Fabrication of hollow fiber membranes using amphiphilic block copolymers as pore-forming additives

Loh, Chun Heng

2014

Loh, C. H. (2014). Fabrication of hollow fiber membranes using amphiphilic block copolymers as pore-forming additives. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/55443>

<https://doi.org/10.32657/10356/55443>

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PORE-FORMING ADDITIVES

LOH CHUN HENG

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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PORE-FORMING ADDITIVES

LOH CHUN HENG

School of Civil and Environmental Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2014

ACKNOWLEDGEMENT

This thesis would not have been possible without the guidance and help of many people who contributed and extended their valuable assistance in the preparation and completion of this study.

First of all, I would like to express my gratitude to my supervisor, Associate Professor Wang Rong, for the support, guidance and advice she has extended to me throughout my study. I am sincerely and heartily grateful to her for her encouragements and patience. It would not have been possible without her help.

I sincerely thank Prof. William B. Krantz (visiting professor Singapore Membrane Technology Centre (SMTC)) for the helpful workshops and suggestions regarding to the communication skills, Prof. Anthony G. Fane as the SMTC director; and qualification exam reviewer committee, Prof. Ng Wun Jern, Associate Prof. Tang Chuyang and Prof. Hu Xiao, for their kind suggestions and comments.

It is my pleasure to thank everyone for their help, support and sharing throughout my research work. I would like to thank Dr. Shi Lei, Dr. Sunee Wongchitphimon, Dr. Laurentia E.K. Setiawan, Mr. Zhang Lizhi, and Mr. Chou Shuren for their many valuable advices and discussions, Dr. Shi Lei for his guidance in various instruments trainings, and SMTC Laboratory Manager Dr. Chong Tzyy Haur for his involvement and guidance in laboratory safety and equipment purchasing.

Many thanks are also due to FYP students: Mr. Li Guoliang (2010), Ms. Kuah Hui Mun (2011) and Ms. Koh Bao Yur (2012) for their diligent assistance.

I am thankful to Mrs. Lim Tay Chew Wang, Mr. Aidil Bin Md Idris, Mrs. Koh Tang Lai Sim, Mr. Tan Han Khian, Ms. Maria Chong Ai Shing, Ms. See Shen Yen, Pearlyn and other staffs in CEE Environmental Laboratory for helping me out with various purchasing and equipment usage.

It is difficult to find words to express my appreciation to my friends and colleagues for their lovely companionships and helps. Special thanks to my office and lab buddies as well as my group mates: Xuesong, Zhang Yuan, Zuo Guangzhi, Wang Penghua, Liao Yuan, Tiao Miao, Chen Guizi, Yao Lei, Liu Chang, Stanislaus Raditya Suwarno, Teo Chee Wee, Dr. Yang Xing, Dr. Rajabzadeh K. Saeid, and Dr. Yogesh B. Singh. It is my pleasure to be part of SMTC family so that I have had an enjoyable PhD life.

I also would like to acknowledge the Environment and Water Industry Programme Office (EWI) of Singapore for funding the project (EWI RFP 0904 IRIS-02-03). I am also grateful to Nanyang Technological University for providing my scholarship and to the SMTC for providing the necessary facilities.

Last but not least, this thesis is dedicated to my beloved parents: Chua Hooi and Ong Ah Eng and my brothers and sisters: Loh Chun Hiang, Loh Chun Hao, and Loh Wan Theng, who always support me in my endeavors, always give me strength and encouragement to pursue my dreams and never leave me in doubt of their love for me.

Loh Chun Heng

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- Loh, C. H. and R. Wang (2013). •Insight into the role of amphiphilic pluronic block copolymers as pore forming additive in PVDF membrane formation 1st International Conference on Desalination using Membrane Technology, Sitges, Spain, 7-10 Apr 2013 (Oral presentation).

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LIST OF ABBREVIATION S

Abbreviation	Description
ATR	attenuated total reflectance
BSA	bovine serum albumin
CA	celluloseacetate
CMC	critical micelle concentration
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DMSO	dimethylsulphoxide
EO	oxyethylene / ethylene oxide
FE-SEM	field emission scanning electron microscope
FTIR	Fourier transform infrared spectroscopy
GPC	gel permeation chromatography
HMPA	hexamethylphosphoramide
IPA	2-propanol
MF	microfiltration
MWCO	molecular weight cutoff
NF	nanofiltration
NIPS	nonsolventinduced phase separation
NMP	N-methyl-2-pyrrolidone
PA	polyamide
PAN	polyacrylonitrile
PC	polycarbonate
PEEK	polyether ether ketone
PEG	polyethylene glycol
PEI	polyetherimide
PEO	poly(ethylene oxide)
PES	polyethersulfone
PFSA	perfluorosulfonic acid
PI	polyimide

PO	propylene oxide
POEM	poly(oxyethylenemethacrylate)
PP	polypropylene
PPESK	poly(phthalazine ether sulfone ketone)
PPG	polypropylene glycol
PPO	poly(propylene oxide)
PSf	polysulfone
PTFE	polytetrafluoroethylene
PVDF	poly(vinylidene fluoride)
PVP	poly(vinyl pyrrolidone)
PWP	pure water permeation
RO	reverse osmosis
SEM	scanning electron microscope
SMM	surface modifying macromolecule
TEP	triethyl phosphate
TIPS	thermally induced phase separation
TMP	trimethyl phosphate
TMU	tetramethylurea
TOC	total organic carbon
UF	ultrafiltration
XPS	X-ray photoelectron spectroscopy

ABSTRACT

The use of additives is an important mean to tailoring the membrane structures and properties during membrane fabrication. Amphiphilic Pluronic triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) have received much attention recently due to their unique behavior, such as high surface activity and micellization in water, which potentially change the surface properties and pore structure of membranes. However, the mechanism of membrane formation with the presence of amphiphilic polymers is still not fully understood. Therefore, a more comprehensive investigation on the role of amphiphilic polymers in membrane formation is required before they can become potential alternatives to the conventional additives.

A systematic study has been firstly carried out to investigate the effect of Pluronic copolymers with different molecular architectures and contents as a pore forming additive on the fabrication of polyethersulfone (PES) ultrafiltration (UF) hollow fibers, and to identify the most preferential features of Pluronic for making high-performance membranes. It is observed that the pure water permeation (PWP) and molecular weight cutoff (MWCO) of the as-spun hollow fibers are dependent on the structure of the additives. Among all the membranes spun with 5 wt% additives, the hollow fibers spun using Pluronic F127 (EO₁₀₀, PO₆₅, EO₁₀₀, where EO is ethylene oxide, PO is propylene oxide) and F108 (EO₁₃₂, PO₅₀, EO₁₃₂) as the additives possess the highest PWP, the lowest MWCO, and the narrowest pore size distribution. It is possible that due to the long PPO and PEO blocks in these Pluronic, PEO brush layer that reduces the apparent membrane pore size has formed on the internal pore surface and hence the solute rejection of the resultant membranes is improved. When Pluronic F127 concentration was 10 wt%, the as-spun hollow fiber exhibited the highest PWP of 114 L/m²·h·bar and the lowest MWCO of 9 kDa.

Due to the good performance of Pluronic F127 in PES membrane fabrication, it has been selected as the amphiphilic additive to further study the formation of poly(vinylidene fluoride) (PVDF) membranes. In this work, the

fundamental study has been carried out on flat sheet membranes instead of hollow fibers because the former involve less fabrication parameters. The surface tension-concentration curve reveals that no micelles are formed in Pluronic F127 in N-methyl-2-pyrrolidone (NMP) solutions while the thermodynamics and kinetics are found to be similar for the systems containing Pluronic and polyethylene glycol (PEG), respectively. Based on the characteristics of the prepared membranes, Pluronic shows a stronger pore-forming ability than PEG. Instead of the commonly used concept of instantaneous or delayed demixing, it is believed that the stronger pore-forming ability of Pluronic is caused by the hydrophobic interaction between Pluronic and PVDF that delays the solidification process. The loss of Pluronic after 2-propanol treatment causes an increase in water permeation and a decrease in rejection, further proving that the presence of Pluronic on the membrane pore surface can narrow down the pore size.

Pluronic F127 has also been used as the additive to fabricate PVDF hollow fiber membranes. However, tremendous growth of macrovoids is observed in the fibers prepared with Pluronic, even with a concentration as low as 1 wt%. The big macrovoids in hollow fibers are unfavorable to the mechanical strength. Therefore, a second additive which is either LiCl or water has been added together with Pluronic in the spinning dope to examine the synergetic effects of mixed additives on macrovoid formation. The macrovoid growth is suppressed when either LiCl or water is used as the second additive. An increase in PWP and MWCO and an enhancement in mechanical properties can be observed for the fibers prepared with water as the second additive. On the other hand, the addition of LiCl causes an increase in PWP yet a decrease in MWCO of the resultant fibers. However, the mechanical strength is not improved by the addition of LiCl.

A stability study has been carried out on PVDF/Pluronic membranes and Pluronic is observed to be not completely stable in PVDF membrane matrix in long term. Considering this stability issue, as well as the strong pore-forming ability of Pluronic F127 and the effectiveness of Pluronic/LiCl mixed additive to form smaller surface pores as observed in the above PVDF study, the Pluronic/LiCl mixed additive consisting of a very low concentration of Pluronic has been used in

further study which investigated the effects of spinning conditions on PVDF hollow fiber fabrication. It is found that the use of merely 20 wt% of Pluronic is sufficient to impose significant impacts on the morphology, filtration performance, and mechanical properties of the resultant fibers. Hollow fibers spun using higher coagulant temperature, higher take speed, and water as the bore fluid exhibit better mechanical properties and filtration performance. PVDF hollow fiber membranes with PWP of 118 L/m²·h·bar and MWCO of 5 kDa were obtained when spun with optimized spinning conditions and using 3 wt% of LiCl and 0.2 wt% of Pluronic as the mixed additive. The fibers can withstand a pressure of 5.5 bar from the lumen.

In conclusion, this study provides a better understanding on the role of amphiphilic Pluronic block copolymers as an additive in membrane formation based on the studies on the fundamental mechanisms of membrane formation, the effects of block copolymers on apparent membrane pore size, the synergetic effects of mixed additives, and the influence of spinning conditions. This expands the current list of additives used in membrane fabrication where amphiphilic polymers are revealed to be potential alternatives to the conventional additives preparing membranes for various applications.

CHAPTER 1. Introduction

1.1. Background

The original meaning of membrane, is the skin that covers the separate members of the body (Webster's Online Dictionary 2006). In modern world, membrane can refer to either a biological membrane or a synthetic membrane. A biological membrane is a selective barrier around or within a cell and carries out very complex tasks in living organisms, frequently using active transport. On the other hand, a synthetic membrane also acts as a selective barrier between two phases but its function is not as complicated. In addition, the transport through synthetic membranes is normally passive, which means external driving forces are required to achieve certain tasks. Synthetic membranes have been widely used in separation processes involving sea water, brackish water, gases, vapors, bioproducts, food products etc., for decades.

Synthetic membranes can be classified by the materials, fabrication methods, structures, sieving size, applied driving force or applications. Based on the size range of particles being retained, membranes can be classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), as shown in Figure 1-1. In terms of applications, these four terms usually refer to pressure driven membrane processes involving water-based media. In addition to these processes, there are a number of different membrane processes such as gas separation, pervaporation, membrane distillation, dialysis, electrodialysis, forward osmosis, and pressure retarded osmosis. Different driving forces such as pressure, concentration, and temperature difference as well as chemical and electrical potentials are applied depending on the processes.

Different configurations of membranes are available such as flat sheet (many in spiral wound modules), tubular, and hollow fiber. Flat-sheet membranes in spiral wound modules provide large surface area per volume but that configuration can induce high pressure drop due to the friction created when the liquid flows along the space (Verissimo et al. 2005). Tubular modules are less

susceptible to fouling but they are expensive and have low packing capacity (Mulder 1996). Compared with tubular and spiral wound modules, hollow fiber modules have a higher packing capacity, which means they provide a larger area for separation to take place in a given volume. In addition, the configuration of hollow fibers makes them able to withstand a certain back pressure, thus extend the options of backflushing (Frank et al. 2001, Setiawan 2012). Therefore, there is a higher flexibility for the system design and operation of membrane processes using hollow fibers.

Figure 1-1. Classification of membranes according to their sieving size [figure adopted from (Mueller et al. 2011)]

Depending on the membrane processes and operating environment different types of hollow fiber membranes are to be fabricated. Nowadays, most of the hollow fibers are fabricated by polymeric materials via nonsolvent phase separation technique. In general, the hollow fiber membranes need to be highly permeable, highly selective, resistant to chemical, thermal, and mechanical stresses, and less susceptible to fouling. A large number of studies have been carried out to prepare hollow fibers with these desired properties through various means such as exploring various materials (Sliem et al. 2010, Wu et al. 2010), adding additives (Zhao et al. 2007, Carlos Mierzwa et al. 2012), changing fabrication

conditions (Yang et al. 2007, Tang et al. 2012) and carrying out posttreatments (Qin et al. 2005a, Khulbe et al. 2010). Among these, the choice of membrane materials is crucial for actual applications because it determines the chemical and thermal resistance of resultant membranes. Polyethersulfone (PES) and poly(vinylidene fluoride) (PVDF) are two of the most commonly used polymers in the preparation of hollow fibers for MF and UF applications. While both materials have good thermal stability and mechanical properties, PVDF has higher chemical resistance and hydrophobicity than PES. This makes PVDF a potential candidate in applications of membrane contactor, membrane distillation, and applications involving harsh environment (Liu et al. 2011).

While material selection determines the stability of membranes towards working environment, the choice of additives can highly affect membrane permeability and selectivity. The use of additives is a convenient and versatile tool for tailoring membrane structures and properties. When an additive is added into a polymer solution, the thermodynamics or kinetics of the system are altered. Consequently, the structure of prepared membranes is affected due to the change in membrane formation pathway. A wide range of additives has been studied in membrane preparation and they were observed to behave very differently in the phase inversion process. In order to fulfill different requirements on membranes used in various applications, the exploration of new additives is still ongoing. Amphiphilic polymers, which consist of at least a hydrophilic segment and a hydrophobic segment, have recently received much attention as additives in polymeric membrane preparation due to their unique behavior in the membrane system (Qian et al. 2007, Zhao et al. 2008a, Rahbari-Sisakht et al. 2012). Unlike conventional hydrophilic additives, amphiphilic polymers show not only pore forming but also surface-modifying ability (Zhao et al. 2008a). In addition, it is believed that homopolymers and amphiphilic polymers interact with membrane materials differently and thus membranes with different properties and structures can be formed (Liu et al. 2013).

The behavior of amphiphilic polymers especially those commercially available ones in aqueous solution has been well studied. However, there is still a

lack of information on how the amphiphilic polymers behave in organic solvent and interact with other polymers. It is expected that the interaction between the amphiphilic polymer and the membrane polymer in a solution and in the resultant membrane is one of the key factors determining the membrane's final performance. Therefore, a more comprehensive understanding on the role of amphiphilic polymers in membrane formation is required before they can become potential alternatives to the conventional additives when preparing membranes for a specific application.

1.2. Objectives

This study aims to understand the role of amphiphilic block copolymers as the additives in hollow fiber membrane formation. PES and PVDF have been selected as the membrane materials in this study since both of the polymers are among the most commonly used materials for separation applications. The primary objectives of the study are

- (1) to investigate the effects of different types of amphiphilic block copolymers on PES hollow fiber membrane properties
- (2) to understand the mechanism for PES and PVDF membrane formation when amphiphilic block copolymers are used as an additive
- (3) to examine how the presence of amphiphilic block copolymers impacts PVDF membrane performance;
- (4) to control the macrovoid formation of PVDF hollow fiber membranes using amphiphilic block copolymers as an additive
- (5) to develop PVDF hollow fiber membranes with high permeability and selectivity, as well as good mechanical strength, by using appropriate amount of amphiphilic block copolymers in the polymer dope and optimizing the spinning conditions

1.3. Thesis outline

This thesis contains seven chapters, which are highlighted as follows:

- Chapter 1: Introduction „ the background and objectives of the study are provided.
- Chapter 2: Literature Review- This chapter is categorized into two parts. The first part provides an introduction to polymeric membrane preparation techniques in particular nonsolvent-induced phase separation. The dope formulation and spinning conditions allow fiber membrane fabrication and are discussed. The second part of the literature study reviews the preparation of polymeric membranes using amphiphilic polymers. A more specific review on the properties of commercially available block copolymers, Pluronic, and their usage in membrane fabrication are also included.
- Chapter 3: Fabrication of PES Hollow Fiber Membranes Using Amphiphilic Pluronic Block Copolymers as Pore-forming Additives - As a preliminary study aiming to understand the roles of amphiphilic block copolymers as an additive in membrane formation, this chapter investigates the effects of different types of Pluronic on the formation of PES hollow fiber membranes. Preferential features of Pluronic have been identified for making high performance hollow fiber membranes.
- Chapter 4: Fundamental Study on the Role of Pluronic as an Additive in PVDF Membrane Formation, This chapter aims to understand the mechanism of PVDF membrane formation when Pluronic is used as the additive. The effects of Pluronic and PEG on membrane formation have been compared. Pluronic has also been intentionally washed out to examine how the presence of Pluronic affects membrane performance.
- Chapter 5: Effects of Second Additives on the Properties of PVDF/Pluronic Hollow Fiber Membranes „ The synergetic effects of mixed additives, which comprise Pluronic and a second additive, on PVDF hollow fiber membrane formation have been investigated. The

filtration performance and mechanical properties of the resultant membranes have been tested.

Chapter 6: Stability of PVDF/Pluronic Membranes and the Use of Low concentration Pluronic in PVDF Hollow Fiber Spinning,, The long-term stability of Pluronic in PVDF membrane matrix has been examined. Mixed additives, which consist of LiCl and low concentration of Pluronic, have been used to fabricate PVDF hollow fiber membranes. Spinning conditions have been varied to obtain high-performance PVDF hollow fibers.

Chapter 7: Conclusions and recommendations, In this chapter, the important conclusions in this study are provided and future works to be carried out are recommended.

CHAPTER 2. Literature Review

2.1. Synthesis of polymeric membranes

Being the most important component in any membrane separation process, the membrane serves as a barrier to separate two phases and selectively permits the passage of certain components in a specific manner (Lonsdale 1989). The materials used to prepare membranes include polymers, ceramics, liquids, metals, and glass. Among these, polymeric membranes are most commonly used in various applications due to their low cost and superior properties. Depending on the types of polymers used and the desired membrane structures, polymeric membranes can be fabricated by various techniques including casting, stretching, track etching, and phase inversion (Mulder 1996). While the first three techniques mainly produce membranes in the microfiltration (MF) range (pore size of 0.05–20 μm), membranes with a very wide range of pore size (0.001–10 μm) can be obtained via phase inversion. In addition, the preparation of membranes by phase inversion can be done using a large variety of polymers. The prepared membranes can be further modified by dipcoating, interfacial polymerization, plasma polymerization, etc. to produce composite membranes. To date, phase inversion is the most important technique for commercial membrane production.

2.1.1. Phase inversion

The first asymmetric membrane by phase inversion technique was developed by Loeb and Sourirajan using cellulose acetate in 1963 (Loeb and Sourirajan 1963). Until now, the materials used for membrane production via phase inversion have been extended to various synthetic polymers such as polyacrylonitrile (Yin et al. 2012), poly(etherimide) (Zhang et al. 2012), polysulfone (Ohya et al. 2009), polyethersulfone (Idris et al. 2007), and Poly(vinylidene fluoride) (Wang et al. 2011). In phase inversion, a polymer with typical concentration of 1–25% by weight is dissolved into a solvent or solvent mixture, and the final solution is a homogeneous dope for membrane synthesis. The dope is then subjected to demixing

(i.e., phase separation) by applying some conditions such as changing the temperature or composition of the system. In thermodynamic point of view, the mixing and demixing of the solution is controlled by the Gibbs free energy change during the process, which can be expressed (Mulder 1996):

$$\Delta G_M = \Delta H_M - T \Delta S_M \quad (2.1)$$

where ΔG_M is the Gibbs free enthalpy of mixing, ΔH_M the enthalpy of mixing, ΔS_M the entropy of mixing. The mixing process is spontaneous if $\Delta G_M < 0$.

To minimize the Gibbs free energy of mixing in the system, a thermodynamically unstable solution will undergo demixing in which a single phase liquid solution separates into a polymer-rich phase and a polymer-poor phase. After the polymer-rich phase is solidified by crystallization, gelation, or vitrification, it forms the matrix of membrane while the polymer-poor phase forms the membrane pores (Mulder 1996; Ren and Wang 2010). There are different approaches to prepare asymmetric polymeric membranes via phase inversion process, including:

- (1) Thermally induced phase separation (TIPS), in which a polymer solution is prepared at a high temperature and demixing is induced by cooling down the homogenous solution;
- (2) Nonsolvent-induced phase separation (NIPS), in which a change in a local composition of the polymer solution is induced by diffusion of solvent or nonsolvent between the solution and its external environment. The change in composition will lead to demixing and precipitation.

NIPS of a homogenous polymer solution can be induced by (1) immersion precipitation: immersion of the polymer solution into a nonsolvent bath such that solvent/nonsolvent exchange occurs; (2) vapor absorption: the absorption of nonsolvent by the polymer solution when it is subjected to a vapor containing nonsolvent until precipitation; (3) solvent evaporation: evaporation of a volatile solvent from a polymer solution containing two or more solvents of different volatility (Ren and Wang 2010).

a. Thermodynamics of immersion precipitation

In this thesis the membranes will be mainly prepared via the immersion precipitation technique. The technique involves at least 3 components: polymer, solvent, and nonsolvent and can be rationalized with the aid of an isothermal phase diagram as shown in Figure 2-1. A typical homogenous polymer dope prepared for membrane fabrication falls within Region I, which represents a stable one-phase state. Once the polymer dope is immersed into a nonsolvent bath, the nonsolvent starts to diffuse from the bath into the dope while the solvent in the dope diffuses out. After a period of time the solvent/nonsolvent exchange process brings the dope into Region II, a thermodynamically unstable state. In this region, the dope undergoes liquid-liquid demixing in which two separate phases (polymer rich and polymer lean phase) are formed. The solidification of the polymer phase occurs in either region III or IV. Region III is a solid-liquid two phase state in which the polymer is swollen in a mixture of solvent/nonsolvent. In region IV, the polymer chains are frozen in a glassy state (Mulder 1996 Ren and Wang 2010).

Figure 2-1. Isothermal phase diagram of a ternary system for immersion precipitation process (figure adopted from (Ren and Wang 2010))

The structure of membranes prepared via immersion precipitation is determined by the precipitation path as shown schematically in Figure 2-2. In the case of solvent evaporation, the polymer solution undergoes a glass transition and a

glassy and dense film is formed. (path 1) For immersion precipitation process, the membrane formation follows path 1-2, 2-2, or 2-3 which is dependent on the relative rate of solvent out-diffusion to non-solvent in-diffusion. For path 2-1 and 2-3, the system was first brought into a metastable zone (located between the binodal and spinodal curve) where liquid-liquid demixing is mainly based on nucleation and growth mechanism. Nascent membrane with continuous polymer matrix and dispersed pores is formed due to the nucleation and growth of polymer lean phase in the case of path 1-2. In contrast, nucleation and growth of polymer rich phase occurring in path 2-3 results in low integrity powdery agglomerates which is not a practical membrane structure. On the other hand, if the demixing path goes directly into the unstable region (path 2-2), liquid-liquid demixing occurs via spinodal decomposition mechanism, leading to a interpenetrating network of polymer-rich and polymer-lean phases (Kimmerle and Strathmann 1999, Mulder 1996, Ren and Wang 2010).

Figure 2-2. Schematic diagram of membrane formation in different precipitation paths [figure adopted from (Ren and Wang 2010)]

The demixing process can be described based on the interval between the immersion of dope into the coagulant (nonsolvent) and the onset of liquid-liquid demixing. Instantaneous demixing refers to the process in which liquid-liquid demixing begins immediately after the immersion of dope into the coagulant

whereas it takes some time before the dope undergoes demixing in the case of delayed demixing (Mulder 1996 Ren and Wang 2010). Thermodynamically instantaneous demixing occurs if the initial homogeneous solution is relatively close to its metastable/unstable state, otherwise the system undergoes delayed demixing. Generally, instantaneous demixing produces membranes with thin skin layer and highly porous (normally with the presence of macrovoids) substructure, while membranes with spongelike structure are formed if delayed demixing occurs. An example on how instantaneous and delayed demixing affects membrane structure is demonstrated in the following section.

b. Kinetics of immersion precipitation

Although membrane formation is highly related to the thermodynamics of the involved system, the kinetics of the phase inversion process have also found to govern the final membrane structure in many cases (Kasay et al. 2002a Wongchitphimon et al. 2011). The kinetics normally refer to the rate of solvent-nonsolvent exchange during phase inversion. If the exchange rate of solvent-nonsolvent is slow, the onset of liquid-liquid demixing of the system will be delayed. In other words, delayed demixing can occur even though a homogeneous system is thermodynamically close to the nodal or spinodal curve.

During phase inversion, the solvent diffusion velocity (V_{out}) is always larger than the nonsolvent diffusion velocity (V_{in}) as evidenced by the smaller thickness of final membrane compared with the initial thickness of polymer dope (Wang and Ma 2012). The explanations include the much higher viscosity of dope than that of coagulant, the mass transfer resistance generated by the formation of outermost skin layer, and the better affinity between polymer-solvent than polymer-coagulant. Based on the concept that V_{out} is predominantly higher than V_{in} , Wang and Ma proposed that V_{in} should be a controlling factor that determines the membrane structure when kinetics dominate the system (Wang and Ma 2012).

The relationships between thermodynamics, kinetics, (and membrane structures can be demonstrated by the presence of a typical hydrophilic nonsolvent additive in the polymer dope, as shown in Figure 2-3 and Figure 2-4. With

increasing additive concentration, the thermodynamic stability of the dope tends to be reduced while V_{in} is increased because of the higher hydrophilicity of the dope. Both the thermodynamic and kinetic factors facilitate instantaneous demixing which changes the membrane morphology from sponge structure (S or S>M in Figure 2-4) to macrovoid structure (M>S or M in Figure 2-4). However, when the additive concentration exceeds a certain amount, dope viscosity becomes so high that the in-diffusion of nonsolvent is highly restricted. Hence, V_{in} becomes lower and delayed demixing occurs because the kinetic starts to predominate over thermodynamics of the system. As a result, the membrane morphology changes gradually from macrovoid structure (M or M>S in Figure 2-4) back to sponge structure (S>M or S in Figure 2-4). For systems containing semicrystalline polymer, particulate structure (S+P or P in Figure 2-4) may form due to crystallization when liquid-liquid demixing is delayed (Wang and Ma 2012).

Figure 2-3. Schematic depiction of the effects of additive on nonsolvent diffusion velocity on membrane structure [figure adapted from (Wang and Ma 2012)]

c. Macrovoid formation

It is well known that macrovoids are normally formed when instantaneous demixing occurs as mentioned in previous parts, but the mechanism of macrovoid formation is still under debate. In the literature, the initiation and growth of macrovoids has been described by various mechanisms such as interfacial hydrodynamic instability induced by surface tension gradient (Matz 1972), osmotic

pressure in polymer-lean nucleus (McKelvey and Koros 1996) shrinkage of polymer matrix (Strathmann and Kock 1977) and excess intermolecular potential gradients caused by concentration gradients (Ray et al. 1985).

Figure 2-4. Typical types of morphology of phase conversion membranes included in Figure 2-3 (M: fully macrovoids; M>S: mainly macrovoids with some sponge structure; S>M: mainly sponge structure with some macrovoids; S: fully sponge; S+P: mixture of sponge and particulate structures; P: particulate structure) adopted from (Wang and Ma 2011).

Once a polymer dope is immersed in coagulant, exchange of solvent and nonsolvent occurs immediately at the coagulant-membrane interface and phase separation takes place. According to McKelvey and Koros, a planar front (i.e., interface between phase separation region and homogeneous dope) gradually migrates inward from the outermost interface at a rate proportional to $1/\text{time}^2$ (McKelvey and Koros 1996). At a given location in the nascent membrane, the composition changes with time. If the composition lies within the unstable region on the phase diagram, nucleation and growth of polymer-lean phase will start to take place. In general, a nucleus grows isotropically due to the diffusion of

solvent from the surrounding environment until the nucleus wall is solidified (Figure 2-5 A).

Figure 2-5. Schematic diagram for macrovoid growth [figure adopted from Li 2005]

In the case where a nucleus is in contact with the moving front of phase separation region, the rate of solvent/nonsolvent exchange at the back side of the nucleus is dramatically enhanced (Figure 2-5 B). Due to the inflow of nonsolvent from the back side, the osmotic pressure in the nucleus increases significantly which fastens the inflow of solvent from the front side of the nucleus. Both inflow of solvent and nonsolvent enlarge the volume of the nucleus. However, the composition inside the nucleus is not uniform where the back side has more nonsolvent, which causes the wall at the back side of the nucleus to become more rigid while the front side of the nucleus is still highly plasticized. Consequently, the nucleus cannot expand isotropically but grows towards the front side forming a tear-like shape. Finally, a macrovoid is formed by continuous growing of the nucleus until the rest part of the wall becomes solidified (McKelvey and Koros 1996; Li 2005).

2.1.2. Dope formulation in membrane fabrication

a. Polymer materials

By using NIPS technique, polymeric membranes have been prepared from various materials such as cellulose acetate (CA), polysulfone (PSf), polyethersulfone (PES), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyetherimide (PEI), polycarbonate (PC), polyamide (PA), polyimide (PI), polyether ether ketones (PEEK), and poly(phthalazine ether sulfone ketone) (PPESK) (Wang and Ren 2008). Among these, PSf, PES, and PVDF are more commonly used in the fabrication of commercial MF and UF membranes. Their structures are shown in Figure 2-6 and their properties are briefly introduced as follows.

Figure 2-6. Chemical structure of PSf, PES, and PVDF

Polysulfone and polyethersulfone

Both PSf and PES are amorphous polymers with glass transition temperature of 195°C and 230 °C, respectively. Compared with many other commonly used polymers such as CA and PAN, these polymers have higher chemical resistance, better tolerance to high temperatures, stability over a wide range of pH, and high processability. Hence, they are widely used to make MF/UF membranes and can be the support layer of composite membranes. Although PSf and PES membranes demonstrate good chemical resistance to alcohols, acids, and aliphatic hydrocarbons, they display low tolerance to ketones and aromatic hydrocarbons (Wang and Ren 2008; Amirilargani et al. 2011). When comparing PES with PSf,

PES shows a higher affinity to water because it is more polar. As a result, PES has been shown to be a more suitable candidate for separation involving water media while PS might be more suitable for gas application (Barth et al. 2000).

Poly(vinylidene fluoride)

PVDF is a semicrystalline polymer with glass transition and melting temperatures of 40 °C, -30 °C and 155, 192 °C, respectively. The low glass transition temperature implies that PVDF is in rubbery state at room temperature, making this polymer highly ductile. Typically, PVDF has three different types of crystal phases named α , β , and γ . α and β form nonpolar and polar (all-trans) conformation, respectively, while γ form has an intermediate polar conformation. PVDF is typically 50-70% crystalline and its crystallinity is determined by various factors including polymerization rate, cooling rate, molecular weight, and molecular weight distribution. PVDF demonstrates good mechanical and thermal stability, and has high chemical resistance to most organic solvents except those that are highly polar. In addition, PVDF can undergo dehydrofluorination in concentrated alkaline solution. Due to the hydrophobic nature, PVDF membranes are suitable in membrane distillation and membrane contactor applications. However, the hydrophobicity of PVDF is undesirable in some applications as it may lead to higher fouling tendency. Therefore, surface modification of PVDF to enhance its hydrophilicity has also been widely studied (Roussel et al. 1992; Ameduri 2009; Liu et al. 2011).

b. Polymer concentration

The membrane morphology is highly influenced by the concentration of polymer in the dope solution. Generally, a membrane prepared from a dope containing a higher polymer concentration possesses a denser skin and lower porosity support which in turn reduces the membrane permeation and enhances the selectivity (GarcíaPayo et al. 2009; Choi et al. 2010).

The polymer concentration highly affects the dope viscosity, which is a very important parameter that affects membrane fabrication process. Generally, the

viscosity of dope for hollow fiber spinning should be high enough to ensure a stable and continuous flow from the spinner during the spinning process. The critical polymer concentration can be determined by plotting the relationship of dope viscosity versus polymer concentration (Li et al. 2002). Above the critical concentration, the slope of the plot dramatically increases due to different degrees of polymer chain entanglement, as shown in Figure 2-7. The polymer concentration used for hollow fiber membrane spinning is normally chosen to be close to the critical value.

Figure 2-7. Critical concentration for a polymer dope [figure adopted from (Li et al. 2002)]

c. Solvents

To prepare a homogeneous dope for membrane fabrication, a polymer must be dissolved in a suitable solvent. The relative affinity between a solvent and a polymer can be assessed using Hansen's three dimensional solubility parameters expressed as (Matsuura 1994)

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2.2)$$

where d_t is the solubility parameter of a polymer or solvent, d_D , d_P , and d_H represents the dispersion interaction, polar bonding, and hydrogen bonding components for the solubility parameter, respectively. Basically, the solubility of a polymer in a solvent is better if the solubility parameter difference (Δd) between them is smaller.

It has been observed that the choice of solvent could affect the formation of a membrane and hence its performance. Bottino et al. (1991) used eight different solvents, including N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethylsulphoxide (DMSO), N-methyl-2-pyrrolidone (NMP), hexamethylphosphoramide (HMPA), tetramethylurea (TMU), triethyl phosphate (TEP), and trimethyl phosphate (TMP), to prepare PVDF microporous membranes. The water flux and porosity of the resultant membranes were observed to be highly related to the solvent used. The effect of solvent types on water flux and porosity was in the sequence of HMPA > DMSO > NMP > TEP > DMAc > DMF > TMU, while the water flux of membranes produced from the last 4 types of solvents is extremely small compared with the others. The phenomenon was explained by the different mutual diffusivity of the solvent and coagulant (water) used.

After Bottino, comparisons have also been made between DMAc and NMP in membrane fabrication by other researchers as these solvents are among the most commonly used. In preparation of PVDF hollow fibers for gas separation, the resultant membranes possessed smaller finger-like macrovoids and smaller pore size when DMAc was used as the solvent (Choi et al. 2010). This observation is in accordance with the study by Bottino et al. Another study reported a similar observation on the size of macrovoids of PES membranes prepared with DMAc and NMP as the solvent. It was believed that in PES/DMAc/water system the polymer rich phase vitrified earlier than that in PES/NMP/water system. As a result, macrovoid growth in the former system was suppressed (Saeidi and Sadatnia 2008).

By using TEP as the solvent, the growth of macrovoids in PVDF hollow fibers was completely suppressed, which was favorable to enhance mechanical strength. However, a much thicker skin layer was formed compared with DMAc

based membranes. Formation of such thick skin layer is unfavorable to water permeation, but it could be improved by other means such as the addition of pore forming additives (Abed et al. 2012)

d. Additives

Among various strategies used to control membrane structure, the addition of nonsolvent additives into a polymer dope solution has been found to be an effective and simple method for adjusting the pore size and porosity of membranes. A wide range of additives has been used as pore-forming additives in membrane fabrication, which includes polymer/macromolecules, organic molecules, inorganic salts or acids, weak cosolvents, and strong solvents. They cause different changes on the properties of polymer dope and hence demonstrate various functions on membrane formation. Selected additives are discussed in the following paragraphs.

Polymeric additives

Polymeric additives such as polyethylene glycol (PEG) and poly(vinyl pyrrolidone) (PVP) are widely used as pore-forming additives in membrane fabrication. The polymers used are usually highly hydrophilic, which enhance the intake of nonsolvent (water) from the coagulant. In addition, the membrane materials are usually thermodynamically incompatible with these additives, making the homogeneous dope less stable. Both changes in hydrophilicity and thermodynamic stability of the dope suggest that instantaneous demixing is likely to occur, which facilitates the formation of more porous membrane structure (Shi et al. 2007, Wongchitphimon et al. 2011). Feng et al. suggested that the dope solution completely separates into 2 phases during demixing process and large pores are formed after the additive-rich phase leached out into the water due to their hydrophilic nature (Feng et al. 2006)

Several studies on the effect of molecular weight of PEG on hollow fiber preparation revealed that the size of macrovoids and the water flux increased with increasing PEG molecular weight (Xu and Qusay 2004, Wongchitphimon et al.

2011, Shen et al. 2013b). On the other hand, the addition of PVP into the dope led to the formation of bigger macrovoids, suggesting that instantaneous demixing occurred as the hydrophilic nature of PVP enhanced the water intake (Kong and Li 2001, Shi et al. 2007). However, further increase in PVP concentration to a certain level caused a significant increase in dope viscosity, which delayed the drying process and suppressed the macrovoid formation (Sonnet al. 2007, Yuan and Dai 2008).

Organic molecules

Organic molecules with hydrophilic nature such as ethylene glycol and glycerol, are frequently used as an additive in membrane preparation. As a nonsolvent in a dope solution, ethylene glycol (EG) has two functions on membrane formation: the first is to induce rapid phase separation to obtain thin skin, the second is as a pore facilitating agent to produce porous structure (Wang et al. 2008). It has been reported that an increase in EG concentration from 4 to 8 wt% in dope solution resulted in an increase of pore size of the hollow fiber (Khayet et al. 2002a). In addition, membranes prepared with the addition of EG exhibited higher porosity and narrower pore size distribution (Wang et al. 2008).

The use of glycerol as an additive was observed to reduce the thermodynamic stability of polymer dopes and thus facilitate the growth of fingerlike macrovoids (Shi et al. 2008). When comparing glycerol with water as the additive, glycerol was found to exhibit a stronger pore-forming ability, which produced membranes with larger pores and wider pore size distribution (Anchayawut et al. 2006). In addition to glycerol and EG, other organic additives such as ethanediol (Khayet et al. 2002b), and 1,2-propanediol (Qin et al. 2005) have also been studied as pore forming agent in membrane fabrication. In general, membranes obtained with the addition of organic molecules displayed higher porosity and higher hydrophobicity compared with the membranes prepared with polymeric additives. Hence, they could be useful additives in the preparation of membranes for hydrophobic applications such as membrane distillation.

Inorganic salts

Lithium chloride (LiCl) is well known for its strong interaction with some solvents such as NMP, DMAc and DMF. Hence the addition of LiCl significantly increases the viscosity of the dope solution containing these solvents (Kong and Li 2001, Hou et al. 2009, Ahmed et al. 2010, Idris et al. 2010). As a result, the presence of LiCl in the dope delays the onset of demixing and suppresses formation of macrovoids. In addition, it was found that membrane pore size was reduced while porosity was increased with increasing LiCl concentration in the polymer dope (Naim et al. 2012).

Other lithium-based salts such as lithium fluoride (LiF) (Idris et al. 2010), lithium bromide (LiBr) (Idris et al. 2009, Idris et al. 2010), lithium nitrate (LiNO_3) (Qin et al. 2005), and lithium perchlorate (LiClO_4) (Yeow et al. 2005) have also been used as performing additives and their behavior in membrane formation process was found to be different from each other. Membrane prepared with LiBr displayed higher water permeability and good solute rejection compared with that prepared with LiCl and LiF (Idris et al. 2010). Possible reasons included the higher molecular weight of LiBr and its relatively mild effect on dope viscosity.

Inorganic salts with similar cations but different anions have been compared as the additives in membrane fabrication. Mierzwa et al. studied the effects of $(\text{NaPO}_3)_6$, Na_2SO_4 , Na_2CO_3 , NaCl, and NaF as the additives on the structure and performance of PES membranes (Carlos Mierzwa et al. 2012). Membranes made with $(\text{NaPO}_3)_6$, Na_2SO_4 , and NaCl were observed to have higher permeability than the others while the membrane made with $(\text{NaPO}_3)_6$ displayed a narrower pore size distribution. However, the mechanism was not discussed in the study.

Weak solvents

Alcohols such as methanol, ethanol, and propanol can be added into a polymer dope in a relatively large amount due to their solvent nature to polymers. It was observed that the morphology of PES hollow fibers spun with the addition of ethanol changed from fingerlike to sponge-like structure when the

ethanol concentration increased from 0 to 25 wt% and Qusay 2004b. The pure water permeation also increased with increasing ethanol concentration while the solute rejection was smallest at ethanol concentration of 15 wt%. Similar observation on the morphology change with increasing ethanol concentration has been reported by Yuan et al. (Yuan et al. 2009). This was because that the addition of ethanol caused a significant delay in demixing process in which crystallization of polymer occurred before liquid-liquid demixing.

The presence of solvent might also affect the dope viscosity. Ahmed et al. reported that when acetone was added as a solvent in a PES/DMF dope, the effect of viscosity enhancement due to the presence of LiCl became less pronounced. This was because the interaction between LiCl and acetone is weak compared with that between LiCl and DMF (Ahmed et al. 2010). On the other hand, the highly volatile nature of acetone can also be used to control membrane morphology. Ong et al. observed that PVDF membranes with dense skin layer, fully sponge structure, and good mechanical strength were obtained when acetone was evaporated for 20 min before immersing the casted dope into coagulant (Ong et al. 2011).

Strong nonsolvent (water)

Water is a strong coagulant in polymer dope and the presence of water in the dope makes the system closer to its metastable/unstable state. This promotes instantaneous demixing during membrane formation. Khayet et al. (Khayet and Matsuura 2001) fabricated PVDF flat sheet membranes for membrane distillation using pure water as the pore-forming additive. They reported that the pore size and porosity of the membranes, and therefore permeate flux of membrane distillation increased as the water content in the casting solution was increased. Achariyawut et al. observed a narrow pore size distribution on the membrane prepared using water as the additive (Achariyawut et al. 2006). In a study regarding membrane formation of Poly(methyl methacrylate)/NMP/water system, the addition of high quantity of water was observed to suppress macrovoid formation (Lion et al. 2002). The phenomenon was attributed to the water induce gelation of the polymer. Similar observation on macrovoid suppression by the presence of water in dope has

been reported by Ren et al. (Ren et al. 2010). They believed that phase inversion process was faster when the system was very close to the binodal curve on phase diagram, and hence macrovoids were unable to form and grow.

Mixed additives

The use of a mixture of two compounds as the solvent additives has been found to produce membranes with higher performance than using single additive. For instance, the addition of propionic acid or acetic acid together with LiCl in a dope produced hollow fiber with higher porosity and controlled maximum pore size, when compared with the use of single additive (Kong and Li 2001). A mixture of PEG and water as the additive to prepare PES hollow fibers has also been studied (Liu et al. 2003). It was found that the addition of water in a large amount into the PEG-containing dope could suppress the formation of macrovoid and the resultant membrane exhibited both high water flux and rejection. The better membrane performance was due to the synergistic effects of mixed additives.

Others

In addition to the additives discussed above, other chemicals such as phosphorous acid (Atchariyawut et al. 2006) and acetic acid (Wang et al. 2006a) have also been studied as porosity-forming agent in membrane fabrication. Recently, polymers with amphiphilic nature have also received much attention as additives due to their unique behavior during membrane formation. A deeper discussion on these polymers will be provided in Section 2.1.3.

2.1.3. Spinning of hollow fiber membranes

During hollow fiber membrane spinning, a homogenous dope is pumped through the outer channel of a spinneret while bore fluid (inner coagulant) is pumped through the inner channel, as shown in Figure 2-8. The nascent fiber passes through a certain length of air gap before immersing into a coagulant bath. The formed fibers are collected by a drum rotating at a constant speed, which is so called take-up speed. Spinning of hollow fiber membranes is a more complicated

process compared with film casting as the phase separation takes place from both the shell and lumen of the nascent fibers. Spinning parameters such as air gap, take up speed, flow rate of dope and bore fluid and coagulant temperature can highly affect the hollow fiber formation, as discussed in the following paragraphs.

Figure 2-8. Spinneret structure and hollow fiber spinning

a. Composition of coagulant and bore fluid

The composition of coagulant has significant effect on membrane morphology. Water is considered a strong coagulant as it promotes instantaneous demixing during phase inversion, leading to the formation of a membrane with a dense skin layer and macrovoids underneath it. The use of weak (or so-called •soft,) coagulant causes delayed demixing in the dope solution, resulting in the formation of porous and spongy nascent membranes with the absence of dense skin layer (Kong and Li 2001, Khayet et al. 2002, Sukitpaneenit and Chung 2009).

Bonyadi et al. (Bonyadi and Chung 2007) demonstrated the formation of a more porous membrane surface morphology with the use of water/methanol (20/80, w/w) coagulant, compared with the membranes prepared with the use of water

coagulant. However, in hollow fiber spinning process, the use of external coagulant other than water may not be economically practical as the volume of external coagulant required is very large. On the other hand, the use of weak solvent as the bore fluid to induce a slower phase separation at the lumen side of hollow fiber is widely reported. Kong and Li reported that the elimination of lumen skin by using a soft bore fluid (i.e., ethanol or water/ethanol mixtures) increased the membrane permeation when compared with the membrane with both shell and lumen skins (Kong and Li 2001). The mixture of a strong coagulant and a solvent such as water/NMP has also been used as the bore fluid to eliminate the inner skin layer of hollow fibers (Atchariyawut et al. 2006; Ohya et al. 2009). Nevertheless, it should be noted that the bore fluid must not be too weak or else phase inversion may not take place (Ren et al. 2006). Therefore, the concentration of water must exceed a certain value when using the mixture of water/solvent as the bore fluid.

PVDF hollow fibers with rough surface and interconnected globule structure (similar to Figure 2-4 (S+P) and (P)) have been prepared by using a mixture of alcohols and water as the external coagulant (Sukitpaneemit and Chung 2009). It has been shown that the onset of liquid-liquid demixing can be significantly delayed when the coagulant contains a large amount of alcohol. This allows occurrence of solid-liquid demixing accompanying crystallization, since liquid-liquid demixing and solid-liquid demixing is competitive to each other in a system containing semi-crystalline polymers. During crystallization, the nuclei of PVDF crystal are able to grow and membranes comprising globules are finally formed (Lee et al. 2003a; Sukitpaneemit and Chung 2009). Due to the rough surface, PVDF membranes with such type of morphology have been reported to be highly hydrophobic relative to that with a smooth surface (Kuo et al. 2008; Bonyadi and Chung 2009). However, the mechanical properties of such kind of hollow fibers are deteriorated because the interconnection between the globules is relatively weak.

b. Coagulant temperature

In the preparation of PVDF hollow fiber membranes using water as bore fluid, solid-liquid demixing was claimed to be dominant at coagulant temperature of 14 °C while liquid-liquid demixing was the dominating mechanism at 50 °C as the

crystallization of PVDF was suppressed at higher temperature (Choi et al. 2011). As a result, the hollow fiber produced at the lower coagulant temperature exhibited larger pores, leading to a higher gas permeance and a lower selectivity. Wongchitphimon et al. (Wongchitphimon et al. 2011) also reported that PVDF hollow fibers with smaller macrovoids and improved molecular weight cutoff (MWCO) were obtained when a higher coagulant temperature was employed, which agreed the observation of Choi et al. (Choi et al. 2011).

However, contradictory observations have also been reported in several studies. For instance, PVDF hollow fibers with larger inner surface pores were obtained by increasing internal coagulant (i.e., bore fluid) temperature (Tang et al. 2012). CA hollow fibers also exhibited larger surface pores and macrovoids when they were prepared at a higher coagulant temperature, resulting in a higher water flux and lower solute rejection (Chou et al. 2007). The reasons might be due to the higher solvent-nonsolvent exchange rate at elevated temperature which enhanced the leaching of additive from the nascent fibers. Although the mechanism is not clear, it can be seen from the contradictory findings that the effects of coagulant temperature on the properties of resultant fibers vary in different cases.

c. Air gap

Based on Chung's study (Chung 1997), air gap can introduce external elongation stress which results in entropy change in solution. There are three effects introduced by the external stress: (1) creating phase instability; (2) facilitating phase separation; (3) inducing orientation. The first two will lead to the formation of bigger pores on the membrane surface, while the third results in an oriented membrane structure. Several studies (Kishulbe et al. 2007, Teoh and Chung 2009, Tang et al. 2012) have reported an increase in pore size and permeation of hollow fibers when the air gap was increased. The findings suggested that the first two mechanisms of Chung's theory were dominated when the air gap was increased. On the other hand, different observations have also been reported: an increase of air gap to a certain level results in hollow fibers with lower permeation, higher solute rejection, or smaller surface pores (Khayet 2003, Qin et al. 2005). This phenomenon might be attributed to the induced orientation caused by the air gap,

leading to the formation of a denser membrane structure due to a greater molecular orientation and chain packing (Chayet 2003).

Corrugation in the lumen of hollow fiber has always been found in the phase inversion process as illustrated in Figure 2-9, and the explanations on this phenomenon are diversified (Bonyadi et al. 2007, Shi et al. 2007). Several studies reported that the degree of corrugation in the inner contour was alleviated by increasing the air gap which might be due to: (1) the release of stress/instability outward in the nascent fibers before the outer surface was vitrified; (2) the formation of a more rigid inner skin caused by a longer precipitation time before the nascent fiber entering the coagulant (Bonyadi et al. 2007, Shi et al. 2007).

Figure 2-9. Effect of air gap on the inner contour of hollow fiber membranes (Figure adapted from (Bonyadi et al. 2007)).

d. Flow rate of dope and bore fluid

The flow rate of dope and bore fluid mainly control the outer diameter, inner diameter, and thickness of spun hollow fibers. It was observed that the thickness of hollow fibers increased and decreased with increasing dope flow rate and bore fluid flow rate, respectively (Wu et al. 2007, Zhang et al. 2013b). In addition, hollow fibers with larger pore size on the inner surface were obtained when a higher bore fluid flow rate was used during spinning. This might be attributed to the fast solidification of inner surface induced by enhanced mass transfer (Zhang et al. 2013b). The deformation of fiber inner contours could also be eliminated when a

higher bore fluid flow rate was used because the inward radial forces were balanced (Wang et al. 2009)

e. Takeup speed

The takeup speed of a spinning process should be at least equal to the free falling speed of the nascent fibers to prevent them from coiling in the coagulant bath. An increase of takeup speed has been found to induce tensile stress on the nascent fiber and affect the membrane properties. It was reported that the pore size of the hollow fibers was increased with a larger takeup speed (Chou and Yang 2005, Shen et al. 2013). The reasons might be attributed to the merging of pores or expansion of defects under the elongation stress. In contrast, Sukitpaneenit et al. and Sun et al. observed a reduction in membrane surface pore size with increasing takeup speed (Sun et al. 2010, Sukitpaneenit and Chung 2011). The possible mechanisms include: (1) the elongation stress changes the properties of spinning dope; (2) rapid shrinkage of hollow fibers causes the solvent to diffuse out, which increases polymer concentration; (3) spinodal decomposition occurs due to the enhanced thermodynamic instability induced by the elongation stress.

For the first time, Wang et al. reported a complete elimination of macrovoids in hollow fiber by employing high takeup speed (Wang et al. 2004). The possible causes for this phenomenon were elaborated based on four different aspects: (1) chain packing induced by high elongation stress; (2) phase instability created by high elongation stress; (3) rapid shrinkage of fibers; (4) reduction in hollow fibers' wall thickness (Peng et al. 2008).

2.2. Amphiphilic polymers for membrane fabrication

In recent years, the use of amphiphilic polymers as additives has received much attention in membrane preparation. Many of the amphiphilic polymers consist of at least a hydrophobic water-insoluble segment and a hydrophilic, water-soluble segment. Different from conventional pore-forming additives, amphiphilic polymers normally serve as membrane surface modifiers. During the wet phase inversion process, the amphiphilic polymer additive

segregated to the polymer/water interface due to the low interfacial energy between the hydrophilic segment and water, while the hydrophobic, water-insoluble segment of the amphiphilic polymer firmly anchored in the polymer matrix (Hester et al. 1999, Zhao et al. 2008). Various types of amphiphilic polymers including ionic polymers, linear block copolymers, and branched copolymers have been used in membrane fabrication. Their surface modifying and performance functions are discussed in the following sections.

2.2.1. Membranes prepared with amphiphilic polymers

a. Self-synthesized amphiphilic polymers

The preparation of antifouling membranes has been an important topic in membrane applications. Since the interaction between organic foulants and membrane surface is mainly contributed by electrostatic force and hydrophobic interaction, membranes with hydrophilic and charged surface are preferred to reduce fouling (Larsson 1980, Khulbe et al. 2010). One of the effective and convenient methods is to blend amphiphilic polymers into casting dope.

By far, there have been a number of studies reporting the synthesis of amphiphilic block copolymers for membrane surface modifying via blending methods. Generally, it is preferable to have copolymers that consist of a water-insoluble backbone similar or same to the polymer used as the membrane material (homopolymer) to ensure the compatibility between the copolymer additive and the membrane matrix. On the other hand, Poly(ethylene oxide) (PEO) and poly(oxyethylene methacrylate) (POEM) are popular choices for the hydrophilic segments. The studies on the blending of synthesized block copolymer with homopolymer to prepare hydrophilic membranes include blend of PAN with PAN-PEO (Asatekin et al. 2007), blend of PSf with PSf-PEO (Hancock et al. 2000), blend of PVDF with poly(methyl methacrylate)-PEO (Hester and Mayes 2002), blend of PVDF with polysiloxane-PEO or hyperbranched polyester-PEO (Zhao et al. 2008), Moghareh Abed et al. 2013, blend of PES with polystyrene-PEO (Ma et al. 2007), and others. The salt membranes in all the above studies exhibited

lower contact angle and better fouling resistance compared to the membranes prepared without the addition of amphiphilic copolymers. In addition, the water permeability of the membranes was also enhanced with increasing copolymer concentration in the case that the total polymer concentration was kept constant. However, in situation where the concentration of homopolymer was kept constant, an increase in copolymer concentration (i.e., the total polymer concentration increased) reduced the water permeability (Roux et al. 2006).

Amphiphilic block copolymers with hydrophobic ends have also been synthesized and added into polymer dope to prepare hydrophobic membranes. For instance, surface modifying macromolecule (SMM) consists of polyurethane backbone endcapped with low polarity fluorine-based polymer chains has been synthesized (RahbariSisakht et al. 2012). Due to the presence of the hydrophobic fluorine chains, the SMMs have a tendency to minimize the interfacial energy by migrating to the air/film interface during membrane formation, resulting in the increase in hydrophobicity of the membrane surface without significant effect on the bulk membrane properties. Since the migration of SMMs takes time, the casted film needs to be placed in the air for a period of time before it is immersed into the coagulant. Khayet observed an increase in contact angle with increasing solvent evaporation time in the membranes prepared with the blend of PEI and SMM, due to the migration of more SMMs toward the membrane surface (Khayet 2004). The synthesized SMMs were also used to prepare PES membranes and the surface segregation of the SMMs resulted in an increase in the advancing contact angle of the resultant membranes to a value as high as 116° (Plesm et al. 1999). The hydrophobic membranes prepared with SMMs have been used in membrane distillation and membrane contactors (Khayet et al. 2005; Qtaishat et al. 2009; RahbariSisakht et al. 2012).

Ionic polymers with amphiphilic nature have also been synthesized for membrane preparation. Lang et al. added perfluorosulfonic acid (PFSA), which comprised fluorine-based backbone and terminated by a sulfonate ionic group, into PVDF dope to prepare antifouling hollow fibers (Lang et al. 2007; Lang et al. 2012). Light transmittance experiment verified that the presence of PFSA promotes

instantaneous demixing of the system. As a result, membranes with much higher permeation were obtained. In addition, due to its good compatibility with PVDF, PFSA was found to stay in the membrane which enhanced the antifouling properties. Li et al. synthesized an amphiphilic zwitterionic copolymer PVDF-poly(sulfobetaine methacrylate) and used it as an additive in the preparation of PVDF membranes (Li et al. 2012). By keeping the concentration of total polymer constant, water permeation was enhanced with increasing copolymer concentration. The hydrophilicity and antifouling properties of the resultant membranes were also improved.

b. Commercially available amphiphilic polymers

While most of the amphiphilic polymers used for membrane fabrication were self-synthesized, there are several studies reported the use of commercially available surfactants. One of the advantages of commercial products over self-synthesized ones is that more information related to the products is available because they have normally been used and studied in various fields. In addition, the reproducibility of commercial chemicals is normally better. Therefore, commercially available amphiphilic polymers are more suitable to be used for fundamental study on pore-forming mechanism compared with the self-synthesized ones.

In a study using commercial surfactant Tween 80 (Figure 2-10 (a)) as the additive to prepare PVDF membranes, the formation of micelles by amphiphilic polymers in casting dope was observed to affect the membrane formation process (Zhang et al. 2012). It was believed that reverse micelles which solubilized water molecules were reformed when water is added into the PVDF dope containing Tween 80 as the additive and DMAc as the solvent. The author claimed that the presence of the micelles confined the movement of water during phase separation, leading to the formation of smaller macrovoids. The effects of two amphiphilic surfactants with different hydrophilicity, which are Tween 80 and Span 80 (Figure 2-10 (b)), on macrovoid formation have been compared (Zhang et al. 1998). Span 80 was more hydrophobic than Tween 80 due to the difference in their hydrophilic heads as shown in Figure 2-10. It was observed that macrovoid formation was enhanced

when the miscibility between the amphiphilic additive and the coagulant was better. For instance, large macrovoids were formed when water and the more hydrophilic Tween 80 was used as the coagulant and additive, respectively. In contrast, macrovoid growth was suppressed when the coagulant-additive pair had a low miscibility. The less miscible coagulant-water pairs included water-Span 80 and n-hexane-Tween 80.

Figure 2-10. Chemical structures of commercially available amphiphilic polymers

Rahimpour et al. used commercial products of anionic (Figure 2-10 (c)), cationic (Figure 2-10 (d)), and nonionic amphiphilic polymers (Figure 2-10 (e)) to prepare PES membranes (Rahimpour et al. 2007). It was observed that the addition of all these surfactants enhanced the membrane porosity and water permeation while the surface pore size became smaller. Among the three types of surfactants, the membrane prepared using the nonionic copolymers exhibited the highest performance in milk concentration application due to a lower fouling tendency.

The effects of amphiphilic polymers on membrane formation have also been studied via virtual simulation. Liu et al. have done a computer simulation on membrane formation with the addition of amphiphilic block copolymers (Liu et al. 2013). Based on the simulation, membranes with interconnected pore structure can be obtained by using copolymers containing longer hydrophilic segment.

Pentablock and triblock copolymers were also found to have a better pore-forming ability compared with diblock copolymers. The study revealed that the size and the block arrangement of block copolymers can be crucial to membrane formation.

In addition to the above mentioned polymers, commercial triblock copolymers comprise of PEO and poly(propylene oxide) (PPO) has also been used in membrane preparation. Due to the low cost, easy availability, and unique behavior in aqueous solution, this family of commercial polymers has received attention in membrane field since 2005 (Wang et al. 2005). More details on these copolymers will be discussed in Section 2.2.

c. Highly ordered structures

Preparation of membranes with very narrow pore size distribution by utilizing copolymers have been reported. Akthakul et al. synthesized block copolymer PVDF-POEM and used it to prepare flat sheet membranes via evaporation casting (Akthakul et al. 2004). Due to the incompatibility between PVDF and POEM, micro-phase separation of the hydrophobic backbone and hydrophilic side chains occurred during membrane formation process. As a result, the copolymer self assembled into bi-continuous phase of PVDF and POEM domain, as shown in Figure 2-11 (a). The hydrophilic POEM domains provided selective transport channels with a defined size of around 2 nm.

Due to the self-assembly of the copolymer induced by partially evaporating the volatile solvent, Peinemann et al. successfully prepared a membrane with highly ordered top layer and sponge-like substructure using the block copolymer of polystyrene and poly(4-vinylpyridine) as the membrane material (Peinemann et al. 2007). As shown in Figure 2-11 (b), the surface of the resultant membrane was highly ordered with pore diameter around 40 nm.

2.2.2. Pluronic block copolymers and their properties

Pluronic is a trade name registered under BASF for amphiphilic triblock copolymers of hydrophilic PEO and hydrophobic PPO, which are often denoted as

PEO-PPO-PEO and PPO-PEO-PPO (Alexandridis et al. 1994). The chemical structures of typical Pluronic and its homopolymer counterpart, PEG, are presented in Figure 2-12. Pluronic copolymers have been widely used as surfactants, components in drug delivery systems, cell culture media and others for decades due to their unique surface activity, reversible thermorheological phase behavior, and micellization in water (Nakashima and Bahadur 2006). In recent years, Pluronic has also been used in membrane preparation.

Figure 2-11. (a) TEM image of PVDFOEM nanodomain morphology; (b) SEM images of cross-section (1) and surface (2) morphology of polystyrene-poly(4-vinylpyridine) block copolymer membrane. Scale bars correspond to (a) 20 nm and (b) 500 nm [figure adopted from Akthakul et al. 2004 & (Peinemann et al. 2007)].

Figure 2-12. Chemical structures of (a) Pluronic and (b) polyethyleneglycol.

a. Membranes prepared with Pluronic

Wang et al. blended Pluronic with PES to prepare antifouling membranes via immersion precipitation using water as the coagulant (Wang et al. 2005). Significant amount of Pluronic molecules were proven to remain in the resultant membranes despite that they were water soluble. The enrichment of Pluronic on the membrane surface enhanced the membrane hydrophilicity and reduced protein adsorption. The observations revealed that the hydrophobic PPO block in the Pluronic interacted with PES and made the Pluronic anchor in the membrane matrix stable. On the other hand, the addition of Pluronic showed no significant impact on the membrane pure water permeability.

Since then, a series of studies on PES membrane preparation have been carried out using Pluronic as an additive (Wang et al. fabricated antifouling PES membranes using PES as the pore-forming additive and a small amount of Pluronic as the surface modifier (Wang et al. 2006). The contact angle was observed to decrease from 60° to 48° with the addition of merely 1.6 wt% of Pluronic (Zhao et al. used Pluronic as both pore-forming and surface-modifying additive (Zhao et al. 2008). The water flux increased while the rejection decreased with increasing Pluronic concentration from 3.6 to 18 wt%. The author claimed that the increase in Pluronic micelle size with increasing Pluronic concentration was the reason responsible to the bigger surface pores. Susanto and Ulbricht compared the effects of PVP, PEG, and Pluronic, which had similar molecular weight, as the additive on the properties of PES membranes (Susanto and Ulbricht 2009). Water permeability of the membrane prepared with Pluronic was the highest while the solute rejection was similar for the membranes prepared with different additives. Membranes prepared with Pluronic showed the best filtration performance and stability, but Pluronic was observed to be not completely stable in PES membrane matrix. The effects of coagulant temperature on the performance of PES/Pluronic membranes were also studied (Peng et al. 2010). The pore size became larger when the membranes were prepared at a higher coagulant temperature. This might be because the Pluronic micelles became larger with increasing temperature.

In addition to PES, Pluronic has also been blended with other polymer materials such as CA (Lv et al. 2007), polyvinyl chloride (Liu et al. 2012), and PVDF to prepare antifouling membranes. By far, studies on PVDF membrane preparation using Pluronic as an additive via immersion precipitation are limited. In one of the studies, the polymorphism and thermoresponsive behavior of PVDF/Pluronic membranes were examined (Du et al. 2012). It was observed that the addition of Pluronic in the PVDF dope facilitated the formation of β and β' crystal phases. Water flux was found to be enhanced significantly when the operating temperature was increased during the filtration process. The phenomenon was explained by the temperature-dependent solubility of Pluronic, which will also be discussed in the following section.

b. Properties of Pluronic solutions (micellization)

The properties of Pluronic in aqueous solution have been widely studied. The water solubility of Pluronic becomes lower at higher temperature. Therefore, Pluronic chains are in extended conformation at lower solution temperature whereas they tend to aggregate and form micelles or become gel when the temperature is increased (Jørgensen et al. 1997; Du et al. 2012). At a certain temperature, Pluronic can form micelles in water above critical micelle concentration (CMC), where the hydrophobic PPO blocks locate at the core and the hydrophilic PEO blocks comprise the corona of the micelles. Since the water solubility of the hydrophobic PPO block is significantly deteriorated with increasing temperature, the CMC is smaller at elevated temperature. In addition, the size of PPO and PEO blocks in Pluronic molecules can also affect the micellization. It has been shown that micelles are formed at a lower concentration when the PPO block is larger. On the other hand, an increase in PEO block length slightly decreases the CMC, indicating that micelles are more difficult to form for the more hydrophilic molecules. However, the effect of PEO block length on CMC is less pronounced compared with that of PEO block, indicating that the hydrophobic block primarily controls the micellization process (Alexandridis et al. 1994).

The driving force in Pluronic micelle formation has been proposed based on the Gibbs free energy equation which is similar to equation (2.1). CMC, the

standard enthalpy of Pluronic micellization, ΔH , is observed to be positive (i.e., endothermic process). However, the micellization is spontaneous which indicates that the free energy, ΔG , should be negative. This implies that the driving force of Pluronic micellization should be the negative contribution of entropy, which is related to the hydrophobic effect. When organic compounds are present in water, the interaction between the two species causes an ordered structure in the water and reduces the water entropy. The aggregation of the organic compounds can restore the hydrogen bonding between water molecules to some extent, causing an increase in water entropy which overcomes the entropy loss due to the packing of hydrophobic blocks in the micelle (Alexandridis and Alan Hatton 1995).

Despite the widely studied properties of Pluronic in aqueous solution, investigations on the behavior of Pluronic micellization in organic solutions are very limited: most of them are carried out in *p*-xylene. Some types of Pluronic have been reported to form reverse micelles in *p*-xylene at room temperature, while some can only form reverse micelles in *p*-xylene at elevated temperature in the presence of water. Unlike the Pluronic micellization in water, the micellization of Pluronic is an exothermic process in *p*-xylene. The CMC decreases with increasing Pluronic molecular mass and increasing PEO block length. The reverse micelles of Pluronic can solubilize a certain amount of water in the organic solvent and the water solubilization capacity per oxyethylene (EO) unit decreases with increasing PEO block content (Alexandridis and Andersson 1997, Guo et al. 2000, Ghaouar et al. 2011).

CHAPTER 3. Fabrication of PES Hollow Fiber Membranes Using Amphiphilic Pluronic Block Copolymers as Pore-Forming Additives

3.1. Introduction

It is noticed that Pluronic has different molecular architectures, and mass fraction and chain length of PEO hydrophilic block in Pluronic may also vary. It is expectable that the interactions of Pluronic with the polymer dope solution and the coagulant may be different when different Pluronics are used in membrane preparation. To date, the role of Pluronic as a pore-forming additive was demonstrated mainly by using Pluronic F127. No systematic study was reported with respect to the effects of Pluronic molecular architectures (i.e., the relative position of hydrophobic PPO and hydrophilic PEO chains), PEO mass fraction, and PEO chain length on the membrane performance when Pluronic was added into a polymer dope as a pore-forming additive. In addition, all of the membranes prepared via nonsolvent-induced phase separation (NIPS) method using Pluronic as an additive were casted in the form of flat sheet. It has been widely recognized that hollow fiber fabrication is a more complex process compared with film casting, as the former involves two coagulation processes, etc. Thus, the performance of hollow fiber membranes spun with the addition of Pluronic could be different from that of flat sheet membranes.

To understand the role of amphiphilic block copolymers as an additive in the membrane formation, an attempt was made to systematically investigate the effects of different types of Pluronics (different molecular architectures, PEO mass fractions and PEO chain lengths) as an additive on the fabrication of PES ultrafiltration (UF) hollow fiber membranes. PES has been chosen as the membrane material in this study due to its very high chemical and thermal stability, and because it is a very commonly used polymer material which has been well studied in the phase inversion process (Seben and Wang 2010). Since the commonly used additive, polyethylene glycol (PEG), only comprises of PEO block, a comparison

between Pluronic and PEG as additives was also made to study the importance of the presence of PPO chain in Pluronic for membrane formation. It is anticipated that this study can provide a better understanding of the role of various Pluronics as additives in the phase inversion process, and identify the most preferential features of Pluronic for making hollow fiber membranes.

3.2. Experimental

3.2.1. Membrane material and chemicals

PES (Ultrason E6020P, MW = 51,000, BASF), was dried at 50°C under vacuum for at least 1 day before use. N-methyl-2-pyrrolidone (NMP) purchased from Merck was used as solvent. Pluronic copolymers with different range of molecular weights and PEO/PPO ratios were purchased from Sigma. PEG (MW = 10,000) (PEG10k) was purchased from Merck, Singapore. Dextran with different molecular weights ranging from 6,000 to 500,000 Da (Sigma) was used to determine the molecular weight cutoff (MWCO) of hollow fiber membranes. All the reagents were used as received.

The physical properties of Pluronic copolymers studied, as well as PEG10k, are listed in Table 3-1, and their chemical structures are illustrated in Figure 2-12. The notation of Pluronic products (PEO_nPPO_mPEO) comprises of a letter followed by a two or three digit number. The first letter L (liquid), P (paste), or F (flake) reflects their physical appearance. The last digit shows the mass fraction of PEO block, and the first one or two digits are indicative of the chain length of PPO block. For example, Pluronic L64 is in liquid form, it contains 40 wt% of PEO, and its PPO chain length is shorter than that in Pluronic F108 and F127 (Alexandridis et al. 1994). For the Pluronic products with reverse block arrangement (Pluronic R, PPO-PEO-PPO), the nomenclature is similar to their counterparts.

Table3-1. Properties of Pluronic and PEG

Polymer	MW ^a	Mass fraction of PEO(wt%)	EO units ^b	PO units ^b	Block arrangement ^c
17R4	2700	40	22	2 x 15	PPOPEOPPO
L64	2900	40	2 x 13	30	PEOPPOPEO
F68	8400	80	2 x 76	29	PEOPPOPEO
F127	12600	70	2 x 100	65	PEOPPOPEO
F108	14600	80	2 x 132	50	PEOPPOPEO
PEG10k	10000	100	227	-	-

^a Molecular weight^b Number of repeating units of PEO and PPO^c The relative position of PPO and PEO segments

3.2.2. Cloud point determination

The determination of cloud point for the PES/NMP/water system with and without the addition of an additive was achieved by titrimetric method at room temperature. In this method, a series of PES/NMP/additive solutions containing 10 wt% of PES and 5 wt% of additive was prepared. PES concentration used in this experiment was smaller than that of spinning dopes because the dope viscosity was too high for operation when water was added in the dopes containing 18 wt% of PES. A small amount of MilliQ water acting as nonsolvent was added into each homogenous solution and local gelation occurred. Stirring was required to make the solution homogenous again. The process was repeated until reaching cloud point, at which permanent turbidity was observed visually. The amount of water required to achieve cloud point was recorded. An average from two experiments was taken for each sample and the standard deviations are within 0.2 wt%.

3.2.3. Spinning dope preparation and dope viscosity measurements

A polymer dope solution for spinning was prepared by dissolving 18 wt% of PES and a desired amount of additive in NMP using a jacket flask. The additive concentrations in the dopes are shown in Table 3-2. The dope solution was mechanically stirred for at least 2 days at 60 °C. The homogenous dope prepared

was then cooled down to room temperature (20 ± 2 °C) and subsequently degassed under vacuum for overnight before spinning.

Table3-2. Additive concentration, viscosity, and dope/bore fluid flow rates for spinning dopes containing 18wt% of PES

Dope	Additive	Concentration (wt%)	Viscosity of dope (Pa·s)	Dope/bore fluid flow rates (g/min)
#0	N.A.	0	1.5	6.5/ 5.0
#r4-5	Pluronic 17R4	5	2.2	6.5/ 5.0
#64-5	Pluronic L64	5	2.2	6.5/ 5.0
#68-5	Pluronic F68	5	2.6	6.5/ 5.0
#127-5	Pluronic F127	5	2.8	6.5/ 5.0
#108-5	Pluronic F108	5	3.0	6.5/ 5.0
#p10-5	PEG10k	5	3.2	6.5/ 5.0
#127-10	Pluronic F127	10	4.3	6.0/ 6.0
#127-15	Pluronic F127	15	7.0	5.5/ 6.0

Rheological characteristic of the spinning dope solutions was measured by a rheometer (Physica MCR 101, Anton Paar). The measurements were carried out using a 25 mm measuring plate (CP25) under steady state shear rate ranging from 0.01 to 100 s^{-1} at 25 °C. The viscosity of dope solutions was taken at the shear rate of 10 s^{-1} .

3.2.4. Spinning of PES hollow fiber membranes

The PES hollow fiber membranes were fabricated via dry/wet spinning process. The dope and bore fluid were extruded through a spinneret at a controlled rate and went through an air gap before immersing into a coagulation bath containing tap water. In the spinning of the dopes containing 5wt% of additive the dope and bore fluid flow rates were kept constant. For the spinning of other dopes which contained a higher concentration of additive, different dope and bore fluid flow rates were employed in order to achieve a reasonable thickness spun membrane (Table3-2). The nascent hollow fiber was collected at a free take up speed and subsequently stored in a water bath for 2 days to remove

residual solvent. The detailed spinning conditions are listed in Table 3-2 and Table 3-3.

Table 3-3. Spinning parameters for PES hollow fiber membranes

Spinning parameters	Value
Spinneret dimension (mm)	ID = 1.0, OD = 2.0
Dope flow rate (g/min)	Refer to Table 3-2
Bore fluid (wt%)	NMP/water (70/30)
Bore fluid flow rate (mL/min)	Refer to Table 3-2
External coagulant	Tap water
Coagulant temperature (°C)	25 ± 1
Air gap (cm)	0.3
Take-up speed	Free fall
Room temperature (°C)	20 ± 2
Room humidity (%)	70 ± 3

3.2.5. Pure water permeation and MWCO measurement

A crossflow setup, as shown schematically in Figure 3-1, was used for pure water permeation (PWP) and MWCO characterization of hollow fiber membranes. The hollow fiber membranes were kept wet in water before tested for their PWP and MWCO. Each hollow fiber module was made by sealing 10 pieces of hollow fibers in plastic tubing. Two modules were prepared and tested for each batch of the hollow fibers. The effective length of the hollow fibers was 26 cm and distilled water as feed was circulated through the shell side of the hollow fibers. Compaction on the membranes was done under the pressure of at least 1 bar for 1 hour and the permeate was subsequently collected for 5 minutes under 1 bar. The PWP of the hollow fibers (1 bar) was calculated using the formula:

$$J = \frac{Q}{A \times t} \quad (3.1)$$

where Q is the permeate collected over a duration of time for the hollow fiber (L/h); ΔP the pressure difference between the feed and permeate side of hollow fibers; A the outer surface area of hollow fibers in the module.

Figure 3-1. Crossflow setup for PWP and MWCO characterization

The MWCO of a hollow fiber membrane is defined as the molecular weight at which 90% of the solute is retained by membranes. The compacted hollow fibers were used for MWCO test and 1500 ppm of a dextran aqueous solution with a molecular weight distribution ranging from 6,000 to 500,000 Da was used as the feed. The permeate was collected after 30 minutes of feed circulation under 1 bar to make sure that the system was stabilized. Gel permeation chromatography (GPC) (PL-GPC50 Plus, A Varian, Inc.) was used to characterize the dextran molecular weight distribution in the feed and permeate. Rejection of hollow fibers was then calculated according to the formula expressed as:

$$R = \frac{C_f - C_p}{C_f} \quad (3.2)$$

where R is the rejection coefficient for dextran molecule with a certain molecular weight M ; C_f and C_p the concentrations of dextran with a molecular weight M in the feed and permeate solutions, respectively.

3.2.6. Other characterizations of PES hollow fiber membranes

The pore size distribution parameters (which include the geometric mean pore diameter D^* and geometric standard deviation f^*) of spun hollow fibers

were determined by substituting the data of dextran rejection (section 3.2.5) into the Extreme model as mentioned in the study of Ren et al. (2006a). For each membrane two sets of rejection data were used in the model: Rej_1 % 0.65, 0.70, Rej_2 % 0.95, and their corresponding dextran molecular weight M_1 and M_2 , respectively.

The cross-sectional morphology of hollow fiber membranes was observed using a scanning electron microscope (SEM) (EVO 50, Carl Zeiss AG). The hollow fibers were broken in liquid nitrogen and sputtered with gold prior to the test.

In order to examine the presence of Pluronic and PEG10k in PES hollow fibers, attenuated total reflectance Fourier transform infrared spectroscopy (ATR FTIR) was carried out by IR Prestige 64 spectrophotometer from Shimadzu. The outer surface of dried membranes was directly analyzed and the IR spectra were obtained by 45 scans at a resolution of 4th cm⁻¹. The chemical composition of the membrane surface were analyzed by X-ray photoelectron spectroscopy (XPS, Theta Probe, Thermo Scientific), cover a range of 0–1300 eV. High resolution spectra of C1s peak from which the relative amount of hydrocarbon (C and C-H) and ether carbon (C-O) can be obtained were also collected. Atomic percentage of ether carbon over total carbon in the samples can then be calculated. Both XPS operation and fitting of high resolution spectra were carried out by Institute of Materials Research and Engineering, Singapore.)

3.3. Results and discussion

3.3.1. Cloud point and viscosity of PES dope solutions

The structure of membrane is strongly controlled by thermodynamic and kinetic properties of the polymer dope system. Cloud point experiment, which pertains to the thermodynamics of phase inversion, was carried out to determine the amount of water needed to initiate phase separation, and the results are listed in Table 3-4. It can be seen that the water amount and cloud point is reduced from 12.7 wt% to around 12.0 wt% for the different types of Pluronic and to 10.0 wt% for

PEG10k when they are added into the dopes, indicating that these additives exhibit non-solvent properties and tend to reduce the thermodynamic stability of the system (Yeow et al. 2003). However, varying the Pluronic molecular architecture and PEO chain length appear to have little influence on the system's thermodynamic state. It can also be seen that there is a significant reduction in water tolerance with the addition of PEG10k into the PES dope compared with that of various Pluronics.

Table3-4. Amount of water required for phase separation in PES/NMP/additive systems

Additive	None	17R4	L64	F68	F127	F108	PEG10k
Water amount at cloud point (wt%)	12.7	11.9	12.0	12.2	12.2	12.2	10.0

The kinetics of phase inversion, which always refers to the diffusion rate of the solvent and the diffusion rate of the nonsolvent during membrane formation, is highly related to the viscosity of the polymer dope solution: a high viscosity hinders the exchange of solvent/nonsolvent during the phase inversion process and vice versa. The viscosity of the dope prepared for spinning is presented in Table3-2. The results reveal that the addition of polymeric additives enhanced the viscosity of the solution. The increases of the additive's molecular weight and the concentration result in an increase in dope viscosity. This phenomenon is attributed to the increasing effect of the entanglement between the polymer chains with increasing polymer chain length and polymer concentration (Ohya et al. 2009). On the other hand, it is also observed that the viscosity of dope #5 is the highest among the group with the same concentration of 5 wt% additives, which might be due to the better affinity of PEG10k with NMP than Pluronic with NMP.

3.3.2. Effect of additives on membrane morphology

Figure 3-2 shows the cross-sectional morphology of PES hollow fiber membranes prepared with/without the addition of different additives. It is observed that all the membranes exhibit an asymmetric structure consisting of finger-like

Figure3-2. Crosssectional morphology of hollow fiber membranes (a) #0, (b) #5, (c) #10, (d) #645, (e) #685, (f) #1275, (g) #1085, and (g) #p105 spun with different types of Pluronic and PEG10k as additives (18wt% of PES) bars correspond to 20 μ m

macrovoids developed underneath the outer surface of the fibers, as a sponge-like structure near the lumen of the fibers. Compared with the morphology of membrane #0, which was prepared without any additives, larger finger-like macrovoids have been developed across the membranes prepared with Pluronic and PEG10k (Figure 3-2). There is no significant difference in the morphology of hollow fibers spun with different additives when comparing Figure 3-2 (b) to (g).

On the other hand, the observed larger finger-like macrovoids in hollow fibers prepared with various additives indicate that PEG10k and various types of Pluronic, regardless of the molecular architectures and contents, act as pore formers in membrane formation. This observation is believed to be associated with thermodynamic and kinetic effects caused by the addition of the additives into the dope system. The results of cloud point test discussed in chapter 2 reveal that the addition of Pluronic and PEG10k reduce the thermodynamic stability of the dope systems. In addition, the hydrophilic nature of PEO chain in Pluronic and PEG10k accelerates the indiffusion rate of nonsolvent during membrane formation. It is likely that both the reduction in thermodynamic stability and increase in nonsolvent indiffusion rate promote instantaneous demixing, which enhances macrovoid formation. The increase in macrovoid size observed in Figure 3-2 ((a) vs. (f) and (g)) also suggests that the impact of a four-fold increase in viscosity (see Table 3-2) on phase inversion is insignificant compared with the thermodynamic effect induced by the additive addition.

3.3.3. Presence of additives in membrane matrix

Since all the Pluronics used in this study are highly soluble in water according to the manufacturer, it is interesting to know whether the additives can stay in the membrane matrix or are completely washed out. It is thought that the presence of these amphiphilic block copolymers in the membrane matrix might have an impact on the membrane rejection properties, which will be discussed in a later section. Therefore, the chemistry of the spun hollow fibers was determined using ATR-FTIR. Figure 3-3 shows the ATR-FTIR spectra for hollow fiber #0, #1275, #p105, and pure Pluronic F127 as examples to assess the presence of the

additives in the spun hollow fibers. Both Pluronic and PEG macromolecules are characterized by the absorbance peaks at 1107 cm^{-1} corresponding to the ether, O groups in PPO/PEO blocks (Susanto and Ulbricht 2009, Mei et al. 2010). However, the ether peak of Pluronic and PEG is found to be fully overlapped with the very strong ether peak of PES. Therefore, the intensity of peak at 1107 cm^{-1} relative to the C-H peak at 1578 cm^{-1} which is contributed from the aromatic ring in PES molecule, is used to evaluate the change of surface chemistry of the membranes after the addition of various additives. This method has also been described by Susanto et al. (Susanto et al. 2009). The increase in peak intensity ratio of each membrane with respect to that of control membrane #0 is calculated as follows:

$$= \frac{I_{1107}}{I_{1578}}, \quad = \frac{I_{1107}}{I_{1578}} \quad (3.3)$$

where I_r is the ratio of the peak intensity at 1107 cm^{-1} , I_{1107} , to that at 1578 cm^{-1} , I_{1578} ; I_{r0} the peak intensity ratio of control membrane #0

Figure 3-3. ATR-FTIR spectra of membranes (a) #0, (b) #127-5, (c) #p105, (d) pure Pluronic F127

Table 3-5 presents the relative peak intensity ratio of each membrane. The increase in relative C=O peak is observed in all the other membranes prepared with additives while the degree of increment varies with different types of additives used. Hollow fiber membranes #127 and #1085, which were spun with two Pluronics consisting of the longest PEO and PPO chains among all types of Pluronic used, exhibit the highest relative peak increase with a larger than 10%. An increase of around 6 to 8% in relative peak is also observed in hollow fibers #r45 and #645, while there is insignificant relative C=O peak increase in hollow fiber #685 and #p105. Considering that the chain length of Pluronic L64 and Pluronic 17R4 is shorter than that of other Pluronics, it is understood for membrane #L64 and #r45 to have a lower value of relative peak increase. Hence, it can be seen that a significant portion of Pluronic F127, F108, L64, and 17R4 remains in the membrane matrix. However, the presence of Pluronic F68 and PEG10k in the membrane matrix is not as significant as others considering their high content of C=O bond per molecule due to high molecular weight.

Table 3-5. PWP, MWCO, ATR-FTIR analyses, and pore size distribution parameters (D^*) of hollow fibers spun using different additives

Membrane code	PWP (L/m ² ·h·bar)	MWCO (kDa)	ATR-FTIR relative peak increase at 1107/1578 cm ⁻¹ (%)	D^* (nm)	σ^*
#0	0.4 ± 0.02	- ^a	N.A.	-	-
#r4-5	24 ± 0.5	180	7.8	9.7	1.5
#645	46 ± 0.7	220	6.0	12.8	1.4
#685	130 ± 18	150	2.9	11.3	1.4
#1275	104 ± 6	15	11.6	7.3	1.1
#1085	107 ± 12	18	10.5	8.1	1.1
#p105	86 ± 9	130	4.1	8.8	1.5

^a MWCO test was not done on membrane #0 due to its extremely low PWP

The presence of Pluronic and PEG in the membrane matrix is thought to be related to their solubility in water as well as their interaction with PES chains. As amphiphilic polymers, Pluronic macromolecules contain hydrophilic PEO block and hydrophobic PPO block. For the Pluronic with PEO-PEO arrangement,

the hydration of the ethylene oxide (EO) groups, which results in the hydrogen bonding of at least two water molecules to each EO group, controls Pluronic solubility in water (Wu et al. 2005). In other words, the solubility of Pluronic increases with the increase of the mass fraction of PEO contained in the Pluronic (BASF 1996). In the case of Pluronic with reverse block arrangement (Pluronic R), the hydrophilic PEO block is located at the middle of the molecule, and therefore there is a steric hindrance that may prohibit the EO group from hydrating with more water molecules. This steric effect on hydration consequently makes the Pluronic R less hydrophilic and less soluble in water compared with their counterparts (Wu et al. 2005). On the other hand, the length of PPO block in Pluronic affects its interaction with PES. A sufficiently long length of PPO block is essential to anchor Pluronic copolymer at the membrane surface (Cavey and Olliff 1999; Wang et al. 2005).

To facilitate the analysis of the observed FTIR results, the additives used in this study are compared in four different groups:

- (1) Pluronics that have almost the same length of PPO and PEO block but reverse block arrangement, L64 and 17R4 mentioned in the previous paragraph, Pluronic 17R4 is less water soluble than Pluronic L64 due to steric effect on hydration. Therefore, the former is slightly more stable in the membrane matrix despite their similar chemical composition, as evidenced by the larger increase in IR relative peak of $1105/1178\text{ cm}^{-1}$.
- (2) Pluronics with constant PPO length and increasing PEO chain length, L64 and F68. Pluronic F68 is much more soluble in water than Pluronic L64 as the former contains 80 wt% of hydrophilic PEO compared with the 40 wt% PEO in the latter. Expectedly, most of the additive leached out from the membrane #65 and thus its IR relative peak intensity is almost the same as that of the control membrane.
- (3) Pluronics with similar mass fraction of PEO but increasing PPO chain length, F68, F108, and F128. Since all of these copolymers contain 70 or 80 wt% of PEO, they should have similar solubility in water. In terms of their interaction with PES chain, however, the length of PPO block in Pluronic

F108 and F127 is longer than that in Pluronic F68, hence anchoring the molecule in membrane matrix more stably.

- (4) PEG10k PEG is very soluble in water compared with Pluronic as it is fully comprised of hydrophilic EO groups and PPO block is absent. The slight increase in relative C peak in membrane #p10 prepared using PEG10k as an additive might be attributed to the weak physical entrapment in membrane matrix due to its relatively high molecular weight.

3.3.4. Chemical composition on membrane surface

It has been reported that Pluronic molecules tend to segregate to the membrane surface due to the hydrophilic nature of PEO chains and their thermodynamic incompatibility with PES chains (Wang et al. 2005; Wang et al. 2006b; Wang et al. 2006c). In this study, hollow fibers #0, #125, and #p10 were selected for XPS analysis to examine the surface segregation of Pluronic molecules. Figure 3-4 shows the XPS spectra of the three hollow fibers and the peaks for carbon, oxygen, and sulfur are observed. The surface elemental compositions of these membranes are also listed in Table 3-6. It is observed that the amount of oxygen increases while the amount of sulfur decreases when Pluronic F127 is used as the additive. The percentage of ether carbon (O/C over total carbon) in membrane #125 is also greater than that in membrane #0. This confirms there is an observable amount of Pluronic F127 molecules on the membrane surface. From Table 3-6, it can also be seen that the experimental percentage of ether carbon for membrane #125 (21.9%) is close to its theoretical value (22.3%). This means that the Pluronic amount on the membrane surface is not significantly higher than that in the bulk membrane, which might be interpreted as there is no segregation of Pluronic molecules to the membrane surface. However, considering the low interfacial energy between the PEO blocks of Pluronic and water, it is still possible that there is segregation in microscopic scale, which Pluronic molecules tends to reorientate themselves and, in microscopic distance, migrate to not only membrane surface but also the surface of pores inside the membrane (Hessler et al. 1999; Asatekin et al. 2007). Therefore, even if there is segregation in microscopic scale,

Pluronic might still be uniformly distributed in the membrane in macroscopic scale since pores are distributed across the whole membrane.

Figure3-4. XPS spectra of PES control membranes and PES membranes spun with Pluronic F127 and PEG10k as additives.

Table3-6. Surface elemental compositions of hollow fibers spun using different additives

Membrane code	XPS atoms percent				
	C	O	S	C, O ^a	C, O ^b
#0	72.8	20.7	6.5	16.9	16.7
#127-5	72.8	23.2	4.0	21.9	22.3
#p10-5	73.6	19.8	6.6	17.3	23.2

^aexperimental percentage of ether carbon over total carbon calculated from high resolution spectra of C1s peak

^btheoretical percentage of ether carbon over total carbon

On the other hand, the amount of oxygen and sulfur, as well as the percentage of ether carbon in membrane #510 does not differ much from that in membrane #0. Moreover, the content of ether carbon in membrane #p10 is much smaller than its theoretical value, as shown in Table 3-6. The result is in accordance to the ATR-FTIR analysis which has showed that there is only a small amount of PEG10k remains in the membrane matrix. This is because most of the molecules of PEG10k on the membrane surface have been leached out into the water since the hydrophobic PPO block is absent in the PEG10k molecules.

3.3.5. Effect of additives on membrane performance

a. Pluronics with different block arrangements (Pluronic L64 vs. 17R4)

The PWP, MWCO, and pore size distribution parameters (D^* , f^*) of hollow fiber membranes prepared with different additives are presented in Table 3-5. When comparing hollow fiber #45 to #645 prepared using Pluronic 17R4 and L64, respectively, it is observed that the PWP of membrane #54 is only 24 L/m²·h·bar, while that of membrane #64 is almost doubled. The geometric mean pore size of membrane #64 is also larger than that of membrane #54. It can be concluded that despite the similarity in chemical composition, the molecular architecture of Pluronic has a significant influence on the membrane formation.

Referring back to the cloud points in Table 3-4 and the viscosity data in Table 3-2, which show that the thermodynamic stability and viscosity of the dopes #45 and #645 did not differ much, the formation of larger pores and consequently a higher PWP of membrane #64 might be mainly attributed to the difference in hydrophilicity between the two Pluronics. As mentioned earlier in the previous section, Pluronic 17R4 is less hydrophilic than Pluronic L64 due to the steric effect on hydration of the former. The higher hydrophilicity of Pluronic L64 might result in a faster indiffusion rate of nonsolvent (water) during the phase inversion process and therefore more rapid precipitation rate. It has been reported that a rapid precipitation caused by the hydrophilicity of the dope results in higher surface porosity and more porous sublayer, leading to a higher water permeability (Kao and Li 2001).

b. Pluronics with a higher PEO content (Pluronic L64 vs. F68, F108 and F127) PEG10k

As shown in Table 3-5, with the addition of Pluronic F68, which has a longer hydrophilic PEO chain than Pluronic L64, the PWP of hollow fiber #685 increases dramatically to 130 L/m²·h·bar. Hollow fiber #1275 and #1085 spun with the addition of Pluronic F127 and F108, respectively, also exhibit relatively

high PWP of around 105 L/m²h-bar. This significant increase in permeation might be attributed to the higher PEO content (70 or 80 wt%) in these Pluronic, which enhances their hydrophilicity and thus results in more porous membrane surface as explained previously. The slightly lower PWP for membrane #127 and #108 compared with membrane #58 might be due to the presence of PEO brush layer on the surface of pores which narrows down the pore size, as will be discussed in the next few paragraphs.

On the other hand, PEG10k is the most hydrophilic molecule among all the additives used, as it comprises of 100% EO group. In contrast, PWP of membrane #p15 spun using PEG10k as an additive is around 86 L/m²h-bar and this is not as high compared with membranes #58, #127, and #108. Although the mechanism is not fully understood, the relatively low flux of membrane #p15 might be attributed to the formation of thicker skin layer.

Figure 3-5 shows the pore size distribution of the hollow fibers with PWP above 80 L/m²h-bar. It can be seen that the pore size distribution of membranes #127 and #108 is much narrower, and their geometric mean pore size is also smaller, compared with membranes #58 and #p15. In addition, the MWCO of membrane #127 and #108 is extremely low (15 and 18 kDa, respectively) compared with other membranes despite their relatively high PWP, as presented in Table 3-5. These interesting observations on the high performance of membranes #127 and #108 could not be simply explained based on the thermodynamic and kinetic effects. Therefore, a hypothesis is made to explain this observation based on the surface segregation phenomenon of amphiphilic block copolymers in membrane formation. It is possible that a PEO brush layer has been formed on the surface of membrane internal pores due to the surface segregation of the amphiphilic polymers, as reported by Asatekin et al. (Asatekin et al. 2007) and Wang et al. (Wang et al. 2006). As illustrated in Figure 3-6, this PEO brush layer formed by the Pluronic F127 and F108 might have reduced the apparent pore size of the membranes, leading to the improvement of the solute rejection evidenced by the sharp decrease in MWCO. Similarly, poly(vinylidene fluoride) (PVDF) membranes with high rejection has also been reported due to the assembly of amphiphilic

copolymer which formed a selective transport channel of defined size (Athakul et al. 2004). On the other hand, Pluronic L64 has much shorter PEO chains which might form a thinner PEO brush layer; Pluronic F68 does not present much in the membrane matrix based on the ATR-FTIR analysis in section 3.3.3 therefore the PEO brush layer formed might not be significant to affect the solute passage through the pores. These explain the relatively high MWCO for membranes #64 and #68 compared with membranes #127 and #108.

Figure 3-5. Pore size distribution of the PES hollow fibers spun with Pluronic F68, F127, F108, and PEG10k as additives

As for membrane #105, a uniform PEO brush layer may be unable to form on the surface of internal pores due to the absence of PPO block and its relatively low presence on the membrane surface as discussed in section 3.4, hence the MWCO and pore size distribution of membrane #513 is not as good as that of membranes #127 and #108 despite its long PEO chain. To prove the impact of the PEO brush layer on the solute rejection, further investigation has been carried out (on PVDF membranes) which will be discussed in the next chapter.

3.3.6. Effect of Pluronic F127 concentration on membrane morphology and performance

Both Pluronic F127 and F108 have been proved to be good additives in hollow fiber membrane formation in this study. Pluronic F127 was selected for

further investigation on the effect of its concentration on membrane formation. Figure 3-7 shows the cross-sectional morphology of hollow fibers spun using Pluronic F127 at different concentrations. The finger-like macrovoids developed from the outer side of hollow fibers become narrower when the concentration of Pluronic F127 in the dope solution is increased from 5 to 10 wt% (membrane #127e 10). At Pluronic F127 concentration of 15 wt% (membrane #157), more sponge-like structures are found in between the macrovoids, as observed in Figure 3-7 (C). It seems that macrovoid formation has been suppressed with increasing Pluronic F127 concentration. This might be due to the sharp increase in dope viscosity from 2.8 to 4.3 and 7.0 Pa·s (Table 3-2) as the Pluronic concentration changed from 5 to 10 and 15 wt%, respectively. A significant increase in viscosity caused by strong polymer chain entanglement tends to delay the rate of phase separation, hence suppressing the formation of macrovoids.

Figure 3-6. Illustration of PEO brush layer formation on the surface of membrane internal pores

Figure 3-7. (a, b, c) Crosssectional morphology and (A, B, C) their enlarged view near the outer edge of hollow fiber membranes spun with different Pluronic F127 concentrations of 5 wt%, 10 wt% and 15%, respectively

The ATR-FTIR relative peak increase presented in Table 3-7 illustrates a sharp increase in peak at $1105/1578^{-1}\text{cm}^{-1}$ from 11.6 to 31.6% as Pluronic concentration increases from 5 to 15 wt%. This implies that Pluronic F127 has good presence in the membrane matrix if more Pluronic initially presents in the dope solution. From Table 3-7 it can also be seen that the PWP of hollow fibers spun using Pluronic F127 as an additive increases slightly from 104 to 114 L_m/bar when Pluronic concentration increases from 5 to 10 wt%. In contrast, the PWP decreases to 86 L_m/bar as Pluronic F127 concentration further increases to 15 wt%. The MWCO of these hollow fibers shows an opposite trend in which the value first decreases from 15 to 9 kDa and then increases to 22 kDa with increasing Pluronic F127 concentration.

Table3-7. PWP , MWCO, and ATR-FTIR analyses of hollow fibers spun using different concentrations of Pluronic F127

Concentration of Pluronic F127 (wt%)	PWP (L/m ² ·h·bar)	MWCO (kDa)	ATR-FTIR relative peak increase at 1105/1578 cm ⁻¹ (%)
5	104 ± 6	15	11.6
10	114 ± 0.4	9	12.7
15	86 ± 3	22	31.6

The change in PWP for the hollow fibers spun with different Pluronic F127 contents is mainly affected by the morphology (membrane porosity) whereas the MWCO of hollow fibers is dependent on the membrane surface pore size. It is possible that membrane #127 is more porous compared with membrane #125, hence its PWP is improved. On the other hand, membrane #15127 has more spongelike structure which might impose a higher resistance for water transport causing a decrease in PWP.

It is supposed that the pore size of the membrane skin layer becomes larger with increasing the concentration of Pluronic F127, as reported by Zhai et al. (Zhao et al. 2008), and the MWCO of hollow fibers should increase accordingly. On the other hand, the thickness of PEO brush layer formed on the membrane internal pores is believed to increase as the amount of Pluronic F127 in the membrane matrix increases, as evidenced by the ATR-FTIR results. This increase in PEO brush layer thickness imposes an additional resistance for the solutes to pass through the pores. The observed trend of MWCO might be attributed to these contradictory effects induced by increasing concentration of Pluronic F127. The optimum Pluronic F127 concentration is found to be 10 wt%, at which the spun hollow fiber exhibits the highest PWP of 114 L/m²·h·bar and the lowest MWCO of 9 kDa.

3.4. Conclusions

Pluronics with different molecular architectures, PEG mass fractions and chain lengths were used as additives in PES hollow fiber membranes fabrication.

Extensive experiments reveal that in order to obtain hollow fibers with high water permeation and low MWCO, Pluronic with the following features is more preferential:

- (1) A molecular architecture with PEO-PPO-PEO arrangement. This structure is more hydrophilic than the reverse PPO-PPO structure because the latter exhibits steric hindrance on hydration;
- (2) A large PEO mass fraction (70, 80 wt%) as it has higher hydrophilicity;
- (3) Long PEO chains because a thick PEO brush layer may be formed on membrane (pore) surfaces. This PEO brush layer may have significant impact on solute transport through the pores and thus it improves the solute rejection;
- (4) A long PPO block as it not only provides stable anchorage to the membrane surfaces but also helps in the formation of a uniform PEO brush layer.

Both Pluronic F127 and F108 exhibit the above properties and hollow fibers spun using these two additives have high PWP and low MWCO. An increase in Pluronic F127 concentration in the dope solution tends to increase pore size and thus the water permeation, whereas a better rejection can be achieved probably due to the formation of a PEO brush layer with a large thickness on the membrane pores, which reduces the apparent pore size on the membrane surface. When Pluronic F127 concentration is 10 wt%, the spun hollow fiber exhibits the highest PWP of 114 L/m².h.bar and the lowest MWCO of 9 kDa.

CHAPTER 4. Fundamental Study on the Role of Pluronic as an Additive in PVDF Membrane Formation

4.1. Introduction

In the previous chapter, Pluronic F127 and F108 are found to be effective in preparing high performance polyethersulfone (PES) hollow fiber membranes. These Pluronics have similarity to conventional additives that they are highly hydrophilic, but the presence of hydrophobic block makes the Pluronics behave differently in PES membrane systems. Considering its unique characteristics, it would be interesting to apply Pluronic in another commonly used membrane material, poly(vinylidene fluoride) (PVDF), which is more hydrophobic than PES, for membrane fabrication.

PVDF is a semicrystalline polymer with good thermal stability, chemical resistance, and mechanical properties (Wang et al. 1999, Awanis Hashim et al. 2011, Feng et al. 2011). Among the common hydrophobic polymers, PVDF has a higher processing ability compared with polytetrafluoroethylene (PTFE) and polypropylene (PP) as the former can be easily dissolved in common solvents (Sants et al. 2007). All the above advantages make PVDF one of the most popular choices as a membrane material for various applications including microfiltration (Baroña et al. 2007), ultrafiltration (Ma et al. 2009), pervaporation (Ong et al. 2011), membrane distillation (Hou et al. 2009, Yang et al. 2011), and gas-liquid membrane contactor (Atchariyawut et al. 2006).

Due to the hydrophobic nature of PVDF material, however, it has been found that the penetration of coagulant (water) into the polymer dope solution is restricted during the phase inversion process (Wang et al. 2000). As a result, the slow coagulation rate of PVDF might cause difficulty in the preparation of highly porous membranes. One efficient method to improve the porosity of PVDF membranes is to introduce suitable hydrophilic additives as a pore former into the polymer dope solution. A wide range of additives has been used as a pore former in

PVDF membrane fabrication, which includes hydrophilic polymers, inorganic salts or acids, weak solvents, and strong solvents (Shi et al. 2008).

In our preliminary study to prepare PVDF/Pluronic hollow fibers, the addition of Pluronic into PVDF systems was found to seriously jeopardize the mechanical properties of resultant membranes due to the formation of extremely large macrovoids (will be further discussed in the next chapter). Unlike in PES system, it seems that Pluronic has a tremendous effect on pore structure of PVDF membranes, indicating that Pluronic has a much stronger pore-forming ability in PVDF system. Nevertheless, despite that a few publications involving the use of Pluronic in PVDF membrane preparation have been published, there is still a lack of understanding on the mechanism of membrane formation in the PVDF/Pluronic system. This is because those publications mainly focused on the enhancement of electrolyte uptake and ionic conductivity (Cui et al. 2008), the thermoresponsive behavior (Du et al. 2012), and the anti-biofouling behavior of PVDF/Pluronic membranes (Venault et al. 2012) while none of them focused on the use of Pluronic as an additive to control the pore structure (i.e. filtration performance) of PVDF membranes. Therefore, it is desirable to understand the mechanism behind it or to fully utilize the distinctive characteristics of Pluronic.

Similar to the studies of other membrane formation system, the information on thermodynamics and kinetics is essential for understanding the mechanism of membrane formation in PVDF/Pluronic system. In addition, due to the amphiphilic properties of Pluronic, it is important to know if Pluronic forms micelle in the polymer solution since this will certainly affect the membrane formation. Micellization of Pluronic in an aqueous solution has been well studied (Alexandridis et al. 1994) but so far no information is available on the micellization of Pluronic in common organic solvents or solvent-induced phase separation (NIPS) process to the best of our knowledge.

In the present study, aiming to understand the fundamental mechanism of membrane formation, casting of flat sheet membranes was carried out instead of hollow fiber spinning because the latter involves many spinning conditions which make the system more complicated. The effect of Pluronic as an additive on PVDF

membrane formation was investigated by examining the characteristics and performance of resulting membranes. Since Pluronic has a similar chemical structure to polyethylene glycol (PEG) with just an additional hydrophobic block, PEG with similar molecular weight to the Pluronic used in this work was also selected as an additive for comparison purpose. With the ~~also~~ information of thermodynamics/kinetics/micellization ~~and~~ the comparison between Pluronic and PEG, an attempt was made to understand the mechanism of membrane formation in PVDF/Pluronic system. In addition, to examine how the presence of Pluronic in the membrane matrix affects the ~~performance~~ of the membranes, the Pluronic molecules that are entangled in the prepared membranes were purposely washed out by solvent treatment. This study is anticipated to provide a more comprehensive understanding on the role of Pluronic in PVDF membrane formation, and explore its potential as an alternative to the conventional additives when preparing membranes with desired structures.

4.2. Experimental

4.2.1. Membrane material and chemicals

PVDF (Kynar 761, MW = 444,000, Arkema) was dried at 50°C under vacuum for at least 1 day before use. Pluronic F127 (SigmaAldrich) was used as the additives. propanol (IPA, Merck) ~~was~~ used to wash out the remaining additives from the prepared membranes. All the reagents were used as received. Other chemicals used have been described in CHAPTER 3 Section 3.2.1.

4.2.2. Determination of critical micelle concentration

To find out whether Pluronic forms micelles in N-methyl-2-pyrrolidone (NMP), an attempt was made to determine the critical micelle concentration from the surface tension-concentration curve as described by ~~et al.~~ (Lin et al. 1999). The surface tension of Pluronic/NMP solutions with different Pluronic concentrations was measured by the Wilhelmy plate method using a tensiometer.

(DCAT11, Dataphysics) at 24.0 ± 0.5 °C. Surface tension measurement was carried out and repeated at an interval of 10 min until the readings within an hour were stable. This was to ensure that the equilibrium value was obtained. An average of the last 5 readings was used in the plotting of surface tension (concentration) curve. The critical micelle concentration of Pluronic in NMP can be obtained from the graph if there is an abrupt change in gradient (Lent et al. 1999; Desai et al. 2001).

4.2.3. Phase diagram and Hansen solubility parameters

The determination of cloud point for the PVDF/NMP/water system with and without the addition of additives was achieved by titrimetric method at room temperature, as described in CHAPTER 3 Section 3.2.2. The amount of water required to achieve the cloud point was recorded. The weight fractions of PVDF, NMP, and water at the cloud point were then used to plot the ternary phase diagram.

The Hansen solubility parameters of polymer, solvent, and additives were used to calculate the total solubility parameter difference between polymer and solvent/additive ($\Delta\delta$) (Setiawan et al. 2012). The values of Hansen solubility parameters were either adopted from literature (Bettino et al. 1983) or calculated according to the group contribution method (Barton 1983).

4.2.4. Casting of PVDF membranes, measurement of dope viscosity, and post treatment

Polymer solutions with 18 wt% of PVDF and varied concentration of additives were prepared using NMP as the solvent. The dope solution was stirred for at least 2 days at 60 °C. The homogenous dope prepared was then cooled down to room temperature and allowed to stand overnight to get rid of bubbles before casting. The homogeneous polymer solutions were casted on a glass plate using a motorized film applicator (Elcometer 4340) at room temperature. The thickness of the film was controlled at 250 μ m by an adjustable blade. The film with the glass plate was then immediately immersed into a coagulant bath (tap water). The resulting membranes were subsequently stored in a water bath with water being

replaced frequently for at least 2 days to remove residual solvent. The dope compositions are listed in Table 4-1. Rheological characteristic of the dope solutions was measured by a rheometer as described in CHAPTER 3 Section 3.2.3

Table 4-1. Compositions of polymer dope and their characteristics

Membrane code	Dope composition (wt%)	Viscosity (Pa·s)	$\epsilon_{dl} = \frac{d_{solvent} + d_{additive}^b - d_{polymer}}{d_{polymer}}$ (MPa) ^{1/2}
P0	PVDF/NMP (18/82)	3.7 ± 0.1	0.2
P1	PVDF/P127/NMP (18/1/81)	3.9 ± 0.2	0.3
P3	PVDF/P127/NMP (18/3/79)	4.4 ± 0.1	0.5
P5	PVDF/P127/NMP (18/5/77)	5.2 ± 0.3	0.7
P10	PVDF/P127/NMP (18/10/72)	7.8 ± 0.2	1.2
G5	PVDF/PEG/NMP (18/5/77)	5.4 ± 0.4	0.7

^aP127: Pluronic F127

^b $d_{solvent} + d_{additive}$ is calculated based on mole fraction of solvent and additives (Setiawan et al. 2012)

In CHAPTER 3 it is demonstrated that the presence of poly(ethylene oxide) (PEO) brush layer on membrane pore surface might be responsible for the high performance of the resultant membranes. However, this hypothesis needs to be further confirmed by more evidence. In this chapter, Pluronic molecules that are entangled in the prepared membranes were purposely washed out by soaking the membranes in IPA for at least 4 hours. The IPA-treated membranes were subsequently immersed into water to wash out the residual IPA. By comparing membranes before and after the washing out of Pluronic, it is possible to examine how the presence of Pluronic in the membrane matrix affects the performance of the membranes. The observations can be useful to verify the mentioned hypothesis.

4.2.5. Membrane characterizations and analysis

The cross-sectional and surface morphologies of hollow fiber membranes were observed using a field emission scanning electron microscope (SEM, JEOL JSM7600F). For the observation of cross-sectional morphology, the membranes were broken in liquid nitrogen and sputtered with platinum prior to the test.

To determine the overall porosity of membranes, gravimetric method was employed. First, the weight of a wet membrane was measured after carefully wiping away the excess water. The membrane was then dried at a temperature of 60 °C and the weight of the dried membrane was measured. The membrane porosity is calculated using the following equation (Chou et al. 2009)

$$P = \frac{(W_1 - W_2) / \rho_{\text{water}}}{(W_1 - W_2) / \rho_{\text{water}} + W_2 / \rho_{\text{PVDF}}} \quad (4.1)$$

where P is the membrane porosity, W_1 and W_2 the weight of wet and dry membrane, respectively, ρ_{water} the specific gravity of water, ρ_{PVDF} the specific gravity of PVDF which has a value of 1.78 according to the Kynar product information.

The surface contact angle was measured by the sessile drop method using a goniometer (Dataphysics OCA) to examine the hydrophilicity of the prepared membranes. The initial static contact angles were obtained immediately after dropping Milli-Q water on the membrane surface. At least 5 measurements were repeated at different locations of a dried membrane.

The presence of Pluronic and PEG in the prepared membranes was examined by Fourier transform infrared spectroscopy (FTIR) as mentioned in Section 0. To test the pure water permeation (PWP) and dextran rejection, a membrane was sealed in a customized module with an effective area of 4.0 cm². The details of testing have been described in Section 3.2.5. Most of the membranes prepared in this chapter showed a molecular weight cutoff (MWCO) larger than 500 kDa, which was the maximum limit. Therefore, instead of MWCO data, the rejection of 50-kDa Dextran is reported.

4.3. Results and discussion

4.3.1. Micelle characterization of Pluronic in NMP

It is well known that Pluronic can form micelles in an aqueous solution and the micellization is dependent of temperature, concentration, and types of Pluronic

(Alexandridis et al. 1994) The micellization process is driven by the hydrophobic effect, which states that there is a gain in entropy caused by restoring of hydrogen bonding structure in water when the hydrophobic parts of the Pluronic molecules aggregate (Alexandridis and Alan Hatton 1995). On the other hand, the micellization of Pluronic in dipolar aprotic solvents such as NMP has not been studied. To understand the membrane formation involving Pluronic as an additive, it is important to know the behavior of Pluronic in the used solvent. Therefore, an attempt has been made to find out whether Pluronic can form micelles in NMP.

Figure 4-1 shows the plot of the surface tension of Pluronic solutions versus concentration of Pluronic in NMP. The surface tension decreases linearly with increasing Pluronic concentration within the range of 0.05 wt% to 18 wt%. An abrupt change in gradient, which is indicative of micelle formation, is not observed in the plot. Moreover, the addition of Pluronic in NMP merely reduces the surface tension from 42.0 (0 wt% Pluronic) to 38.9 mN/m at a concentration of 18 wt%. Comparing this observation to the literature report of the reduction in surface tension of water from 72 to 45 mN/m at a Pluronic concentration of 0.001 wt%, Pluronic seems to have very low surface activity in NMP (Desai et al. 2001). This reveals that unlike the amphiphilic behaviour of Pluronic in water, the solubility of PEO and poly(propylene oxide) (PPG) blocks in NMP is considered similar. Both the absence of the gradient change in the surface tension-concentration plot and the low surface activity of Pluronic in NMP suggest that micelle is unlikely to form in the Pluronic/NMP solution.

4.3.2. Phase diagram and viscosity of polymer dopes

Figure 4-2 illustrates the effect of different additives on the isothermal phase diagram for the PVDF/NMP/water system. The cloud point curves shift slightly towards the left when either Pluronic or PEG presents in the dopes, indicating that both additives promote thermodynamic instability in the system since the water tolerance of the system is reduced. This can be explained by the increase in total solubility parameter difference between solvent and PVDF (δ) when the additives are added as shown in Table 4-1, which was calculated based on the

Hansen solubility parameters provided Table 4-2. When comparing PEG and Pluronic, it seems from the phase diagram that their influence on the degree of water tolerance is similar. This reveals that the presence of an additional PPO block in Pluronic molecules has no significant impact on the thermodynamics of the system, which is in agreement with presented in Table 4-1.

Figure 4-1. Surface tension versus log(concentration) curve of Pluronic F127 in NMP

The viscosities of dopes, which can affect the rate of solvent exchange during the membrane formation process, are also listed in Table 4-1. As expected, the viscosity increases with increasing Pluronic content since the increase in polymer content can cause a higher degree of chain entanglement. Similar to the influence on thermodynamics, the effect of Pluronic addition on the dope viscosity has no much difference to that of PEG. For instance, the dope containing 5 wt% of Pluronic and 5 wt% of PEG has a viscosity of 5.2 and 5.4 Pa·s, respectively. The observation on both thermodynamics and viscosity confirms that Pluronic and PEG exhibits very similar behavior in NMP.

Figure 4-2. Ternary phase diagram of PVDF/NMP/water system with the presence of different additives

4.3.3. Hydrophilicity and chemistry of PVDF membranes

a. Effects of Pluronic and PEG as additives

The effect of Pluronic concentration on the membrane contact angle is illustrated in Figure 4-3. As shown in the figure, the contact angle of PVDF membranes without IPA treatment decreases from 64° to 45° when the Pluronic concentration in the dope solution is increased from 0 to 10 wt%. The enhancement in surface hydrophilicity with increasing Pluronic concentration is expected since Pluronic tends to migrate towards the membrane/water interface (Mao et al. 2005). The presence of Pluronic in the membranes can be further evidenced by the FTIR analysis which is presented in Figure 4-4 (a). It shows that when the Pluronic concentration is greater than 3 wt%, an absorbance peak at 1107 cm^{-1} corresponding to the ether group (C-C) in Pluronic molecules can be obviously observed.

Table 4-2. Hansen solubility parameters

	d_H (MPa) ^{1/2}	d_D (MPa) ^{1/2}	d_P (MPa) ^{1/2}	d_t (MPa) ^{1/2}
PVDF ^a	9.2	17.2	12.5	23.2
NMP ^a	7.2	18.0	12.3	23.0
PEO ^b	8.5	15.3	7.9	19.2
PPO ^b	7.1	14.7	7.1	17.8
Pluronic F127 ^c	8.2	15.2	7.7	18.9

^avalues adopted from Bottino et al. (Bottino et al. 1983)

^bvalues calculated according to group contribution method (Barton 1983)

^cvalues calculated based on 1:1 molar fraction of PEO and PPO

Figure 4-3. Contact angles of PVDF membranes prepared with Pluronic or PEG as the additive. (nonIPA: before IPA treatment; IPA: after IPA treatment)

On the other hand, this ethereal peak is totally absent in the FTIR spectra of the membranes prepared with the addition of PEG as the additive, even when the PEG concentration is as high as 5 wt%, as shown in Figure 4-5. The PEG used in this study has a molecular weight of around 10,000 Da which is close to Pluronic molecular weight of 12,600 Da. From here it can be assured that chain entanglement is not the main reason for the ability of Pluronic to stay in the membranes, since PEG with similar molecular weight is observed to be totally

leached out during the membrane formation process. Instead, the presence of PPO block in Pluronic molecules, which induces hydrophobic interaction between PVDF and the additive, should be responsible for the much better stability of Pluronic in membranes compared with PEG. This idea on the PVDF-Pluronic interaction is helpful in the understanding of membrane formation involving amphiphilic block copolymer as an additive, as elaborated in a later section.

Figure 4-4. FTIR spectra of PVDF membranes prepared with Pluronic concentration (a) before and (b) after IPA-treatment

b. Effects of IPA treatment

The change in contact angle due to the IPA treatment is also illustrated in Figure 4-3. For the IPA-treated membranes prepared with the addition of Pluronic at a concentration of 3 wt% or more, an increase in contact angle can be clearly observed compared with the membranes without IPA treatment. The Pluronic molecules that are originally attached near the membrane surface appear washed out during the soaking of the membranes in IPA, resulting in the increase in contact angle. On the other hand, there is no much change in contact angle for the

membranes prepared with a lower Pluronic content or with PEG. This is probably because the amount of Pluronic and PEG presents near the membrane surface is not significant to enhance the membrane hydrophilicity even before the IPA treatment.

Figure 4-5. FTIR spectra of PVDF membranes prepared with Pluronic or PEG as the additive

From Figure 4-3 it can also be observed that the contact angle of IPA-treated membranes prepared with Pluronic as the additive is higher than that of pure PVDF membranes. This phenomenon might be attributed to the enhanced surface porosity of the membranes prepared with Pluronic, which will be illustrated in the following section. According to Cassie and Baxter, the apparent contact angle of a surface is higher than the intrinsic contact angle of the material when the material surface is porous (Cassie and Baxter 1944).

The change in Pluronic content in the membrane matrix before and after IPA-treatment can be qualitatively examined by comparing the FTIR spectra of the membranes shown in Figure 4-4 (a) and (b). The absorbance peaks at 1107 cm⁻¹ have disappeared after the membranes were soaked in IPA, indicating that even Pluronic molecules that are originally embedded in the membrane matrix have been

washed out. Moreover, it can be seen from the FTIR analysis that the chemistry of PVDF itself is not affected by the IPA treatment since the spectra of membranes prepared with little or no Pluronic (i.e., membranes P1 and P0) show no difference before and after the IPA treatment. This also confirms that the change in membrane contact angle due to IPA treatment is solely caused by the loss of Pluronic but not the change in PVDF chemistry.

4.3.4. Membrane morphology and porosity

The morphology of prepared membranes before and after the IPA treatment was compared under SEM and no significant difference was observed. Therefore, only the images of surface and cross-sectional morphology for the IPA treated membranes are presented in this study.

a. Effects of Pluronic as the additive

Figure 4-6 shows the top surface and the cross-sectional morphologies of PVDF membranes after IPA treatment. Compared with membrane P0 with no additive, the surface of membrane P1 becomes highly porous with the addition of merely 1 wt% Pluronic. The surface porosity is further enhanced when the concentration of Pluronic is 3 wt% or more for membrane P3 and P5. On the other hand, the addition of Pluronic also significantly promotes macrovoid growth: compared with membrane P0, the size of macrovoids becomes much bigger and they occupy the whole cross-section for membrane P1 to P5. Correspondingly, significant enhancement in overall porosity from less than 80% to around 88% can be observed after the addition of 1 wt% Pluronic and the degree of porosity enhancement has already reached the plateau status with further increasing Pluronic concentration (Figure 4-7). The observations reveal that Pluronic acts as a very effective pore former in PVDF systems.

Figure 4-6. Top surface and cross-sectional morphologies of PVDF membranes prepared with different Pluronic concentrations (after-IPA treatment)

Figure4-7. Overall porosity of prepared PVDF membranes

b. Proposed mechanism of membrane formation with Pluronic or PEG as additive

Figure4-8 presents the top surface and the ~~cross~~ cross-sectional morphologies of PVDF membranes prepared with Pluronic or PEG as the additive. It is observed that the membrane prepared with Pluronic (membrane P5) exhibits a significantly higher surface porosity and pore size than the membrane prepared with PEG (membrane G5). The macrovoids are fully developed across the ~~cross~~ cross-section of membranes in both membranes P5 and G5, but the size of macrovoids ~~appears~~ appears larger for membrane P5 when comparing the SEM images at the same magnification. The overall porosity of membrane G5 is also lower than that of membrane P5 as shown in Figure 4-7. The above observations reveal that Pluronic has a stronger pore forming ability than PEG in PVDF membrane formation.

The concept of thermodynamics and kinetics is commonly used to explain the membrane formation via phase inversion processes. However, it can be seen from section4.3.2 that the addition of Pluronic and PEG causes similar degree of

thermodynamic instability and does not occur. In addition, the size of Pluronic and PEG in NMP is expected to be similar due to the fact that micelles are unlikely to be formed in Pluronic/NMP solution, as discussed in section 4.1. Accordingly, the significant difference in surface pore, porosity, and macrovoid size between the membranes prepared with Pluronic and PEG cannot be explained by the general rule of instantaneous or delayed demixing based on the thermodynamics of the system and the viscosity-controlled rate of solvent/solvent exchange during the membrane formation process. Instead, it is believed that the strong pore-forming ability of Pluronic in PVDF membrane formation is attributed to the hydrophobic hydrophobic interaction between Pluronic and PVDF, as elaborated below.

Figure 4-8. Top surface and cross-sectional morphologies of PVDF membranes prepared with 5 wt% of Pluronic (left) and PEG (right) (after IPA treatment)

The surface images in Figure 4-8 show that both the membranes prepared with Pluronic and PEG consist of dispersed pores and continuous PVDF phase, indicating that nucleation and growth of polymer phase may have dominated the membrane formation process (Mulder 1996; Ren and Wang 2010). In this situation,

the in-diffusion of nonsolvent and out-diffusion of solvent bring the system to a thermodynamically metastable condition, resulting in the nucleation of polymer lean phase. The nuclei can grow continuously until the surrounding polymer phase becomes solidified via crystallization, gelation, or vitrification (Mulder 1996). During PVDF membrane formation involving Pluronic, water diffusing into the polymersystem may induce the hydrophobic-hydrophobic interaction between PPO block and PVDF, which has been discussed in section 4.003. In other words, Pluronic molecules would preferably attach to PVDF macromolecules in the presence of water in the surrounding environment. Due to the high mobility and flexibility of PEO chains in an aqueous environment, it is possible that the rearrangement of PVDF chains is disrupted by the attached Pluronic molecules (Wang et al. 2005; Shi et al. 2009). As a result, the solidification of polymer-rich phase tends to be delayed compared with the PVDF/PEG system, in which the hydrophobic-hydrophobic interaction is absent, giving more time for the polymer lean nuclei to grow to a bigger size. This leads to the larger surface pores on the resultant membranes.

This concept can also be extended to explain the macrovoid formation because the process also involves the growth of nucleus, which is opposed by the solidification of surrounding polymer-rich phase according to McKelvey et al. (McKelvey and Koros 1996). Since the interaction between PVDF and PEG is weak compared with the PVDF/Pluronic interaction, the polymer-rich phase in the system containing PVDF and PEG solidifies earlier than their counterpart containing Pluronic. This results in a shorter duration for macrovoid growth and the membranes prepared with PEG exhibit a less porous structure with smaller macrovoids. The relationship between the macrovoid formation and the occurrence of solidification has also been reported by Barzin et al. (Barzin and Sadatnia 2008). In their study, it has been shown that the growth of macrovoids in PES/dimethylformamide/water system is suppressed because the polymer phase of the system vitrifies earlier than that of PES/NMP/water system. This observation agrees with our proposed mechanism.

c. Comparison between PES/Pluronic and PVDF/Pluronic systems

Unlike the tremendous effect of Pluronic on macrovoid growth in PVDF membranes, the macrovoid size of PES/Pluronic membranes is similar to that of PES/PEG membranes, as can be seen in Figure 3-2. It seems that the interaction between PPO blocks in Pluronic and PES macromolecules does not significantly affect macrovoid growth in PES system. The reason might be attributed to the different glass transition temperatures (T_g) of PVDF and PES. At room temperature, PVDF ($T_g \approx 35^\circ\text{C}$) is in rubberlike state, while PES ($T_g \approx 230^\circ\text{C}$) is in glassy state in which the movement of polymer chains is much restricted (Ameduri 2009; Ren and Wang 2010). As a result, PES has a much higher solidification rate than PVDF and it is believed that PES/PPO interaction does not play an important role in macrovoid growth of PES membranes.

4.3.5. Filtration performance of PVDF membranes

a. Effects of IPA-treatment

Figure 4-9 (a) presents the PWP of membranes prepared with different additives. Comparing the membranes before and after IPA treatment, it can be seen that the PWP increases significantly after IPA treatment for membranes prepared with 3 wt% or more of Pluronic. Apparently, the enhancement in PWP is caused by the loss of Pluronic from the membranes due to IPA soaking, which has been confirmed by contact angle measurement and FTIR analysis in section 4.3.1. This phenomenon is related to the migration of Pluronic towards the polymer/water interface, including surface of membrane pores, as discussed previously in CHAPTER 3 Section 0. When the amount of Pluronic migrated to the surfaces is large enough, PEO brush layer can be formed which narrows down the membrane pores. Thus by washing out the Pluronic using IPA treatment, the membrane pores increase to its inherent size, leading to the enhancement in PWP (Figure 3-6).

The change in pore size after IPA treatment is also revealed by dextran rejection of the membranes. As shown in Figure 4-9 (b), a decrease in dextran

rejection can be seen for membranes P3, P5, and P10 after treatment. On the other hand, membranes prepared with either PEG or low concentration of Pluronic show no significant change in PWP and solute rejection after treatment, further confirming that the smaller apparent pore size before IPAtreatment is due to the presence of Pluronic at the pore surface for the membranes with higher amount of Pluronic. From here it is known that the membrane pore size can indeed be reduced significantly when PEO brush layer is formed at the membrane pore surface, providing that the amount of Pluronic in the membrane is sufficiently high. Similarly, it can be further confirmed that the low MWCO of PES hollow fiber membranes spun with the addition of Pluronic F127 and F108 is attributable to the formation of PEO brush layer as mentioned in CHAPTER 3

Figure 4-9. (a) Pure water permeation (b) dextran rejection of prepared PVDF membranes (not IPA: before IPAtreatment; IPA: after IPAtreatment)

b. Effects of Pluronic concentration

Referring to Figure 3-6 in CHAPTER 3 which illustrates the formation of PEO brush layer formation on membrane pore surface, the filtration performance of

membranes depends on the inherent pore size, when there is no PEO brush layer, or the apparent pore size, at the presence of PEO brush layer. As shown in Figure 4-9 (a), the PWP of IPA-treated membranes increases with increasing Pluronic concentration and reaches a value of 490^2 L/hbar at a Pluronic concentration of 10 wt%. Correspondingly, the membrane rejection for 500Da dextran of the membranes decreases with increasing Pluronic concentration as shown in Figure 4-9 (b). This reveals that the inherent pore size, of the membrane surface becomes larger with increasing Pluronic concentration. However, the apparent pore size, of the membrane surface shows a trend of increase with increasing Pluronic concentration based on the filtration performance of membranes without IPA-treatment. This is because PEO brush layer does not come into effect at low Pluronic concentration. The formation of PEO brush layer only becomes significant enough to reduce the apparent pore size at Pluronic concentration of at least 3 wt%. On the other hand, the pore size of membranes prepared with 5 wt% PEG is higher than the apparent pore size of the membrane prepared with the same concentration of Pluronic but lower than its inherent pore size.

4.4. Conclusions

The role of Pluronic as an additive in PVDF membrane formation has been studied in this work, while PEG with similar molecular weight and the same ether group has also been used for comparison purpose. It is found that there is no significant difference in thermodynamic instability and viscosity between the system containing Pluronic and PEG. Surface tension study also reveals that no micelles are formed in Pluronic/NMP systems. However, hydrophobic interaction seems to exist between PEG blocks in Pluronic molecules and PVDF macromolecules. This interaction is believed to affect PVDF membrane formation by disrupting the PVDF chain rearrangement during the solidification process. Consequently, the membranes prepared with Pluronic exhibit larger surface pore size, porosity, and macrovoids than the membranes prepared with PEG, indicating that Pluronic has a strong pore-forming ability due to its unique properties. When comparing membranes before and after IPA treatment, it is shown that the presence

of Pluronic in the membrane pores can significantly affect the filtration performance of the membranes due to the formation of PEO brush layer. Thus, IPA treatment also leads to an increase in PWP and an increase in dextran rejection of the membranes by removing the PEO brush layer that narrows down the pores.

CHAPTER 5. Effects of Second Additives on the Properties of PVDF/Pluronic Hollow Fiber Membranes

5.1. Introduction

Due to the interaction between poly(vinylidene fluoride) PVDF and poly(propylene oxide) PPO/poly(ethylene oxide) PEO blocks, Pluronic shows a strong pore-forming ability in PVDF membrane formation. This unique behavior of Pluronic is beneficial to produce highly porous PVDF membranes which are desirable for permeation performance. However, the strong effect of Pluronic on pore formation is also accompanied with the enhancement of macrovoid growth. It has been reported that when large macrovoids are formed in membrane cross section, the mechanical strength of the membrane is jeopardized (Sheet al. 2008). In other words, by using Pluronic as the additive it is expected to produce highly permeable membranes at a price of sacrificing mechanical properties. Therefore, there is a need to control the macrovoid formation while maintaining high porosity of the membrane during fabrication process.

The control of macrovoid formation has always been an important topic in the research of membrane preparation. The effects of various membrane preparation conditions on the membrane morphology have been studied. For instance, the morphology of the resultant hollow fibers changes from finger-like to sponge-like when the PVDF concentration increases (Yuliwati and Ismail 2011, Tang et al. 2012). It has also been reported that the type of coagulant can have a significant impact on membrane morphology (Jy. et al. and Lin et al. reported the use of ethanol and 1-octanol respectively, as the soft coagulant to make macrovoid-free and particulate-like PVDF membranes (Lin et al. 2003, Li et al. 2011). The phenomenon is attributed to the occurrence of solid-liquid demixing accompanying crystallization of PVDF due to the slower onset of liquid-liquid demixing.

Since the macrovoid formation is a competition between the growth of polymer-lean nucleus and the solidification of the surrounding polymer-rich phase (McKelvey and Koros 1996) it is possible to suppress the macrovoid growth by

either hindering the nucleus growth or accelerating the solidification, which can be achieved by adjusting the properties of the polymer dope solution. For instance, membranes with smaller macrovoids have been obtained when a highly viscous casting dope is used, since a high viscosity tends to delay the demixing and suppress the macrovoid growth (Fontananova et al. 2006, Wang et al. 2011). It has been reported that when PVDF is dissolved in a weaker solvent such as triethyl phosphate, a little amount of nonsolvent is sufficient to induce gelation or solidification (Yeow et al. 2004, Abed et al. 2012). As a result, macrovoids are not able to develop and a fully sponge structure is normally observed on the resultant membranes.

In this study, attempts were made to control the macrovoid formation of PVDF/Pluronic membranes by adjusting the dope properties using a second additive. The effects of Pluronic and the second additive on the membrane properties, including morphology, filtration performance, and mechanical properties, were studied. Lithium chloride and water were selected because the former has been reported to enhance the dope viscosity significantly while the latter is a strong coagulant which is expected to accelerate the solidification process (Kong and Li 2001, Hou et al. 2009, Idris et al. 2010). At the point of study, the use of mixed additives in PVDF/Pluronic membrane fabrication has not been reported. The aim of the study was to utilize the synergetic effect of the mixed additives, i.e., the strong pore-forming ability of Pluronic and the macrovoid-suppressing ability of the second additives, to prepare highly porous PVDF hollow fiber membranes with reasonably good membrane morphology and mechanical properties.

5.2. Experimental

5.2.1. Membrane material and chemicals

PVDF (Kynar 761, MW = 444,000, Arkema) was dried at 50 °C under vacuum for at least 1 day before use. Pluronic F 127, lithium chloride (LiCl, anhydrous, MP Biomed), and M10 water were used as the solvent additives in membrane preparation. Other chemicals used are described in Section

5.2.2. Preparation of spinning dope, measurement of dope viscosity and construction of phase diagram

A polymer dope solution for spinning was prepared by simultaneously dissolving desired amount of predried PVDF and the additives which consist of Pluronic F127, LiCl, or water in N-methyl-2-pyrrolidone (NMP) using a jacket flask. The dope solution was mechanically stirred for at least 24 h at 60 °C. The homogenous dope prepared was then cooled down to room temperature and subsequently degassed under vacuum for overnight before spinning.

Rheological characteristic of the spinning dope solutions was measured by a rheometer (Physica MCR 101, Anton Paar) and the cloud points of the PVDF/NMP/water system with and without additives were determined by titration method. The detailed procedures have been illustrated in Section 3.2.3 and Section 4.2.3

5.2.3. Spinning of PVDF hollow fiber membranes

The PVDF hollow fiber membranes were fabricated via dry/wet spinning process as described in Section 0. For the spinning of different dopes, the dope flow rate was kept constant while different bore fluid flow rates were employed in order to achieve a reasonable thickness of spun membranes. The nascent hollow fiber was collected at free falling take-up speed and subsequently stored in a water bath for at least 2 days to remove residual solvent. The dope compositions and detailed spinning conditions are listed in Table 5-1 and Table 5-2, respectively.

Table 5-1. Additive concentration in dope solutions containing 18wt% of PVDF

Dope/ membrane code	Pluronic F127 concentration (wt%)	2nd additive & concentration (wt%)
P0	0	-
P1	1	-
P3	3	-
P3L3	3	LiCl, 3
P3W3	3	water, 3

Table 5-2. Spinning parameters for PVDF hollow fiber membranes

Spinning parameters	Value
spinneret dimension (mm)	ID = 1.0, OD = 2.0
dope flow rate (g/min)	6.0
bore fluid (wt%)	NMP/water (70/30)
bore fluid flow rate (mL/min)	3 - 6
external coagulant	tap water
coagulant temperature (°C)	25 ± 1
air gap (cm)	1
take-up speed (m/min)	8.6, 10.0
room temperature (°C)	20 ± 2
room humidity (%)	70 ± 3

5.2.4. Membrane characterizations and analysis

The mechanical properties of the membranes were measured using a Zwick Roell BT1-FR0.5TN.D14 tensile tester. A hollow fiber was clamped at the both ends with an effective length of 25 mm and was pulled in tension at a constant elongation velocity. Young's modulus, tensile stress at break, and elongation at break were obtained by averaging five times of measurement results.

The outer and inner diameters of the membranes were determined using a digital microscope (KEYENCE, VHX500F). The surface and cross-sectional morphologies of the hollow fibers were observed under field emission scanning electron microscope (FE-SEM) and scanning electron microscope (SEM), respectively, as elaborated in Section 4.2.5 and Section 4.3.

To determine the overall porosity of hollow fiber membranes, a gravimetric method that is different from the method used in CHAPTER 4 was employed. This is because the excess water in the lumen of wet fibers, which is more difficult to wipe away, can lead to inaccurate measurement if the method used for determining the porosity of flat sheet membranes is used. The porosity of hollow fiber membranes was determined according to the following equation (Tang et al. 2012):

$$P = 1 - \frac{W_{\text{wet}}}{W_{\text{dry}}} = 1 - \frac{m_{\text{wet}}}{m_{\text{dry}}} \quad (5.1)$$

where ϵ is the membrane porosity, W the weight of dry membrane, V_{membrane} the volume of membrane which can be determined based on its inner diameter, ρ_{PVDF} the specific gravity of PVDF which has a value of 1.78 according to the Kynar product information. It should be noted that deviation of inner/outer diameter along the length of hollow fiber may lead to some uncertainty on this membrane porosity measurement.

The pure water permeation (PWP) and molecular weight cutoff (MWCO) were tested using procedures described in Section 2.5. The experiments were operated under a pressure of 0.34 bar since some of the fibers are mechanically weak.

5.3. Results and discussion

5.3.1. Phase diagram and viscosity of polymer system

Figure 5-1 illustrates the effect of different additives on the isothermal phase diagram for the PVDF/NMP/water system. Comparing with the dope without any additive, the cloud point curve shifts slightly towards the left when Pluronic is the only additive in the dope. When both Pluronic and LiCl are added in the dope, the cloud point curve becomes further closer to the PVDF/NMP axis. This indicates that the presence of the additives promotes thermodynamic instability in the system and the impact due to the presence of both Pluronic and LiCl is much stronger. This phenomenon is attributed to the strong interaction between LiCl and NMP, which causes a decrease in the ability of the solvent to dissolve PVDF. As a result, the polymer solutions become thermodynamically unstable after the addition of LiCl (Sidiawan et al. 2012a).

The viscosity of the dopes prepared for spinning is presented in Figure 5-2. The results revealed that an increase in Pluronic F127 concentration from 0 to 3 wt% in PVDF dopes causes an increase in the dope viscosity from 3.6 to 5.0 Pa·s, while the reason has been discussed in Section 2. When comparing the dope with and without the addition of a second additive, it can be observed that the dope

viscosity increases with the addition of second additives into the dope. This dope viscosity enhancement effect is more evident for LiCl than that for water. For instance, the viscosity increases significantly from 5.0 Pa·s for dope P3 to 13.3 Pa·s for dope P3L3, which is the case with the addition of LiCl as the second additive; whereas, a slight increase in viscosity from 5.0 Pa·s for dope P3 to 6.3 Pa·s for dope P3W3, which shows the case with the addition of water, observed. This phenomenon has also been reported by other studies (Kang and Li 2001, Shi et al. 2008, Hou et al. 2009). The significant enhancement of viscosity caused by the addition of LiCl can be attributed to the formation of loose complexes between LiCl and the solvent, as well as the interaction between cation and electron donor in the polymer molecule (Shi et al. 2008).

Figure 5-1. Phase diagram of PVDF/NMP/water system with different additives

5.3.2. Macrovoid development and porosity of PVDF hollow fibers

a. Effects of Pluronic as additive

Figure 5-3 (a, b, c) shows the cross-sectional morphology of PVDF hollow fibers prepared with/without the addition of Pluronic F127. Membrane P0, which

was prepared without any additive, exhibits an asymmetric structure consisting of finger-like macrovoids developed underneath the outer surface of the fibers, and a spongelike structure near the lumen of the fibers. Tremendous change in the morphology is observed after the addition of 1 wt% of Pluronic. With the addition of 1 and 3 wt% of Pluronic F127 (membrane P1 and P3), the macrovoids almost fully develop across the cross-section and the size of macrovoids is significantly increased compared with the morphology of membrane P0. Accordingly, the overall porosity of the membranes also increases from 79% to 85% after the addition of Pluronic, as shown in Table 5-3. It is also noticed that irregular contour is formed at the lumen of the fibers with the addition of Pluronic F127.

Figure 5-2. Dope viscosity with different additives

The formation of much larger macrovoids in the spun hollow fibers presented in Figure 5-3 (b) and (c) is consistent with the observation on flat sheet membranes in Section 3.4. As discussed in the previous chapter, it is believed that the presence of hydrophobic interaction between PVDF macromolecules and PPO block is responsible for such a tremendous enhancement in macrovoid growth. These big macrovoids formed in membrane P1 and P3 are not desirable as the mechanical strength of the membranes will be strongly deteriorated.

Therefore, an attempt has been made to suppress the macrovoid formation by the addition of 2nd additives, including LiCl and water, into the dope containing 3 wt% Pluronic F127, as discussed in the following section.

Figure5-3. Crosssectional morphology of hollow fiber membranes (a) P0, (b) P1, (c) P3, (d) P3L3, and (e) P3W3 scale bars correspond to 20 μm

Table5-3. Dimensions, porosity, and MWCO of PVDF hollow fiber membranes

Membrane code	Outer diameter (μm)	Inner diameter (μm)	thickness (μm)	porosity (%)	MWCO (kDa)
P0	940 $\pm$ 9	610 $\pm$ 10	165 $\pm$ 2	79.2 $\pm$ 0.1	11
P1	1100 $\pm$ 20	780 $\pm$ 25	160 $\pm$ 5	85.4 $\pm$ 0.1	70
P3	1050 $\pm$ 12	730 $\pm$ 18	160 $\pm$ 4	83.4 $\pm$ 0.1	490
P3L3	1190 $\pm$ 12	860 $\pm$ 12	165 $\pm$ 7	82.2 $\pm$ 0.1	50
P3W3	1140 $\pm$ 13	830 $\pm$ 10	155 $\pm$ 5	83.6 $\pm$ 0.1	>500

b. Effects of second additive

Figure 5-3 (d, e) presents the cross-sectional morphology of PVDF hollow fiber membranes prepared with the addition of second additives, while the concentration of Pluronic F127 is kept constant at 3 wt%. The morphology observed to change from big macrovoids to narrower finger structure when LiCl or water is added into the Pluronic-containing dopes. On the other hand, the overall porosity of the fibers spun with two additives does not differ much from that spun with single additives.

With the presence of LiCl in the dope, the thermodynamic stability of the membrane formation system is significantly deteriorated. This brings the cloud point curve of the system much closer to the initial dope composition, as presented in Figure 5-1. In other words, demixing of the LiCl-containing system will be initiated with the presence of much lesser amount of water compared with the systems with only Pluronic as the additive. Therefore, instantaneous demixing is expected to be promoted, which in turn encourages the macrovoid growth (Mulder 1996). On the other hand, the presence of LiCl also enhances the dope viscosity significantly as discussed in 3.1. The high viscosity tends to hinder the growth of polymer-lean nucleus and consequently macrovoids with much smaller size are formed (Wongchitphimon et al. 2011). It can be seen from the above that the thermodynamics and kinetics of the LiCl-containing system renders contradictory effects on macrovoid formation. However, the effect of enhanced viscosity is to be dominant in this case based on the observation on resultant membrane morphology.

The addition of water into the dope brings the system much closer to its cloud point condition which promotes instantaneous demixing and thus the growth of large macrovoids is expected. This is in contrast to the observation in this study. Since the viscosity enhancement of the water-containing spinning dope is not as pronounced as that of the LiCl-containing system, it seems that there are other reasons responsible for the macrovoid suppression in this case. One possible explanation is that the presence of water not only promotes instantaneous demixing

but also causes solidification of PVDF to occur more easily. Hence, the growth of macrovoids might be inhibited by the surrounding solidified polymeric phase despite the fast demixing process. Similar macrovoid suppression during membrane formation has also been observed with the addition of water-polyethersulfone (PES) and polyetherimide (PEI) systems (Liu et al. 2003; Ren et al. 2010). Another reason for the macrovoid suppression might be related to the interaction between water and Pluronic in the dope. The hydrophilic groups of the Pluronic tend to interact with water molecules that have already existed in the spinning dope. In turn, the intake of water from the coagulant bath into the nascent fibers is expected to be slower. As a result, the macrovoid growth is suppressed when both water and Pluronic presents in the spinning dope. Similar mechanism has been proposed by Zhang et al. for the macrovoid suppression of PVDF membranes using water and Tween 80, an amphiphilic surfactant as the additive (Zhang et al. 2012a).

5.3.3. Filtration performance of PVDF hollow fibers

The PWP and MWCO of hollow fiber membranes prepared with different conditions, including Pluronic F127 concentration and types of second additive, are presented in Figure 5-4 and Table 5-3, respectively. It was observed that membrane P0, which is prepared without any additive, exhibits a very low PWP of 6 L/m²·h·bar. With the addition of 1 and 3 wt% of Pluronic F127, the PWP of membrane P1 and P3 increases sharply to 76 and 78 L/m²·h·bar, respectively while the MWCO also increases significantly from 11 to 490 kDa. The significant improvement of PWP might be attributed to the enhanced surface overall porosity while the large MWCO indicates the formation of large surface pores when Pluronic F127 was added as an additive to the polymer dope. These phenomena are in good accordance with the observations obtained in the previous chapter, which reveal the good pore-forming ability of Pluronic F127 in the formation of PVDF membranes.

The effect of the addition of a second additive into the Pluronic-containing dope on the membrane performance can be examined by comparing membranes P3, P3L3, and P3W3 in Figure 5-4 and Table 5-3. With the addition of LiCl as the

second additive into the dope containing 3 wt% Pluronic F127, the PWP of membrane P3L3 increases largely to 253 L/m²h·bar compared with membrane P3 with a PWP of 78 L/m²h·bar. Surprisingly, a significant reduction of MWCO from 485 to 53 kDa is also observed with the addition of LiCl. On the other hand, an even sharp increase in PWP to more than 600 L/m²h·bar is observed on membrane P3W3 with the addition of water as the second additive while its MWCO is larger than 500 kDa (rejection of 500 kDa dextran % 70%)

Figure 5-4. PWP of hollow fibers spun with different additives

The enhancement of PWP for membrane P3L3 despite a reduction in surface pore size and overall porosity might be attributed to the formation of a thinner skin layer. However, it was unable to determine the thickness of skin layer because skin layer cannot be seen under high magnification of FESEM due to difficulty in preparing perfect membrane cross-section. The observations on MWCO are in good accordance with the membrane surface pore size observed under FESEM, as shown in Figure 5-5. Comparing membrane P3 and P3L3, it is observed that the surface pores become much smaller when LiCl is added as the second additive into the Pluronic-containing dope. Meanwhile, a significant increase in the surface pore size can be observed on membrane P3W3 when water is used as the second additive. Both the addition of LiCl and water into the dope solutions promote thermodynamic instability as presented in Figure 5-1, indicating that instantaneous demixing that

promotes the growth of polymer nuclei is likely to occur (Wang et al. 2008, Hou et al. 2009). However, Similar to the effect on macrovoid growth, the enhanced dope viscosity that inhibits the growth of polymer phase on the membrane surface seems to prevail over the effect of instantaneous demixing with the presence of LiCl. In contrast, the presence of water does not enhance the dope viscosity as much compared with LiCl. Accordingly, the effect of instantaneous demixing which promotes the growth of nuclei dominates the membrane skin formation process in the system containing 3 wt% of water. As a result, much larger surface pores are formed when water is used as the second additive.

Figure 5-5. Outer surface (left) and spongy structure near lumen (right) of hollow fibers prepared with/without second additives

5.3.4. Mechanical properties

The mechanical properties of PVDF hollow fibers spun with different additives are presented in Figure 5-6 and Figure 5-7. It is observed that the Young's modulus, tensile stress at break, and elongation at break of hollow fibers P1 and P3, which are spun with the addition of Pluronic, are significantly smaller than that of hollow fibers P0 without any additive. The weaker mechanical strength of membranes P1 and P3 can be attributed to two reasons. One of the reasons is that their cross-section is fully occupied by big macrovoids as can be seen in Figure 5-3. The other reason is the loose packing of PVDF macromolecular chains in the resultant membranes since the rearrangement of PVDF chains is disrupted during the membrane formation process due to the interaction between PVDF and Pluronic.

Figure 5-6. Young's modulus and tensile stress at break of hollow fibers spun with different additives

It is found that LiCl and water have different impacts on the mechanical properties of spun fibers when they are used as a second additive. As shown in Figure 5-6 and Figure 5-7, membrane P3W3 exhibited improved mechanical

properties compared with membrane P3. The reason is attributed to the presence of macrovoids due to the use of water as the second additive, as discussed in 5.3.2. However, despite the similar cross-sectional morphology of membrane P3W3 and P3L3, the mechanical properties of the latter are not improved. This is contradictory with normal observation in which membranes with smaller macrovoids exhibited a higher mechanical strength. It seems that the structural morphology of the as-spun fibers, which is presented in Figure 5-5, might be responsible for the phenomenon. As can be observed in the figure, the skin region near the lumen side of membrane P3L3 exhibits a relatively loose packing, similar to that of membrane P3, compared with that of membrane P3W3. Since the skin region acts as the mechanical support of the fibers, membrane P3L3 shows a lower mechanical strength.

Figure 5-7. Elongation at break of hollow fibers spun with different additives

5.4. Conclusions

The effects of Pluronic concentration and addition of a second additive on PVDF hollow fiber membrane properties have been studied. Big macrovoids are formed in the hollow fibers when Pluronic is used as the additive.

Consequently, the mechanical properties are deteriorated. By adding a second additive, which is either LiCl or water, the macrovoid growth can be suppressed. The hollow fiber spun with Pluronic and LiCl as the mixed additives exhibits a higher PWP yet a smaller MWCO compared with that spun with single additive. However, the mechanical properties are not improved in membrane P3L3. On the other hand, both PWP and MWCO of spun fiber significantly increase when Pluronic and water are used as the mixed additives. Furthermore, the mechanical properties are observed to be better to the smaller macrovoids. It is concluded that highly permeable PVDF hollow fibers with reasonably high mechanical properties can be obtained by utilizing the synergetic effects of Pluronic and water as the additives.

CHAPTER 6. Stability of PVDF/Pluronic Membranes and the Use of Low-concentration Pluronic in PVDF Hollow Fiber Spinning

6.1. Introduction

Pluronic has been found to be a potential alternative to conventional additives for the fabrication of poly(vinylidene fluoride) (PVDF) membranes due to its strong pore-forming ability and interesting behaviors, as shown in previous chapters. However, further investigations are still required on the PVDF/Pluronic hollow fiber membranes. One of the issues is the stability of Pluronic in the membranes when it is in water environment. A slight decrease of Pluronic content in polyethersulfone (PES) membranes after soaking the membranes in either water or sodium hypochlorite solution was reported, indicating that Pluronic may not be completely stable in the PES membrane matrix (Susanto and Ulbricht 2009). It is not clear whether this conclusion observed in PES membranes is applicable to PVDF membranes since the interaction between Pluronic and PVDF can be different from that between Pluronic and PES. It has been shown in CHAPTER 4 that Pluronic can be washed out by propanol (IPA)-treatment and the loss of Pluronic from the PVDF/Pluronic membranes changes the filtration performance of the membranes. Accordingly, if the Pluronic molecules can gradually leach out from the membrane matrix to the water environment, it is expected that the long term performance of PVDF/Pluronic membranes will not be consistent. Therefore, it is important to study the stability of Pluronic in PVDF membrane matrix if the membranes are to be applied for practical applications.

Another factor that can be further adjusted or improved in PVDF/Pluronic hollow fiber membranes is the filtration performance. In the previous chapter, the use of mixed additives including Pluronic/LiCl and Pluronic/water has been observed to be a powerful mean to enhance the water permeability of PVDF hollow fibers. While the membranes prepared with Pluronic/water are considered to be loose ultrafiltration (UF) or tight microfiltration (MF), the combination of

Pluronic/LiCl as the additive seems to be a useful tool for preparing membranes with much smaller pores. Therefore, it would be interesting to further investigate the synergetic effects of Pluronic/LiCl on the preparation of hollow fibers for UF applications. On the other hand, as discussed in Section 5.3.4, the mechanical properties of PVDF hollow fibers spun with Pluronic/LiCl are observed to be not satisfactory possibly due to a loose packing in the sponge-like region. This is possible to be improved by adjusting the spinning conditions and additive concentration which affect the microstructure of the resultant membranes (Sukitpaneenit and Chung 2009; Peng et al. 2011).

In this study, the stability of Pluronic in PVDF membranes has been firstly examined by observing the change in characteristics of PVDF/Pluronic membranes with different water-soaking durations. Spinning of PVDF hollow fibers using the mixed additives of Pluronic/LiCl has been carried out by varying Pluronic amount at constant LiCl concentration. Low Pluronic concentrations ranging from 0 to 0.5 wt% were used in this study due to the following reasons: (1) Considering Pluronic may not be completely stable in PVDF membrane matrix, the use of low Pluronic concentration imposes less impact on long-term performance of spun membranes; (2) The pore-forming effect of Pluronic is tremendously strong in PVDF system even at a concentration as low as 1 wt% (CHAPTER 4 and CHAPTER 5); (3) the mechanical properties of PVDF membranes are highly affected by the presence of Pluronic (Section 5.3.4). The effects of spinning conditions including air gap, bore fluid composition, coagulant temperature, and take-up speed on the properties of spun fibers have also been studied. The objective of this study is to fabricate high-performance PVDF UF hollow fibers with good mechanical strength through the synergetic effects of Pluronic/LiCl and the optimization of spinning conditions.

6.2. Experimental

6.2.1. Membrane materials and chemicals

The materials and chemicals used for membrane preparation are the same as those mentioned in Section 5.2.1. In addition to dextran, Bovine serum albumin (BSA, MW = 67,000 Da) obtained from Sigma-Aldrich, Singapore was also used to assess the selectivity of spun fibers.

6.2.2. Casting/spinning of PVDF membranes

The preparation of polymer dope, the flat sheet membrane casting, and hollow fiber spinning procedures have been described in Section 4.2.3, Section 4.2.4, and Section 4.2.5, respectively. For the hollow fiber spinning, the concentrations of PVDF and LiCl were kept constant at 18 wt% and 3 wt%, respectively. Tap water was used as the external coagulant while the bore fluid was varied from water to a mixture of N-methyl-2-pyrrolidone (NMP)/water. Various other spinning conditions including air gap, take-up speed, and coagulant temperature were changed to study their effects on membrane properties and performance. To obtain fibers with circular inner contour and desirable dimensions, the dope and bore fluid flow rates were also adjusted for different cases. The detailed spinning conditions for each membrane are listed in Table 6-1.

6.2.3. Membrane characterizations and analysis

The surface/cross-sectional morphologies and chemistry of spun hollow fibers were obtained using instruments mentioned in Section 4.2.5. The procedures for measuring mechanical properties and overall porosity of spun fibers were discussed in Section 5.2.4. Pure water permeation (PWP) and molecular weight cut off (MWCO) of the fibers was assessed by experiments similar to Section 5.2.5 while the operating pressure was maintained at 1.0 bar. In addition to MWCO test using dextran, BSA rejection test, in which a BSA aqueous solution with a

Table6-1. Spinning conditions of PVDF hollow fiber membrane (PVDF: 18 wt%, LiCl: 3 wt%)

Membrane code	Pluronic concentration (wt%)	Bore fluid composition (wt%)	air gap (cm)	Dope flow rate (g/min)	Bore fluid flow rate (mL/min)	take-up speed (m/min)	Coagulant temperature (°C)
P00-80	0	NMP/water (80/20)	1	6	3.5	8.6	25
P00-00	0	water	25	5	2.5	7.2	25
P00-00H	0	water	25	5	2.5	7.2	50
P02-80	0.2	NMP/water (80/20)	1	6	3.5	8.6	25
P02-00	0.2	water	25	5	2.5	7.2	25
P02-00H	0.2	water	25	5	2.5	7.2	50
P05-80	0.5	NMP/water (80/20)	1	5	3.5	8.6	25
P05-00	0.5	water	25	4	3	7.2	25
P05-00H	0.5	water	25	4	3	7.2	50
P05-00H-A	0.5	water	20	4	3	5.7	50
P05-00H-B	0.5	water	20	4	3	7.2	50

concentration of 1 g/L was used as the feed, was also carried out. The concentration of BSA in the feed and permeate was determined by measuring their total organic carbon (TOC) using TOC Analyzer (Shimadzu, TOC SH).

The contact angle of PVDF flat sheet membranes was measured by the method mentioned in Section 4.2.5. The hydrophilicity of and hollow fiber membranes was examined by dynamic contact angle using goniometer (DCAT11 Dataphysics, Germany) according to Wilhelmy method. Three immersion cycles in Milli-Q water were carried out for each specimen with a repetition of 5 times for all the samples. The advancing contact angle of the second cycle was recorded.

6.3. Results and discussion

6.3.1. Stability of Pluronic in PVDF membranes

As mentioned in Section 6.1, the stability of Pluronic in PVDF membranes has not yet been studied. It is reasonable to expect that the long-term performance might be affected if Pluronic can gradually leach out from the membrane matrix. Therefore, the impacts of water soaking duration on the characteristics and performance of PVDF membranes were studied. In the stability test, PVDF flat sheet membranes prepared with 5 wt% Pluronic were soaked in water for different durations and fresh water was replaced frequently. Flat sheet membranes instead of hollow fibers were used because when the latter is immersed in water, the condition inside the lumen of fiber is relatively stagnant since the inner diameter of fiber is very small. Consequently, the leaching of Pluronic (if any) from hollow fibers is expected to be slower than that from flat sheet membranes. By using flat sheet membranes in the stability test, any change in the Pluronic amount can be more obviously observed in a shorter period of soaking duration.

As shown in Figure 6-1, after soaking in water for 3 days, the membrane shows a contact angle of $54 \pm 5^\circ$. However, the contact angle increases to $68 \pm 1^\circ$ after 19 days of water soaking. Since Pluronic can migrate to the membrane surface during the phase inversion process to improve membrane hydrophobicity (Wang et al. 2005), the increase of the contact angle with increasing the duration of water soaking implies the possibility of Pluronic loss from the membrane surface. The presence of Pluronic in the membrane matrix near the surface can also be examined by the spectra of attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) in Figure 6-1. In the figure, the ether peak at 1107 cm^{-1} is found in both the spectra of the membranes with different soaking durations. It seems that a significant amount of Pluronic is still present in the PVDF membrane even after soaking in water for 19 days, despite the fact that there is an increase in contact angle. In fact, ATR-FTIR has a penetration depth from 300 nm to a few micrometers at wave numbers lower than 2000 cm^{-1} , which means that not only the surface chemistry but also the chemical information within membrane matrix is obtained (Tang et al. 2009). Therefore, it is believed that Pluronic molecules at the outermost surface of PVDF membranes are not stable and can gradually leach out into water as evidenced by the contact angle increase, while Pluronic molecules that are embedded in the membrane matrix are somewhat more stable as observed from the ATR-FTIR analysis. This phenomenon can be expected since the Pluronic molecules at the outermost surface have a higher mobility compared with their counterparts in the compact structure inside the membrane.

The effects of water soaking duration on the PWP and MWCO of PVDF membranes prepared with the addition of Pluronic are illustrated in Figure 6-2. There is a slight increase in both PWP and MWCO after the membranes were soaked in water for 19 days. It has been discussed in CHAPTER 4 that the presence of Pluronic might narrow down the membrane pores due to the formation of poly(ethylene oxide) (PEO) brush layer on the pore surface. Accordingly, the change in PWP and MWCO due to a longer water soaking duration might be attributed to the leaching out of Pluronic from the membrane surface, which causes a change in the apparent pore size of the membranes due to the absence of PEO brush layer.

Figure6-1. Contact angle of PVDF flat sheet membranes (5 wt% Pluronic) after water soaking of 3 and 19 days.

Figure6-2. Effects of water soaking duration on the performance of PVDF membranes prepared with 5 wt% of Pluronic

Considering the issues including that Pluronic may not be completely stable in PVDF membrane matrix and the others mentioned in Section 6.1, it seems that the use of a lower concentration of Pluronic might be an appropriate mean to produce a high performance PVDF hollow fiber membranes. Therefore, this chapter focuses on the spinning of PVDF/Pluronic hollow fibers with addition of 0 to 0.5 wt% of Pluronic.

6.3.2. Membrane morphology and porosity

a. Effects of air gap and bore fluid composition

Figure 6-3 shows the effect of air gap on the crosssectional structure of hollow fibers spun with 50 wt% of NMP and water as the bore fluid. Deformation of inner contour is observed for fibers spun with 50 wt% of NMP and the situation does not improve with increasing air gap up to 20cm. Similarly, when water is used as the bore fluid, inner contour deformation also exists when the air gap is below or equal to 20 cm. However, the membrane structure becomes more regular when the air gap is increased from 20 cm onwards and a fully circular structure is obtained at an air gap of 25 cm.

Due to the fact that the rate of solvent diffusing out from a polymer dope is always higher than that of nonsolvent diffusing into the dope, shrinkage is always observed in nascent membranes during phase inversion (Wang and Ma 2012). In hollow fiber spinning process, the shrinkage of nascent fiber in coagulant bath induces inward radial force which in turn deforms the inner contour of the fiber if the lumen skin is not rigid enough (Bonyadi et al. 2007). For dry-jet wet spinning, phase inversion has already started at the interface between the bore fluid and the dope before the dope is in contact with the external coagulant. With a larger air gap, there is more sufficient time for the demixing or the solidification of polymer to occur near the lumen of the nascent fiber. As a result, a more rigid lumen skin can be formed before the dope entering the coagulant bath. Therefore, the irregular inner contour of the fiber spun with water as the bore fluid can be eliminated when the air gap is large enough.

Figure 6-3. Effect of air gap on inner contour of PVDF hollow fibers spun with 0.5 wt% of Pluronic (upper row: 50 wt% NMP as bore fluid; lower row: water as bore fluid)

For fibers spun with 50 wt% NMP as the bore fluid, a slower demixing process occurs compared with the case using water as the bore fluid. Consequently, the formed lumen skin is still not strong enough to resist inward radial stress when the dope enters the coagulant bath. However, when the NMP concentration in the bore fluid is further increased to 80 wt%, no solidified skin is formed in the lumen of nascent fibers (Sonyadi et al. 2007). As a result, the induced stress can be relaxed and hollow fibers with regular cross-section can be obtained at air gap as low as 1 cm, as shown in Figure 6-4 (a1). It should be noted that the spinning using 80 wt% NMP as the bore fluid could only be carried out at very low air gap because the polymer flow became unstable when the air gap was large. Therefore, the air gap used was different for hollow fibers spun with different bore fluids.

Figure 6-4 shows the morphology of membranes prepared using the same amount of additives but different bore fluids. The cross-section of membrane CB-80 (80 wt% NMP as the bore fluid) exhibits a structure with macrovoids developed from the shell and sponge-like structure near the lumen, while its outer surface is

dense and inner surface is highly porous with big pores. On the other hand, macrovoids are developed from both the shell and lumen in membrane P05-00 (water as the bore fluid) while the outer surface has larger pores than the inner surface possibly due to the high air gap. The observed structures are in accordance to those in literatures since the instantaneous demixing induced by strong coagulant (water) facilitates the formation of dense skin and macrovoids while delayed demixing causes the formation of spongy structure and the elimination of skin layer when a soft coagulant (80 wt% NMP) is used (Mulder 1996 Madaeni and Rahimpour 2005).

Figure 6-4. Morphologies of hollow fibers (a) P05-80 and (b) P05-00 (1: cross section; 2: outer surface; 3: inner surface)

b. Effects of Pluronic concentration

Figure 6-5 presents the cross-sectional morphology of hollow fibers spun with different Pluronic concentrations and spinning conditions. Regardless of the spinning conditions, a significant increase in macrovoid size can be observed with the addition of merely 0.2 wt% of Pluronic. Further increase of Pluronic concentration from 0.2 wt% to 0.5 wt% has a smaller impact on the macrovoid size. On the other hand, the overall porosity of the spun membranes is also improved significantly with increasing Pluronic concentration, as shown in Figure 6-6. As discussed in CHAPTER 4 the strong pore-forming ability of Pluronic might be attributed to the interruption to the rearrangement between PVDF macromolecules due to the interaction between Pluronic and PVDF. The above observations suggest that the interruption is significant enough to possess an impact on the macrovoid formation even with the presence of just 0.2 wt% of Pluronic.

Figure 6-7 shows the morphology of outer surface for hollow fibers spun with different Pluronic concentrations and spinning conditions. For fibers spun with 80 wt% NMP as the bore fluid, the outer surfaces are dense with no visible pores at 50,000x magnification regardless of the Pluronic concentration. For fibers spun with water as the bore fluid, the membrane surface is not significantly affected with the addition of 0.2 wt% Pluronic (membranes 00-00 and 02-00). Highly porous surface can be observed on membrane 05-00 when the Pluronic concentration is 0.5 wt%.

c. Effects of take-up speed

When the dope and bore fluid flow rates are kept constant, a higher take-up speed imposes a higher stretching force on the nascent fiber. Therefore, the dimensions of the hollow fibers become smaller. The cross-sections of the fibers are not significantly affected by different take-up speeds, as can be seen in Figure 6-8. However, the surface of membrane 05-00H-B spun at a take-up speed of 5.7 m/min becomes less porous and the pore size becomes smaller compared with that of membrane 05-00H-A spun with a lower take-up speed.

Figure6-5. Crosssectional morphology of PVDF hollow fibers

Figure 6-6. Overall porosity of PVDF hollow fibers (PX-80 includes P00-80, P02-80, and P05-80. Similar manner for P-X00 and PX00H)

In literature, the effect of take-up speed on the membrane pore size and the explanations on the phenomenon are diversified. Chou reported an increase in pore size with increasing take-up speed possibly due to the expansion of pores under elongation stress (Chou and Yang 2005). In contrast, Sukitpaneemit et al. observed smaller surface pores when a higher take-up speed is used, while the proposed mechanisms were related to the enhanced spinodal decomposition of demixing and rapid shrinkage of the nascent fibrils (Sukitpaneemit and Chung 2011). In this study, the mechanism of liquid-liquid demixing is believed to be nucleation and growth at a higher take-up speed since dispersed pores with continuous PVDF phase is observed. Hence the spinodal decomposition mechanism cannot explain the reduction in surface pore size and porosity in this case. Instead, it is believed that the shear stress caused by the higher take-up speed is responsible for this phenomenon. Under a high shear stress, the orientation of PVDF macromolecular chains is induced and hence a close packing is formed which in turn produces a less porous structure (Shi et al. 2009).

Figure6-7. Outer surface of PVDF hollow fibers

Figure 6-8. Outer surface and crosssectional morphology of PVDF hollow fibers spun at different take up speed

d. Effects of coagulant temperature

The effect of coagulant temperature on the morphology of membrane cross section and the outer surface can be observed in Figure 6-5 and Figure 6-7, respectively. It seems that the cross-sectional morphology does not change much with increasing coagulant temperature from 25 to 50 °C, except that the size of macrovoids developed from the shell become smaller for membranes P02-00H and P05-00H compared with that of membranes P02-00 and P05-00, respectively. The suppression of macrovoids at higher coagulant temperature has also been observed by Wongchitphimon et al. (Wongchitphimon et al. 2011) for PVDF/polyethylene glycol/NMP system. At a higher temperature, the thermodynamic stability of a polymer dope system is enhanced which in turn delays the onset of liquid-liquid demixing (Yeow et al. 2003; Khayet et al. 2010; Wongchitphimon et al. 2011). When the nascent fibers are immersed into the coagulant bath with a temperature of 50 °C, the temperature of the dope in contact with the water is increased. Therefore, delayed demixing occurs and smaller macrovoids are developed from the shell of fibers compared with the case using a lower coagulant temperature.

On the other hand, the pore size of membrane surface becomes significantly larger when the coagulant temperature is increased to 50°C, especially for membrane P2-00H and P5-00H which is spun with the addition of 0.2 wt% and 0.5 wt% Pluronic, respectively. This phenomenon is in contrast with the study reported by Choi et al. in which the pore size of PVDF membranes (without any additive) was observed to decrease significantly with increasing coagulant temperature (Choi et al. 2010). The difference might be aroused due to the use of LiCl and Pluronic as the additives in this study:

- (1) With the presence of LiCl, the suppression of nucleus growth induced by high dope viscosity is the dominating factors of pore formation. The viscosity of polymer dope decreases with increasing temperature. As a result, the effect of nucleus growth suppression becomes less pronounced at a higher temperature and larger pores are formed.
- (2) Water solubility of the center poly(propylene oxide) (PPO) block in Pluronic decreases significantly at elevated temperatures (Alexandridis et al. 1994). In other words, PPO is much more hydrophobic at higher temperature. When the outer surface of nascent fiber is in contact with hotter water, it is possible that the hydrophobic-hydrophobic interaction between PPO and PVDF becomes stronger. This leads to a more pronounced disruption on the rearrangement of PVDF macromolecules, which facilitates the formation of larger pores.

6.3.3. Filtration performance

As can be seen in Figure 6-4, it is noticed that when 80 wt% NMP is used as the bore fluid, the membrane outer surface is much denser than the inner surface. This indicates that the selective layer is located at the shell side of -spun fibers. However, relatively dense skins are formed at both the shell and lumen side of the fibers when water is used as the bore fluid. In order to determine the location of the selective skin, filtration tests operated under outside-in (feed at shell side) and inside-out (feed at lumen side) modes were carried out for membranes P5-P0 and P05-00H which are spun using water as the bore fluid.

Table 6-2 presents the PWP and MWCO of membranes P05-00 and P05-00H tested under outside-in and inside-out modes. It is observed that the PWP is higher for the inside-out mode when the area of surface that is directly in contact with the feed is taken for calculation. However, the absolute flux is similar when the fibers are tested under both modes. On the other hand, the MWCO is smaller when the feed is located at the lumen side, indicating that the surface pore size at the lumen is smaller. The higher MWCO tested under outside-in mode is attributed to the concentration polarization in the membrane matrix, since some dextran molecules that has passed through the outer skin are accumulated near the inner skin.

Table 6-2. Effects of operating modes and take up speed on PWP and MWCO of PVDF hollow fibers

Membrane code	Outside-in		Inside-out		
	PWP ^a (L/m ² ·h·bar)	MWCO (kDa)	PWP ^a (L/m ² ·h·bar)	PWP ^b (L/m ² ·h·bar)	MWCO (kDa)
P05-00	143 ± 3	270	144 ± 2	209 ± 3	65
P05-00H	147 ± 2	> 500	129 ± 11	190 ± 16	30
P05-00H-A	-	-	144 ± 12	206 ± 17	60
P05-00H-B	-	-	130 ± 1	190 ± 1	25

^acalculated based on outer surface area

^bcalculated based on inner surface area

Figure 6-9 presents the PWP and MWCO of PVDF hollow fibers spun with different conditions. According to the location of the selective skin, the feed was run at the shell side and the lumen side for fibers spun with 80 wt% NMP and water as the bore fluid, respectively. The PWP is calculated based on the surface area that is directly in contact with the feed. It can be seen that the PWP increases with increasing Pluronic concentration in the spinning dope. For the fibers spun with 80 wt% NMP as the bore fluid, the PWP increases tremendously by about 190% from 25 to 72 L/m²·h·bar with the addition of merely 0.2 wt% of Pluronic. For the fibers spun with water as the bore fluid, the presence of 0.2 wt% Pluronic also enhances the PWP significantly by 46% and 39% when the coagulant temperature is 25 °C and 50 °C, respectively. Despite the pronounced enhancement in PWP, the MWCO of the fibers is not affected much by the low concentration of Pluronic.

Figure 6-9. PWP and MWCO (kDa) of PVDF hollow fibers (PX-80 includes P0-80, P02-80, and P05-80. Similar manner for PX10 and PX00H)

The PWP is further enhanced significantly at 0.5 wt% of Pluronic concentration. A remarkable increase in MWCO is also observed when the Pluronic concentration is increased from 0.2 to 0.5 wt%. For instance, The PWP increases from 87 to 209 L/m²h·bar and the MWCO changes from 4 to 65 kDa, when comparing membranes P02-00 and P05-00. The increase in PWP and MWCO is due to the enhancement in membrane surface and overall porosity as discussed in Section 6.3.2

The effects of bore fluid composition on PWP and MWCO are not comparable since the location of selective skin is different in the two cases. On the other hand, no obvious trend can be observed for the impacts of the coagulant temperature on the PWP and MWCO. As shown in Figure 6-9, the PWP increases at a higher coagulant temperature when the Pluronic concentration is 0.2 wt% or less, while the MWCO is not affected much. Both PWP and MWCO of the fibers spun with 0.5 wt% of Pluronic decreases at higher coagulant temperature. The changes in PWP at different coagulant temperatures can be attributed to the different overall porosities of as-spun membranes as shown in Figure 6-6. As for the

MWCO, it is believed that the increasing coagulant temperature does not significantly affect the membrane structure near the lumen side because the inner surface is not in direct contact with the external coagulant. Accordingly, the inner surface pore size is expected to be similar for hollow fibers spun at different coagulant temperature. This is true for the spun fibers in this study except for the fibers spun with 0.5 wt% of Pluronic, while the reason is unclear.

The impact of take-up speed on the filtration performance of spun fibers can be assessed in Table 6-2. Comparing fibers P05-00H-A and P05-00H-B which are spun with different take-up speeds, the PWP is observed to be similar. However, the MWCO of the fibers becomes smaller when the take-up speed is increased, indicating that hollow fibers with smaller surface pores can be obtained at the presence of elongation stress. This is due to the formation of close packing by shear-induced PVDF chain orientation as discussed in Section 6.3.2.

6.3.4. Presence of Pluronic in PVDF membranes

The presence of Pluronic in spun PVDF hollow fibers can be assessed by their FTIR spectra as shown in Figure 6-10. No peak can be observed at the wave number of 1107 cm^{-1} for all the fibers spun with different Pluronic content. This reveals that little or no ether group exists in the membranes. In addition, the contact angle of the fibers does not change significantly with increasing Pluronic concentration up to 0.5 wt% as listed in Table 6-3. It seems that the chemical properties of the fibers are not affected by the addition of Pluronic in the spinning dopes when its concentration is lower or equal to 0.5 wt%. In other words, Pluronic functions as a pore former but not surface modifier at low concentration. It is anticipated that the stability of Pluronic in membrane matrix is no longer an issue since the membranes contain very insignificant amount of Pluronic.

6.3.5. Mechanical properties

The mechanical properties of spun fibers tested under tensile mode are presented in Figure 6-11. The Young's modulus, tensile stress at break, and

elongation at break of all the fibers are observed to be reduced with increasing Pluronic concentration, except for the elongation at break of hollow fibers spun with 80 wt% NMP as the bore fluid. As discussed in Section 5.2.4, the interaction between PVDF and Pluronic molecules that interrupts the rearrangement of PVDF macromolecular chains might be responsible for the reduction in mechanical strength of as-spun fibers. The Young's modulus and tensile stress of the fibers decrease significantly with the addition of merely 0.2 wt% Pluronic. This reveals that the PVDF-Pluronic interaction is significant enough to impact the mechanical properties at a very low Pluronic concentration. Similar phenomena have also been observed in previous sections where the addition of 0.2 wt% Pluronic imposes a great impact on membrane structures and filtration performance.

Figure 6-10. FTIR spectra for PVDF hollow fibers spun with different amount of Pluronic

In Figure 6-11, it seems that the increase in coagulant temperature does not impose significant impact on the mechanical properties of the as-spun fibers. Similarly, the effect of take-up speed on the mechanical properties of membranes is also observed to be insignificant (data not shown). However, when comparing the fibers spun using different bore fluid, the fibers spun with 80 wt% NMP as the bore fluid were observed to have a significantly lower value of Young's modulus, tensile

stress, and elongation than the fibers spun with water as the bore fluid. For both of the bore fluids, the resultant fibers consist of both macrovoids and sponge-like structures (Figure 6-5) and the region with sponge-like structure acts as the mechanical support. A closer look at the sponge-like structure located at the middle of the cross section for hollow fibers P00-80 and P05-00 is presented in Figure 6-12 (A) and (B), respectively. One can clearly see that membrane P00-00, which is spun using water as the bore fluid, has a more compact structure compared with its counterpart. The difference in the packing density of sponge-like region between the two fibers is even more obvious near the lumen side, as shown in Figure 6-12 (a) and (b). Although the region near the lumen of membrane P05-00 is fully sponge-like while that of membrane P00-00 is mainly occupied by macrovoids, the latter consists of a much denser sponge-like structure in between the macrovoids. The tighter packing observed in the sponge-like region of the hollow fibers spun with water as the bore fluid is believed to be the reason for its higher mechanical strength.

Table 6-3. Dimensions, contact angle, and collapsing pressure of PVDF hollow fibers

Membrane code	Outer diameter (μm)	Inner diameter (μm)	Thickness (μm)	Contact angle (°)	Collapsing pressure ^a (bar)
P00-80	900	600	150	71.4 ± 2.4	4
P00-00	890	640	125	75.6 ± 2.1	4.5
P00-00H	920	650	135	77.5 ± 1.5	>5
P02-80	980	620	180	77.5 ± 0.8	3
P02-00	920	610	155	78.9 ± 0.7	3
P02-00H	920	630	145	78.4 ± 1.1	4
P05-80	990	670	160	75.4 ± 3.4	1.5
P05-00	920	630	145	73.0 ± 0.6	1.5
P05-00H	950	640	155	76.0 ± 1.3	2.5

^apressure was applied at the shell side of hollow fibers

The collapsing pressure of spun hollow fibers has also been tested to reflect the actual tolerance of the membranes towards hydrostatic pressure during applications. As listed in Table 6-3, the collapsing pressure of fibers decreases significantly with increasing Pluronic concentration, which is in accordance with

the observed trend in the tensile properties. Interestingly, it was observed that the hollow fibers spun at a higher coagulant temperature can tolerate a higher pressure than their counterparts, regardless of the Pluronic concentration. One of the reasons may be due to the smaller macrovoids developing from the surface of the fibers.

Figure 6-11. Mechanical properties of PVDF hollow fibers: (a) Young's modulus; (b) Tensile stress at break; (c) Elongation at break. PX-80 includes P0-80, P02-80, and P05-80. Similar manner for PX00 and PX00H)

According to the collapsing pressure listed in Table 6-3, the hollow fibers spun with 0.2 wt% of Pluronic are rigid enough for UF applications as they can tolerate a pressure of at least 3 bar. Selected membranes with a selective skin located at the lumen side have also been tested for the burst pressure, which indicates the tolerance of the fibers towards pressure acting from the lumen. The burst pressure was taken at the pressure at which the PWP appears to continuously increase over time because it indicates the emergence of defects. Membranes P02

00 and P02-00H are observed to exhibit a burst pressure of 4.5 and 5.5 bar, respectively, which are greater than their collapsing pressure. For the fibers spun with 0.5 wt% of Pluronic, the collapsing pressures are relatively low, (2.5 bar), indicating that they are more suitable for low pressure applications.

Figure 6-12. (A, B) Spongelike structure and (a, b) crosssection near lumen of hollow fibers (A, a) P05-80 and (B, b) P05-00

The performance of PVDF hollow fiber membranes prepared in this study has been compared with those in literature as listed in Table 6-4. It can be seen that the hollow fiber P02-00H prepared in this study exhibit a very low MWCO and very high BSA rejection, while its PWP is reasonably high. In addition, hollow fiber P02-00H is also stronger than most of the other membranes in terms of tensile stress and elongation at break.

6.4. Conclusions

The longterm stability of Pluronic in PVDF membranes has been tested. It is observed that Pluronic may gradually leach out from the membrane matrix when the membrane is soaked in water. The stability issue can be eliminated by using

very low amount of Pluronic for membrane fabrication. It is found that the use of merely 0.2 wt% of Pluronic is sufficient to impose significant impacts on the morphology, filtration performance, and mechanical properties of the resultant fibers. The observations once again reveal the extremely strong performance ability of Pluronic in PVDF system due to the interaction between PVDF and Pluronic.

By using the mixture of Pluronic and LiCl as the additives and adjusting the spinning conditions, PVDF hollow fibers with high performance have been obtained. The effects of spinning conditions on the membrane properties include:

- (1) Spinning at high air gap can help to eliminate the irregular inner contour of hollow fibers.
- (2) The inner skin layer is removed when 80 wt% NMP is used as the bore fluid, while relatively dense skins are formed at both the shell and lumen side of the fibers when water is used as the bore fluid. The mechanical strength is better for the fibers spun with water as the bore fluid, probably due to the closer packing of spongelike region.
- (3) At a higher coagulant temperature, the macrovoids developed from the shell side of the fibers become smaller while the surface pores are larger. Hollow fibers spun at a higher coagulant temperature can withstand a higher pressure.
- (4) The surface pore size of the fibers becomes smaller at a higher uptake speed due to the stress-induced arrangement of PVDF macromolecules.

Table6-4. Comparison of various PVDF UF hollow fiber membranes

Additives used (wt%)	PWP ^a (L/m ² ·h·bar)	MWCO ^b (kDa)	BSA rejection ^c (%)	Tensile stress (MPa)	Elongation (%)	Collapsing pressure (bar)	Reference	Remarks
Pluronic F127 (0.2) + LiCl (3)	118 (lumen)	5	99	4.0	310	4 (shell) 5.5 (lumen)	this work (P02-00H)	
PVDF copolymer (5)	131	200	84	2.2	230	3	(Moghareh Abed et al. 2013)	
PVDF copolymer + PEG (8)	275*	N.A.	95	0.4	150	N.A.	(Shen et al. 2013b)	PWP tested at 0.4 bar
Fe ³⁺ + Cu ²⁺ + PEG	35	N.A.	92	2.6	100	N.A.	(Zhang et al. 2013b)	
PVDF copolymer + TiO ₂ (1)	974	N.A.	93*	3.3	80	N.A.	(Zhang et al. 2013a)	Rejection of dextran 500 kDa
PEG (5)	137 (lumen)	150	N.A.	7.5	160	N.A.	(Abed et al. 2012)	
PFSA (3)	27	24*	N.A.	2.6	70	N.A.	(Lang et al. 2012)	MWCO tested using PEG
water (3)	30	40	N.A.	N.A.	N.A.	N.A.	(Feng et al. 2011)	
PVP (5)	190	N.A.	83	N.A.	N.A.	N.A.	(Lang et al. 2011)	
PFSA (1) + ethanol (1)	12*	8	95*	N.A.	N.A.	N.A.	(Yuan et al. 2009)	PWP tested at 2 bar; Rejection of PEG 10 kDa
PFSA (3)	137	N.A.	97	N.A.	N.A.	N.A.	(Lang et al. 2007)	
phosphorus acid (3)	89	290	N.A.	N.A.	N.A.	N.A.	(Atchariyawut et al. 2006)	
1,2-ethanediol	19*	367*	N.A.	N.A.	N.A.	N.A.	(Khayet et al. 2002b)	PWP tested at 4.8 bar; MWCO tested using PEG
LiCl (2) + 1-propanol (7)	87	N.A.	84*	N.A.	N.A.	12	(Wang et al. 2000)	Rejection of dextran 110 kDa
PVP (8)	110	N.A.	61*	N.A.	N.A.	N.A.	(Wanget al. 1999)	Rejection of dextran 500 kDa

^aoperating pressure was 1 bar unless otherwise stated^bMWCO was tested using dextran unless otherwise stated^cBSA was used for rejection test unless otherwise stated

*see remarks

CHAPTER 7. Conclusions and Recommendations

7.1. Overall conclusions

The thesis presents the fabrication of poly(ethersulfone) (PES) and poly(vinylidene fluoride) (PVDF) hollow fiber membranes using amphiphilic block copolymers as pore-forming additives. Unlike conventional additives, amphiphilic block copolymers possess interesting behavior: they tend to segregate to the polymer/water interface due to the presence of hydrophilic segments, while the hydrophobic, water-insoluble segment of the copolymer can be firmly anchored in the polymer matrix. Copolymers of Pluronic, which is the trade name of amphiphilic triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), were selected to be studied because they are commercially available and relatively low cost compared with other self-synthesized copolymers. A series of Pluronic products with different molecular architectures were used to fabricate PES hollow fiber membranes and Pluronic F127 was observed to be most effective in preparing high-performance membranes (CHAPTER 3). Pluronic F127 was then used in PVDF flat sheet membrane casting to understand the mechanism of pore formation (CHAPTER 4), followed by the study on how the presence of second additives affects the properties of PVDF/Pluronic hollow fiber membranes (CHAPTER 5). Finally, the stability of Pluronic in PVDF membranes was examined and optimization of dope compositions/spinning conditions was carried out (CHAPTER 6).

The major conclusions observed in each chapter are summarized as follows:

CHAPTER 3

- PES hollow fibers with high pure water permeation (PWP) and low molecular weight cutoff (MWCO) can be obtained by using Pluronic molecules with PEO-PPO-PEO arrangement, large PEO mass fraction (70, 80 wt%), a long PEO chain and PPO chain. Pluronics that fulfill these properties are not only

more hydrophilic but also able to form a PEO brush layer on membrane pore surface which enhances the solute rejection.

- Both Pluronic F127 and F108 exhibit the above properties and PES hollow fibers spun using these two additives have high PWP and low MWCO.
- The optimum Pluronic F127 concentration was found to be 10 wt% where the as-spun hollow fiber exhibits the highest PWP of 114 L/m²·h·bar and the lowest MWCO of 9 kDa.

CHAPTER 4

- The properties of polymer dopes containing Pluronic F127 or polyethylene glycol (PEG) 10k were compared because both molecules have similar molecular weight and the same ether group but the latter does not have hydrophobic PPO block. No significant difference in thermodynamic instability and viscosity was observed between the two systems.
- Surface tension study revealed that Pluronic micelles are unlikely to be formed in N-methyl-2-pyrrolidone (NMP) solutions.
- PVDF membranes prepared with Pluronic exhibit larger surface pore size, porosity, and macrovoids than membranes prepared with PEG, indicating that Pluronic has a stronger pore-forming ability. The phenomenon might be attributed to the hydrophobic interaction between PPO blocks in Pluronic molecules and PVDF macromolecular chains which disrupts the PVDF chain rearrangement during the solidification process.
- Pluronic in the prepared membranes can be washed out by 2-propanol (IPA)-treatment. An increase in PWP and MWCO was observed in the treated membranes due to the removal of PEO brush layer that narrows down the pores.

CHAPTER 5

- Big macrovoids are formed in PVDF hollow fibers when Pluronic is used as the additive. Consequently, the mechanical properties are deteriorated.

- Macrovoid growth can be suppressed by adding LiCl or water as a second additive in the spinning dopes. The mechanical properties are improved for hollow fibers spun with Pluronic/water but not for hollow fibers spun with Pluronic/LiCl, mainly due to the difference in microstructural morphology between the two systems.
- Both PWP and MWCO are significantly enhanced when water is used as the second additive. On the other hand, PWP is enhanced yet MWCO is reduced when LiCl is added in the spinning dope as the second additive.

CHAPTER 6

- It was observed that Pluronic might not be completely stable in PVDF membrane matrix.
- The use of merely 0.2 wt% of Pluronic is sufficient to impose significant impacts on the morphology, filtration performance, and mechanical properties of the resultant PVDF hollow fibers.
- Spinning conditions affect the membrane properties: the mechanical strength of as-spun fibers is stronger when water is used as the coagulant and when the coagulant temperature is higher; the surface pores are larger when a higher coagulant temperature or a lower take-up speed is used.
- PVDF hollow fiber membrane with PWP of $11.8 \text{ m}^2 \cdot \text{h} \cdot \text{bar}$ and MWCO of 5 kDa was obtained when spun with optimized spinning conditions and using 3 wt% of LiCl and 0.2 wt% of Pluronic as the mixed additive. The fibers can withstand a pressure of 5.5 bar from the lumen of the fiber.

7.2. Recommendations for future research

The following tasks are recommended for future study:

7.2.1. Different types of amphiphilic block copolymers

Other types of amphiphilic block copolymers can be considered as the pore forming additives, especially copolymers with different hydrophobic segments. It has been observed in this study that the interaction between the hydrophobic block of the additive and the PVDF macromolecular chains can have significant impact on pore formation. Copolymers consist of other hydrophobic blocks may lead to different pore forming behaviors. For instance, if an amphiphilic block copolymer comprised of a hydrophobic block that is more compatible to PVDF, the effect of PVDF additive interaction on macrovoid formation will be an interesting topic to study. In addition, the stability of this copolymer in PVDF membrane matrix will be higher than that of Pluronic. This can lead to the formation of a stable brush layer on membrane pores, which improve the selectivity of resultant membranes in long term. Potential candidates for the hydrophobic block that is compatible to PVDF include PMMA and PVDF itself (Rajabzadeh et al. 2009). However, there is no commercial product for this type of block copolymers, which means that self-synthesis of block copolymers will be involved in this study. This imposes an additional challenge to the future work.

7.2.2. Role of Pluronic in membrane formation of different polymeric materials

To broaden the applications of Pluronic, the use of Pluronic in other polymer systems can be further studied. Either PES or PVDF, which is relatively hydrophobic, was used as the membrane material in this study. If a hydrophilic material such as cellulose acetate (CA) is used, different interaction between the polymer and Pluronic is expected. Lv et al. has demonstrated that CA membranes with a thinner selective layer and a higher porosity could be obtained when Pluronic F127 was used as the additive, indicating that Pluronic also serves as a pore former in CA system (Lv et al. 2007). However, they also observed that most of Pluronic F127 has been leached from the CA membranes, revealing that the interaction between PPO blocks of Pluronic and CA macromolecules might be weaker.

To understand how CA/Pluronic interaction affects pore formation in the system, systematic studies need to be carried out. For instance, PEG and polypropylene glycol (PPG) can be used as the comparative additives to Pluronic in CA membrane fabrication to study the role of the hydrophilic and hydrophobic blocks of Pluronic in CA membrane formation.

7.2.3. Fabrication of PVDF MF membranes

Further investigations on the system containing PVDF as the membrane material and Pluronic/water as the mixed additive can be carried out. While the mixed additives of Pluronic/LiCl are effective to prepare ultrafiltration (UF) membranes (CHAPTER 6), the Pluronic/water system has shown potential for microfiltration (MF) membrane fabrication (CHAPTER 5). So far, most of the PVDF MF hollow fiber membranes are fabricated via thermally induced phase separation (TIPS) technique (Rajabzadeh et al. 2006; Chasen et al. 2012). These membranes typically possess sponge-like structure and high degree of crystallinity. Therefore, PVDF MF membranes prepared using Pluronic as the additive via nonsolvent-induced phase separation (NIPS) can be highly competitive to the conventional TIPS membranes, since membranes obtained via NIPS normally exhibit porous structure with finger-like macrovoids which can be beneficial to mass transfer. In addition, the hydrophobicity of PVDF can be maintained by washing out Pluronic from the prepared membranes via IPA treatment. By doing so, the applications of PVDF/Pluronic membranes can be further extended to hydrophobic applications such as membrane distillation and membrane contactor.

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