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**EFFECT OF NONSOLVENT ADDITIVE ON THE SURFACE MORPHOLOGY AND
THE GAS SEPARATION PERFORMANCE OF
POLY(2,6-DIMETHYL-1,4-PHENYLENE)OXIDE MEMBRANES**

by

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**Submitted in Partial Fulfilment
of the requirements of the degree of
DOCTOR OF PHILOSOPHY**

**School of Graduate Studies
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ABSTRACT

Integrally skinned asymmetric membranes were prepared from poly(2,6-dimethyl-1,4-phenylene)oxide (PPO) using different nonsolvent additives. These nonsolvent additives consisted of branched and linear alcohols ranging from C₃ to C₁₀. Permeation data of these membranes were obtained from a constant pressure permeation system for pure gases of CO₂, CH₄, O₂ and N₂. An empirical correlation relating the pure gas permeance ratio of CO₂/CH₄ and the structural components of the nonsolvent additives has been proposed.

The surface of the membranes was characterized by atomic force microscopy (AFM). It was observed that there were two types of surface morphologies: merged nodules and discrete nodules. The appearance of the nodules were reflected in the mean roughness data, R_a. It was revealed that membranes with smaller and merged nodules resulted in higher pure gas permeance ratios for O₂/N₂ and CO₂/CH₄ with the exception of 3,5,5-trimethyl-1-hexanol and 3-ethyl-2,2-dimethyl-3-pentanol. The microscopic studies showed that the membranes containing discrete nodules resulted in lower pure gas permeance ratios for O₂/N₂ and CO₂/CH₄. It was observed that nonsolvent additives that possess a long straight hydrocarbon chain such as 2-ethyl-1-hexanol, 1-octanol and 2-decanol produced the highest pure gas permeance ratios.

The polymer solutions from which the membranes were made were characterized through intrinsic viscosity and surface tension measurements. The intrinsic viscosity studies revealed that as the intrinsic viscosity increased, the chances of entanglement of the polymer molecules increased. As a result, the pure gas permeance for CO₂/CH₄ increased with the exception of 3,5,5-trimethyl-1-hexanol. The surface tension studies showed that as the surface tension of the solutions increased, the pure gas permeance for CO₂/CH₄ and O₂/N₂ increased. This was due to the increase of the capillary forces within the spherical

particles of the polymer-rich phases.

Plasma-etching is a powerful tool for investigating the structure of the skinlayer of asymmetric membranes. This process involves the gradual etching of the skinned membrane surface by highly reactive particles from an oxygen gas plasma. The rate of etching was low at 0.1×10^{-6} m/min. The membranes were etched at 30, 60, 120 and 190 sec. Pure gas permeances using CO₂, CH₄, O₂ and N₂ were determined for the etched and unetched membranes. The morphology of these membranes was determined from scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM of the cross-section of the membranes showed that there is a transition in the membrane structure from the dense layer to the layer with visible pores. AFM images of the top surfaces of the membranes showed that mean roughness of the nodules increased linearly as the membrane is exposed to longer periods of etching time.

RÉSUMÉ

Plusieurs membranes asymétriques furent préparées à partir du poly(2,6-diméthyl-1,4-oxide phénylique) (POP) utilisant des additifs nonsolvables. Ces additifs nonsolvables consistaient d'alcools types branchés et types linéaires avec une étendue du C_3 au C_{10} . Les données de perméation de ces membranes furent obtenues d'un système de perméation à pression constante pour le gaz CO_2 , CH_4 , O_2 et N_2 sous format pure. Une corrélation empirique reliant rapport de perméabilité CO_2/CH_4 avec celui des composantes structurales des additifs nonsolvables fut proposée.

Les surfaces des membranes furent caractérisées par l'utilisation de la microscopie à force atomique (MFA). Deux types de morphologie de surface furent observés: nodules fusionnés et nodules détachés. La rudesse de la surface démontrait l'apparence des nodules à la surface. Il a été révélé que les membranes avec les nodules plus petits et fusionnés ont produit des rapports O_2/N_2 et CO_2/CH_4 plus élevés sauf pour celui du 3,5,5-triméthyl-1-hexanol et du 3-éthyl-2,2-diméthyl-3-pentanol. Les études microscopiques ont démontré que les membranes contenant les nodules détachés produisirent des rapports O_2/N_2 et CO_2/CH_4 plus bas. Il fut observé que les additifs nonsolvants possédant une longue chaîne d'hydrocarbure droite comme celles du 2-éthyl-1-hexanol, 1-octanol et du 2-decanol produisirent le plus grand rapport de perméabilité des gaz purs.

Les solutions de polymère utilisées pour fabriquer les membranes furent caractérisées par des mesures de viscosité intrinsèques et tension de surface. Les études de viscosité intrinsèques ont révélé qu'une augmentation de celle-ci augmentait aussi le mélange des molécules des polymères. Ceci a pour effet d'augmenter la perméabilité du CO_2/CH_4 sauf pour le 3,5,5-triméthyl-1-hexanol. Les études de tension de la surface démontrèrent qu'en augmentant la tension de la surface des solutions, la perméabilité du CO_2/CH_4 et O_2/N_2 augmenta aussi. Ceci était due à une augmentation des forces capillaires à

l'intérieure des particules sphériques des phases riches en polymère ce qui produit la fusion de celles-ci.

L'enlèvement au plasma est un puissant outil pour étudier la structure de la couche extérieure des membranes asymétriques. Le procédé comprend l'enlèvement graduelle de la couche supérieure par des particules hautement réactives d'un plasma émanant d'une source de gaz d'oxygène. La vitesse d'enlèvement de la matière était de 0.1×10^{-6} m/min. Les membranes furent exposées pour 30, 60, 120 et 190 secondes. La perméance des gaz purs y compris le CO_2 , CH_4 , O_2 et de N_2 fut déterminée pour les membrane exposées et non exposées au plasma. La morphologie de ces membranes fut déterminée en utilisant la microscopie à électron cherchant (MEC) et le MFA. Le MEC de profile des membranes ont démontré qu'il y a une transition dans la structure de la membrane débutant de la couche dense à la couche dotée de pores visibles. Des images MFA du dessus des surfaces des membranes ont montré que la rudesse moyenne des nodules accroit linéairement lorsque la membrane est exposée à des périodes d'enlèvement plus longue.

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NOMENCLATURE

Abbreviations

AFM	atomic force microscopy
CED	cohesive energy density
DEOXO	catalytic deoxygenation system
EOR	enhanced oil recovery
MeOH	methanol
MMBtu	million British thermal unit
MMscfd	million standard cubic feet per day
SCFH	standard cubic feet per hour
OcOH	octanol
PPO	poly(2,6-dimethyl-1,4-phenylene)oxide
PSA	pressure swing adsorption
TCE	trichloroethylene
VPSA	vacuum pressure swing adsorption

Parameters/Symbols

c_p	concentration of polymer in solution (g/dL)
$f(x,y)$	surface of membrane relative to the center plane
ΔE	energy of evaporation (J/mol)
F_c	force resulting from capillary pressure (N)
F_G	force which resists deformation of the polymer particle (N)
ΔG_m	free enthalpy of mixing (J/mol)
ΔH_m	enthalpy of mixing (J/mol)
J_{vi}	volumetric flux of component i (mol/m ² .s)
K	constant from Mark-Houwink equation (dimensionless)
l	thickness of active layer of membrane (m)

L_x	length of scanned surface in the x -direction (nm)
L_y	length of scanned surface in the y -direction (nm)
M	number averaged polymer molecular weight (g/gmol)
N_0	Avogadro's number (6.023×10^{23} molecules/gmol)
p_i	partial pressure of component i (N/m ²)
P	permeability coefficient (mol/m.s.Pa)
P_c	capillary pressure (mN/m ²)
P/l	pure gas permeance (mol/m ² s.Pa)
r	radius of the "throat" that passes through the centers of the touching particles (m)
R	gas constant (J/mol.K)
R_0	dilute solution macromolecule radius (cm)
R_a	mean roughness of nodules (nm)
R_h	hydrodynamic radius of macromolecule (cm)
$R_{\max}$	maximum pore radius (m)
ΔS_m	enthalpy of mixing (J/mol.K)
T	temperature (K)
T_g	glass transition temperature (K)
v_i	volume fraction of component i in solution (dimensionless)
$v_{polymer}$	bulk (crystalline) polymer volume (cm ³ /molecule)
V_i	molar volume of component i in solution (m ³ /mol)
V_m	molar volume of solution (m ³ /mol)

Greek symbols

α	pure gas permeance rate ratio
β	constant from Mark-Houwink equation (dimensionless)
γ	surface tension, (dyne/cm) or (mN/m)
δ	solubility parameter, (J/m ³) ^{0.5} or (MPa) ^{0.5}
δ_d	solubility parameter due to dispersion forces, (J/m ³) ^{0.5} or (MPa) ^{0.5}

δ_p	solubility parameter due to polar forces, $(\text{J/m}^3)^{0.5}$ or $(\text{MPa})^{0.5}$
δ_h	solubility parameter due to hydrogen bonding forces, $(\text{J/m}^3)^{0.5}$ or $(\text{MPa})^{0.5}$
$\delta_{d,a}$	solubility parameter due to dispersion forces in nonsolvent additive, $(\text{J/m}^3)^{0.5}$ or $(\text{MPa})^{0.5}$
$\delta_{p,a}$	solubility parameter due to polar forces in nonsolvent additive, $(\text{J/m}^3)^{0.5}$ or $(\text{MPa})^{0.5}$
$\delta_{h,a}$	solubility parameter due to hydrogen forces in nonsolvent additive, $(\text{J/m}^3)^{0.5}$ or $(\text{MPa})^{0.5}$
$\delta_{d,ppo}$	solubility parameter due to dispersion forces in PPO, $(\text{J/m}^3)^{0.5}$ or $(\text{MPa})^{0.5}$
$\delta_{p,ppo}$	solubility parameter due to polar forces in PPO, $(\text{J/m}^3)^{0.5}$ or $(\text{MPa})^{0.5}$
$\delta_{h,ppo}$	solubility parameter due to hydrogen bonding forces in PPO, $(\text{J/m}^3)^{0.5}$ or $(\text{MPa})^{0.5}$
Δ	difference in solubility parameter between nonsolvent additive and PPO, $(\text{J/m}^3)^{0.5}$ or $(\text{MPa})^{0.5}$
ϵ	swelling factor (dimensionless)
η	viscosity of solution (Pa.s)
$[\eta]$	intrinsic viscosity (dL/g)
η_s	viscosity of the solvent (Pa.s)
η_{sp}	specific viscosity (dimensionless)
λ	mean free path (m)
μ_i	chemical potential of component i (J/mol)
μ_i°	chemical potential of component i at a standard reference state (J/mol)

Subscripts

i	component i
j	component j
f	feed
p	permeate

CHAPTER 1

INTRODUCTION

1.1 Motivation

There are three areas which are critical toward the success of membrane-based gas separations (Koros and Fleming, 1993). These areas are material selection, membrane formation and module and system configuration. The former two areas are what constitute the bulk of this study.

Poly(2,6-dimethyl-1,4-phenylene) oxide (PPO) has long been regarded as an attractive material for gas separation membrane applications (Toi et al., 1982; Yasuda and Rosengren, 1970; Chern et al., 1987). Looking back at the history of PPO membranes, the asymmetric membranes were originally developed for ultrafiltration applications (Broens et al., 1977). The PPO membranes were made from trichloroethylene (TCE) as the solvent and methanol as the nonsolvent bath. The resulting membranes had skin and the walls of the pores in the sublayer that were too dense and were not permeable to water.

The idea of introducing a more porous structure to the skin layer was achieved by adding

a nonsolvent additive, 1-octanol to the PPO/TCE solution (Broens et al., 1977,1978). The resulting membranes were tested for both their ultrafiltration properties (Broens et al., 1977) and their gas separation properties (Buys et al., 1981).

There have been extensive studies on the science behind PPO membrane formation. Some of these works include studies of phase separation phenomena in polymer solutions made from cellulose acetate, polysulfone, polyacrylonitrile and PPO (Broens et al., 1980); and the relationship of PPO/TCE/1-octanol and methanol to membrane formation (Wijmans et al., 1985). This research will be elaborated in the Literature Review section of this study.

The development of PPO asymmetric membranes for gas separation applications continued with the introduction of hollow fiber PPO membranes for the separation of CO_2/CH_4 and O_2/N_2 by Bauer et al. (1991) and Smid et al. (1991). Other studies on using PPO include modifying the structure of the polymer itself by adding carbonyl, methyl esterified carboxyl and bromine substituents (Story and Koros, 1992), preparing silylated derivatives of PPO (Perego et al., 1991) and preparing sulfonated derivatives of PPO (Kruczek and Matsuura, 1998). These modified membranes were tested for their gas performance.

1.2 Problem Statement

The focus of this research was to develop and evaluate new types of asymmetric poly(2,6-dimethyl-1,4-phenylene)oxide (PPO) membranes for gas separation applications, particularly, for CO_2/CH_4 and O_2/N_2 . Within this research was the subproject to elucidate the role of nonsolvent additives in the formation of the top skin layer morphology. Past studies have shown that nonsolvent additives have played an important role in the gas performance of PPO membranes. These additives used in the phase inversion process have been shown to increase gas permeation while maintaining selectivity. In particular,

the interactions among the PPO polymer, nonsolvent additive and solvent require elucidation.

1.2.1. Objectives

The following are the objectives of this research:

- (i) Development of new types of asymmetric PPO membranes using nonsolvent additives consisting of linear and branched alcohol molecules.
- (ii) Determination of the transport characteristics of these membranes by determining permeances toward pure gases of CO₂, CH₄, O₂ and N₂.
- (iii) Formulation of an empirical model to relate the structure of the nonsolvent additives to the transport characteristics of the membranes.
- (iv) Characterization of the skin-side surface morphology of these asymmetric membranes through optical microscopy.
- (v) Characterization of the molecular interactions among polymer/nonsolvent additive/solvent in their solutions by intrinsic viscosity measurements.
- (vi) Determination of the effect of interfacial tensions in polymer solutions and hence, the role of capillary pressure in nodule aggregation.
- (vii) Determination of the morphology of the skin layer through oxygen plasma etching studies.

1.2.2. Expected Contributions

The finding of this work will provide the following contributions to the fields of chemical engineering, membranology, separation technology, surface science, transport phenomena and mathematical modelling.

- (i) Optimization of conditions to prepare PPO asymmetric membranes for gas separation performance by various solvent-nonsolvent additive combinations.
- (ii) Determination of the role of structural elements of the additives which affect

membrane formation and hence, its performance.

- (iii) Quantitative and qualitative data resulting from the optical microscopy studies, which will provide an insight into the role of nodules in the gas separation process.
- (iv) Determination of the behaviour of the polymer molecules in solution prior to nodule formation, based on intrinsic viscosity and surface tension measurements.
- (v) Elucidation of the process of nodule formation on the skin layer of PPO asymmetric membranes.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Gas Separation Technology

2.1.1 History of Membrane Gas Separation Technology

Membrane gas separation technology application traces its roots to the 1830's when the first demonstrations of gas separations were carried out by using natural rubber membranes by Graham (Graham, 1866). More than a century later, in the 1940's, membranes were used for the separation of Uranium 235 (Werner, 1986). In the 1960's, commercial attempts to recover helium from natural gas using homogeneous membrane were unsuccessful due to low productivity (Stern, 1964; Stern et al., 1965). In order to improve productivity, the thickness of the membrane had to be reduced. This would, however, bring on increased pinhole defects on the membrane.

The discovery of Loeb and Sourirajan (1960) was seen as a breakthrough for developing commercially viable membranes for gas separation applications. They developed an asymmetric cellulose acetate membrane for reverse osmosis. This membrane consisted of two layers: the top layer formed a dense (skin) layer which carried out the liquid/liquid separation and the bottom layer formed a porous sublayer which provided the mechanical

support. However, two problems occurred when the membranes were dried. First, the porous structure would collapse and second, the selective layer would lose its separating properties. This problem was solved by Vos and Burris (1969) who developed a surfactant-aided method. The surfactant reduced the interfacial tension between the membrane pore walls and the water held in the pores. Thus, when the water evaporated, the porous structure remained rigid. Eventually, Gantzel and Merten (1970) would apply the discoveries of Loeb and Sourirajan for the separation of H_2/N_2 using cellulose acetate membranes.

Adequate productivities remained a problem until the mid-1970's with the development of a "composite" membrane (Ward et al., 1976) and the introduction of lamination to reduce pinholes (Salemme, 1977). Although both elements i.e. composite membrane and lamination were technically successful, it was found that the fabrication process and the properties of the membrane modules were not economically feasible for large scale commercial applications.

In the 1970's, DuPont (Hoehn, 1974; Pye et al., 1976) identified glassy polymers made up of selected polyimides, polyesters and polyamides with high intrinsic permeabilities. These polymers demonstrated the ability to be transformed into reverse osmosis asymmetric membranes (Panar et al., 1973). Therefore, in 1979, the focus for membrane research and applications was turned towards reverse osmosis.

Gas separation technology was largely ignored until the early 1980's when Monsanto developed and commercialized asymmetric bisphenol-A polysulfone hollow fibres, known commercially as the PRISM® separator (Henis and Tripodi, 1980). Due to the "energy crisis", Monsanto became strongly involved in the recovery of hydrogen from ammonia purge stream, refinery and petrochemical purge stream applications (Bollinger et al., 1982); and would later make this technology a reality (Graham, 1983).

Gas separation technology was then extended towards more demanding areas such as recovery of carbon dioxide from tertiary oil recovery in the 1980's (Graham, 1983). This technology was not as successful as the recovery of hydrogen and the focus was shifted to treatment of landfill gas and BTU upgrading of standard natural gas. These treatments became successful with the introduction of hollow fiber and spiral wound configurations by Dow and Separex, respectively (Schell, 1982; Cooley and Dethloff, 1985).

In the early '80s, several companies in the US, Japan and Europe became actively involved in membrane development. These companies included, Bend Research, Membrane Technology and Research Inc., Albany International and AG Technology. Universities also became strongly involved in the science of membrane development. In Canada, various groups at the National Research Council studied the effect of preparation variables such as shrinkage temperature and solvent used in the solvent-exchange process on the performance of a series of cellulose acetate membranes (Rangarajan et al., 1984; Minhas et al., 1985a, 1987; Lui et al. 1988a, 1988b). These studies showed that these variables greatly influenced the pore size and pore size distribution of the membrane.

In 1977, the Oxygen Enrichment Company introduced the the first commercial membrane oxygen enricher (Kondo, 1992). Although applicable to small scale production, large scale applications such as enriched air combustion have not been successful due to the high power requirement (Kondo, 1992). Along with the separation of oxygen, came the co-production of nitrogen. Prasad et al. (1994) observed that "the oxygen selective nature of present polymeric membranes renders them practically more suitable to the 'rejection' of oxygen from air to produce nitrogen."

As with hydrogen separation, Monsanto became a leader with small-scale generation of inert gas for shipping (Kelley, 1985), followed by the production of the Prism Alpha system in 1988. The system (still based on bisphenol-A polysulfone) offered three times the productivity while maintaining the same selectivity when compared to the original

Prism system. This performance was achieved by reducing the thickness of the selective layer. Table 2.1 shows some selected separation performance of membranes. The selectivities, α given represent the separation of pure gases except for the work by Story and Koros (1992). They used a gas mixture of CO_2/CH_4 .

As observed by Kesting and Fritzsche (1993), from 1960 to 1980, significant progress was made in almost every area of membranology: applications, research tools, membrane formation processes, chemical and physical structures, configurations and packaging. Yet, the field of gas separation has not fully matured.

2.1.2 Industrial Requirements and Applications of Carbon Dioxide/Methane Separation

Natural gas consists of a highly variable mixture of gases and vapours. The main component is CH_4 , with other impurities such as N_2 , CO_2 , He, H_2S and C_2H_6 as well as hydrocarbons ranging from C_2H_6 to C_8H_{18} (Medici, 1974). Some of these compounds have to be removed. Non-combustible gases such as N_2 and CO_2 lower the calorific value of the gas and add to the compression costs of transportation. Potentially corrosive gases such as CO_2 and H_2S , in the presence of water vapour, reduce the operating life of the metal pipeline. Also, the condensed vapours block pipelines and cause build-up of liquid resulting in operating problems.

Companies such as British Gas (Hamilton and Lavery, 1993) have begun to expand their natural gas treatment operations worldwide by exploiting remote or offshore reserves of natural gas. An example is the North Morecambe field on the UK continental shelf where appreciable amounts of CO_2 (up to 5.5%) have been found. The variability in gas quality in different fields means that there is a growing need for efficient and cost-effective gas treatment. Operational needs of the industry require the gas to be treated to meet transmission and storage specifications. When gas production is located offshore, most

Table 2.1. CO₂/CH₄ and O₂/N₂ separation performance of selected membranes.(i) Gas Pair: CO₂/CH₄

α	Membrane	Reference
58	Polyimide	Yamamoto et al. (1990)
14.3	Silyl- Poly(phenylene oxide)	Perego et al. (1991)
23.2	Carboxyl- Poly(phenylene oxide)	Story and Koros (1992)
13.8	Radel A PSF film	Ghosal et al. (1993)
33	Polyimide	White et al. (1995)
27	Polyimide	Hachisuka et al. (1996)
17.7	Polytrimethylsilylpropane film	Borisov et al. (1997)
25	Poly(phenylene oxide)	Khulbe et al. (1997)
43.4	Sulfonated- Poly(phenylene oxide)	Kruczek and Matsuura (1998)

(ii) Gas Pair: O₂/N₂

α	Membrane	Reference
4-5	Poly(phenylene oxide)	Pusch and Walch (1982)
4	Poly(phenylene oxide)	Wijmans et al. (1985)
5.1	Polycarbonate	Hellums et al. (1989)
2.9	Polyvinylalcohol	Zhang et al. (1989)
7.2	Polyimide	Yamamoto et al. (1990)
4.1	Silyl- Poly(phenylene oxide)	Perego et al. (1991)
4.5	Poly(phenylene ether)	Smid et al. (1991)
6.4	Radel A PSF film	Ghosal et al. (1993)
3.55	Poly(4-methyl-1-pentene)	Lin et al. (1996)
5	Poly(phenylene oxide)	Khulbe et al. (1997)
6.7	Sulfonated- Poly(phenylene oxide)	Kruczek and Matsuura (1998)

of the gas processing is performed at the onshore terminal. This is due to size and weight restrictions on offshore platforms. However, a minimum of treatment is still necessary. Current technologies employed in the purification of natural gas include cryogenics, physical adsorption, chemical absorption and direct conversion. These systems require large and complex plants with expensive operating and maintenance costs. Therefore, there is an economic incentive to find new or improved techniques for natural gas processing.

Membrane technology has several advantages over the competing processes stated above. Membranes are generally smaller and more compact. The advantages of their operation include fast startup and shutdown, minimum maintenance and operator attention, modularity and no moving parts (unless recompression is required).

The second industry that requires the recovery of CO₂ is in the oil fields where enhanced oil recovery (EOR) via CO₂ injection is practised (Zolandz and Fleming, 1992).

Recovery of CO₂ from the offgas is desirable due to economic and environmental reasons. The recovered CO₂ can be reinjected into the oil field. A minimum level of 95% CO₂ purity is required so that CO₂ may dissolve the oil in the underground strata. The minimum requirements also help to keep the injection costs low and to reduce the risk of damaging the underground strata.

The membrane application for this process is unique because first, over the life of the typical injection project, the volume of produced gas increases and second, the CO₂ content of that gas also increases with time. Other technologies cannot provide the flexibility of additional processing capacities (as needed) compared to the modularity of membranes. An example is the SACROC® unit owned and operated by Cynara, a subsidiary of Dow (Parro, 1984). This unit provided the additional processing capacity to the existing hot potassium carbonate plant.

The third application of membranes is in the recovery of methane from biogases such as landfill gas (Zolandz and Fleming, 1992). A typical composition of the gas is 40-45% CO₂, 50-56% CH₄ and 0.5-1% trace contaminants. The collected gas is compressed and pretreated before contacting with the membrane. An example of the process is where the enriched methane gas (at 90-96% recovery) is produced at a feed pressure in the range of 100-400 psig, and CO₂ is produced as a by-product at lower pressures.

An economic study of CO₂ recovery options based on cellulose acetate was carried out by McKee et al. (1991a, 1991b) at Kellogg. Figure 2.1 shows the comparison in technologies among amine, hybrid and membrane processes for the treatment of natural gases. The dashed lines represent the boundaries of preference between a single-stage membrane system and conventional amine process. Amine systems are generally preferred for operating parameters of high feed rate and low CO₂ concentrations. As the price of the feed gas increases, the range of operability for the amine system increases. Membranes are preferable at low flowrates due to the low capital investment regardless of feed gas price. As the CO₂ content increases, the savings due to membranes also increases. The hybrid system refers to a membrane/amine contactor configuration proposed in the same study. This system is favourable at the same feed rate as amine process but for high CO₂ concentrations. The range of operability increases as the price increases.

2.1.3 Industrial Requirements and Applications of Oxygen/Nitrogen Separation

Commercial-scale use of oxygen-enriched gas from membranes has not reached its full potential (Zolandz and Fleming, 1992) even though considerable effort has been invested in the research, development and commercialization of large scale applications such as enriched air combustion. According to Kondo (1992), membrane modules offered in the oxygen enrichment market have capacities ranging from 10 to 500 SCFH and oxygen purities ranging from 28 to 60%. These membrane modules have been limited to medical

(a) Economic region when feed gas = \$0.50/MMBtu.

(b) Economic region when feed gas = \$1.00/MMBtu.

Figure 2.1. Cost comparison of membrane, amine and hybrid systems. This was based on the recovery of CO₂ from the other components in natural gas. The dashed lines represent the boundaries of preference between a single-stage membrane system and conventional amine process (McKee et al., 1991a, 1991b).

(c) Economic region when feed gas = \$1.50/MMBtu.

(d) Economic region when feed gas = \$2.00/MMBtu.

Figure 2.1 (cont'd). Cost comparison of membrane, amine and hybrid systems.

uses. Compared to small-scale pressure swing adsorption (PSA) units, the modules are lighter and more inexpensive (Golan and Kleper, 1987). A small number of the membrane oxygen enrichment modules are used in specialty fields such as fermentation and copper smelting (Kondo, 1992).

In recent years, the demand for nitrogen has exceeded that of oxygen in industries such as petrochemicals, pharmaceuticals and food processing/packaging. Although nitrogen is produced primarily by cryogenic means, membrane air separation has established its commercial foothold in the production of nitrogen.

Laverty and O'Hair (1990) described a membrane process for the offshore production of nitrogen where it is injected into the oil-bearing strata. The two advantages of using nitrogen is that it can be generated offshore (from air separation) and it need not be recovered. It may also be injected into the reservoir to prevent reservoir subsidence. However, with the current low selectivities of O_2/N_2 of 6 or less and the inability of current membranes to produce high purity products containing only ppm levels of impurities, this process is not economically feasible.

In 1994, the production of nitrogen from air using membranes reached to over 2000 tons per day. Some of the production units that exist have capacities ranging from less than one ton per day to over 100 tons per day. The purity levels range from 95 to 99.95%. Although the market for nitrogen enriched air is shared by various technologies including cryogenic and PSA systems, it is estimated that by the year 2000, membranes will generate nearly 10% of the world nitrogen production.

Currently available commercial membranes for air separation include Prism Alpha membranes created by Permea and Generon II by Dow, of which both systems were created in 1985. Generon II was upgraded with a new membrane polymer. Its product flow rate is ten times higher and its product recovery is double that of the original

membranes (Heitz and Milne, 1990). Large-scale nitrogen production plants have also been installed, such as Linde NitroGen™ which produces 17,000 ft³/h of 97% pure nitrogen for a pharmaceutical industry (Zolandz and Fleming, 1992).

Figure 2.2 shows the boundaries where the different competitive technologies control in nitrogen production. Membrane systems dominate the market at nitrogen capacities from 1,000 to 100,000 SCFH and purity levels from 95 to 99.95%, by PSA from 10,000 to 100,000 SCFH and purity of 95-99.95% and by cryogenics at capacities higher than 100,000 SCFH and above 99.95% purity (Prasad and Thompson, 1990).

Figure 2.2. Economic operating regimes for recovery of N₂ from air (Prasad and Thompson, 1990).

2.2 Selection of Membrane Materials

Substantial amounts of data on the permeation of gases and vapours through rubbery and glassy polymers have been available for over 15 years (Stern, 1994). From the data gathered, the following conclusions were drawn. First, as the gas permeability of a polymer increases, its selectivity to different gas pairs generally decreases. Second, glassy polymers (their glass transition temperature, T_g is above the ambient temperature) tend to have high selectivities but low permeabilities while rubbery polymers (their T_g is below the ambient temperature) tend to have low selectivities but high permeabilities.

Before the introduction of glassy polymers, rubbery polymers were the basis for membrane materials. As noted above, this was due to the higher intrinsic permeability produced by rubbery membranes. However, this problem has been solved with the development of high-flux asymmetric or composite membranes made from glassy polymers (Stern, 1984; Koros and Chern, 1987; Kesting, 1985; Cabasso, 1987). Membranes made from glassy polymers have higher gas selectivity and good mechanical properties compared to that of rubbery polymers.

2.2.1 Poly(2,6-dimethyl-1,4-phenylene)oxide

There have been various studies on the relationship between structure and permeability of poly(phenylene oxide) and of its chemical modifications (Toi et al., 1982; Chern et al., 1987; Story and Koros, 1992; Ghosal and Chern, 1992; Ilinitich et al., 1992; Aguilar-Vega and Paul, 1993; Gagné, 1996; Khulbe et al., 1997; Kruczek and Matsuura, 1998). Among glassy polymers such as polycarbonates, polysulfones and cellulose acetates, PPO has higher permeability even though its overall selectivity is lower. Therefore, PPO is a promising polymer to develop membranes with potential in gas separation and is used in this study.

PPO was first produced by A.S. Hay (1986) by the copper-catalyzed oxidative coupling of 2,6-dimethylphenol. The melting point of PPO is 533 K. Figure 2.3 shows the basic structure of PPO. The presence of the aromatic ring on the main chain tends to dominate the structure and makes the polymer chain quite stiff although the presence of the ether group allows the chain to have a small degree of flexibility (Hay, 1986; and Sundarajan, 1990). This flexibility as well as the low-chain packing density of PPO allows for the high permeability of PPO to light gases (Story and Koros, 1992). Due to the presence of the aromatic ring, the polymer has excellent chemical and thermal stability (Mulder, 1992).

Figure 2.3. Basic structure of PPO.

PPO has a very high T_g (493 K) since its main chain contains an aromatic group. In the glassy state, the polymer segments cannot rotate freely around the chain (Mulder, 1992). Therefore, the free volume of the polymer is virtually constant. The free volume is defined as the volume unoccupied by the macromolecules.

PPO is a semi-crystalline polymer (Wijmans and Smolders, 1984). It consists of an amorphous region without any ordering and an ordered crystalline region as shown in Figure 2.4 (Mulder, 1992). The degree of crystallinity does not provide any information on the size and shape of the crystallites. The crystal lattice contains sections of adjacent linear polymeric chains. Crystallization is intermolecular with a number of segments of various chains arranged parallel to each other. Crystallites have a large influence on the mechanical and transport properties of polymers.

Figure 2.4. Amorphous region without ordering and an ordered crystalline region of PPO polymer.

2.3 Preparation and Formation of PPO Membranes

2.3.1 Phase Inversion Membranes Prepared by Immersion Precipitation

Most commercially available membranes are prepared from the phase inversion method. Phase inversion membranes are formed when a polymer in a liquid state is transformed into the solid state in a controlled manner. These membranes have an asymmetric structure as shown in Figure 2.5. It consists of a dense skin layer with the thickness of 0.1-0.5 μm and a porous sublayer of 0.1-0.2 mm in thickness. Both the skin layer and the porous sublayer are made from the same material.

One of the well-defined techniques used in the production of PPO phase inversion membranes is the technique of immersion precipitation. It has been studied by many authors (Manjikian et al., 1965; Koenhen et al., 1977; Guillotin et al., 1977; Kesting, 1985). A polymer solution consisting of polymer and solvent is cast onto a suitable

Figure 2.5. Cross-section of an asymmetric membrane.

support like a glass plate. The cast film is immersed in a nonsolvent coagulation media where precipitation occurs when the solvent and nonsolvent coagulation bath are exchanged. The resulting membrane structure is formed due to a combination of mass transfer and phase separation.

2.3.2 Phenomena of Phase Separation

The phase inversion process is highly complex since it is a combination of phase equilibria, the kinetics of phase separation and changes in morphological structures in non-dilute systems. There are three types of phase separation phenomena that occur in PPO polymer solutions and are thought to be responsible for the asymmetry of the membranes (Broens et al., 1977, 1980; Koenhen et al., 1977; Smolders, 1980). These phenomena are

- (i) liquid-liquid demixing
- (ii) crystallization of the polymer
- (iii) gelation

Each layer of the asymmetric membrane contains different changes in composition brought about by the phase separation phenomena. The formation of the skin layer is caused by gelation, possibly induced by crystallization and the formation of the sublayer is caused by liquid-liquid demixing followed by gelation of the polymer-rich phase.

Liquid-Liquid Demixing

The mechanism for this phenomena was proposed by Koenhen et al. (1977) for the system of polyurethane/dimethylformamide/water. Figure 2.6 shows the isothermal cross-section of a ternary system with a liquid-liquid demixing gap. The critical point, C' , is located at low to very low polymer concentrations. Above, and on the left side of the critical point, the homogeneous solution is thermodynamically stable. As the nonsolvent coagulation media is added, the components are still miscible. When the binodal line is reached, the solution becomes thermodynamically unstable and liquid-liquid demixing will occur. The composition within the two phase region always lies on a tie line and splits into two liquid phases of different compositions represented by two intersections between the tie line and the binodal.

Figure 2.6. Isothermal cross-section of a ternary system with a liquid-liquid demixing gap.

One of the ways in which liquid-liquid demixing can occur is by nucleation and growth of the second phase. In Figure 2.6, the point B' on the binodal line contains a concentrated polymer solution with a low amount of nonsolvent coagulation media (concentrated phase). Point D' contains a large amount of nonsolvent coagulation media with a minute amount of polymer in it (dilute phase). As the polymer solution becomes

thermodynamically unstable and when a continuous concentrated phase (B') is formed, a nucleus of composition D' starts to appear in the continuous phase. This nucleus, together with many other nuclei will grow to droplets and will coalesce. The growth of this phase will cease with the gelation of the surrounding polymer solution.

The nucleation of either the concentrated phase or the dilute phase depends upon the composition of the initial polymer solution with respect to the critical point, C'_r . Referring to the phase separation process described above, the nucleation and growth of the dilute phase occurs when the initial polymer concentrations lie on branch C'_rB' which is generally expected for solutions containing more than 10 wt.% of polymer (Broens et al., 1980).

Crystallization and Gelation

Crystallization is a type of phase separation. Studies have been reported of crystallization of PPO from toluene solutions (Koenhen et al., 1977). Other authors have reported that PPO can crystallize into irregular spherical shapes from different solvents (Barrales-Rienda and Pepper, 1967; Akers et al., 1968; Savolainen, 1974). It is also known that crystallization of PPO is only possible in the presence of certain solvents (Barrales-Rienda and Fatou, 1971; Janeczczek et al., 1978; Turska and Janeczczek, 1978).

The formation of ordered structures from polymer solutions depends upon the thermodynamic quality of the solution and the ability of the macromolecules to crystallize in the time available (Wunderlich, 1973). The thermodynamic quality of a polymer solution decreases when any one of the following occurs: loss of solvent, lowering of temperature or introduction of a nonsolvent. Crystallization is a kinetically slower process than liquid-liquid demixing for a polymer solution of medium concentration.

From medium to high concentrations, however, the increase in polymer supersaturation increases the rate of nucleus formation for crystallization. Liquid-liquid demixing remains the same since it is more dependent on the content of the nonsolvent coagulation media for its nucleation process. Along with the increase in the rate of nucleation and the limited growth rate for crystallization, the solution will contain numerous submicroscopical ordered regions, not much larger than the nucleus itself.

These ordered regions act as physical crosslinks in the polymer solution and together with other crosslinks of a different kind, a thermoreversible polymer gel is formed. The type of gel formation described above is the leading principle for structure formation in the skin of the membranes and for gelation of pore walls in the porous sublayer.

2.3.3 Phase Separation and Asymmetric PPO Membranes

Skin Formation

The determining factor in the formation of a skin layer on an asymmetric membrane is the local polymer concentration in the top layer of the polymer solution film. There are two methods in which this factor is demonstrated. First, the technique of precipitation of the polymer by controlled evaporation of the solvent in which a symmetric membrane is formed without a skin. Second, the technique of immersion precipitation in which an asymmetric membrane is formed.

In immersion precipitation, the polymer solution film is immersed into the nonsolvent coagulation media. The solvent will diffuse from the top layer of the film into the nonsolvent coagulation media at a rapid rate. As a result, the polymer concentration on the top layer increases. Gelation takes place when the nonsolvent coagulation media diffuses into the polymer solution film. The higher the polymer concentration becomes before nucleation in the skin sets in, the more numerous and the smaller will be the nuclei

due to supersaturation (Broens et al., 1980).

Nodular Structure

The physical structure of asymmetric membranes can be divided into (Kesting and Fritzche, 1993)

- (i) mechanical states of matter in which the structures are differentiated through density, mobility and order and
- (ii) morphology in which the structure is characterized by optical microscopy.

A linear macromolecule that exists in the glassy state is also known as an amorphous polymer, that is, it does not exhibit long-range order. There is no clear evidence about the disposition of the polymer molecules within the glassy state. However, it has been suggested that the order of the polymer begins with interactions between polymer segments whether of intramolecular or intermolecular origin.

Privalko and Lipatov (1974) adopted a folded chain model to represent the state of the polymer molecules. This is contrary to the proposal by Boyer (1985,1987). He proposed that the polymer molecules can be represented by models of simple collapsed random coils. Both studies conclude, however, that the collapsed random coil models are highly interpenetrating and should have far more entanglements than are found experimentally.

A combination of studies by Privalko and Lipatov (1974) and Boyer (1985, 1987) was proposed by several authors (Hsiue et. al., 1983; Yeh, 1972a, 1972b) in which the model of a “random-coil” folded-chain fringed micelle can be viewed as a sphere in three dimensions. These spherical particles are known as nodules. Their formation from spherical aggregates due to the buildup of ordered structural units (nuclei) in the skin was observed for a PPO ultrafiltration membrane by Broens et al. (1980) and was discussed in the previous section. There is no clear evidence about the disposition of polymer molecules within a nodule. However, polymer physicists (Boyer, 1987) agree that the

polymer molecules have some amorphous order in the form of folded-chain segments that run more or less parallel to one another over distances of at least 10 Å (Pace and Datyner, 1980).

Most of the early evidence of nodules comes from transmission and scanning electron microscopy studies (Schultz and Asunmaa, 1970; Kesting, 1973; Panar et al., 1973; Alegranti et al., 1975; Broens et al., 1977; Sanderson and Pienaar, 1978) and from filtration (water flux) and gas adsorption measurements (Broens et al., 1978; Le Moigne and Gramain, 1978). Yeh and Geil (1967) observed spherical structures with some paracrystalline order in poly(ethylene terephthalate). These structures were called crystalline nodules by Keith (1969). An assembly of closely packed spherical particles with diameters of 188 Å were observed by Schultz and Asunmaa (1970) for cellulose acetate reverse osmosis membranes through scanning electron micrographs.

The origin of nodules has been attributed to micelles (Panar et al., 1973), para-crystallites (Kesting, 1973), aggregates (Kamide and Manabe, 1985), inhomogeneities in the polymer solution (Kunst et al., 1976; Kunst and Vajnaht, 1977) or perturbations (Ray et al., 1985). Panar et al. (1973) studied the scanning electron micrographs of a polyamide-hydrazide asymmetric membrane. The surface structure showed a monolayer of micelles of about 400 to 800 Å in diameter. These spherical micelles appeared to be deformed and partly fused.

Kesting (1973) studied the gradual etched surfaces of cellulose acetate reverse osmosis membranes. The dense skin layer contained nodules that appeared to be ellipsoidal. The aggregation of these nodules revealed the presence of some crystalline structure. Therefore, it was concluded that these nodules represented an early phase in the development of crystallinity and they were called paracrystallites.

Kunst and Vajnaht (1977) identified inhomogeneities, otherwise known as

supermolecular aggregation in cellulose acetate casting solutions by measuring their rheological behaviour. The three variables studied, in characterizing the state of supermolecular polymer ordering in the polymer solution, were the nature of the solvent, the polymer concentration and the temperature.

Kamide and Manabe (1985) proposed a theory about the formation of aggregates through the study of phase separation phenomena of polymer solutions. As the polymer-rich phase separates as primary particles between 10 and 30 nm in diameter, these particles would collide and amalgamate into secondary particles of 50 to 300 nm in diameter. The secondary particles subsequently coagulate to form pores.

Ray et al. (1985) presented a model based on a thin-film stability theory. This model is illustrated in Figure 2.7. The liquid layer is bounded above by a gas phase. This system is subjected to random disturbances of arbitrary wave length. The molecules in the liquid phase are strongly affected by the solid phase through intermolecular interactions such as London dispersion forces or permanent dipole interactions. Therefore, the potential energy of molecules at the liquid/gas interface is altered. This can result in the growth of some wavelengths of the spectrum of random perturbations of the liquid/gas interface and the subsequent break-up of the thin film.

While most of the early studies on nodule structure were focused on membranes for liquid separation, Fritzsche et al. (1990a) also found nodules in the surface of asymmetric integrally skinned gas separation membranes of polysulfone.

Two conditions are required for the formation of nodules (Wienk et al., 1996). First, the diffusion process of solvent and nonsolvent coagulation media is rapid compared to that of the slow-moving polymer molecules. Second, nodules are formed over a surface layer

Gas phase

Figure 2.7. Liquid layer with an adjacent interface representing the thin-film stability theory (Ray et al., 1985).

which is less than $1.0\ \mu\text{m}$ in thickness and contains over 90% of the polymer concentration. Due to this high concentration, nucleation of a polymer-rich phase is not likely to take place. Therefore, the binodal and spinodal curves derived from equilibrium conditions cannot be used to explain the phenomenon of nodule formation.

Kimmerle and Strathmann (1990) postulated that nodules evolved from spheres formed during the nucleation of the polymer rich phase. Others (Pinnau and Koros, 1993; Boom et al., 1992) have suggested that due to the rapid diffusion rate of the solvent-nonsolvent coagulation media in forming the top layer, the polymer solution becomes unstable and crosses the spinodal curve. As a result of spinodal decomposition, the nodules are formed.

Wienk et al. (1996) proposed a new mechanism whereby two processes occur simultaneously in the nodule formation of gas separation membranes. First, the entanglement of adjacent clusters of polymer molecules due to the rapid solvent-nonsolvent coagulation media diffusion and the eventual disentanglement of polymer segments between the spheres. Second, the excess out-diffusion of solvent leads to

increased polymer concentration on the top layer which eventually leads to the vitrification of the polymer matrix. Hence, vitrification and disentanglement occur simultaneously. If vitrification is more rapid than disentanglement, the result is a gas separation membrane (Pinnau and Koros, 1993).

Experiments performed by Beerlage (1994) support this mechanism. He postulated that during membrane preparation strong tensions tend to be frozen in. Through solvent-nonsolvent coagulation media exchange and drying, enough free volume was created inside the flat nodules to relax these tensions. The flat molecular conformations rearrange into spherical conformations, and a large surface shrinkage results.

Porous Sublayer

In the formation of the porous sublayer, the formation of the skin will increase the resistance for the diffusion of the solvent out and the nonsolvent coagulation media into the sublayer of the polymer solution. As a result, phase separation will take place at a much lower polymer concentration compared to that in the skin. As mentioned above, this type of phase separation is liquid-liquid demixing.

There are two types of morphologies found in the porous sublayer of an asymmetric membrane. First, the formation of conical voids or “fingerlike cavities” is an important feature for ultrafiltration membranes. Second, a sponge structure is formed from the nucleation of the dilute phase and gelation of the polymer-rich phase.

There are two types of sponge structures that are formed from liquid-liquid demixing. A uniform pore structure is formed when the nucleation density does not vary much over the film thickness. This happens if the concentration of the polymer, at the locus where liquid-liquid demixing sets in, does not increase too much over the depth of the solution layer. The uniform pore structure is found in gas separation membranes. An open pore

sponge structure is obtained when a certain amount of coalescence of the drops occurs before the walls of the concentrated polymer solution between the pores solidify (Broens, et al., 1980).

2.3.4 Phase Separation in Quaternary Polymer Systems

Role of Nonsolvent Additive

The addition of a nonsolvent additive is used to improve the overall morphology and performance of membranes. Previous studies have shown that an interaction develops between the nonsolvent additive and polymer resulting in the swelling of the polymer (Keilin, 1964a, 1964b; King and Cantor, 1972; and King et al., 1972) or the formation of supermolecular aggregates (Kesting and Menefee, 1969; Kunst et al., 1976; Vásárhelyi et al., 1987; Ronner et al., 1989; Kesting and Fritzsche, 1993).

The concept of a swelling agent (a combination of solvent and nonsolvent additive) for PPO asymmetric membranes was first used by Broens et al. (1977). One of their studies was concerned with the formation of ultrafiltration membranes on the PPO/TCE/OcOH/MeOH system. The range of octanol as nonsolvent additive in the polymer solution was varied from 10 to 22 wt.%. Evidence taken from scanning electron micrographs showed that at concentrations of less than 15 wt.% of octanol, the membranes were not water permeable. Hence, the membranes were suitable for gas separation as shown by Buys et al. (1981). It was also observed that the addition of octanol caused structural changes in the skin layer, introducing a grainy structure. This structure consisted of densely packed crystalline nodules which contained voids through which water permeation by ultrafiltration was successful. The grainy structure has been found in a number of other polymers (Schultz and Asunmaa, 1970; Kesting, 1973; Panar et al., 1973; Alegranti et al., 1975).

Wijmans et al. (1985) studied the complicated quaternary relationship of PPO/TCE/OcOH/MeOH system. Cloud points were measured for five different ratios of OcOH and MeOH and the results are shown in Figure 2.8. It was concluded that MeOH was a stronger nonsolvent (coagulant) for PPO than OcOH. As mentioned earlier, crystallization is dominant at high PPO concentrations while liquid-liquid demixing is dominant at high nonsolvent coagulant concentrations. However, these two types of phase separation cannot be determined as liquid-liquid demixing is immediately followed by crystallization in the concentrated phase. Growth of the nuclei during crystallization was determined to be diffusion controlled from pulse-induced critical scattering experiments. The nucleation and growth process of PPO crystallization was determined to be governed by the concentration of PPO, and not by OcOH and/or MeOH.

As mentioned, membranes produced from concentrations of less than 15 wt.% of octanol were suitable for gas separation (Buys et al., 1981). Gas permeation characteristics were also determined using O_2/N_2 by Pusch and Walch (1982). Their highest attainable ideal separation factor was 5.0. Convective transport was taking place through defects or very small pores.

Figure 2.8. Cloud-point compositions at 25°C for five pseudo-ternary systems (Wijmans et al., 1985).

When the polymer solution film consisting of PPO/TCE/OcOH is immersed in the MeOH coagulation media, TCE and OcOH diffuse into the bath and the PPO concentration increases. The penetration of the MeOH into the film moves the liquid-liquid demixing boundary to the left of the phase diagram as shown in Figure 2.8. It is very difficult to visualize the coagulation by coagulation paths but increasing the OcOH content increases the occurrence of liquid-liquid demixing in the film. Thereby, this increases the number of pores and the pore radius in the top layer and produces membranes that are more suitable for water permeation.

A limited number of fundamental studies have been done on the effect of nonsolvent additive on asymmetric membrane formation. Beerlage (1994) described the association of a complex formation between dicarboxylic acids and polyimide. The acid is the nonsolvent additive for the polyimide/dimethylformamide system. This complex formation results in the decrease of the flexibility of the polyimide chain, thereby changing the properties of the polymer and the ultrafiltration characteristics of the membrane.

Solubility Parameter Approach in Predicting the Swelling of Linear Polymer Networks

The miscibility of two or more components is described by:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (2.1)$$

where ΔG_m is the free enthalpy of mixing. It is negative if two components mix together spontaneously. ΔH_m is the enthalpy of mixing. It determines the solubility.

The solubility parameter approach gives a qualitative description for describing polymer

solubility or polymer-penetrant interactions. Hildebrand and Scott (1949) derived the following equation which connects the energy of mixing of two components to their individual energies of evaporation.

$$\Delta H_m = V_m \left[\left(\frac{\Delta E_1}{V_1} \right)^{0.5} - \left(\frac{\Delta E_2}{V_2} \right)^{0.5} \right]^2 v_1 v_2 \quad (2.2)$$

where V_m , V_1 and V_2 are molar volumes of the solution, components 1 and 2, respectively; v_1 and v_2 are the volume fractions of components 1 and 2, respectively; and ΔE is the energy of evaporation. $\Delta E/V$ is also known as the cohesive energy density, CED, and the square root of the CED is known as the solubility parameter, δ .

$$\delta = \sqrt{\left(\frac{\Delta E}{V} \right)} \quad (2.3)$$

Therefore, equation (2.2) becomes:

$$\Delta H_m = V_m [\delta_1 - \delta_2]^2 v_1 v_2 \quad (2.4)$$

The solubility parameter, δ , is a result of three contributions (Hansen, 1967).

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2.5)$$

where δ_d is the solubility parameter due to dispersion forces; δ_p is the solubility parameter due to polar forces; and δ_h is the solubility parameter due to hydrogen bonding forces.

The affinity of a nonsolvent additive with respect to the polymer is inversely proportional to its distance, Δ from the polymer in the $\delta_d, \delta_p, \delta_h$ -space.

$$\Delta = \left[(\delta_{d,a} - \delta_{d,ppo})^2 + (\delta_{p,a} - \delta_{p,ppo})^2 + (\delta_{h,a} - \delta_{h,ppo})^2 \right]^{0.5} \quad (2.6)$$

where the subscripts *a* and *ppo* refer to nonsolvent additive and PPO, respectively.

Therefore, the interaction between the nonsolvent additive and the polymer can be predicted (Froehling et al., 1976) provided that there are no specific interactions upon mixing the two or more components. If there is a large difference between δ_1 and δ_2 , then the affinity between polymer and nonsolvent additive decreases. However, if $\delta_1 \approx \delta_2$, ΔH_m approaches zero and since ΔS_m is always positive, polymer and nonsolvent additive are miscible.

The physical properties of the nonsolvent additives are given in Table 2.2 (Acros Organics, 1996; Aldrich Chemical Company, 1995). All products had purities above 96%. These nonsolvent additives were chosen to represent a wide range of linear and branched alcohols, from propanol to decanol. The nonsolvent additives include isomers like 2-ethyl-1-hexanol and 1-octanol. The solubility parameters of the nonsolvent additives are given in Table 2.3. The results from Table 2.3 indicate that PPO and the nonsolvent additives are more miscible with each other compared with that of PPO and methanol since Δ for PPO/methanol is much larger compared to PPO/nonsolvent additives. This indicates that methanol is more suitable as the nonsolvent coagulation media.

Table 2.2. Physical properties of nonsolvent additives.

Nonsolvent additives	Molecular weight	Melting point (K)	¹ Boiling point (K)	² Density kg/m ³ (X 10 ⁻³)
2-propanol	60.1	183.65	355.4	0.785
2,2-dimethyl-3-pentanol	116.2		405	0.825
2,3-dimethyl-3-pentanol	116.2		413	0.833
2,4-dimethyl-3-pentanol	116.2		412-413	0.829
4,4-dimethyl-2-pentanol	116.2		410-410.5 98,125 Pa	0.815
2,4,4-trimethyl-1-pentanol	130.23		441-442 98,659 Pa	0.818
3-ethyl-3-pentanol	116.2		414 99,059 Pa	0.824
3-ethyl-2,2-dimethyl-3-pentanol	144.26	254	447	0.852
2-methyl-2-hexanol	116.2		414-415	0.812
2-methyl-3-hexanol	116.2		414-416 101,992 Pa	0.821
3,5,5-trimethyl-1-hexanol	144.26		466-467	0.824
2-ethyl-1-hexanol	130.23	197	456-459	0.833
6-methyl-2-heptanol	130.23		444-445	0.803

¹Boiling point at 101,325 Pa unless otherwise indicated.

²Density at 293 K relative to water at 277 K.

Table 2.2 (cont'd). Physical properties of nonsolvent additives.

Nonsolvent additives	Molecular weight	Melting point (K)	² Boiling point (K)	³ Density (kg/m ³) (X 10 ⁻³)
2,6-dimethyl-4-heptanol	144.26		451	0.809
1-octanol	130.23	258	469	0.827
2-nonanol	144.26	237-238	466-467	0.827
2-decanol	158.29		484	0.827

Table 2.3. Solubility parameters of nonsolvent additives and solubility parameter differences, Δ of PPO and nonsolvent additive (Matsuura, 1994).

Additive	δ_d (MPa ^{0.5})	δ_p (MPa ^{0.5})	δ_h (MPa ^{0.5})	δ (MPa ^{0.5})	Δ (MPa ^{0.5})
Poly(phenylene oxide)	12.3	2.7	4.9	13.51	n/a
methanol	18.82	14.91	24.47	28.26	23.97
2-propanol	16.91	7.48	17.34	25.35	14.10
2,2-dimethyl-3-pentanol	16.08	3.70	12.20	20.52	8.28
2,3-dimethyl-3-pentanol	16.08	3.70	12.20	20.52	8.28
2,4-dimethyl-3-pentanol	15.96	3.74	12.27	20.47	8.29
4,4-dimethyl-2-pentanol	16.08	3.70	12.20	20.52	8.28
2,4,4-trimethyl-1-pentanol	16.18	3.31	11.54	20.15	7.72
3-ethyl-3-pentanol	16.58	3.75	12.27	20.97	8.59
3-ethyl-2,2-dimethyl-3-pentanol	15.97	2.94	10.88	19.54	7.02
2-methyl-2-hexanol	16.58	3.75	12.27	20.97	8.59
2-methyl-3-hexanol	16.46	3.79	12.34	20.92	8.59
3,5,5-trimethyl-1-hexanol	16.27	3.00	10.98	19.85	7.26
2-ethyl-1-hexanol	16.99	3.08	11.13	20.55	7.81
6-methyl-2-heptanol	16.52	3.38	11.66	20.50	8.00
2,6-dimethyl-4-heptanol	15.75	2.86	10.72	19.26	6.77
1-octanol	17.45	3.46	11.79	21.34	8.64
2-nonanol	16.99	3.08	11.13	20.55	7.81
2-decanol	17.38	2.83	10.67	20.59	7.69

2.4 Characterization of Membranes

2.4.1 Characterization by Gas Transport

One of the methods used in the characterization of gas separation membranes is measuring their gas permeability. The permeability method will be described in Chapter 3, Materials and Methods. A membrane will separate gases only if some components pass through the membrane more rapidly than others. Transport in glassy polymers is most often controlled by penetrant size. Therefore, kinetic diameters of the gases used in this study based on zeolite sorption cutoffs, as given in Table 2.4, would be useful in predicting the permeability of gases.

Table 2.4. Kinetic sieving dimensions of CO₂, O₂, N₂ and CH₄ based on zeolite sorption cutoffs (Breck, 1974).

Molecule	CO ₂	O ₂	N ₂	CH ₄
Kinetic diameter (Å)	3.3	3.46	3.64	3.8

Models of Membrane Gas Transport

Mechanisms for gas transport through polymer membranes can be divided into two major groups and are illustrated in Figure 2.9. First, the mechanism of solution-diffusion occurs when gas molecules dissolve into the membrane and then diffuse across it. The sorption, unsteady and steady-state permeation using this mechanism has been described by the free volume theory and the dual sorption theory.

Cohen and Turnbull (1959) first described the diffusion of permeant between the polymer segments, from one “hole” to the other within the polymer. The “hole” is created from the fluctuations of local density due to thermal motion of the polymer. This theory was used by Stern et al. (1972) for interpretation of their permeability data through membranes.

(a) Solution-diffusion model

Gas dissolves into the membrane material and diffuses across it.

(b) Pore model

Knudsen diffusion through the pores. Pores with diameter less than the mean free path of the gas molecules allow lighter molecules to preferentially diffuse through the pore.

Figure 2.9. Mechanisms for gas separation using membranes.

The dual sorption model describes gas solubility in glassy polymers. Sorption occurs in two idealized environments (Barrer et al., 1958; Michaels et al., 1963). The first environment is the uptake of the permeant by dissolving into the polymer and is described by Henry's law relation. The second environment is the uptake by filling up the unrelaxed volume or "microvoids" in the polymer matrix and is described by a Langmuir type of sorption isotherm. The development of the application of the dual sorption model for permeation through glassy polymers has been extensively studied (Barrer et al., 1958; Michaels et al., 1963; Paul and Koros, 1976; Chan et al., 1978; Koros and Paul, 1978a, 1978b; Stannett et al., 1979; Chern et al., 1983; Koros and Chern, 1987).

The second mechanism of gas transport through membranes is described by pore models typical of the one shown in Figure 2.9(b). The pore models were originally proposed for liquid transport (Glückauf, 1965; Merten, 1966; Bean et al., 1969; Jacazio et al., 1972; Dresner, 1974; Jonsson and Boesen, 1975). Unlike the solution-diffusion mechanism, pore models such as the fine-pore model assumed the presence of open micropores on the active surface layer of the membrane.

Sourirajan (1970) proposed the preferential sorption-capillary flow model originally for reverse osmosis transport. The influence of the interaction force among the solute, solvent and membrane material on the flow of mass through the open capillaries is considered. This model can be extended for gas transport through membranes. Figure 2.10 shows the flow of two layers in the membrane pore. One layer of the pore contains the adsorbed gas molecules that have a strong interaction with the pore wall. These molecules are tightly packed and form a condensed phase at the gas-pore wall interface. The other layer contains the bulk gas phase and does not interact with the pore wall. These gas molecules diffuse through the membrane easily.

Three mechanisms were proposed to describe the free gas flow in a pore (Rangarajan et al., 1984). These mechanisms depended upon the size of the pore relative to the mean

free path of the permeating gas molecules. The mean free path, λ , is the distance a molecule travels before colliding with another molecule. Depending on the range of pore sizes present in the membrane, the contribution of these three mechanisms rely on the maximum pore radius, $R_{\max}$. Knudsen mechanism was dominant if the pore radius was much smaller than λ i.e. less than 0.5λ . Slip flow would occur if the pore radius was

Figure 2.10. Adsorbed gas layer in a membrane pore.

between 0.5λ and 50λ . For pore sizes higher than 50λ but less than $R_{\max}$, viscous flow would be the mechanism of gas transport. All mechanisms operate simultaneously if $R_{\max}$ is higher than 50λ .

Surface flow is the flow of the condensed phase of adsorbed molecules on the pore wall. Gilliland et al. (1958) proposed this two-dimensional force balance which is established between the spreading pressure of the adsorbed film and the frictional force exerted on the film when it moves at a steady velocity on a smooth surface. The surface is the interface formed between the adsorbed film and the membrane pore wall. Extensive studies have been carried out to correlate data of permeation of gases through polymeric membranes by the pore model (Rangarajan et al., 1984; Mazid et al., 1985; Minhas et al., 1985b; Lui et al., 1988a, 1988b; Tremblay et al., 1988; Yong et al., 1989a, 1989b).

Pores in integrally-skinned phase inversion membranes are seen as static two-dimensional

spaces between the structural elements which constitute their borders (Kesting, 1989). Separation of penetrants for gas separation membranes are controlled by their pores and/or pore rim elements, which constitute the intramolecular chain segment. The pores and their rim elements work in a manner similar to sieves which separate penetrants based mostly on the size and shape of both pores and penetrants. The approximate diameter of the pores are 2-5 Å. The size of penetrants used in this study is given in Table 2.4. Gas permeation occurs through the primary pores, which are found in the low density areas between the adjacent nodules and through pores found between the chains within the interior of the nodules.

Driving Force for Gas Separation

Gas separation in membranes occurs through pressure-driven diffusion. This process is spontaneous only if the change in chemical potential of the diffusing species is negative. For a component i in an ideal gas mixture, the chemical potential is given by

$$\mu_i = \mu_i^0(T) + RT \cdot \ln(p_i) \quad (2.7)$$

$\mu_i^0(T)$ is the chemical potential of pure component i at the system temperature T and the reference pressure of 1 atm. The change in chemical potential across the membrane from the feed f to the permeate p is given as

$$\begin{aligned} \mu_{ip} - \mu_{if} &= [\mu_i^0(T) + RT \cdot \ln(p_{ip})] - [\mu_i^0(T) + RT \cdot \ln(p_{if})] \\ &= RT \cdot \ln\left(\frac{p_{ip}}{p_{if}}\right) \end{aligned} \quad (2.8)$$

Since the difference in chemical potential must be negative, $\ln (p_{ip}/p_{if})$ must also be negative. Therefore, p_{ip} must be less than p_{if} . This difference in partial pressure provides the driving force for the transport of gas across the membrane.

From Fick's first law the equation for the flux of a given component i across the membrane is given by

$$J_{vi} = \left(\frac{P_i}{l} \right) (p_{if} - p_{ip}) \quad (2.9)$$

where J_{vi} is the volumetric flux of i across the membrane, P_i is the permeability of i in the membrane polymer, l is the thickness of the active layer, p_{if} is the partial pressure of i on the feed f side of the membrane and p_{ip} is the partial pressure of i on the permeate p side of the membrane. Pressure will be used in many equations although the fugacity driving force is more thermodynamically correct. If the pressure is less than 50 atm, the difference between pressure and fugacity is small (Zolandz and Fleming, 1992).

The pure gas permeance ratio, α_{ij} is determined by

$$\alpha_{ij} = \frac{P_i/l}{P_j/l} \quad (2.10)$$

2.4.2 Correlations Predicting Permeability and Permselectivity for Polymers and Polymeric Membranes.

Various correlations have been proposed to predict the permeability and permselectivities of permeants through polymers. Correlations based on the Hildebrand solubility

parameter in a solution-diffusion model were proposed by LaPack et al. (1994). The study was based on a silicone elastomer membrane made up of poly(dimethylsiloxane) and fumed silica. The feed and membrane phases were characterized by the Hildebrand solubility parameters and the equilibrium partitioning of substances between these two phases were modelled as solutions. The model had good predictive value over three or four orders of magnitude for the permselectivities of permanent gases, alkanes, chlorinated and brominated hydrocarbons, alcohols and aromatic hydrocarbons.

Li (1975) reported a generalized correlation to predict gas permeabilities through polymers using T_g of the polymer and the critical temperature, critical volume and molecular weight of the permeant. Teplyakov and Meares (1990) proposed correlations for inorganic and C_1 and C_4 hydrocarbon gases through different polymers using the solution-diffusion equation. Patil et al. (1995) proposed correlations for permeabilities through polymers based on parameters derived from the molecular structure of the permeant. It consisted of hydrocarbon gases and alcohols. The parameters were derived from molecular descriptors such as molecular connectivity, average molecular polarizability and molecular weight of the permeant.

Robeson et al. (1997) proposed a group contribution approach to predicting the permeability of O_2 , N_2 and He gases and permselectivities of O_2/N_2 and He/ N_2 through aromatic polymers such as polysulfones, polycarbonates, polyarylates, poly(aryl ketones) and poly(aryl ethers). The group contribution approach comes from the logarithmic relationship between the volume fraction of a specific group comprising the polymer repeat structure and the permeability contribution of that specific group. Some of the above studies will be used in this study to find correlations between the nonsolvent additives and the gas separation properties such as permeances and pure gas permeance ratios of the membranes.

2.4.3 Surface Characterization by Atomic Force Microscopy and Scanning Electron Microscopy

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) are among the available techniques that are used to obtain information about the structure of a surface, its composition and the oxidation states present.

The ability to control the position of a fine tip in order to scan surfaces with subatomic resolution has brought scanning probe microscopies to the forefront in surface imaging techniques. Atomic force microscopy (AFM) is a newly developed high-resolution

Figure 2.11. Schematic illustration of atomic force microscope.

technique to study the morphology of surfaces of thin films (Marti et al., 1988; Frommer, 1992; Marti and Amrein, 1993). This technique is illustrated in Figure 2.11.

Surface forces in the range from 10^{-13} to 10^{-6} N can be measured by mounting a fine tip to a piezoelectrically positioned cantilever spring. The surface forces are a combination of capillary, electrostatic, van der Waals and frictional forces and are measured from the deflection of the cantilever.

To date, the study of morphology of synthetic membranes by AFM has been carried out by several authors (Dietz et al., 1991,1992; Fritzsche et al., 1992a, 1992b; Khulbe et al., 1996a, 1996b, 1997, 1998). Khulbe et al. (1996a) studied the surface structure of PPO gas separation membranes. They found that the top and bottom surfaces of the asymmetric membranes were significantly different from each other. The top surface was relatively flat while the bottom surface was very porous revealing a microfiltration structure. In another study (Khulbe et al., 1996b), they compared the surface structures of asymmetric and homogeneous PPO membranes made from two different solvents, trichloroethylene and chloroform. A difference in morphology was observed for both solvents. It was concluded that when a more volatile solvent (chloroform) was used, the resulting nodules contained more free volume, thereby, increasing nodule diameter.

Surfaces of membranes can be compared through roughness parameters such as the mean roughness, R_a and the mean diameter of nodules. The mean roughness is the mean value of the surface relative to the center plane, the plane for which the volume enclosed by the image above and below this plane are equal, and is calculated as:

$$R_a = \frac{1}{L_x L_y} \int_0^{L_y} \int_0^{L_x} |f(x,y)| dx dy \quad (2.11)$$

where $f(x,y)$ is the surface relative to the center plane and L_x and L_y are dimensions of the surface.

Figure 2.12. Schematic illustration of scanning electron microscope.

Scanning electron microscopy (SEM) is widely used to examine surfaces down to a resolution of 50 nm or so, depending on the nature of the sample. Figure 2.12 shows a schematic illustration of a scanning electron microscope. A focused electron beam is used to scan the surface and the intensity of the secondary electrons is monitored. These electrons are viewed on a cathode-ray tube (CRT) (Lee, 1993) by modulating its raster (or image forming area). The output is scanned in synchronization with the focused electron beam. Each point on the CRT raster corresponds to a point on the surface of the sample. The intensity of the secondary electrons production from the corresponding point on the surface determines the quality of the image at each point. Image quality is seen in terms of good contrast and high resolution. High resolution is produced by having a large number of lines scanned while good contrast is produced if a high intensity signal is received.

Characteristically, SEM images have a wide range of contrast; that is, detail can be seen

both in very dark and in very light areas. The images also have a great depth of focus, such that, rough surfaces show in startling clarity and feeling of depth (Baker and Princen, 1971; Princen, 1976; Lee, 1993).

2.4.4 Structure Determination by Plasma-Etching

The gradual etching of a membrane surface by highly reactive particles from a gas plasma is very useful for investigating the structure of membranes. Oxygen at low pressure is passed through a radio-frequency coil and by electrodeless radio-frequency excitation, the oxygen molecules disassociate into free radicals and ions as shown in Figure 2.13. These particles can react with a variety of polymers, and this reaction is reflected in the weight loss.

The rate of ablation is dependent on the chemical structure of the polymer (Hansen et al., 1965; Lawton, 1974; Yasuda, 1985). Hansen et al. (1965) found that while in most cases a simple ablation of the surface was observed, in other polymers such as polyethylene and polypropylene, a highly oxidized surface layer was created. The oxygen plasma consists of a mixture of oxygen atoms, oxygen ions, electronically and vibrationally excited oxygen molecules and ground state molecular oxygen. All these species attack specific sites of the polymer and at different rates. Atomic oxygen can distinguish between sites which are more readily attacked by molecular oxygen and those which are less readily attacked.

The plasma treatment is a low temperature process and is limited to the surface of the polymer. Therefore, the bulk properties of the polymer do not change (Hansen, 1965, 1968; Schornhorn and Hansen, 1967; Byrne and Brown, 1972; Hudis, 1972; Yasuda et al., 1973). The weight loss is not dependent on the thickness of the polymer sample. The surface of the polymer is rapidly oxidized due to the rapid reaction of oxygen atoms or molecular oxygen with the hydrocarbon radicals formed together with alkoxy or hydroxy

radicals during the initial stages of treatment. Hansen et al. (1965) showed that polymer surfaces that were highly oxidized exhibited remarkably low contact angles with water while those surfaces that oxidized and volatilized showed little or no change in contact angles.

Yasuda et al. (1973) studied the effects of gas plasma as functions of gas pressure, discharge power, exposure time and type of plasma gas. There were two types of gases, nitrogen and helium. Nitrogen plasma caused less radiation damage on the polymers than helium. It was found that gas pressure did not have an effect on the weight loss of the polymer sample. As for discharge power, the weight loss reached a plateau at very high discharge power.

There have been several studies on the use of plasma treatment to study surface morphology (Anderson and Holland, 1960; Anderson, 1963; Magill and Harris, 1962; Yasuda et al., 1973; Padhye et al., 1976; Fritzsche et al. 1987, 1990b; Bauer et al., 1991). Fritzsche et al. (1990b) studied the effect of etching experiments on asymmetric polysulfone hollow fibers spun from *N*-methyl pyrrolidone:formamide complex. As the outer regions of the membrane were etched, the separation factor of He/N₂ declined.

Figure 2.13. Generation of gas plasma and etching of membrane.

More defects in the skin were exposed with increasing etching time. Therefore, most of

the contribution to the total amount of gas flow through the membrane was attributed to the gas flow through these defects. They also showed that it was possible to determine the sublayer resistance after etching. Bauer et al. (1991) studied the etching effect on the sublayer of asymmetric PPO hollow fiber membranes. From permeability experiments using He/N₂ and O₂/N₂, it was shown that the gas resistance of the sublayer had a large influence on the overall selectivity of the membrane.

2.5 Characterization of Mixed Solvent Systems

2.5.1 Characterization of Polymer Solvent Systems through Intrinsic Viscosity Studies

Viscosity has been regarded as a valuable tool in the characterization of polymer solutions due to the simplicity and accuracy in measurement. Viscosity measurements performed at low concentrations yield the intrinsic viscosity, $[\eta]$, defined by

$$[\eta] = \lim_{c_p \rightarrow 0} \frac{\eta - \eta_s}{c_p \eta_s} = \lim_{c_p \rightarrow 0} \frac{\eta_{sp}}{c_p} \quad (2.12)$$

It is the ratio of specific viscosity, η_{sp} , to concentration, c_p , at infinite dilution (Rodriguez, 1982). η_s is the viscosity of the solvent. The intrinsic viscosity is a characteristic function for the single molecule in solution. It depends mostly on the molar mass, structure and conformation of the polymer molecules, on the solvent power and on temperature. The dimension of $[\eta]$ is volume per unit mass and is thought of as the sum of effective hydrodynamic volumes of the separate, non-interacting molecules that make up a gram of polymer. An increase in viscosity observed in polymer solutions is due to a greater amount of work necessary to overcome frictional forces exerted by the dissolved molecules on the fluid.

The flow properties of polymer solutions are based on the following assumptions (Bohdanecký and Kovář, 1982).

- (i) The solvent is incompressible and its viscosity of the solution is Newtonian.
- (ii) The molecular structure of the solvent is neglected and the solvent is regarded as a continuous medium that exerts forces upon polymer molecules.
- (iii) Intramolecular hydrodynamic interaction occurs due to the disturbances in fluid velocity at points of location on elements of the polymer chain.
- (iv) Rigid molecules undergo translational and rotational motions and flexible molecules undergo deformation when exposed to an external field of force.

The study of intrinsic viscosity of binary solvent systems exhibiting co-solvency is of particular interest. This system is defined by the polymer which is insoluble in either of the two liquids but is readily dissolved by their mixture within a certain composition range (Bohdanecký and Kovář, 1982). In this thesis, chloroform is a better solvent for PPO than the nonsolvent additives.

Such studies have been carried out by Tuzar and Bohdanecký (1969) for poly(2-hydroxyethyl methacrylate)/water/dioxane and by Wolf and Molinari (1973) for polystyrene/acetone/diethyl ether. The polymer-solvent interaction involves the composition and molar volumes of the two liquids, the interaction between the solvent-nonsolvent components as well as the interactions between polymer segments and the solvent-nonsolvent components (Prigogine, 1957; Flory, 1970; Pouchlý and Patterson, 1976).

The hydrodynamic structure of nonentangled linear polymer solutions is determined by (Maron et al., 1959; Maron and Chiu, 1963; Rudin and Johnston, 1971, 1972; Johnston and Sourirajan, 1974)

$$v_{polymer} \epsilon = \frac{4\pi R_h^3}{3} \quad (2.13)$$

where $v_{polymer}$ is the bulk (crystalline) polymer volume, ϵ is the swelling factor that accounts for the increase in volume pervaded by a polymer molecule when in a solvent and R_h is the hydrodynamic radius of the volume occupied by each polymer molecule. In dilute solutions, equation (2.13) becomes

$$\frac{4\pi R_0^3}{3} = \frac{[\eta]M}{2.5N_0} \quad (2.14)$$

where R_0 is the dilute solution macromolecule radius, M is the number-averaged polymer molecular weight and N_0 is Avogadro's number. The Mark-Houwink (Mark, 1938) equation describes the general relationship between $[\eta]$ and M as follows

$$[\eta] = KM^\beta \quad (2.15)$$

where the constants K and β depend upon the temperature of the solution and the choice of solvent used to dissolve the polymer. Therefore, equations (2.14) and (2.15) show that the hydrodynamic volume occupied by a polymer molecule in a dilute solution is dependent upon the type or strength of solvent. Additives such as inorganic salts and solvents used in polymer solutions can influence $[\eta]$, K and β for a given polymer. This in turn would affect the dilute macromolecule radius (Wood and Sourirajan, 1991).

2.5.2 Characterization of Polymer Solution through Surface Tension and the Effect of Capillary Pressure

It has been suggested that the coalescence of the nodular network occurs primarily at the membrane-air interface due to capillary pressure of the nodules (Pinnau and Koros, 1993). This idea was adapted from studies on the formation of latex films from polymer emulsions (Brown, 1956; Brodnyan and Konen, 1964; Imoto, 1973; Mason, 1973; Lamprecht, 1980; Kast, 1985; Eckersley and Rudin, 1990). In the study by Brown for water-based polymer emulsions, the cast latex film consisted of latex spheres in contact with each other while water “filled up” the void spaces in between the spheres. These spheres formed a continuous film surface with isolated concave areas of water. This results in the capillary pressure exerted in a direction normal to the water-polymer interface (Figure 2.14).

The condition for film formation depends upon the forces due to capillarity and resistance to deformation.

$$F_C > F_G \quad (2.16)$$

where F_C is the force resulting from the capillary pressure and F_G is the force which resists deformation. In an analogy to the latex system, Pinnau and Koros (1993) suggested that the polymer-rich phase formed a continuous film surface by the coalescence of nodules while the polymer-poor phase filled up the void spaces in between.

The basic equation of capillarity given in 1805 by Young (1855) and by Laplace (1806) relates the pressure due to the curvature of air-liquid interface, P_c to the radius of capillary, r .

Figure 2.14. Effect of capillary pressure on the contracting forces in the voids of latex films (Brown, 1956).

$$P_c = \frac{2\gamma}{r} \quad (2.17)$$

where γ is the surface tension of the interstitial fluid and r is the radius of the “throat” that passes through the centers of three touching spherical particles (Brown, 1956).

Surface tension is a definite and accurately measurable property of the liquid-liquid interface. In this work, it is of interest to understand how surface tension depends on polymer-poor phase/polymer-rich phase interaction.

CHAPTER 3

MATERIALS AND METHOD

The experimental work was divided into the following parts:

- (i) Membrane casting, in which the optimum concentration of 2-ethyl-1-hexanol was determined and the other nonsolvent additives were used.
- (ii) Characterization of the membranes from (i) through gas permeation, in which coupons were cut out from these membranes and tested for their permeation properties.
- (iii) Characterization of the top surface i.e. nodule structure of membranes from (i) by using Tapping Mode Atomic Force Microscope.
- (iv) Measurements of intrinsic viscosity, which was carried out on polymer solutions without nonsolvent additives and polymer solutions with nonsolvent additives.
- (v) Measurements of surface tension, which was carried out on mixed solutions consisting of solvent and nonsolvent additive. Both (iv) and (v) were carried out to investigate the interaction among polymer, solvent and nonsolvent additives.
- (vi) Etching the top surface of the membrane using oxygen plasma to investigate the layers of the skin.
- (vii) Measurements of contact angle on etched membranes to investigate the possibility of chemical reaction at the surface during the plasma-etching process.

3.1 Membrane Casting

3.1.1 Determination of Optimum Concentration of 2-ethyl-1-hexanol

The casting solution consisted of PPO, 2-ethyl-1-hexanol as the nonsolvent additive and chloroform as the solvent. The PPO powder was obtained from General Electric. Intrinsic viscosity of PPO was 1.79 dL/g. In order to determine the optimum concentration of 2-ethyl-1-hexanol, various casting solutions were made. While the solution had consistent amounts of PPO at 12.6 wt.%, the concentration of 2-ethyl-1-hexanol was varied from 0 to 12.6 wt.%. The concentration of chloroform was adjusted accordingly, from 87.4 to 74.8 wt.%. The casting solutions were made at room temperature.

Chloroform was first added to 2-ethyl-1-hexanol in a glass bottle. PPO was then added to the mixture. The bottle was sealed with black electrical tape and was placed on a mechanical roller for 24 hours. The bottle was removed when the mixture was noticeably clear which indicated that the PPO polymer had “dissolved” in the chloroform/2-ethyl-1-hexanol mixture.

The solution was pressure-filtered at 30 psig with N₂ through a Teflon filter (5 µm pore size) to ensure that contaminants and polymer aggregates were removed. The filtrate i.e. homogeneous solution was collected in another bottle and was degassed by leaving it under storage for 24 hours. It is important to note that storage time and filtration treatment of the casting solution affects the morphology of the resulting membranes (Ma et al., 1995). Prefiltered polymer solutions that were unused for casting membranes within two weeks of preparation were discarded and fresh casting solutions were prepared.

Membranes were cast on a glass plate in a fumehood using a metal casting bar, which

was previously machined to give the desired wet thickness of the membrane. The casting apparatus is shown in Figure 3.1. The thickness of the as-cast membrane was 4 mil (101.6 μm). The membrane together with the glass plate was immediately placed in a nonsolvent coagulation media consisting of methanol. The nonsolvent coagulation media

Figure 3.1. Schematic diagram of casting bar, glass plate and nonsolvent coagulation media.

was kept at the temperature of the fumehood. The temperature and humidity of the fumehood were recorded. The membrane was kept in the nonsolvent coagulation media for 48 hours to complete the gelation of the polymer.

When the membrane was removed from the nonsolvent coagulation media, the membrane peeled off from the glass plate, spontaneously. The membrane was then placed in a vacuum oven at a pressure of 0 Pa and room temperature for a minimum of a week to remove any residual organic compounds.

3.1.2 Use of Other Nonsolvent Additives

The nonsolvent additives listed in Table 2.1 were purchased from Acros Organics with the exception of 6-methyl-2-heptanol and 3,5,5-trimethyl-1-hexanol, which were purchased from Aldrich Chemical Company. The method of making polymer solutions using nonsolvent additives other than 2-ethyl-1-hexanol was as follows. The solution consisted of 12.6 wt.% PPO, 5 wt.% nonsolvent additive and 82.4 wt.% chloroform. The method of casting membranes was the same as described in section 3.1.1. After the membranes were cast, they were placed in the vacuum oven until the membranes were ready to be used.

3.2 Characterization of Membranes Through Gas Permeation Experiments

For each nonsolvent additive used, two suitable coupons were cut out from up to four membranes made. These coupons were used for gas permeation experiments. The area of the coupons was 9.24 cm². The coupon was mounted onto the porous mesh of a test cell. Figure 3.2 shows a schematic of the cell and the order in which filter paper, polyethylene O-ring and coupon were placed. The filter paper provided physical support to the coupon whilst the polyethylene O-ring was an added precaution to prevent gas leaks from the cell. Both parts of the cell were then fitted and clamped together with a large screw.

The membranes were put in cells which were a part of the constant pressure testing system as shown in Figure 3.3. The permeation of pure N₂ was then carried out. The membranes were first pressurized at 120 psig for a minimum of 12 hours with N₂. This is to ensure that the membrane was completely compressed and that other foreign gases did not remain in the testing system.

Figure 3.2. Schematic diagram of the layout of the testing cell.

Figure 3.3. Schematic diagram of gas testing apparatus consisting of a constant pressure system.

After 12 hours, the pressure of the system would be lowered to 100 psig, which is the testing pressure. The pressure of the permeate stream was at atmospheric conditions. The retentate line was closed. Then, permeability testing would take place. The pure gas permeation rates of N_2 were measured using a Hewlett-Packard bubble flowmeter (Hewlett Packard 0101-0113). The bubble flowmeter could be used for gas volumes of up to 1 mL, 10mL and 100mL. The pressure and temperature of the atmosphere were also recorded. Permeability readings would be taken until the change in permeability was less than 5% which indicated that steady-state had been reached. The permeability data were corrected to standard temperature and pressure. The permeation experiments were repeated for pure gases of O_2 , CH_4 and CO_2 , in that order.

3.3 Characterization of Nodule Structure Using Tapping Mode Atomic Force Microscope (TMAFM)

Samples of approximately 0.5 cm^2 in area were cut from each membrane and glued onto metal disks. Only the top surfaces were studied. The images of the top surfaces were obtained using TMAFM on a Nanoscope III equipped with a 1553D scanner from Digital Instruments. The membrane surfaces were imaged in three different scan sizes: $18.1 \times 18.1\text{ }\mu\text{m}$, $2 \times 2\text{ }\mu\text{m}$ and $0.5 \times 0.5\text{ }\mu\text{m}$. The size and the distribution of characteristic features of the surface can only be revealed in a particular range of scan sizes. Therefore, the smallest scan size, $0.5 \times 0.5\text{ }\mu\text{m}$, was used.

The captured image as shown on the bottom left window of Figure 3.4 is divided into a number of grids. Measurements of nodule diameters and heights were taken from cross-sectional views of the data along the reference line. Figure 3.4 shows an example of the measurement of the diameter of nodules. For a pair of cursors, the horizontal distance represents the diameter of a nodule and the measurement is given in the bottom right window of Figure 3.4. The height of the nodules was also measured for the membranes used in plasma-etching experiments. Figure 3.4 shows that for a pair of cursors, the

vertical distance represents the height of a nodule and the measurement is given in the bottom right window of Figure 3.4. The mean diameter and height of the nodules is based on the average of at least 50 measurements. The roughness, R_a , of each grid is given in the upper right window of Figure 3.4. Mean roughness, R_a , of each sample is the average value of R_a for all grids in the captured image.

Figure 3.4. Cross-sectional view of nodules and measurement of nodule height and diameter of analysis from atomic force microscopy.

3.4 Measurements of Intrinsic Viscosity on Polymer Solutions

Intrinsic viscosity was measured for dilute polymer solutions involving nonsolvent additives and a polymer solution without nonsolvent additive.

3.4.1 Polymer Solution Without Nonsolvent Additive

This measurement was used to verify the intrinsic viscosity of PPO in chloroform. In order to measure the polymer solution without nonsolvent additive, 0.5 wt.% of PPO was dissolved in 100 mL chloroform. A syringe (Hamilton Gastight Syringe) was used to obtain 5 mL of solution. The syringe was then weighed. The chloroform solution (about 3 mL) was injected into an Ubbelohde viscometer (size: 50) (Jupiter Instrument Company Viscometer Assembly). The syringe was weighed again. The weight measurements were used for calculations of intrinsic viscosities.

The viscometer assembly was then immersed in a constant temperature bath. The temperature was kept at 25°C and controlled to $\pm 0.2^\circ\text{C}$. The viscometer consisted of an optical system for sensing the change in light level as a liquid meniscus passed a certain point in the glass capillary tube. The viscometer was connected to a viscosity timer (Model 821, Jupiter Instrument Company). An electronic circuit uses the change in light intensity to activate and deactivate the viscosity timer. It has three selectable time bases, 0.01, 0.10 and 1.00 seconds to accommodate a wide range of flow periods.

The solution in the viscometer was diluted by 2 mL of pure chloroform. This was done using another syringe which was weighed before and after injecting pure chloroform into the viscometer. The flow time of this solution was then measured. The flow times were reproducible to $\pm 0.1\%$. The process of dilution was repeated three times by using 1 mL of pure chloroform.

3.4.2 Polymer Solution With Nonsolvent Additive

In order to measure the intrinsic viscosity of a polymer solution with nonsolvent additive, 0.5 wt.% of PPO was dissolved in 100 mL solution consisting of chloroform and nonsolvent additive. The solvent-nonsolvent ratio was kept constant at 16.48:1 in all viscosity measurements. The method of flow time measurement and dilution is the same as with the polymer solution without nonsolvent additive except a chloroform-nonsolvent additive mixture (16.48:1) was used instead of pure chloroform.

3.5 Measurements of Surface Tension on Mixed Solvent Solutions Using the Drop Weight Method

Figure 3.5 shows a schematic diagram of the experimental set-up for measuring the surface tension of chloroform and chloroform/nonsolvent additive mixtures. Ten mL solutions consisting of 5.7 wt.% nonsolvent additive and 94.3 wt.% chloroform were prepared. This proportion was similar to the preparation of casting solutions in section 3.1.2. The solution was poured into the automated syringe pump (Model 341B SAGE INSTRUMENTS). The flowrate of the syringe pump was set according to the type of syringe in use. In order to ensure that air bubbles were not present in the syringe, the initial flowrate of the syringe was set at 0.5 mL/min.

At the beginning of the experiment, the initial weight of the container for drop collection was recorded. The normal flowrate for most measured liquids is 0.1 mL/min. However, in the case of chloroform, the flowrate was determined to be at 0.15 mL/min so that the rate at which the droplets fell was fast enough to overcome inertia but was slow enough such that the weighing balance could stabilize.

- 1 Syringe pump**
- 2 Weighing balance**
- 3 Tubing**
- 4 Container for drop collection and weighing**
- 5 Recorder**

Figure 3.5. Schematic diagram of surface tension experiment.

Figure 3.6 shows a detailed schematic illustrating the drop weight method. Once the flowrate of the solution has been established and the initial weight has been recorded, the syringe pump is turned on to deliver controlled drops. When a drop forms at the tip of the teflon needle and falls into solution, the recorder (GA44, METTLER) prints the increased weight as soon as it stabilizes. The electronic balance (AJI50, METTLER) records the weight of the solution up to 4 decimal places. The diameter of the needle used in surface tension calculations was 2.87×10^{-3} m. 50 drops or more were recorded for each sample and this is considered statistically acceptable. The final weight was also recorded.

Figure 3.6. Detailed schematic illustrating the drop weight method.

3.6 Membranes Subjected to Oxygen Plasma-Etching Experiments

Membranes were made from solutions consisting of 12.6 wt.% PPO, 5 wt.% 2-ethyl-1-hexanol (nonsolvent additive) and 82.4 wt.% chloroform. The method for making membranes has been described in section 3.1.1. This experiment consisted of two parts. First, etching of the top surface layer of the membrane and second, measuring the CO_2 , CH_4 , O_2 and N_2 permeation of the etched membranes. The latter part has been described in section 3.2.

The plasma system (SP 100, ANATECH) operates at 0-100 Watts at a radio frequency (RF) of 13.56 MHz. It is divided into three parts.

(i) Control console

It consists of the main microprocessor, power supply, RF control, gas flow control, metering and switch controls.

(ii) Chamber compartment

This part is shown in Figure 3.7. It contains the main process chamber, RF coil,

main vacuum valve and gauge pressure circuit.

(iii) Vacuum system

It comprises of vacuum pump and hoses and is connected to the chamber compartment.

The membrane coupon was weighed and then clamped between two rectangular glass rods, exposing the surface area on both sides of the coupon (18.48 cm^2). The entire contraption was put in a vertical position in the middle of the chamber compartment (Yasuda et al., 1973). It was then closed. The valve of the compressed oxygen cylinder was opened to allow low pressure O_2 in the chamber. As discussed in Section 2.4.4, the pressure of the plasma gas does not have an effect on the weight loss of the polymer. The desired process time was set. The power level was set at 89 Watts in order to maintain a consistent rate of weight loss of polymer.

Once the program selections were made, the etching cycle was started. The chamber compartment is evacuated of foreign gases by the vacuum pump. It also removes any residual gases produced during the etching process. The low pressure oxygen is passed through the RF coil. By an electrodeless discharge process, the coil produces oxygen atoms and ions from the oxygen. These atoms and ions will impinge on the membrane and thus, etching starts to occur. If it is successful, a blue light will be emitted in the chamber. The timer will start its timing sequence. At the end of the timing sequence, the RF will be removed, extinguishing the plasma. The gas valve will close and the chamber will vent to the atmosphere. The sample is then removed from the chamber and weighed to determine the weight loss.

Figure 3.7. Schematic diagram of part of the ANATECH plasma system: process chamber compartment.

3.7 Contact Angle Measurements

Contact angles of water on the top surface of the etched and unetched membranes were measured after 5 minute deposition. This time was already established for the water droplet to attain equilibrium. The membrane samples had a surface area of 0.5 to 1 cm². The samples were placed on a glass slide with the top surface exposed. The glass slide was mounted onto the contact angle goniometer (SCHERR TUMICO). A droplet of water was placed on the slide. The goniometer uses a magnifying lens of 20X to view the angle directly. Three measurements were taken for each sample.

3.8 Statistical Considerations

- (i) Gas permeation rates were measured in duplicates and the results are presented as averages.

- (ii) In measuring the nodule sizes, not less than 50 measurements were taken. The results are presented as averages with a 95% confidence interval.
- (iii) Intrinsic viscosity measurements of each polymer solution were done in triplicates. The results are presented as averages with a 95% confidence interval.
- (iv) In the surface tension experiments, 50 drops or more were recorded for each nonsolvent additive sample.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Optimum Concentration of 2-ethyl-1-hexanol

The nonsolvent additive, 2-ethyl-1-hexanol and its effect on membrane gas performance has been studied (Albers and Greinadus, 1984; Smid et al., 1991; Gagné, 1996). The membranes used by Smid et al. (1991) were made from polyphenylene ether/2-ethyl-1-hexanol/trichloroethylene. They prepared asymmetric hollow fiber membranes from casting solutions containing TCE and 2-ethyl-1-hexanol in various ratios and calculated the apparent skin thickness of these membranes so prepared. It was found that the apparent skin thickness decreased with an increase in nonsolvent additive/solvent ratios. A previous study by Albers and Greinadus (1984) reported a 100 fold increase in the flux of O_2 on changing the concentration of 2-ethyl-1-hexanol in the polymer solution (polyphenylene ether/2-ethyl-1-hexanol/TCE) from 0 wt.% to 17 wt.% while the polymer concentration remained at 20 wt.%. Gagné (1996) studied the permeances of CO_2 and CH_4 in asymmetric membranes prepared from PPO/2-ethyl-1-hexanol/TCE. It was found that as the concentration of 2-ethyl-1-hexanol was increased from 12.5 wt.% to 16.7 wt.%, the pure gas permeance of both these gases increased significantly. However, the pure gas permeance ratios decreased.

In a series of preliminary experiments, 0, 5, 6.8, 8, 10 and 12.6 wt.% of 2-ethyl-1-hexanol were added to the PPO solution, where the concentration of PPO was fixed at 12.6 wt.%. This fixed concentration was determined by Gagné (1996) for developing asymmetric PPO membranes for gas separation. Table 4.1 and 4.2 show the temperature of the fumehood during the casting of these membranes. This was done to ensure that there were not any substantial differences in the temperatures which may affect the final membrane structure and hence, its performance. The membranes were cast in a fumehood because the solvent, chloroform has a low boiling point and is considered harmful if breathed in at high concentrations.

Following the preparation of these membranes as discussed in Chapter 3, the formed membranes were then subjected to gas permeation experiments. Table 4.1 and 4.2 show the results of these experiments for O₂/N₂ separation and CO₂/CH₄ separation, respectively. It was found that the pure gas permeance ratios, $\alpha_{O_2/N_2} = 5.51$ and $\alpha_{CO_2/CH_4} = 24.5$, were the highest when 5 wt.% of 2-ethyl-1-hexanol was added. Therefore, 5 wt.% was chosen as the concentration of nonsolvent additive in the following experiments.

Table 4.1 Casting conditions and permeance data for N₂ and O₂ for different concentrations of 2-ethyl-1-hexanol (nonsolvent additive).

Coupon code	Additive concentration (wt %)	¹ Temperature (K)	² P// N ₂	² P// O ₂	³ α O ₂ /N ₂
MAY2995	0	295.2	5.38E-11	2.47E-10	4.61
JULY0495	5.0	295.8	7.17E-10	3.95E-09	5.51
JULY1495	6.8	296.2	1.56E-09	7.13E-09	4.58
NOV1595	8.0	294.7	3.10E-09	3.1E-09	1.00
NOV1095	10.0	294.8	3.2E-09	3.2E-09	1.00

Table 4.2 Casting conditions and permeance data for CO₂ and CH₄ for different concentrations of 2-ethyl-1-hexanol (nonsolvent additive).

Coupon code	Additive concentration (wt %)	¹ Temperature (K)	² P// CH ₄	² P// CO ₂	³ α CO ₂ /CH ₄
MAY2995	0	295.2	5.85E-11	1.20E-09	20.5
JULY0495	5.0	295.8	9.54E-10	2.35E-08	24.5
JULY1495	6.8	296.2	2.50E-09	4.86E-08	19.5
NOV1595	8.0	294.7	1.60E-09	1.45E-08	9.06
NOV1095	10.0	294.8	2.17E-09	9.97E-09	4.59

¹Casting temperature (of the fumehood) ³Pure gas permeance rate ratio

²Units of permeance: mol/m².s.Pa

4.2 Empirical Correlation between Structure of Additives and Permeation Data of Poly(2,6-dimethyl-1,4-phenylene)Oxide Membranes

4.2.1 Gas Performances of N₂, O₂, CH₄ and CO₂ of Poly(2,6-dimethyl-1,4-phenylene)Oxide Membranes

Of the 17 nonsolvent additives listed in Table 2.2, four nonsolvent additives were not suitable for making asymmetric membranes even though the calculation of their solubility parameters indicated otherwise. These nonsolvent additives were 2,3-dimethyl-3-pentanol, 4,4-dimethyl-2-pentanol, 6-methyl-2-heptanol and 2-nonanol. The rejected membranes turned out to be translucent and brittle unlike the other membranes which were opaque and mechanically strong.

Table 4.3 shows the casting conditions of the membranes that were subjected to O₂ and N₂ permeance testing. Two coupons from each batch of membranes cast were used with the exception of 2-ethyl-1-hexanol, 2-decanol and 3-ethyl-3-pentanol. In total, 13 nonsolvent additives were tested. This table also shows the permeances and permeance ratios of the individual coupons.

Table 4.4 shows the casting conditions of the membranes that were subjected to CO₂ and CH₄ permeance testing. Two coupons from each batch of membranes cast were used with the exception of 2-ethyl-1-hexanol and 2-decanol. It should be pointed out that the membranes made from 3-ethyl-3-pentanol and 2-methyl-2-hexanol had pinholes during testing and had to be discarded. In total, 11 nonsolvent additives were tested. This table also shows the permeances and permeance ratios of the individual coupons.

Figures 4.1 and 4.2 show the average values of the pure gas permeances of N₂ and O₂, respectively. The 13 different nonsolvent additives are represented by the numbers on the X-axis and are given in the legend provided. The error bars reflect the reproducibility of

the pure gas permeances of the membranes. Figure 4.1 shows that the pure N₂ permeance values range from 2.04×10^{-10} mol/m².s.Pa for 1-octanol to 1.68×10^{-9} mol/m².s.Pa for 3-ethyl-2,2-dimethyl-3-pentanol. Figure 4.2 shows that the pure O₂ permeance values range from 8.98×10^{-10} mol/m².s.Pa for 1-octanol to 5.46×10^{-9} mol/m².s.Pa for 3-ethyl-2,2-dimethyl-3-pentanol.

Figure 4.3 shows the pure O₂/N₂ permeance ratio. It can be seen that the highest α_{O_2/N_2} is for 2-ethyl-1-hexanol at 5.51 and the lowest α_{O_2/N_2} is for 2-methyl-3-hexanol at 3.02.

Figures 4.4 and 4.5 show the average values of the pure gas permeances of CH₄ and CO₂, respectively. Figure 4.4 shows that the lowest pure CH₄ permeance is 1.15×10^{-10} mol/m².s.Pa for 1-octanol and the highest value is 1.35×10^{-9} mol/m².s.Pa for 3-ethyl-2,2-dimethyl-3-pentanol. Figure 4.5 shows that the pure CO₂ permeance values range from 2.9×10^{-9} mol/m².s.Pa for 1-octanol to 2.34×10^{-8} mol/m².s.Pa. for 2-ethyl-1-hexanol.

Figure 4.6 shows the pure gas permeance ratios for CO₂ and CH₄. α_{CO_2/CH_4} values range from 11.7 for 3-ethyl-2,2-dimethyl-3-pentanol to 25.2 for 1-octanol. However, its (P/I)_{CO₂} is 2.9×10^{-9} mol/m².s.Pa which is low compared to that of 2-ethyl-1-hexanol. It has the highest (P/I)_{CO₂} and its α_{CO_2/CH_4} value is also high at 24.5.

Table 4.3 Casting conditions and permeance data for N₂ and O₂ for different nonsolvent additives.
Footnotes for the superscripts are found at the end of Table 4.3.

Coupon Code	³ Temperature (K)	³ Humidity (%)	⁴ P// N ₂	⁴ P// O ₂	α O ₂ /N ₂
2-ethyl-1-hexanol	295.75	41	7.17E-10	3.95E-09	5.51
1-octanol	294.05	20	¹ 2.40E-10 ² 1.68E-10	¹ 1.11E-09 ² 6.90E-10	4.63 4.11
2-propanol	294.35	66	¹ 4.12E-10 ² 4.38E-09	¹ 1.29E-09 ² 1.39E-09	3.13 3.18
2-decanol	294.25	74	2.80E-10	1.26E-09	4.5
3,5,5-trimethyl-1-hexanol	295.05	19	¹ 1.28E-09 ² 1.46E-09	¹ 4.07E-09 ² 5.11E-09	3.18 3.50

Table 4.3 (cont'd). Casting conditions and permeance data for N₂ and O₂ for different nonsolvent additives.

Coupon Code	³ Temperature (K)	³ Humidity (%)	⁴ P// N ₂	⁴ P// O ₂	α O ₂ /N ₂
2,4-dimethyl-3-pentanol	295.65	12	¹ 1.33E-09 ² 1.03E-09	¹ 4.98E-09 ² 3.72E-09	3.74 3.61
2,4,4-trimethyl-1-pentanol	296.09	16	¹ 8.64E-10 ² 6.02E-10	¹ 3.14E-09 ² 2.84E-09	3.63 4.72
2,2-dimethyl-3-pentanol	295.87	19	¹ 4.99E-10 ² 1.04E-09	¹ 2.23E-09 ² 3.91E-09	4.47 3.76
3-ethyl-2,2-dimethyl-3-pentanol	295.82	18	¹ 1.94E-09 ² 1.42E-09	¹ 6.04E-09 ² 4.87E-09	3.11 3.43
2-methyl-3-hexanol	295.76	17	¹ 4.84E-10 ² 5.18E-10	¹ 1.45E-09 ² 1.57E-09	3.00 3.03

Table 4.3 (cont'd) Casting conditions and permeance data for N₂ and O₂ for different nonsolvent additives.

Coupon Code	³ Temperature (K)	³ Humidity (%)	⁴ P// N ₂	⁴ P// O ₂	α O ₂ /N ₂
2,6-dimethyl-4-heptanol	294.54	18	¹ 9.96E-10 ² 1.13E-09	¹ 4.21E-09 ² 4.45E-09	4.23 3.94
3-ethyl-3-pentanol	295.98	16	¹ 1.24E-09	¹ 5.22E-09	4.22
2-methyl-2-hexanol	294.15	17	¹ 9.04E-10 ² 1.05E-09	¹ 3.01E-09 ² 3.38E-09	3.33 3.22

^{1,2}denote coupons 1 and 2, respectively³Casting conditions of the fumehood⁴Units of permeance: mol/m².s.Pa

Table 4.4 Casting conditions and permeance data for CO₂ and CH₄ for different nonsolvent additives.
Footnotes for the superscripts are found at the end of Table 4.4.

Coupon Code	³ Temperature (K)	³ Humidity (%)	⁴ P// CH ₄	⁴ P// CO ₂	α CO ₂ /CH ₄
2-ethyl-1-hexanol	295.75	41	9.54E-10	2.34E-08	24.5
1-octanol	294.05	20	¹ 1.05E-10 ² 1.25E-10	¹ 2.44E-09 ² 3.36E-09	23.2 26.9
2-propanol	294.35	66	¹ 2.59E-10 ² 2.95E-09	¹ 4.07E-09 ² 5.61E-09	15.7 19.0
2-decanol	294.25	74	2.50E-10	5.59E-09	22.4
3,5,5-trimethyl-1-hexanol	295.05	19	¹ 8.94E-10 ² 1.27E-09	¹ 1.28E-08 ² 2.04E-08	14.3 16.1

Table 4.4 (cont'd) Casting conditions and permeance data for CO₂ and CH₄ for different nonsolvent additives.

Coupon Code	³ Temperature (K)	³ Humidity (%)	⁴ P// CH ₄	⁴ P// CO ₂	α CO ₂ /CH ₄
2,4-dimethyl-3-pentanol	295.65	12	¹ 6.28E-10 ² 5.60E-10	¹ 1.07E-08 ² 9.49E-09	17.0 16.9
2,4,4-trimethyl-1-pentanol	296.09	16	¹ 7.68E-10 ² 6.93E-10	¹ 1.19E-08 ² 8.96E-09	15.5 12.9
2,2-dimethyl-3-pentanol	295.87	19	¹ 3.99E-10 ² 6.39E-10	¹ 7.13E-09 ² 8.51E-09	17.9 13.3
3-ethyl-2,2-dimethyl-3-pentanol	295.82	18	¹ 1.33E-09 ² 1.38E-09	¹ 1.61E-08 ² 1.57E-08	12.1 11.4
2-methyl-3-hexanol	295.76	17	¹ 3.32E-10 ² 3.41E-10	¹ 5.14E-09 ² 4.95E-09	15.5 14.5

Table 4.4 (cont'd) Casting conditions and permeance data for CO₂ and CH₄ for different nonsolvent additives.

Coupon Code	³ Temperature (K)	³ Humidity (%)	⁴ P// CH ₄	⁴ P// CO ₂	α CO ₂ /CH ₄
2,6-dimethyl-4-heptanol	294.54	18	¹ 8.35E-10	¹ 1.15E-08	13.8
			² 1.04E-09	² 1.26E-08	12.1
3-ethyl-3-pentanol	295.98	16	---	---	
2-methyl-2-hexanol	294.15	17	---	---	

^{1,2}denote coupons 1 and 2, respectively³Casting conditions of the fumehood⁴Units of permeance: mol/m².s.Pa

Legend

(1) 2-ethyl-1-hexanol	(2) 1-octanol	(3) 2-propanol
(4) 2-decanol	(5) 3,5,5-trimethyl-1-hexanol	
(6) 2,4-dimethyl-3-pentanol	(7) 2,4,4-trimethyl-1-pentanol	
(8) 2,2-dimethyl-3-pentanol	(9) 3-ethyl-2,2-dimethyl-3-pentanol	
(10) 2-methyl-3-hexanol	(11) 2,6-dimethyl-4-heptanol	
(12) 3-ethyl-3-pentanol	(13) 2-methyl-2-hexanol	

Figure 4.1. Pure N₂ permeance of nonsolvent additives.

Legend

(1) 2-ethyl-1-hexanol	(2) 1-octanol	(3) 2-propanol
(4) 2-decanol	(5) 3,5,5-trimethyl-1-hexanol	
(6) 2,4-dimethyl-3-pentanol	(7) 2,4,4-trimethyl-1-pentanol	
(8) 2,2-dimethyl-3-pentanol	(9) 3-ethyl-2,2-dimethyl-3-pentanol	
(10) 2-methyl-3-hexanol	(11) 2,6-dimethyl-4-heptanol	
(12) 3-ethyl-3-pentanol	(13) 2-methyl-2-hexanol	

Figure 4.2. Pure O₂ permeance of nonsolvent additives.

Legend

(1) 2-ethyl-1-hexanol	(2) 1-octanol	(3) 2-propanol
(4) 2-decanol	(5) 3,5,5-trimethyl-1-hexanol	
(6) 2,4-dimethyl-3-pentanol	(7) 2,4,4-trimethyl-1-pentanol	
(8) 2,2-dimethyl-3-pentanol	(9) 3-ethyl-2,2-dimethyl-3-pentanol	
(10) 2-methyl-3-hexanol	(11) 2,6-dimethyl-4-heptanol	
(12) 3-ethyl-3-pentanol	(13) 2-methyl-2-hexanol	

Figure 4.3. Pure O_2/N_2 permeance rate ratio of nonsolvent additives.

Figure 4.4. Pure CH_4 permeance of nonsolvent additives.

Figure 4.5. Pure CO₂ permeance of nonsolvent additives.

Legend

(1) 2-ethyl-1-hexanol	(2) 1-octanol	(3) 2-propanol
(4) 2-decanol	(5) 3,5,5-trimethyl-1-hexanol	
(6) 2,4-dimethyl-3-pentanol	(7) 2,4,4-trimethyl-1-pentanol	
(8) 2,2-dimethyl-3-pentanol	(9) 3-ethyl-2,2-dimethyl-3-pentanol	
(10) 2-methyl-3-hexanol	(11) 2,6-dimethyl-4-heptanol	

Figure 4.6. Pure CO₂/CH₄ permeance rate ratio of nonsolvent additives.

4.2.2 Empirical Correlation

This work is the first attempt to find a suitable correlation between the gas performance data and the structures of the nonsolvent additives. Figures 4.7(a) - (m) show the structures of the nonsolvent additives which are straight-chained and branched alcohol molecules. The linear additivity rule was applied to the structural components of the additives. For this purpose, alcohol molecules were broken into structural components which were chosen arbitrarily. However, the rules used in choosing them were consistent for each nonsolvent additive. The nonsolvent additives were separated into CH_3 -, $-\text{CH}_2$ -, $-\text{CH}$ -, $-\underset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-$ and $-\text{OH}$ groups. Table 4.5 shows the grouping of all the nonsolvent additives.

(a) 2-ethyl-1-hexanol

(b) 1-octanol

(c) 2-propanol

(d) 2-decanol

Figure 4.7. Structural components of nonsolvent additives.

(e) 3,5,5-trimethyl-1-hexanol

(f) 2,4-dimethyl-3-pentanol

(g) 2,4,4-trimethyl-1-pentanol

(h) 2,2-dimethyl-3-pentanol

(i) 3-ethyl-2,2-dimethyl-3-pentanol

(j) 2-methyl-3-hexanol

Figure 4.7 (cont'd). Structural components of nonsolvent additives.

(k) 2,6-dimethyl-4-heptanol

(l) 3-ethyl-3-pentanol

(m) 2-methyl-2-hexanol

Figure 4.7 (cont'd). Structural components of nonsolvent additives.

Table 4.5. Grouping of alcohol molecules.

Additives	Grouping of alcohol molecules				
	-CH ₃	-CH ₂ -	-CH-	-C-	OH
(1) 2-ethyl-1-hexanol	2	5	1	0	1
(2) 1-octanol	1	7	0	0	1
(3) 2-propanol	2	0	1	0	1
(4) 2-decanol	2	7	1	0	1
(5) 3,5,5-trimethyl-1-hexanol	4	3	1	1	1
(6) 2,4-dimethyl-3-pentanol	4	0	3	0	1
(7) 2,4,4-trimethyl-1-pentanol	4	2	1	1	1
(8) 2,2-dimethyl-3-pentanol	4	1	1	1	1
(9) 3-ethyl-2,2-dimethyl-3-pentanol	5	2	0	2	1
(10) 2-methyl-3-hexanol	3	2	2	0	1
(11) 2,6-dimethyl-4-heptanol	4	2	3	0	1
(12) 3-ethyl-3-pentanol	3	3	0	1	1
(13) 2-methyl-2-hexanol	3	3	0	1	1

LaPack et al. (1994) developed correlations based on the solution-diffusion model to predict the permeability and permselectivity of various permeants through membranes. While the correlation developed by LaPack et al. (1994) was shown to have good predictive value, the development of the model was complicated since the Hildebrand solubility parameters were incorporated into the solution-diffusion model.

Patil et al. (1995) used the method of molecular connectivity of the permeants to predict their permeabilities through various polymers. This method was attempted in this work

to predict the permeances and permeance ratios of the permeants through PPO membranes. However, this method was unsuccessful. The coefficient of regression, r^2 was less than 0.9 and some predicted values had no physical meaning.

Furthermore, several linear 1st, 2nd and 3rd order polynomial equations were proposed in order to derive an empirical correlation between the structural components in the alcohol molecules and gas performance data (i.e. pure gas permeances and pure gas permeance ratios). However, a satisfactory model could not be found in each case. It was then decided that perhaps, not all the structural components were required in deriving an empirical correlation. As before, several linear polynomial 1st, 2nd and 3rd order equations were proposed between some of the structural components in the alcohol molecules and gas performance data.

Various models were used to fit the O_2/N_2 permeation data. These attempts were unsuccessful because the range in which α_{O_2/N_2} fell was very narrow, from 3.0 to 5.5. In all cases the coefficient of regression, r^2 , was less than 0.9 and the predicted values had no physical meaning.

A correlation was determined for the pure CO_2/CH_4 permeance ratio and alcohol structure, while all others were unsuccessful. The method of fitting the data and significance tests on the adequacy of the fitted model are given in Appendix B. The results of the significance test will be discussed here. This model is

$$\begin{aligned} \alpha_{CO_2/CH_4} = & 21.264 + 0.2744 X_{CH_3} - 1.377 X_{CH_2} - 0.5987 X_{CH_3}^2 \\ & + 0.4452 X_{CH_2}^2 + 0.2074 X_{CH_3} X_{CH_2} \end{aligned} \quad (4.1)$$

The following assumptions were made in proposing the above equation.

- (i) 1st and 2nd order $-CH_3$ and $-CH_2-$ groups have a higher influence over α_{CO_2/CH_4} .
- (ii) Groups of $\overset{|}{-CH-}$ and $\overset{|}{-C-}$ do not influence or slightly influences α_{CO_2/CH_4} .
- (iii) The equation does not distinguish among isomers nor among nonsolvent additives that have the same number of $-CH_3$ and $-CH_2-$ groups.

- (iv) The effect of molecular interactions among the alcohol groups do not influence or slightly influences $\alpha_{\text{CO}_2/\text{CH}_4}$.

The second order linear polynomial was tested for its adequacy by putting it through significance tests to make sure that the equation was not merely coincidental. The first part required that residual plots be drawn. However, these plots did not reveal any oddities in the predictability of the correlation. In the second part of the test, the variance of experimental error was estimated from replicate data points. In this work, one replicate data point was obtained from 2,4,4-trimethyl-1-pentanol and 2,6-dimethyl-4-heptanol, both of which have the same number of structural groups. $\alpha_{\text{CO}_2/\text{CH}_4}$ for 2,4,4-trimethyl-1-pentanol and 2,6-dimethyl-4-heptanol, respectively are 14.3 and 13.2. The replicate data was obtained from independent tests carried out at the same operating conditions.

The result of the aforementioned significance test showed that the inadequacy in the fitted straight line model was not significantly larger (at the 0.05 significance level) than the experimental error. Therefore, this model is adequate to describe the permeation properties with the type of nonsolvent additive and has physical meaning.

The coefficient of regression for the above equation (4.1) is 0.84. Figure 4.8 shows the observed and predicted $\alpha_{\text{CO}_2/\text{CH}_4}$ values. The measured value for 1-octanol is 25.2 and for 2-decanol is 22.4. The predicted pure CO_2/CH_4 permeance ratio for 1-octanol is about 37% more than the measured value while for 2-decanol, it is about 54% more than the measured value. There are two factors that contribute to the over-predicted values of $\alpha_{\text{CO}_2/\text{CH}_4} = 34.6$ for 1-octanol and $\alpha_{\text{CO}_2/\text{CH}_4} = 34.5$ for 2-decanol. First, the alcohol structures of 1-octanol and 2-decanol contain the most number of $-\text{CH}_2-$ groups which is 7. Also, from equation (4.1), the third highest constant is for the square of X_{CH_2} which is 0.4452.

Further analysis shows that if five $-\text{CH}_2-$ groups were in place of seven groups for 1-octanol and 2-decanol, the predicted pure CO_2/CH_4 permeance ratios would be more reasonable. The new predicted pure CO_2/CH_4 permeance ratio for 1-octanol is about 4% more than the measured value ($\alpha_{\text{CO}_2/\text{CH}_4} = 26.2$), while for 2-decanol, it is about 15% more than the measured value ($\alpha_{\text{CO}_2/\text{CH}_4} = 25.7$). The new coefficient of regression for the above model is 0.89. Figure 4.9 shows the observed and new predicted $\alpha_{\text{CO}_2/\text{CH}_4}$ values. The above results suggest that, while a large number of methylene group, $-\text{CH}_2-$, helps to increase the permeability ratio, $\alpha_{\text{CO}_2/\text{CH}_4}$, the 6th and 7th $-\text{CH}_2-$ can no longer contribute to its increase.

Figure 4.8. Predicted versus observed values of $\alpha_{\text{CO}_2/\text{CH}_4}$ with the over-predicted values of 2-decanol and 1-octanol.

Figure 4.9. Predicted versus observed values of $\alpha_{\text{CO}_2/\text{CH}_4}$ with the adjusted values of 2-decanol and 1-octanol.

4.3 Effect of Nodule Size and Roughness on Pure O₂/N₂ and CO₂/CH₄ Permeance Ratios

Surface morphology studies were done on 11 membrane samples, each representing an additive. Roughness data were obtained and the results are shown in Table 4.6. It shows the pure gas permeance ratios and roughness data (mean diameter and mean roughness, R_a of nodules) for different additives.

Figure 4.10 shows the mean pure gas permeance ratios of O₂/N₂ versus the mean diameter of nodules. It is found that the membrane that contained 2-ethyl-1-hexanol as its additive has the highest pure O₂/N₂ permeance ratio, $\alpha_{O_2/N_2} = 5.51$ and lowest mean nodule diameter, 27.8 nm. Figure 4.11 shows the pure gas permeance ratios of CO₂/CH₄ versus the mean diameter of nodules. Here again, it is seen that 2-ethyl-1-hexanol has the second highest pure CO₂/CH₄ permeance ratio, $\alpha_{CO_2/CH_4} = 24.5$ with the corresponding lowest mean nodule diameter.

The mechanism of nodule formation proposed by Wienk et al. (1996) showed that due to the rapid exchange of solvent and nonsolvent coagulant, the polymer molecules surround themselves with other polymer segments in order to diminish contact with the nonsolvent coagulant. The polymer chains do not extend, instead they become highly entangled coils and cluster into groups. Adjacent clusters are connected by chain entanglements and by shared polymer chains. At the beginning of the solvent-nonsolvent coagulant exchange process, the polymer clusters are highly interconnected. As the process continues, the polymer segments between the spheres become disentangled. This disentanglement leads to pore formation. The excess out-diffusion of solvent increases the polymer concentration in the top layer and results in vitrification of the polymer matrix which starts in the centers of the polymer clusters. Vitrification and disentanglement often occur simultaneously. The correlation of decreasing pure gas permeance ratio with increasing nodule size can be explained by the rapid disentanglement of the polymer

molecules compared to the vitrification process. As a result, more pores are also formed.

An important observation in this study was the physical appearance of nodules. There were two types of nodules identified: merged and discrete. Table 4.6 shows the amount of discrete or merged nodules over the total number of nodules (represented as a percentage) for the entire sample area studied. Figures 4.12 and 4.13 show examples of cross-sectional views of the merged (2-ethyl-1-hexanol) and discrete (2,4-dimethyl-3-pentanol) nodules, respectively. The merged nodules are defined by depressions that have a flat appearance on Figure 4.12. The discrete nodules are defined by the distinct depressions on Figure 4.13. The appearance of the nodules are also reflected in the mean roughness data, R_a . As shown in Table 4.6, if R_a is above 0.63 nm, the nodules were discrete and if R_a is below 0.62 nm, the nodules tend to merge.

Another important observation is the membranes with merged nodules formed an upper boundary in Figures 4.10 and 4.11 with only two exceptions (3,5,5-trimethyl-1-hexanol and 3-ethyl-2,2-dimethyl-3-pentanol). The percentages of merged nodules of these two exceptions are 56.7 and 71.4, which are the lowest and the third lowest among merged nodules, respectively (Table 4.6). This means that merged nodules result in higher pure gas permeance ratios. The merged nodules also reflect the rapidness of vitrification compared to that of disentanglement. The merged nodules show that vitrification is more rapid than disentanglement for 2-ethyl-1-hexanol, 1-octanol and 2-decanol. As a result, fewer number of pores are formed and the pure gas permeance ratios are high. It is also noted that while merged nodules result in higher pure gas permeance ratios, the size of nodules also plays an important role i.e. smaller nodules which range from 27.8 to 65.2 nm tend to result in higher pure gas permeance ratios.

In Figures 4.10 and 4.11, membranes with discrete nodules were located on the lower boundary of the plot. The discrete nodules show that the disentanglement process is close to completion when vitrification occurs. Therefore, more pores are formed and the pure

gas permeance ratios are low. Here, the range in the sizes of nodules is from 43.2 nm to 66.2 nm.

It should be recalled that a similar conclusion was obtained by Khulbe et al. (1997) for dense homogeneous membranes. Nodule aggregates were observed on the surface of a membrane which was cast from a PPO solution in CS_2 solvent. The selectivity of the membrane was found to be very high for CO_2/CH_4 and O_2/N_2 gas pairs (Khulbe et al., 1997). It can therefore be concluded that the aggregation, or the merging, of polymer nodules on the membrane surface is highly desirable to obtain a membrane of high selectivity. It should be specially noted that the above conclusion is valid for both integrally skinned asymmetric and dense homogeneous membranes. It should also be recalled that the selectivity of the dense homogeneous membrane decreased with an increase in the roughness parameter, R_a . The increase in roughness of the membrane results in disentanglement of nodules and discrete nodules are observed under AFM.

Looking into the structural components of three membranes which showed the highest pure gas permeance ratios, they were prepared by adding 2-ethyl-1-hexanol (shown as 1m), 1-octanol (shown as 2m) and 2-decanol (shown as 4m). In Table 4.5, it is found that all of them have a large number of $-\text{CH}_2-$ groups. The ratios defined as (number of $-\text{CH}_2-$ / number of $-\text{CH}_3$) are 5/2, 7/1 and 7/2, respectively, for 1m, 2m and 4m, indicating that all additives possess a long straight hydrocarbon chain. On the other hand, the above ratios for 3,5,5-trimethyl-1-hexanol (5m) and 3-ethyl-2,2-dimethyl-3-pentanol (9m) are 3/4 and 2/5, respectively, indicating high degrees of branching in the hydrocarbon structure. Note that the latter two additives were considered exceptional since they did not form the upper bounds in the plots shown in Figures 4.10 and 4.11.

Table 4.6. Roughness, diameter and appearance of nodules for membranes with the corresponding pure gas permeance ratios for O_2/N_2 and CO_2/CH_4 containing different nonsolvent additives.

Additive	α_{O_2/N_2}	α_{CO_2/CH_4}	Mean diameter (nm)	Appearance of nodule	R_a (nm)
(1) 2-ethyl-1-hexanol	5.51	24.5	27.8	90% merge	0.59
(2) 1-octanol	4.39	25.2	57.4	85.5% merge	0.54
(3) 2-propanol	3.16	17.5	43.2	61.6% discrete	0.64
(4) 2-decanol	4.50	22.4	44.7	65.5% merge	0.38
(5) 3,5,5-trimethyl-1-hexanol	3.43	15.4	56.7	56.7% merge	0.31
(6) 2,4-dimethyl-3-pentanol	3.69	17.0	45.7	100% discrete	0.63
(7) 2,4,4-trimethyl-1-pentanol	4.08	14.3	65.6	68.8% discrete	0.67
(8) 2,2-dimethyl-3-pentanol	3.99	15.1	114.1	76.9% merge	0.60
(9) 3-ethyl-2,2-dimethyl-3-pentanol	3.24	11.7	65.2	71.4% merge	0.45
(12) 3-ethyl-3-pentanol	4.20	n/a	56.5	100% merge	0.62
(13) 2-methyl-2-hexanol	3.27	n/a	66.2	56.6% discrete	0.76

Figure 4.10. Pure O_2/N_2 permeance ratio as a function of nodule diameter.

Figure 4.11. Pure CO₂/CH₄ permeance ratio as a function of nodule diameter.

Figure 4.12. Cross-sectional view of merged nodules from 2-ethyl-1-hexanol from analysis of atomic force microscopy.

Figure 4.13. Cross-section of discrete nodules from 2,4-dimethyl-3-pentanol from analysis of atomic force microscope.

4.4 Characterization of Mixed Solvent Systems

4.4.1 Effect of Intrinsic Viscosity on Polymer-Solvent-Nonsolvent Additive Systems on Pure O₂/N₂ and CO₂/CH₄ Permeance Ratios

Since the nodule size is predetermined by the size of polymer in solution, a correlation between pure gas permeance ratios and intrinsic viscosity of the dilute polymer systems is expected. A sample measurement and calculation of the intrinsic viscosity is given in Appendix D. The plots of η_{sp}/c versus c to determine if these measurements were linear are reflected in the calculated correlation coefficients of more than 0.96 in all cases (Table 4.7).

Table 4.7 Intrinsic viscosity measurements of polymer-solvent-nonsolvent additive systems for each nonsolvent additive and the corresponding pure CO₂/CH₄ permeance ratio.

Additive	$\alpha_{\text{CO}_2/\text{CH}_4}$	$[\eta]$ (dL/g)	Coefficient of regression, r^2
(1) 2-ethyl-1-hexanol	24.5	1.675	0.997
(2) 1-octanol	25.2	1.648	0.998
(3) 2-propanol	17.5	1.487	0.998
(4) 2-decanol	22.4	1.637	0.998
(5) 3,5,5-trimethyl-1-hexanol	15.4	1.616	0.999
(6) 2,4-dimethyl-3-pentanol	17.0	1.384	1.000
(7) 2,4,4-trimethyl-1-pentanol	14.3	1.292	0.999
(10) 2-methyl-3-hexanol	15.0	1.281	0.999

Figure 4.14 shows the correlation between the pure gas permeance ratios for CO₂/CH₄

and the intrinsic viscosities for eight additives. The intrinsic viscosities ranged from 1.28 dL/g for 2-methyl-3-hexanol to 1.68 dL/g for 2-ethyl-1-hexanol. All the values were below the intrinsic viscosity of the polymer solution without any nonsolvent additives at 1.79 dL/g.

It can be seen that as the intrinsic viscosity increases, the pure gas permeance ratios for CO_2/CH_4 increases with the exception of 3,5,5-trimethyl-1-hexanol. The increase in intrinsic viscosity means that polymer tends to spread in the solution rather than to be coiled (and as a result to be isolated from each other). In this case, the extension of a polymer molecule in a solution of a given concentration is a function of the polymer-solvent-nonsolvent additive interaction. In a "good" mixed solvent system, the interaction between the polymer and mixed solvent system is pronounced and the polymer becomes more relaxed compared to that of a "poor" mixed solvent system. As a result, the chance of entanglement between polymer molecules in solution increases, thereby, decreasing available free volume among polymer molecules. This result is manifested in the increasing pure CO_2/CH_4 permeance ratios as shown in Figure 4.14. It is seen that the three points with the greatest intrinsic viscosity, representing 2-ethyl-1-hexanol, 1-octanol and 2-decanol, form an upper boundary in which their nodules merge. It should be reminded that these additives have (number of $-\text{CH}_2-$ / number of $-\text{CH}_3$) ratios of much higher than unity.

In a "poor" mixed solvent system, the interaction between the polymer and mixed solvent system is not as pronounced and the polymer molecules are rigid. Since there is little interaction among the polymer molecules, their condition allows for increasing free volume. This is manifested in the low pure CO_2/CH_4 permeance ratios for 2-propanol, 2,4-dimethyl-3-pentanol, 2,4,4-trimethyl-1-hexanol and 2-methyl-3-hexanol as shown in Figure 4.14. It is also observed that discrete nodules are found among the aforementioned additives, namely 2-propanol, 2,4-dimethyl-3-pentanol and 2,4,4-trimethyl-1-hexanol.

Legend

(1) 2-ethyl-1-hexanol	(2) 1-octanol	(3) 2-propanol
(4) 2-decanol	(5) 3,5,5-trimethyl-1-hexanol	
(6) 2,4-dimethyl-3-pentanol	(7) 2,4,4-trimethyl-1-pentanol	
(10) 2-methyl-3-hexanol		

Figure 4.14. Pure CO_2/CH_4 permeance ratio as a function of intrinsic viscosity.

4.4.2 Effect of Surface Tension of Mixed Solvent Systems on Pure O₂/N₂ and CO₂/CH₄ Permeance Ratios

The effect of surface tension on the formation of nodules at the outermost region of the membrane has been discussed (Kesting, 1989; Pinnau and Koros, 1993). For the wet phase inversion process, Kesting (1989) described the transition from sol 1 to gel to sol 2. The formation of nodule aggregates is due to the simultaneous effect of solvent concentration gradients and surface tension forces. Pinnau and Koros (1993) described the effect of capillary pressure in the interstitial space filled with the polymer-poor phase in contact with air. This resulting force acts normal to the membrane-air interface until the spherical particles fuse together, to minimize surface area.

The results of the surface tension measurements carried out on mixed solvent systems consisting of nonsolvent additive/solvent are shown in Table 4.8. The values of the surface tension measurements range from 25.29×10^{-3} N/m for 2-methyl-3-hexanol to 26.65×10^{-3} N/m for 2-ethyl-1-hexanol. The standard deviations of these measurements are not higher than 0.59%.

The effect of the surface tension of chloroform-nonsolvent additive systems on the formation of nodules are reflected in the correlation between surface tension and pure O₂/N₂ (Figure 4.15) and CO₂/CH₄ (Figure 4.16) permeance ratios. Both figures show that as the surface tension increased, the pure gas permeance ratios increased. Also, merged nodules are found in the range of surface tensions greater than 26.4×10^{-3} N/m. When the surface tension is less than 26.4×10^{-3} N/m, nodules are discrete. The only exception of this rule is 3-ethyl-3-pentanol.

In Figure 4.15, the use of 2-ethyl-1-hexanol, 1-octanol and 2-decanol as nonsolvent additives produces higher surface tensions resulting in higher pure O₂/N₂ permeance ratios. On the other hand, lower surface tensions resulting in lower pure O₂/N₂

permeance ratios are reflected in the use of 2-propanol, 2,4-dimethyl-3-pentanol, 2-methyl-3-hexanol and 2-methyl-2-hexanol as nonsolvent additives. In Figure 4.16, the higher surface tensions resulting from using 2-ethyl-1-hexanol, 1-octanol and 2-decanol as nonsolvent additives, increases the pure CO₂/CH₄ permeance ratios. The capillary forces of spherical particles in the polymer-rich phases of these solutions are high. As a result, these particles coalesce more readily than nonsolvent additives of 2-propanol, 2,4-dimethyl-3-pentanol and 2-methyl-3-hexanol. This coalescence results in the manifestation of merged nodules, which may lead to increasing nodule diameter or increasing roughness.

Table 4.8 Experimental values of surface tension for chloroform-nonsolvent additive mixtures and their standard deviations.

Sample	$\gamma \times 10^3$ (N/m)	% std.dev.
Chloroform	26.82	0.51
2-ethyl-1-hexanol	26.65	0.59
1-octanol	26.84	0.53
2-propanol	25.88	0.49
2-decanol	26.53	0.59
3,5,5-trimethyl-1-hexanol	26.44	0.44
2,4-dimethyl-3-pentanol	26.10	0.45
2,4,4-trimethyl-1-pentanol	26.42	0.52
2-methyl-3-hexanol	25.29	0.50
3-ethyl-3-pentanol	25.56	0.48
2-methyl-2-hexanol	26.27	0.54

Both the experiments of intrinsic viscosity and surface tension have proven to be simple and accurate techniques for obtaining information of the interaction among the various

variables such as polymer, solvent and nonsolvent additive. The intrinsic viscosity provides quantitative representation of the behaviour of polymer, solvent and nonsolvent additive at infinite dilution. The interaction between polymer and solvent/nonsolvent additive system can be identified as "good", where the polymer molecules are relaxed as opposed to the system being "poor", where the molecules are rigid.

Information from experiments of surface tension gives a preliminary idea of the formation of nodules on the surface of the membrane. The surface tension provides a quantitative measure of the liquid-liquid i.e. solvent-nonsolvent additive interface. Since this measure is directly proportional to the capillary pressure of the solvent-nonsolvent additive interface, it may be extended to represent the capillary pressure of the polymer nodules.

Legend

(1) 2-ethyl-1-hexanol	(2) 1-octanol	(3) 2-propanol
(4) 2-decanol	(5) 3,5,5-trimethyl-1-hexanol	
(6) 2,4-dimethyl-3-pentanol	(7) 2,4,4-trimethyl-1-pentanol	
(10) 2-methyl-3-hexanol	(12) 3-ethyl-3-pentanol	
(13) 2-methyl-2-hexanol	m-merged	d-discrete

Figure 4.15. Pure O₂/N₂ permeance rate ratio as a function of surface tension.

Legend

(1) 2-ethyl-1-hexanol	(2) 1-octanol	(3) 2-propanol
(4) 2-decanol	(5) 3,5,5-trimethyl-1-hexanol	
(6) 2,4-dimethyl-3-pentanol	(7) 2,4,4-trimethyl-1-pentanol	
(10) 2-methyl-3-hexanol		
m-merged	d-discrete	

Figure 4.16. Pure CO_2/CH_4 permeance rate ratio as a function of surface tension.

4.5 Effect of Plasma-Etching on Pure CO₂/CH₄ and O₂/N₂ Permeances and Permeance Ratios.

Coupons for plasma-etching studies were produced from membranes which were prepared by using 2-ethyl-1-hexanol as the nonsolvent additive. The details of the procedure for preparing the membranes were discussed in Chapter 3. Table 4.9 shows these coupons and their etching times.

Table 4.9. Coupon codes and their plasma etching time.

Sample #	Maximum etching time (sec)
C10	30
C131	60
C11	120
C9	190

Figure 4.17 shows the weight loss of PPO coupons during etching. The weight loss of the coupons is gradual and after 190 sec of etching time, the membrane loses 8.8% of its weight.

Figures 4.18 and 4.19 show the pure N₂ and O₂ permeances (P/l) versus the etching time. Data from coupons C10, C131 and C11 show that as the etching time is increased from 0 to 120 seconds, P/l decreases. After 120 seconds, P/l increases as indicated by the data from coupon C9. In Figure 4.20, the pure O₂/N₂ permeance ratios of coupons C10 and C11 increased as the etching time was increased from 0 to 30 seconds. α_{O_2/N_2} then decreased when the etching time of all the coupons was increased from 40 to 190 seconds.

Figure 4.17 Mass loss of membrane as a function of etching time.

Figure 4.18. Permeance of N₂ as a function of etching time.

Figure 4.19. Permeance of O_2 as a function of etching time.

Figure 4.20. Pure O₂/N₂ permeance rate ratio as function of etching time.

Figure 4.21 shows that $(P/I)_{CH_4}$ decreased as the etching time increased from 0 to 120 seconds for coupons C10, C131 and C11. Data from coupon C9 show that after 120 seconds, the $(P/I)_{CH_4}$ increased by 126% of its original value from 1.31×10^{-9} to 2.97×10^{-9} mole/m².s.Pa. For $(P/I)_{CO_2}$ versus etching time, Figure 4.22 shows that as the etching time increased from 0 to 120 seconds, $(P/I)_{CO_2}$ decreased. It leveled off after the membrane was etched from 120 to 190 seconds. In Figure 4.23, α_{CO_2/CH_4} reached a maximum for coupons C10 and C11 after the coupons were etched for 20 seconds. After coupon C9 was etched for 190 seconds, α_{CO_2/CH_4} decreased by 81% of its original value from 17.8 to 3.33.

Figures 4.24(a)-(e) show scanning electron micrographs (SEM) of the cross-section of the unetched and etched membranes at the magnification of 900X. The SEM pictures of coupons C10, C131, C11 and C9 were taken after etching times of 30, 60, 120 and 190 seconds, respectively. Coupon C131 was used to take the SEM picture of the unetched membrane. All the coupons show that there is a transition in the membrane structure from the dense layer to the layer with visible pores. With the exception of coupon C9 (Figure 4.24(e)), the other coupons reveal a smooth surface on the top surface of the membrane. The surface of coupon C9 has had the highest etching time at 190 seconds and reveals a surface that is torn-up. Therefore, coupon C9 was not included in the following AFM analysis since the results obtained would not be representative of the conditions on the top surface.

Figures 4.25(a)-(e) show three dimensional AFM images of the top surfaces of the unetched and etched membranes. It is observed that for Figures 4.25(a)-(c), the surface of the top layer is smooth and for Figure 4.25(d), the roughness of the surfaces increases. It is reflected in Figure 4.26 for mean roughness, R_a versus etching time where R_a increases linearly as the membrane is exposed to longer periods of etching time. The unlabelled point at 0 sec of etching time refers to the unetched membrane.

Legend

▼ C10 (30 sec)
● C11 (120 sec)

■ C131 (60 sec)
▲ C9 (190 sec)

Figure 4.21. Permeance of CH_4 as a function of etching time.

Figure 4.22. Permeance of CO₂ as a function of etching time.

Legend

▼ C10 (30 sec)	■ C131 (60 sec)
● C11 (120 sec)	▲ C9 (190 sec)

Figure 4.23. Pure CO₂/CH₄ permeance rate ratio as a function of etching time.

Figure 4.24(a). SEM picture of unetched membrane.

Figure 4.24(b). SEM picture of membrane etched at 30 sec (coupon C10).

Figure 4.24(c). SEM picture of membrane etched at 60 sec (coupon C131).

Figure 4.24(d). SEM picture of membrane etched at 120 sec (coupon C11).

Figure 4.24(e). SEM picture of membrane etched at 190 sec (coupon C9).

Figure 4.25(a). Three-dimensional view of unetched membrane.

Figure 4.25(b). Three-dimensional view of membrane etched at 30 sec.

Figure 4.25(c). Three dimensional view of membrane etched at 60 sec.

Figure 4.25(d). Three dimensional view of membrane etched at 120 sec.

Figure 4.25(e). Three dimensional view of membrane etched at 190 sec.

Results of regression analysis

$R_a = 0.009637x + 0.488$ where x is the etching time.

The coefficient of regression, $r^2 = 0.96$.

Figure 4.26. Roughness as a function of etching time.

The height and diameter of the nodules were measured from the AFM images as described in Chapter 3. Figures 4.27 and 4.28 show the mean height and mean diameter, respectively, of the nodules as a function of etching time. An example of the calculation is given in Appendix F. In Figure 4.27, the mean nodule height decreases by 35.5% from 1.66 ± 0.35 nm for the unetched membrane to 1.07 ± 0.26 nm for 30 seconds of etching time. As the etching time increases however, so does the mean nodule height. For the mean diameter, Figure 4.28 shows that the diameter of the nodules increases as the etching time increases.

Table 4.10 shows the average thicknesses of the skin layer at various etching times. The thickness of the skin layer was calculated from intrinsic permeability values (Appendix F). The original thickness of the skin layer was calculated to be $0.68 \mu\text{m}$. At 190 sec, the membrane retains 46.35% of its original thickness.

Table 4.10. Thickness of skin layer as a function of etching time.

Etching time (sec)	Average thickness (μm)	% of original thickness
0	0.68	N/A
170	0.41	60.38
190	0.31	46.35

Figure 4.29 shows two macromolecular aggregates packed together. By using the height from roughness data and diameter for 60 and 120 second etching time, the radius of curvature, R of the aggregate can be calculated and this is given in Table 4.11. Sample calculations are given in Appendix F. The highest difference in radius of curvature between the etched and unetched membranes is 18.2 % (120 sec etching time). This suggests that the nodules dimension was unchanged by etching and that the surface of the skin layer was etched in a particular manner.

Figure 4.27. Nodule height as a function of etching time.

Figure 4.28. Nodule diameter as a function of etching time.

Figure 4.29. Radius of curvature, R based on a spherical macromolecular aggregate.

Table 4.11. Calculated radius of curvature, R based on a spherical macromolecular aggregate at various etching times and percentage difference between unetched and etched membranes.

Maximum etching time (sec)	Height from roughness measurements (nm)	Mean diameter (nm)	R (nm)	% difference
0	0.5947	27.8	162.8	N/A
60	1.0475	38.86	181.0	11.2
120	1.6864	50.83	192.4	18.2

It had been assumed that plasma-etching had a layering effect on the surface of the membranes but this would have been reflected in the AFM images in which the mean height of a nodule would decrease for the etching times higher than 30 seconds. As the surface of the top layer of the membrane is continually etched for 60 and 120 seconds, the mean height of the nodule increases (Figure 4.27) and the mean diameter of the nodule increases (Figure 4.28) with an increase in etching time compared to that of the unetched membrane. Both these observations reflect the manner in which the membranes are

etched. A possibility is to assume that the low density areas of the membrane i.e. between the nodules, are etched faster than the high density areas (nodules). These low and high density areas are depicted in Figure 4.30. This can be proven by adding the length of the crevices between the nodules to the diameter of the nodules of coupons C131 and C11 to yield a constant value, regardless of the etching time. Appendix F shows an example of this calculation. The results are shown in Table 4.12. The length of the crevices are given in Figure 4.31. As Kesting (1989) pointed out, the dominant pore rim element for gas separation membranes is the displacement between parallel intramolecular chain segments in the interior of the nodule as well as in the low density areas between the nodules. Therefore, unlike reverse osmosis membranes where its pore rim element is the intermolecular chain segments in interstices between nodules, gas permeation cannot be largely controlled in the interstices between nodules for gas separation membranes. This permeation behaviour is reflected in Figures 4.18, 4.19 and 4.21 where there is an increase in the permeance of N_2 , O_2 and CH_4 after an etching time of 120 seconds.

Figure 4.30. Low and high density areas for spherical macromolecular aggregates.

c length of crevice
 ma diameter of macromolecular aggregate
 n diameter of nodule

Figure 4.31. Mean diameter of nodule and length of crevice.

Table 4.12. Mean diameter of nodule plus length of crevice for coupons C131 and C11.

Coupon	Maximum etching time (sec)	Mean diameter of nodule plus length of crevice (nm)
131	60	52.93 ± 5.43
11	120	54.50 ± 4.66

Contact angle measurements were carried out on the etched and unetched membranes and the results are shown in Table 4.13. The unetched membrane, coupons C131 and C11 showed similar contact angles. Coupon C10 has a slightly lower contact angle than the aforementioned coupons. The slight change in contact angles for coupons C10, C131 and C11 shows that PPO was attacked quite slowly by atomic oxygen and that the primary oxidation products were attacked more rapidly than the polymer itself. If a highly oxidized layer had been created, these surfaces would have exhibited very low contact angles. Bauer et al. (1991) also concluded that phenomena such as chemical reactions or melting of the topmost layer of asymmetric PPO hollow fiber membranes due to etching,

was not possible. Coupon C9 showed an advancing contact angle of 90° which simply showed that the surface had been roughened, as proven by the SEM picture (Fig. 4.24(e)).

Table 4.13. Contact angle measurements of etched and unetched membranes.

Coupon #	Etching time (sec)	Contact angle
Unetched	0	53.33°
10	30	49.50°
131	60	51.30°
11	120	50.00°
9	190	90.00°

CHAPTER 5

CONCLUSIONS

1. For 5 wt.% of nonsolvent additive, the PPO/chloroform/2-ethyl-1-hexanol/methanol system provided the highest pure gas permeance ratio for O₂/N₂ at 5.5.
2. For 5 wt.% of nonsolvent additive, the PPO/chloroform/2-ethyl-1-hexanol/methanol system also provided the highest permeance for CO₂ at 2.35 X 10⁻⁸ mol/m².s.Pa while maintaining a high pure gas permeance ratio for CO₂/CH₄ at 24.5.
3. $\alpha_{\text{CO}_2/\text{CH}_4}$ can be predicted by applying the linear additivity rule to the structural components of nonsolvent additives. The model is

$$\alpha_{\text{CO}_2/\text{CH}_4} = 21.264 + 0.2744 X_{\text{CH}_3} - 1.377 X_{\text{CH}_2} - 0.5987 X_{\text{CH}_3}^2 + 0.4452 X_{\text{CH}_2}^2 + 0.2074 X_{\text{CH}_3} X_{\text{CH}_2} \quad (4.1)$$

While a large number of methylene group, -CH₂-, helps to increase $\alpha_{\text{CO}_2/\text{CH}_4}$, the 6th and 7th -CH₂- can no longer contribute to its increase. The discussion of fitting the experimental permeation properties with the type of nonsolvent by nonlinear regression does have physical significance

4. The technique of atomic force microscopy (AFM) has provided a useful tool for measuring and characterizing nodules on the surfaces of asymmetric PPO membranes. Two types of nodules were identified: merged and discrete.
5. Membranes containing merged nodules resulted in higher pure gas permeance ratios for O_2/N_2 and CO_2/CH_4 with the exception of 3,5,5-trimethyl-1-hexanol and 3-ethyl-2,2-dimethyl-3-pentanol. The merged nodules showed that vitrification of the polymer molecules was more rapid than disentanglement especially for 2-ethyl-1-hexanol, 1-octanol and 2-decanol.
6. Membranes containing discrete nodules resulted in lower pure gas permeance ratios for O_2/N_2 and CO_2/CH_4 .
7. As for the size of the nodules, membranes with smaller nodules on its top surface resulted in higher pure gas permeance ratios for O_2/N_2 and CO_2/CH_4 .
8. Intrinsic viscosity and surface tension measurements have proven to be valuable tools for the characterization of mixed solvent systems. Both methods are simple and provide accurate measurements.
9. Higher intrinsic viscosities of the dilute PPO/chloroform/nonsolvent additive systems resulted in higher pure gas permeance ratios for CO_2/CH_4 , with the exception of 3,5,5-trimethyl-1-hexanol. The three nonsolvent additives, 2-ethyl-1-hexanol, 1-octanol and 2-decanol which had high intrinsic viscosities, produced nodules that merged.
10. Higher surface tensions of the chloroform/nonsolvent additive systems resulted in higher pure gas permeance ratios for CO_2/CH_4 and O_2/N_2 . Higher surface tensions resulted in merged nodules with the exception of 3,5,5-trimethyl-1-hexanol while

lower surface tensions resulted in discrete nodules.

11. Plasma-etching is a powerful tool in determining the structure of the skin of the asymmetric PPO membrane. This structure is reflected in the gas performance data for pure N₂, O₂, CH₄ and CO₂.
12. Scanning electron microscopy and atomic force microscopy have provided useful information regarding the cross-sectional surfaces and the top surfaces of the membrane, respectively.
13. Scanning electron microscopy showed that there is a transition in the membrane structure from the dense layer to the layer with visible pores for all the coupons. With the exception of coupon C9 (etching time higher than 120 seconds), the other coupons revealed a smooth surface on the top surface of the membrane.
14. The AFM images of the top surfaces of the unetched and etched membranes show that mean roughness, R_a increases linearly as the membrane is exposed to longer periods of etching time.
15. As the surface of the top layer of the membrane is continually etched from 60 to 120 seconds, the low density areas of the membrane i.e. between the nodules, are etched faster than the high density areas (nodules).
16. Small contact angle change for coupons C10, C131 and C11 from the unetched membrane, showed that PPO was attacked quite slowly by atomic oxygen and that the primary oxidation products were attacked more rapidly than the polymer itself. The advancing contact angle of 90° for coupon C9 showed that the surface had been roughened.

CHAPTER 6

RECOMMENDATIONS

The following are recommendations for the continuation of this work.

1. Light scattering experiments can be carried out on PPO/chloroform/nonsolvent additive casting solutions in order to study their extent of polymer supermolecular ordering. Data obtained from such measurements with the properties of prepared asymmetric PPO membranes may shed more light on the early stage of membrane formation and contribute to more controllable membrane preparation.
2. The characterization of PPO membranes made from different nonsolvent additives can also be carried out by using mixed gases of CO_2/CH_4 and O_2/N_2 gas pairs to obtain permeance data. These data may be correlated along with mean diameter of nodules, intrinsic viscosity and surface tension to further investigate the role of merged and discrete nodules in gas permeance.
3. Properties of solvents used in the preparation of membrane casting solutions are an important factor affecting membrane morphology and performance.

Asymmetric PPO membranes have already been prepared from solvents such as chloroform, trichloroethylene (Wijmans et al., 1985) and mixtures of trichloroethylene/chloroform (Gagné, 1996) using 2-ethyl-1-hexanol as the nonsolvent additive. The surface morphology of these membranes can be characterized by atomic force microscopy and compared with each other in terms of nodule size, roughness and if possible, other notable features.

4. The effect of plasma-etching can be investigated on membranes with discrete nodules such as PPO/chloroform/2-propanol. These membranes can be characterized by gas permeation, atomic force microscopy, scanning electron microscopy and contact angle measurements and then compared with membranes with merged nodules.

APPENDICES

Appendix A

Casting conditions and permeance data for N₂, O₂, CH₄ and CO₂ for different nonsolvent additive.

The following tables, tables A.1 and A.2 contain abbreviations for the chemical structures of the nonsolvent additives which is given below. The superscripts, 1 and 2 in both tables refer to coupon 1 and coupon 2 which were tested for their gas permeation properties.

Coupon code	Abbreviation
2E1H	2-ethyl-1-hexanol
1OCOH	1-octanol
2PROH	2-propanol
2DEOH	2-decanol
355T1H	3,5,5-trimethyl-1-hexanol
24D3P	2,4-dimethyl-3-pentanol
244T1P	2,4,4-trimethyl-1-pentanol
22D3P	2,2-dimethyl-3-pentanol
3E22D3P	3-ethyl-2,2-dimethyl-3-pentanol
2M3H	2-methyl-3-hexanol
26D4H	2,6-dimethyl-4-heptanol
3E3P	3-ethyl-3-pentanol
2M2H	2-methyl-2-hexanol

Table A.1 Casting conditions and permeance data for N₂ and O₂ for different nonsolvent additives.

COUPON CODE	CASTING TEMP. (K)	CASTING HUMIDITY (%)	P// N ₂ mol/s.m ² .Pa	P// O ₂ mol/s.m ² .Pa	α O ₂ /N ₂	Mean P// N ₂ mol/s.m ² .Pa	Mean P// O ₂ mol/s.m ² .Pa	α O ₂ /N ₂
2EIH	295.75	41	7.17E-10	3.95E-09	5.51	7.17E-10	3.95E-09	5.51
IOCOH	294.05	20	1.240E-10 1.68E-10	1.11E-09 6.90E-10	4.63 4.11	2.04E-10	8.98E-10	4.40
2PROH	294.35	66	4.12E-10 4.38E-09	1.29E-09 1.39E-09	3.13 3.18	4.25E-10	1.34E-09	3.15
2DEOH	294.25	74	2.80E-10	1.26E-09	4.5	2.80E-10	1.26E-09	4.50
355T1H	295.05	19	1.28E-09 1.46E-09	4.07E-09 5.11E-09	3.18 3.50	1.37E-09	4.59E-09	3.34
24D3P	295.65	12	1.33E-09 1.03E-09	4.98E-09 3.72E-09	3.74 3.61	1.18E-09	4.35E-09	3.69
244T1P	296.09	16	8.64E-10 6.02E-10	3.14E-09 2.84E-09	3.63 4.72	7.33E-10	2.99E-09	4.18
22D3P	295.87	19	4.99E-10 1.04E-09	2.23E-09 3.91E-09	4.47 3.76	7.70E-10	3.07E-09	4.12
3E22D3P	295.82	18	1.94E-09 1.42E-09	6.04E-09 4.87E-09	3.11 3.43	1.68E-09	5.46E-09	3.27
2M3H	295.76	17	4.84E-10 5.18E-10	1.45E-09 1.57E-09	3.00 3.03	5.02E-10	1.51E-09	3.02
26D4H	294.54	18	9.96E-10 1.13E-09	4.21E-09 4.45E-09	4.23 3.94	1.06E-09	4.33E-09	4.09
3E3P	295.98	16	1.24E-09	5.22E-09	4.22	1.24E-09	5.22E-09	4.22
2M2H	294.15	17	9.04E-10 1.05E-09	3.01E-09 3.38E-09	3.33 3.22	9.78E-10	3.20E-09	3.27

Table A.2. Casting conditions and permeance data for CO₂ and CH₄ for different nonsolvent additives.

COUPON CODE	CASTING TEMP. (K)	CASTING HUMIDITY (%)	P// CH ₄ mol/s.m ² .Pa	P// CO ₂ mol/s.m ² .Pa	α CO ₂ /CH ₄	Mean P// CH ₄ mol/s.m ² .Pa	Mean P// CO ₂ mol/s.m ² .Pa	α CO ₂ /CH ₄
2E1H	295.75	41	9.54E-10	2.34E-08	24.5	9.54E-10	2.34E-08	24.5
1OCOH	294.05	20	¹ 1.05E-10 ² 1.25E-10	¹ 2.44E-09 ³ 3.36E-09	23.2 26.9	1.15E-10	2.9E-09	25.2
2PROH	294.35	66	¹ 2.59E-10 ² 2.95E-09	¹ 4.07E-09 ² 5.61E-09	15.7 19.0	2.77E-10	4.84E-09	17.5
2DEOH	294.25	74	2.50E-10	5.59E-09	22.4	2.50E-10	5.59E-09	22.4
35ST1H	295.05	19	¹ 8.94E-10 ² 1.27E-09	¹ 1.28E-08 ² 2.04E-08	14.3 16.1	1.08E-09	1.66E-08	15.4
24D3P	295.65	12	¹ 6.28E-10 ² 5.60E-10	¹ 1.07E-08 ² 9.49E-09	17.0 16.9	5.93E-10	1.01E-08	17.0
244T1P	296.09	16	¹ 7.68E-10 ² 6.93E-10	¹ 1.19E-08 ² 8.96E-09	15.5 12.9	7.30E-10	1.04E-08	14.3
22D3P	295.87	19	¹ 3.99E-10 ² 6.39E-10	¹ 7.13E-09 ² 8.51E-09	17.9 13.3	5.19E-10	7.84E-09	15.1
3E22D3P	295.82	18	¹ 1.33E-09 ² 1.38E-09	¹ 1.61E-08 ² 1.57E-08	12.1 11.4	1.35E-09	1.59E-08	11.7
2M3H	295.76	17	¹ 3.32E-10 ² 3.41E-10	¹ 5.14E-09 ² 4.95E-09	15.5 14.5	3.38E-10	5.06E-09	15.0
26D4H	294.54	18	¹ 8.35E-10 ² 1.04E-09	¹ 1.15E-08 ² 1.26E-08	13.8 12.1	9.38E-10	1.21E-8	13.0
3E3P	295.98	16	---	---	---	---	---	---
2M2H	294.15	17	---	---	---	---	---	---

Appendix B

Empirical Correlation between Alcohol Structure (Group Contribution) of Nonsolvent Additive and Pure CO₂/CH₄ Permeance ratio.

The model proposed to fit the alcohol structures of nonsolvent additives and pure CO₂/CH₄ permeance ratios was a 2nd order linear polynomial.

$$E(Y) = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2 \quad (B.1)$$

The equation describes the relationship of the -CH₃- (given as X₁) and -CH₂- (given as X₂) groups with $\alpha_{\text{CO}_2/\text{CH}_4}$. The 1st and 2nd order -CH₃- and -CH₂- groups have a higher influence over $\alpha_{\text{CO}_2/\text{CH}_4}$ compared to -CH-, -C- and -OH groups.

Model Assumptions

The following assumptions were made in proposing the above equation.

- (i) The other groups such as -CH-, -C- and -OH do not influence or slightly influences the results of $\alpha_{\text{CO}_2/\text{CH}_4}$.
- (ii) The equation does not distinguish among isomers nor among nonsolvent additives that have the same number of -CH₃ and -CH₂- groups.
- (iii) The effect of molecular interactions among the alcohol groups have been neglected.

Parameter estimation

The parameters in equation (B.1) were estimated using linear least squares fit based on the orthogonal factorization method available from MATLAB (The MathWorks Inc., 1992). The parameters are shown in Table B.1.

Table B.1: Estimated values for the parameters for equation (B.1).

Parameters	b_0	b_1	b_2	b_{11}	b_{22}	b_{12}
Values	21.264	0.2744	-1.377	-0.5987	0.4452	0.2074

Significance tests were done on the adequacy of the fitted model (McLean, 1997). Table B.2 shows the measured response values for data point u , y_u , and the fitted response value for data point u , $\hat{y}_u$.

The residual sum of squares is given by

$$\Sigma e_u^2 = \Sigma (y_u - \hat{y}_u)^2 = \Sigma [(y_u - ym_u) + (ym_u - \hat{y}_u)]^2 \quad (B.2)$$

where n is the total number of data points used for fitting the model. Therefore, $\Sigma e_u^2 = 54.33$ for 11 data points and has $(n - p) = 11 - 6 = 5$ degrees of freedom. n is the number of residuals that have been constrained by the p linear equations to ensure that Σe_u^2 is minimized and p is the number of estimated parameters in the fitted model.

Since 2,4,4-trimethyl-1-pentanol and 2,6-dimethyl-4-heptanol have the same number of structural groups, there is one pair of replicate response value. α_{CO_2/CH_4} for 2,4,4-trimethyl-1-pentanol and 2,6-dimethyl-4-heptanol are 14.3 and 13.2, respectively. Therefore, the estimate of pure error variance, σ^2 is given by the following expression

$$\sigma^2 = \frac{\Sigma (y_u - ym)^2}{(m - 1)} = 0.366 \quad (B.3)$$

where ym is the sample mean of all measured response values at the operating conditions for data point u and m is the number of replicates at a certain operating condition. σ^2 has 1 degree of freedom, q .

From equation (B.2), it can be seen that Σe_u^2 is a combination of two terms. The first term on the right hand side comes from pure error only and the second term comes from pure error and inadequacy in the form of the model being fitted. The value of this second term is

$$\Sigma (ym_u - \hat{y}_u)^2 = 53.96 \quad (B.4)$$

It has $(n - p - q) = 11 - 6 - 1 = 4$ degrees of freedom.

The significance of any model inadequacy is tested using the test ratio, R .

$$R = \frac{\Sigma (ym_u - \hat{y}_u)^2 / (n - p - q)}{\sigma^2} = \frac{53.96}{(4)0.366} \quad (B.5)$$

This value is compared with the F probability density function, $F_{4,1,0.05} = 235$. R is less than F which shows that any inadequacy in equation (B.1) is not significantly larger (at the 0.05 significance level) than the experimental error.

Table B.2. Measured response values, y_u , and fitted response values, $\hat{y}_u$ for nonsolvent additives.

Additive	No. of CH ₃ groups	No. of CH ₂ groups	y_u	$\hat{y}_u$
2-ethyl-1-hexanol	2	5	24.5	25.74
1-octanol	1	5	25.2	26.22
2-propanol	2	0	17.5	19.42
2-decanol	2	5	22.4	25.74
3,5,5-trimethyl-1-hexanol	4	3	15.4	15.15
2,4-dimethyl-3-pentanol	4	0	17.0	12.78
2,4,4-trimethyl-1-pentanol	4	2	14.3	13.47
2,2-dimethyl-3-pentanol	4	1	15.1	12.68
3-ethyl-2,2-dimethyl-3-pentanol	5	2	11.7	8.77
2-methyl-3-hexanol	3	2	15.0	16.00
2,6-dimethyl-4-heptanol	4	2	13.2	13.47

Appendix C

Example of data collection and calculation of diameter of nodules from AFM samples.

Additive: 2-decanol

The sample was subdivided into grids and the roughness data measured for each grid.

Table C.1. Measurements of diameter from cross-section of AFM samples for 2-decanol.

Grid #	Diameter (nm)
Sample SP1500nm	
1	27.344 41.016 35.156 29.297 17.578 27.344 31.250 25.391 19.531 25.391 33.203 68.359
2	31.250 41.016 33.203 44.922 21.484 19.531 33.203 25.391 23.438 52.734 21.484
3	27.344 31.250 19.531 44.922 21.484 33.203 33.203 33.203 31.250 21.484
4	60.547 39.063 56.641 44.922 64.453 37.109 41.016
Sample SP2500nm	
1	151.93 61.973 49.979 59.974
2	53.977 59.974 75.967 43.981 55.976
3	65.972 63.972 35.985 71.969
4	41.982 45.980 67.971 45.980 93.960
5	53.977 65.972 85.963
6	57.975 51.978 29.987 41.982

Statistical analysis for diameter of nodules

Mean	44.68426 nm
Standard Error	2.749503 nm
Median	41.016 nm
Standard Deviation	22.1672 nm
Minimum	17.578 nm
Maximum	151.93 nm
Sum	2904.477 nm

Count	65
Confidence level (0.95)	5.388926 nm

Appendix D

Sample Calculation of Intrinsic Viscosity, $[\eta]$.

D.1 Sample Calculation of Intrinsic Viscosity, $[\eta]$ without nonsolvent additive.

Necessary data: Density of chloroform (CHCl_3) = 1.4789 g/mL.

Original solution consists of 0.2 g PPO and 59.156 g chloroform (CHCl_3).
Therefore, total weight of solution is 59.356 g.

Initial concentration, c_1

$$c_1 = 0.015006 \text{ g PPO} / 3.001213 \text{ mL CHCl}_3 = 0.5 \text{ g PPO} / 100 \text{ mL of CHCl}_3$$

Flowtime measurements for this solution, t_1 , were = 196.1 sec, 196.47 sec, 196.45 sec. Therefore, the average t_1 = 196.34 sec.

1st dilution with CHCl_3 . Calculation of c_2 .

Weight of CHCl_3 from c_1	=	4.438494 g
Weight of 1st dilution	=	<u>2.793200 g</u>
Therefore, total weight of CHCl_3 after dilution	=	7.231694 g
total volume of CHCl_3 after dilution	=	4.889914 mL

Weight of PPO in solution	=	0.015006 g
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Therefore, $c_2 = 0.015006 \text{ g PPO} / 4.889914 \text{ mL CHCl}_3 = 0.306878 \text{ g PPO} / 100 \text{ mL of CHCl}_3$.

Flowtime measurements for this solution, t_2 , were = 154.49 sec, 154.33 sec, 154.19 sec. Therefore, the average t_2 = 154.34 sec.

2nd dilution with CHCl_3 . Calculation of c_3 .

Weight of CHCl_3 from c_2	=	7.231694 g
Weight of 2nd dilution	=	<u>1.444300 g</u>
Therefore, total weight of CHCl_3 after dilution	=	8.675994 g
total volume of CHCl_3 after dilution	=	5.866518 mL

Weight of PPO in solution	=	0.015006 g
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Therefore, $c_3 = 0.015006 \text{ g PPO} / 5.866518 \text{ mL CHCl}_3 = 0.255792 \text{ g PPO} / 100 \text{ mL of CHCl}_3$.

Flowtime measurements for this solution, t_3 , were = 144.21 sec, 144.19 sec, 144.11 sec. Therefore, the average $t_3 = 144.17 \text{ sec}$.

3rd dilution with CHCl₃. Calculation of c_4 .

Weight of CHCl ₃ from c_3	=	8.675994 g
Weight of 3rd dilution	=	<u>1.560300 g</u>
Therefore, total weight of CHCl ₃ after dilution	=	10.23629 g
total volume of CHCl ₃ after dilution	=	6.921559 mL

Weight of PPO in solution	=	0.015006 g
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Therefore, $c_4 = 0.015006 \text{ g PPO} / 6.921559 \text{ mL CHCl}_3 = 0.216802 \text{ g PPO} / 100 \text{ mL of CHCl}_3$.

Flowtime measurements for this solution, t_4 , were = 136.35 sec, 136.49 sec, 136.47 sec. Therefore, the average $t_4 = 136.44 \text{ sec}$.

4th dilution with CHCl₃. Calculation of c_5 .

Weight of CHCl ₃ from c_4	=	10.23629 g
Weight of 4th dilution	=	<u>1.296500 g</u>
Therefore, total weight of CHCl ₃ after dilution	=	11.53279 g
total volume of CHCl ₃ after dilution	=	7.798224 mL

Weight of PPO in solution	=	0.015006 g
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Therefore, $c_5 = 0.015006 \text{ g PPO} / 7.798224 \text{ mL CHCl}_3 = 0.192429 \text{ g PPO} / 100 \text{ mL of CHCl}_3$.

Flowtime measurements for this solution, t_5 , were = 131.99 sec, 132.09 sec, 132.07 sec. Therefore, the average $t_5 = 132.05 \text{ sec}$.

Calculation of intrinsic viscosity of PPO and CHCl₃

Normalized flowtime measurement is given by

$$\eta = \frac{t_n - t_{\text{CHCl}_3}}{t_{\text{CHCl}_3}} \quad (\text{D.1})$$

where t_n is the flowtime measurement of each dilution from 1 to n and t_{CHCl_3} is the flowtime measurement of $CHCl_3$ only and is equal to 97.68 sec.

Table D.1. Calculation of normalized flowtime, η_n to obtain η_n/c_n for intrinsic viscosity of PPO only.

n	t_n (sec)	η_n	c_n (g PPO/ dL $CHCl_3$)	η_n/c_n (dL/g)
1	196.34	1.01003	0.5	2.020066
2	154.34	0.580057	0.306878	1.890189
3	144.17	0.475942	0.255792	1.860662
4	136.44	0.396806	0.216802	1.830270
5	132.05	0.351863	0.192429	1.828533

From regression analysis of plot of η_n/c_n versus c_n , $[\eta]$ was determined to be 1.696745 dL/g with regression coefficient, r^2 of 0.995.

D.2 Sample Calculation of Intrinsic Viscosity, $[\eta]$ with nonsolvent additive.

Nonsolvent additive: 1-Octanol (OCOH)

Necessary data: Density of 1-octanol = 0.827 g/mL

Density of chloroform ($CHCl_3$) = 1.4789 g/mL.

Original polymer solution consists of 0.2133 g PPO, 2.4286 g OCOH and 40.024 g chloroform ($CHCl_3$). Therefore, total weight of polymer solution is 42.6659 g.

Total weight of OCOH and $CHCl_3$ in original polymer solution is 42.4526 g.

Initial concentration, c_1

$c_1 = 0.021244$ g PPO/ 2.987842 mL $CHCl_3$ and OCOH = 0.711 g PPO/ 100 mL of $CHCl_3$ and OCOH.

Flowtime measurements for this solution, t_1 , were = 300.3 sec, 300.8 sec, 300.5 sec. Therefore, the average $t_1 = 300.5$ sec.

1st dilution with $CHCl_3$ and OCOH. Calculation of c_2 .

Volume of $CHCl_3$ and OCOH from c_1 = 2.987842 mL

Volume of 1st dilution = 2.617790 mL
Therefore, total volume of CHCl_3 and OCOH after dilution = 5.605632 mL

Weight of PPO in solution = 0.021244 g

Therefore, $c_2 = 0.021244 \text{ g PPO} / 5.605632 \text{ mL CHCl}_3 \text{ and OCOH} = 0.378968 \text{ g PPO} / 100 \text{ mL of CHCl}_3 \text{ and OCOH}$.

Flowtime measurements for this solution, t_2 , were = 216.4 sec, 215.5 sec, 215.5 sec. Therefore, the average $t_2 = 215.8 \text{ sec}$.

2nd dilution with CHCl_3 and OCOH . Calculation of c_3 .

Volume of CHCl_3 and OCOH from c_2 = 5.605632 mL
Volume of 2nd dilution = 1.168409 mL
Therefore, total volume of CHCl_3 and OCOH after dilution = 6.774041 mL

Weight of PPO in solution = 0.021244 g

Therefore, $c_3 = 0.021244 \text{ g PPO} / 6.774041 \text{ mL CHCl}_3 \text{ and OCOH} = 0.313602 \text{ g PPO} / 100 \text{ mL of CHCl}_3 \text{ and OCOH}$.

Flowtime measurements for this solution, t_3 , were = 194.0 sec, 195.5 sec, 194.1 sec. Therefore, the average $t_3 = 194.5 \text{ sec}$.

3rd dilution with CHCl_3 and OCOH . Calculation of c_4 .

Volume of CHCl_3 and OCOH from c_3 = 6.774041 mL
Volume of 3rd dilution = 1.368397 mL
Therefore, total volume of CHCl_3 and OCOH after dilution = 8.142438 mL

Weight of PPO in solution = 0.021244 g

Therefore, $c_4 = 0.021244 \text{ g PPO} / 8.142438 \text{ mL CHCl}_3 \text{ and OCOH} = 0.260899 \text{ g PPO} / 100 \text{ mL of CHCl}_3 \text{ and OCOH}$.

Flowtime measurements for this solution, t_4 , were = 178.1 sec, 177.6 sec, 178.9 sec. Therefore, the average $t_4 = 178.2 \text{ sec}$.

4th dilution with CHCl_3 and OCOH . Calculation of c_5 .

Volume of CHCl_3 and OCOH from c_4 = 8.142438 mL

Volume of 4th dilution = 1.117246 mL
 Therefore, total volume of CHCl_3 and OCOH after dilution = 9.259684 mL

Weight of PPO in solution = 0.021244 g

Therefore, $c_2 = 0.021244 \text{ g PPO} / 9.259684 \text{ mL CHCl}_3 \text{ and OCOH} = 0.22942 \text{ g PPO} / 100 \text{ mL of CHCl}_3 \text{ and OCOH}$.

Flowtime measurements for this solution, t_s , were = 169.1 sec, 168.7 sec, 168.7 sec. Therefore, the average $t_s = 168.8 \text{ sec}$.

Calculation of intrinsic viscosity of PPO, CHCl_3 and OCOH .

Normalized flowtime measurement is given by

$$\eta = \frac{t_n - t_{mix}}{t_{mix}} \quad (\text{D.2})$$

where t_n is the flowtime measurement of each dilution from 1 to n and t_{mix} is the flowtime measurement of CHCl_3 and OCOH and is equal to 114.73 sec.

Table D.2. Calculation of normalized flowtime, η_n to obtain η_n/c_n for intrinsic viscosity of PPO and nonsolvent additive.

n	t_n (sec)	η_n	c_n (g PPO/ dL CHCl_3)	η_n/c_n (dL/g)
1	300.5	1.619193	0.711	2.277346
2	215.8	0.880938	0.378968	2.32457
3	194.5	0.695285	0.313602	2.217089
4	178.2	0.553212	0.260899	2.120404
5	168.8	0.471280	0.229420	2.054226

From regression analysis of plot of η_n/c_n versus c_n , $[\eta]$ was determined to be 1.647515 dL/g with regression coefficient, r^2 of 0.998.

Appendix E

Sample calculation of Surface Tension for Chloroform (Solvent)

Experimental data for chloroform

Table E.1. Experimental data for chloroform to determine surface tension using the drop weight method.

Drop #	0	1	2	3	4	5	6	7
Weight (g)	-0.0003	0.0149	0.0304	0.0458	0.0612	0.0767	0.0921	0.1076
Δ weight (g)	0	0.0152	0.0155	0.0154	0.0154	0.0155	0.0154	0.0155
Drop #	8	9	10	11	12	13	14	15
Weight (g)	0.123	0.1384	0.1538	0.1692	0.1847	0.2	0.2155	0.2308
Δ weight (g)	0.0154	0.0154	0.0154	0.0154	0.0155	0.0153	0.0155	0.0153
Drop #	16	17	18	19	20	21	22	23
Weight (g)	0.2462	0.2617	0.2772	0.2926	0.3079	0.3234	0.3388	0.3543
Δ weight (g)	0.0154	0.0155	0.0155	0.0154	0.0153	0.0155	0.0154	0.0155
Drop #	24	25	26	27	28	29	30	31
Weight (g)	0.3696	0.3851	0.4005	0.4159	0.4313	0.4469	0.4622	0.4776
Δ weight (g)	0.0153	0.0155	0.0154	0.0154	0.0154	0.0156	0.0153	0.0154
Drop #	32	33	34	35	36	37	38	39
Weight (g)	0.4931	0.5085	0.5239	0.5393	0.5547	0.57	0.5855	0.6009
Δ weight (g)	0.0155	0.0154	0.0154	0.0154	0.0154	0.0153	0.0155	0.0154
Drop #	40	41	42	43	44	45	46	47
Weight (g)	0.6164	0.6317	0.6471	0.6625	0.678	0.6934	0.7088	0.7241
Δ weight (g)	0.0155	0.0153	0.0154	0.0154	0.0155	0.0154	0.0154	0.0153

Table E.1 (cont'd). Experimental data for chloroform to determine surface tension using the drop weight method.

Drop #	48	49
Weight (g)	0.7396	0.755
Δ weight (g)	0.0155	0.0154

Known values

Total volume	=	0.528 mL
Total no. of drops	=	49
Flow rate of pump	=	0.15 mL/min
Room temperature	=	23.5°C
Diameter of nozzle	=	0.287 cm
Evaporation rate	=	0.0041 g/min
Average mass	=	0.0154 g
Std. dev. of mass	=	8E-05 g

Preliminary calculations

$$\text{Total experimental time} = \frac{\text{Total volume}}{\text{Flow rate of pump}} = 3.52 \text{ min}$$

$$\begin{aligned} \text{Evaporation loss per drop} &= \frac{(\text{Total experimental time})(\text{Evaporation rate})}{\text{Total no. of drops}} \\ &= 0.0003 \text{ g} \end{aligned}$$

$$\% \text{ standard deviation} = \frac{\text{Standard deviation} * 100}{\text{Average mass}} = 0.5$$

For one drop, the total average mass is calculated by

$$\text{Total average mass, } m = \text{Average mass} + \text{Evaporation loss} = 0.0157 \text{ g}$$

$$\text{Average volume} = \frac{\text{Total volume}}{\text{Total no. of drops}} = 0.0108 \text{ mL}$$

$$\text{Density of chloroform} = \frac{\text{Total average mass per drop}}{\text{Average volume}} = 1.4576 \frac{\text{g}}{\text{mL}}$$

Calculation of surface tension

According to Tate's Law,

$$\gamma = \frac{mg}{2\pi rf} = \frac{(0.0157 \text{ g})(980 \text{ cm}^2/\text{sec})}{(2\pi)(0.287/2 \text{ cm})(1)}$$
$$= 26.82 \frac{\text{dyne}}{\text{cm}}$$

where g is the gravitational constant ($980 \text{ cm}^2/\text{sec}$), r is the radius of the nozzle and f is the correction factor (1 for chloroform).

Comparison of surface tension with available literature value

At 25°C , the literature value for the surface tension of chloroform (Lange's Handbook of Chemistry, 1992) is 26.67 dyne/cm .

The experimental value for the surface tension of chloroform corrected to 25°C is 26.62 dyne/cm .

The % difference between the literature value and the experimental value is 0.18.

Appendix F

F.1 Results of pure CO₂/CH₄ and O₂/N₂ permeances and permeance ratios as a function of their etching times.

Table F.1. Results of pure CO₂/CH₄ and O₂/N₂ permeances and permeance ratios as a function of their etching times.

Coupon: C10

Etching time (sec)	P/l _{N₂} (mol/m ² .s.Pa)	P/l _{O₂} (mol/m ² .s.Pa)	α _{O₂/N₂}
0	1.355E-09	4.896E-09	3.61
10	9.598E-10	3.837E-09	4.00
20	5.830E-10	2.692E-09	4.62
30	5.631E-10	2.637E-09	4.68

Etching time (sec)	P/l _{CH₄} (mol/m ² .s.Pa)	P/l _{CO₂} (mol/m ² .s.Pa)	α _{CO₂/CH₄}
0	1.703E-09	2.050E-08	12.0
10	1.348E-09	1.507E-08	11.2
20	6.134E-10	1.121E-08	18.3
30	5.855E-10	9.762E-09	19.7

Coupon: C131

Etching time (sec)	P/l _{N₂} (mol/m ² .s.Pa)	P/l _{O₂} (mol/m ² .s.Pa)	α _{O₂/N₂}
0	1.237E-09	5.083E-09	4.11
20	1.070E-09	4.526E-09	4.23
40	9.466E-10	3.984E-09	4.21
60	7.026E-10	2.938E-09	4.18

Etching time (sec)	P/l _{CH₄} (mol/m ² .s.Pa)	P/l _{CO₂} (mol/m ² .s.Pa)	α _{CO₂/CH₄}
0	1.271E-09	2.315E-08	18.2
20	1.121E-09	1.679E-08	15.0
40	9.768E-10	1.490E-08	15.3
60	7.311E-10	1.196E-08	16.4

Table F.1 (cont'd). Results of pure CO₂/CH₄ and O₂/N₂ permeances and permeance ratios as a function of their etching times.

Coupon: C11

Etching time (sec)	P/l_{N_2} (mol/m ² .s.Pa)	P/l_{O_2} (mol/m ² .s.Pa)	α_{O_2/N_2}
0	1.618E-09	5.916E-09	3.66
10	7.771E-10	3.161E-09	4.07
20	5.638E-10	2.416E-09	4.28
30	4.981E-10	2.275E-09	4.57
80	4.754E-10	1.812E-09	3.81
100	5.006E-10	1.625E-09	3.25
120	5.237E-10	1.548E-09	2.96

Etching time (sec)	P/l_{CH_4} (mol/m ² .s.Pa)	P/l_{CO_2} (mol/m ² .s.Pa)	α_{CO_2/CH_4}
0	2.513E-09	3.623E-08	14.4
10	1.282E-09	1.138E-08	8.87
20	6.542E-10	1.270E-08	19.4
30	6.111E-10	9.174E-09	15.0
80	5.405E-10	7.710E-09	14.3
100	5.410E-10	6.427E-09	11.9
120	5.758E-10	5.968E-09	10.4

Coupon: C9

Etching time (sec)	P/l_{N_2} (mol/m ² .s.Pa)	P/l_{O_2} (mol/m ² .s.Pa)	α_{O_2/N_2}
0	1.141E-09	5.505E-09	4.82
140	7.911E-10	2.381E-09	3.01
150	1.070E-09	2.580E-09	2.41
170	1.801E-09	3.216E-09	1.79
190	2.360E-09	3.674E-09	1.56

Table F.1 (cont'd). Results of pure CO₂/CH₄ and O₂/N₂ permeances and permeance ratios as a function of their etching times.

Coupon C9

Etching time (sec)	P/l_{CH_4} (mol/m ² .s.Pa)	P/l_{CO_2} (mol/m ² .s.Pa)	$\alpha_{\text{CO}_2/\text{CH}_4}$
0	1.312E-09	2.335E-08	17.8
60	---	1.801E-08	---
110	---	9.557E-09	---
140	9.341E-10	1.114E-08	11.9
150	1.268E-09	1.034E-08	8.15
170	2.296E-09	1.018E-08	4.43
190	2.969E-09	9.901E-09	3.33

F.2 Example of data collection and calculation of height of nodules from AFM samples.

Coupon: C11

Table F.2. Height of nodules measured from AFM samples for coupon etched for 120 sec.

The sample was subdivided into grids and the height of nodule measured for each grid.

Grid #	Height (nm)				
Sample File1900nm					
1	4.844	2.192	5.104	2.624	2.278
	2.624	2.797	3.230		
2	4.931	8.651	6.603	3.576	4.498
	4.844	4.556			
3	6.978	1.903	2.826	4.816	7.180
	3.489	4.066	4.008		
4	4.989	6.257	5.421	7.843	5.306
	2.566	5.681	5.306	9.112	7.987
	7.295	2.278	4.873	4.931	
File2900nm					
1	5.911	11.88	8.881	4.354	3.114
	1.672				
2	3.864	7.468	3.403	4.556	4.152
	1.990	5.075			
3	6.834	4.729	4.816	5.998	2.566
	4.960	8.189			
4	3.143	3.230	3.374	4.556	9.372
	6.402	3.114			
5	3.547	3.46	8.103	3.922	2.682
	5.421	3.835			

Statistic analysis for height of nodules

Mean	4.8878 nm
Standard Error	0.2494 nm
Median	4.729 nm
Standard Deviation	2.1017 nm
Minimum	1.672 nm
Maximum	11.9 nm

Sum	347.036 nm
Count	71
Confidence level (0.95)	0.4889 nm

F.3 Calculation of thickness of skin layer as a function of etching time

Intrinsic permeability data was obtained for PPO/trichloroethylene system (Khulbe et al., 1997) and given in Table F.1. This system was chosen because its gas performance was similar to the unetched asymmetric membrane where $\alpha_{\text{CO}_2/\text{CH}_4}$ is 24.0 and $\alpha_{\text{O}_2/\text{N}_2}$ is 5.3. Pure feed gases were used and the feed pressure was at 80 psig.

Table F.3. Intrinsic permeability data obtained for PPO/trichloroethylene system (Khulbe et al., 1997).

Gas	Permeability (Barrer)	Permeability (cm ³ (STP).cm /cm ² .s.cm Hg)
CO ₂	61.8	6.18E-09
CH ₄	2.55	2.55E-10
O ₂	12.8	1.28E-09
N ₂	2.4	2.40E-10

Table F.4. Permeability data for coupon C9 (etching time: 190 sec) using CH₄ and N₂. Feed pressure for these pure gases was 100 psig.

Gas: CH₄

Etching time (sec)	P/l (mole /m ² .s.Pa)	P/l (cm ³ (STP) /cm ² .s.cm Hg)	Thickness (μm)
0	1.3122E-09	3.9187E-06	0.65
170	2.2960E-09	6.8568E-06	0.37
190	2.9691E-09	8.8670E-06	0.29

Gas: N₂

Etching time (sec)	P/l (mole /m ² .s.cPa)	P/l (cm ³ (STP) /cm ² .s.cm Hg)	Thickness (μm)
0	1.1413E-09	3.4084E-06	0.70
170	1.8012E-09	5.3791E-06	0.45
190	2.3603E-09	7.0488E-06	0.34

F.4. Calculation of radius of curvature, R of a macromolecular aggregate at various etching times.

Figure 4.29. Radius of curvature, R of a macromolecular aggregate.

The following equations were used to calculate R of an aggregate (assuming that it is spherical) at various etching times.

$$h = R - R\cos\theta \quad (\text{F.1})$$

$$d = 2R\sin\theta$$

$$d^2 = 4R^2\sin^2\theta \quad (\text{F.2})$$

From (F.1)

$$h = R(1 - \cos\theta)$$

$$\frac{h}{R} = 1 - \cos\theta$$

Therefore,

$$\cos\theta = 1 - \frac{h}{R}$$

$$\cos^2\theta = \left(1 - \frac{h}{R}\right)^2 \quad (\text{F.3})$$

From (F.2)

$$\sin^2\theta = \left(\frac{d}{2R}\right)^2 \quad (\text{F.4})$$

Combining (F.3) and (F.4)

$$\left(1 - \frac{h}{R}\right)^2 + \left(\frac{d}{2R}\right)^2 = 1$$

$$4(R-h)^2 + d^2 = 4R^2$$

$$4R^2 - 8Rh + 4h^2 + d^2 = 4R^2$$

Therefore

$$8Rh = 4h^2 + d^2$$

$$R = \frac{4h^2 + d^2}{8h} = \frac{h}{2} + \frac{d^2}{8h} \quad (\text{F.5})$$

If $h = 0.5947 \text{ nm}$ and $d = 27.8 \text{ nm}$, then $R = 162.7 \text{ nm}$.

F.5. Length of crevices and nodule diameter from etched membrane.Notes: d_1 : diameter of nodule #1 d_2 : diameter of nodule #2 d_{cre} : (diameter of crevice)/2 d_{total} : (diameter of nodule + diameter of crevice) $\approx$ diameter of nodule for the unetched membrane.

Nodule #1 and #2 lie in series. The crevice is in between nodule #1 and #2. If the nodule has a measured crevice on both sides, then the diameter is an average of both these crevices.

Table F.5. Length of crevices and nodule diameter from etched membrane for coupon #11 (etching time: 120 sec).

d_1 (nm)	d_{cre} (nm)	d_2 (nm)	d_{cre} (nm)	d_{total} (nm)
38.517	5.7775			44.2945
50.072	5.7775	50.072	13.481	59.70125
65.479	5.7775			71.2565
23.11	5.7775	23.11	7.7035	29.8505
		38.517	7.7035	46.2205
73.182	9.629			82.811
30.814	9.629	30.814	5.7775	38.51725
		34.665	5.7775	40.4425
61.627	13.481			75.108
		34.665	13.481	48.146
26.962	7.7035			34.6655
		30.814	7.7035	38.5175
34.665	9.629			44.294
		53.924	9.629	63.553
23.11	5.7775			28.8875
		57.775	5.7775	63.5525
88.589	15.407			103.996
		30.814	15.407	46.221
26.962	5.7775			32.7395
		46.22	5.7775	51.9975
38.517	9.629			48.146

Table F.5 (cont'd). Length of crevices and nodule diameter from etched membrane for coupon #11 (etching time: 120 sec).

d_1 (nm)	d_{cre} (nm)	d_2 (nm)	d_{cre} (nm)	d_{total} (nm)
		26.962	9.629	36.591
53.924	19.2585			73.1825
57.775	19.2585	57.775	17.498	76.15325
		26.962	17.498	44.46
50.072	11.555			61.627
26.962	11.555	26.962	9.629	37.554
		57.775	9.629	67.404
34.665	7.7035			42.3685
46.22	7.7035	46.22	7.7035	53.9235
		38.517	7.7035	46.2205
34.665	7.7035			42.3685
		50.072	7.7035	57.7755
46.22	13.481			59.701
		46.22	13.481	59.701
50.072	5.7775			55.8495
53.924	5.7775	53.924	19.2585	66.442
		57.775	19.2585	77.0335
42.369	7.7035			50.0725
		53.924	7.7035	61.6275
80.886	9.629			90.515
		53.924	9.629	63.553
57.775	13.481			71.256
		26.962	13.481	40.443
26.962	3.8515			30.8135
		38.517	3.8515	42.3685
34.665	7.7035			42.3685
42.369	7.7035	42.369	17.3325	54.887
		53.924	17.3325	71.2565

Statistical analysis for d_{total}

Mean	54.4987 nm
Standard Error	2.3786 nm
Median	51.9975 nm
Mode	42.3685 nm
Standard Deviation	16.6505 nm
Minimum	28.8875 nm

Maximum	103.996 nm
Sum	2670.4343 nm
Count	49
Confidence Level(0.950000)	4.6621 nm

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