Separation

By
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Abstract
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Production of biofuels at an industrial scale is a challenge that must be addressed for a green, sustainable future. One of the major goals to achieve in order to successfully manufacture biofuels in large-scale is *in situ* product recovery of the biofuels. This is an important issue for producing biofuels via biological pathways and also via chemical pathways. In fermentation, *in situ* product recovery is crucial because of product inhibition. Product inhibition is severe enough to terminate fermentation at around 20 g/L of product concentration, thus limiting the productivity and resulting in high separation costs as well as high operation costs due to batch processing. In chemical reactions for producing biofuels, *in situ* product removal is important in minimizing the formation of side products in the reaction, which also limits the productivity.

We approach this challenge by using pervaporation, a membrane-based separation method. We have designed PDMS-derived block copolymers, which are novel materials for this application, for *in situ* product recovery of biofuels by pervaporation. We aim to study the physical properties of these block copolymer membranes to apply them in fermenters and chemical reactors for product recovery.

Here, we first studied the structure-property relationship of PDMS-derived block copolymer membranes. The block copolymer that we have designed self-assembles into various morphologies when solvent-cast under different conditions. Comparing the morphologies of the membranes to the permeabilities of the membranes allowed us to understand the effect of morphology on permeation. The lamellar structure was the most detrimental to the permeability of the membrane; it resulted in a five-fold decrease in biofuel permeability and a three-fold decrease in biofuel selectivity. The reason for this decrease was found to be originating from the diffusion step in the permeation process.

Next, the effect of support layer resistance was studied by measuring the permeabilities of membranes of different thicknesses and by direct imaging. In order to maximize the flux of block copolymer pervaporation membranes, using an additional porous membrane layer is inevitable. However, pore penetration of the block copolymer into the porous membrane results in a dramatic increase in support layer resistance. This explains the permeability decrease with decreasing
membrane thickness, and by assuming a certain pore penetration layer thickness, we were able to successfully use the resistance model to fit the permeability data. In addition, we succeeded in visually confirming pore penetration of the block copolymer via transmission electron microscopy.

The PDMS-derived block copolymer membrane was also applied in an in situ pervaporation setup attached to an ongoing acetone-butanol-ethanol (ABE) fermentation. We were able to successfully demonstrate a pervaporative-fermentation experiment where the ABE removal rate of the block copolymer membrane was matched to the rate of production in the fermenter. This resulted in a semi-continuous mode of operation for 109 hours.

Finally, crosslinked block copolymers were studied for the application of in situ pervaporation during chemical reactions to produce biofuels. These reactions are operated above the temperatures that normal polymer membranes can withstand. Thus, we studied the possibility of forming crosslinks in the non-transporting block of the block copolymer to enhance the heat tolerance to the block copolymer membranes. We were able to form crosslinks within the polyethylene domain of a polyethylene-\(b\)-polydimethylsiloxane-\(b\)-polyethylene membrane, and discovered that the crosslinks enhanced the temperature stability of the membrane without hindering permeability.
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Lastly, I would like to thank my family and friends who are not mentioned here for their love and their faith in me. Thank you.
Chapter 1. Introduction

1.1 In situ Product Removal of Biofuels

Biofuels are sustainable energy sources where solar energy is converted into biomass via biological pathways. The biomass is further converted by physical, chemical, or biological processes into chemicals that resemble the liquid fossil fuels currently used the most widely in the world [1].

![Figure 1.1 A scanning electron microscopy image of C. acetobutylicum. The scale-bar on the bottom-left represents 2 µm.]

Lignocellulosic fermentation is one of the most utilized biological processes to produce biofuels. In this type of fermentation, microorganisms such as yeast, *Escherichia coli*, and Clostridia (Figure 1.1) are employed to convert the sugars from lignocellulosic biomass to biofuels or biofuel-like molecules, such as ethanol, butanol, and acetone [2-4]. A simplified process of producing biofuels by fermentation is shown in Figure 1.2. However, this way of manufacturing biofuels is not yet economically feasible at an industrial scale [5]. One of the major challenges hindering the economic viability is product inhibition. Most of the biofuels produced in fermentation are toxic to the microorganisms. Thus, as biofuel concentration increases in the fermenter, the cell viability decreases, ultimately resulting in cell death when a certain biofuel concentration is reached. Product inhibition begins occurring at very low biofuel concentrations, and around 2 g/L, cell death starts taking place [6]. A typical final concentration of the products, acetone, n-butanol, and ethanol, of a *Clostridium acetobutylicum* fermentation is shown in Table 1.1.
Figure 1.2 Schematic of the process for producing biofuels from lignocellulosic biomass via fermentation. Dark boxes represent processes and light boxes represent feed or products.

Table 1.1 Final concentration of products of a batch, acetone-butanol-ethanol (ABE) fermentation with C. acetobutylicum.

<table>
<thead>
<tr>
<th>Product</th>
<th>Final concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>4</td>
</tr>
<tr>
<td>n-butanol</td>
<td>13</td>
</tr>
<tr>
<td>ethanol</td>
<td>2</td>
</tr>
</tbody>
</table>

Due to product inhibition, final concentrations of products are very low, which not only results in low productivity but also in high separation costs. In addition to this, the toxicity of the products limits the fermentation process to be operated in a batch mode. Therefore, removal of the products in situ has become a topic of great interest for many biofuel researchers [7, 8].

Some of the methods that can be used for in situ biofuel recovery during fermentation are gas stripping, liquid-liquid extraction, adsorption, perstraction, and pervaporation. The advantages and disadvantages of each method are discussed extensively in Reference [9, 10]. However, as of today, none of these technologies are yet utilized for the industrial-scale production of biofuels.

There are also chemical pathways to product biofuels [11-13]. Similarly, in situ product recovery can be applied to chemical processes to produce biofuels [14]. Here, in situ product removal is beneficial because it can allow the chemical reaction to go in the direction of producing more products and also minimize the formation of side products.

1.2 Pervaporation

Pervaporation, a word derived from ‘permeation’ and ‘evaporation’, is a separation method where a dense, selective membrane is placed between a liquid feed, or the liquid from which products are to be removed, and a vacuum pump. The molecules in the feed are selectively adsorbed onto the
membrane and then are diffused through the membrane to the opposite side of the membrane. The separated product on the vacuum side of the membrane is called the permeate, and it is collected with cold traps. A schematic of the pervaporation process is shown in Figure 1.1.

![Figure 1.1 Schematic of pervaporation.](image)

The separation mechanism of pervaporation is most commonly explained by the solution-diffusion model [15]. This model proposes that the permeation of small molecules through a dense membrane occurs in two separate steps: adsorption onto the membrane surface and diffusion across the membrane. The model assumes that there is thermodynamic equilibrium of the permeating species on both sides of the feed/membrane interface. This equilibrium determines the chemical potential of the permeating species on the feed side of the membrane. By controlling that on the other side of the membrane by the vacuum pump, a chemical potential gradient is formed, thus driving the permeating species to the vacuum side of the membrane.

The essence of the solution-diffusion model is represented by the following equation:

\[ J_i = \frac{P_i}{l} \left( x_i \gamma_i p_i^{sat} - y_i p_{permeate} \right) \]  

(1.1)

where \( J_i \) is the flux of \( i \), \( P_i \) is the permeability of \( i \), \( l \) is the membrane thickness, \( x_i \) is the mole fraction of \( i \) in the feed, \( \gamma_i \) is the activity coefficient of \( i \) in the feed, \( p_i^{sat} \) is the saturation vapor pressure of \( i \) in the feed, \( y_i \) is the mole fraction of \( i \) in the permeate, and \( p_{permeate} \) is the pressure in the permeate. The terms in the parenthesis account for the thermodynamic driving force of permeation. In the case of \textit{in situ} product removal application, the driving force is pre-determined by the conditions of the biofuel reaction.
Chapter 1

$P_i$ is flux normalized by membrane thickness and thermodynamic driving force. It is defined as the product of two terms: solubility of $i$ ($K_i$) and diffusivity of $i$ ($D_i$). It describes an intrinsic property of a membrane material, and it is the most commonly used term to compare the effectiveness of permeation for different membranes [16]. Although $P_i$ is a qualitative term at a certain temperature, $P_i$ may differ with temperature because both $K_i$ and $D_i$ are affected by temperature [17]. $D_i$ increases with temperature, and $K_i$ can either increase or decrease, which is determined by the heat of sorption of the transporting chemical species onto the membrane surface. Oftentimes in pervaporation, the heat of sorption is negative, thus resulting in the decrease of $K_i$ with increasing temperature [18].

Even though pervaporation has many advantages such as high selectivity and non-toxicity, there are many challenges that hinder application of pervaporation in \textit{in situ} product recovery. Amongst them is the limitation of $P_i$ and $l$ of the membrane. Crosslinked polydimethylsiloxane (PDMS) is the most widely used membrane material for the removal of biofuels from fermentations [19-24]. However, the chemical crosslinks which help maintain the physical structure of the crosslinked PDMS limit the recyclability of the membrane, and because of the crosslinks, the membrane is susceptible to swelling. Also, the effect of crosslinks on membrane permeability is not yet well understood.

Currently, no commercial membrane material for biofuel removal via pervaporation exceeds the qualities of those of the crosslinked PDMS. In this dissertation, we study an alternative material for pervaporation of biofuels by designing PDMS-derived block copolymers.

1.3 Block Copolymer Membranes

A block copolymer is a polymer that has two or more chemically different polymers attached to each other via covalent bonds. By adjusting the relative ratio of each blocks of the polymer, tuning the chemical structures of each block, and changing the molecular weight of the block copolymer, block copolymers can be fine-tuned to have physical properties of those between the different blocks of the polymer.

Block copolymers have been widely studied as membrane material for transport of various species: ions, water, etc [25-28]. The largest advantage in using block copolymers is the tunable physical properties, as mentioned above. In the field of selective transport through block copolymer membranes, one block is chosen for facilitating transport of the desired species, while the other block is chosen to increase the mechanical stabilities of the polymer. The mechanical block is usually not permeable, and this results in the decrease of the transporting portion in the membrane due to the volume taken up by the mechanical block. Therefore, for block copolymer membranes designed for molecular transport, it is ideal to minimize the volume ratio of the mechanical block within the volume ratio necessary for the desired physical properties.

Transport through block copolymer membranes is further complicated by self-assembly of the polymers into different nano-morphologies. This occurs because of the immiscibility of the...
different blocks in the block copolymer. The self-assembly, as well as the geometry of the morphology, are determined by the Flory-Huggins interaction parameter ($\chi$), the degree of polymerization ($N$), and the volume fraction of each block [29]. The morphologies range widely from spherical morphologies, cylindrical morphologies, and to lamellar morphologies (Figure 1.4).

![Figure 1.4 Schematic of different block copolymer morphologies taken from Reference [30] and [31].](image)

These morphologies have the potential to further hinder transport through block copolymer membranes, mostly due to the increase in tortuosity of the path that the permeating species have to take. Although there have been attempts to simulate and calculate the effect of morphology on permeation [32, 33], the effect of path tortuosity in molecular transport through block copolymers has not yet been elucidated.

### 1.4 Outline of Dissertation

We discuss the properties of PDMS-derived block copolymer pervaporation membranes in the following chapters of this dissertation. In Chapter 2, we provide the structure-property relationship of the block copolymer membranes. By changing the casting-solvent quality, we are able to direct different morphologies with the same block copolymer. We compare the permeabilities of the membranes with different morphologies. In Chapter 3, we discuss the permeability loss observed with decreasing membrane thickness. This originates from the composite structure of the membrane, or more specifically, from the penetration of the thin, selective, block copolymer layer into the porous support layer. We use the resistance model to explain our observations in permeability and use direct imaging to study the pore penetration layer. In Chapter 4, we demonstrate the feasibility of an *in situ* pervaporative-fermentation unit with the block copolymer membranes. In Chapter 5, we discuss the potential of fabricating crosslinked block copolymer membranes for *in situ* product removal of biofuels at high temperature chemical reactors.
Chapter 2. Effect of Block Copolymer Morphology Controlled by Casting-Solvent Quality on Pervaporation of Butanol/Water Mixtures*

Abstract

Motivated by the need for developing membranes for biofuel purification, we made pervaporation membranes by casting a polystyrene-\textit{b}-polydimethylsiloxane-\textit{b}-polystyrene (SDS) triblock copolymer using toluene, cyclohexane, and hexane as casting solvents. The three solvents have different affinities for each of the blocks of the SDS, which enables the creation of membranes with different nano-morphologies using the same block copolymer. These membranes were used in pervaporation experiments with butanol/water mixtures as the feed solution. We quantify the effect of morphology on butanol and water permeabilities. Poorly-ordered granular morphology, obtained from hexane-cast membranes, is optimal for selective butanol transport. Butanol permeability was a more sensitive function of morphology than water permeability. Butanol uptake measurements showed that morphology had negligible effects on solubility. Therefore, we attribute the dependence of permeability on morphology to differences in diffusivities.

2.1 Introduction

As mentioned in the previous chapter, pervaporation is a membrane-based separation method which is advantageous because of its high product selectivity. The most widely used membrane material for the \textit{in situ} removal of biofuel during fermentation is crosslinked polydimethylsiloxane (PDMS) [20, 21, 34]. An ideal membrane would be selectively permeable to the biofuels while withstanding the mechanical stresses necessary for operation. One approach for obtaining mechanically rigid membranes that are permeable is based on block copolymer self-assembly [35, 36]. One of the blocks is designed to enable selective permeation while the other is generally impermeable but rigid, which enables control of mechanical properties.

* This chapter was reported in the \textit{Journal of Membrane Science} \textbf{523}, 588-595 (2017), and is adapted with permission from co-authors X. Chelsea Chen, John M. Prausnitz, and Nitash P. Balsara.
In a series of previous publications, we have studied permeation through polystyrene-\(b\)-polydimethylsiloxane-\(b\)-polystyrene (SDS) block copolymer membranes; polystyrene is a glassy and rigid polymer at room temperature, and functions as the mechanical block \([37, 38]\). The selective permeation of biofuels through these membranes was better than that of commercial crosslinked PDMS membranes. Experiments wherein the biofuel (a mixture of butanol, acetone, and ethanol) produced by fermentation was removed by pervaporation through the SDS membrane showed better productivity than fermentation experiments with the crosslinked PDMS membrane \([38]\).

It is well known that in bulk, block copolymers self-assemble into a variety of nano-scale equilibrium morphologies \([29, 31]\). The equilibrium morphologies of block copolymers and solvents mixtures are affected by the selective solvation of individual blocks in the solvents \([39, 40]\). When block copolymer membranes are made by solvent-casting, it is possible to trap non-equilibrium metastable states \([41]\). Previous studies of pervaporation through block copolymer membranes have focused on transport through equilibrium morphologies \([33, 42, 43]\). The geometries and sizes of the nanostructures were controlled by changing chain length and/or composition of the block copolymer.

In this paper, we prepared films for pervaporation by casting block copolymer films from different solvents followed by thorough drying. A dilute mixture of butanol in water is used as a model solution for a biofuel fermentation broth, and was used as the feed solution in all pervaporation experiments. The same block copolymer was used in all experiments; thus, the nominal compositions of all the films are identical. We show that the solvent used for casting the membranes has a significant effect on selective permeation. Analysis of the morphology by small angle X-ray scattering and electron microscopy, along with butanol uptake experiments, are used to understand the underpinnings of these observations.

2.2. Experimental

2.2.1. Membrane preparation

![Chemical structure of polystyrene-\(b\)-polydimethylsiloxane-\(b\)-polystyrene triblock copolymer.](image)

**Figure 2.1** Chemical structure of polystyrene-\(b\)-polydimethylsiloxane-\(b\)-polystyrene triblock copolymer.
A polystyrene-\textit{b}-polydimethylsiloxane-\textit{b}-polystyrene (SDS) triblock copolymer of molecular weight 22-104-22 kg/mol and polydispersity index of 1.3 was purchased from Polymer Source (Dorval, Canada). The chemical structure of the polymer is shown in Figure 2.1. The polymer consists of 60 wt% SDS triblock copolymer, 30 wt% polystyrene-\textit{b}-polydimethylsiloxane diblock copolymer of molecular weight 22-52 kg/mol, and 9 wt% homopolymer polystyrene (Viscotek GPC, Malvern). The polydimethylsiloxane (PDMS) volume fraction, determined by $^1$H nuclear magnetic resonance (NMR) on toluene-d8 solutions, was 0.70. Using the nominal densities of PS and PDMS (1.04 and 0.970 g/cm$^3$) [44, 45], the estimated PDMS volume fraction calculated using the block molecular weights supplied by Polymer Source is 0.72. Given the polydisperse nature of the sample, this difference is not surprising. Casting solvents, toluene, hexane, and cyclohexane, were purchased from Sigma Aldrich and were used as received.

1 g of SDS was dissolved into about 30 ml of the solvent of interest. The solution was then poured into a 3-in diameter Teflon petri dish. The dish was lightly covered with aluminum foil and a glass beaker. The solution was dried for 3-4 days. Afterward, the Teflon dish was placed in a vacuum chamber for one day to ensure the absence of any remaining solvent in the membrane. The absence of remaining solvent was checked by dissolving the membrane in a deuterated solvent that was different from the casting solvent and conducting NMR experiments to confirm the absence of the casting solvent. After the drying step, non-porous, free-standing membranes with thicknesses ranging from 100 to 150 µm were obtained.

\section*{2.2.2 Scanning Transmission Electron Microscopy}

To prepare scanning transmission electron microscopy (STEM) samples, a piece of the bulk membrane was mounted onto a cryomicrotome (Leica FC6) and cooled to -140 ~ -120 °C. Thin sections with thicknesses of approximately 80 nm were obtained and transferred onto a lacey carbon-coated copper grid (Electron Microscopy Sciences). STEM was done on a Tecnai F20 UT FEG instrument using a high angle annular dark field detector (HAADF) with an acceleration voltage of 200 keV. The samples were not stained. The contrast of the images is resulted from the z-contrast between the silicon of the PDMS phase and the carbon of the PS phase.

\section*{2.2.3 Small angle X-ray scattering}

Small angle X-ray scattering (SAXS) experiments were conducted at the Advanced Light Source (Lawrence Berkeley National Lab, Berkeley) from beamline 7.3.3. The sample-to-detector distance was 4 m, and the X-ray energy was 10 keV. Exposure time was 30 sec for each sample. The collected 2D image was then azimuthally averaged and X-ray intensity was plotted as functions of the magnitude of the scattering wave vector, $q$, which is defined as $q = 4\pi \sin(\theta/2)/\lambda$, where $\theta$ is the scattering angle and $\lambda$ is the wavelength of the X-ray.
2.2.4 Butanol uptake measurement

Three membrane pieces were cut from the three different membranes: toluene-cast, cyclohexane-cast, and hexane-cast. The weight of the pieces ranged from 0.01 g to 0.1 g, and the thickness of the membranes were 100-150 µm. Each piece was placed in a 5 ml vial containing 1-butanol. All of the membrane samples were insoluble in butanol. The vials containing the membrane samples were placed in an oil bath at temperatures of interest. The vials were kept for about 24 hr at each of the temperatures before the membrane samples were taken out and measured. The samples taken out of the butanol were dapped dry with paper towels before measuring the mass of the swollen samples. The ratio of the mass of the swollen membrane to that of the dry membrane is defined as butanol uptake. The butanol uptake was used to calculate the volume fraction of butanol in the membrane, \( \phi_b \), using pure component densities (butanol: 0.81 g/cm\(^3\) [46], PS: 1.05 g/cm\(^3\), PDMS: 0.96 g/cm\(^3\) [47]) and neglecting volume change on mixing. (We attempted to measure water uptake and found that it was negligible.)

2.2.5 Pervaporation

Aqueous 1 wt% 1-butanol solution was used as feed for all of the pervaporation experiments. The butanol was purchased from Sigma Aldrich and was used as received. The pervaporation experiments were performed on a benchtop pervaporation unit purchased from Sulzer Chemtech as described in Reference 13. The collected permeate was analyzed by high performance chromatography (Prominence UFLC instrument, Shimadzu). The pervaporation experiments were repeated on 2-3 membranes. The data reported in this paper were obtained from the same membrane that was used in the uptake measurements. The pervaporation experiments using this membrane were run four times. We report the average value and take the standard deviation as a measure of experimental uncertainty.

2.2.6 Permeability and diffusivity

Permeabilities of butanol and water (\( P_b \) and \( P_w \)) through the membranes were calculated from data obtained from pervaporation experiments using methods described in Reference [37]. Membrane selectivity relative to butanol (\( \alpha_b \)) is defined as

\[
\alpha_b = \frac{P_b}{P_w}
\]  

(2.1)

Following previous studies [37], we assume that butanol diffuses only through the PDMS phase of the membrane. Thus, permeability through block copolymer membranes is given by

\[
P_i = f_{P_i}\phi_{PDMS}P_i^0 \quad (i = b \text{ or } w)
\]  

(2.2)
where $\phi_{PDMS}$ is the volume fraction of PDMS in the block copolymer (0.70), $P_i^0$ is the intrinsic permeability of species $i$ through pure PDMS, and $f_{Pi}$ is a morphology factor that accounts for geometric constraints on permeability.

For a dilute solution of butanol, $P_i$ is expressed as [15]

$$P_i = K_i D_i$$  \hspace{1cm} (2.3)

where $K_i$ is the solubility of $i$ and $D_i$ is the diffusivity of $i$. $K_i$ was obtained by equilibrating liquid butanol with the block copolymer membrane. In general,

$$K_i = \frac{c_i}{x_i \gamma_i P_i^{sat}}$$  \hspace{1cm} (2.4)

where $c_i$ is the molar concentration of $i$ in the membrane, $x_i$ is the mole fraction of $i$ in the liquid, $\gamma_i$ is the activity coefficient of $i$ in the liquid, and $P_i^{sat}$ is the saturated vapor pressure of $i$ in the liquid [16, 48]. For an aqueous 1 wt% butanol solution, $x_b = 0.0024$.

Focusing on butanol permeability, we define $K_b^0$ and $D_b^0$ to be solubility and diffusivity of butanol in pure PDMS. Rewriting Equation 2.3 in terms of these parameters, we obtain

$$P_b = f_{Pb} \phi_{PDMS} (K_b^0 D_b^0)$$  \hspace{1cm} (2.5)

In principle, $f_{Pb}$ can be separated into a morphology factor affecting sorption ($f_{Kb}$) and a morphology factor affecting diffusion ($f_{Db}$):

$$f_{Pb} = f_{Kb} f_{Db}$$  \hspace{1cm} (2.6)

Equation 2.5 becomes

$$P_b = f_{Kb} K_b^0 f_{Db} \phi_{PDMS} D_b^0$$  \hspace{1cm} (2.7)

where
\[ K_b = f_{K_b} K_b^0 \] (2.8)

and

\[ D_b = f_{D_b} D_b^0 \] (2.9)

Based on usual definitions of morphology factors [33, 49], we expect diffusion to be affected by morphology but not solubility, i.e., we expect \( f_{K_b} \) to be unity and \( f_{P_b} = f_{D_b} \).

To obtain information on the thermodynamic properties of the butanol-polymer system, that is, to find the Flory-Huggins parameter \( \chi_{b,p} \), we measured the butanol uptake for a membrane equilibrated in pure butanol. In this case,

\[ \gamma_b x_b = 1 = \Gamma_b \phi_b \] (2.10)

where \( \Gamma_b \) is the activity coefficient of butanol in the membrane based on volume fraction and \( \phi_b \) is the volume fraction of butanol in the membrane. Using Flory-Huggins theory for mixtures of a high molecular-weight homopolymer and solvent [50]

\[ \ln \Gamma_b = 1 - \phi_b + \chi_{b,p} (1 - \phi_b)^2 \] (2.11)

Using Equation 2.10, pure butanol uptake measurements enabled determination of \( \chi_{b,p} \). Table 2.1 shows results obtained for the three membranes.

The volume fraction of butanol in the membrane equilibrated in the pervaporation feed solution (1 wt% butanol) is then estimated using \( \chi_{b,p} \).

\[ \gamma_b x_b = \Gamma_b \phi_b \] (2.12)

noting that the \( \gamma_b \) and \( x_b \) now refer to the feed solution. \( \gamma_b \) at each temperature was estimated using the non-random two-liquid (NRTL) equation for binary butanol-water mixtures [51]. For temperatures between the data provided in Reference [51], linear extrapolation was used to estimate \( \gamma_b \).
Chapter 2

2.3. Results and Discussion

The three solvents chosen for casting the membranes exhibit varying affinities for the blocks of the polystyrene-\(b\)-polydimethylsiloxane-\(b\)-polystyrene (SDS) block copolymer. Toluene dissolves both blocks, cyclohexane is a theta solvent for polystyrene (PS) and a good solvent for polydimethylsiloxane (PDMS), and hexane is a poor solvent for PS and a good solvent for PDMS. Using the three different solvents for solvent-casting resulted in drastically different morphologies.

In Figure 2.2, we show SAXS profiles of membranes cast from different solvents before they were used in pervaporation experiments and after completing the experiments. All of the profiles exhibit a well-defined primary scattering peak at scattering vector \(q = q^*\). This indicates the presence of periodic structures with domain spacings \(d = 2\pi/q^*\). The domain spacing represents the average center-to-center distance between adjacent PDMS microdomains. The domain spacings for membranes cast from toluene, cyclohexane, and hexane are 65.3 nm, 45.7 nm, and 35.2 nm, respectively. The domain spacing decreases with decreasing solvent quality. A higher order scattering peak at \(q = 2q^*\) is seen in the toluene-cast membrane, indicating lamellar morphology. In the case of the cyclohexane-cast membrane, a shoulder is seen at \(q = \sqrt{3}q^*\), suggesting a

Table 2.1 Measured \(\phi_b\) in 100% butanol, \(\Gamma_b\) in 100% butanol, \(\chi_{b,p}\), \(\gamma_b\) in aqueous 1% butanol, calculated \(\phi_b\) in aqueous 1% butanol, and \(\Gamma_b\) in aqueous 1% butanol for the three membranes at different temperatures.

<table>
<thead>
<tr>
<th>casting solvent</th>
<th>temperature (^\circ\text{C})</th>
<th>measured (\phi_b) ((100% \text{ butanol}))</th>
<th>(\Gamma_b) ((100% \text{ butanol}))</th>
<th>(\chi_{b,p})</th>
<th>(\gamma_b) ((1% \text{ butanol}))</th>
<th>calculated (\phi_b) ((1% \text{ butanol}))</th>
<th>(\Gamma_b) ((1% \text{ butanol}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>37</td>
<td>0.217</td>
<td>4.60</td>
<td>1.21</td>
<td>43.3</td>
<td>0.0118</td>
<td>8.79</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.333</td>
<td>3.00</td>
<td>0.983</td>
<td>43.2</td>
<td>0.0151</td>
<td>6.88</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.371</td>
<td>2.69</td>
<td>0.916</td>
<td>42.7</td>
<td>0.0158</td>
<td>6.50</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.568</td>
<td>1.76</td>
<td>0.716</td>
<td>35.7</td>
<td>0.0160</td>
<td>5.35</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>37</td>
<td>0.290</td>
<td>3.45</td>
<td>1.05</td>
<td>43.3</td>
<td>0.0140</td>
<td>7.42</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.357</td>
<td>2.80</td>
<td>0.936</td>
<td>43.2</td>
<td>0.0156</td>
<td>6.63</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.413</td>
<td>2.42</td>
<td>0.863</td>
<td>42.7</td>
<td>0.0167</td>
<td>6.16</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.597</td>
<td>1.68</td>
<td>0.695</td>
<td>35.7</td>
<td>0.0163</td>
<td>5.24</td>
</tr>
<tr>
<td>hexane</td>
<td>37</td>
<td>0.277</td>
<td>3.60</td>
<td>1.07</td>
<td>43.3</td>
<td>0.0137</td>
<td>7.61</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.336</td>
<td>2.98</td>
<td>0.968</td>
<td>43.2</td>
<td>0.0151</td>
<td>6.85</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.414</td>
<td>2.41</td>
<td>0.861</td>
<td>42.7</td>
<td>0.0167</td>
<td>6.15</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.598</td>
<td>1.67</td>
<td>0.694</td>
<td>35.7</td>
<td>0.0164</td>
<td>5.24</td>
</tr>
</tbody>
</table>

\(\gamma_b\) taken from Reference 51.
cylindrical morphology. The scattering profiles obtained before and after pervaporation are nearly identical. The largest difference is seen in the hexane-cast membrane wherein the domain spacing changes from 35.2 nm to 37.4 nm. It is evident that the membrane morphologies are effectively trapped during the pervaporation experiments.

**Figure 2.2** Small angle X-ray scattering (SAXS) intensity as a function of the magnitude of the scattering Q vector for the toluene-cast, the cyclohexane-cast, and the hexane-cast membranes. Each of the solid curves represents the SAXS profile before the membrane was used in pervaporation experiments. The dotted curves represent the SAXS profiles after the membranes were used in pervaporation experiments. ▼ denotes the positions of the primary and secondary peaks.
Figure 2.3 Dark-field scanning transmission electron microscopy (STEM) images of the (a) toluene-cast, (b) cyclohexane-cast, and (c) hexane-cast membranes. The brighter phase is the PDMS-rich phase, and the darker phase is the PS-rich phase. The white scale bar represents 100 nm. All of the images were taken at the same magnification. The red arrows represent the domain sizes calculated from SAXS.

Further confirmation of the different morphologies was made by scanning transmission electron microscopy (STEM). Figure 2.3 shows the STEM images of toluene-cast, cyclohexane-cast, and hexane-cast membranes. The toluene-cast membrane has lamellar morphology, cyclohexane-cast membrane has cylindrical morphology with PS cylinders, and the hexane-cast membrane has a poorly-ordered granular morphology with dark PS domains in a bright PDMS matrix. The equilibrium morphology of the block copolymer is expected to be cylindrical based on the fact that
the PDMS volume fraction is 0.70. It is evident that the morphologies of our block copolymer membranes depend on interactions between the blocks and the solvent, [39, 40] and perhaps other parameters such as evaporation rates. The domain spacings observed by STEM are consistent with the domain spacings calculated from the SAXS profiles; the SAXS domain spacings are represented by red arrows in Figure 2.3.

![Figure 2.3](image)

**Figure 2.4** Butanol-water binary component pervaporation results at 37, 50, 60, and 80 °C. (a) Butanol permeabilities ($P_b$), (b) water permeabilities ($P_w$), and (c) butanol selectivities ($\alpha_b$) are plotted as functions of temperatures for the hexane-cast (●), the cyclohexane-cast (■), and the toluene-cast (▲) membranes.
The butanol permeabilities ($P_b$) and water permeabilities ($P_w$) of the three membranes were measured by pervaporation experiments using aqueous 1 wt% butanol solutions as feed. Permeabilities were determined at different temperatures: 37, 50, 60, and 80 °C. $P_b$ and $P_w$ are plotted as functions of temperature in Figure 2.4a and b, respectively. $P_b$ and $P_w$ of the three membranes decreased monotonically as the pervaporation temperature was increased. This is consistent with literature [52]. (Both butanol and water fluxes increase with temperature due to an increase in the driving forces for pervaporation, see $p_{b\text{sat}}$ in Table 2.2.) The hexane-cast and cyclohexane-cast membranes showed similar $P_b$ and $P_w$ at all temperatures. $P_b$ obtained from these two membranes are within experimental error, while small differences outside the experimental error are seen in $P_w$. The toluene-cast membrane has the lowest $P_b$ and $P_w$ across all temperatures.

$P_b$ of the toluene-cast membrane are about 20% of those of the hexane-cast and cyclohexane-cast membranes, and $P_w$ of the toluene-cast membrane are about 50% of those of the other membranes. Figure 2.4c is a plot of the butanol selectivities ($\alpha_b$) of the three membranes versus temperature. $\alpha_b$ is insensitive to temperature. $\alpha_b$ for the hexane- and cyclohexane-cast membranes are about 3.8 while that of the toluene-cast membrane is 1.3.

Table 2.2 Vapor pressure for pure butanol ($p_{b\text{sat}}$) and concentration of butanol in membrane ($c_b$) for the three membranes at different temperatures.

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>$p_{b\text{sat}}$ (mmHg)</th>
<th>$c_b$ (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>toluene-cast</td>
<td>cyclohexane-cast</td>
</tr>
<tr>
<td>37</td>
<td>15.0</td>
<td>129</td>
</tr>
<tr>
<td>50</td>
<td>33.6</td>
<td>165</td>
</tr>
<tr>
<td>60</td>
<td>59.2</td>
<td>172</td>
</tr>
<tr>
<td>80</td>
<td>162.3</td>
<td>175</td>
</tr>
</tbody>
</table>

In attempt to explain the differences in $P_b$, $P_w$, and $\alpha_b$, apparent PDMS volume fractions were derived from the STEM images. Although the same SDS was used to cast all three membranes, we did not want to disregard the possibility of non-equilibrium effects. The PDMS volume fractions were measured to be 0.52 and 0.54 for the toluene-cast membrane and the cyclohexane-cast membrane, respectively. (We did not attempt to estimate PDMS volume fraction for the hexane-cast membrane.) These numbers are different from the PDMS volume fraction determined by NMR, 0.70. It appears that the PDMS volume fraction determined by STEM is consistently lower than that determined by NMR. We are not sure about the reason for this difference. It may be related to STEM sample preparation.

\footnote{$p_{b\text{sat}}$ taken from Reference 48.}
Figure 2.5 (a) Butanol uptake, (b) butanol solubility ($K_b$), and (c) butanol diffusivity ($D_b$) as functions of temperature in hexane-cast(●), cyclohexane-cast(■), and toluene-cast(▲) membranes.

Butanol uptake measurements were conducted to estimate butanol solubility in the three membranes. Figure 2.5a shows results of uptake experiments measured by immersing the membranes in pure butanol. These butanol uptake measurements were used to calculate the volume fraction of butanol in the membrane, $\phi_b$, using pure component densities as described experimental section. $\phi_b$ for the three membrane are listed in Table 2.1. This enables calculation of $I_b$ for pure butanol using Equation 2.10, and $\chi_{b,p}$ using Equation 2.11. Assuming $\chi_{b,p}$ is independent of butanol concentration, we then simultaneously solve Equation 2.11 and 2.12 to
determine \( \bar{I}_b \) and \( \phi_b \) for an aqueous 1 wt% butanol solution, using \( \gamma_b \) from literature [51] for the aqueous 1 wt% butanol solution. The measured \( \phi_b \) and \( \bar{I}_b \) for pure butanol, \( \chi_{b,p} \), and \( \gamma_b \), calculated \( \phi_b \), and \( \bar{I}_b \) for the aqueous 1 wt% butanol solution at different temperatures for the three membranes are given in Table 2.1.

In Table 2.2, we give the temperature dependence of \( P_b^{\text{sat}} \) and \( c_b \) of the three membranes. This information, along with \( \gamma_b \) in Table 2.1, is used to calculate \( K_b \) for each membrane using Equation 2.4. The temperature dependence of \( K_b \) in three membranes is shown in Figure 2.5b. While butanol uptake and \( c_b \) increases significantly with increasing temperature, \( K_b \) decreases with temperature due to the temperature dependence of the other parameters in Equation 2.4. The butanol uptake and \( K_b \) of the membranes do not depend on the solvent used for casting the membranes (Figures 2.4a,b). Differences in \( P_b \) seen in Figure 2.4a thus cannot be attributed to differences in solubility, \( K_b \). The solubility measurements, however, provide an explanation for the decrease in butanol permeability with increasing temperature.

From \( P_b \) and \( K_b \), butanol diffusivities (\( D_b \)) were calculated using Equation 2.3 and plotted as functions of temperature (Figure 2.5c). As expected, \( D_b \) increases monotonically with increasing temperature for all three membranes. The toluene-cast membranes exhibited the lowest \( D_b \) at all temperatures, while the hexane-cast membrane and the cyclohexane-cast membrane exhibited similar \( D_b \) at all temperatures because both \( P_b \) and \( K_b \) are similar. For comparison, \( D_b \) in aqueous 1 wt% butanol solution at 25 °C has been reported in literature to be \( 9.2 \times 10^{-6} \) cm²/s [53]. \( D_b \) in the membranes measured at 37 °C were about an order of magnitude smaller; they were calculated to be \( 1.2 \times 10^{-7} \) cm²/s, \( 5.1 \times 10^{-7} \) cm²/s, and \( 6.6 \times 10^{-7} \) cm²/s, respectively for toluene-cast, cyclohexane-cast, and hexane-cast membranes.

We use the framework described in the experimental section (Equations 2.2-9) to study the effect of morphology on permeation. In this framework, the morphology factor \( (f) \) accounts for the microphase-separated geometry of the block copolymer. For lamellar morphologies, \( f = 2/3 \), while for morphologies with continuous transporting phases, \( f = 1 \) [33, 49]. In both cyclohexane- and hexane-cast membranes, the transporting PDMS-rich microphase is continuous and we thus expect \( f = 1 \) in these systems. By definition, neither \( \phi_{PDMS} \) nor \( P_i^0 \) are affected by the casting solvent. Our framework thus predicts that butanol and water permeabilities through cyclohexane- and hexane-cast membranes should be within experimental error. Our measurements are more-or-less consistent with this prediction (Figure 2.4). Our framework also enables analysis of permeation through toluene-cast membranes. We estimate \( P_i^0 \) using data obtained from the hexane-cast membrane assuming that \( f_{Pi} = 1 \). \( P_i^0 \) thus obtained are thus a factor of \( 1/0.70 \) larger than the butanol and water permeabilities of the hexane-cast membranes in Figures 2.3a and b. Using \( P_i^0 \), we determine \( f_{Pi} \) for the toluene-cast membrane with lamellar morphology. Figure 2.6a shows the results obtained. Both \( f_{Piw} \) and \( f_{Pi} \) are more-or-less independent of temperature. The average value of \( f_{Piw} \) is 0.50, which is somewhat lower than the expected value of 0.67. This suggests that defects in the lamellar phase slow down transport of water molecules. It is not uncommon to obtain morphology factors that are lower than theoretical limits [54, 55]. What is surprising, however, is that \( f_{Pi} \) is a factor of three smaller than \( f_{Piw} \). The fact that water permeability is unaffected by morphology suggests that water molecules may be permeating through both PS- and PDMS-rich microphases.
Since permeability depends on solubility and diffusivity, $f_{Pb}$ can, in principle, be affected by both parameters. This is explicitly quantified in Equation 2.6. The morphology factor related to solubility, $f_{Kb}$, for the toluene-cast membrane, is estimated from measurements of $K_b$ in toluene- and hexane-cast membranes in a manner that is analogous to our determination of $f_{Pb}$ for the toluene-cast membrane. From Equation 2.8, it is evident that $f_{Kb}$ is given by the ratio $K_{b,\text{toluene}}/K_{b,\text{hexane}}$. In Figure 2.6b, we plot $f_{Kb}$ versus temperature. The morphology factor associated with diffusivity is then given by $f_{Db} = f_{Pb} / f_{Kb}$ (see Equations 2.3-9). In Figure 2.6b, we also plot $f_{Db}$ versus temperature. It is evident that both $f_{Kb}$ and $f_{Db}$ are independent of temperature. To a good approximation $f_{Kb}$ is unity (average value 0.95) while $f_{Db}$ is about 0.17. This indicates that morphology affects diffusivity, not solubility. We hypothesize that defects such as T-junctions are responsible for hindering butanol transport through the toluene-cast lamellar SDS membrane. Further work is needed to either prove or disprove this hypothesis.

2.4 Conclusions

We used toluene, cyclohexane, and hexane, which have varying affinities for each of the blocks in SDS, as solvents for casting pervaporation membranes. The difference in the casting solvents resulted in different morphologies: the toluene-cast membrane exhibited a lamellar morphology, the cyclohexane-cast membrane exhibited a cylindrical morphology with a PDMS-rich matrix, and the hexane-cast membrane exhibited a poorly-ordered granular morphology with a PDMS-rich matrix (Figures 2.1 and 2.2). These membranes were used in pervaporation experiments with an aqueous butanol solution as the feed. This enabled quantification of butanol and water
permeabilities (Figure 2.4). We expect permeability to be largely restricted to the PDMS-rich microphase. Since all of the membrane have the same composition, our experiments thus provide a unique window into the effect of morphology on simultaneous transport of butanol and water. The poorly-ordered granular morphology is optimal for selective butanol transport. Surprisingly, butanol permeability is more strongly affected by morphology than water permeability (Figure 2.6a). Butanol uptake measurements showed that morphology had negligible effect on solubility (Figure 2.6b). The observed dependence of permeability on morphology is thus attributed to differences in diffusivities.

It is evident that the choice of solvent used for casting block copolymer membranes can have a large effect on membrane permeability. Further work is needed to elucidate the relationship between block copolymer processing, morphologies of block copolymer membranes, and transport mechanisms of mixtures of molecules through block copolymer membranes.

### 2.5 Nomenclature

- $\phi_b$: volume fraction of butanol in membrane
- $P_b$: butanol permeability
- $P_w$: water permeability
- $\alpha_b$: butanol selectivity
- $\phi_{\text{PDMS}}$: volume fraction of PDMS phase
- $P_i^0$: permeability of $i$ through pure PDMS
- $f_{Pi}$: morphology factor associated with the permeability of $i$
- $K_i$: solubility of $i$
- $D_i$: diffusivity of $i$
- $c_i$: molar concentration of $i$ in the membrane
- $x_i$: mole fraction of $i$ in the liquid
- $\gamma_i$: activity coefficient of $i$ in the liquid
- $p_i^{\text{sat}}$: saturated vapor pressure of $i$ in the liquid
- $K_b^0$: butanol solubility in pure PDMS
- $D_b^0$: butanol diffusivity in pure PDMS
- $f_{Kb}$: morphology factor associated with butanol solubility
- $f_{Db}$: morphology factor associated with butanol diffusivity
- $\chi_{b,p}$: Flory-Huggins parameter for the butanol-polymer system
$\Gamma_b$ butanol activity coefficient in the membrane based on volume fraction
Chapter 3. Effect of Pore Penetration on Butanol and Water Permeabilities of Nanostructured Composite Pervaporation Membranes§

3.1 Introduction

As mentioned the previous chapters, pervaporation is advantageous in the fact that the separated product, or the permeate, is more enriched with biofuels than from other separations, and also in the fact that it is non-invasive toward the microorganisms in fermentation. In pervaporation, a dense, selective membrane is placed between the liquid feed and the permeate vapor. Vacuum is applied on the permeate side of the membrane, and the chemical potential gradient across the membrane acts as the thermodynamic driving force for permeation. The solubility and the diffusivity of the molecular species in respect to the membrane material determine permeability, or the intrinsic quality of permeation through the membrane.

Permeability is the product of diffusivity and solubility. This definition is derived from the solution-diffusion theory used widely in describing molecular transport of small molecules through non-porous, dense membranes [15]. At a certain temperature, diffusivity and solubility are both qualitative terms; thus permeability is also a qualitative term when the temperature is kept constant. However, permeability fluctuations as a result of decreasing membrane thickness have been observed [56-58]. We believe that this issue needs to be clearly understood in order for the commercialization of membrane separation methods for fermentation.

Permeability decrease with decrease in thickness has been predicted in many studies [59-62]. The two most well-known hypotheses for this are concentration polarization of the selective species on the feed side of the membrane and resistance from the porous support layer. Concentration polarization has been known to decrease the permeability of the selective species [60, 63]. This occurs because of a boundary layer forming on the feed side of the membrane due to faster depletion of the selective species than of the non-selective species. In this case, decrease in the permeability of the selective species can be observed with decreasing membrane thickness, decreasing feed flow rate, and decreasing feed concentration.

The resistance from the support layer is also widely known to have a detrimental effect on permeabilities [61, 62]. The use of support layers is inevitable in membrane separation because in order to have high flux, the thickness of the membrane has to be reduced as much as possible. This

§ This chapter contains collaborative work adapted with permission from collaborators Xi Jiang, Wonjae Ko, and Nitash P. Balsara.
makes the use of support membranes unavoidable. Thus, most membranes used in separation are made as composite membranes, where there is a micro-porous support membrane underneath a thin, selective, dense layer of membrane on the top [61].

The resistance originating from the use of support layers has been studied in two different scenarios: one where the selective layer has penetrated into the pores of the support layer, and one where it has not. In the first case, most of the resistance from the support layer is said to have come from the selective membrane material in the pores of the support membrane [61, 64, 65]. The effect of a pore penetration layer on permeabilities has been applied to the creation of gutter layers in gas separation membranes [66]. Gutter layers are created with a different selective material, and are used to intentionally fill the pores closest to the selective layer on top. The addition of gutter layers can significantly change the permeability and selectivity of the composite membrane. However, penetration of selective material into the porous support layer has not been directly observed by imaging.

In the second case where no pore penetration is assumed, the increase in the tortuosity of the permeate’s path is the reason for the resistance [62, 67, 68]. Wijmans and Hao calculated that the resistance coming from the support membrane, without a gutter layer, starts affecting the permeability when the selective membrane layer is less than 1 µm thick [62].

In this study, we performed a systematic study of the support resistance by measuring the butanol and water permeability of membranes with different thicknesses. A block copolymer was chosen as the selective membrane material because of its good mechanical properties and good permeabilities without the need for crosslinks. The morphology of the block copolymer was controlled by using the solvent casting using hexane as casting-solvent. Block copolymer membranes of thicknesses ranging from 1.7 – 125 µm were cast on top of porous PTFE membranes. With the permeability data, we try to estimate the pore penetration layer thickness in the composite membranes, and fit the permeability data by calculating the resistance originating from the pore penetration layer. At same time, we use direct imaging to find evidence of pore penetration in the composite membrane.

3.2 Methods

3.2.1 Polymer Membrane Casting

Polystyrene-\textit{b}-polymethylsiloxane-\textit{b}-polystyrene (SDS) triblock copolymers of molecular weight 144 kg/mol was purchased from Polymer Source (Dorval, Canada). The molecular weight of the polystyrene (PS) block is each 22 kg/mol, and the molecular weight of the polymethylsiloxane (PDMS) is 104 kg/mol. The polydispersity index of the polymer is 1.3 and 60 wt% of the polymer is the SDS triblock copolymer, 30 wt% is polystyrene-\textit{b}-polymethylsiloxane diblock copolymer of molecular weight 22-52 kg/mol, and 9 wt% is homopolymer PS.

Porous polytetrafluoroethylene (PTFE), which was used as the support layer for the composite membrane, was purchased from Sterlitech (Kent, WA). The thickness of the PTFE membrane was 13 µm, and the pores are 0.2 µm in diameter. By comparing the density of the PTFE membrane to
the density of PTFE (2.2 g/cm$^3$ [44]), the volume fraction of the pores in the PTFE was calculated to be 0.20.

Varying masses of SDS were dissolved into hexane to make membranes of different thicknesses. The amount of hexane used to dissolve SDS was tuned such that the resulting solution had SDS concentrations of about 2 wt%. The SDS/hexane solutions were poured into 100 mL Teflon petri dishes with porous PTFE membranes on the bottom. The Teflon dish was then lightly covered with aluminum foil and a funnel and left to dry for 4-7 days. After the membrane had been dried, the Teflon dish containing the membrane was brought into a vacuum chamber and was subsequently dried for one day. The dried membranes were then cut into circles of 37 cm$^2$ in area and used in pervaporation experiments. The thickness of the thickest membrane was determined by using a micrometer and taking 20 measurements throughout different areas in the membrane. The thickness of the support PTFE membrane was measured separately using a micrometer, and the SDS layer of the thickest membrane was determined by subtracting the PTFE membrane’s thickness from the SDS-PTFE composite membrane’s thickness. The thicknesses of other membranes were determined by measuring the mass of each membrane, and comparing the mass to that of the thickness membrane to deduce the thickness.

3.2.2 Transmission Electron Microscopy (TEM)

SDS-PTFE composite membrane which is 125 µm thick was cryo-micromted at -160°C by using Diatome cryo diamond knife and Leica UC6. The thickness of sectioned thin film was about 100 nm. Sectioned thin films were imaged by using FEI Tecnai F20 at 200kv in HAADF-STEM mode at room temperature. The bright phase in large scale images is the porous PTFE membrane because of its larger thickness which was induced by pores collapsing, and the dark phase is the SDS membrane.

3.2.3 Pervaporation and Permeability Measurements

A benchtop pervaporation setup (Sulzer) was used to measure permeabilities of the membranes. 2 L feed of butanol-water solutions were used in the experiments. Butanol was purchased from Sigma Aldrich (used as received). The feed solution was circulated at the rate of 6.2 L/min, which corresponds to 1.3 m/sec at the membrane surface. Each membrane was left for at least 30 min at the beginning of an experiment to ensure that temperature equilibrium has been reached in the membrane. Vacuum of 2~3 mbar was applied on the other side of the membrane, and the permeate was collected in cold trap with isopranol and dry ice solution, and the collection time was adjusted so that ~0.5 g of permeate would be collected for each time-point. The collected permeate were then thawed, and the mass was measured. The butanol concentration of the permeate was measured by high-performance liquid chromatography (Prominence UFLC instrument, Shimadzu). Four permeate collections was performed for each experiment, and the resulting permeability data from the four cold traps were averaged.

Permeabilities of the SDS-PTFE composite membranes were calculated by the following equation derived from the solution-diffusion theory [15]:

\[
P = \frac{k \cdot \Delta C \cdot A}{L}
\]
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\[ J_i = \frac{P_{i,t}}{l_t} \left( x_i \gamma_i P_i^{sat} - y_i P_{permeate} \right) \]  

(3.1)

where \( J_i \) is the flux of species \( i \) through the membrane, \( P_{i,t} \) is the total permeability of \( i \) for the composite membrane, \( l_t \) is the total thickness of the composite membrane, \( x_i \) is the mole fraction of \( i \) in the feed, \( \gamma_i \) is the activity coefficient of \( i \) in the feed, \( P_i^{sat} \) is the saturation vapor pressure of \( i \) in the feed, \( y_i \) is the mole fraction of \( i \) in the permeate, and \( P_{permeate} \) is the pressure in the permeate.

Selectivity of butanol (\( \alpha_b \)) is defined as:

\[ \alpha_b = \frac{P_{b,t}}{P_{w,t}} \]  

(3.2)

where \( P_{b,t} \) is the butanol permeability and \( P_{w,t} \) is the water permeability of the SDS-PTFE composite membrane.

### 3.2.4 Support Resistance Calculations

![Figure 3.1](image)

Figure 3.1 (a) Schematic of the SDS-PTFE composite membrane cross-section. (b) Resistances of the composite membrane expressed analogously in an electric circuit.

The support resistance when assuming the presence of a pore penetration layer was calculated by using the same methodologies as described in the resistance model in Reference [61]. The SDS-PTFE composite membrane is consisted of three layers: the selective, SDS-only layer, the pore penetration layer, where SDS has penetrated into the pores of the PTFE, and the porous, PTFE-
only layer. The resistance from the SDS-PTFE membrane can be categorized into $R_1$, $R_2$, $R_3$, and $R_4$ (Figure 3.1a). $R_1$ is the resistance of the selective layer, $R_2$ is the resistance from the SDS in the pore penetration layer, $R_3$ is the resistance of the PTFE in the pore penetration layer, and $R_4$ is the resistance in the porous layer. The resistances can be analogously described in terms of electric circuits (Figure 3.1b). The total resistance of the composite membrane, $R_t$, can be expressed as:

$$R_t = R_1 + \frac{R_2 R_3}{R_2 + R_3} + R_4$$

(3.3)

Resistances, in relation to permeability, can be expressed as:

$$R = \frac{l}{PA}$$

(3.4)

where $l$ is the thickness, $P$ is the permeability, and $A$ is the cross-sectional area of the resistance of interest. $R_3$ is infinitely larger than $R_2$ because PTFE is an impermeable material, and $R_4$ is essentially 0 for our system. From these assumptions and Equation 3.3 can be re-written as the following:

$$\frac{l + l_p}{P_{i,t} A_t} = \frac{l}{P_{i,SDS} A_t} + \frac{l_p}{P_{SDS} A_p}$$

(3.5)

where $l$ and $l_p$ are the thicknesses for the selective layer and the pore penetration layer, respectively, $P_{i,t}$ is the permeability of $i$ in the composite membrane, or the permeability that we measure, $P_{i,SDS}$ is the permeability of the SDS, $A_t$ is the total membrane area, $A_p$ is the area that is occupied by the SDS in the pore penetration layer.

### 3.3 Results and Discussion

Polystyrene-$b$-polydimethylsiloxane-$b$-polystyrene (SDS) was solvent-cast on top of porous PTFE membranes with hexane as the casting-solvent. Eight SDS-PTFE composite membranes with SDS thicknesses ranging from 1.73 µm to 125 µm were cast using the same method to ensure that the block copolymer morphology of the membranes were the same. A TEM image of the selective, SDS-only layer of the 125 µm-thick composite membrane is shown in Figure 3.2a. The brighter phase in the TEM image is the PDMS phase of the SDS, and the darker phase is the PS phase. By Fourier transforming the TEM image (Figure 3.2b) and by subsequent azimuthal averaging, the
domain spacing of the self-assembled structures can be calculated (Figure 3.2c). The domain spacing, calculated here as 29 nm, corresponds well with the domain spacing of 35 nm calculated from a previously obtained small angle X-ray scattering data from a free-standing, hexane-cast membrane [69] (Figure 3.2c).

Figure 3.2 TEM image of the selective, SDS-only layer of the (a) SDS-PTFE composite membrane. The lighter region is the PDMS phase, and the darker region is the PS phase. (b) The Fourier-transformed image of (a). (c) Azimuthally averaged intensity of (b) plotted as a function of scattering q vector (green) and small angle X-ray scattering profile of freestanding SDS (red) [69]. Inverted triangles (▼) denote the primary peaks of each curve, from which domain spacings in the parentheses are calculated.

The butanol and water permeabilities of SDS-PTFE membranes ($P_{b,t}$ and $P_{w,t}$) ranging in thicknesses were measured in pervaporation experiments using binary butanol-water solutions. The feed butanol concentration was 1 wt% and $P_{b,t}$ and $P_{w,t}$ were measured at four different temperatures: 40, 50, 60, and 70 °C (Figure 3.3). Both $P_{b,t}$ and $P_{w,t}$ increase with increasing membrane thickness, and start plateauing at around 40 μm. $P_{b,t}$ of the thickest membrane at 40 °C, which is 125 μm thick, is eight times of that of the thinnest membrane at 40 °C, which is 1.73 μm thick (Figure 3.3a). The permeability difference between the thickest and the thinnest membranes is smaller for $P_{w,t}$; the $P_{w,t}$ of the thickest membrane is four times of that of the thinnest membrane at 40 °C (Figure 3.3b). Similar trends are observed at all temperatures, although increase in temperature results in the decrease of permeabilities for all membranes. The increase in temperature also decreases the permeability difference gap between the thickest membrane and
the thinnest membrane. At 70 °C, $P_{b,t}$ difference between them is four-fold, and $P_{w,t}$ difference between them is three-fold.

**Figure 3.3** (a) $P_{b,t}$ (butanol permeability of SDS-PTFE composite membrane) and (b) $P_{w,t}$ (water permeability of the SDS-PTFE composite membrane) plotted as functions of $l$ (membrane thickness). Data obtained at 40 °C (●), 50 °C (♦), 60 °C (▲), and 70 °C (■) are shown with fits using $l_p$ (pore penetration layer thickness) = 2.2 µm in dotted lines. (c) $P_{b,SDS}$ (butanol permeability of SDS, ○) and $P_{w,SDS}$ (water permeability of SDS, ◊) at different temperatures are calculated from $l_p = 2.2$ µm.
We used the resistance model described in the experimental section and the permeability data to fit for the pore penetration layer thickness, \( l_p \), and the permeability of the SDS-only layer, \( P_{i,\text{SDS}} \). \( l_p \) of 2.2 µm resulted in the best fit for \( P_{b,t} \) and \( P_{w,t} \) data at all four temperatures. This value was used to draw the fit curves in Figure 3.3a and b. Using a single value of \( l_p \) results in a reasonably good fit with an average \( R^2 \) value of 0.93 for \( P_{b,t} \) and an average \( R^2 \) value of 0.83 for \( P_{w,t} \). \( P_{b,\text{SDS}} \) and \( P_{w,\text{SDS}} \) at each temperature are calculated from \( l_p \) and are shown in Figure 3.3c. Both \( P_{b,\text{SDS}} \) and \( P_{w,\text{SDS}} \) decrease monotonically with increasing temperature.

**Figure 3.4** (a) \( P_{b,t} \) and (b) \( P_{w,t} \) plotted as functions of \( l \) at different butanol feed concentrations: 0.5 wt% (▲), 1 wt% (●), and 2 wt% (■). Fits using \( l_p = 4.1 \) µm are in
dotted lines. (c) $P_{\text{b,SDS}}$ (○) and $P_{\text{w,SDS}}$ (◊) at different feed concentrations are calculated from $l_p = 4.1 \, \mu m$.

We also measured $P_{\text{b,t}}$ and $P_{\text{w,t}}$ using different feed concentrations (0.5 wt%, 1 wt%, and 2 wt% butanol) at 40 °C (Figure 3.4). Although the general trend of decreasing $P_{\text{b,t}}$ and $P_{\text{w,t}}$ with decreasing membrane thickness is observed for each data set at each feed concentration, there are not any noticeable trends in $P_{\text{b,t}}$ and $P_{\text{w,t}}$ with the change in feed butanol concentrations.

The same set of resistance model analyses was performed on the data from the different feed concentration experiments. Equation 3.5 was used to calculate the best-fitting $l_p$ for the $P_{\text{b,t}}$ and $P_{\text{w,t}}$ data. This was calculated to be $l_p = 4.1 \, \mu m$, and was used to draw the dotted fit curves in Figure 3.4a and b. $R^2$ is 0.83 for $P_{\text{b,t}}$ fits, and 62 for $P_{\text{w,t}}$ fits. $P_{\text{b,SDS}}$ and $P_{\text{w,SDS}}$ at each feed concentration are calculated from $l_p$ and are shown in Figure 3.4c. Both $P_{\text{b,SDS}}$ and $P_{\text{w,SDS}}$ are independent functions of feed concentration.

![Figure 3.5](image-url) (a) $\alpha_b$ (butanol selectivity) plotted as functions of $l$ for different temperatures: 40 °C (●), 50 °C (♦), 60 °C (▲), and 70 °C (■). (b) $\alpha_b$ plotted as functions of $l$ for different feed concentrations: 0.5 wt% (▲), 1 wt% (●), and 2 wt% (■).
The lack of feed concentration dependence in $P_{b,t}$ and $P_{w,t}$ is one of the reasons that we do not attribute the permeability fluctuations to concentration polarization. The other reason is the observed decrease in $P_{w,t}$ with decreasing membrane thickness, as well as in $P_{b,t}$. These are strong evidences that concentration polarization is not the reason for the permeability decreases we observe with decreasing membrane thickness. If concentration polarization were limiting the mass transfer on the feed side of the membrane, $P_{b,t}$ would be expected to increase with increasing feed concentration, and only $P_{l,t}$ of the selective species, butanol, would be affected, and $P_{w,t}$ would not be affected.

The largest limitation of the resistance model is that it is not able to explain the butanol selectivity ($\alpha_b$) decrease observed in the permeability data (Figure 3.5). There is a slight decrease in $\alpha_b$ with decreasing $l$. $\alpha_b$ is independent of temperature (Figure 3.5a) and feed butanol concentration (Figure 3.5b). However, from Equation 3.5, it can be inferred that the resistance model only predicts a single value of $\alpha_b$ for all $l$ values.

By rearranging Equation 3.5, the ratio of the apparent permeability to the actual permeability of the selective layer can be expressed as:

$$\frac{P_{l,t}}{P_{l,SDS}} = \frac{l + l_p}{l + l_p / (A_p/A_t)}$$

From this equation, it can be inferred that when $l >> l_p$ and $A_p/A_t \rightarrow 1$, $P_{l,t}/P_{l,SDS}$ goes to unity. These trends are shown visually in Figures 3.6a and b. By using the $P_{b,SDS}$ value at 40 °C and assuming different $l_p$ values ranging from 0.001 – 2 µm, we are able to make butanol permeability estimations for membranes of different SDS thicknesses at 40 °C (Figure 3.6a). As $l_p$ becomes smaller, the permeability becomes less affected by the membrane thickness, and the onset point of thickness at which permeability starts being affected decreases. However, we can see that even at a pore penetration layer thickness of 500 nm, the resistance is still severe enough to affect membrane thicknesses of around 10 µm. Figure 3.6b shows the calculations for butanol permeability at 40 °C as $A_p/A_t \rightarrow 1$. This was calculated by assuming a constant $l_p$ of 4.41 µm. As $A_p/A_t$ goes to unity, there is less suppression of the permeabilities. This anaylisis does not take into account the increase in resistance arising from the porous layer.
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Figure 3.6 Butanol permeability data (●) from 40 °C, 1 wt% butanol experiments, best fit to the data obtained by using $l_p$ of 4.41 µm and 0.2 porosity (dotted black line), and butanol permeability forecasts assuming (a) different $l_p$ and (b) different porosities.

We further tried to validate the resistance model by direct imaging of the SDS-PDMS composite membranes. By gluing epoxy on either sides of the membrane prior to cryo-microtoming, we have
succeeded in observing penetration of the SDS layer into the porous PTFE membrane (Figure 3.7). Figure 3.7a shows a cross-sectional TEM image of the SDS-PTFE composite membrane at the two membranes’ interface. The bright, top-left region is the porous PTFE membrane; the dark, bottom-right region is the SDS membrane. Figure 3.7b shows an image that is higher in magnification with the same configuration. In the SDS membrane region, similar morphologies as in Figure 3.2a can be observed, where the brighter matrix is the PDMS phase and the darker, granular structure is the PS phase. In addition to this, nano-structured SDS inside the PTFE membrane can also be observed. It is clear that most of the pores in the support layer are filled with the SDS copolymer; two empty pores are evident in the middle of the support layer. To the extent of our knowledge, this has never been captured in a TEM image before, and we attribute our success to using a nano-structured membrane material.

Figure 3.7 (a) Cross-sectional TEM image of the SDS-PTFE interface where the bright, top-left is the porous PTFE and the dark, bottom-right is the SDS. (b) The same image at a higher magnification.

3.4 Conclusion

We have studied the effect of pore penetration layer in SDS-PTFE composite membranes by pervaporation experiments and direct imaging. We observed a significant decrease in both butanol and water permeabilities as the thickness of the membranes was reduced from 125 µm to 1.73 µm. We were able to visually confirm penetration of the SDS layer into the porous PTFE membrane, thus forming a pore penetration layer inside the PTFE, and were able to fit the permeability data by calculating the resistance arising from the pore penetration layer based on the resistance model. While this resistance does explain most of our observations, there is a limitation in the resistance model that it does not account for the slight selectivity decrease that we also observe. Based on the
model, we have also predicted the effect of pore penetration thickness and porosity on permeabilities.

### 3.5 Nomenclature

- $J_i$: flux of $i$
- $P_{i,t}$: permeability of $i$ for the composite membrane
- $l_t$: thickness of the composite membrane.
- $x_i$: mole fraction of $i$ in the feed
- $\gamma_i$: activity coefficient of $i$ in the feed,
- $p_{i,\text{sat}}$: saturation vapor pressure of $i$ in the feed
- $y_i$: mole fraction of $i$ in the permeate
- $p_{\text{permeate}}$: pressure in the permeate
- $\alpha_b$: selectivity of butanol
- $R_1$: resistance of the selective layer
- $R_2$: resistance of the SDS in the pore penetration layer
- $R_3$: resistance of the PTFE in the pore penetration layer
- $R_4$: resistance in the porous layer
- $R_t$: total resistance of the composite membrane
- $l$: thickness of the selective layer
- $l_p$: thickness of the pore penetration layer
- $P_{i,\text{SDS}}$: permeability of $i$ in SDS
- $A_t$: total membrane area
- $A_p$: pore penetration area
Chapter 4. Block Copolymer Pervaporation Membrane for 
in situ Product Removal during Acetone-Butanol-Ethanol 
Fermentation**

Abstract

We address two major challenges facing commercialization of acetone-butanol-ethanol (ABE) fermentation: product inhibition and low productivity. We studied a polystyrene-\(b\)-polydimethylsiloxane-\(b\)-polystyrene (SDS) triblock copolymer membrane for selective removal of butanol from aqueous solutions by pervaporation. The SDS membrane exhibited higher permeabilities than a commercially available cross-linked polydimethylsiloxane (PDMS) membrane. Both types of pervaporation membrane were also used for \textit{in situ} product removal of ABE biofuels in \textit{Clostridium acetobutylicum} fermentations operated in a semi-continuous mode. Membrane performance and its effect on the fermentation process were assessed by measuring flux, OD\(_{600}\) and concentrations of different components in the fermenter as a function of time. Volumetric ABE productivity increased from 0.45 g/L∙h in simple batch fermentation to 0.66 g/L∙h in the case of pervaporative-fermentation with the PDMS membrane. A further increase in productivity to 0.94 g/L∙h was obtained in the case of pervaporative-fermentation with the SDS membrane. Overall, total ABE production improved by a factor of three, viable fermentation time increased by a factor of two, and cell density increased by a factor of 2.5 upon applying SDS membrane pervaporation, relative to the batch process. Upon decreasing the fermentation volume from 1.25 L to 1 L, continuous ABE production for 109 h was achieved where the total mass of ABE produced was 90 g.

4.1 Introduction

There is considerable effort underway to replace fossil fuels with biofuels produced from renewable resources [9]. Biobutanol is more attractive than first generation bioethanol because it has higher energy density, lower miscibility with water, and lower vapor pressure. \textit{Clostridium acetobutylicum}, \textit{C. beijerinckii}, and \textit{C. saccharoperbutylacetonicum} are commonly used microbes for producing biobutanol. In addition to butanol, however, these microbes also produce acetone.

** This chapter was reported in the \textit{Journal of Membrane Science} 484, 57-63 (2015), and is adapted with permission from co-authors Zachary C. Baer, X. Chelsea Chen, A. Evren Ozcam, Douglas S. Clark, and Nitash P. Balsara.
and ethanol. Acetone-butanol-ethanol fermentation (ABE fermentation) by *C. acetobutylicum* occurs in two phases: an acidogenesis phase wherein the microbes mainly produce acetic acid and butyric acid, followed by a solventogenesis phase wherein the microbes mainly produce ABE [6, 9, 70].

Two significant challenges facing commercialization of ABE fermentation are: (1) product inhibition (This means that the products of fermentation are toxic to the microorganisms), and (2) low ABE productivity. ABE fermentation normally stops when the total ABE concentration is 2 wt% [6]. Conventional production of biofuel is carried out in a batch process. In the case of ABE fermentation, biofuel is only produced during the second phase of batch fermentation. Afterwards, the fuel is typically separated from the reaction broth by distillation. The availability of *in situ* product removal methods will lead to better utilization of the microorganisms and higher volumetric productivities, and may ultimately enable continuous biofuel production [8, 71]. Methods for *in situ* product removal include liquid-liquid extraction [72, 73], adsorption [19], and pervaporation [20-23, 74]. However, none of these technologies has been scaled-up for industrial use.

The purpose of this study is to compare different pervaporation membranes for continuous ABE fermentation at high cell densities. Pervaporation has advantages over other technologies in that it has better selectivity toward the ABE and is less invasive to the cells [75, 76]. However, the flux of biofuels through currently available membranes is low, and this limits the efficacy of the separation process. The membrane material most widely used for biofuel purification is polydimethylsiloxane (PDMS) [19-23, 74]. For example, Van Hecke et al. [23] attached a pervaporation module with a PDMS membrane to a two-stage chemostat, and increased total ABE productivity from 0.13 g/L∙h to 0.30 g/L∙h. From an industrial point of view, it would be desirable to retain the cells in the reactor and remove only the fuel. Also, higher culture densities promote greater productivities [77]. The possibility of using a PDMS membrane for this mode of operation was recently explored by Li et al. [74], who concluded that fermentation productivity is improved when assisted by pervaporation.

A shortcoming of PDMS is that it is a soft rubber. Increasing the rigidity of PDMS membranes is usually accomplished by increasing cross-linking density. In this paper, we use block copolymer self-assembly to improve the mechanical properties of PDMS-based membranes. Polystyrene (PS) blocks are covalently bonded at the ends of PDMS chains to produce a polystyrene-*b*-polydimethylsiloxane-*b*-polystyrene (SDS) triblock copolymer. Microphase separation results in the formation of mechanically rigid PS cylinders in a PDMS matrix. Thin films of SDS were coated onto a commercial polyethersulfone support and used in a pervaporation module that was attached to an ABE fermentation reactor. The fermentation was started in batch mode until the acidogenesis phase was completed. The reactor was then operated in a continuous mode with a feed stream comprising concentrated medium and an ABE product stream separated by pervaporation. Advantages due to the high flux of ABE through the SDS membrane are quantified by repeating the same experiment with a commercially available PDMS membrane in the pervaporation module.
4.2 Experimental

4.2.1 Membrane Preparation

A SDS copolymer with PS block molecular weights of 22 kg/mol and PDMS block molecular weight of 104 kg/mol was purchased from Polymer Source. 60 wt% of the sample was the SDS triblock copolymer, 30 wt% was the polystyrene-\textit{b}\textendash{}polydimethylsiloxane diblock copolymer, and 9.3 wt% was PS homopolymer (Viscotek GPC, Malvern). The polydispersity index of the polymer was 1.3 and the volume fraction of PDMS was 72% in the triblock copolymer. The same polymer was used in reference [37]. A supporting membrane (Biomax PBHK100205), purchased from Millipore, consisted of a porous polyethersulfone layer with a pore size cutoff of 100 kg/mol, and a non-woven polyester layer beneath the polyethersulfone. 1 g of SDS was dissolved in 20 mL of cyclohexane (Sigma Aldrich, used as received). The supporting membrane was cut into a 10x10 cm square and attached onto a 3 in diameter silicon wafer using double-sided tape, with the polyethersulfone layer facing upward. The silicon wafer with the supporting membrane attached was placed on a spin coater, and 6 mL of the SDS/cyclohexane solution was placed on the membrane, thoroughly covering the entire area of the membrane. The polymer was spin-coated at 300 rpm for 40 sec. The membrane was then dried at room temperature for a day. A commercially available supported PDMS membrane was purchased from Pervatech. Each pervaporation experiment was conducted on a different piece of circular SDS or PDMS membrane (area = 37 cm²).

4.2.2 Scanning and Transmission Electron Microscopy

Cross-sectional scanning electron microscopy (SEM) samples were obtained by cryo-fracturing the membranes with support in liquid nitrogen. Samples were sputter coated with 5 nm of Au before imaging. SEM images were obtained on a Zeiss ULTRA 55 analytical SEM operating at 5 kV.

Thin transmission electron microscopy (TEM) samples with thicknesses of approximately 120 nm were microtomed at -120 °C on a Leica EM FC6 and picked up on lacey carbon coated copper grids (Electron Microscopy Sciences). TEM experiments were conducted on a Philips CM 200 FEG using acceleration voltage of 200 keV. Double tilt series images were collected in the angle range -60° ~ 60° for each tilt series. Exposure time for image collection was set to 1 second. Fiducial gold with 5 nm diameters were deposited on the sample to facilitate alignment of the tilt series images. Alignment and reconstruction were done using the IMOD tomographic reconstruction software package. The reconstructed tomogram was segmented and colored using Avizo Fire.

4.2.3 Aqueous Butanol Pervaporation Experiments

Pervaporation experiments with 2 wt% aqueous butanol solutions were conducted on a bench top unit manufactured by Sulzer Chemtech, as described in reference [37], [28]. The SDS and PDMS membranes were placed in a membrane holding module and the butanol solution feed was pumped
across the membrane at a rate of 3 L/min. The membrane temperature was maintained at 37 °C. On the permeate side of the membrane, a vacuum of ~2 mbar was applied using a vacuum pump (Welch, model 2014) and the permeate stream was condensed in a cold trap using dry ice/isopropanol at -70 °C. The permeate was collected in a cold trap for 30-60 min. The permeate phase-separates into a butanol-rich phase and a water-rich phase. After measuring the mass, the permeate was diluted with water to form a single phase solution and the ABE concentrations were measured by high performance liquid chromatography (HPLC) using a Prominence UFLC instrument (Shimazu). The compositions of both the feed and permeate streams were monitored by HPLC as a function of time. Average values of four separate permeate collections are presented.

4.2.4 Fermentation

All fermentations were carried out with *Clostridium acetobutylicum* ATCC824 purchased from the American Type Culture Collection (Manassas, VA, USA). *C. acetobutylicum* cultures were inoculated and cultivated in clostridia growth medium (CGM, in g L⁻¹: glucose 70, yeast extract 5, ammonium acetate 2, sodium chloride 1, potassium phosphate monobasic 0.75, potassium phosphate dibasic 0.75, L-cysteine-hydrochloride monohydrate 0.5, magnesium sulfate heptahydrate 0.1, ferrous sulfate heptahydrate 0.01, manganese sulfate monohydrate 0.01). All cultures were maintained in CGM with 25 wt% glycerol for long-term storage at -80 °C. Fermentation precultures were started by the addition of 0.5 mL glycerol stock in 10 mL of CGM and incubated at 37 °C overnight.

Fermentations at the 1.25 L and 1.0 L scale were carried out in 3-L bioreactors (Bioengineering AG, Switzerland) with a 2-L working volume. Seed cultures of CGM (100 mL) were inoculated with the preculture described above (4 mL), and grown in 150 mL anaerobic serum bottles at 37 °C until the OD₆₀₀ (optical density at a wavelength of 600 nm) reached 2.0. 60 mL of the seed culture was used to inoculate the bioreactor. The bioreactor was equipped with an automatic controller that maintained pH ≥ 5.0 during the fermentation, using a 5 M KOH solution. Nitrogen gas was sparged into the bioreactor at a rate of 200 mL/min to maintain an anaerobic environment. To minimize losses of volatiles, specifically the loss of acetone through the gas exhaust port, a cooling condenser attached to a RTE7 water bath (4 °C) was used. Agitation in the bioreactor was set to 200 rpm and the fermentation temperature was held at 37 °C.

A Shimadzu Prominence HPLC system equipped with both an RID and DAD detector was used to analyze metabolite concentrations for glucose, acetate, butyrate, acetone, butanol, and ethanol. Samples were injected onto a Bio-Rad Aminex HPX-87H column with a Cation H guard column equilibrated to 35 °C. A mobile phase of 5 mM H₂SO₄ was pumped through the column at 0.7 mL/min. Concentrations were determined based on a six-point calibration. Glucose consumption rates were determined from real-time glucose concentration measurements on a YSI Biochemistry Analyzer equipped with a glucose membrane.

The glucose concentration in the reactor was measured in real time every 4-6 hours and used to determine the microbe’s glucose consumption rate. Based on the calculated glucose consumption rates from the previous time points a concentrated feed (500 g/L glucose, 50 g/L yeast extract) was
pulsed into the fermenter in order to maintain a glucose concentration between 5-40 g/L between time points.

### 4.2.5 Pervaporative-Fermentation

The bioreactor described above was also used in the pervaporation experiments. Figure 4.1 shows a schematic of the pervaporative-fermentation setup. Part of the fermentation broth was circulated into a pervaporation module that was identical to that used in the aqueous butanol pervaporation experiments described above. The main difference was that liquid nitrogen was used in the cold trap due to the volatility of acetone and ethanol.

The pervaporation module was connected after 18 hours of simple batch fermentation to ensure commencement of the solventogenesis phase. This marked the start of the continuous pervaporative-fermentation experiment wherein glucose in the reactor was monitored and concentrated media was manually fed into the bioreactor. The glucose concentration in the reactor was measured every 4-6 hours and the amount of glucose consumed by the microbes during that time was added in the reactor via a concentrated feed (500 g/L glucose, 50 g/L yeast extract).

![Figure 4.1 Schematic diagram of the pervaporative-fermentation setup.](image-url)
4.2.6 Permeability Calculations

The relation between molar flux of permeated species \( i \), \( J_i \), and permeability of species \( i \), \( P_i \), is given by Wijmans and Baker [15].

\[
J_i = \frac{P_i}{t} \left( x_i y_i p_{i,\text{sat}} - y_i p_{\text{permeate}} \right)
\]

Here, \( t \) is the thickness of the membrane, \( x_i \) is the feed mole fraction, \( y_i \) is the activity coeffient, \( p_{i,\text{sat}} \) is the saturated vapor pressure at feed conditions, \( y_i \) is the permeate mole fraction, and \( p_{\text{permeate}} \) is total permeate pressure. Activity coefficients were calculated by the van Laar equation, and saturation vapor pressures of the pure components were calculated from the Antoine equation [48].

Selectivity of species \( i \) (\( \alpha_i \)) is a measure of the enrichment of species \( i \) in comparison to water by permeation through the membrane. Subscripts \( B \) and \( W \) denote butanol and water.

\[
\alpha_B = \frac{P_B}{P_W}
\]

Separation factor (\( \beta_i \)) of species \( i \), which is used commonly to determine membrane separation performance, was calculated with the following equation.

\[
\beta_B = \frac{Y_B}{Y_w} / \frac{X_B}{X_w}
\]

Here, \( X_i \) and \( Y_i \) are weight concentrations of \( i \) in the feed and permeate.

4.3 Results and Discussion

4.3.1 Membrane Characterization

The cross-sectional structure of the supported SDS and PDMS membranes used in pervaporative-fermentation was studied by SEM and the results are shown in Figure 4.2. The thickness of the commercial PDMS membrane is about 0.5 µm while that of our SDS membrane is 2 µm. The nanoscale morphology of the SDS copolymer was studied by transmission electron microtomography experiments conducted on thin sections of a free-standing membrane made by solvent casting with the same solution that was used to make the supported SDS membranes, and the results are shown in Figure 4.3. The cross-sectional view in Figure 4.3a shows hexagonally packed bright PS cylinders in a dark PDMS matrix. The average length of the PS cylinders is relatively short, and this is more clearly seen in the three-dimensional tomogram shown in Figure
4.3b. It is likely that this short cylinder length is due to the finite polydispersity index of our copolymer. The ends of the cylinders can be regarded as topological defects, and the high concentration of topological defects may be related to the presence of uncoupled diblock copolymer and PS homopolymer in the sample and the relatively high polydispersity index of the block copolymer. Selective transport of organics through the membrane occurs primarily through the dark PDMS matrix phase in Figure 4.3 [37].

Figure 4.2 Scanning electron microscopy image of the (a) PDMS and (b) SDS membrane cross-sections. The porous support layers are on the left side of the images, and the gray, dense regions to the right of the support layers are the selective (PDMS and SDS) layers.
Pervaporation experiments with a 2 wt% aqueous butanol solution were performed using both SDS and PDMS membranes. Butanol was chosen as the organic constituent because it is the major product and the most toxic biofuel produced in *C. acetobutylicum* fermentations [6]. Table 4.1 shows the results of these experiments where the flux and permeability of butanol and water through the two membranes are listed. Despite the fact that the commercial PDMS membrane is significantly thinner than the SDS membrane, the butanol flux through the SDS membrane is 2.5-fold greater than that through the PDMS membrane. The water flux through the SDS membrane is only 1.5-fold larger than that through the PDMS membrane. It is likely that the lower flux through the PDMS membrane is due to the cross-linked nature of the membrane; the PDMS chains in the SDS membrane are not cross-linked. One might expect lower flux through the SDS membranes due to the presence of rigid PS domains that do not transport butanol and water.

**Figure 4.3** (a) Transmission electron microscopy image of a free-standing SDS membrane. (b) Reconstructed 3D image of region inside the yellow box in (a).
effectively. However, rapid butanol and water transport, due to the non-cross-linked nature of the PDMS chains in SDS more than compensates for this effect. Stretching of the PDMS blocks due to microphase separation may also affect transport properties of the SDS membranes [25, 37]. The differences in fluxes between the membranes are manifested in the butanol and water permeability reported in Table 4.1. Butanol selectivity, $\alpha$, is significantly higher for the SDS membrane (Table 4.1).

Table 4.1 Data from the binary butanol/water pervaporation experiment is shown from the SDS membrane and the PDMS membrane. Flux of each component was measured and the separation factor, permeability, and selectivity were calculated.

<table>
<thead>
<tr>
<th>membrane material</th>
<th>thickness ($\mu$m)</th>
<th>butanol flux (g/m²·h)</th>
<th>water flux (g/m²·h)</th>
<th>separation factor $\beta$</th>
<th>butanol permeability $\times 10^{12}$ (mol·m/m²·s·Pa)</th>
<th>water permeability $\times 10^{12}$ (mol·m/m²·s·Pa)</th>
<th>selectivity $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>2</td>
<td>420</td>
<td>1600</td>
<td>24</td>
<td>13</td>
<td>8.2</td>
<td>1.6</td>
</tr>
<tr>
<td>PDMS</td>
<td>0.5</td>
<td>170</td>
<td>1100</td>
<td>16</td>
<td>1.3</td>
<td>1.3</td>
<td>1.0</td>
</tr>
</tbody>
</table>

In a previous publication, we described pervaporation of aqueous ethanol mixtures through SDS membranes [37]. The thicknesses of the membranes used in that study were 100–150 μm. In contrast, the membranes used in this study were 2-μm thick. The butanol permeability through a 150-μm thick SDS membrane is $25 \times 10^{-12}$ mol·m/m²·s·Pa. The butanol permeability reported in Table 4.1 is much lower than this value. Further work is needed to identify the reasons for the observed thickness dependence of permeabilities through block copolymer membranes. Similarly, the permeabilities of 100-μm thick PDMS membranes reported in Reference [78] is significantly higher than that given in Table 4.1 for a 0.5-μm thick membrane. Offeman and Ludvik have shown that the permeability of ethanol through PDMS membranes decreases with decreasing thickness [79].

4.3.2 Pervaporative-Fermentation

Results were obtained for three fermentation experiments: (1) A simple batch fermentation in which pervaporation was not used to remove the products from the bioreactor. (2) Pervaporative-fermentation with the SDS membrane. (3) Pervaporative-fermentation using the commercial PDMS membrane. The fermentation volume was 1.25 L for the three experiments.
Figure 4.4 (a) Butanol concentrations, (b) cell optical density, and (c) butanol removal rate through the membranes versus fermentation time for the simple batch fermentation (○), pervaporative-fermentation with PDMS membrane (□), and pervaporative-fermentation with SDS membrane (Δ). Lines in plots were drawn to guide the eye and arrows depict when the pervaporation module was initiated.

Figure 4.4a shows the butanol concentration in the bioreactor ([BuOH]_r) at different time points during the three fermentations. Butanol, the major product in *C. acetobutylicum* fermentations, is produced after the acidogenesis phase of cell metabolism ends, which is around 10 hours into the fermentation. The arrow in Figure 4.4a represents the time at which circulation to the pervaporation module was initiated in the pervaporative-fermentation experiments (t = 18 h). The concentration of butanol at t = 18 h ranges between 2 and 4 g/L in all experiments. In the simple
batch process, \([BuOH]\), rises rapidly and saturates at about 13 g/L and butanol production ceases at \(t = 28\) h. The increase in \([BuOH]\), obtained during pervaporative-fermentation using both SDS and PDMS membranes are similar. Butanol concentrations in both cases increase more slowly, reaching a maximum of about 13 g/L at \(t = 62\) h.

Figure 4.4b shows the optical density of cells (OD\(_{600}\)) at different timepoints during the three fermentations. OD\(_{600}\) values lie between 6 and 8 at \(t = 18\) h when circulation to the pervaporation module was initiated. In the simple batch process, OD\(_{600}\) reaches a maximum of 10 at \(t = 32\) h and decreases slightly at longer times due to cell death. In pervaporative-fermentation with the PDMS membrane, OD\(_{600}\) increases monotonically until \(t = 45\) h and saturates at a value of 15 for \(46 \leq t \leq 64\) h. A decrease in OD\(_{600}\) after 64 h signifies cell death and sporulation. In pervaporative-fermentation with the SDS membrane, OD\(_{600}\) increases monotonically until \(t = 54\) h, and saturates at a value of about 27 for \(54 \leq t \leq 62\) h before decreasing due to cell death. The data in Figure 4.4b show that the differences in permeabilities of the SDS and PDMS membranes (Table 4.1) have a qualitative effect on pervaporative-fermentation. It is interesting to note that these differences occur even though the time dependence of \([BuOH]\), in both cases is similar (Figure 4.4a).

Figure 4.4c presents the butanol removal rate during pervaporative-fermentation using SDS and PDMS membranes. The advantage of higher butanol permeability of the SDS membrane is clearly seen in these data. The butanol removal rate obtained with the SDS membrane is significantly higher at all times. It appears that the higher butanol removal rate in the SDS membrane enables the cells to reach a higher density during pervaporative-fermentation.

![Figure 4.5](image)

**Figure 4.5** Total amount of butanol produced versus fermentation time for the simple batch fermentation, pervaporative-fermentation with SDS membrane, and pervaporative-fermentation with PDMS membrane. Lines in the plot were drawn to guide the eye.
Figure 4.5 shows the total mass of butanol produced (butanol in the bioreactor and butanol removed by pervaporation) as a function of time during the three fermentations. In the simple batch fermentation, production ceased after $t = 32$ h, and 13 g of butanol were produced in total. In pervaporative-fermentation with the PDMS membrane, butanol was produced steadily until $t = 64$ h, and a total of 33 g of butanol was produced. In pervaporative-fermentation with the SDS membrane, production of butanol ended around $t = 62$ h, and 49 g of butanol was produced in total.

Table 4.2 summarizes biofuel production characteristics obtained during the three fermentations. All three fermentations began with the same number of cells. Nonetheless, significant differences in the amount of glucose consumed and ABE produced are evident in the two pervaporative-fermentations. The volumetric productivity in the simple batch fermentation was 0.45 g/L·h. In the pervaporative-fermentation with the PDMS membrane, the volumetric productivity was 0.66 g/L·h, and in the pervaporative-fermentation with the SDS membrane, the volumetric productivity was 0.94 g/L·h. The specific productivity (g/L·h·OD$_{600}$) is similar in all cases, suggesting the increase in volumetric productivity for pervaporative-fermentations was not due to improvement of cell performance, but because of the large increase in cell population. The efficacy of glucose to ABE conversion, defined by the yield (moles of glucose equivalent converted to ABE/moles of glucose consumed), is also similar in all cases. This suggests that the underlying metabolic processes for ABE production are not affected by pervaporation. Losses of biofuels due to nitrogen sparging have not been accounted for. Acetone is the most volatile fermentation product. That the ABE compositions reported here are similar to those reported in the literature suggest that losses due to sparging are not significant.

**Table 4.2** Glucose consumption, ABE produced, volumetric productivity, specific productivity, and yield are measured and calculated for the simple batch fermentation, pervaporative-fermentation with the PDMS membrane, and pervaporative-fermentation with the SDS membrane. Yield is defined as (moles of glucose equivalent converted to ABE/moles of glucose consumed). The glucose equivalences were calculated assuming 1:1, 1:1, and 1:2 stoichiometric ratios for glucose to acetone, butanol, and ethanol.

<table>
<thead>
<tr>
<th>fermentation type</th>
<th>glucose consumed (g)</th>
<th>ABE produced (g)</th>
<th>volumetric productivity (g of ABE/L·h)</th>
<th>specific productivity (g of ABE/OD$_{600}$ L·h)</th>
<th>yield (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>simple batch</td>
<td>83.45</td>
<td>5.83</td>
<td>16.56</td>
<td>4.80</td>
<td>0.45</td>
</tr>
<tr>
<td>PDMS</td>
<td>198.57</td>
<td>17.18</td>
<td>32.65</td>
<td>3.71</td>
<td>0.66</td>
</tr>
<tr>
<td>SDS</td>
<td>275.67</td>
<td>20.13</td>
<td>48.98</td>
<td>8.63</td>
<td>0.94</td>
</tr>
</tbody>
</table>
Table 4.3 Flux of each component was measured for both SDS and PDMS membranes. \( \beta_{\text{butanol}} \), \( \beta_{\text{acetone}} \), and \( \beta_{\text{ethanol}} \) are separation factors for butanol, acetone, and ethanol.

<table>
<thead>
<tr>
<th>membrane material</th>
<th>water flux ((\text{g/m}^2\cdot\text{h}))</th>
<th>butanol flux ((\text{g/m}^2\cdot\text{h}))</th>
<th>acetone flux ((\text{g/m}^2\cdot\text{h}))</th>
<th>ethanol flux ((\text{g/m}^2\cdot\text{h}))</th>
<th>( \beta_{\text{butanol}} )</th>
<th>( \beta_{\text{acetone}} )</th>
<th>( \beta_{\text{ethanol}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>1300</td>
<td>220</td>
<td>91</td>
<td>23</td>
<td>21</td>
<td>22</td>
<td>5.8</td>
</tr>
<tr>
<td>PDMS</td>
<td>770</td>
<td>110</td>
<td>55</td>
<td>6</td>
<td>14</td>
<td>19</td>
<td>6.4</td>
</tr>
</tbody>
</table>

The efficacy of the SDS and PDMS membranes during pervaporative-fermentation are quantified in Table 4.3 where average permeate fluxes of water and ABE are given. The fluxes are consistently higher for the SDS membrane than for the PDMS membrane. It is interesting to note that the separation factors (\( \beta \)) of acetone and butanol are also higher for the SDS membrane, although the ethanol separation factor was higher for the PDMS membrane.

Table 4.4 Permeabilities of butanol and water calculated from the pervaporative-fermentation data and compared with permeability values from the binary butanol/water pervaporation experiments.

<table>
<thead>
<tr>
<th>membrane material</th>
<th>butanol permeability ( \times 10^{12} ) (mol/m²·s·Pa)</th>
<th>water permeability ( \times 10^{12} ) (mol/m²·s·Pa)</th>
<th>selectivity ( \alpha )</th>
<th>butanol permeability ( \times 10^{12} ) (mol/m²·s·Pa)</th>
<th>water permeability ( \times 10^{12} ) (mol/m²·s·Pa)</th>
<th>selectivity ( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>13</td>
<td>8.2</td>
<td>1.6</td>
<td>8.4</td>
<td>6.2</td>
<td>1.4</td>
</tr>
<tr>
<td>PDMS</td>
<td>1.3</td>
<td>1.3</td>
<td>1.0</td>
<td>0.91</td>
<td>0.94</td>
<td>0.96</td>
</tr>
</tbody>
</table>
Table 4.4 compares the permeabilities obtained from aqueous butanol pervaporation experiments and the pervaporative-fermentation experiments with the SDS and PDMS membranes. The fermentation broth was modeled as a binary butanol/water mixture, i.e., binary activity coefficients were used to compute the effective driving force. The measured permeabilities of both butanol and water are slightly lower in the pervaporative-fermentation experiment. It is likely that this is due to our use of binary activity coefficients in our analysis of pervaporation of the complex fermentation broth. Membrane fouling in the fermentation experiments may also be responsible for some of the deviations seen in Table 4.4. We observed relatively small decreases in fluxes through the membranes as fermentation proceeded (e.g., the water flux decreased by 11% and 3% for SDS and PDMS membranes, respectively). Given the complexity of the pervaporative-fermentation experiment, the general agreement seen in Table 4.4 is noteworthy.

![Figure 4.6](image)

**Figure 4.6** Total amount of butanol (▲), acetone (■), and ethanol (●) produced versus fermentation time for a 1 L pervaporative-fermentation with the SDS membrane. Lines in the plot were drawn to guide the eye.

In addition to the three fermentation experiments discussed above, we conducted another pervaporative-fermentation experiment with smaller fermentation volume. Decreasing the fermentation volume to 1 L while using the same SDS membrane allowed the butanol removal rate to match the butanol production rate. Therefore, butanol concentration was maintained below the toxic level at all times during fermentation, and continuous production was observed. ABE production increased monotonically to 90 g (27 g acetone, 57 g butanol, 6 g ethanol) for 109 h until it was manually stopped (Figure 4.6).
Table 4.5 Data compiled from different pervaporative-fermentation experiments at 37 °C.

<table>
<thead>
<tr>
<th>Reference</th>
<th>microorganism</th>
<th>active membrane material</th>
<th>membrane thickness (µm)</th>
<th>total flux (g/m²∙h)</th>
<th>butanol separation factor ($β_{\text{butanol}}$)</th>
<th>volumetric productivity (g of ABE/L∙h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liu et al., 2011 [21]</td>
<td>C. acetobutylicum</td>
<td>PDMS</td>
<td>5</td>
<td>~700</td>
<td>9-22</td>
<td>-</td>
</tr>
<tr>
<td>Chen et al., 2013 [22]</td>
<td>C. acetobutylicum</td>
<td>PDMS</td>
<td>8, 16</td>
<td>784, 556</td>
<td>10.3, 7.03</td>
<td>0.314</td>
</tr>
<tr>
<td>Van Hecke et al., 2013 [23]</td>
<td>C. acetobutylicum</td>
<td>PDMS</td>
<td>1</td>
<td>621</td>
<td>16.8–19.8</td>
<td>0.37–1.13</td>
</tr>
<tr>
<td>Li et al., 2014 [74]</td>
<td>C. acetobutylicum</td>
<td>PDMS/silicate-1</td>
<td>7</td>
<td>486</td>
<td>31.6</td>
<td>0.97</td>
</tr>
<tr>
<td>This work</td>
<td>C. acetobutylicum</td>
<td>SDS</td>
<td>2</td>
<td>1634</td>
<td>21</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>C. acetobutylicum</td>
<td>PDMS</td>
<td>0.5</td>
<td>941</td>
<td>14</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>C. acetobutylicum</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ATCC 824</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DP 217</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ATCC 824</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.5 compares the results of the present study with published results on ABE pervaporative-fermentations [21-23, 74]. The total flux (water and ABE biofuel) obtained in our PDMS based pervaporative-fermentation is higher than that of prior studies. This may be attributed to our use of a thinner PDMS membrane (Table 4.5). The total flux obtained with the SDS membrane is significantly higher than in all other ABE pervaporative-fermentations. The butanol separation factor is highest when PDMS/silicalite-1 membranes are used but the addition of silicalite-1 appears to lead to a significant decrease in flux. The volumetric productivity of SDS pervaporative-fermentation is comparable to results reported by Van Hecke et al. and Li et al. We conclude, based on both our results and previously published work, that SDS membranes are more effective for in situ product removal for pervaporative ABE fermentation than cross-linked PDMS membranes.

4.4 Conclusions

We demonstrate the efficacy of polystyrene-\textit{b}-polydimethylsiloxane-\textit{b}-polystyrene membranes for \textit{in situ} product removal of biofuels by pervaporation during \textit{C. acetobutylicum} ABE fermentations. Using pervaporative-fermentation, we were able to alleviate two major problems hindering commercialization of ABE fermentation: product inhibition and low productivity. Pervaporative-fermentation with the SDS membrane resulted in higher volumetric ABE productivity, ABE production, and cell density, when compared with the batch process and the pervaporative-
fermentation using a state-of-the-art commercial PDMS membrane. Aligning the fermentation volume with the pervaporation module’s capacity to remove biofuel enabled continuous ABE production at high cell density. The effective permeabilities of butanol and water obtained during pervaporative-fermentation were consistent with results from pervaporation experiments on binary butanol/water mixtures. Further work on optimizing factors such as membrane composition and thickness for pervaporative-fermentation is warranted and ongoing.
Chapter 5. Crosslinked PDMS-derived Triblock Copolymer Membranes for High Temperature Pervaporation††

5.1 Introduction

The efficiency of the permeation mechanism in pervaporation for a specific chemical species is determined by the solubility and diffusivity of the species for the membrane material. The two most significant advantage of using pervaporation for separation are that it is a highly selective process, and that it can be employed as an *in situ* product recovery method [80, 81].

It has been shown in many researches that pervaporation can be used as an effective *in situ* product recovery method for biofuel production via fermentation [20-22, 74]. In addition to fermentation, pervaporation has also been demonstrated as an *in situ* product removal method for a chemical reaction which produced furfural, a precursor molecule for liquid fuels, from biomass-derived xylose [14]. *In situ* product removal is important to the productivity of this chemical reaction because by selectively removing the target product of the reaction, less side products from furfural is formed as furfural is continually removed from the reactive solution.

To the extent of our knowledge, prior to Reference [14], pervaporation has never been applied as an *in situ* product removal method for biofuel production by chemical catalysts. Here, it was found in laboratory-scale to have similar effectiveness as that of liquid-liquid separation, a commonly used separation technique for furfural production from xylose, and was predicted in simulation to potentially have better yields and selectivities than that those of liquid-liquid extraction. However, due to the high reaction temperature of the reaction environment (140 °C), an external loop was required in order to integrate the membrane process with the existing reaction. The furfural-containing reactive solution was cooled down before flowing past the pervaporation membrane, and was heated back up to reaction temperature once looping back to the reactor. This type of an external loop results in high energy costs, as well as in reduction of productivity.

The temperature limitation exists for most pervaporation membranes because they are made from polymers. While polymers do not start degrading at very high temperatures (normally above 200 °C) [82], they undergo phase changes such as melting and glass transition [83] at the high temperatures (above 100 °C) necessary for operating most chemical reactions utilized for

†† This chapter contains collaborative work adapted with permission from collaborators Alex Wang and Nitash P. Balsara.
producing biofuels [11-13, 84], including the one studied in Reference [14]. These phase changes are detrimental to the mechanical properties of the polymer, thus making it hard for the polymer membrane to maintain a stable physical boundary between the liquid feed and the permeate vapor. Therefore, overcoming the temperature limitation of polymeric pervaporation membranes is a crucial challenge that must be overcome to employ pervaporation as in situ product recovery process for a chemical reactions used to product biofuels.

We have shown previously that polydimethylsiloxane (PDMS)-derived block copolymers are very effective membrane materials for removing biofuels or biofuel-like organics from aqueous solutions [37, 85]. Attaching mechanically rigid polymer blocks, such as polystyrene (PS) or polyethylene (PE), to either sides of PDMS blocks enabled the resulting pervaporation membrane to retain the good permeability and good selectivity of PDMS while being physically robust enough to form membranes of small thicknesses and large areas. However, these polymers also cannot withstand high temperatures; the glass transition temperature ($T_g$) of PS is 100 °C, $T_g$ of PDMS is -123 °C, and the melting temperature ($T_m$) of PE ranges from 101 to 145 °C, depending on the linearity [44].

In this study, we use the same design concept of fabricating PDMS-derived triblock copolymers. In order to make them compatible to high temperatures, we study the possibility of forming crosslinks within the mechanical polymer block. Here, we synthesize two polymers, polybutadiene-$b$-polydimethylsiloxane-$b$-polybutadiene (BDB) and polyethylene-$b$-polydimethylsiloxane-$b$-polyethylene (EDE), and investigate the potential of fabricating crosslinked polymeric pervaporation membranes where crosslinks are formed within the polybutadiene and polyethylene block of each polymer. We discuss the necessary membrane casting and crosslinking conditions. We further compare the crosslinked triblock copolymer membrane to its uncrosslinked analog by performing differential scanning calorimetry (DSC) measurements and high temperature pervaporation experiments.

5.2 Experimental

5.2.1 Polymer Synthesis

![Chemical structures of (a) polybutadiene-$b$-polydimethylsiloxane-$b$-polybutadiene (BDB) and (b) polyethylene-$b$-polydimethylsiloxane-$b$-polyethylene (EDE)](image)

Figure 5.1 Chemical structures of (a) polybutadiene-$b$-polydimethylsiloxane-$b$-polybutadiene (BDB) and (b) polyethylene-$b$-polydimethylsiloxane-$b$-polyethylene (EDE)
Polybutadiene-\(b\)-polydimethylsiloxane-\(b\)-polybutadiene (BDB) of molecular weight 147 kg/mol was synthesized as in Reference [86], and polyethylene-\(b\)-polydimethylsiloxane-\(b\)-polyethylene (EDE) of molecular weight 149 kg/mol was synthesized by hydrogenating the BDB [86]. The chemical structure of BDB and EDE are depicted in Figure 5.1. Both polymers have polydimethylsiloxane (PDMS) blocks of 87 kg/mol, and each of the polybutadiene (PB) block is 30 kg/mol, while each of the polyethylene (PE) block is 31 kg/mol.

### 5.2.2 Solubility Parameter Calculation [87]

The Hansen solubility parameter for dispersion (\(\delta_D\)), for polar (\(\delta_P\)), and for hydrogen bonding (\(\delta_H\)) interactions for PB, PDMS, PE, and various solvents were obtained from Reference [87]. Each polymer’s Ra, a weighted difference between the Hansen solubility parameters of the polymer and those of a solvent, was calculated by the following equation:

\[
Ra^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2
\]

Here, the subscripts 1 and 2 denote the polymer and the solvent, respectively. The relative energy difference (RED) is calculated by dividing the Ra by Ro, the interaction diameter of the polymer determined experimentally.

\[
RED = \frac{Ra}{Ro}
\]

The Ro is the maximum Ra that enables dissolution of the polymer. Thus, it can be inferred that for a polymer/solvent pair with RED > 1, the polymer would not dissolve in the solvent.

### 5.2.3 Membrane Casting and Crosslinking

BDB and EDE described above were solvent-cast to form membranes and then were subsequently heated for the crosslinking process. Chloroform, \(o\)-xylene, toluene, cyclohexane, and tetrahydrofuran (all were from Sigma Aldrich, used as received) were used as casting-solvents. Around 0.5 g of polymer was used to cast each membrane, and the polymer/solvent solution for membrane casting was around 0.5 g/10 mL in polymer concentration. For the polymer solutions used to cast crosslinked membranes, 5 wt% of the polymer weight of dicumyl peroxide (Sigma Aldrich) was added to the solution right before casting. Dicumyl peroxide was not added to the polymer solutions for casting uncrosslinked membranes.
A stainless-steel ring with 2 in-diameter was placed on top of a non-porous polytetrafluoroethylene (PTFE) sheet, and polymer/solvent solution was poured into the metal ring. For the crosslinked membrane used in pervaporation, a PTFE petri dish of 3 in-diameter was used instead of the stainless-steel ring for casting. This was due to the slight decrease in membrane area during crosslinking. The entire setup was placed on top of a temperature-controlled membrane castor so that temperature could be controlled as needed. The ring was covered lightly with aluminum foil and a funnel was placed on the top of the foil. After making sure the polymer/solvent solution was dry, which on average required about 12 hours, the stainless-steel ring, polymer membrane, and PTFE sheet was brought into a vacuum oven.

For the uncrosslinked membranes, the vacuum oven was used to dry the membrane for 24 hours at room temperature. For the crosslinked membranes, the oven was brought up to the target temperature under vacuum, and was maintained at that temperature for 24 hours. After the 24 hours, the oven was cooled and the polymer membrane was peeled off of the stainless-steel ring and the PTFE sheet.

5.2.4 Gel Ratio

To determine the percentage of the membrane that has been crosslinked, we put a piece of the crosslinked polymer membrane in boiling cyclohexane (~80 °C) with agitation. The solution was stirred for 24 hours under constant temperature, and the undissolved membrane pieces were taken out of the solution and dried in a vacuum oven for another 24 hours. The weight of the membrane before and after the cyclohexane treatment was compared, and the gel ratio, defined here as the ratio of the two masses, was calculated.

5.2.5 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was conducted to measure the $T_m$ and $T_c$ of the polymers. Polymer membrane samples of around 4 mg in weight were sealed in aluminum pans. An initial heating scan was performed where temperature was increased at a rate of 5 °C/min to 160 °C. Cooling and heating scans were performed, where the temperature range was from -70 °C to 160 °C at cooling and heating rates of 5 °C/min and -5 °C/min, respectively. Data from the cooling and the second heating scans are reported.

5.2.6 Pervaporation

A bench-top pervaporation unit was custom-built by modifying a membrane separation unit (Millipore). This unit consists of a 82 mL-, cylindrical reaction vessel where the membrane is placed on the bottom. The effective area of the membrane was 13.9 cm$^2$. The commercially purchased unit was altered to include a thermocouple and a sampling tube accessed from the top.
of the unit, and a heating tape around the reactor for temperature control. Vacuum of ~3 mbar was applied on the other side of the membrane, where the permeate was collected in a cold trap placed in liquid nitrogen. Pervaporation experiments using furfural aqueous solution were performed at different temperatures. The furfural concentration of the feed solution was in the range of 2.8 – 12 g/L. High performance liquid chromatography (Ultra High Performance Liquid Chromatograph system, Shimadzu) was used to analyze the concentration of the feed and permeate solutions. Normalized flux was calculated to compare the pervaporation data obtained from different membranes and different feed concentrations. It is defined here as flux normalized by the feed concentration and the membrane thickness and was used as an alternative to permeability. Permeability could not be calculated due to lack of activity coefficient data for furfural at high temperatures. Separation factor ($\beta$) was calculated using the following equation:

$$\beta = \frac{Y_F}{Y_W} / \frac{X_F}{X_W}$$ (5.3)

where $X$ and $Y$ denote weight concentrations in the feed and the permeate, respectively, and subscripts $F$ and $W$ denote furfural and water, respectively.

5.3 Results and Discussion

5.3.1 Crosslinked Triblock Copolymer Membranes

![Figure 5.2 RED of various solvents with respect to (a) PDMS and PB, and (b) PDMS and PE. In (a), $\Delta$, $\Diamond$, and $\Box$ denote toluene, chloroform, and tetrahydrofuran, respectively. In (b), $\Diamond$ denotes o-xylene.](image)
The solubility of each of the polymers in various solvents was estimated by calculating the relative energy differences (RED) from Hansen solubility parameters [87]. The choice in casting-solvents is important in determining not only the dissolution of the polymer, but also in the quality of the final membrane [69, 88]. This is due to the nano-structures formed by self-assembly in block copolymer membranes [29]. The final structure of the polymer membrane can be affected by the choice in casting-solvent, and because one of the blocks is impermeable, the difference in morphology can result in less efficient permeation [33, 69, 89, 90]. RED can be used to estimate the solubility, an indication of affinity, between a polymer and a solvent. The RED between each block of the polymers (BDB and EDE) and various solvents were calculated using Equations 5.1-2 from the experimental section (Figure 5.2).

In the case of BDB, three of the solvents with the highest solubilities for BDB were used as casting-solvents: chloroform, toluene, and tetrahydrofuran (THF) (Figure 5.2a). Only chloroform was able to completely dissolve BDB at room temperature; toluene and THF was required to be heated to 80 °C and 60 °C, respectively, for complete dissolution of BDB. Each solution was solvent-cast at the temperature used for dissolution, and was subsequently crosslinked at 120 °C. Figure 5.3 shows the membranes after crosslinking. The chloroform-cast membrane is fractured into many pieces (Figure 5.3a). The toluene-cast membrane, for an unknown reason became yellow, and has large-scale grains and fractures (Figure 5.3b). The THF-cast membrane also very inhomogeneous with large-scale grains and fractures (Figure 5.3c).

Although all three of the membranes exhibited gel ratios of around 0.9, indicating good crosslinking efficiency, none of the membrane were suitable for pervaporation because of the fractures in the membranes. One of the reasons for the inhomogeneity and fractures might be that some crosslinks are forming while the membrane is being casted. PB is a readily-crosslinked material due to the presence of double bonds, so the casting temperature required for dissolving the block copolymer could have induced some crosslinking the PB phase before the membrane was completely dry. Another reason for this might be the poor intrinsic mechanical properties of the BDB.

In the case of EDE, all of the solvents had higher affinity for the PDMS block than for the PE block (Figure 5.2b). The crystallinity of the PE block prevented the EDE from dissolving even in the best solvent for both blocks, chloroform, at room temperature. Fortunately, PE starts crosslinking at much higher temperatures than PB; thus, there were not any limitations in heating the EDE/solvent solution. However, the four best solvents for EDE, chloroform, hexane, dioxane, and vinyl acetate, have boiling temperatures of below the $T_m$ of PE, which in literature is in the range of 101- 145 °C [44]. Therefore, o-xylene, which has a boiling temperature of 144 °C, was selected as the casting-solvent for EDE.
Figure 5.3 Images of the (a) chloroform-cast, (b) toluene-cast, and (c) tetrahydrofuran-cast BDB membranes. The diameter of each of the membranes is 2 in.

Figure 5.4 Images of the EDE membranes cast with o-xylene at (a) 95 °C, (b) 105 °C, and (c) 115 °C.
EDE completely dissolved in o-xylene at 95 °C. However, casting at 95 °C resulted in an inhomogeneous membrane with macroscopic granular structures (Figure 5.4a). Increasing the casting temperature to 105 °C resulted in the disappearance of the granular structures, and the membrane is homogeneous and no macroscopic features were visible to the eye as well as with an optical microscope (Figure 5.4b). Increasing the casting temperature even further to 115 °C resulted in the formation of bubbles trapped inside the membrane (Figure 5.4c). We think this is happening because the casting temperature is nearing the boiling temperature. From this, we conclude that 105 °C is the optimal casting temperature for the EDE/o-xylene solution.

The EDE membrane casted at 105 °C was further annealed at 200 °C in a vacuum oven. The gel ratio for the crosslinked EDE membrane was found to be 0.82. The degree of crosslinking is lower than that of the crosslinked BDB because of the lack of double bonds in the PE, which makes it more difficult for the radical initiators to create radicals in the polymer. Unlike the crosslinked BDB membrane, the crosslinked EDE membrane appeared to be homogeneous and could be used to hold sufficient vacuum in the pervaporation setup.

5.3.2 Comparison of EDE and Crosslinked EDE Membranes

The properties crosslinked EDE (xEDE) membrane, were compared to those of an uncrosslinked EDE membrane by DSC and pervaporation experiments. The uncrosslinked EDE membrane was prepared by the absence of dicumyl peroxide and the crosslinking processing step at 200 °C. The DSC cooling and heating curves are compared in Figure 5.5. For the EDE membrane, T_m of the PE block is observed at 102.9 °C, and two T_c (crystallization temperature) of the PE block are observed at 60.5 °C and 88.7 °C (Figure 5.5a). For the xEDE membrane, T_m of PE is at 89.4 °C, and only one T_c of PE, at 73.8 °C, can be observed (Figure 5.5b). For both membranes, T_m of PDMS is observed at similar temperatures: -40.5 °C and -41.5 °C for EDE and xEDE, respectively. The T_g of PDMS was not observable in our temperature range, as it is usually known in literature to be below -100 °C [44].

The difference between T_m of PE for EDE and that for xEDE is more than 10 °C. A similar difference is observed for T_c of PE. We attribute the significant decrease in T_m and T_c of PE in xEDE to the presence of crosslinks. Since there are crosslinks placed randomly in the PE domain of xEDE, the crystallization of PE is more susceptible for disruption. The second, smaller T_c peak observed in EDE disappears in the xEDE; this also may due to the crosslinks limiting a second type of crystallization in the PE. Using a similar reasoning, it can be inferred from the similarity of T_m for PDMS in EDE and xEDE that there are not any significant number of crosslinks formed within the PDMS domain.
The normalized furfural and water fluxes of EDE and xEDE at temperatures from 50 °C to 110 °C are compared in Figure 5.6. The normalized furfural flux data of the EDE and xEDE resemble each other very closely at all temperatures (Figure 5.6a). The normalized water fluxes of the two membranes also are very similar (Figure 5.6b), as well as the furfural separation factor (β) (Figure 5.6c). The increase in flux with increasing temperature is observed as expected; this is due to the increase in the thermodynamic driving force. The similarities in flux and β suggests that the permeation mechanism through the PDMS domain is not affected by the addition of crosslinks in the PE domain.

Even though the flux data from EDE and xEDE are similar, the temperature range at which each membrane failed to maintain a physical barrier between the feed and permeate was different. The EDE membrane failed between 95 - 110 °C. The xEDE failed between 110 - 140 °C. The failure temperature range for the EDE membrane corresponds well to the $T_m$ of PE (102.9 °C). The xEDE was able to maintain the structural integrity even after the melting of the PE at 89.4 °C. This can be attributed to the presence of chemical crosslinks present in the PE phase.

Figure 5.5 Differential scanning calorimetry curves for (a) EDE and (b) crosslinked EDE membranes.
5.4 Conclusions

In this study, we have studied the possibility of forming crosslinks within the structural blocks of block copolymer pervaporation membranes in the goal of fabricating pervaporation membranes with good high-temperature tolerance. Two potential membrane materials, polybutadiene-\(b\)-polydimethylsiloxane-\(b\)-polybutadiene (BDB) and polyethylene-\(b\)-polydimethylsiloxane-\(b\)-
polyethylene (EDE), were studied, and only the EDE was able to form crosslinked, homogeneous membranes. By comparing crosslinked an uncrosslinked EDE, we were able to demonstrate that the presence of crosslinks result in higher heat resistance without any loss in permeation properties.
Chapter 6. Summary

The objective of this research was to gain better understanding of PDMS-derived block copolymer membranes for application in \textit{in situ} biofuel recovery. By tuning the mechanical block and the transporting block, we aimed to design a pervaporation membrane with good transporting property and good structural stability. We have studied the physical properties determining the permeation mechanisms of biofuels through these block copolymer membranes, as well as the application of the membranes in \textit{in situ} processes.

In Chapter 2, we studied the influence of block copolymer morphology on the permeation properties of block copolymer membranes. Morphologies where the matrix was consisted of the transporting block resulted in a much higher permeability and selectivity than those of lamellar morphologies. The difference in the permeabilities was discovered to be originating from the effect of morphology on the diffusion mechanism.

In Chapter 3, the effect of pore penetration of the block copolymer layer on permeability was studied. We were able to directly image the pore penetration layer via transmission electron microscopy, and by assuming a certain pore penetration layer thickness, we were able to successfully calculate the effect of the resistance originating from the pore penetration layer and fit it to the thickness dependent permeability observations.

In Chapter 4, we assembled an \textit{in situ} pervaporative-fermentation and used the PDMS-derived block copolymer membrane for \textit{in situ} product recovery. We succeeded in demonstrating a semi-continuous pervaporative-fermentation experiment.

In Chapter 5, the possibility of forming crosslinks within the mechanical block of the block copolymer membranes to enhance the temperature stability was studied. We were able to form polyethylene-\textit{b}-polydimethylsiloxane-\textit{b}-polyethylene membrane which had crosslinks within the polyethylene domain. The presence of the crosslinks enhanced the heat tolerance of the membrane without resulting in any permeability loss.
References


