

The Effect of Surfactant and Compatibilizer on Inorganic Loading and Properties of PPO-based EPMM Membranes

by

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Thesis submitted to the
Faculty of Graduate and Postdoctoral Studies
in partial fulfillment of the requirements for the degree of

Master of Applied Science in Chemical Engineering

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Faculty of Engineering
University of Ottawa

September 2012

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STATEMENT OF CONTRIBUTION OF COLLABORATIONS

I hereby declare that I am the sole author of this thesis. All the experimental and analytical work related to this thesis was performed by me under the supervision and training received from Professor Boguslaw Kruczek.

My supervisor, Dr. Kruczek, provided me with an excellent collaboration throughout this work with laboratory training, supervision, discussions, support, and editorial comments for all of my written work. The quality of this thesis has been tremendously improved through his guidance.

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ABSTRACT

Hybrid membranes represent a promising alternative to the limitations of organic and inorganic materials for high productivity and selectivity gas separation membranes. In this study, the previously developed concept of emulsion-polymerized mixed matrix (EPMM) membranes was further advanced by investigating the effects of surfactant and compatibilizer on inorganic loading in poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)-based EPMM membranes, in which inorganic part of the membranes originated from tetraethylorthosilicate (TEOS).

The polymerization of TEOS, which consists of hydrolysis of TEOS and condensation of the hydrolyzed TEOS, was carried out as (i) one- and (ii) two-step processes. In the one-step process, the hydrolysis and condensation take place in the same environment of a weak acid provided by the aqueous solution of aluminum hydroxonitrate and sodium carbonate. In the two-step process, the hydrolysis takes place in the environment of a strong acid (solution of hydrochloric acid), whereas the condensation takes place in weak base environment obtained by adding excess of the ammonium hydroxide solution to the acidic solution of the hydrolyzed TEOS. For both one- and two-step processes, the emulsion polymerization of TEOS was carried out in two types of emulsions made of (i) pure trichloroethylene (TCE) solvent, and (ii) 10 w/v% solution of PPO in TCE, using different combinations of the compatibilizer (ethanol) and the surfactant (n-octanol). The experiments with pure TCE, which are referred to as a gravimetric powder method (GPM) allowed assessing the effect of different experimental parameters on the conversion of TEOS. The GPM tests also provided a guide for the synthesis of casting emulsions containing PPO, from which the EPMM membranes were prepared using a spin coating technique.

The synthesized EPMM membranes were characterized using ^{29}Si nuclear magnetic resonance (^{29}Si NMR), differential scanning calorimetry (DSC), inductively coupled plasma mass spectrometry (ICP-MS), and gas permeation measurements carried out in a constant pressure (CP) system.

The ^{29}Si NMR analysis verified polymerization of TEOS in the emulsions made of pure TCE, and the PPO solution in TCE. The conversions of TEOS in the two-step

process in the two types of emulsions were very close to each other. In the case of the one-step process, the conversions in the TCE emulsion were significantly greater than those in the emulsion of the PPO solution in TCE. Consequently, the conversions of TEOS in the EPMM membranes made in the two-step process were greater than those in the EPMM membranes made in the one-step process. The latter ranged between 10 - 20%, while the highest conversion in the two-step process was 74% in the presence of pure compatibilizer with no surfactant. Despite greater conversions and hence the greater inorganic loadings, the EPMM membranes prepared in the two-step process had glass transition temperatures (T_g) only slightly greater than the reference PPO membranes. In contrast, despite relatively low inorganic loadings, the EPMM membranes prepared in the one-step process had T_g s markedly greater than PPO, and showed the expected trend of an increase in T_g with the inorganic loading. These results indicate that in the case of the one-step process the polymerized TEOS was well integrated with the PPO chains and the interactions between the two phases lead to high T_g s. On the other hand, this was not the case for the EPMM membranes prepared in the two-step process, suggesting possible phase separation between the polymerized TEOS and the organic phase. The latter was confirmed by detecting no selectivity in the EPMM membranes prepared by the two-step process. In contrast, the EPMM membranes prepared in the one-step process in the presence of the compatibilizer and no surfactant showed 50% greater O₂ permeability coefficient and a slightly greater O₂/N₂ permeability ratio compared to the reference PPO membranes.

RÉSUMÉ

Les membranes hybrides représentent une excellente solution de rechange aux matériaux organiques et inorganiques pour une productivité et sélectivité élevée des membranes pour la séparation de gaz. Dans cette étude, le concept précédemment élaboré de membranes mixtes préparées par un procédé de polymérisation (EPMM) a été plus avancé en cherchant les effets d'agents tensio-actifs et de compatibilisateurs sur la partie inorganique dans les membranes EPMM à base de (2,6-diméthyle-1,4-phénylène oxyde) (PPO), dans lequel la partie inorganique provenait de tétraéthylorthosilicate (TEOS).

La polymérisation de TEOS, qui consiste en l'hydrolyse et la condensation du TEOS, a été réalisée au cours i) du procédé en une seule étape et ii) du procédé en deux étapes. Dans le procédé en une seule étape, l'hydrolyse et la condensation surviennent dans le même environnement d'un acide faible fourni par la solution aqueuse de l'hydroxonitrate d'aluminium et de carbonate de sodium. Dans le procédé en deux étapes, l'hydrolyse a lieu dans l'acide fort (solution d'acide chlorhydrique), tandis que la condensation a lieu dans la solution alcaline faible en ajoutant un excès de la solution d'hydroxyde d'ammonium à la solution acide de l'hydrolyse du TEOS. Pour tous les deux procédés, la polymérisation en émulsion de TEOS est intervenue dans deux types d'émulsions i) solvant pur du trichloréthylène (TCE), et ii) une solution à 10 w/v% de la PPO dans TCE, à l'aide de différentes combinaisons du compatibilisateur (éthanol) et le tensio-actif (n-octanol). Les expériences avec TCE pur, qui sont désignées comme une méthode gravimétrique de poudre (GPM) a permis une évaluation rapide de l'effet de différents paramètres expérimentaux sur la conversion de TEOS. Les tests GPM également fournissent un guide pour la synthèse des émulsions de coulée contenant PPO, à partir de laquelle les membranes EPMM ont été préparées en utilisant la technique de l'enduction centrifuge.

Les membranes EPMM synthétisées ont été caractérisées à l'aide de ^{29}Si résonance magnétique nucléaire (^{29}Si NMR), la calorimétrie différentielle à balayage (DSC), Spectromètre de masse à plasma à couplage inductif (ICP-MS), et des mesures de pénétration de gaz ont été réalisées dans le système à pression constante (CP).

L'analyse ^{29}Si NMR a vérifié la polymérisation de TEOS dans les émulsions en TCE pur, et à partir de la solution PPO dans TCE. Les conversions de TEOS dans le procédé en deux étapes dans tous les deux types d'émulsions étaient très proches les uns des autres. Dans le cas du procédé en une seule étape, les conversions de l'émulsion en TCE étaient significativement plus élevées que celles des l'émulsions de la solution de PPO dans le TCE. Par conséquent, les conversions de TEOS dans les membranes EPMM pour les processus en deux étapes sont supérieures à celles dans les membranes EPMM réalisées dans les processus en une seule étape. Ce dernier variait entre 10 % et 20 %, tandis que la conversion la plus élevée dans les processus en deux étapes était de 74,38 %, en présence du compatibilisateur, mais pas de l'agent tensio-actif.

Malgré de plus grandes conversions et donc plus grandes quantités inorganiques, les membranes EPMM préparées dans le procédé en deux étapes possèdent des températures de transition vitreuse (T_g) qui ne sont que légèrement supérieures aux membranes PPO de référence. En revanche, malgré de petites quantités inorganiques, les membranes EPMM préparées dans le procédé en une seule étape avaient des T_g supérieures par rapport aux membranes PPO, et cela montre une augmentation de T_g avec la charge inorganique en général.

Ces résultats indiquent que dans le cas du procédé en une seule étape, le TEOS polymérisé était bien intégré avec les chaînes PPO et les interactions entre les deux phases conduisent à des T_g élevées. D'un autre côté, ce n'était pas le cas pour les membranes EPMM préparées dans le procédé en deux étapes, ce qui suggère la possibilité de la séparation de phase entre les TEOS polymérisés et les chaînes d'OPP. Celui-ci n'a été confirmé par aucune sélectivité des membranes EPMM préparées dans le procédé en deux étapes. En revanche, les membranes EPMM préparées dans le procédé en une seule étape en présence du compatibilisateur et aucun agent tensio-actif ont montré un coefficient 50 % plus grand de perméabilité de O_2 et un ratio de perméabilité légèrement plus grand de O_2/N_2 par rapport aux membranes PPO de référence.

ACKNOWLEDGEMENTS

I would like to thank the people that helped me with my Master's studies at University of Ottawa.

Foremost, I would like to express my sincere appreciation and utmost gratitude to Dr. Boguslaw Kruczek for his guidance in the completion of this thesis, endless support and assistance even in his busiest times. Undoubtedly, without his patience and endless help, this study would not be possible. I will always appreciate his support which was far beyond the regular requirements for an academic supervisor.

I would like to thank to Louis Tremblay, Gérard Nina and Franco Ziroldo, for their outstanding technical support.

I would like to thank my husband and my parents for their support, encouragement and understanding throughout this work.

I would like to thank to Dr. Andre Y. Tremblay for the support on the ultrasounds dismembrator.

Finally, I would like to thank former Master graduate Qiang Wang for his time and effort on his training for synthesizing the membranes. I would also like to thank Chanh Park, Muhammad Tawalbeh and all my friends in Chemical and Biological department at University of Ottawa.

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NOMENCLATURE

ABBREVIATION

ab	acid-base catalyzed system (HCl-NH ₄ OH)
aq	Aluminum hydroxonitrate solution
CP	Constant Pressure
DSC	Differential Scanning Calorimetry
EPMM	Emulsion Polymerized Mixed Matrix
EtOH	Ethanol
F	Feed
GPM	Gravimetric Powder Method
HMW	High Molecular Weight
HPC	Hydroxypropyl Cellulose
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LMW	Low Molecular Weight
MFC	Mass Flow Controller
MFM	Mass Flow Meter
NMR	Nuclear Magnetic Resonance
NV	Needle Valve
PPO	Poly (2,6-dimethyl-1,4-phenylene oxide)
PT	Pressure Transducer
R	Retentate
S	Sweep
SC	Spin Coating
SE	Solvent Evaporation
SP	Sweep and Permeate
TCE	Trichloroethylene
TEOS	Tetraethylorthosilicate
TMOS	Tetramethylorthosilicate

SYMBOLS

A	Arrhenius constant	[s ⁻¹]
A'	permeant area of the membrane	[cm ²]
d_K	kinetic diameter	Å
D	diffusivity coefficient	[cm ² s ⁻¹]
ΔC_p	specific heat capacity	[J g ⁻¹ °C ⁻¹]
E^*	activation energy	[J mol ⁻¹]

h	degree of hydrolysis	
L	membrane thickness	[cm]
M_w	molecular weight	[g mol ⁻¹]
P	permeability coefficient	[Barrer [*]]
p	pressure	[cm Hg]
Q	gas permeation rate	[cm ³ (STP) s ⁻¹]
R	universal gas constant	[J mol ⁻¹ K ⁻¹]
S	solubility coefficient	[cm ³ (STP) cm ⁻³ cmHg ⁻¹]
t_c	net sonication time of the emulsion three in two-step process	[min]
t_g	gelation time	[min]
t_h	net sonication time of the emulsion two in two-step process	[min]
t_r	net sonication time of the emulsion two in one-step process	[min]
T	absolute temperature	[K]
T_g	glass transition temperature	[°C]
T_C	critical temperature	[K]

GREEK SYMBOLS

α^*	Ideal selectivity = permeability ratio = permselsctivity
η	Viscosity

SUBSCRIPTS

A,B	components in the binary gas mixture
f	membrane feed side
p	membrane permeate side

^{*} 1 Barrer = 10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹

Chapter 1. INTRODUCTION

1.1. Motivation

Membrane separations offer a number of benefits, technically and economically, over other separation technologies. These include, low capital investment requirements, lightweight compact units, easy operation, being environmentally friendly, minimum maintenance costs, and high process flexibility (Abedini and Nezhadmoghadam, 2010).

In the last decade, membrane gas separation technology has grown significantly and today it can be counted as a competitive gas separation method in industry, which is used in a wide variety of applications such as nitrogen and oxygen-enriched air production, helium recovery from natural gas, hydrogen recovery from gas mixtures, air dehumidification, etc. (Baker, 2004).

Hybrid membranes, which consist of homogeneously interpenetrating polymeric and inorganic matrices, have been developed as an interesting alternative to overcome the limitations of organic and inorganic materials (Chung et al., 2007). These materials often exhibit enhanced properties compared to their individual organic and inorganic components, and offer the potential to combine the specific transport properties of organic and inorganic materials with the purpose of producing highly permselective membranes. In other words, they may combine the advantages of the inorganic materials such as rigidity, selectivity, thermal stability and the advantages of the organic polymers such as flexibility, permeability, and easy processing. In addition, they may exhibit special properties as a consequence of the interaction between polymer chains and inorganic particles (Cong et al., 2007).

The major challenge in the development of hybrid membranes is to prevent the formation of non-selective voids or defects, which lead to a significant decrease in the

selectivity (Koros and Mahajan, 2000). Therefore, improvement of compatibility between inorganic and organic phases is the main theme in the research involving hybrid membranes. There are two major approaches for improvement of compatibility between phases; one chemical and the other one physical. The chemical approach involves chemical modification of organic and/or inorganic phases to increase the interactions between them by means of weak chemical bonds. In the physical approach, the size of nanoparticles is decreased in order to allow more intimate contact between the phases and hence a greater role of Van der Waals forces. The problem with the second approach is that inorganic nanoparticles strongly interact between themselves, which leads to undesirable aggregation of nanoparticles before they have a chance for an intimate contact with the polymer segments.

Recently, Sadeghi et al., (2007) developed a new method, referred to as emulsion polymerized mixed matrix (EPMM) for the synthesis of nanocomposite materials within a continuous organic phase. This was achieved by growing the inorganic nanoparticles from a silica precursor in a continuous phase of the polymer solution. The aqueous phase, which is used for growing inorganic particles, is dispersed in the polymer solution and acts as micro-reactors. The silica precursor, soluble in a continuous phase of the polymer solution, polymerizes in contact with the aqueous phase. It should be noted that the size of the synthesized inorganic particles largely depends on the droplet size of the emulsion. Therefore, the compatibility between inorganic and organic phases can be improved by minimizing the droplet size in the emulsion.

The material selection for both organic matrix and inorganic phases is a key aspect in the development of mixed-matrix membranes (Koros and Mahajan, 2000). In

the present study, tetraethylorthosilicate (TEOS) was used as an inorganic precursor that was polymerized in the aqueous phase in the presence of different catalysts, which was dispersed in a continuous phase of the solution of poly(2,6-dimethyl-1,4-diphenyl oxide) (PPO) in trichloroethylene (TCE). Ethanol and n-octanol were used as a compatibilizer and a surfactant in the emulsion, respectively. Such prepared emulsions were used for casting of PPO-based EPMM membranes, which were then thoroughly characterized.

1.2. General research objectives

The main objectives of this work were to increase the understanding of the parameters affecting emulsion polymerization of silica precursors in the continuous phase of polymer solution, and eventually the preparation of EPMM membranes capable to separate gases. This required:

- The study of the effect of the catalyst and the reaction path (one- and two-step processes) on the conversion of TEOS and the loading of silica nanoparticles in the PPO-based EPMM membranes.
- The investigation of the effect of surfactant and compatibilizer as well as their different combinations on the conversion of TEOS and the inorganic loading in the PPO-based EPMM membranes.
- The investigation of the role of viscosity of the continuous organic phase by carrying out the comparative studies with pure solvent and the actual polymer solutions.
- To utilize differential scanning calorimetry (DSC), ^{29}Si nuclear magnetic resonance (^{29}Si NMR) spectroscopy, inductively coupled plasma mass

spectrometry (ICP-MS), and gas permeation in order to gain a better understanding of the phenomena taking place in the synthesis of the EPMM membranes.

- The syntheses of PPO-based EPMM membranes.

1.3. Specific research objectives and tasks

This thesis is a continuation of the work of former graduate students, Forouzan Sadeghi (Sadeghi, 2007) and Qiang Wang (Wang, 2011). The protocols developed in previous studies, in particular, one-step reaction in weak acidic conditions in the presence of surfactant (Sadeghi, 2007), and one-step gravimetric powder method (GPM) along with one-step synthesis of the PPO-based EPMM membranes (Wang, 2011), were utilized in this work. However, in addition to these protocols, to accomplish the general objectives of this research, the following specific objectives were set:

- Development of the protocol for a two-step process in the presence of both pure solvent (GPM tests) and polymer solution (the actual EPMM membranes), which required:
 - Design of single phase experiments (gelation tests) to establish pH for acid catalyzed hydrolysis of TEOS – step one, and base catalyzed condensation – step two reactions, respectively.
 - Implementation of the results from the gelation tests for the polymerization of TEOS in the environment of pure solvent and polymer solution.
 - Optimization of the time for the hydrolysis reaction based on the GPM tests.
 - Optimization of the time for condensation reaction based on the GPM tests.

- Study the effect of a liquid additive consisting of surfactant (n-octanol) and/or compatibilizer (ethanol) on the conversion of TEOS in one- and two-step reaction processes.
- Modification of the existing vacuum oven for thermal post-treatment of a new batch of high molecular weight PPO, which was very sensitive to the presence of traces of oxygen at elevated temperatures.
- Establishing the minimum temperature of thermal post-treatment for the complete removal of unreacted TEOS from the synthesized EPMM membranes.
- Implementation of state of art techniques, such as DSC, ^{29}Si NMR, and ICP-MS for systematic characterizations of synthesized inorganic powders and PPO-based EPMM membranes, and proper interpretation of the obtained results.
- Implementation of the constant pressure gas permeation system for the preliminary characterization of gas transport properties of the synthesized EPMM membranes.
- Comparative study on suitability of low and high molecular PPO batches for the preparation of EPMM membranes.

1.4. Organization of the thesis

This thesis is divided into five chapters. The current chapter provides an overview of the project. Chapter 2 presents a comprehensive literature review on organic–inorganic nanocomposite membranes for gas separation, properties of PPO, chemistry of silicon alkoxides, and the mechanism of TEOS polymerization in different environments. Chapter 3 provides a detailed description of the experimental procedures, including

polymerization of TEOS in a single phase, along with emulsion polymerization in the environments of pure solvent (gravimetric powder method) and the polymer solution (PPO-based EPMM membranes). This is followed by the description of membrane casting and membrane characterization. Chapter 4 presents the results obtained in this research project and provides a thorough discussion from the perspective of the general objectives of this work. This chapter is divided into three parts dedicated to (i) single phase reactions, (ii) two-phase reactions in the environment of pure solvent, and (iii) two phase reactions in the polymer solution environment. Chapter 5 provides the conclusions of this dissertation along with recommendations for future work on EPMM membranes. Details on pH measurements, sample calculations, and ^{29}Si NMR spectra are presented in the Appendices.

Chapter 2. LITERATURE REVIEW

The aim of this project is to determine the effect of surfactant and compatibilizer on incorporation of inorganic materials, originating from tetraethylorthosilicate (TEOS), into the polymer matrix of poly (2,6-dimethyl-1,4-phenylene oxide) in one- and two-step processes. The ultimate goal is to synthesize these composite materials in a form of thin films, which will be referred to as emulsion polymerized mixed matrix (EPMM) membranes.

2.1. Organic–inorganic nanocomposite membranes for gas separation

Gas separation by polymeric membranes is one of the fastest growing branches of membrane technology (Chung et al., 2007). Polymeric membranes are advantageous because of their high flexibility, solution processability, and the ability to withstand high pressures, while in general membrane separation is associated with lower energy consumption compared to other unit operations (Koros and Mahajan, 2000). Generally, all the rubbery polymer membranes and most of the glassy polymer membranes are considered as nonporous membranes. The solution-diffusion model is the most widely used model for non-porous polymer membranes, in which permeants first dissolve in the membrane material, and then diffuse from upstream to the downstream face of the membrane, where they desorb to external phase. The permeants are separated because of the differences in their solubilities in the membrane and the differences in the rates at which they diffuse through the membrane (Wijmans and Baker, 1995). In this model, the permeability coefficient (P) is considered as a material constant, which is proportional to a thermodynamic factor called the solubility coefficient (S), and a kinetic parameter called diffusion coefficient (D) (Koros and Fleming, 1993).

$$P = SD \quad (2.1)$$

The gas solubility of polymeric membranes depends on the (i) penetrant condensability, (ii) the nature of polymer-penetrants interactions, and (iii) free volume in the polymers. On the other hand, gas diffusivity largely depends on the kinetic diameter (d_K) of the penetrants (Rowe et al., 2010). In the case of gas separation, the application of polymeric membranes is limited because of a trade-off between the gas permeability and selectivity, low stability at high temperatures, and generally low selectivity. On the other hand, inorganic membranes overcome these limitations, but they are expensive and difficult to fabricate due to their fragile structures (Cong et al., 2007). Among many inorganic membranes, silica membranes have been studied extensively, because of their high selectivity and excellent thermal resistance (Ma et al., 2010).

The emerging new type of membrane materials for gas separation applications are the organic/inorganic nanocomposites, which are generally composed of inorganic nanoscale fillers dispersed in an organic polymer matrix. Nanocomposites exhibit special properties as a result of interactions between polymer chains and inorganic particles. In turn, nanocomposite membranes are expected to have the advantages of the inorganic materials such as rigidity, selectivity, thermal stability, along with the advantages of the organic polymers such as flexibility, high permeability, and processability (Cong et al., 2007). The interactions between the polymer chains and inorganic particles, and the degree of cross-linking of the polymer matrix are the controlling factors in manufacturing of nanocomposites. For instance, in the case of weak interactions, voids are formed at the inorganic/organic interface, and as a result the nonselective passing of penetrants takes place through these voids (Chung et al., 2007). Inorganic nanoscale phase may consist of

nanotubes, layered silicates, nanoparticles of metals, metal oxides, semiconductors, etc. Among these, polymer/silica nanocomposites are of special interest for gas separation membranes (Basu et al., 2010).

In the case of nanocomposite membranes, the inorganic nanofillers can influence the gas separation in two ways. First, the interactions between the polymer-chain segments and inorganic particles can disrupt the packing of the polymer-chain thus increasing the free volume, thereby enhancing the gas diffusivity in the nanocomposite. Second, functional groups (e.g. hydroxyl group) incorporated to the inorganic phase can interact with polar gases, hence, enhancing the penetrant solubility in the hybrid membranes (Ge et al., 2011). Although the nanocomposite materials are being developed as an alternative to the conventional polymeric and inorganic materials, there still exists the important problem of generating non selective voids, which is mainly due to the incompatibility between the inorganic and polymer interfaces (Zou et al., 2008). These voids can reduce the overall separation efficiency of the membrane, which will be discussed in the next section.

2.1.1. Organic–inorganic interface morphology

Synthesizing an ideal nanocomposite membrane with no defects at the interface of polymer and inorganic particle is extremely difficult due to the difference between the properties of polymer and inorganic particles as well as a strong aggregation tendency among the inorganic particles. The formation of these defects at the polymer–inorganic interface will affect the overall properties of the membrane (Hillock et al., 2008). These interface defects can be classified into three main categories: (i) interface voids, (ii)

rigidified polymer layer around the particles, and (iii) particle pore blockage (Aron et al., 2010). Figure 2.1 shows the ideal morphology, interface voids, and rigidified polymer layer in a mixed matrix membrane.

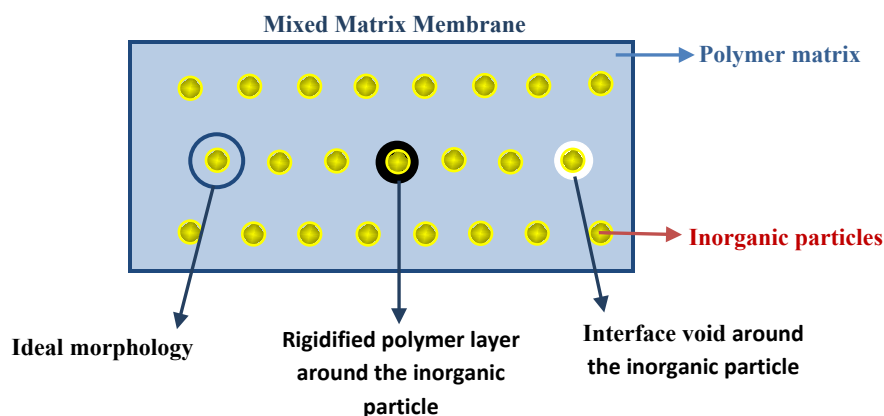


Figure 2.1 Schematic diagram of nanoscale morphology of mixed matrix structure including the ideal morphology, interface voids, and the rigidified polymer layer in the polymer–particles interface. Based on Aron et al. (2010)

The interface voids are formed due to the poor contact of polymer–inorganic particles, which can lead to a non-selective membrane (Aron et al., 2010). On the other hand, in the case of intimate contact between the polymer matrix and inorganic particles, the other two defects including rigidified polymer chain and particle pore blockage may occur (Chung et al., 2007). The polymer chain rigidification may be formed during the solvent evaporation, due to a decrease in the chain mobility of polymer segments in the vicinity of the particle surface. Since the rigid polymer chains cannot freely move around their axis, the probability of existence of defects between them is much greater than between the chain of regular mobility in the bulk polymer. Moreover, if the directions of

stress around the inorganic particles are not uniform, additional interface voids may be formed at the interface of the inorganic particle with the polymer (Aron et al., 2010).

These two types of defects, interface voids and rigidified polymer layers in a mixed matrix membrane, may be formed regardless of the porosity or non-porosity of the inorganic particles. On the other hand, pore blockage defects are unique in the case of porous inorganic particles. Although the polymer chains do not have a tendency to enter the small pores in inorganic particles, they could block the pores to varying degrees. Moreover, particle pores can be plugged totally or partially with either a residual solvent or minor component in a feed gas or polymer chains, before, during or after the membrane fabrication process. Pore blockage can decrease the gas permeability of the hybrid membrane. In addition, when the pore size of the filler is comparable to the molecular diameter of the feed gas, and even smaller penetrants cannot pass through the pores, the selectivity of the membrane may also decrease (Chung et al., 2007).

2.1.2. Preparation of nanocomposite membranes

The ultimate properties of the nanocomposite depend on particle sizes as well as an interfacial interaction between the dispersed and continuous phases (Chan et al., 2002). According to the interfacial interactions, nanocomposite materials can be classified into two different categories: (i) physical or weak phase interactions (e.g., hydrogen, Van der Waals bonds), and (ii) strong chemical bonds (e.g., covalent, ion-covalent bonds) which increase the compatibility between two phases of nanocomposites (Cong et al., 2007).

Generally, the morphology of the nanocomposites depends largely on the preparation method. There are three general methods that have been reported for the preparation of polymer/silica nanocomposites: blending, sol-gel processes, in situ polymerization (Dlamini et al., 2011). Recently, the emulsion polymerized mixed matrix (EPMM) method has been developed by Sadeghi et al. (2008), which is an extension of the sol-gel and in situ polymerization methods. The inorganic phase can be a silica precursor or silica nanoparticles, while the organic phase also can be a monomer or a polymer. Figure 2.2 indicates the materials used for the preparation of polymer/silica nanocomposites in the aforementioned methods. Inorganic nanoparticles are used directly in the blending and in situ polymerization methods, while in the sol-gel and EPMM methods silica precursors are introduced.

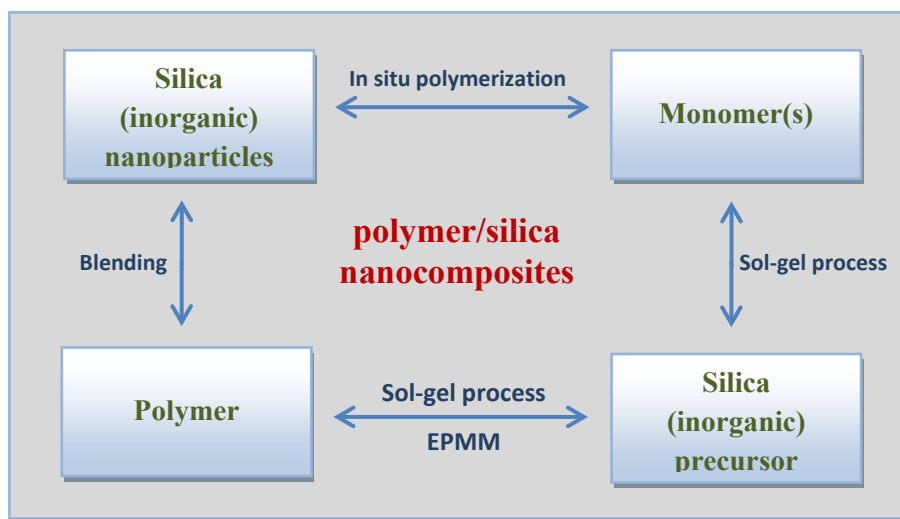


Figure 2.2 Schematic of four general preparative methods of polymer/silica nanocomposites based on the starting materials of organic and inorganic phase. Based on Zou et al., (2008).

2.1.2.1. Blending

Blending is the direct mixing of inorganic nanoparticles into a continuous polymer phase, which is the simplest method of preparing nanocomposites. The main challenge in this method is the dispersion of the nanoparticles in the polymer matrix. This is because of the tendency of nanoparticles to aggregate (Wei et al., 2010). Surface modification of the nanofillers to increase their interactions with the polymer matrix is used to prevent/minimize the aggregation and to enhance the dispersion of nanoparticles in the polymer phase (Tripathi and Shahi, 2011). Blending can be performed as a solution blending, or as a melt blending.

Solution blending is carried out by dissolving the polymer in a solvent to form a solution and then dispersing the inorganic nanoparticles in the polymer solution, which is cast to form a membrane. Alternatively, nanoparticles may be first dispersed in a solvent, which is followed by addition of the polymer and dissolving it in the presence of nanoparticles. The nanocomposite membrane is ultimately obtained after the evaporation of the solvent, which follows casting of the polymer solution containing nanoparticles. This method can be used for a wide variety of inorganic nanoparticles. However, finding a solvent which on the one hand dissolves the polymer, and on the other hand has sufficiently strong interactions with nanoparticles, is not easy. Moreover, it is necessary to remove the solvent after membrane casting in the evaporation step, during which nanoparticles may aggregate (Wei et al., 2010).

Melt blending is performed by dispersing the nanoparticles in a polymer melt, which is a viscous liquid. The disadvantage of this method comes from high viscosity of the polymer melt, which makes dispersing of inorganic particles very challenging

(Tripathi and Shahi, 2011). In some cases, high viscosity melts prevent using this type of method, in particular when high concentrations of inorganic particles in the nanocomposite are desired. It is also important to keep in mind that not all polymers can be melted (Zou et al., 2008).

2.1.2.2. Sol-gel process

In the sol-gel method, organic monomers or polymers are mixed with inorganic precursors forming a single phase solution. Then the inorganic precursors hydrolyze and condense in a continuous polymer phase. The characteristic feature of the sol-gel method is the transition of a colloidal solution (liquid) into a gel (solid), which consists of two steps: hydrolysis of alkoxides in order to produce hydroxyl groups, and then the polycondensation of the hydroxyl groups (Brinker, 1988). In polymer/silica nanocomposites, acid or base catalysts are used to activate the reactivity of the silicon. If the dispersion of organic and inorganic particles occurs at the nanometer level, the final membranes prepared by this method will be homogeneous (Cong et al., 2007).

The sol-gel method for the preparation of organic/inorganic nanocomposites has been widely studied due to its moderate reaction conditions (room temperature and ambient pressure) and the ability to control the concentrations of organic and inorganic components in the solution. However, it is not easy to control the film thickness and the size of the synthesized inorganic particles. Moreover, finding a suitable solvent, which is compatible with both the organic polymer and inorganic precursor, is still the major challenge in this method (Lee et al., 1999).

2.1.2.3. In situ polymerization

In the case of in situ polymerization, the nanoparticles, containing functional groups (i.e. hydroxyl and carboxyl groups), are dispersed into a continuous phase of organic monomers. Then the prepared solution is coated on a support. The polymerization of monomers is initiated by a high energy radiation, plasma or other conditions, which cause the generation of radicals, cations or anions from the functional groups of the inorganic particles (Alonso et al., 2011). In this method, inorganic nanoparticles can be connected to the polymer chains by covalent bonds and the nanocomposites are formed in situ during the polymerization, which prevents the formation of gaps at the interphase (Cong et al., 2007).

The advantages of this method are the high speed of the process and the better performance of the final membrane due to the formation of covalent bonds between organic and inorganic phases. On the other hand, it is difficult to control the membrane thickness and also avoid the aggregation of inorganic nanoparticles, which can affect the final properties of the membrane. Moreover, the necessity of finding the appropriate solvent is a big challenge of this method. These concerns have limited the application of this method in industry (Zou et al., 2008).

2.1.2.4. Emulsion polymerized mixed matrix (EPMM) method

The emulsion polymerized mixed matrix (EPMM) method for the preparation of organic/inorganic nanocomposites has been developed by Sadeghi et al. (2008) in order to enhance the compatibility between organic and inorganic phases. In this method, the chemical reaction occurs in the emulsion, thus overcoming a single-phase requirement

necessary in the sol-gel and in situ polymerization methods. The aqueous phase containing the inorganic precursor is broken into small droplets by sonication, and then each droplet acts as a micro-reactor for growing the inorganic phase while the reaction occurs at the interphase between the continuous phase of polymer solution and the dispersed aqueous micro-droplets. The compatibility between organic and inorganic phases, which largely affects the final properties of the membranes, can be improved by minimizing the droplet size in the emulsion. Hence, the EPMM method overcomes the main problem in the previous methods, which was finding a solvent compatible with both the organic and inorganic phases (Sadeghi et al., 2008).

2.2. Properties of poly (2,6-dimethyl-1,4-phenylene oxide)

Poly (2,6-dimethyl-1,4-phenylene oxide), PPO, is a glassy polymer with a glass transition temperature (T_g) ranging from 206.85°C (Wrasidlo, 1972) to 224.85°C (Karasz and Reily, 1965), which largely depends on the molecular weight of the polymer. PPO membrane shows one of the highest permeability to gases among glassy polymers, due to the absence of polar groups in its main chain. In addition, it has excellent mechanical properties as well as good chemical and thermal stability. The phenyl rings in the polymer backbone make PPO hydrophobic, stiff, and resistant to a number of chemical agents. The hydrophobicity of PPO causes the lack of solubility in conventional membrane dipolar aprotic solvents. Due to the lack of solubility and also a relatively low selectivity for gases, a series of modifications were performed to make PPO a more attractive material for the gas separation membranes (Fu et al., 1994).

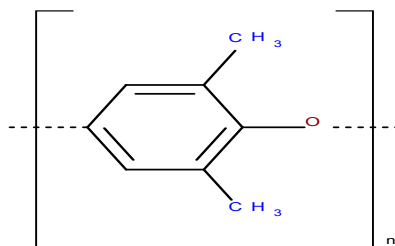


Figure 2.3 Repeat unit of poly (2,6-dimethyl-1,4-phenylene oxide)

The oxygen permeability of PPO membrane have been reported between 16.71 (Chowdhury, 2001) and 16.8 Barrer (Baker, 2004). In addition, the nitrogen permeability is in the range of 3.52 (Chowdhury, 2001) and 3.8 Barrer (Baker, 2004). Generally, there are two main ways to improve the selectivity of PPO membrane. The first way is the chemical modification of PPO by the electrophilic substitution reactions such as: bromination, sulfonylation and acylation (Benham and Kinstle, 1988), while the other way is the incorporation of inorganic nanoparticles (silica nanoparticles) in the PPO matrix (Sadeghi et al., 2008).

It should also be noted that the properties of the solution-cast PPO membrane also depend on the properties of the solvent. Khulbe et al. (2000) reported the preparation of dense PPO membranes from various casting solvents, such as carbon disulphide (CS₂), benzene, trichloroethylene (TCE), toluene, chlorobenzene, and bromobenzene. It was then concluded that the physical properties of solvents, such as surface tension, boiling point, and viscosity, play an important role in the ultimate performance of the resulting membranes for gas separation. The PPO-TCE and PPO-CS₂ membranes in Khulbe et al. (2000) had better performance for gas permeation than the membranes prepared with other solvents.

2.3. Chemistry of silicon alkoxides

2.3.1. Silica

A quarter of the earth's crust consists of silicon. Silicon can be prepared by heating sand (silica) with a magnesium powder. Silica (SiO_2) is the most important compound of silicon, which can be present in a crystalline form (e.g., quartz) or an amorphous form (e.g., onyx). Naturally, silicon occurs in a +4 oxidation state with a coordination number of 4. In addition, it has a partial positive charge of +0.32 in tetraethylorthosilicate (TEOS), which is less electropositive than most transition metals (Brinker and Scherer, 1990).

2.3.2. Silicon alkoxide precursor

Different tetraalkoxysilanes such as tetramethoxysilane, TMOS, and tetraethoxysilane, TEOS are used as the silicon alkoxide precursor in hybrid materials. TMOS is more expensive than TEOS and can also emit dangerous fumes, which can lead to blindness. Thus, TEOS is preferred for the preparation of silica gels (Rao et al., 1993). It consists of four ethyl groups attached to SiO_4^{4-} ion, which is called orthosilicate. Figure 2.4 presents the chemical structure of the TEOS (Brinker and Scherer, 1990). The solubility of TEOS in water is negligible so it is dissolved in ethanol in order to make it soluble in water. The normal boiling point of TEOS is approximately 165.8°C (Rao et al., 1993).

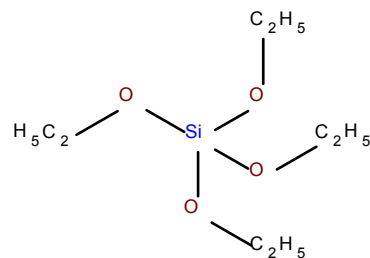


Figure 2.4 The chemical structure of TEOS

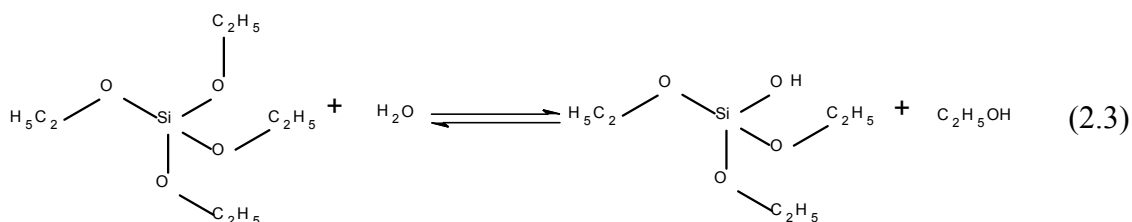
The traditional method of preparing tetraalkoxysilane is reacting tetrachlorosilane with ethanol. When ethanol is used, the product is TEOS and the by-product is hydrogen chloride, which is shown by the following reaction (Klein, 1985):



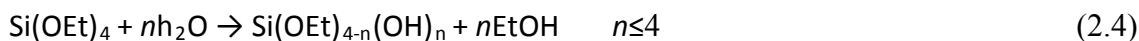
Polyalkoxy siloxanes are polymers containing siloxane groups, Si-O-Si, which are formed by the condensation reactions of alkoxides. These polymers have high thermal resistance. Thermal degradation of siloxane bonds occurs at temperatures above 300°C (Ni, et al., 2000).

2.3.3. Polymerization of tetraethylorthosilicate

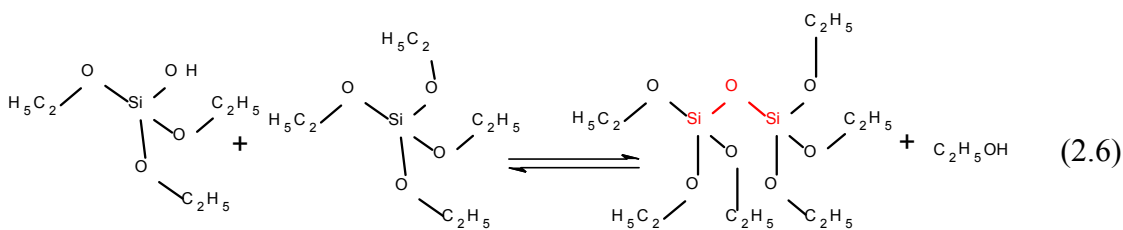
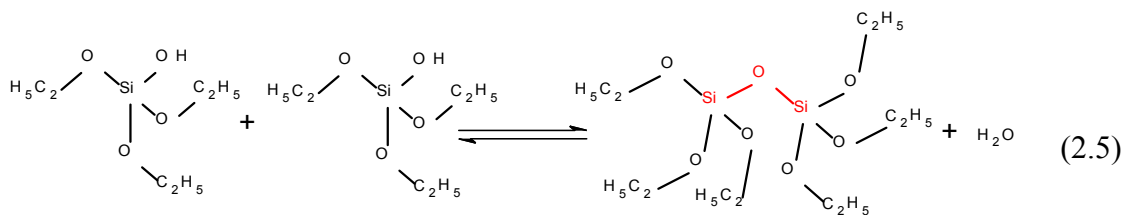
The first step in the polymerization of TEOS is hydrolysis. During the hydrolysis of TEOS in water the oxygen atom of the water molecule attacks the silicon atom of TEOS and the alkoxide group is replaced by the hydroxyl group, as shown by



It should be emphasized that TEOS molecules can be hydrolyzed more than once, because they contain more than one alkoxide group. Therefore, the hydrolysis of TEOS in a more general form is represented by



The hydrolyzed TEOS undergoes a polycondensation reaction, leading to water as a by-product (water condensation), or ethanol as a by-product (ethanol condensation). These two forms of condensations, which are classified as oxolation (water producing) and alcoxolation (alcohol producing), lead to siloxane bonds (Si-O-Si). These two condensation reactions are depicted by Reactions 2.5 and 2.6, respectively (Klein, 1985).



The condensation reaction occurs preferentially between a hydrolyzed and non-hydrolyzed species. This leads to the formation of a dimer, which further reacts with a monomer to form a trimer, and then trimers react with other monomers to form tetramers. Finally, the trimers and tetramers react with each other forming of a continuous network or gel. The ^{29}Si NMR can determine the condensation products,

which are formed in the following order: monomer, dimer, linear trimer, cyclic trimer, cyclic tetramer, and higher order rings (Brinker and Scherer, 1990).

Since water and alkoxysilane are immiscible, a mutual solvent is normally employed as a compatibilizer (e.g. alcohol). On the other hand, since alcohol produced as the by-product of the hydrolysis reaction is sufficient to homogenize the two-phase system; gels can be formed from silicon alkoxide-water mixtures without any additional alcohol. It is important to note that alcohol is not simply a solvent; it can participate in the esterification or alcoholysis reactions and shift Reactions 2.3 and 2.6 to the left (Brinker and Scherer, 1990).

Since the type of alkoxysilane and its functionality in Reactions (2.3), (2.5), and (2.6) are the same, the major variables in the polymerization of TEOS are the catalyst (OH^- or H^+), its concentration (i.e., pH), the ratio of $[\text{H}_2\text{O}]/[\text{TEOS}]$, and the reaction temperature. These variables control polymerization growth and the aggregation of the silica species when the transition occurs from the sol state to the gel state (Chang and Ring, 1992). The reaction rates of the hydrolysis and condensation are accelerated by using acid and base catalysts, respectively. It is important to note that the reaction rate is also influenced by the strength and the concentration of the catalyst (Brinker and Scherer, 1990).

The influence of pH on the gelation process was studied by Brinker and Scherer (1990). The pH value of the solution affects the sol-gel process by modifying the relative rates of the hydrolysis and condensation, and controlling the reaction mechanism (Chang and Ring, 1992). The dependence of the relative rate of reaction (v_{rel}) for both hydrolysis and condensation as a function of pH is shown in Figure 2.6. According to this figure, at $\text{pH} > 7$ the kinetics of condensation is faster than the kinetics of hydrolysis (Dorcheh and

Abbasi, 2008). It should be noted that the effect of pH on the relative reaction rates shown in Figure 2.5 is applicable only when HCl and NH_4OH are used as acidic and basic catalysts, respectively.

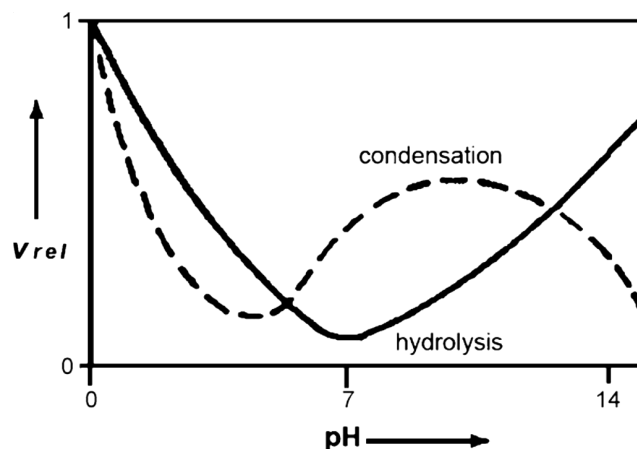
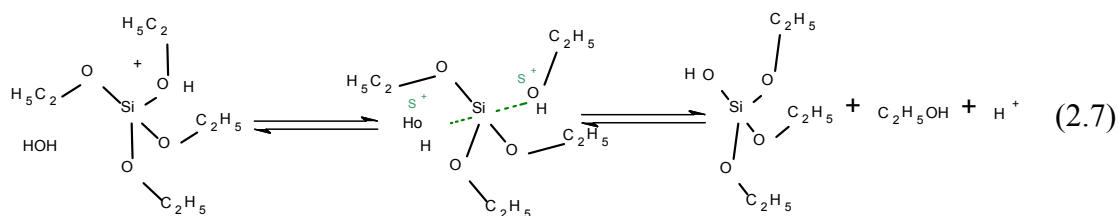


Figure 2.5 Dependence of the relative hydrolysis and condensation rates on the pH of the solution (Dorcheh and Abbasi, 2008)

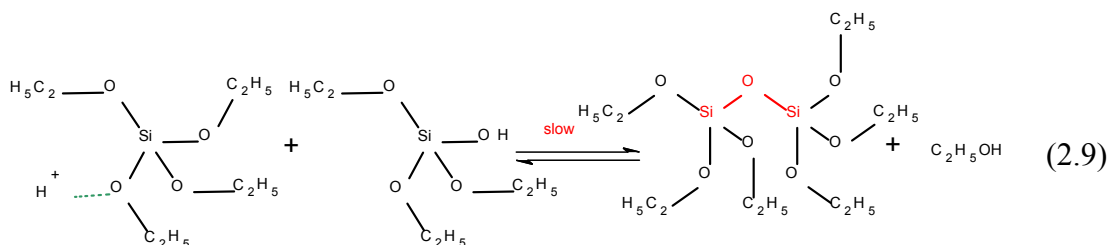
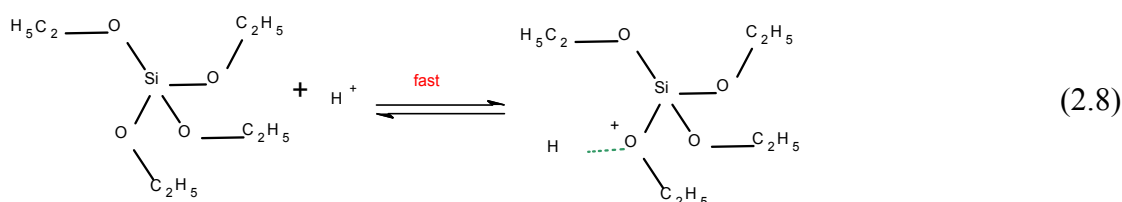
2.3.3.1. Acid-catalyzed hydrolysis

Under acidic conditions, the alkoxide group is protonated. Since electron density is withdrawn from the silicon atom, it becomes more electrophilic and is attacked by the water molecule. As a result, the water molecule acquires a partial positive charge and correspondingly the positive charge of the protonated alkoxide group is reduced, converting it to the ethanol molecule (Brinker and Scherer, 1990). The acid-catalyzed hydrolysis of TEOS is shown by the Reaction (2.7):



2.3.3.2. Acid-catalyzed condensation

The acid-catalyzed condensation mechanism involves a protonated silanol atom. Since the protonated silanol atom is more electrophilic, it is more susceptible to a nucleophilic attack. It is important to note that the condensation reactions can occur between neutral atoms and the protonated silanols (Brinker and Scherer, 1990). The acid-catalyzed condensation of TEOS is shown in the Reaction (2.8) (2.9):

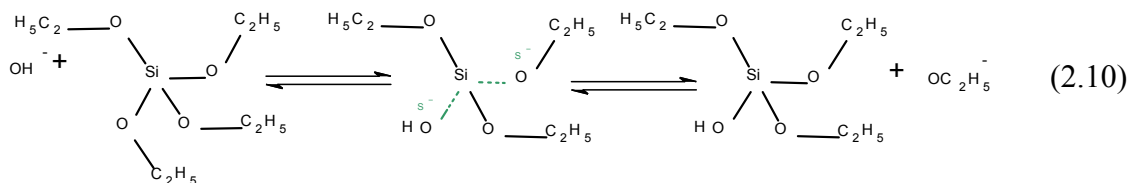


The acidic catalyst accelerates condensation step; however, the hydrolysis reaction is still the rate controlling step in the polymerization of TEOS (Brinker and Scherer, 1990).

2.3.3.3. Base-catalyzed hydrolysis

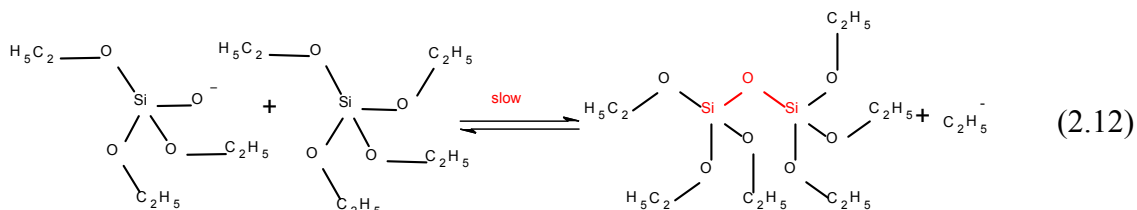
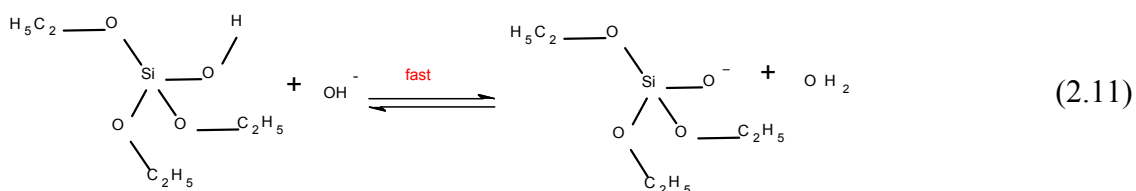
Under basic condition, TEOS initially reacts with hydroxide ions to form a transition state complex. Since the nucleophilic attack is very sensitive to the steric effects of the substitutes and also to the electron density around the atom of silicon, the fewer bulky alkoxy groups surrounding the silicon atom, the more rapidly the attack by

the OH^- groups occurs. Hence, the controlling step is the removal of the first alkoxy group. Then, the monomeric partially hydrolyzed products are hydrolyzed at a faster rate to produce monomeric silicic acid (Harris et al. 1990). The base-catalyzed hydrolysis of TEOS is shown by the Reaction (2.10):



2.3.3.4. Base-catalyzed condensation

In the base catalyzed condensation, the hydroxyl anion attacks the product of the hydrolysis reaction and deprotonates the silanol group. The Si-O-Si bond is formed by the reaction between the neutral silicon atoms and the deprotonated silanol groups (Brinker and Scherer, 1990). These two steps are shown by the Reactions (2.11) and (2.12), respectively.



2.3.4. Acid- or base-catalyzed silica gel

A gel is defined as a solid three-dimensional molecular network, which entraps some liquid inside. As the liquid evaporates from the gel at ambient conditions, it changes to a xerogel. An aerogel is formed when the removal of the liquid does not damage the solid structure, which requires supercritical drying (Goksu et al., 2010). The sol-gel process for the preparation of aerogel and xerogel is shown schematically in Figure 2.6.

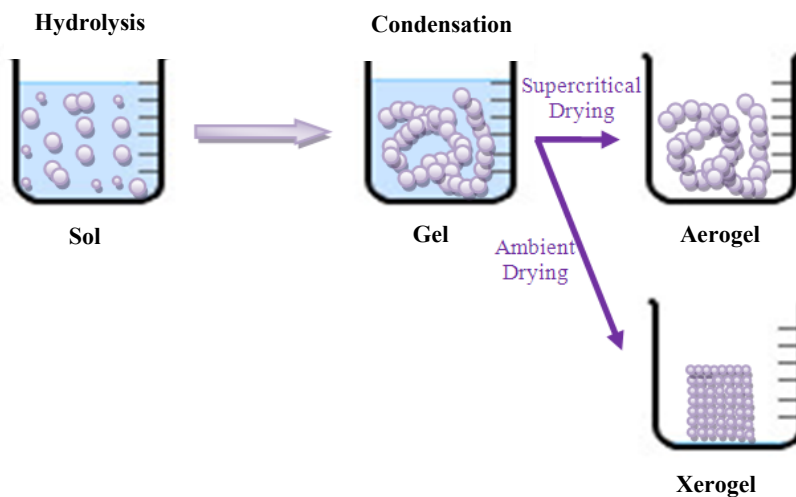


Figure 2.6 General scheme for preparing aerogel and xerogel by sol-gel processing.
Based on Goksu et al., 2010

Acid and base catalyzed gels, aerogels or xerogels are different in rheological properties and they are formed by different mechanisms as mentioned above. At low pH levels, hydrolysis is rapid, producing a significant increase of Si-OH-containing monomers. These monomers are then polymerized and have tendency to form linear polymers, which are occasionally lightly branched. The chains entangle and cause

additional branches to form a cross-linked gel shown in Figure 2.7. This type of gel is called a polymeric gel (Chang and Ring, 1992).



Figure 2.7 Gel structure under acidic condition (Nagarale et al., 2006)

Under basic conditions, the rate of the condensation reaction is faster than the rate of the hydrolysis reaction so the reactions proceed by quickly polymerizing the hydrolyzed TEOS. As a result, more highly branched clusters are formed and the condensed silica species are linked with each other to form a three-dimensional network. This type of gel, schematically shown in Figure 2.8, is usually referred to as a colloidal gel (Chang and Ring, 1992).

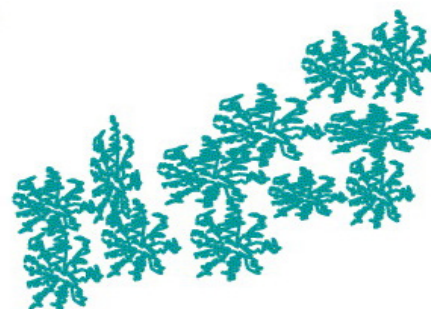


Figure 2.8 Gel structure under basic condition (Nagarale et al., 2006)

X-ray scattering confirms that the base-catalyzed gels are more densely cross-linked than the acid-catalyzed gels. Moreover, the gels prepared with acid catalysts are often less transparent than their base counterparts (Brinker and Scherer, 1990).

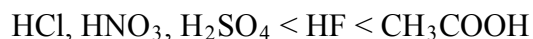
The gelation kinetics is also highly dependent on the temperature, because as the temperature increases the reaction rates of both hydrolysis and condensation increase (Chang and Ring, 1992). At a constant temperature, the acid-catalyzed systems require more gelation time (t_g) compared to the base-catalyzed systems, and it was found that the gelation times follow the sequence (Chang and Ring, 1992):

$$t_g \text{ (acidic condition)} > t_g \text{ (neutral condition)} > t_g \text{ (basic condition)}$$

It should be noted that, pH and temperature are not the only factors that control the hydrolysis rate and the gelation time. The nature of the catalysts also affects the kinetics of the sol-gel process. For example, Dorcheh and Abbasi (2008) investigated the sol-gel process of TEOS in ethanol using five different acid catalysts at the same concentration and reported that the gelation time increased in the following sequence:



The corresponding pH values were:



Thus, the lower pH solutions (e.g. HCl, HNO₃, and H₂SO₄) resulted in slower kinetics of gelation than the higher pH solutions (e.g. HF and CH₃COOH), which is exactly the opposite of the relationship shown in Figure 2.6. The latter, as already indicated is valid using the same acid catalysts (HCl) (Dorcheh and Abbasi, 2008).

2.3.5. Classification of silica gels

Since the kinetics of the hydrolysis and condensation of TEOS are slow at room temperature, catalysts are added for accelerating these reactions. Figure 2.9 presents the classification of the synthesized silica gels based on their preparation process. If the hydrolysis and condensation take place simultaneously, the process is classified as a one-step process and the t_g is a result of both reactions, so that it is difficult to distinguish the conditions of each. In a two-step process, the hydrolysis and condensation are not simultaneous. In this case, it is possible to take advantage of high hydrolysis rate at acidic conditions and high condensation rates at base conditions. Therefore, the two-step acid-base catalyzed is an optimum procedure for the fast formation of the inorganic structure. It should be noted that for both processes, the ultimate properties of the formed gel largely change with alteration of the catalysts (Boonstra and Bernards, 1988).

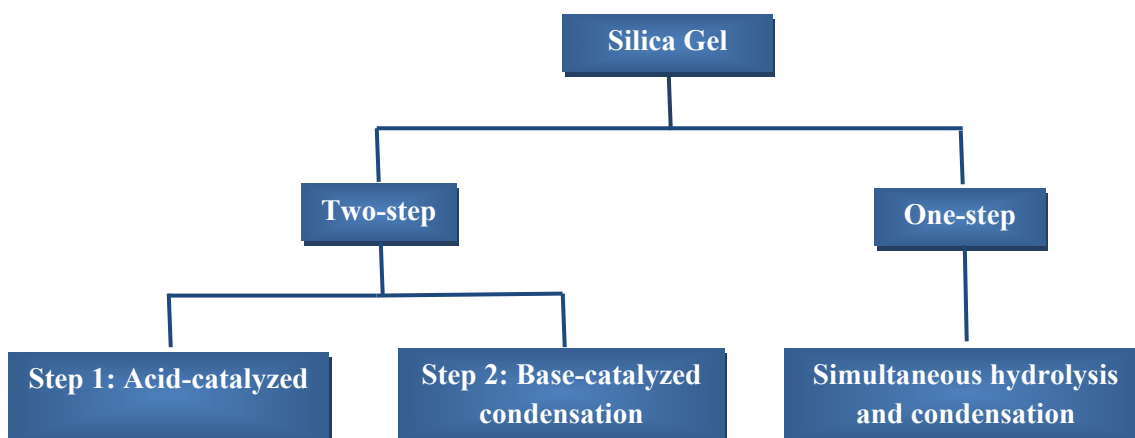


Figure 2.9 Single-step vs. two-step method for silica gel

2.3.6. Single-step base-catalyzed polymerization

As mentioned before, the gelation kinetics of $\text{Si}(\text{OR})_4$ at room temperature is very slow, and the gelation kinetics can be accelerated by using bases, which carry strong negative charges. Proton acceptors (bases) accelerate the condensation reaction more than the hydrolysis reaction, which then results in the formation of denser colloidal silica particles and colloidal gels. Aqueous NH_3 is the basic catalyst most frequently utilized for the silica gel formation (Aegerter, 2011).

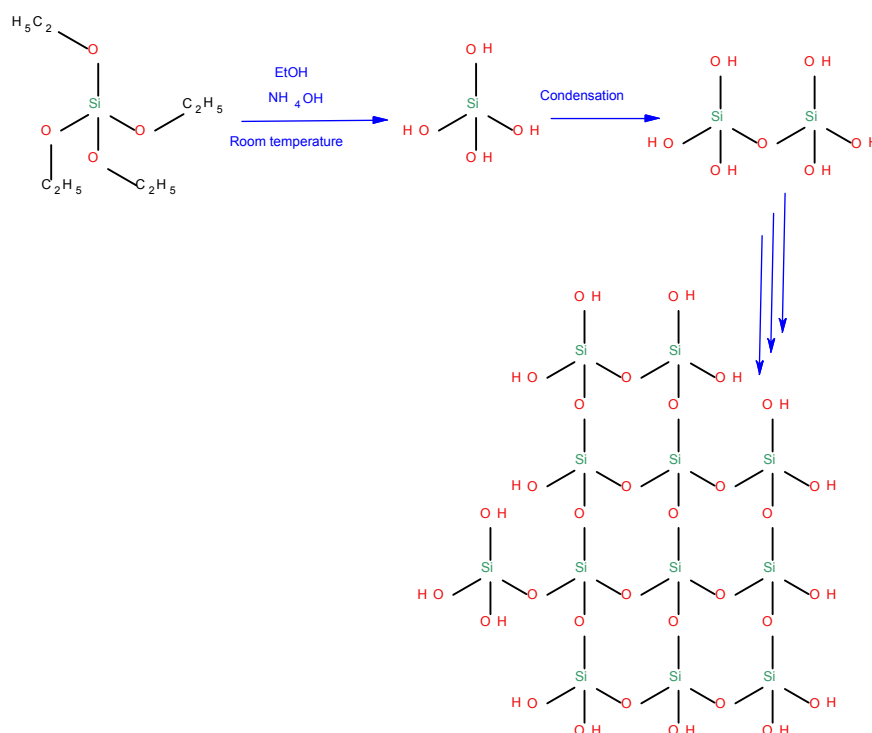


Figure 2.10 Polymerization of TEOS in the presence of NH_4OH . Based on Green et al., (2003)

Figure 2.10 presents schematically the single-step polymerization of TEOS in the presence of NH_4OH . The concentrations of H_2O and NH_3 play an important role in controlling the balance between the hydrolysis rate of TEOS and the condensation rate of

its hydrolyzed monomers. Increasing the concentrations of H_2O and NH_3 results in the production of higher amounts of OH^- groups, which attacks the Si atoms and speed up the hydrolysis reaction (Green et al., 2003).

2.3.7. Single-step acid-catalyzed polymerization

Another method to accelerate the gelation kinetics of $\text{Si}(\text{OR})_4$ alkoxide is adding acids (H^+), which completely changes the reaction mechanism. In this case, the hydrolysis rate is faster than the condensation rate, and the silica gels with a texture similar to that of polymeric gels derived from organic chemistry are obtained (Aegerter, 2011).

Colby et al. (1986) reported the gelation time of solutions containing TEOS and ethanol with H_2O and HCl as a catalyst (molar ratio: 1:4:4:0.05) to be 380 hours at 25°C . However, when the temperature increased to 70°C , the gelation time, although still long, decreases to 20 hours. The gelation time follows a typical Arrhenius-type relation with temperature.

$$1/t_g = A \exp(-E^*/RT) \quad (2.13)$$

where A is the Arrhenius constant, E^* is the apparent activation energy, and T is the absolute temperature. The plots of $\ln(t_g)$ versus $1/T$ are linear as shown in Figure 2.11 (Colby et al. 1986). In addition, the t_g is a function of the $\text{H}_2\text{O}/\text{TEOS}$ ratio. For the complete hydrolysis, this ratio should be four. When the ratio is less than four, the gelation time increases (Bechtold, 1980).

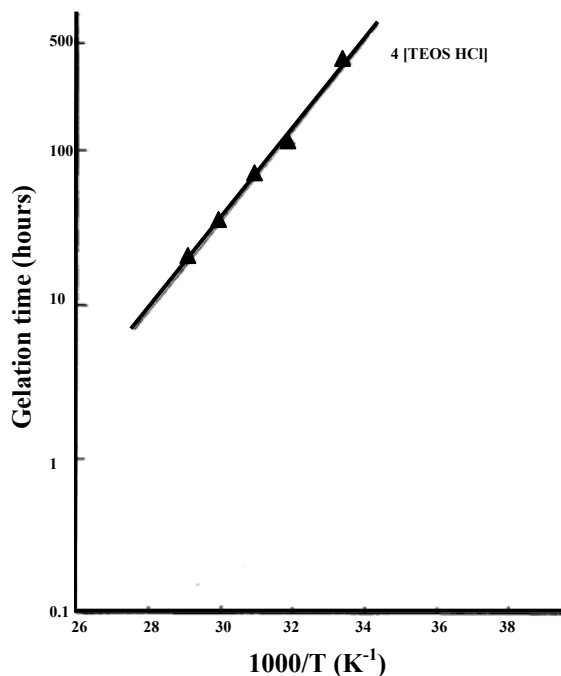


Figure 2.11 Plot of $\ln(t_g)$ versus $1/T$ for $\text{Si}(\text{OR})_4 : 4\text{C}_2\text{H}_5\text{OH} : 4\text{H}_2\text{O} : 0.05 \text{ HCl}$. Taken from Colby et al., (1986).

2.3.8. Two-step acid-base catalyzed

The split of the simultaneous hydrolysis and condensation of TEOS into an acidic hydrolysis step and a basic condensation step was suggested by Brinker et al. (1990). A two-step process combines the advantages of the individual steps, which are a high rate of hydrolysis by using an acid catalyst and a high condensation rate by using a base catalyst, leading to a decreased gelation time.

For the formation of silica gel with a two-step sol-gel process, the solution of TEOS in water and ethanol is first hydrolyzed in the presence of HCl, and then NH_4OH solution is added in the second step. Both the acid and base solutions contain water and ethanol. The latter is used to avoid the effects of immiscibility during water addition in the hydrolysis and gelation steps (Boonstra and Bernards, 1988). The hydrolysis time (t_h)

is defined by the time interval between the acid and base additions. The gelation time (t_g) is then the time interval between the addition of the base and the moment when no more fluidity of the solution is observed. It is important to note that t_g in the basic step is strongly influenced by the hydrolysis in the acid step (Boonstra and Bernards, 1988).

In general, for short hydrolysis times, a long gelation times are observed when $\text{Si}(\text{OC}_2\text{H}_5)_3\text{OH}$ is the main hydrolysis product. In the extreme case of very short t_h , the gelation does not occur even after several days. By extending the hydrolysis, the concentration of $\text{Si}(\text{OEt})_{4-n}(\text{OH})_n$ increases and as a result, the gelation time in the basic step decreases. In acidic step, once all the added water is consumed, dimerisation of silanols becomes the dominant reaction and therefore the concentration of $\text{Si}(\text{OEt})_{4-n}(\text{OH})_n$ decreases and finally the gelation time increases in the basic step (Boonstra and Bernards, 1988).

Various other parameters, such as the hydrolysis temperature, the concentrations of HCl , NH_4OH , and ethanol affect the gelation time. In general, the gelation time is proportional to the concentration of HCl , NH_4OH and the hydrolysis temperature. On the other hand, increasing the ethanol concentration leads to an increase in the gelation time because ethanol dilutes the solution, consequently retarding the condensation reaction. In other words, dilution of the solution increases the distance between the species, which are condensed partially and thereby increases the gelation time (Boonstra and Bernards, 1989).

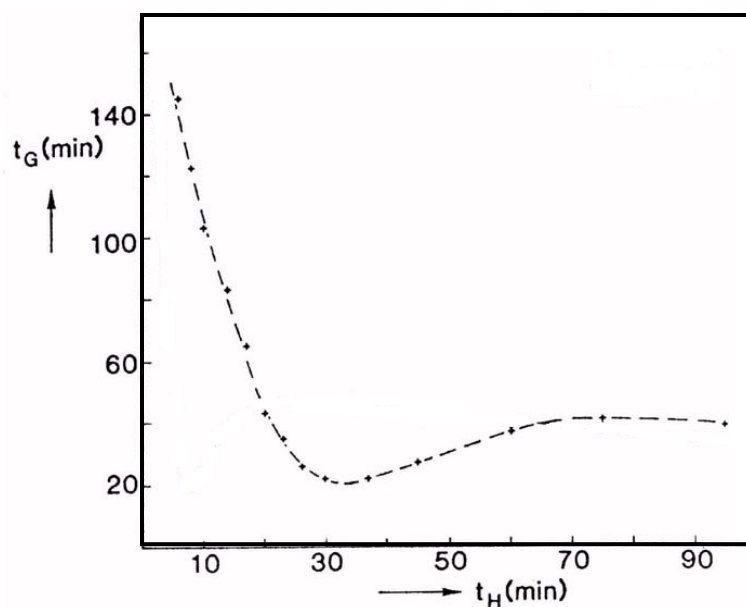


Figure 2.12 Dependence of the gelation time on the hydrolysis time (Boonstra and Bernards, 1988). Component molar ratio 1TEOS : 4EtOH : 2.5H₂O at $T = 25^\circ\text{C}$

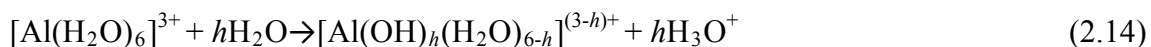
2.3.9. Aluminum silicate chemistry

Acidic conditions also exist when salts of strong acids and weak basis dissolve in an aqueous solution. The example of such a salt is an aluminum nitrate or aluminum hydroxonitrate. Since the latter, similarly to TEOS undergoes the hydrolysis and condensation, these two processes must be first discussed before considering polymerization of TEOS in the presence of aluminum hydroxonitrate.

2.3.9.1. Hydrolysis and condensation of Al (III)

Aluminum is the second most abundant metal in the earth's crust, which shows the trivalent state in compounds and solutions (Brinker and Scherer, 1990). The aluminium aqua ion in acidic conditions, with $\text{pH} < 3$ is octahedrally coordinated and

forms the non-hydrolyzed species of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (Bourrie et al., 1989). When the pH is greater than 3, the hydrolyzed species can be formed according to the following reaction (Feng et al., 2008):



where h is the equivalent to the $[\text{OH}]_{\text{tot}}/[\text{Al(III)}]_{\text{tot}}$ ratio (i.e., the molar ratio of hydrolysis) according to the net Reaction (2.14). Subsequent condensation leads to the formation of polynuclear hydroxides (Brinker and Scherer, 1990). The distribution of polynuclear species is largely dependent on the hydrolysis conditions such as time, temperature, and the base concentration. By changing the base concentration, various hydrolysis products have been reported with different h values (Botter et al., 1980). Baes and Mesmer (1976) reported the production of two small polynuclear species at low base concentrations, which are $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_4]^{4+}$ and $[\text{Al}_3(\text{OH})_4(\text{H}_2\text{O})_9]^{5+}$. On the other hand, at higher base concentrations large polynuclear species $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ is produced.

This study focuses on $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ or Al_{13}^{7+} , which forms the so called keggin structure. In this form, the Al-complex is a symmetrical polyprotic acid consisting a tetrahedral $\text{AlO}_{4/4}^+$ in the center and surrounded by 12 identical functional groups of $\text{AlO}_{1/4}(\text{OH})_{4/2}(\text{H}_2\text{O})^{0.5+}$ (Figure 2.13) (Furrer et al., 1992).

Hydrolysis of Al_3^+ occurs rapidly in the presence of sodium carbonate and Al_{13}^{7+} is formed as the hydrolysis proceeds. The formation of keggin structure requires a high degree of hydrolysis. On the other hand, the addition of sodium carbonate leads to the formation of Al_{13}^{7+} at any hydrolysis degree. It should also be noted that the formation of Al-complex depends also on concentration. As the base is added, a precipitate forms,

which should be dissolved immediately, because otherwise it leads to an insoluble materials (Akitt and Farthing, 1981).

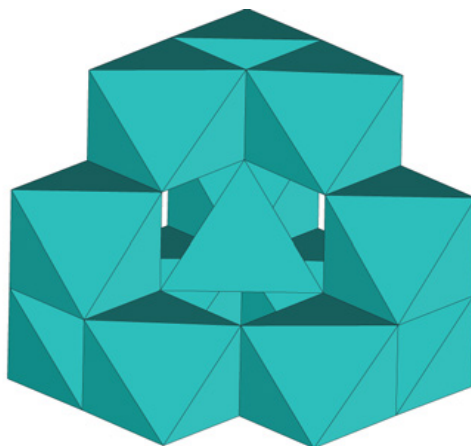


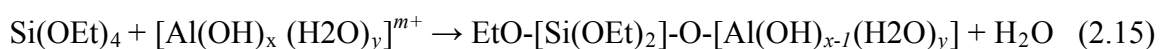
Figure 2.13 Keggin structure of $\text{Al}_{13}^{7+} : \text{AlO}_{4/4}^{+}$ in the center surrounded by 12 identical functional units of $\text{AlO}_{1/4}(\text{OH})_4/(\text{H}_2\text{O})^{0.5+}$ (Franceti and Bukovec, 2008)

2.3.9.2. Hydrolysis and condensation of TEOS in the presence of aluminum hydroxonitrate

Eliseev et al. (1999) investigated the polymerization of TEOS in an aqueous solution of aluminum hydroxonitrate. The experiments illustrated that the TEOS hydrolysis in the presence of aluminum hydroxonitrates with a high degree of hydrolysis ($h > 1.9$) takes place very rapidly (gelation time $\approx 10 - 20$ min), and the final gel is opaque. At a lower degree of hydrolysis ($h < 1.9$) the gelation requires more time (3-4 days) and the produced gel is transparent. In other words, opaque gels are formed whenever the kinetics of hydrolysis is restricted by the condensation processes whereas

the formation of transparent gels is characteristic of the gelation limited by the hydrolysis of TEOS (Eliseev et al., 1999).

During the hydrolysis of TEOS in the presence of the aluminum complex, the nucleophilic agent can be either the H₂O molecule or the OH⁻ group coordinated with the aluminum cation. The OH⁻ groups in the keggins structure have a lower partial charge compared to the free water molecules and as a result they can possess stronger nucleophilic activity. Therefore, the reaction mechanism of TEOS in the presence of aluminum hydroxonitrate includes the attack of the OH⁻ groups on a TEOS molecule based on the following equation:



The ²⁷Al NMR studies of the gel indicates that all the aluminum incorporated into the gel matrix is in the keggins structure, [AlO₄Al₁₂(OH)₂₄(H₂O)₁₂]⁷⁻. The keggins structure is also able to accelerate the polycondensation of TEOS. This complex attacks the TEOS molecules readily and consequently Al-O-Si bond are formed (Eliseev et al., 1999).

Chapter 3. EXPERIMENTAL METHODS

This chapter discusses experimental methods along with the materials and apparatus used in this research project. The experimental methods are divided into three main parts: (i) polymerization of TEOS in a single phase (gelation test), (ii) polymerization of TEOS in the emulsion with the polymer solvent (gravimetric powder method), and (iii) polymerization of TEOS in the emulsion with polymer solution. These three parts represent sequential phases in the process of developing of the final EPPM membranes. Although the purpose of the gelation tests (first phase) was different for one-step (Al-Keg solution) and two-step (hydrochloric acid and ammonium hydroxide) processes, a successful completion of the gelation tests was a necessary condition prior to moving into the second phase, i.e., the gravimetric powder method tests. The latter provided a quick, indirect quantification of the emulsion polymerization of TEOS in a pure solvent system. Again, observing a conversion of TEOS in the emulsion with pure solvent was a necessary condition before moving into final phase of this project, i.e., polymerization of TEOS in the emulsion with polymer solution. It was in this final phase that the actual EPMM membranes were prepared and extensively characterized. Consequently, this final phase was the most important and time consuming part of this research project.

3.1. Polymerization of TEOS in a single phase

This part of the project describes the polymerization of TEOS in the single phase (gelation test) using two different catalysts; Al-Keg solution (one-step acid-catalyzed process) and hydrochloric acid - ammonium hydroxide (two-step acid- and base-catalyzed process). A successful completion of the gelation tests was a necessary

condition prior to carrying out the two-phase reactions in a pure solvent (gravimetric powder method) and a polymer solution (EPMM membranes).

3.1.1. Polymerization of TEOS in a single phase with Al-Keg solution

The main purpose of the gelation test with Al-Keg solution was to determine if the Al-Keg structure was formed in the aqueous solution. Without this structure it would be impossible to hydrolyze TEOS and then to polymerize it. Therefore, the preparation of the aqueous solution was the most critical aspect in the single step polymerization of TEOS.

3.1.1.1. Preparation of aqueous solution

The preparation of the aqueous solution of the aluminum hydroxonitrate and sodium carbonate involved three steps:

- 1) Dissolving 10.50 g of solid aluminum hydroxonitrate powder into 15.0 mL of distilled-deionized water.
- 2) Dissolving 3.00 g of sodium carbonate powder into 13.0 mL of distilled-deionized water.
- 3) Adding slowly the sodium carbonate solution into the aluminum hydroxonitrate solution while stirring the content using a magnetic stirring bar. During the addition of the carbonate solution, a formation of precipitate was observed, which quickly re-dissolved on stirring.

The resulting aqueous solution had no color, and was further stirred continuously for 48 hours at room temperature to ensure a hydrolytic equilibrium (Eliseev et al., 1999).

It should be noted that the concentration of aluminum in the aqueous solution was 1M and the pH value of the solution ranged from 3.6 to 3.8 (Sadeghi et al., 2008).

3.1.1.2. Gelation test

A gelation test was performed to verify a sufficient degree of hydrolysis of the aluminum hydroxonitrate in the solution, which was necessary for the formation of the required keggin structure of the Al complex (Al-Keg structure). The test was performed by mixing the prepared aqueous solution with the solution of TEOS in ethanol. Since TEOS is not soluble in water, a mutual solvent (ethanol) was used. The volume ratio of TEOS: EtOH: aqueous phase was 1:3:1 (Eliseev et al., 1999). Fig. 3.1 schematically presents the preparation of the aqueous solution followed by the gelation test. Formation of a gel in the single-phase system confirmed the formation of the Al-Keg structure in the aqueous solution, and the latter was considered to be suitable for the polymerization of TEOS in the two phase systems (with pure solvent and with polymer solution).

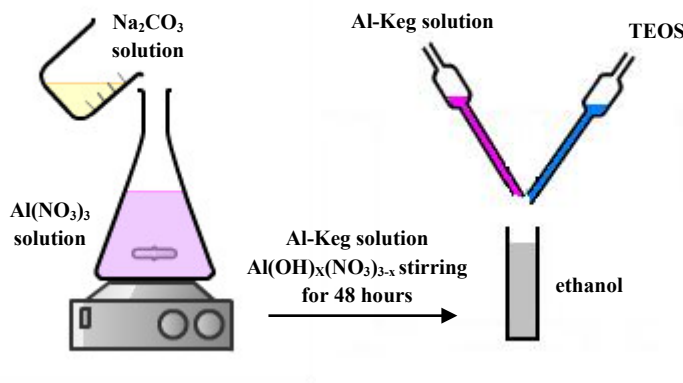


Figure 3.1 The preparation procedure of Al-Keg solution and the gelation test in the presence of aluminum hydroxonitrate

3.1.2. Polymerization of TEOS in a single phase with hydrochloric acid and ammonium hydroxide

Polymerization of TEOS in a single phase by using a two-step process requires the preparation of acid and base solutions. The acid and base solutions were used for the hydrolysis and condensation of TEOS, respectively. A successful gelation test confirmed that these reactions had indeed occurred. The gelation tests also allowed to determine the range of pH in each step for the respective reactions to occur.

3.1.2.1. Preparation of acid solution

The acid solution was prepared by mixing of 5.0 mL of 99% ethanol with 7.5 mL of distilled-deionized water and adding different amount of 20% hydrochloric acid. The effect of the amount of the added acid on the pH of the resulting solution is presented in Appendix A.1.

3.1.2.2. Preparation of base solution

The base solution was prepared by mixing 3.5 mL of ethanol with 7.5 mL of distilled-deionized water and adding a different amount of 15% ammonium hydroxide. The effect of the amount of the added base on the pH of the resulting solution is presented in Appendix A.2.

3.1.2.3. Gelation test

The gelation time in the base environment is strongly influenced by the hydrolysis in the acid environment (Boonstra et al., 1988). Ginneken et al., (1998) reported that in a

two-step procedure gelation occurs with the molar ratio of TEOS: H₂O: C₂H₅OH: HCl: NH₄OH of 1: 1.5 -3.5: 1.9 - 5.9: 3.9×10^{-4} - 1.6×10^{-3} : 1.4×10^{-3} - 5.7×10^{-3} . It should be noted that an excess amount of water and sufficient hydrolysis time accelerate the gelation process by increasing the hydrolysis ratio (Xi et al., 1995). Hence, the gelation experiments in this study were carried out with an excess amount of water. The experimental molar ratio of TEOS: H₂O: C₂H₅OH in this project was 1: 18: 5.1. After adding the acid solution into the solution containing TEOS, the content was stirred by a magnetic stirring bar for 5 minutes, followed by slow addition of the base solution and stirring the content for 10 seconds. The concentrations of acid and base in the respective solutions were varied by adding different amounts of acid and base, which varied from 0.011 to 0.111 drops ml. The gelation process in the two-step procedure discussed above is schematically shown in Figure 3.2.

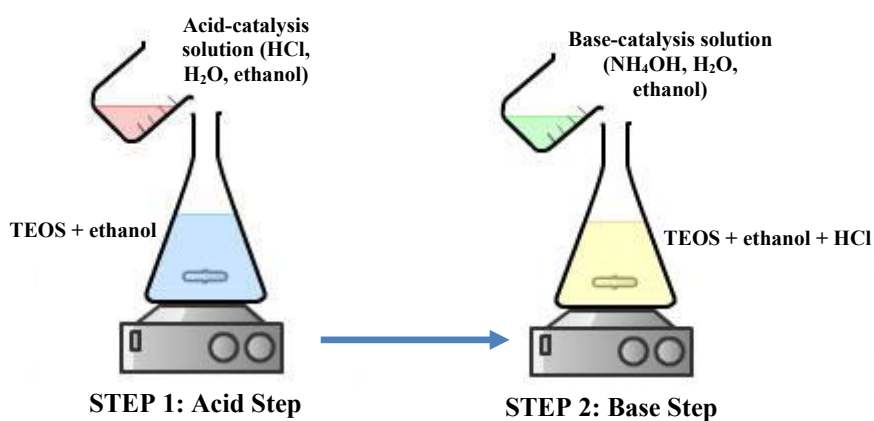


Figure 3.2 The gelation test procedure in the presence of hydrochloric acid - ammonium hydroxide (two-steps acid and base catalyzed process)

3.2. Gravimetric powder method

The ^{29}Si NMR and ICP-MS analyses are two essential characterization techniques that are used to verify the polymerization of TEOS in the final EPMM membranes. However, since the access to these techniques is limited, a gravimetric powder method (GPM) was developed by Wang (2011) for an indirect quantification of the emulsion polymerization of TEOS in a pure solvent system.

In this method, polymerization of TEOS takes place in an emulsion system with only a solvent rather than a polymer solution. This way, extent of the polymerization of TEOS can be assessed based on the mass of solids after the complete evaporation of the reaction content. The unreacted TEOS is considered as a volatile species, because it leaves no detectable solid residuals. On the other hand, the reacted (polymerized) TEOS will remain in the solid phase after the complete evaporation of the reaction content. It is important to note that in the system in which the emulsion is made of a polymer solution rather than a solvent, the polymer would be the major component of the solid phase, thus precluding the accurate assessment of the mass of the reacted TEOS.

Table 3.1 provides the list of all the compounds used for the polymerization of TEOS in different environments. The species listed in this table are classified as either the volatile or non-volatile components.

The GPM tests were performed in the presence of two different catalysts, Al-Keg solution (single-step process) and $\text{HCl-NH}_4\text{OH}$ system (two-step process), respectively. For each catalyst, the GPM tests were performed with four different combinations of the surfactant (n-octanol) and the compatibilizer (ethanol). In each combination the total volume of the liquid additive was 0.3 mL, and the four used concentrations of the

surfactant were: 0, 33.3, 66.7 and 100 v/v%. At each condition several tests were performed to ensure the repeatability of the results, as well as to collect sufficient amounts of the solid phase for further ^{29}Si NMR analysis.

Table 3.1 The species used in the GPM tests and their volatility

Species	Volatility
Water	volatile
TCE	volatile
TEOS	volatile
HCl*	volatile
NH ₄ OH*	volatile
Ethanol	volatile
n-octanol	volatile
Na salt	non-volatile
Al-Si complex	non-volatile
Al salt	non-volatile

*HCl and NH₄OH alone are volatile components, but when used together; they react forming NH₄Cl, which is a non-volatile species

3.2.1. The GPM tests in the presence of aluminum hydroxonitrate

A GPM test in the presence of Al-Keg solution (single-step process) is schematically shown in Figure 3.3. Prior to formation of what is referred to as an *emulsion one* in Fig 3.3, the Al-Keg solution was prepared (Section 3.1.1.1) followed by successful passing of the gelation test (Section 3.1.1.2). The *emulsion one* was prepared by mixing 10 mL of TCE, 0.1 mL of the Al-Keg solution, and 0.3 mL of different combinations of ethanol and n-octanol, followed by ultrasonication of the mixture using an ultra-sound dismembrator 550 from Fisher Scientific. The mixture was sonicated at the power level of 7 for 1 minute, which consisted of two 30 seconds pulses with a 30 seconds rest time in between to avoid overheating of the emulsion. It is important to note that, the power level at this step affects the size of the aqueous phase droplets dispersed in

the continuous phase. Since the droplet size determines the interphase area, by decreasing the droplet size the interphase area is increased and consequently the conversion rate of TEOS should increase. The power level of 7 and the sonication time of 1 minute for this stage were established by Wang (2011), who reported the resulting mean droplet size of 1315 nm.

In the next step, 0.3 mL of TEOS was added into the emulsion one, after which the content was ultrasonicated for 30 minutes. The purpose of ultrasonication in the second step was to facilitate the hydrolysis and condensation reactions. Again, 30 minutes of sonication at the power level of 7 were established by Wang (2011). Similarly to the sonication of the emulsion one, each sonication pulse at the power level of 7 was followed by a 30 seconds rest time. Consequently, for the sonication time of 30 minutes the total reaction time was actually 60 minutes. It is important to note that 0.3 mL of TEOS that was used in the second step was close to 0.29 mL, which represents a stoichiometric amount of TEOS for the reaction with the aluminum hydroxonitrate contained in 0.1 mL of the Al-Keg solution that was present in the emulsion one.

After finishing ultrasonication, the final emulsion was transferred to a petri dish to let the volatile components to evaporate at ambient temperature for 24 hours. After this initial evaporation step, the petri dish with its content was transferred to an oven, where it was heated to 200°C and kept at that temperature for one week. Then the oven was left to cool down to ambient temperature and the mass of the petri dish with the remaining solids was measured.

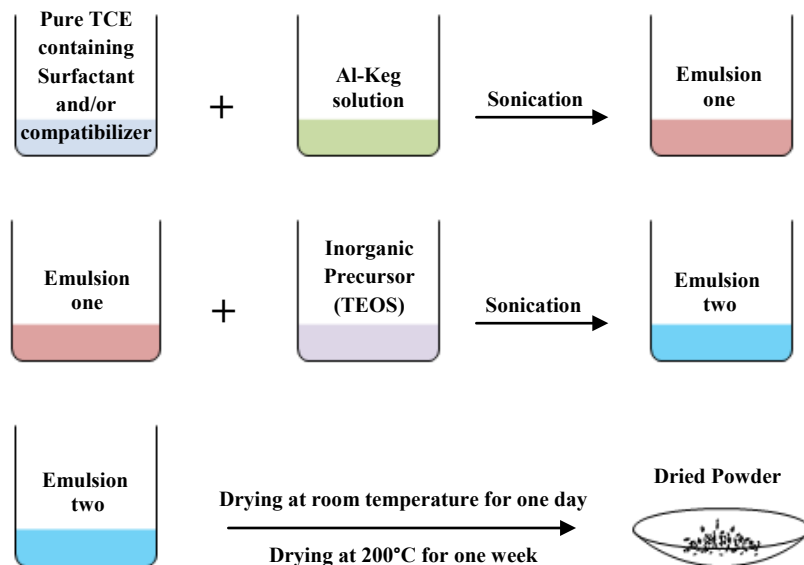


Figure 3.3 The protocol for the gravimetric powder method (GPM) when the Al-Keg solution, which has passed the gelation test, used as a catalyst. Ethanol and n-octanol considered as compatibilizer and surfactant, respectively.

If no chemical reaction occurred, the dried powder in a petri dish would consist only of aluminum hydroxonitrate and sodium carbonate used for the preparation of the Al-Keg solution, and for 0.1 mL of the aqueous solution, the mass of solid residuals would be 0.0305 g (Wang, 2011). In comparison, the average mass of solid residuals remaining after evaporation of 0.1 mL of the aqueous solution was 0.0309 g, which was very close to the theoretical value of 0.0305 g. Consequently, the theoretical mass of 0.0305 g was considered as a threshold value. Thus, if the mass of the dried powder were more than 0.0305 g, the polymerization of tetraethylorthosilicate (TEOS) in the presence of aluminum hydroxonitrate was confirmed.

Table 3.2 summarizes the specific parameters used in the syntheses of four samples, according to the GPM protocol, with Al-Keg solution as an acidic catalyst. The sample names provide the information related to the conditions at which a given sample

was prepared. For instance, GPM/aq/0.2/0.1; indicates a GPM sample prepared using aq, i.e., aqueous solution of aluminium hydroxonitrate and sodium carbonate as a catalyst containing both ethanol – 0.2 mL and n-octanol – 0.1 mL.

Table 3.2 The parameters for the synthesis of the four samples by gravimetric powder method when Al-Keg solution used as a catalyst with four different combinations of the surfactant (n-octanol) and the compatibilizer (ethanol).

GPM/aq/0.3/0.0	GPM/aq/0.2/0.1
10 mL of TCE	10 mL of TCE
0.1 mL of Al-Keg solution	0.1 mL of Al-Keg solution
0.3 mL of ethanol	0.2 mL of ethanol + 0.1 mL of n-octanol
Ultrasonication: 1 minute – Power level of 7	Ultrasonication: 1 minute – Power level of 7
0.3 mL of TEOS	0.3 mL of TEOS
Ultrasonication: 30 minutes - Power level of 7	Ultrasonication: 30 minutes - Power level of 7
GPM/aq/0.1/0.2	GPM/aq/0.0/0.3
10 mL of TCE	10 mL of TCE
0.1 mL of Al-Keg solution	0.1 mL of Al-Keg solution
0.1 mL of ethanol + 0.2 mL of n-octanol	0.3 mL of n-octanol
Ultrasonication: 1 minute – Power level of 7	Ultrasonication: 1 minute – Power level of 7
0.3 mL of TEOS	0.3 mL of TEOS
Ultrasonication: 30 minutes - Power level of 7	Ultrasonication: 30 minutes - Power level of 7

It should also be noted that the output energy of the ultra-sound dismembrator employed in this work can be calculated based on the power level by the following equation:

$$\text{Output Energy (W)} = \frac{\text{Power level}}{10} \times 600 \quad (3.1)$$

3.2.2. The GPM tests in the presence of hydrochloric acid and ammonium hydroxide

A GPM test in the presence of hydrochloric acid and ammonium hydroxide is schematically shown in Figure 3.4. In the first step, the emulsion one was prepared by combining 10 mL of solvent (TCE) with 3 drops of concentrated HCl, 0.1 mL of distilled-deionized water, and surfactant and/or compatibilizer in different proportions, followed by ultrasonication of the content for 1 minute. In the second step, 0.3 mL of TEOS was added into the emulsion one followed by ultrasonication of the content for a specific time (optimization of the ultrasonication time in this step will be presented in Results and Discussion) to facilitate the hydrolysis of TEOS. In the next step, 0.067 mL of NH_4OH were added to the emulsion and ultrasonicated for a specific time to facilitate the condensation reaction. In the final step, the prepared emulsion was poured into a petri dish and dried in the similar way as the emulsion prepared in the presence of Al-Keg solution.

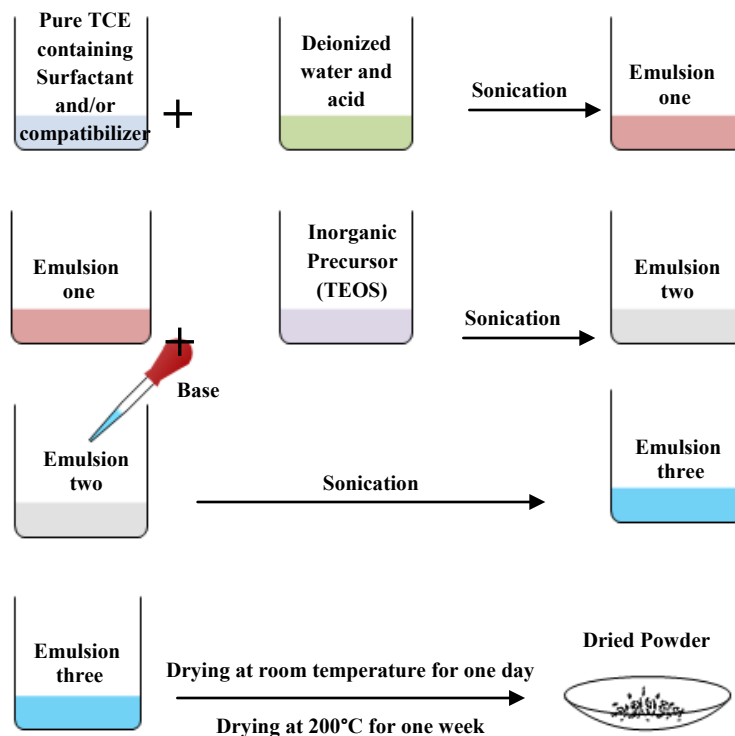


Figure 3.4 The protocol for the gravimetric powder method (GPM) using HCl-NH₄OH as a catalyst system. Ethanol and n-octanol considered as compatibilizer and surfactant respectively.

Table 3.3 summarizes the specific parameters in the synthesis of the four samples, according to the GPM protocol, using HCl-NH₄OH as a catalyst system. If TEOS did not polymerize, the only solid residual would be NH₄Cl. Theoretically, the reaction of 0.033 mL of the concentrated HCl with 0.067 mL of the concentrated NH₄OH should lead to 0.0114 g of residuals. In comparison, the average mass of solid residuals remaining after evaporation of 0.033 mL of the concentrated HCl with 0.067 mL of the concentrated NH₄OH was 0.0109 g, which was very close to the theoretical value. Therefore, if the dried powders mass were more than 0.0114 g, the polymerization of tetraethylorthosilicate (TEOS) in the presence of HCl-NH₄OH was confirmed.

Table 3.3 The parameters for the synthesis of the four samples by gravimetric powder method using HCl-NH₄OH as a catalyst system with four different combinations of the surfactant (n-octanol) and the compatibilizer (ethanol).

GPM/ab/0.3/0.0	GPM/ab/0.2/0.1
10 mL of TCE 0.033 mL HCl + 0.1 of distilled-deionized water 0.3 mL of ethanol Ultrasonication: 1 minute – Power level of 7 0.3 mL of TEOS Ultrasonication: 5 minutes - Power level of 7 0.067 mL of NH ₄ OH Ultrasonication: 30 minutes - Power level of 7	10 mL of TCE 0.033 mL HCl + 0.1 of distilled-deionized water 0.2 mL of ethanol + 0.1 mL of n-octanol Ultrasonication: 1 minute – Power level of 7 0.3 mL of TEOS Ultrasonication: 5 minutes - Power level of 7 0.067 mL of NH ₄ OH Ultrasonication: 30 minutes - Power level of 7
GPM/ab/0.1/0.2	GPM/ab/0.0/0.3
10 mL of TCE 0.033 mL HCl + 0.1 of distilled-deionized water 0.1 mL of ethanol + 0.2 mL of n-octanol Ultrasonication: 1 minute – Power level of 7 0.3 mL of TEOS Ultrasonication: 5 minutes - Power level of 7 0.067 mL of NH ₄ OH Ultrasonication: 30 minutes- Power level of 7	10 mL of TCE 0.033 mL HCl + 0.1 of distilled-deionized water 0.3 mL of n-octanol Ultrasonication: 1 minute – Power level of 7 0.3 mL of TEOS Ultrasonication: 5 minutes - Power level of 7 0.067 mL of NH ₄ OH Ultrasonication: 30 minutes - Power level of 7

3.3. Membrane synthesis

The protocol for the synthesis of the casting emulsions, from which emulsion polymerized mixed matrix (EPMM) membranes were prepared, was similar to the protocol for the preparation of the emulsions for the GPM tests. The EPMM membranes were prepared from the final emulsion using the solvent evaporation (SE) and the spin coating (SC) methods. In addition, these two methods were also used for casting the membranes from a homogeneous polymer solution used for the preparation of the emulsion one. The purpose of the latter membranes was to provide a reference when evaluating the properties of the EPMM membranes.

3.3.1. Preparation of polymer solution

Polymer solution was prepared by dissolving high molecular weight poly (2,6-dimethyl-1,4-phenylene oxide) (HMW-PPO) powder in trichloroethylene (TCE) to form a 10 w/v% solution. To facilitate dissolving of the polymer in solvent the process was carried out under a continuous magnetic stirring for 48 hours. The solution was then filtered through a 1 μ m glass fiber filter to remove any impurities. Such a prepared solution was subsequently used for the preparation of the PPO-based EPMM and pure PPO membranes.

3.3.2. Preparation of casting emulsion for EPMM membranes

The protocol for the preparation of EPMM membranes is similar to the protocol used for the GPM with only two differences (Figures 3.5 and 3.6). First of all, a polymer solution was used instead of a pure solvent for the preparation of the emulsion one. In addition, the final emulsion was ultrasonicated for 90 minutes at the power level of 3 compared to 30 minutes ultrasonication at the power level of 7 in the case of the GPM protocol. The latter changes were dictated by a much greater viscosity of polymer solution compared to the viscosity of pure TCE.

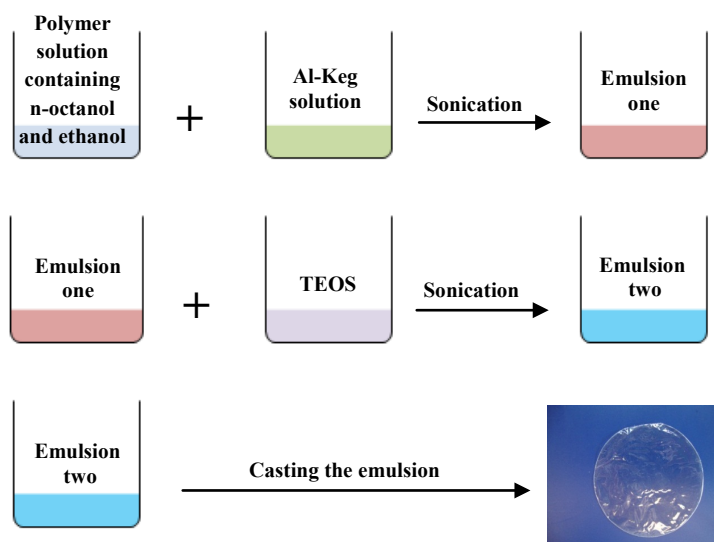


Figure 3.5 The protocol for preparation of EPMM membranes in which TEOS was polymerized in a single-step process. Al-Keg solution had to pass the gelation test. Ethanol and n-octanol played the roles of a compatibilizer and a surfactant, respectively.

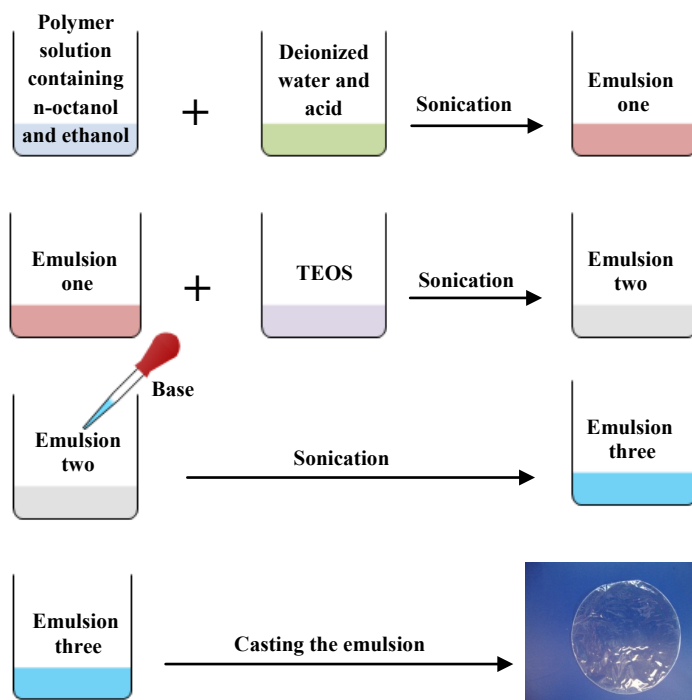


Figure 3.6 The protocol for synthesizing EPMM membranes in which TEOS was polymerized in a two-step process. Ethanol and n-octanol played the roles of a compatibilizer and a surfactant, respectively.

3.3.3. Membrane casting

The EPMM and pure PPO membranes were cast from the final emulsion and polymer solution, respectively, by solvent evaporation (SE) using a levelled glass plate, and/or a spin coating (SC) method.

3.3.3.1. Solvent evaporation method

10 mL of the final emulsion or polymer solution was poured onto a levelled glass plate inside a 9 cm diameter aluminum ring. Since the emulsion (or polymer solution) was not extremely viscous, it spread evenly within the ring by itself. The ring was then covered with a filter paper to prevent dust and other contaminants from being trapped in the membrane, and to slow down the evaporation of solvent. After three days the membrane was peeled off from the plate by lifting the edge of the membrane with a razor blade. If after lifting the edge, the membrane did not peel off, the glass plate with the membrane was immersed in a distilled-deionized water to facilitate the peeling-off process.

3.3.3.2. Spin coating

Compared to the SE method, the spin coating method allows for a better control of the membrane thickness and leads to more uniform membranes. In this project, a 100 series CEE Model Spinner was used. The spinner incorporates a stainless steel spin bowl and a plastic lid, which covers the spin bowl. It has a single-board microcomputer as its main controlling element and a vacuum pump to keep a wafer on the spin chuck.

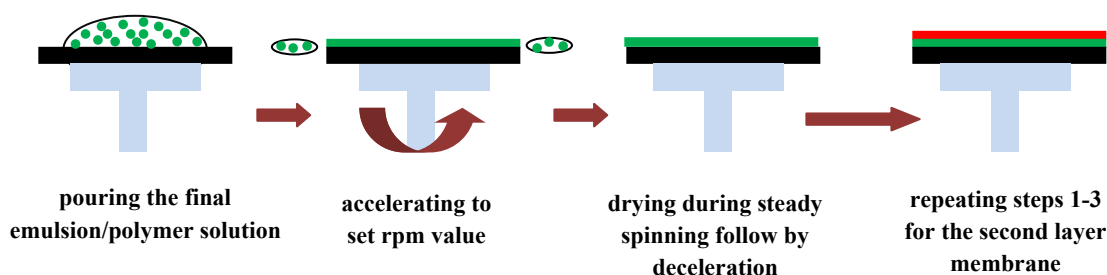


Figure 3.7 Stages of spin coating process

Prior to the actual membrane spin-coating, a dry run was performed to ensure the proper positioning of a 4-inch silicon wafer in the spin-coating machine. The dry run was performed at the speed of 3000 rpm for 10 seconds. After a successful dry run, the entire volume of the final emulsion or polymer solution was poured at the centre of the wafer. Then, the wafer was accelerated to a speed of 600 rpm and maintained at this speed for 200 seconds followed by a rapid deceleration.

Single layer membranes, in particular the EPMM membranes, were very thin and difficult to handle. Therefore, the actual spin-coated membrane consisted of at least two layers. After formation of the first layer, the coated wafer was kept at ambient temperature for at least 2 hours before the formation of the next layer on the top of it. The same spinning parameters were used for the first and any subsequent layer. The spin-coated membranes adhered much stronger to the silicon wafer than the solvent evaporation-cast membranes to the glass plate. Consequently, the removal of all spin-coated membranes required the immersion of the coated wafers in distilled-deionized water for 10 minutes to facilitate the peeling-off process. Tables 3.4 and 3.5 summarize the parameters used for the preparation of EPMM membranes with the Al-Keg solution and the HCl-NH₄OH system as catalysts, respectively.

Table 3.4 Parameters for the synthesis of EPMM membranes prepared by SE and SC methods in one-step process

Samples	HMW-PPO solution (mL)	Catalyst solution	Surfactant	Compatibilizer	Ultrasonication		Inorganic Precursor	Ultrasonication		Casting Method
		Al-Keg solution (mL)	(n-octanol) (mL)	(ethanol) (mL)	Time (min)	Power	TEOS (mL)	Time (min)	Power level	
EPMM/SE/aq/0.3/0.0	10	0.1	-	0.3	1	7	0.3	90	3	SE
EPMM/SE/aq/0.2/0.1	10	0.1	0.1	0.2	1	7	0.3	90	3	SE
EPMM/SE/aq/0.1/0.2	10	0.1	0.2	0.1	1	7	0.3	90	3	SE
EPMM/SE/aq/0.0/0.3	10	0.1	0.3	-	1	7	0.3	90	3	SE
EPMM/SC/aq/0.3/0.0	10	0.1	-	0.3	1	7	0.3	90	3	SC
EPMM/SC/aq/0.2/0.1	10	0.1	0.1	0.2	1	7	0.3	90	3	SC
EPMM/SC/aq/0.1/0.2	10	0.1	0.2	0.1	1	7	0.3	90	3	SC
EPMM/SC/aq/0.0/0.3	10	0.1	0.3	-	1	7	0.3	90	3	SC

Table 3.5 Parameters for the synthesis EPMM membranes prepared by SE and SC methods in two-step process

Samples	HMW-PPO solution (mL)	Deionized water (mL)	HCl (mL)	Surfactant	Compatibilizer	Ultrasonication		NH ₄ OH (mL)	Ultrasonication		Inorganic Precursor	Ultrasonication		Casting Method
				(n-octanol) (mL)	(ethanol) (mL)	Time (min)	Power level		Time (min)	Power	TEOS (mL)	Time (min)	Power level	
EPMM/SE/ab/0.3/0.0	10	0.1	0.033	-	0.3	1	7	0.067	5	3	0.3	90	3	SE
EPMM/SE/ab/0.2/0.1	10	0.1	0.033	0.1	0.2	1	7	0.067	5	3	0.3	90	3	SE
EPMM/SE/ab/0.1/0.2	10	0.1	0.033	0.2	0.1	1	7	0.067	5	3	0.3	90	3	SE
EPMM/SE/ab/0.0/0.3	10	0.1	0.033	0.3	-	1	7	0.067	5	3	0.3	90	3	SE
EPMM/SC/ab/0.3/0.0	10	0.1	0.033	-	0.3	1	7	0.067	5	3	0.3	90	3	SC
EPMM/SC/ab/0.2/0.1	10	0.1	0.033	0.1	0.2	1	7	0.067	5	3	0.3	90	3	SC
EPMM/SC/ab/0.1/0.2	10	0.1	0.033	0.2	0.1	1	7	0.067	5	3	0.3	90	3	SC
EPMM/SC/ab/0.0/0.3	10	0.1	0.033	0.3	-	1	7	0.067	5	3	0.3	90	3	SC

3.3.4. Post treatment of the membrane

The membranes prepared by the SE and SC methods were post-treated to ensure consistent and repeatable properties for a given synthesis protocol. The major objective of the post-treatment process was to remove all the residual components such as solvent, unreacted TEOS, and the compatibilizer/surfactant solution. The post-treatment protocol consisted of two steps:

- Boiling films in distilled-deionized water,
- Heat-treatment in a vacuum oven.

The purpose of boiling membranes in deionized water was to wash out all water-soluble residuals (Sadeghi et al., 2008), which if not removed could lead to the development of defects in the membrane during the heat-treatment process (Wang, 2011). The membranes were boiled in distilled-deionized water for 4 hours.

The purpose of the heat-treatment was to remove the remaining low-volatility and water-insoluble residuals, in particular the unreacted TEOS. The heat-treatment step was carried out in a vacuum oven (VWR Scientific, pressure range: 0-30 inHg) using the following procedure. After the placement of the membranes in custom-made membrane holders inside the oven, the chamber was evacuated and then pressurized to atmospheric pressure using pure nitrogen. This step was repeated several times to ensure the removal of all oxygen from the oven before the heating step. The removal of oxygen was critical, because it can oxidise PPO at elevated temperature.

Originally, after the last evacuation/pressurization cycle the heating was turned on while the chamber was continuously evacuated. However, such post-treated membranes turned out to be brown indicating oxidation of PPO. It is important to note that despite a 0

inHg pressure indicated by a pressure gauge of the vacuum oven, some atmospheric air could be passing through the hot oven because of inherent leaks. Consequently, a custom-made system was built to allow for the heating of the oven while it was filled with nitrogen at atmospheric pressure and continuously purged with a low flow of fresh nitrogen. This way there was no driving force for the flow of atmospheric air into the oven and the heating post-treatment was carried out in the oxygen-free environment, which was indicated by the fact that the membranes did not change their colour even after the heat treatment at 250°C. Such a high temperature for the heat treatment was necessary. This is because according to Hamilton (1995), the complete removal of residuals from glassy polymers requires their heating above the glass transition temperature (T_g). In other words, in glassy polymers residuals can be trapped in so-called Langmuir sites, which are not accessible to the external environment. These Langmuir sites, which are unique to glassy state, disappear in rubbery state. Therefore these residuals can be removed completely by increasing the temperature above the T_g of the polymer, which for the HMW-PPO, the highest T_g is reported in the literature is 224.85°C (Karasz and Reily, 1965). Consequently, the PPO and PPO-based EPMM membranes after the boiling step and air-drying at ambient temperature for 24 hours were heat treated in the modified vacuum oven, in the oxygen-free environment at 235°C for 12 hours. A small flow rate of nitrogen through the oven was maintained until the oven cooled down to ambient temperature.

Such post-treated membranes were ready for different characterization processes, which are described next.

3.4. Membrane characterization

3.4.1. Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermal analysis technique, which monitors heat effects associated with phase transitions as a function of temperature. In a DSC test the heat effects are monitored simultaneously in two aluminum pans, one containing the actual sample (4 mg - 10 mg of the material), and an empty pan, which serves as a reference. The temperature of both pans is increased at the same constant rate, and the resulting difference in the heat flows in the two pans is recorded as a function of temperature.

The glass transition temperature (T_g) is defined as a temperature at which the amorphous part of a polymer is converted from a glass state to a rubber state. At T_g the mechanical behaviour of an amorphous polymer changes significantly. Glass transition is an example of a second order endothermic transition, and consequently it appears as a step rather than a peak on the DSC spectrum. In practice, as shown in Fig 3.8, the T_g is represented as the point of inflection on the heat flow curve.

In this study, the DSC analyses were carried using a QA series TA1000 differential scanning calorimetric analyzer (TA Instruments, New Castle, DE, USA), which was operated under pure nitrogen environment. The samples were scanned from 40°C to 250°C at a constant heating rate of 10°C/min. Then, they were scanned again from 250°C to 40°C at a constant cooling rate of 10°C/min. A cycle consisting of one heating and one cooling ramps was repeated three times. The first cycle helps to remove any volatile residuals from the tested sample, and thus it was disregarded from any further analysis (Ayres et al., 2007). Consequently, the T_g was determined from the

averaged second and third cycles. The scans obtained in these two cycles were typically very similar to each other. Since there was a concern that a single sample may not be representative for the entire membrane, three samples were prepared and tested from various parts of the same membrane.

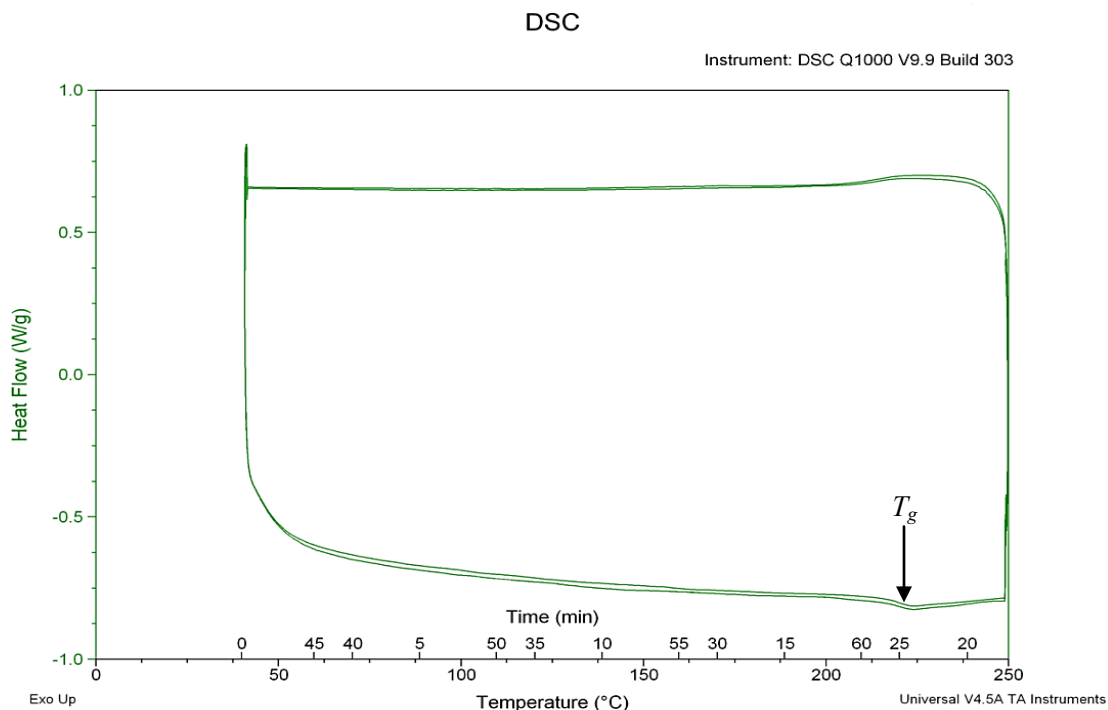


Figure 3.8 A conventional DSC result for a pure HMW-PPO membrane

3.4.2. ^{29}Si NMR

Nuclear magnetic resonance (NMR) spectroscopy is an analytical tool, which allows observing magnetic properties of nuclei in atoms and hence to derive structural information about the molecule. The NMR spectrum can be recorded from the isotopes of elements that contain an odd number of protons and/or neutrons and have a magnetic moment, i.e., from the isotopes of elements with a non-zero spin. In the case of silicon,

there are 24 known isotopes, but among those only ^{28}Si , ^{29}Si , and ^{30}Si are stable, and among the stable ones only ^{29}Si has a non-zero spin (spin 1/2).

In a magnetic field, the applied electromagnetic pulses cause the nuclei to absorb the energy, which is then radiated back. The energy radiated back is at a specific resonance frequency. The structural information about the molecule is determined by comparing the observed frequencies with the known (reference) frequencies.

In the ^{29}Si solid-state NMR, siloxanes are distinguished according to the number of connecting silicon-oxygen bonds. The silicate materials are described by non-branching groups such as a monofunctional (M) and a difunctional (D) groups, and the branching groups of trifunctional (T) and tetrafunctional (Q). Figure 3.9 shows a schematic of a polysiloxane indicating all the building units, where the alkyl (R) groups do not require being homogenous.

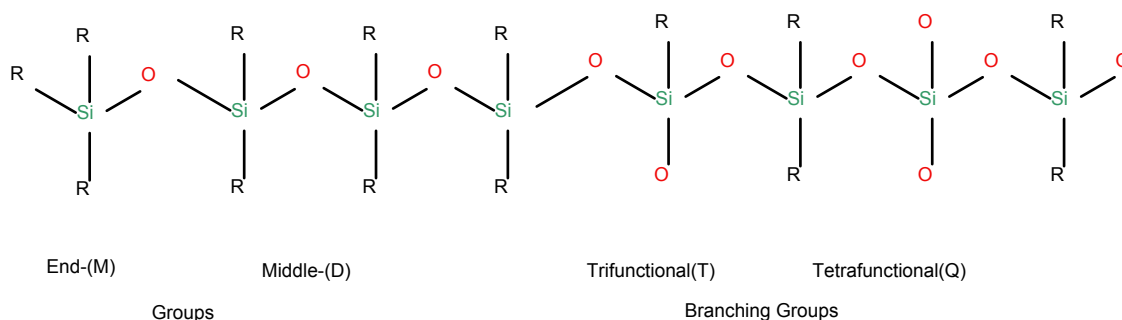


Figure 3.9 The sketch of a polysiloxane with different building units

There are five tetrafunctional branching groups (Q^n). The peak related to Q^4 indicates each Si atom connected to oxygen atoms with four Si neighbours, i.e., with four O(Si) bonds. The Q^3 corresponds to each Si atom, which is linked to three O(Si) groups

and one OH group. The Q^2 then indicates each Si atom, which is linked to two O(Si) groups and two OH groups, and so on. Table 3.6 presents the chemical structure of each peak with the corresponding chemical shift. The peaks at -110, -100 to -104, and -90 ppm correspond to the Q^4 , Q^3 , and Q^2 respectively. The Q^0 is related to the unreacted TEOS, which is located at -82 ppm (Chiang et al., 2008).

Table 3.6 Chemical shifts of different tetrafunctional branching groups

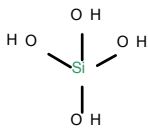
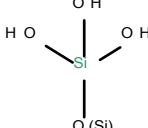
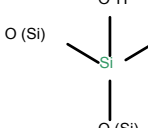
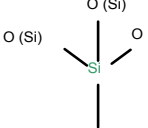
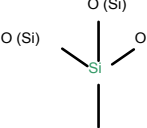
Q^0	Q^1	Q^2	Q^3	Q^4
				
-82 ppm	-86 ppm	-90 ppm	-100 to -104 ppm	-110 ppm

Figure 3.10 shows a typical ^{29}Si NMR spectrum of a silica gel derived from TEOS. The co-existence of Q^2 , Q^3 , and Q^4 verify the polymerization the TEOS, and therefore, the formation of the inorganic network. The absence of Q^0 in Figure 3.8 proves that either all TEOS was fully reacted, or the unreacted TEOS was completely removed from the sample. It should be noted that the area under each peak is related to the number of particular bounds in the sample.

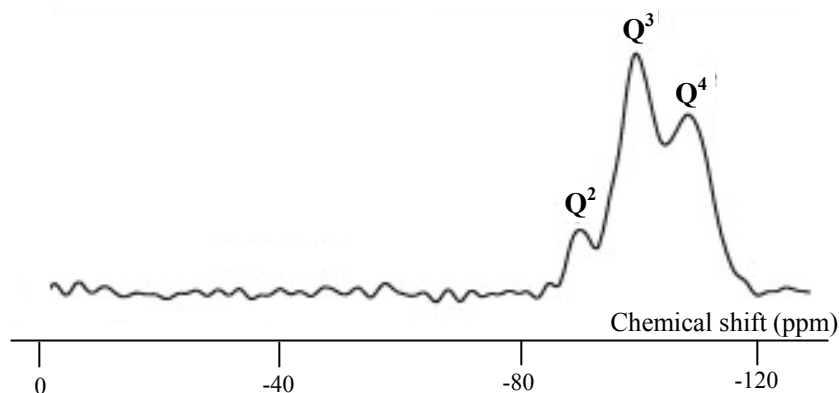


Figure 3.10 The ^{29}Si NMR spectrum of a silica gel derived from TEOS (Chiang et al., 2008)

The ^{29}Si NMR spectrometry analyses were performed on the selected GPM samples and EPMM membranes by Dr. Eric Ye from Nuclear Magnetic Resonance laboratory, Department of Chemistry, Faculty of Science, University of Ottawa. The solid-state ^{29}Si NMR (Bruker Bio Spin Model AVANCE 500) used in this study, which requires samples to be in a powder form, with the minimum amount of 0.01 g for each sample. The EPMM membranes are very flexible and could not be converted into a powder form. Instead, there were cut into very small pieces before sending them to the NMR laboratory.

3.4.3. Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is a fast, sensitive, and powerful technique, which allows for the elemental analysis of a wide variety of materials. This technique is capable of measuring the concentrations as low as several parts per billion. It combines a high temperature ICP source with a mass spectrometer in

which the ICP is used to ionize the atoms of the elements in the sample. These ions are then separated and detected by the mass spectrometer.

The ICP torch produces high temperature Argon plasma, which then collides with a sample resulting in a charge transfer. Then, the ionized molecules, which are in a vapor form, are separated from neutral species by a sample cone. Consequently, these ions form a sharp beam and go through the analyzer. The analyzer separates ions based on their mass-to-charge (M/Z) ratio. Finally, the detector detects the ion and sends the signal to the recorder.

ICP-MS, Hewlett Packard Model Agilent HP 4500, was used in this study for the analysis of Si and Al content in the EPMM membranes. The analyses were performed by Dr. Nimal De Silva in Geochemistry laboratory, Department of Earth Sciences, Faculty of Science, University of Ottawa. Each membrane was split into two parts and each part was analysed separately to verify the accuracy of the final results. The samples were first burned in a furnace at 450°C for 16 hours in order to remove the combustible (organic) portion by thermal decomposition. The actual ICP-MS analyses required the samples to be in a liquid form. Therefore, the ash produced in the thermal decomposition step after its weighing was digested at 120°C in a aqua regia for 10 hours inside Teflon vials, and then diluted using with deionised water.

3.4.4. Constant pressure (CP) system

The synthesized PPO-based EPMM membranes along with the reference PPO membranes were tested using single gas permeation tests carried out with pure oxygen and nitrogen, in order to determine the respective permeability coefficients of these gases

as well as their ratio (ideal selectivity) in the synthesized membranes. The gas permeation tests were performed using a constant pressure (CP) system. In the CP system, the feed side of the membrane is swept with the feed gas at a constant pressure, while the permeate side of the membrane is either open to the atmosphere or swept with a gas at atmospheric pressure. This ensures a constant trans-membrane pressure during the entire gas permeation test.

In this project an automatic four-cell CP system, which is schematically presented in Figure 3.11 was used. The permeation cell, which houses a circular membrane with the diameter of 4.1 cm, is made of a 316 stainless steel and consists of two detachable parts. The lower part of the cell is a high-pressure chamber, which is equipped with the inlet tubes for the flow of the feed (F) stream and the outlet tube for the flow retentate (R) streams. The upper part of the cell is a low-pressure chamber also equipped with the inlet and outlet tubes for the flow of the sweep (S) and sweep + permeate (SP) streams, respectively.

The flow rate of R stream is monitored by an MKS mass flow meter (MFM1) with the reading range of $0-10 \pm 0.1 \text{ cm}^3/\text{min}$. A pressure transducer (PT1) from MKS Instruments having the reading range of 14.7 – 3500 KPa (0 - 500 psig) allows to monitor the pressure in the high pressure chamber of the cell, since the F and the R streams are expected to be at the same pressure. The flow rate of the stream R is controlled by a needle valve (NV). The flow rate of the stream S at the inlet of the upper part chamber is controlled by an MKS mass flow controller (MFC) having the control range of $0-10 \text{ cm}^3/\text{min}$. In the current project no sweep gas was used so that the flow rate of the S stream was zero in all experiments. The flow rate of the SP stream is monitored by an

MKS mass flow meter (MFM2) with the reading range of $0-10 \pm 0.1 \text{ cm}^3/\text{min}$. The line carrying the SP stream is open to atmosphere, i.e. the gas in the SP stream is at atmospheric pressure. The pressure at the permeate side is measured by a pressure transducer (PT2) from MKS Instruments with the reading range of 0-345 KPa (0-50 psia). In addition, the flow rate of the SP and R streams can also be measured by a bubble flow meter, by manually connecting the proper outlet line from a multi-position valve to the bubble flow meter. This feature allows for the calibration of the mass flow meters in the system. In addition, application of the bubble flow meters allows the measurements of the permeation rates as low as 0.01 mL/min.

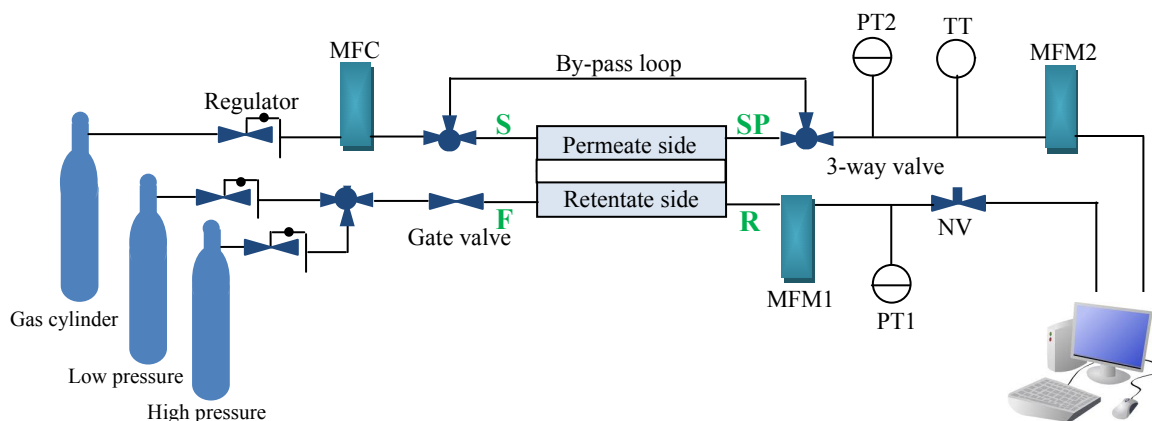


Figure 3.11 The schematic diagram of the automated CP system.

The single gas permeation tests with O_2 and N_2 were carried at the feed pressures of 120 psia. Once the steady state permeation rate was reached, which was indicated by a flat flow rate versus time curve (permeation rate was monitored continuously by the MFM2), the permeation rate was measured several times using the bubble flow meter. The arithmetic average of these readings was considered as a steady state permeation rate Q . The reason for relying on the bubble flow meter rather than on the MFM2 for the

determination of Q was because the permeation rates in all experiments were considerably below 1 cm³/min. The permeability coefficient (P) of the single gas through the membranes was then evaluated from:

$$P = \frac{QL}{A'(p_f - p_p)} \quad (3.2)$$

where Q is the steady state permeation rate of a gas. L , A' , p_f , and p_p are the thickness of the membrane, the permeation area, the feed pressure, and the permeate pressure, respectively.

The selective properties of the membrane were evaluated by the ratio of the permeability coefficients determined in single gas permeation experiments, which is referred to as the ideal selectivity ($\alpha_{A/B}^*$):

$$\alpha_{A/B}^* = \frac{P_A}{P_B} \quad (3.3)$$

where subscript A refers to a more permeable gas (oxygen) and subscript B to a less permeable gas (nitrogen).

3.5. Equipment and materials

Table 3.7 and 3.8 summarizes all the equipments and chemicals used in this study in an alphabet order.

Table 3.7 Equipments employed in this study

Equipments	Part Number	Manufacturer
Bubble flow meter	0.5 ml	Supelco
DSC	QA-1000	TA Instrument
ICP-MS	Agilent HP 4500	Hewlett-Packard
Isotemp oven	Junior-201	Fisher Scientific
Micrometer	0-1"	Miutoyo
pH meter	AB15 Accumet Basic	Fisher Scientific
Si NMR	AVANCE 500	Bruker Bio Spin
Scale	AG204	Mettler Toledo
Stirrer/Hot plates	PC-420	Corning
Ultra-sound dismembrator	550	Fisher Scientific
Vacuum oven	1415M	Sheldon Manufacturing
Viscometer	LVF	Brookfield

Table 3.8 Chemicals and gases used in this research project

Chemicals	Specification	Source
Aluminium nitrate nonahydrous	ACS reagent	Sigma-Aldrich
Ammonium hydroxide	30%	Sigma-Aldrich
Ethanol	99%	Sigma-Aldrich
Hydrochloric acid	36.5%	Fisher Scientific
Nitrogen	Industrial grade	Linde Canada
n-octanol	99.00%	Sigma-Aldrich
Oxygen	Industrial grade	Linde Canada
Poly(2,6-dimethyl-1,4-phenylene oxide) – LMW	Powder	Sigma-Aldrich
Poly(2,6-dimethyl-1,4-phenylene oxide) – HMW	Powder	Sabic
Sodium Carbonate anhydrous	ACS reagent	Sigma-Aldrich
Trichloroethylene (TCE)	ACS reagent	Sigma-Aldrich
Tetraethylorthosilicate (TEOS)	ACS reagent	Sigma-Aldrich

Chapter 4. RESULTS AND DISCUSSION

Similarly to the previous chapter on experimental methods, the results obtained in this research and the pertaining discussion are divided into three sections related to: (i) polymerization of TEOS in a single phase, (ii) polymerization of TEOS in the emulsion with the polymer solvent, and (iii) polymerization of TEOS in the emulsion with polymer solution.

4.1. Gelation test

The purpose of the gelation tests depended on the type of catalysts used in the Al-Keg solution. In the case of the catalysts made by the aluminum hydroxonitrate and sodium carbonate, (single-step process), the purpose was to confirm the suitability of the Al-Keg solution for the emulsion polymerization of TEOS. Consequently, the gelation test was carried out before each emulsion polymerization reaction. In the case of the catalyst made of the hydrochloric acid and ammonium hydroxide (two-step process), the purpose was to establish the amounts of the hydrochloric acid and ammonium hydroxide, which would minimize the gelation time, and consequently use these amounts in the actual emulsion polymerization of TEOS. In both cases, the gelation tests were carried out in a single phase, which was enabled by using a large excess of ethanol.

4.1.1. Aluminum hydroxonitrate

In the case of aluminum hydroxonitrate and sodium carbonate in the aqueous phase as a catalyst, the gelation test was carried out by mixing 2 mL of TEOS with 6 mL of 99% ethanol and 2 mL of the Al-Keg solution in a 20 mL vial. The gelation test was considered as successful, and hence the Al-Keg solution was deemed as suitable for the

emulsion polymerization of TEOS, only when a white gel was formed. The example of a successful gelation test is shown in Figure 4.1. In practice, it took 12-15 minutes for a white gel to appear. The corresponding pH of the aqueous solution was 3.6.

If the white gel did not appear, or if it was transparent rather than white, or if it took more than 15 minutes for the gel to appear, the aqueous solution was discarded and a new one was prepared.



Figure 4.1 Example of a gel obtained in a successful solution polymerization of TEOS in the presence of Al in the aqueous solution

4.1.2. Hydrochloric acid – ammonium hydroxide

The purpose of the gelation test in the case of a two-step process was to determine the amounts of hydrochloric acid and ammonium hydroxide, which would ensure a successful solution polymerization of TEOS in the presence of these species. In this two-step gelation process, the hydrolysis and condensation reactions were carried out in the acidic and basic conditions, respectively.

The acidic solution was prepared by adding different amount of the concentrated hydrochloric acid into a solution containing 7.5 mL of distilled-deionized water and 5.0 mL of ethanol. With 0.033 mL of acid, the pH of the resulting solution was 2.28, and was gradually decreasing with increasing the amount of the acid. After adding a specific

amount of acid, the acidic solution was mixed with the solution containing 10 mL of TEOS and 5 mL of ethanol, and the hydrolysis of TEOS was carried out for 5 minutes by agitating the content using a magnetic stirrer. The agitation time of 5 minutes was determined based on the GPM tests, which are discussed in the next Section.

In parallel, the basic solution was prepared by adding different amount of the concentrated NH_4OH solution into the mixture containing 7.5 mL of distilled-deionized water and 3.5 mL of ethanol. With 0.011 mL of the base, the pH of the resulting solution was 10.81, and was gradually increasing with increasing the amount of the base.

In the second step, the basic solution containing a specific amount of concentrated NH_4OH was mixed with the hydrolysed TEOS in the acidic solution while vigorously stirring the content for 10 seconds. Then, part of the content was transferred into a vial and the time for a gel to appear was measured. In some cases, the gelation was observed almost immediately after combining the hydrolyzed TEOS solution with the basic solution, but in other cases, depending on the amounts of acid and base, no gelation was observed even after several days. Unlike the gelation tests in the presence of aqueous solution containing aluminum hydroxonitrate and sodium carbonate, the gels formed in the two-step process were transparent, as shown in Figure 4.2. This is because the structure of the gels formed in weak acidic conditions differs from that in basic conditions. In the former case, the polymerized TEOS has tendency to form linear polymers, which are occasionally lightly branched (Figure 2.7). In the latter case, the polymerized TEOS forms highly branched clusters resulting in a three-dimensional network (Figure 2.8).

Tables 4.1 and 4.2 summarize the results of the two-step gelation tests. First, Table 4.1 shows the final pH after combining the acidic and basic solutions with different combinations of the concentrated acid and the concentrated base in the respective solutions. It can be noticed that with the same amount of the acid and base in the respective solutions, the final solution is a weak base, and as the amount of the base increases relative to the amount of the acid, pH increases, but in all cases the solution remains a weak base. On the other hand, in the case of excess amount of the acid, the final solution is a relatively strong acid (with pH generally lower than 2). It is important to note that none of the combinations of the acid and base in Table 4.1 gives pH that would be comparable with the pH (c.a. 3.5) that existed in the aqueous solution in the presence of aluminum hydroxonitrate and sodium carbonate.



Figure 4.2 The gel obtained from polymerization of TEOS in the presence of hydrochloric acid-ammonium hydroxide

Table 4.2 presents the summary of the gelation times at different combinations of the acid and base concentrations in the final aqueous solution. For the combinations with an excess amount of acid (the cells above the dark-shaded cells), the gelation did not occur. In other words, gelation was not observed when the pH of the final aqueous solution was 2 or less. In contrast, in the cases with an excess amount of base ($\text{pH} > 8$),

gelation was observed in less than one minute, sometimes even before the final solution was transferred into the vial. This indicates that in all cases TEOS was hydrolyzed in the acidic solution, and lack of gelation was due to a very slow condensation reaction in strong acidic environment.

The comparison of one- and two-step gelation processes indicates that the latter is much faster, provided that weak basic conditions exist for the condensation reaction. None of the combinations of the acid (HCl) and base (NH₄OH) did not allow obtaining weak acidic conditions, such as those existing in a properly prepared aqueous solution using aluminum hydroxonitrate and sodium carbonate, at which condensation reaction would still be possible. In addition, the two-step gelation tests indicate that regardless of the amount of acid used in the first step, condensation reaction (gelation) can occur, provided that the amount of base used can neutralize the acid and the final solution.

Table 4.1 The effect of HCl and NH₄OH concentrations on the pH of the emulsion

	0.011 mL of HCl	0.022 mL of HCl	0.033 mL of HCl	0.044 mL of HCl	0.056 mL of HCl	0.067 mL of HCl	0.078 mL of HCl	0.089 mL of HCl	0.1 mL of HCl	0.111 mL of HCl
0.011 mL of NH ₄ OH	8.99	2.59	2.41	2.25	2.04	1.88	1.53	1.37	1.36	1.36
0.022 mL of NH ₄ OH	9.13	9.07	9.13	2.41	2.13	2.02	1.61	1.33	1.42	1.41
0.033 mL of NH ₄ OH	9.37	9.25	9.15	9.05	2.17	2.25	1.75	1.4	1.45	1.43
0.044 mL of NH ₄ OH	9.7	9.43	9.16	9.18	7.95	2.38	1.85	1.67	1.48	1.45
0.056 mL of NH ₄ OH	9.89	9.47	9.26	9.21	8.06	8.02	2.01	1.86	1.63	1.57
0.067 mL of NH ₄ OH	9.92	9.51	9.32	9.31	8.25	8.46	8.06	7.77	1.89	1.61
0.078 mL of NH ₄ OH	10.11	9.53	9.46	9.38	8.43	8.63	8.22	8.04	7.81	1.87
0.089 mL of NH ₄ OH	10.17	9.64	9.51	9.43	8.74	8.84	8.53	8.67	8.23	7.95
0.1 mL of NH ₄ OH	10.26	9.73	9.62	9.5	9.12	9.05	8.82	8.77	8.65	8.47
0.111 mL of NH ₄ OH	10.33	9.81	9.67	9.58	9.31	9.16	9.04	8.95	8.92	8.82

Table 4.2 The effect of HCl and NH₄OH concentrations on the gelation time

	0.011 mL of HCl	0.022 mL of HCl	0.033 mL of HCl	0.044 mL of HCl	0.056 mL of HCl	0.067 mL of HCl	0.078 mL of HCl	0.089 mL of HCl	0.1 mL of HCl	0.111 mL of HCl	
0.011 mL of NH ₄ OH	20 min	No gelation									
0.022 mL of NH ₄ OH	2 min										t _g > 1 day
0.033 mL of NH ₄ OH											t _g > 1 day
0.044 mL of NH ₄ OH											t _g > 1 day
0.056 mL of NH ₄ OH											t _g > 1 hour
0.067 mL of NH ₄ OH						t _g > 1 hour					
0.078 mL of NH ₄ OH							t _g > 1 hour	10 min			
0.089 mL of NH ₄ OH			t _g < 1 minute						3 min	5 min	
0.1 mL of NH ₄ OH										1 min	
0.111 mL of NH ₄ OH											

4.2. Gravimetric powder method

Before attempting syntheses of PPO-based EPMM membranes, it was important to make sure that emulsion polymerization of TEOS occurs and to optimize the ultrasonication times at different stages of the process. Since in the GPM experiments the emulsion is made with a pure TCE solvent rather than a polymer solution, the conversion of TEOS in a specific reaction condition can be quickly assessed based on the mass of the powder remaining after evaporation and drying of the final emulsion.

4.2.1. Optimizing the sonication time

The term total sonication time is equivalent to the actual reaction time. In the two-step process, the hydrolysis and condensation occur separately. Consequently, the reaction times for these two reactions were optimized in two different sets of experiments. On the other hand, in the one-step process the hydrolysis and condensation occur simultaneously, thus one set of experiments was carried out to optimize the actual reaction time for the polymerization of TEOS in the aqueous solution containing aluminum hydroxonitrate and sodium carbonate.

It is obvious that by increasing the reaction time, the conversion of TEOS increases. However, the conversion is not a linear function of time. Therefore, the purpose of these sets of experiments was to determine the respective times for the above three reactions after which no significant increase in the conversion of TEOS was observed.

Each set of optimization experiments was performed using four different combinations of ethanol (compatibilizer) and n-octanol (surfactant). The total volume of

ethanol and n-octanol (i.e., the liquid additive) in each experiment was 0.3 mL. The four combinations of ethanol and n-octanol in mL were then 0.0 – 0.3, 0.1 - 0.2, 0.2 – 0.1, and 0.3 – 0.0. Consequently, the optimization results will also serve as a basis for the discussion on the effect of the compatibilizer and the surfactant on the conversion of TEOS.

In both the one- and two-step processes ultrasonication was also used for the preparation of the respective emulsion one. These processes were purely physical (no chemical reaction) and were not optimized in this project. Instead, for the ultrasonication time of the emulsion one and the power level the values determined previously by Wang (2011) were used. Similarly, the power level for the three reactions was adopted from the previous experiments performed by Wang (2011).

4.2.1.1. The effect of hydrolysis time on the powder mass in two-step process

Prior to the hydrolysis reaction, the emulsion one was prepared by ultrasonicing the content for 1 minute at the power level of 7. The ultrasonication time (t_h) was increased from 0 minute using 1 minute time increments. The actual hydrolysis time is twice the t_h , because of the ultrasonication procedure, which included 30 seconds pulses followed by 30 seconds rest periods. The hydrolysis time is the time between the addition of 0.033 mL of HCl into the emulsion one and 0.067 mL of NH_4OH into the resulting emulsion two, while ultrasonicing the content at the power level of 7. Consequently, the “0” time refers to the set of experiments in which 0.033 mL of HCl and 0.067 mL of NH_4OH were added simultaneously into the emulsion one. In each experiment after

adding NH_4OH , the condensation reaction carried out by ultrasonication the content for 30 minutes at the power level of 7.

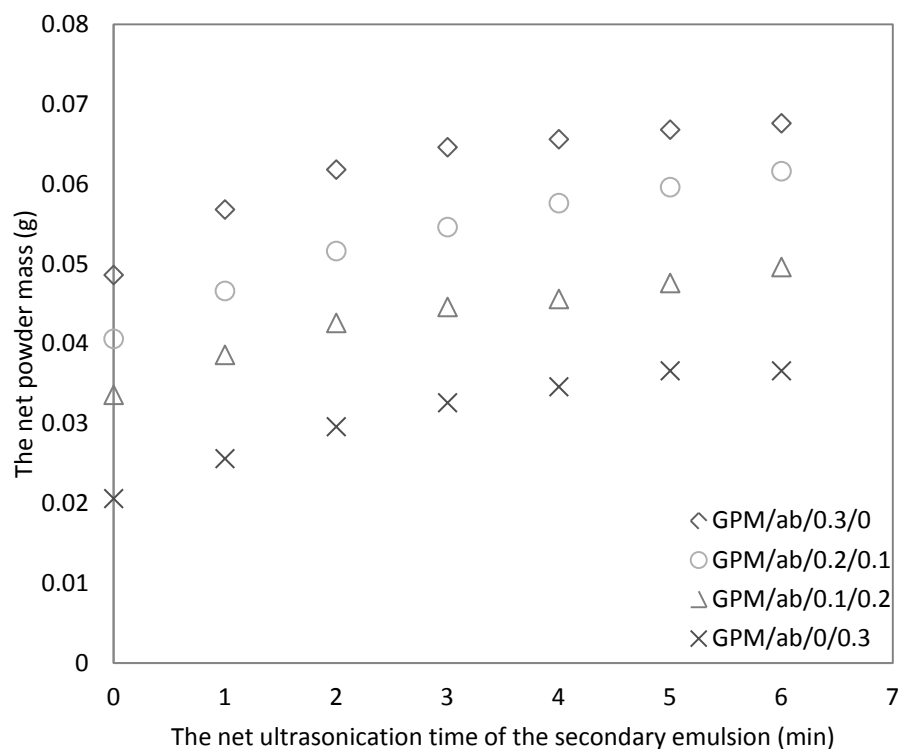


Figure 4.3 The effect of ultrasonication time of the emulsion two (hydrolysis reaction) on the net mass of the dried powder in the two-step acid and base catalyzed process.

Emulsion one, containing different amounts of surfactant and compatibilizer, was sonicated at power level of 7 for 1 minute followed by adding TEOS and sonication at power level of 7 (hydrolysis reaction) for different times; emulsion three was prepared by adding base and ultrasonication at power level 7 for 30 minutes. The actual reaction time is twice the net ultrasonication time.

Figure 4.3 presents the effect of t_h on the net mass of dried powder. The net mass does not include 0.0114 g, i.e., the mass of NH_4Cl that would be formed in the reaction between 0.033 mL of HCl and 0.067 mL of NH_4OH . In all experiments the same volume of TEOS (0.3 mL) was used; consequently the reported masses of the dried powder are indicative of the conversion of TEOS. However, the actual conversion of TEOS at different reaction conditions will be discussed later. It is evident that for each

combination of ethanol and n-octanol, the lowest mass of the dried powder is observed for $t_h = 0$, which could be expected. The mass of the dried powder increases as the t_h increases. However, there is a little change between the mass of the dried powder for $t_h = 5$ minutes and $t_h = 6$ minutes. Consequently, the t_h was not increased beyond 6 minutes, and the t_h of 5 minutes was considered as an optimized time for the ultrasonication during the hydrolysis reaction in the two-step acid-base catalyzed process.

4.2.1.2. The effect of the condensation time on the powder mass in two-step process

The ultrasonication time (t_c) for the condensation reaction is the time between adding 0.067 mL of NH_4OH into the emulsion two, while ultrasonicing the content at the power level of 7, and transferring the resulting emulsion three into a petri dish. The t_c was varied from 10 minutes using 10 minute time increments. Prior to adding NH_4OH , each sample was prepared using the same protocol, which includes 1 minute ultrasonication of the emulsion one at the power level of 7, and 5 minutes ultrasonication at the power level of 7 after addition of 0.033 mL of HCl (hydrolysis reaction). Each experiment was repeated 3 times. Figure 4.4 shows the effect of the ultrasonication time of the emulsion three on the net mass of the dried powder. As expected, the mass of the dried powder increases with t_c . However, after a significant increase in the first 30 minutes, the mass of the dried powder changes only very little for the longer times of 40 and 50 minutes. Despite some variations for a given t_c , which is indicated by error bars representing a standard deviation from three runs, the same trend is observed for all combinations of ethanol and n-octanol. It can also be noticed that the size of the error

bars decreases with increase of the ultrasonication time. Based on the experimental results shown in Figure 4.4, $t_c = 30$ minutes was considered as an optimized time for the ultrasonication of the emulsion three.

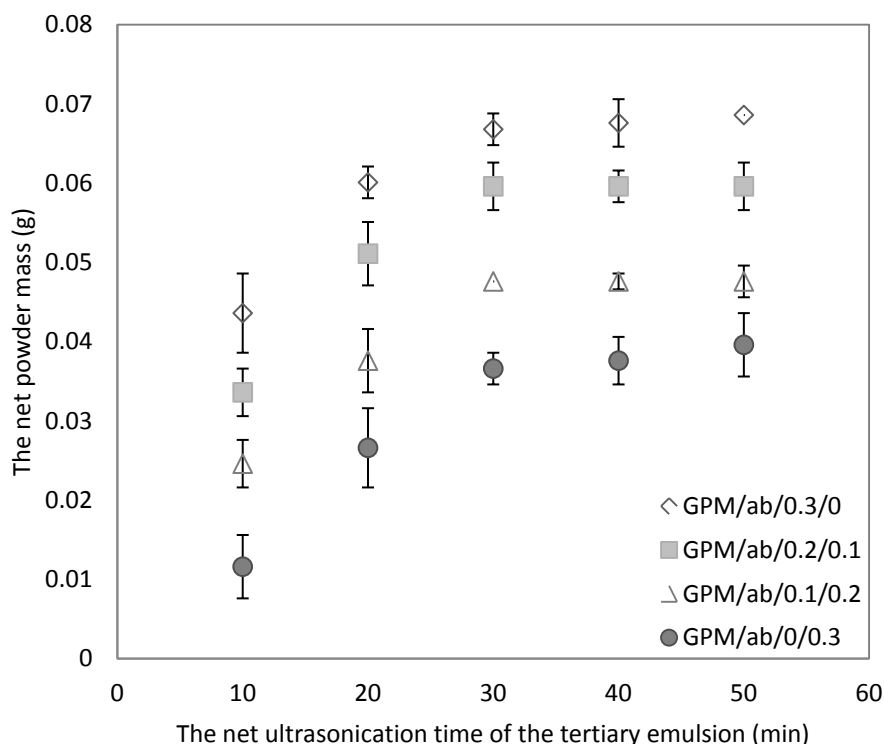


Figure 4.4 The effect of the ultrasonication time of the emulsion three (condensation reaction) on the net mass of the dried powder in the two-step acid and base catalyzed process. Emulsion one containing different amounts of surfactant and compatibilizer was sonicated at power level of 7 for 1 minutes followed by adding TEOS and sonication of the content at power level of 7 for 5 minutes (hydrolysis reaction). Then base is added to the emulsion and sonicated at power level of 7 for different times. The actual reaction time is twice the net ultrasonication time.

4.2.1.3. The effect of reaction time on the powder mass in one-step process

In the one-step process, the reaction time is the time interval between combining the emulsion one with TEOS, while ultrasonicing the content at the power level of 7,

and transferring the resulting emulsion two into a petri dish. The ultrasonication time (t_r) was increased using 10 minute time increments starting from $t_r = 10$ minutes. Similarly to the two-step processes, the actual reaction time is twice the t_r . For each experimental set of conditions, three runs were carried out.

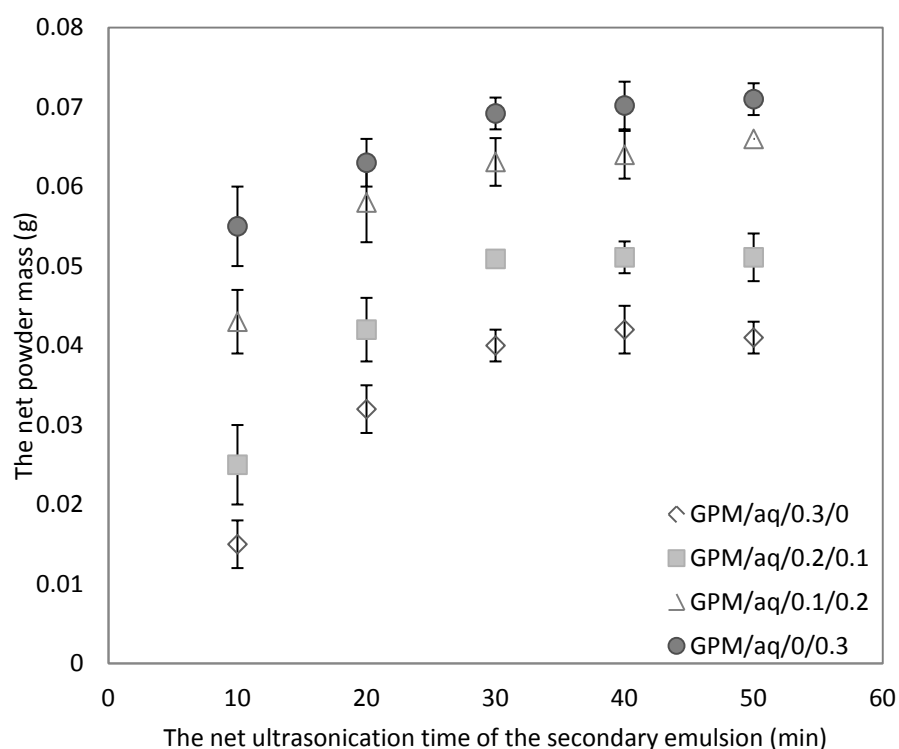


Figure 4.5 The effect of ultrasonication time of the emulsion two on the mass of the dried powder in the one-step process. Emulsion one containing different amounts of surfactant and compatibilizer was sonicated at power level of 7 for 1 minute followed by adding TEOS and sonication at power level of 7 for different times. The actual reaction time is twice the net ultrasonication time.

Figure 4.5 presents the effect of t_r on the net mass of the dried powder. The mass values reported in this figure do not include 0.0305 g, i.e., the mass of residuals remaining of the evaporation of the aqueous solution containing aluminum hydroxonitrate and sodium carbonate. Despite a different reaction system, Figure 4.5 closely resembles Figure 4.4. After a significant increase in the first 30 minutes, the mass

of the dried powder remains practically constant for the longer times of 40 and 50 minutes. The same trend is observed for all combinations of ethanol and n-octanol. It can also be noticed that the size of the error bars decreases with increase of the ultrasonication time. Based on the experimental results shown in Figure 4.5, $t_r = 30$ minutes was considered as an optimized time for the ultrasonication of the emulsion two.

4.2.2. The effect of surfactant and compatibilizer on the dried powder mass

Table 4.3 presents the average total and the net masses of the dried powder for both the two-step and one-step reactions with four different combinations of the compatibilizer and surfactant. The results tabulated in Table 4.3 are shown graphically in Figure 4.6. The data presented in Table 4.3 and Figure 4.6 was compiled from the data previously shown in Figures 4.3-4.5.

It can be noticed that in all cases the net mass of the dried powder was greater than zero, indicating that the emulsion polymerization of TEOS took place in all reactions. For the one-step process catalyzed by a weak acid (solution of aluminum hydroxonitrate and sodium carbonate in water) the mass of the dried powder increases with increase in the amount of the surfactant. In fact, the largest mass of the dried powder is observed in absence of the compatibilizer when the entire 0.3 mL of the liquid additive is n-octanol, while the smallest mass is observed when the entire liquid additive is ethanol. Interestingly, for the two-step process, the results are exactly the opposite, i.e., the largest mass of the dried powder is observed when the entire 0.3 mL of the liquid additive is ethanol, while the smallest mass is observed when the entire liquid additive is

n-octanol. The mass of dried powders in one- and two-step processes appear as “mirror images” of each other. The largest mass in the one-step process is comparable to the largest mass in the two-step process, and similarly the smallest masses in the respective two processes are also comparable. Since in all cases the same amount of TEOS was used the respective maximum and minimum conversions of TEOS are also comparable. This indicates that for the optimized amounts of the surfactant and compatibilizer in the respective processes, the two-step process does not offer any advantage from the point of view of the conversion of TEOS in the emulsion made from a pure TCE solvent over the one-step process.

Table 4.3 The average total and the net mass of the dried powder for both the one- and two-step reactions with four different combinations of the compatibilizer and surfactant

Samples	Dried powder mass(g)	Net powder mass (g)
GPM/aq/0.3/0.0	0.0705	0.0396
GPM/ aq/0.2/0.1	0.0814	0.0505
GPM/ aq/0.1/0.2	0.0936	0.0624
GPM/aq/ 0.0/0.3	0.0997	0.0691
GPM/ab/0.3/0.0	0.0782	0.0668
GPM/ab/0.2/0.1	0.071	0.0596
GPM/ab/0.1/0.2	0.059	0.0471
GPM/ab/0.0/0.3	0.048	0.0367

The opposite effect of ethanol and n-octanol on the emulsion polymerization of TEOS is probably due to a dual role of ethanol, which on the one hand enables the reactions to take place inside the aqueous phase rather than just on the interphase, but on the other hand, since it is a by-product of the hydrolysis reaction, it shifts the equilibrium to the left. Ethanol is more soluble in water than in TCE; therefore, as more ethanol is

produced the size of inorganic droplets will increase. Moreover, in the case of the one-step process, ethanol is a by-product of both hydrolysis and condensation, while in the two-step process water can also be a by-product of the condensation reaction. Therefore, for the same conversion of TEOS more ethanol is produced in the one-step than in the two-step process.

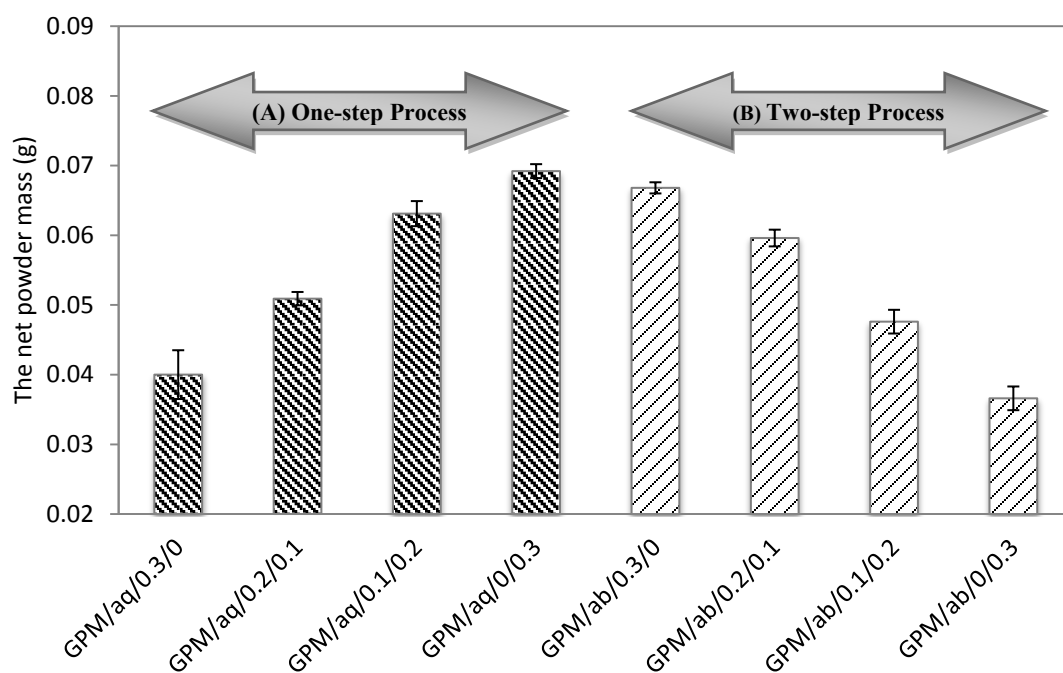


Figure 4.6 The effect of surfactant and compatibilizer on the net dried powder mass for both the (A) one-step and (B) two-step reactions

As the size of inorganic droplets increases, there are two possible outcomes; the droplets may agglomerate with the other ones leading eventually to de-phasing of the emulsion, or to a breakup of the droplets into smaller ones. The second outcome is only possible in the presence of n-octanol (surfactant). In the case of a single-step process, the hydrolysis and condensation are slower than in the two-step process, which was clearly

indicated by the gelation results discussed previously. Therefore, as the aqueous droplets increase and agglomerate, the interfacial area of the emulsion decreases. This will lead to a lower rate of TEOS transport into the inorganic phase resulting in its lower conversion. Thus, n-octanol enhances the conversion of TEOS in the case of slow hydrolysis and condensation in one-step process.

On the other hand, in the case of the two-step process with fast hydrolysis and condensation, the stability of the emulsion is probably not critical. Besides, less ethanol is produced as a by-product. As shown previously in Figures 2.7 and 2.8, the structure of silica gels depends on the pH of the environment in which the condensation takes place.

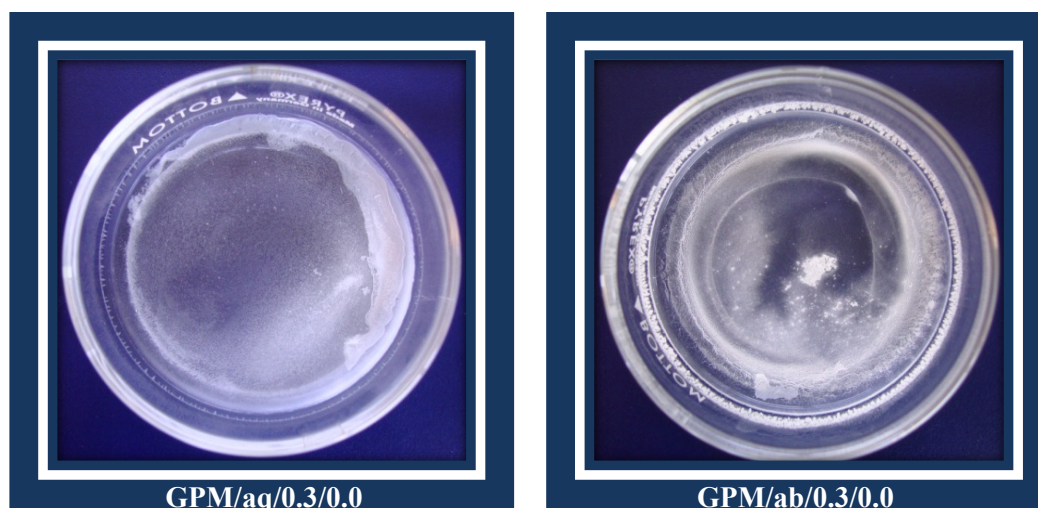


Figure 4.7 The synthesized dried powders using gravimetric powder method: GPM/aq/0.3/0 and GPM/ab/0.3/0; (in GPM/aq/0.3/0, Al-Keg solution and ethanol used as a catalyst and compatibilizer respectively. in GPM/ab/0.3/0, HCl-NH₄OH and ethanol used as a catalyst and compatibilizer respectively)

Although the one- and two-step processes provide similar conversion of TEOS in their respective optimized environments, the appearance of the final powder from the two processes is markedly different. This is shown in Figure 4.7, which presents the

photographs of the final powders. In the acid-base catalyzed system the dried powder forms clusters in the petri dish, which again can be explained by the basic condition for the condensation reaction. On the other hand, in the case of one-step process in which both hydrolysis and condensation occur in weak acidic environment, solid residuals on a petri dish form a film (Figure 4.7).

4.2.3. ^{29}Si NMR spectroscopy of dried powder

The GPM tests have proved that in the emulsion polymerization reactions discussed previously, volatile TEOS had been converted into non-volatile compound(s). However, the GPM tests do not provide the information about the structure of these non-volatile compounds. Moreover, while the net mass of the dried powder is proportional to the conversion of TEOS, the actual conversion of TEOS cannot be determined without the knowledge of the structure of the synthesized dried powder. Such information is provided by ^{29}Si NMR analysis.

Figures 4.8 and 4.9 present the ^{29}Si NMR spectra of the GPM/aq/0/0.3 and GPM/ab/0.3/0 powders, respectively. These powders were selected because of the largest net mass among the powders synthesized in the one- and two-step processes, respectively. Both spectra show the absence of Q^0 and Q^1 peaks, indicating that there was no unreacted TEOS in the analyzed samples, because either all TEOS was converted during the reactions or that unreacted TEOS was effectively removed from the samples before their analysis. In both cases three peaks, corresponding to Q^2 , Q^3 , and Q^4 , are clearly evident, but their relative intensities for the two powders differ significantly. For the powder synthesized in the one-step process (Figure 4.8), Q^3 is a dominant peak,

whereas for the powder synthesized in the two-step process the intensities of Q^3 and Q^4 are comparable. It is also important to emphasize the absence of peaks other than Q^2 , Q^3 and Q^4 in Figure 4.8, indicate that aluminum ions were not incorporated in the synthesized inorganic polymers, and consequently Al-Keg solution played the role of catalyst only in the one-step process.

In conclusion, the ^{29}Si NMR spectra of the synthesized powders shown in Figures 4.8 and 4.9 provide the final proof for successful emulsion polymerization of TEOS in the case where the continuous organic phase is made of a pure solvent (non-viscous environment).

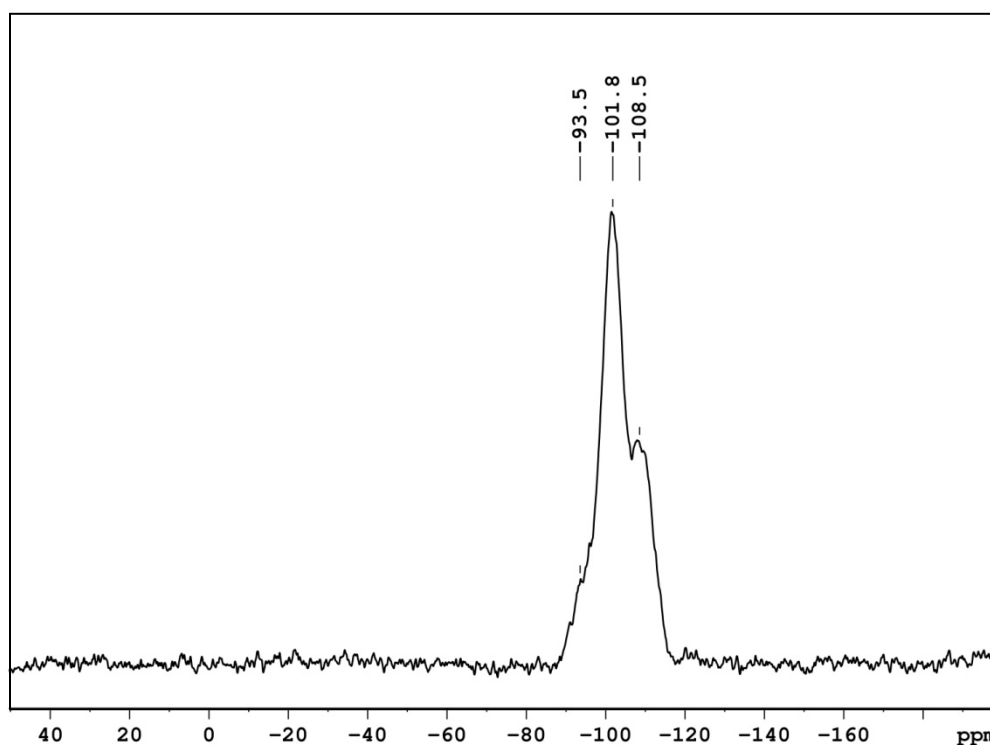


Figure 4.8 ^{29}Si NMR results spectra of the powder synthesized from GPM/aq/0/0.3; (the emulsion one which is contained 10 mL TCE, 0.1 ml Al-Keg solution, and 0.3 ml of n-octanol sonicated for 1 minute. Then 0.3 ml of TEOS is added and sonicated again for 30 minutes)

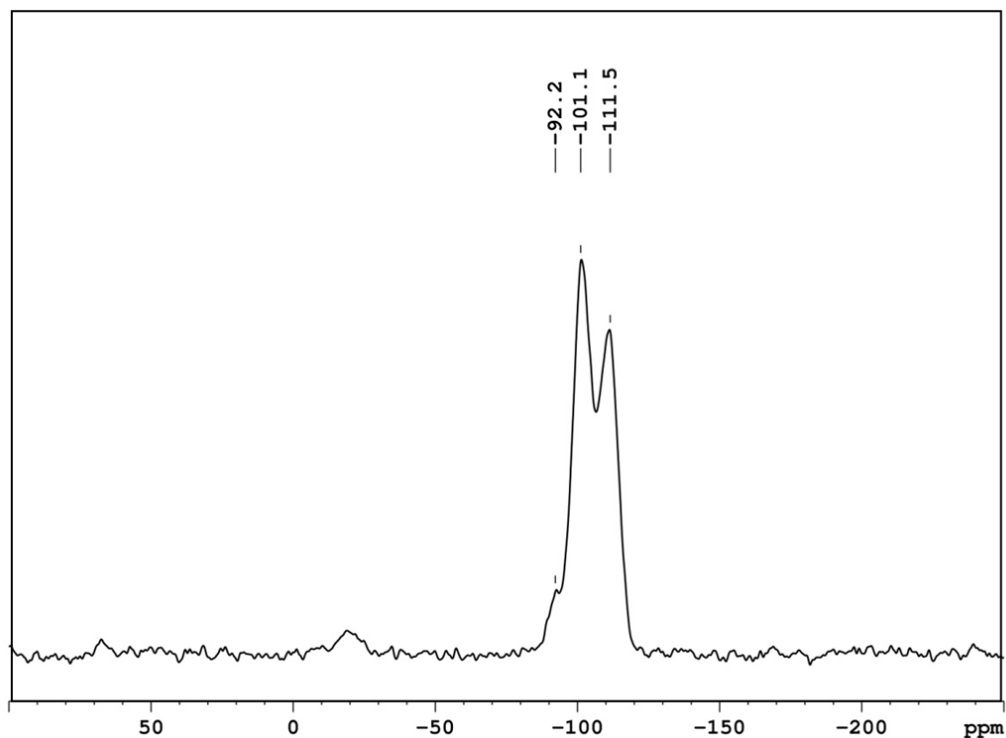


Figure 4.9 ^{29}Si NMR results spectra of the powder synthesized from GPM/ab/0.3/0 using GPM; (the emulsion one which is contained 10 mL TCE, 0.1 ml deionized water, 0.3 ml of ethanol, and 0.033 mL of acid sonicated for 1 minute. Then 0.3 ml of TEOS is added and sonicated again for 5 minute. Finally 0.067 mL of NH_4OH is added to the emulsion and sonicated for 30 minutes)

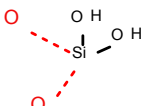
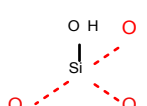
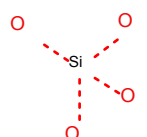
4.2.4. Conversion of TEOS in emulsion polymerization

The net mass of the dried powder along with its ^{29}Si NMR spectrum allows the evaluation of the actual conversion of TEOS in the emulsion polymerization reactions. This requires two assumptions: i) in the case of the one-step process the aluminum hydroxonitrate and sodium carbonate do not copolymerize with TEOS, which was validated by the ^{29}Si NMR analysis; ii) the quantitative contributions of Q^2 , Q^3 and Q^4 are known.

Table 4.4 provides the summary of the TEOS conversion in all reactions considering three hypothetical cases. In the second column of Table 4.4 the conversion is based on the net mass of the powder by assuming that the polymerized TEOS is entirely in the Q^2 form. Then in the third and fourth columns the conversions are provided for the polymerized TEOS entirely in the Q^3 and Q^4 forms, respectively. Consequently, none of these values correspond to the actual conversion of TEOS, but they provide a range of possible conversion for a given net mass of the powder. It can be noticed that for a given net mass of the powder the conversion increases from Q^2 through Q^3 to Q^4 . The details of the conversion calculations are provided in Appendix B.1.

On the other hand, considering the ^{29}Si NMR spectra shown in Figures 4.8 and 4.9, it is reasonable to assume that Q^3 is a dominating peak in the case of the powders synthesized in the one-step process, whereas that Q^3 and Q^4 have approximately equal contributions in the case of powders synthesized in the two-step process. Consequently, the values from the third column in Table 4.4 are taken as the actual conversion in the one-step process, and the arithmetic average of the third and fourth columns is taken as the actual conversion in the two-step process. Such evaluated conversions are plotted in Figure 4.10, which as expected, resembles previously presented Figure 4.6.

Table 4.4 TEOS conversion of the powders synthesized by GPM in one- and two-step processes considering three hypothetical cases

Case Si Bound	Q ²	Q ³	Q ⁴
			
GPM/aq/0.3/0.0			
Net reacted TEOS mass (g)	0.04		
TEOS conversion	0.378	0.428	0.492
GPM/aq/0.2/0.1			
Net reacted TEOS mass (g)	0.0509		
TEOS conversion	0.481	0.544	0.626
GPM/aq/0.1/0.2			
Net reacted TEOS mass (g)	0.0631		
TEOS conversion	0.597	0.675	0.776
GPM/aq/0.0/0.3			
Net reacted TEOS mass (g)	0.0692		
TEOS conversion	0.654	0.738	0.851
GPM/ab/0.3/0.0			
Net reacted TEOS mass (g)	0.0668		
TEOS conversion	0.632	0.715	0.821
GPM/ab/0.2/0.1			
Net reacted TEOS mass (g)	0.0596		
TEOS conversion	0.564	0.637	0.733
GPM/ab/0.1/0.2			
Net reacted TEOS mass (g)	0.0476		
TEOS conversion	0.45	0.509	0.585
GPM/ab/0.0/0.3			
Net reacted TEOS mass (g)	0.0366		
TEOS conversion	0.346	0.391	0.445

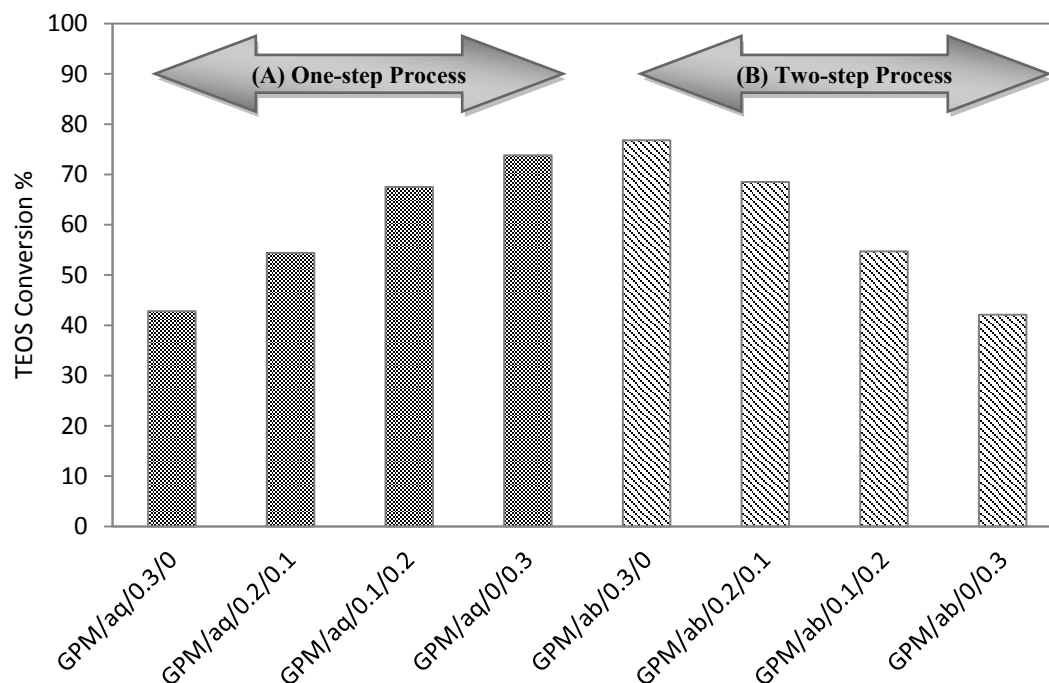


Figure 4.10 The effect of surfactant and compatibilizer on TEOS conversion of powders synthesized by GPM for both the (A) one-step and (B) two-step reactions

In general, the conversion of TEOS, depending on the process and the liquid additive varies from 40 to 75%. For the complete conversion of TEOS, these values are promising in the context of the emulsion polymerization of TEOS in the more challenging environment, in which the continuous organic phase is made of polymer solution rather than a pure TCE solvent.

4.3. PPO-based EPMM membranes

Before discussing the properties of PPO-based EPMM membranes, it is important to establish unbiased reference to which these properties could be compared. Therefore, the first step was to prepare and characterize pure PPO membranes, and to ensure that

pure PPO and PPO-based EPMM membranes undergo similar membrane formation and membrane post-treatment protocols.

4.3.1. The effect of polymer molecular weight on PPO membranes

PPO powders with two different molecular weights (MW) were used for the preparation of polymer solution in this study: low molecular weight (LMW)-PPO and high molecular weight (HMW)-PPO. The properties of these two powders provided by their manufactures are shown in Table 4.5.

Table 4.5 The properties of LMW and HMW-PPO powders provided by their manufactures

	Physical form	$\overline{M}_w$ (g/mol)	T_g (°C)
Low molecular weight (LMW)-PPO	white powder	30000	211
High molecular weight (HMW)-PPO	white powder	350000	220

The polymer solutions were prepared by using TCE as a solvent. The effect of concentration on the viscosity of polymer solutions of LMW and HMW-PPO powders is presented in Figure 4.11. It is evident that for the same concentrations, the viscosity of the HMW solution is significantly greater than that of the LMW solution. Moreover, the difference between these two viscosities increases with the concentration of the solution. This can be explained by an increase in the entanglement density by increasing the concentration of polymer for a given MW. Alternatively, the same result is obtained at a constant polymer concentration by increasing MW (Shenoy et al., 2005). Consequently, an increase in entanglement among polymer chains leads to a significant increase in the viscosity (Kumar and Gupta, 2003). The maximum concentrations for the HMW and

LMW powders, at which they could still completely dissolved, were 11 w/v% and 30 w/v%, respectively. The solution of flexible chain polymers is described in terms of an entanglement network. Such networks can exhibit free penetration of polymer segments, hindered penetration or no penetration at all. The segment interactions lead to a hindrance to penetration, which can be increased by the entanglement density (Schurz, 2011). Despite a much greater solubility of the LMW powder, the viscosity of the HMW solution at the maximum concentration was 2.5 times greater than that of the LMW solution.

Based on the results shown in Figure 4.11, the concentrations chosen for membrane casting by SE and SC techniques were 26 w/v% for the LMW-PPO and 10 w/v% for HMW-PPO. At these two concentrations the respective viscosities of the HMW and LMW solutions were comparable.

Figure 4.12 presents the photographs that HMW and LMW films prepared by the SE and SC techniques. As shown in Figure 4.12C, it was impossible to form a film using the LMW solution and the SE method. As the solvent was evaporating, the film on the plate was cracking, and at the end of the drying process small chunks of polymer remained on the plate rather than in a continuous film. This problem was not observed in the case of the HMW solution, which yielded a uniform film with no visual defects, (Figure 4.12A). The problem of making the film from the LMW-PPO can be explained on the basis of relatively short polymer chains and long film-formation times. The latter allowed the short polymeric chains to align, which resulted in high crystallinity and hence brittleness of the final membrane (Babut et al., 1995).

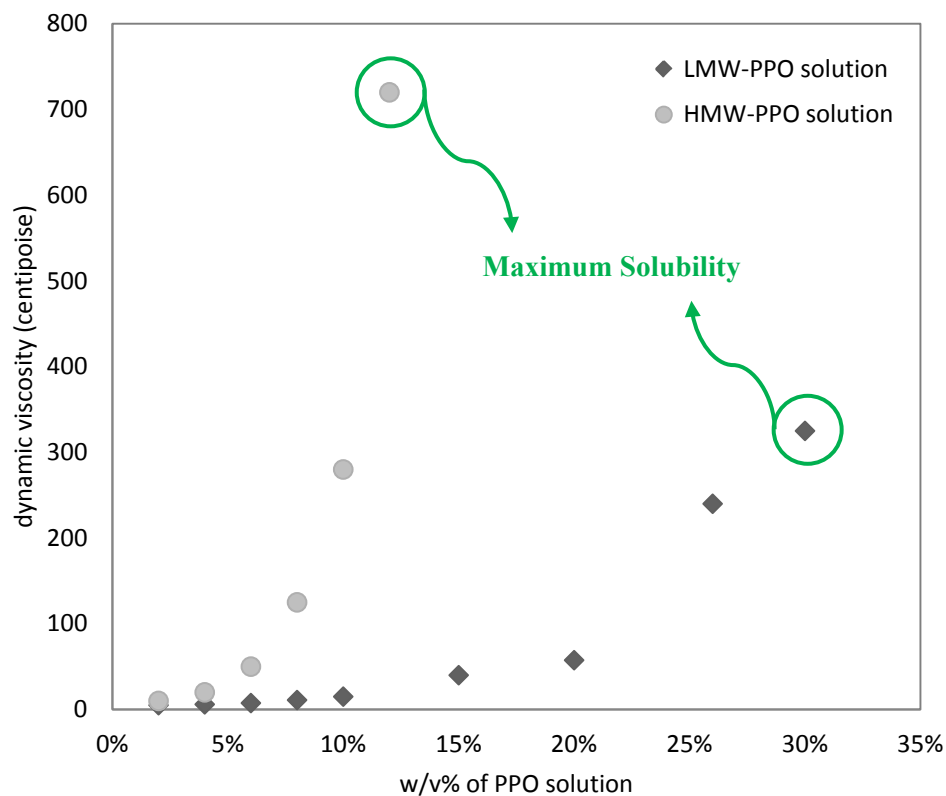


Figure 4.11 The effect of LMW- and HMW-PPO mass concentration on the viscosity of polymer solution (TCE used as a solvent)

On the other hand, there was no problem casting a film from 26 w/v% of LMW-PPO solution by the SC method. As shown in Figure 4.12D, the final LMW film was uniform and transparent without any visual defects, and was similar to the HMW film prepared by the SC technique (Figure 4.12D). In the SC method, a large fraction of polymer solution is lost, and the final membranes are much thinner than those made by the SE method. Moreover, the time for the film to solidify in the SC method was much shorter than that in the SE method. Consequently, short chains did not have time to align leading to quite flexible LMW films, which could be easily handled.

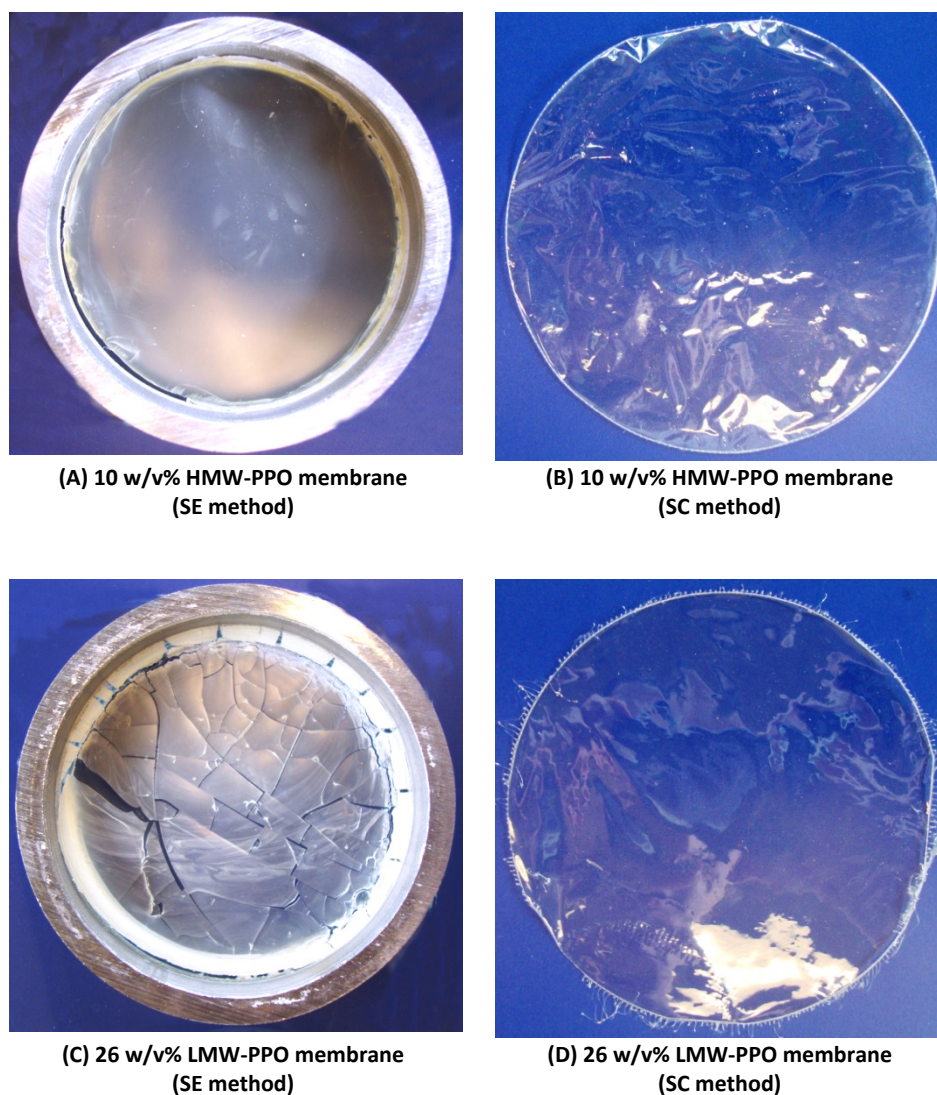


Figure 4.12 The casted film obtained from LMW and HMW-PPO solutions by two different methods; solvent evaporation (SE) and spin coating (SC)

The glass transition temperature (T_g) of both films made by the SC method were measured, and the observed values of 217.8°C and 212.2°C for the HMW- and LMW-PPO, respectively, are slightly different than those provided by the manufactures (Table 4.5). It is important to emphasize that the manufactures' values refer to PPO powders rather than PPO films. In addition, the T_g depends on the heating rate, which in our case

was 10°C/min, while it is not clear what heating rate was used by the manufacturer. The effect of molecular weight on T_g is well known. For a given polymer chemistry, an increase in the MW of polymer increases the chain stiffness and consequently it causes a lower packing density (i.e., a higher free volume) and a higher T_g (Chowdhury et al., 2001).

Table 4.6 The gas transport properties of LMW and HMW PPO membranes

	Parameters		
	O₂ permeability coefficient (Barrer)	N₂ permeability coefficient (Barrer)	Permeability ratio O₂/N₂
HMW-PPO membrane	15.42	3.58	4.31
LMW-PPO membrane	10.1	2.36	4.28

The LMW and HMW PPO films prepared by the SC method were tested in single gas permeation tests with N₂ and O₂ to provide the reference gas transport properties for the PPO-based EPMM membrane. The experimentally measured permeability coefficients for O₂ and N₂ as well as the corresponding permeability ratio for the low and high molecular PPO membranes are summarized in Table 4.6.

The permeability coefficient is a product of the solubility and diffusivity coefficients (Lin and Freeman, 2004). Since PPO does not have any polar group in its backbone, the solubility coefficient is primarily governed by the condensability of penetrants. In turn, the critical temperature (T_c) is a measure of gas condensability; the greater the T_c the greater the condensability and hence the solubility coefficient. For oxygen and nitrogen the T_c is 154 K and 126 K, respectively. In other words, O₂ is more soluble in PPO than N₂. However, the major reason for P_{O_2} being more than four times

greater than P_{N_2} is a greater diffusivity O_2 in PPO than N_2 . In the absence of strong interaction between the penetrant and the membrane, the diffusivity coefficient is primarily determined by the kinetic diameter (d_K) of the penetrant, i.e., the smaller the d_K , the greater the diffusivity coefficient. The corresponding kinetic diameters of O_2 and N_2 are 3.46Å and 3.64Å.

It can also be noticed in Table 4.6 that while the permeability ratio for the HMW and LMW films is comparable, the permeability of the former is nearly 50% greater than the permeability of the latter. This difference in permeabilities is a consequence of a greater free volume of HMW-PPO compared to its LMW counterpart.

Considering a better gas transport properties of HMW-PPO and the fact it is easier to cast membrane from the solutions of HMW-PPO than the solutions of LMW-PPO, which was exemplified by the SE technique, it was decided to focus on PPO-based EPMM membranes originating from the HMW powder.

4.3.2. Synthesis of PPO-based EPMM membranes

The synthesized PPO-based EPMM membranes were first visually evaluated assessing their transparency and then characterized by DSC, ^{29}Si NMR, and ICP-MS. Finally, the gas transport properties of the membranes were investigated by carrying out single gas permeation tests with O_2 and N_2 in a constant pressure (CP) system.

4.3.2.1. Transparency of EPMM membranes

Visual appearance of the synthesized membranes depends on the casing method and the type of the emulsion polymerization process. Table 4.7 summarizes the visual

observations of all synthesized membranes. In general, the membranes prepared using the SC technique, were more transparent than those prepared by the SE method.

Although the same volume of the casting emulsion/solution was used in all cases, a large portion of this volume was lost in the SC process, which contributed to much shorter solidification times compared to the SE process. Furthermore, shorter solidification times in the SC process were also due to the fact that solvent evaporation was a forced convection rather than a natural convection process. In turn, longer solidification times in the case of SE membranes allowed the polymeric chains to align, which enhanced their crystallinity. The crystalline regions scatter the light more than the amorphous regions, making the SE membranes less transparent than the SC membranes (Demirel et al., 2011).

Table 4.7 Visual transparency of the synthesized PPO-based EPMM membranes

	SC method	SE method
PPO film	Transparent	Semi-Transparent
EPMM/aq/0.3/0.0	Transparent	Semi-Transparent
EPMM/aq/0.2/0.1	Transparent	Semi-Transparent
EPMM/aq/0.1/0.2	Transparent	Semi-Transparent
EPMM/aq/0.0/0.3	Transparent	Semi-Transparent
EPMM/ab/0.3/0.0	Semi-Transparent*	Opaque*
EPMM/ab/0.2/0.1	Semi-Transparent*	Opaque*
EPMM/ab/0.1/0.2	Semi-Transparent*	Opaque*
EPMM/ab/0.0/0.3	Semi-Transparent*	Opaque*

* White spots

As far as the effect of the emulsion polymerization types on the appearance of the final membrane is concerned, the EPMM membranes prepared in one-step process were more transparent than those in the two-step process. In addition to being less transparent,

the EPMM membranes prepared in the two-step process were not homogeneous, which can be indicated by the presence of small white spots irregularly distributed in the membrane. This could be an indication of the aggregation of inorganic particles and perhaps the existence of two distinct phases – organic and inorganic, which would be undesirable.

4.3.2.2. Differential scanning calorimetry analysis

All EPMM membranes synthesized in this project along with the reference PPO membranes were analyzed using differential scanning calorimetry (DSC). The primary purpose of this analysis was to determine the glass transition temperature (T_g) of the membranes, which if greater than that of the reference PPO could indirectly indicate successful emulsion polymerization of TEOS in the environment of polymer solution. However, before investigating the effects of the synthesis process and the composition of the liquid additive on the T_g of the EPMM membranes, the DSC analysis was used for establishing the heat post-treatment protocol.

The main purpose of the heat-treatment is to remove the residuals, which could not be removed in the boiling step, in particular TCE solvent, unreacted TEOS, and n-octanol. If these residuals did not remove, they act as plasticizers increasing the mobility of polymer segments, thus reducing the T_g of the polymer. Moreover, the presence of residuals has strong effect on the gas transport properties of the final membrane. Therefore, it is critical to remove residuals prior to gas permeation tests. In addition, in order to determine the actual conversion of TEOS in the EPMM membranes, the latter were tested using inductively coupled plasma mass spectroscopy (ICP-MS). This

technique, as will be shown in the subsequent section, detects all Si-content without distinguishing between the reacted and unreacted TEOS. Therefore, if not removed prior to the ICP-MS analysis, the residual TEOS could falsify the actual conversion of TEOS in the EPMM membranes.

A set of experiments was carried out to investigate the effect of different post-treatment temperatures on the T_g of the synthesized EPMM membranes. The thermal post-treatment was carried out at atmospheric pressure in oxygen-free environment. The results of this investigation are summarized in Figures 4.13 and 4.14, which present the T_g s of EPMM membranes synthesized by SE technique in one- and two-step processes, respectively. For a given type of membrane, three samples from different parts of the same membrane were analyzed. The T_g s shown in Figures 4.13 and 4.14 represent the average from these three samples, while the error bars represent the corresponding standard deviations. In addition, the horizontal line (Figures 4.13 and 4.14) represent the average T_g of the reference PPO membrane prepared by the SE method. Out of the two types of the membrane formation methods, the SE membranes were selected for this investigation, because they were considerably thicker than the SC membranes. If residuals are effectively removed at a given temperature from a thick membrane, it is assumed that they will also be removed from a thin membrane of the same type.

In general, the T_g increases with the heat-treatment temperature. While the dependence of T_g on the heat-treatment temperature is different for the one- and two-step membranes, the common feature of the two types of membranes is the little difference between the T_g s of the membranes post-treated at 235°C and 250°C. This suggests that all residuals were removed at 235°C. The latter was then used as a heat-treatment

temperature for all PPO-based EPMM membranes. It is important to note that 235°C is greater than the boiling points of TEOS, n-octanol, and in particular TCE. These residuals could not be removed completely at lower temperatures, because they are trapped in so-called Langmuir sites, which are not accessible to the external environment. Langmuir sites, which are unique to glassy state, disappear in rubbery state. Consequently, in order to have effective thermal treatment in the case of glassy polymers, the membranes must be exposed to temperatures exceeding the T_g of the polymer.

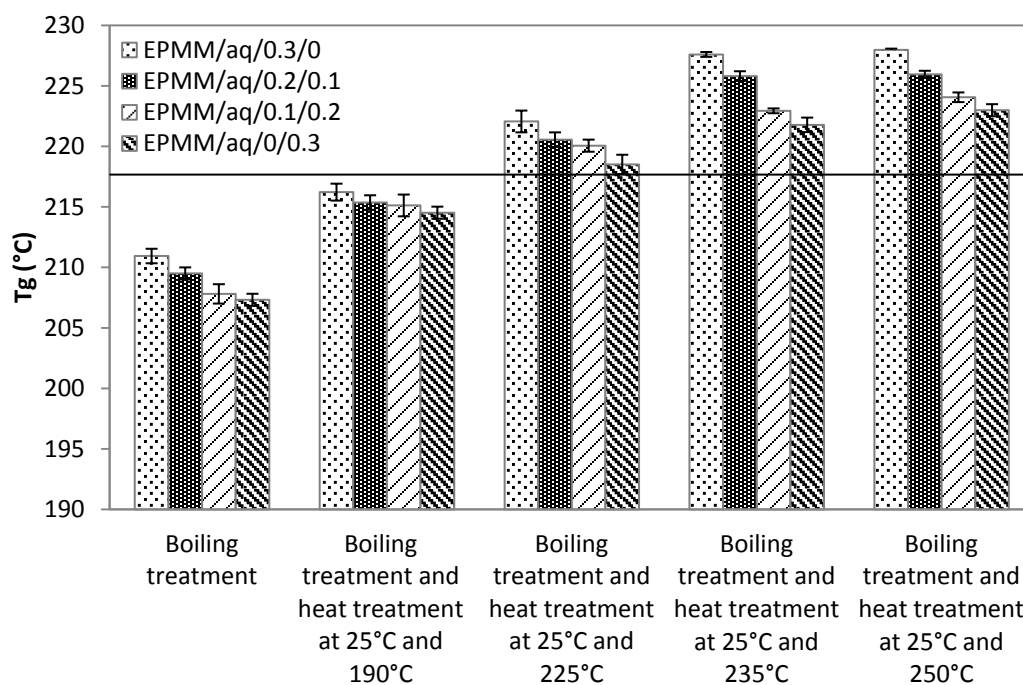


Figure 4.13 The glass transition temperature of the PPO-based EPMM membranes (prepared in one-step process) as a function post treatment conditions

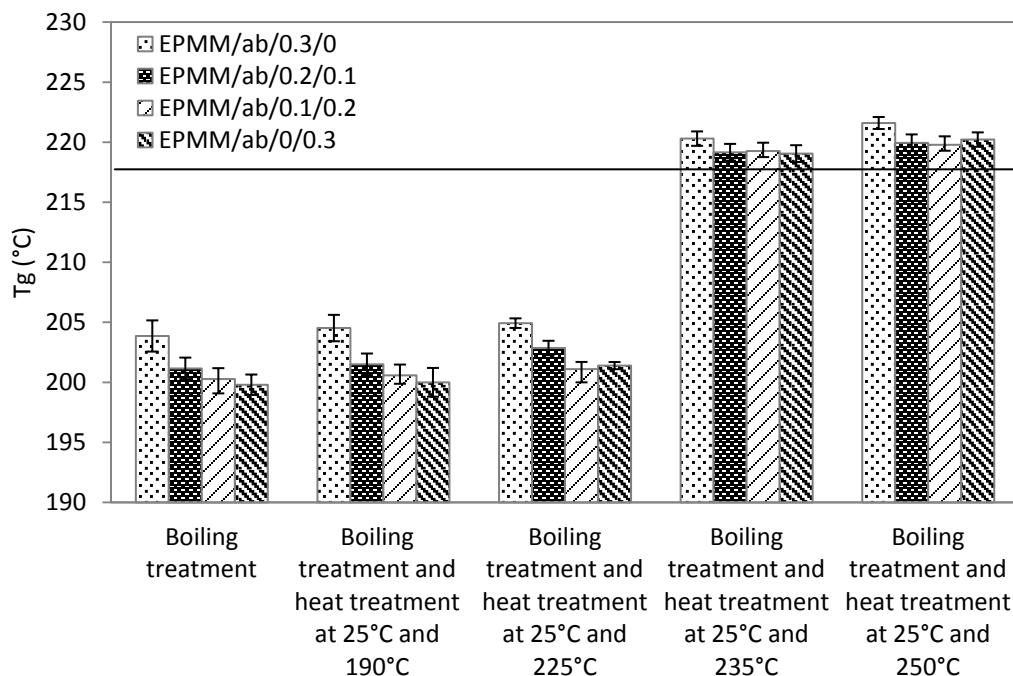


Figure 4.14 The glass transition temperature of the PPO-based EPMM membranes (prepared in two-step process) as a function post treatment conditions

The results previously shown in Figures 4.13 and 4.14 are repotted in Figure 4.15. In addition to the membranes prepared by the SE method, Figure 4.15 also shows the T_g s of the SC membranes synthesized in the one- and two-step processes versus the composition of the liquid additive containing ethanol and n-octanol at different proportions. The horizontal lines in Figure 4.15 represent the average T_g s of the reference PPO membranes prepared by the SC method (solid line) and the SE method (dashed line).

Examination of Figure 4.15 indicates, first of all, that regardless of the type of the emulsion polymerization, the composition of the liquid additive, and the method of membrane preparation the T_g of PPO-based EPMM membranes is greater than the T_g of the reference PPO membranes. The T_g of EPMM membranes range from 219°C to 227.8°C, compared to 218°C of the reference PPO. An increase in T_g indicates a decrease in chain mobility of PPO segments. In turn, this decrease in chain mobility must result

from the presence of polymerized TEOS, which restricts rotations of the polymer segments because of either, occupying the space where these segmental rotations take place, or by interacting with the polymer segments. Therefore, greater T_g of EPMM membranes compared to the reference PPO indicates not only a successful polymerization of TEOS, but also the distribution of the synthesized inorganic particles within the continuous organic phase at a molecular level.

The difference between the T_g of the EPMM membranes and that of the reference PPO depends on the type of the emulsion polymerization reaction, the composition of liquid additive, and the method of membrane preparation, which will be discussed next. However, first remembering that in the case of the SC membranes, a large portion of the casting emulsion was lost from the wafer, there was a concern that the lost portion could contain a greater concentration of the polymerized TEOS than the portion remaining on the wafer, from which eventually the EPMM membrane was formed. This may occur if de-phasing takes place in the emulsion. In this case, the T_g of the SC membranes would be lower than the T_g of the SE membranes since the membrane casted by SE method contains both phases while SC membranes contain organic phase rather than inorganic phase. However, as shown in Figure 4.13, the observed trend is exactly the opposite, i.e., for a given type of the EPMM membrane, the one prepared by the SC method had actually a slightly greater T_g than its SE counterpart.

Figure 4.15 also shows that for a given composition of the liquid additive, the T_g of EPMM membranes synthesized in the one-step process is greater than that of the membranes synthesized in the two-step process. The difference is the greatest when the liquid additive is pure ethanol and gradually decreases with an increase in the

concentration of n-octanol. The EPMM membranes synthesized in the one-step process not only have a greater T_g than those synthesized in the two-step process, but also the corresponding standard deviations for the one-step membranes are smaller than those for the two-step membranes. The standard deviation, which was determined based on T_g s of three samples taken from different parts of the same membrane, indicates a greater homogeneity of the membranes synthesized in the one-step process compared to those synthesized in the two-step process, which is consistent with visual assessment of the membranes discussed previously.

It is important to note that while an increase in T_g is an indication of successful polymerization of TEOS and the magnitude of the increase could also be indicative of the conversion of TEOS, the results shown in Figure 4.15 do not correlate with the conversion of TEOS in the GPM experiments summarized in Figure 4.10. In fact, for the one-step GPM process, the largest conversion of TEOS was observed for the liquid additive being pure n-octanol, while the EPMM membrane synthesized in the one-step process with pure n-octanol has the lowest T_g among its group. In addition, for the two-step membranes, considering the size of the error bars, the T_g does not depend on the composition of the liquid additive. While the environment of pure TCE solvent for the emulsion polymerization of TEOS is very different from that of a viscous PPO solution in TCE, the lack of correlation between Figures 4.10 and 4.15 may indicate that the T_g of EPMM membranes might be affected more by the “quality of dispersion” rather than the quantity of the polymerized TEOS. In turn, the high quality inorganic loading would be the one distributed at a molecular level and thus strongly interacting with the polymer segments of the host polymer.

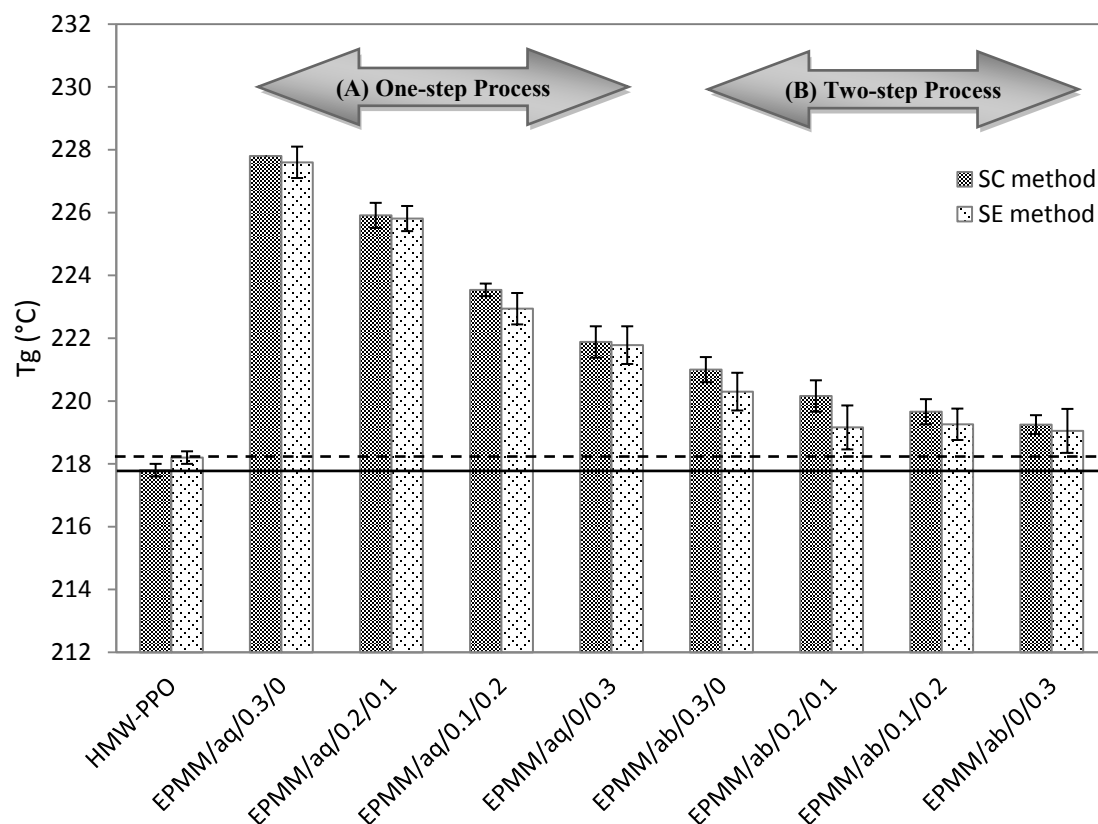


Figure 4.15 The glass transition temperature of HMW-PPO and EPMM membranes, prepared by SC and SE methods in (A) one- and (B) two-step processes

In addition to the measurement of T_g , the DSC analysis also allows an indirect assessment of interactions between the polymer segments. Glass transition is a second order transition, which is characteristic to amorphous polymers; there is no glass transition in crystalline polymers, which when heated to a specific temperature they melt. As an amorphous polymer undergoes glass transition its specific heat changes. The greater the difference between the specific heats (ΔC_p) at the glassy and rubbery states the more evident the glass transition. In other words, as the interactions between the polymers segment increase, the T_g becomes less evident (Almeida et al., 2011).

Figure 4.16 compares the DCS spectra of two membranes synthesized in one-step process, spectrum A is for the membrane in which the liquid additive was pure ethanol (EPMM/aq/0.3/0), while spectrum B is for the membrane in which the liquid additive was pure n-octanol (EPMM/aq/0/0.3). It can be noticed that ΔC_p at glass transition for the spectrum A is considerably smaller than for the spectrum B. It is important to emphasize that out of three samples taken from the EPMM/aq/0.3/0 membrane, only for the one shown in Figure 4.16, the T_g could be detected, and this T_g is the highest among all EPMM membranes synthesized in this research. Lack of detectable T_g could suggest crystalline structure of EPMM/aq/0.3/0. However, this and the other EPMM/aq/0.3/0 membranes were very flexible, easy to handle, and not brittle at all. Consequently, very small ΔC_p at glass transition is probably the result of very fine dispersion of the polymerized TEOS nanoparticles in between amorphous segment of PPO, which effectively prevents free movement (rotation) of many PPO segments at and above the T_g . These immobilized polymer segments would not then contribute to the ΔC_p at glass transition (Almeida et al., 2011).

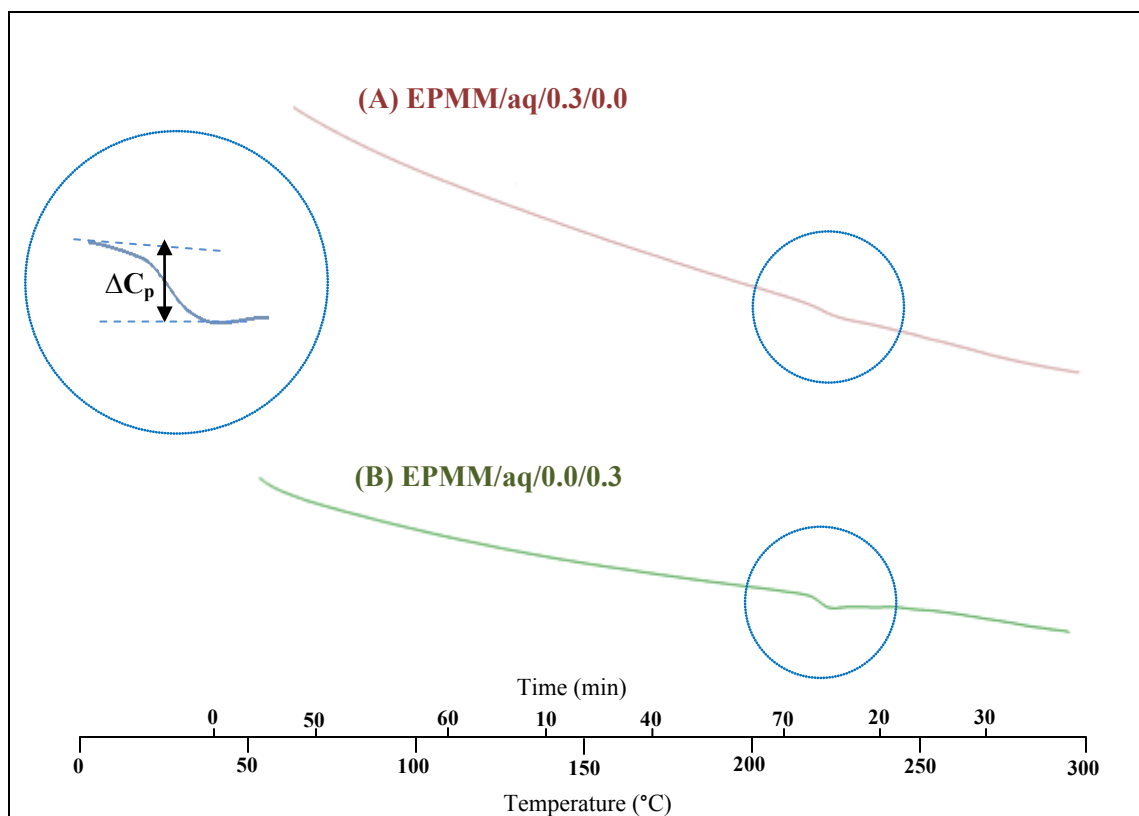


Figure 4.16 The specific heat capacity change (ΔC_p) of two synthesized EPMM membranes in one-step process (A) EPMM/aq/0.3/0.0 (B) EPMM/aq/0.0/0.3

4.3.2.3. ^{29}Si NMR spectroscopy

The ^{29}Si NMR analysis of PPO-based EPMM membranes were carried out to verify the polymerization of TEOS in the polymer matrix as well as the removal of all non-reacted TEOS from the membrane after the post-treatment. Going back to Figure 4.14, one could notice is a big jump in T_g between the two-step membranes post-treated at 225°C and 235°C. This big jump in T_g was attributed to the removal of residuals, including the non-reacted TEOS, from the membranes post-treated at 235°C. To verify this conclusion, two EPMM/ab/0.3/0 membranes, one post-treated at 225°C and the other

one post-treated at 235°C were analysed using ^{29}Si NMR, and the resulting spectra are presented in Figure 4.17A and 4.17B, respectively.

There are three peaks in Figure 4.17A located at -82.5, -89.4, and -96.5 ppm, which can be attributed to Q^0 , Q^1 , and Q^2 respectively. The Q^1 and Q^0 peaks indicate the presence of unreacted TEOS in the membrane post-treated at 225°C. The presence of the Q^2 indicates that some TEOS was actually polymerized. Moreover, the peak at -96.5 ppm is very broad, and probably overlaps with the Q^3 and Q^4 peaks. This is actually confirmed by the spectrum shown in Figure 4.17B obtained for the same type of membrane but post-treated at 235°C, in which the peaks at -100.3 and -108.8 ppm corresponding to Q^3 and Q^4 , respectively, are dominant. Moreover, the peaks corresponding to Q^0 , Q^1 are not present in Figure 4.17B, which proves the anticipated removal of all unreacted TEOS at 235°C.

The spectrum shown in Figure 4.17B is representative for the EPMM membranes synthesized in the two-step process. Despite the fact that the T_g of the EPMM membranes synthesized in the two-step process was only a little bit higher than the T_g of the host PPO, Figure 4.17B provides the direct proof for the emulsion polymerization of TEOS in the two-step process, in the environment of a polymer solution. Compared to the spectrum shown in Figure 4.9, which is representative for the dried powder synthesized in the two-step process, the spectrum in Figure 4.17 shows some important similarities. In particular, in both cases, the peaks Q^3 and Q^4 are dominant, which suggest similar structures of the polymerized TEOS. In addition, a small contribution of the Q^2 peak suggests that in both cases the polymerized TEOS formed branched rather than linear structures.

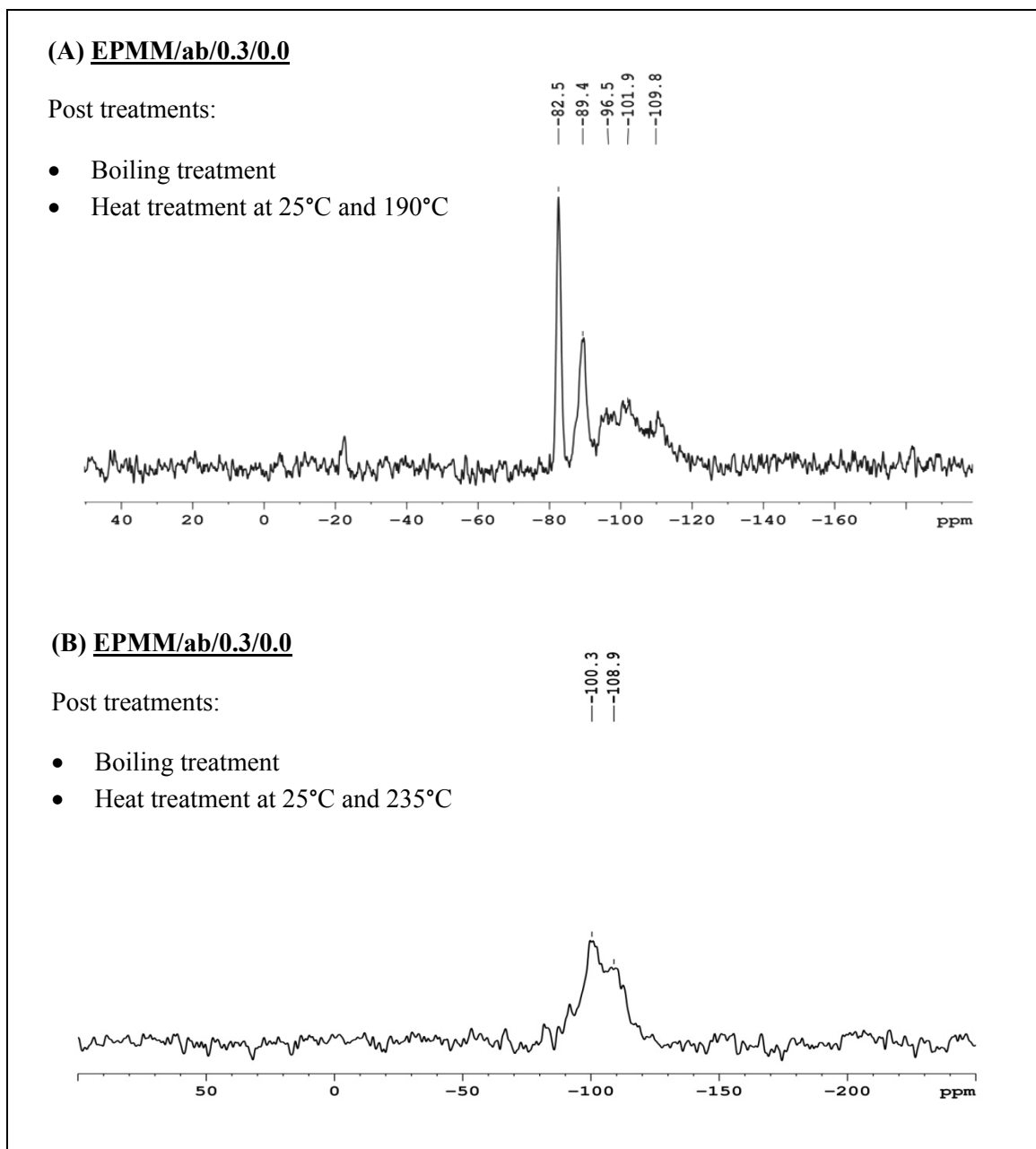


Figure 4.17 The effect of heat treatment temperature on the EPMM/ab/0.3/0 membrane based on ^{29}Si NMR spectra of this membrane heat-treated at (A) 190°C, and (B) 235°C.

Figure 4.18 presents the ^{29}Si NMR spectrum of the EPMM/aq/0.2/0.1 membrane post-treated at 235°C, which can be considered as representative for the EPMM membranes synthesized in the one-step process. Unlike the spectrum shown in Figure

4.17B, there is only one broad peak at -103.8 ppm corresponding to Q^3 , which probably overlaps with smaller Q^2 and Q^4 peaks. This spectrum resembles the one shown in Figure 4.8 for the dried powder synthesized in one-step process, and as such provides the direct proof for the emulsion polymerization of TEOS in the one-step process in the environment of polymer solution. Moreover, the absence of Q^0 and Q^1 peaks in Figure 4.18 confirms that 235°C is sufficient to remove all (if any) unreacted TEOS from the membrane structure.

In addition to the peak at -103.8 ppm, there is also a small peak at -22.6 ppm, which cannot be attributed to any of the Si-O-Si bonds. Interestingly, Wang (2011) also observed this peak in the ^{29}Si NMR spectrum of EPMM/aq/0.3/0, and hypothesized that it could arise from the Si-O-Al bond. However, he could not confirm his hypothesis. It is important to note this peak was not present in the spectrum of the dried powder synthesized in the one-step process (Figure 4.8). Consequently, this peak cannot also be attributed to the residual aluminum complex used in the one-step reactions. This because the EPMM membranes were post-treated in boiling water during which this complex could be washed out, while in the case of dried powder this complex was a part of the total mass of the powder.

The ^{29}Si NMR analysis were also carried out for the EPMM/aq/0/0.3 membrane (pure n-octanol as a liquid additive), but there were no peaks on the resulting spectrum (Appendix C). This is consistent with the results reported by Wang (2011), who also did not observe any peak on the ^{29}Si NMR spectrum of EPMM/aq/0/0.3-type of membrane. Interestingly, the dried powder synthesized at analogous conditions showed the highest conversion of TEOS among the powders synthesized in the one-step process (Figure

4.10). On the other hand, the EPMM/aq/0/0.3 had the lowest T_g among the membranes synthesized in one-step process (Figure 4.15), which to some extent is consistent with the current NMR results. It is important to emphasize that lack of Q^2 , Q^3 , and Q^4 on ^{29}Si NMR spectra, does not automatically imply that the emulsion polymerization of TEOS did not take place. This reaction could still occur, but because of possible low conversion of TEOS, the concentration of the polymerized TEOS could be too small to be detected in the NMR analysis. It is important to keep in mind that ultimately the quantitative information about the conversion of TEOS in the EPMM membranes will be provided by the ICP-MS analysis in the following section.

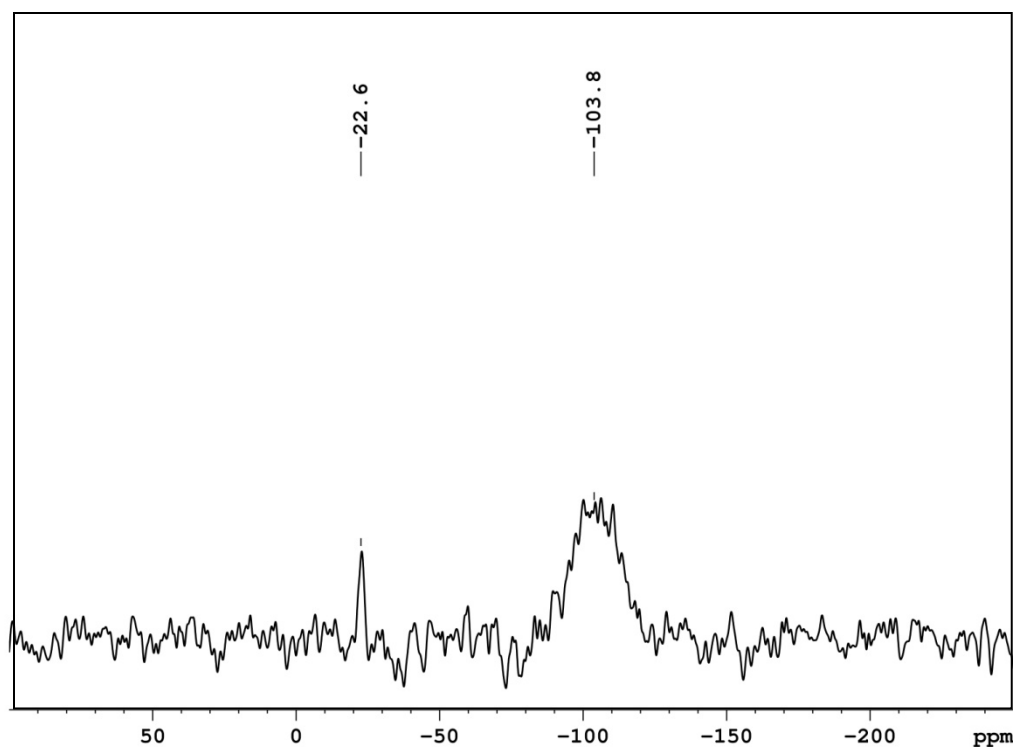


Figure 4.18 ^{29}Si NMR spectrum of the EPMM/aq/0.2/0.1

4.3.2.4. Inductively coupled plasma mass spectroscopy (ICP-MS)

The DSC and ^{29}Si NMR analyses helped to determine the post-treatment conditions allowing complete removal of the unreacted TEOS. Consequently, silicon in such post-treated EPMM membranes comes only from the polymerized TEOS, and the inductively coupled plasma mass spectroscopy (ICP-MS) analysis allows evaluating the actual conversion of TEOS, and the inorganic loading in PPO-based EPMM membranes.

If all TEOS were polymerized, the inorganic loading would depend on the structure of the polymerized TEOS. If all TEOS was converted into a linear polymer, i.e., if peak Q^2 were dominant, the inorganic loading in the resulting EPMM membrane would be 9.57%. The corresponding maximum conversions if all polymerized TEOS were in the Q^3 and Q^4 forms would be 8.56%, and 7.52%, respectively. Therefore, for a given amount of Si, the largest and smallest inorganic loadings are attributed to the forms Q^2 and Q^4 , respectively. This can be explained by the greater mass fraction of Si in the form of Q^4 compared to Q^3 and Q^2 form. On the other hand, the actual conversion of TEOS is independent of actual structure of the polymerized TEOS, since TEOS conversion depends only on the amount of Si in the product. This is further explained in Appendix B.2, which also shows the details of calculations of the conversion and inorganic loading based on the ICP-MS results.

The conversion results are presented graphically in Figure 4.19. It is important to emphasize that for the ICP-MS analysis, each membrane sample was divided into two parts and each part was analysed separately. In all cases, the results from the two parts of the same membrane were in the excellent agreement, which confirms homogeneity of the synthesized EPMM membranes.

Considering Figure 4.19, it is evident that the conversions of TEOS in one-step process, which range from 10% - 20% are significantly smaller than the conversions in two-step process, which range from 50% to 70%. In contrast, in the case of the GPM tests, the conversions in the one- and two-step processes were comparable. Consequently, the environment of polymer solution had a detrimental effect on the conversion in the one-step process, but it did not affect the conversions in the two-step process. Despite relatively low conversions of TEOS in the one-step process and consequently low inorganic loadings in the resulting EPMM membranes, they had significantly greater T_g than the EPMM membranes with much higher inorganic loadings that were synthesized in the two-step process (Figure 4.15). This may appear as a contradiction, because one could anticipate that T_g of EPMM membranes should increase with the inorganic loading, but in reality, there is no contradiction. As already indicated, based on the visual evaluation of the EPMM membranes, those synthesized in one-step process had a uniform appearance as opposed to the EPMM membranes synthesized in the two-step process, which had visible white spots on the surface. Consequently, the combination of visual observation with the DSC and ICP-MS analyses indicate that while the two-step EPMM membranes had high conversions of TEOS; the inorganic phase was not well incorporated into the polymer matrix of the host polymer. On the other hand, low conversions of TEOS in the case of one-step EPMM membranes have a profound effect on their physical properties. Therefore, the inorganic loading cannot be taken as a sole indicator of the properties of EPMM membranes. Equally, if not more important, is the quality of the dispersion of inorganic particles in the continuous phase of the host polymer.

Leaving aside the problem of the quality of dispersion of inorganic phase, a question arises about different effect of polymer solution on the total conversion of TEOS in the one- and two-step processes. A detrimental effect of polymer solution on the conversion of TEOS in one-step EPMM membranes is consistent with the results reported by Parker et al. (2003), who studied polymerization of TEOS in hydroxypropyl cellulose (HPC) solution. A change from a pure solvent to a concentrated polymer results in very significant increase in viscosity (Figure 4.11). Consequently, the diffusivity of TEOS in a viscous polymer solution must be significantly lower than in the pure solvent. In the case of one-step process, because of weak acidic conditions, the rate of hydrolysis, which depends on the rate of the transport of TEOS to the dispersed inorganic phase, is relatively slow even in the environment of pure solvent. Therefore, for the same reaction times, it is logical that the conversion rates in the environment of polymer solution are significantly lower than in the environment of pure solvent.

Unlike the GPM experiments, there is no obvious trend between the composition of the liquid additive and the conversion of TEOS. However, it is evident that the lowest conversion of TEOS for the one-step membranes is observed in the system with pure n-octanol as a liquid additive, which is exactly the opposite of what was observed in the case of the corresponding GPM tests. In the latter case, the key to overcome the problem of low hydrolysis rates was the stability of the emulsion, which was provided by n-octanol. In the case of EPMM membranes, very high viscosity of polymer solution may actually help to maintain stable emulsion regardless of the presence of the surfactant. On the other hand, while the presence of ethanol (compatibilizer) was detrimental to high conversions of TEOS in the one-step GPM tests, it might be desirable in the environment

of polymer solution because it allows the reaction to proceed not only at the interface, but also inside the aqueous phase. At the same time, although ethanol is soluble in both water and TEOS, it is more soluble in the former, which leads to accumulation of ethanol in the aqueous phase; in turn, this shifts the reactions of hydrolysis and condensation to the left, thus preventing high conversions of TEOS. Therefore, finding an alternative solvent to TCE, which on the one hand, could dissolve PPO, but on the other hand, had a better compatibility with ethanol, could help to increase the conversion of TEOS in the single-step membranes.

Unlike the one-step EPMM membranes, the conversions of TEOS in the environment of pure solvent and a viscous polymer solution are comparable in the case of the two-step membranes. This is probably because of very fast hydrolysis in strong acidic conditions and very fast condensation in weak basic conditions. In this case, although the diffusivity of TEOS is very slow, it reacts right away upon reaching to the organic-inorganic interphase.

It should also be emphasized that apart from Si, the EPMM membranes synthesized in the one-step process also contained a small and constant concentration of Al (ranging from 0.15 to 0.19 wt%). There was no correlation between the amounts of Si and Al. This suggests that the detected Al comes more likely from not removed aluminum catalyst rather than Al copolymerized with TEOS (Wang, 2011).

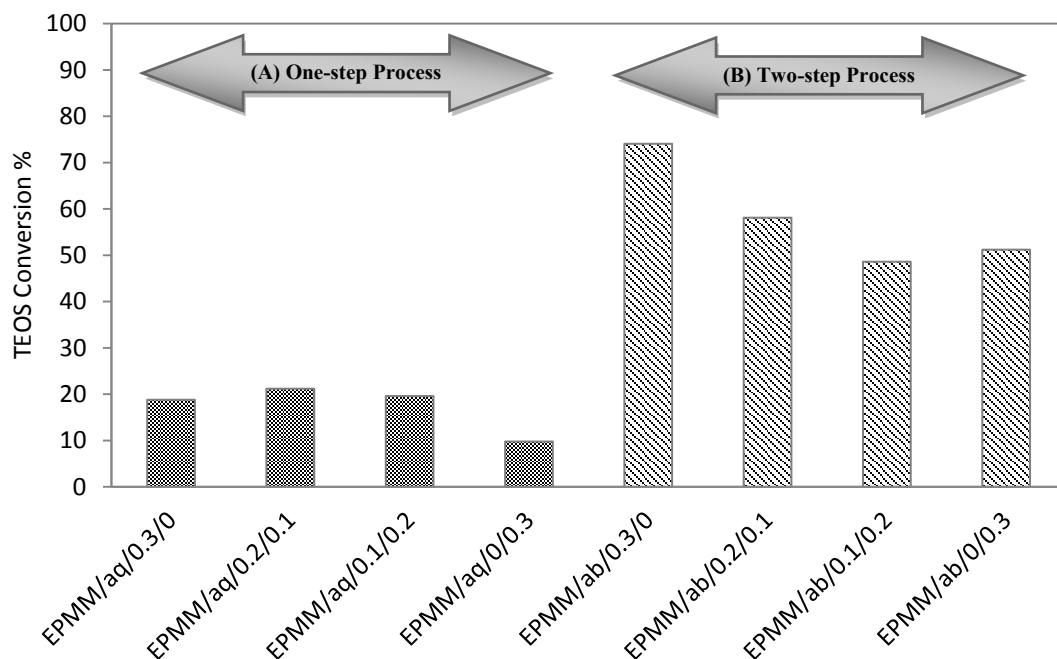


Figure 4.19 TEOS conversions of PPO-based EPMM membranes synthesized in (A) one-step process and (B) two-step process with four different combinations of surfactant and compatibilizer

4.3.2.5. Gas permeation properties

Single gas permeation with oxygen and nitrogen were carried out in a CP system at 120 psia feed pressure and ambient temperature using four types EPMM membranes (three one-step - EPMM/aq/0.3/0, EPMM/aq/0.2/0.1, EPMM/aq/0/0.3, and one two-step - EPMM/ab/0.3/0) along with the reference PPO. For each type of membrane, four coupons were prepared and tested.

It became immediately apparent that all four of EPMM/ab/0.3/0 coupons were defective. They showed very high permeation rates for both O₂ and N₂ but no selectivity. This result was not surprising considering the appearance of the two-step membranes with white spots resulting from de-phasing of organic and inorganic phases. These

membranes are therefore not included in Table 4.8, which summarizes the performance of the other tested membranes.

The O₂ and N₂ permeabilities of the reference PPO shown in Table 4.8 are very close to the values previously reported by Chowdhury (2001) and Baker (2004). All four PPO coupons survived both gas permeation tests. This was not the case for the one-step EPMM membranes, for which, depending on the type of membrane only one or two out of four coupons survived both tests. However, the EPMM/aq/0.3/0 and EPMM/aq/0.2/0.1 membranes that survived both tests show very promising permeation properties. In particular, the oxygen permeability of EPMM/aq/0.3/0 and EPMM/aq/0.2/0.1 was approximately twice that of the reference PPO membranes, while the corresponding O₂/N₂ permeability ratios were similar to the reference PPO. An increase in permeability of more permeable gas without sacrificing the selectivity is always considered as very desirable departure from the trade-off relation between permeability and selectivity (Robeson, 2008). It is important to note, that EPMM/aq/0.3/0 and EPMM/aq/0.2/0.1 membranes showed the highest T_g s among all EPMM membranes synthesized in this research, and they had a double inorganic loading compared to the other one-step membrane (EPMM/aq/0/0.3) listed in Table 4.8. Interestingly, both the O₂ permeability and the O₂/N₂ permeability ratio of the latter membrane were lower than those of the reference PPO.

An increase in permeability of EPMM/aq/0.3/0 and EPMM/aq/0.2/0.1 membranes compared to the reference PPO is probably a result of an increase in free volume. According to Yampolskii et al. (2010), nano-sized inorganic fillers can disrupt molecular chain packing and eventually function as spacer materials. At the same time, strong

interactions between nano-particles and the chains of the host polymer prevent segmental rotations in this extra free volume, which becomes available for additional diffusion of the penetrant in membrane. According to Cornelius (2000), restricting chain segmental motion may lead to an increase in membrane selectivity. In addition, distributed nanoparticles may restrict the chain segmental motion and eventually increase the selectivity, which is not the case for the EPMM/aq/0.3/0 and EPMM/aq/0.2/0.1 membranes.

Table 4.8 Summary of gas permeation properties of the PPO and PPO-based EPMM membranes

	number of successful membranes	Parameters		
		O ₂ permeability coefficient (Barrer)	N ₂ permeability coefficient (Barrer)	O ₂ /N ₂ permselectivity (Barrer)
PPO membrane	4	15.16	3.27	4.63
		16.41	3.59	4.57
		15.72	3.41	4.61
		16.87	3.67	4.59
EPMM/aq/0.3/0.0	2	28.45	6.09	4.67
		25.73	5.6	4.59
EPMM/aq/0.2/0.1	1	26.98	5.99	4.5
EPMM/aq/0.0/0.3	2	12.07	3.6	3.35
		13.95	4.34	3.21

Considering this preliminary gas permeation results along with other physical characterizations of the one-step EPMM membranes, it would be desirable to increase the inorganic loading without compromising its quality.

Chapter 5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusions

The following is the list of main conclusions arising from this research project:

- It is possible to synthesize PPO-based EPMM membranes (one-step process in the environment of weak acid) with the superior properties compared to the reference PPO membranes. In the case of oxygen and nitrogen, gas transport properties are improved by nearly doubling the permeability of the more permeable oxygen, while maintaining the selectivity of the reference PPO membranes.
- Two-step process allows maximization of the conversion of TEOS and hence maximization of inorganic loading in the EPMM membranes, but the resulting membranes were defective due to poor compatibility between organic and inorganic phases.
- Combination of DSC, ^{29}Si NMR, ICP-MS, and gas permeation provides a complete characterization package that allows understanding of the phenomena taking place in the synthesis of EPMM membranes.
- The removal of unreacted TEOS and other liquid residuals requires heating the membranes at temperature considerable above the glass transition of the host polymer for an extended period of time (12 hours). Without this, it is impossible to establish the actual glass transition of the EPMM materials, the conversion of TEOS, and the representative gas transport properties.
- The roles of ethanol (compatibilizer) and n-octanol (surfactant) in conversion of TEOS depend on the viscosity of the continuous organic phase. In the case of one-step reaction, the presence of n-octanol improves the conversion of TEOS by maintaining the stability of the emulsion, but in the environment of viscous

polymer solution, it actually deteriorates the conversion by limiting the reaction to the interphase. It appears that while high viscosity of polymer solution decreases the rate of transfer of TEOS towards dispersed aqueous solution, it also helps to maintain the stability of the emulsion. The presence of the compatibilizer appears to be necessary in the case of one-step process in the environment of polymer solution. Overall, in the case of one-step process, high viscosity of the continuous organic phases leads to a significant decrease in the conversion of TEOS compared to the low viscosity environment of pure solvent.

- In the case of the two-step process, because of very fast hydrolysis in strong acidic conditions and very fast condensation in weak basic conditions, the viscosity of the continuous organic phase does not affect the conversion of TEOS.

5.2. Recommendations

The results obtained in this research project want further studies on the EPMM membranes. While obviously, these studies should go beyond the current polymer (PPO) and the inorganic precursor (TEOS), there are several points in the context of the current EPMM membranes which would be worth of further investigation.

- Separation of O₂ and N₂ is a difficult separation, which may not fully reflect the effect of inorganic loading in the host PPO membranes. Therefore, it is recommended extending the analysis of gas transport to include other gases such as CO₂, CH₄, and H₂. The current testing system allows the experiments involving gas mixtures as well as dynamic tests. These should be utilized to have

a better understanding of the reason(s) for increasing the permeability of EPMM membranes.

- Considering significant decrease in the conversion of TEOS in the environment of viscous polymer solution, it might be interesting to study the effect of PPO concentration in the solution on the conversion of TEOS when other experimental parameters are set constant. Along with this, a small decrease in the concentration of PPO would result in significant decrease in the viscosity of casting emulsion. Consequently, the new parameters for spin coating should be established for different viscosities of the casting emulsion.
- Ethanol, which was used as a compatibilizer and which is also produced as a by-product in the polymerization of TEOS, is more soluble in the aqueous phase than in TCE. Consequently, it tends to accumulate in the inorganic phase, which may have a detrimental effect on the conversion of TEOS because ethanol shifts the reactions to the left and furthermore it increases the size of inorganic droplets. It may therefore be beneficial to find another solvent (or an additive to the current solvent); which while still dissolving PPO had stronger interactions with ethanol. Along with the previous recommendation, a possibility of another compatibilizer and/or silica precursor might be considered in order for the compatibilizer to be different than the by-product of the polymerization of the inorganic precursor.
- Many membranes in the current studies were defective. Obviously, the issue of the defects must be eventually resolved. However, at this stage it would be worthwhile to laminate the membranes with a thin silicone rubber layer. This would allow distinguishing between a non-suitable morphology for gas separation

and random defects of otherwise attractive gas separation materials. The polymerization of TEOS in the basic environment resulted in the defective membranes. In the two-step process involving HCl and NH_4OH , it was impossible to achieve weak acidic conditions, such as those in the one-step process. Therefore, it might be worthwhile to consider a different acid-base system that would allow more gradual changes of pH when adding the base. Ultimately, it would be desired to design a two-step process with a fast hydrolysis at strong acidic condition and condensation at weak acidic conditions.

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APPENDIX A: pH MEASUREMENT

A.1 The effect of HCl droplets on pH of the acid-solution

Acidic solution prepared by adding different amount of HCl to the solution contains 7.5 and 5 mL of deionised water and ethanol respectively.

Table A.1 The effect of HCl droplets on pH of the acid-solution

Acid-solution sample NO.	HCl (mL)	pH	Acid-solution sample NO.	HCl (mL)	pH
1	0.011	2.28	16	0.178	1.1
2	0.022	2.22	17	0.189	1.07
3	0.033	2.15	18	0.2	1.03
4	0.044	2.03	19	0.211	1
5	0.056	1.94	20	0.223	0.98
6	0.067	1.83	21	0.234	0.97
7	0.078	1.71	22	0.245	0.95
8	0.089	1.65	23	0.256	0.93
9	0.1	1.56	24	0.267	0.92
10	0.111	1.45	25	0.284	0.89
11	0.122	1.38	26	0.289	0.87
12	0.134	1.33	27	0.3	0.84
13	0.145	1.26	28	0.311	0.8
14	0.156	1.21	29	0.323	0.79
15	0.167	1.17	30	0.334	0.76

A.2 The effect of NH_4OH droplets on pH of the base-solution

Basic solution prepared by adding different amount of NH_4OH to the solution contains 7.5 and 3.5 mL of deionised water and ethanol respectively.

Table A.2 The effect of NH_4OH droplets on pH of the base-solution

Base-solution sample NO.	NH_4OH (mL)	pH	Base-solution sample NO.	NH_4OH (mL)	pH
1	0.011	10.81	16	0.178	11.54
2	0.022	10.97	17	0.189	11.55
3	0.033	11.13	18	0.2	11.55
4	0.044	11.2	19	0.211	11.56
5	0.056	11.27	20	0.223	11.56
6	0.067	11.32	21	0.234	11.58
7	0.078	11.36	22	0.245	11.58
8	0.089	11.39	23	0.256	11.58
9	0.1	11.42	24	0.267	11.58
10	0.111	11.44	25	0.284	11.58
11	0.122	11.47	26	0.289	11.59
12	0.134	11.5	27	0.3	11.59
13	0.145	11.51	28	0.311	11.6
14	0.156	11.52	29	0.323	11.61
15	0.167	11.53	30	0.334	11.61

APPENDIX B: TEOS CONVERSION

B.1 Calculation of TEOS conversion in dried powders

The sample mass of S-1 (i.e. the mass of dried powder) = 0.0705 g

The net powder mass (i.e. the mass of reacted TEOS) = 0.0705 g - 0.0305 g = 0.04 g

$$\text{Mass fraction of Si in } Q^2 = \frac{28}{28 + 16 \times 3 + 1 \times 2} = 0.359$$

$$\text{Mass fraction of Si in } Q^3 = 0.4058$$

$$\text{Mass fraction of Si in } Q^4 = 0.4667$$

Molecular weight of TEOS = 208 g/mol

Density of TEOS = 0.94 g/mL

TEOS conversion by considering three hypothetical cases (Q^2 , Q^3 , and Q^4 forms):

$$\text{TEOS conversion in } Q^n = \frac{\text{Reacted TEOS}}{\text{TEOS Reactant}}$$

$$Q^2: \text{ TEOS conversion} = \frac{0.04g \times 0.359}{0.94g / mL \times 0.3mL \times \left(\frac{28g / mol}{208g / mol}\right)} = 0.3782$$

$$Q^3: \text{ TEOS conversion} = \frac{0.04g \times 0.4058}{0.94g / mL \times 0.3mL \times \left(\frac{28g / mol}{208g / mol}\right)} = 0.4276$$

$$Q^4: \text{ TEOS conversion} = \frac{0.04g \times 0.4667}{0.94g / mL \times 0.3mL \times \left(\frac{28g / mol}{208g / mol}\right)} = 0.4917$$

B.2 Calculation of inorganic loading and TEOS conversion in the PPO-based EPMM membranes

Taking 1 g of the synthesized PPO-based EPMM membrane:

Based on ICP-MS results for EPMM/aq/0.3/0: amount of Si = 0.7%

In 1 g membrane, the amount of Si = $0.007 \times 1 \text{ g} = 0.007 \text{ g}$

Mass fraction of Si in the forms of $Q^2 = 0.359$, $Q^3 = 0.4058$, and $Q^4 = 0.4667$

Inorganic mass in 1 g of membrane for three forms of Q^2 , Q^3 , and Q^4 are:

$$Q^2 = \frac{0.007}{0.359} = 0.0195 \text{ g}, Q^3 = 0.01725 \text{ g}, \text{ and } Q^4 = 0.015 \text{ g}$$

Inorganic loading for 1 g of PPO:

$$Q^2 = \frac{0.0195}{1 + 0.0195} = 1.93\%, Q^3 = 1.69\%, \text{ and } Q^4 = 1.48\%$$

Mass fraction of PPO in membrane:

$$Q^2: = 1 - \frac{0.007}{0.359} = 0.981$$

$$Q^3: = 0.983$$

$$Q^4: = 0.985$$

TEOS conversion by considering three hypothetical cases (Q^2 , Q^3 , and Q^4 forms) for 1 g PPO:

$$\text{TEOS conversion in } Q^n = \frac{\text{Reacted TEOS}}{\text{TEOS Reactant}} = \frac{\text{Amount of Si in product}}{\text{Amount of Si in reactant}}$$

$$\text{TEOS conversion in } Q^2 = \frac{0.007 \text{ g} / 0.981}{0.94 \text{ g} / \text{mL} \times 0.3 \text{ mL} \times \left(\frac{28 \text{ g} / \text{mol}}{208 \text{ g} / \text{mol}} \right)} = 0.188$$

$$\text{TEOS conversion in } Q^3 = 0.188$$

$$\text{TEOS conversion in } Q^4 = 0.187$$

APPENDIX C: ^{29}Si NMR SPECTRA

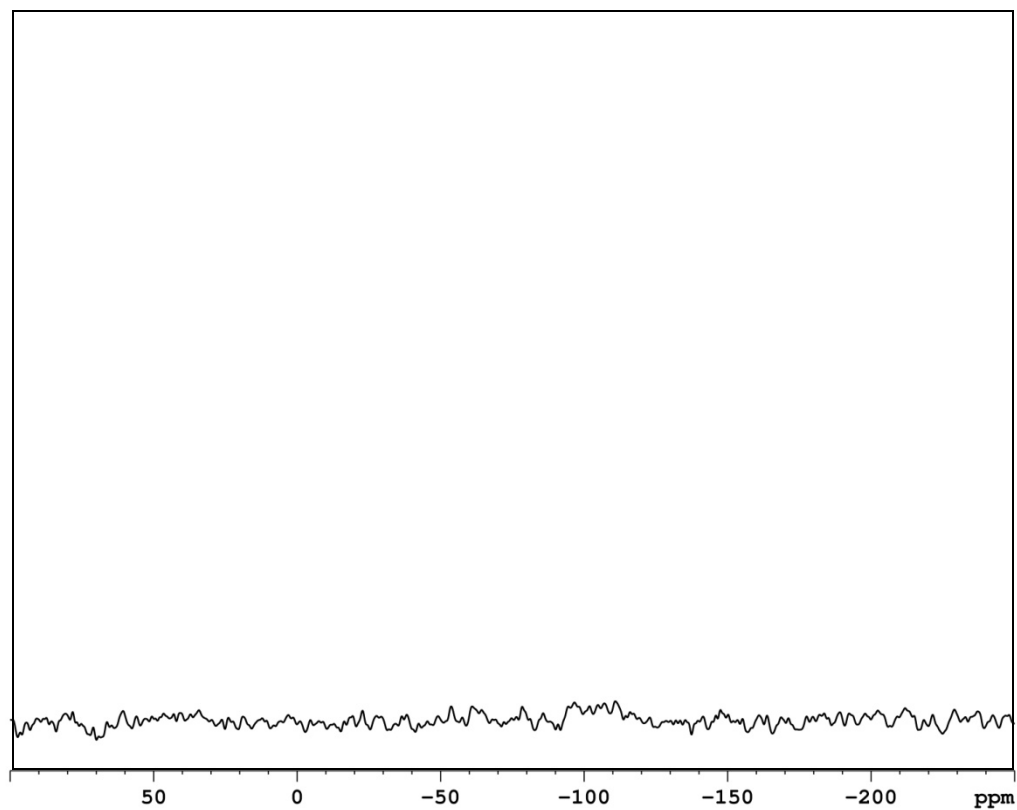
^{29}Si NMR spectrum

Figure C.1 ^{29}Si NMR spectrum of the EPMM/aq/0.0/0.3