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Surface Nanostructuring of Polysulfone Membranes by Atmospheric Pressure Plasma-Induced Graft Polymerization (APPIGP)

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Surface Nanostructuring of Polysulfone Membranes by Atmospheric Pressure Plasma-Induced Graft Polymerization (APPIGP)

A thesis submitted in partial satisfaction
of the requirements for the degree Master of Science
in Chemical Engineering

by

Soo Min Kim

2013

ABSTRACT OF THE THESIS

Surface-nanostructuring of Polysulfone Membranes by

Atmospheric-Pressure Plasma-Induced Graft Polymerization (APPIGP)

by

Soo Min Kim

Master of Science in Chemical Engineering

University of California, Los Angeles, 2013

Professor Yoram Cohen, Chair

Surface nano-structuring of polysulfone (PSf) membrane surrogate surfaces was accomplished by grafting hydrophilic polymers, poly(methacrylic acid) (PMAA) and poly(acrylic acid) (PAA), using the atmospheric pressure plasma-induced graft polymerization (APPIGP) approach. Atmospheric pressure (AP) plasma was used to activate the polysulfone substrate surface, and subsequent graft polymerization of hydrophilic monomers was carried out with an aqueous monomer solution. Optimization of generating the surface initiation sites was guided by water contact angle (θ_w) measurements of the PSf surface after plasma treatment at different gas compositions, radio frequency (RF) power, and the treatment time. Optimal surface activation of the PSf substrate surface was achieved for AP helium plasma of RF power of 50 W and

treatment time of 15 s. Graft polymerization was carried out at initial monomer concentration in the range of 5 – 20 vol% and reaction time of 0.5 – 2 h at 60°C and 70ºC for grafting PMAA and PAA, respectively. Compared to the PSf surrogate surface (θ_w: approx. 97 – 100º), the surface hydrophilicity of the grafted surfaces was improved for all grafting conditions, with the water contact angles of the PMAA- and PAA-grafted polysulfone surfaces decreasing by 28.8% and 34.0%, respectively, both at the lowest initial monomer concentration of 5 vol% and the longest graft polymerization time of 2 hours. Surface topography of the grafted surfaces was evaluated by atomic force microscopy (AFM). Both the surface feature number density and root-mean-square surface roughness (R_{rms}) increased with initial monomer concentration, from 5 – 20 vol%, suggesting that a higher density of surface grafted chains with a wider chain size distribution was achieved with increased initial monomer concentration. All polymer grafted polysulfone surfaces were significantly more hydrophilic than the original polysulfone surface, and high grafting densities were observed. However, relative to lower initial monomer concentration (5 vol%), increased roughness of the surface at high initial monomer concentration (20 vol%) resulted in somewhat reduced surface hydrophilicities quantified by 15.9% and 18.2% contact angle decrease for PMAA- and PAA-grafted PSf, respectively, after 2 h of graft polymerization. Results of the present study are encouraging in indicating that the APPIGP methodology could be beneficial for surface modification of commercial polysulfone membranes for improving the surface hydrophilicity and hence fouling mitigation.

The thesis of Soo Min Kim is approved.

Gerassimos Orkoulas

Robert F. Hicks

Yoram Cohen, Committee Chair

University of California, Los Angeles

2013

DEDICATION

I dedicate this work to my parents, Dong Kwan Kim and Sook Hee Park, who have taught me the value of hard work and helped me pursue my dreams. Your constant love, encouragement, and guidance, have inspired me to find out who I want to be one day and what I want to accomplish in this life.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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1. INTRODUCTION

1.1 Statement of the Problem and Significance of the Study

Microfiltration (MF) and ultrafiltration (UF) membranes are low pressure membranes (LPMs) [1], which operate at relatively low transmembrane pressure (TMP) of typically less than 100 to 200 kPa [2, 3] and have screening pore sizes ranging from several nanometers to several micrometers [4]. MF membranes are used to filter colloidal particles and bacteria, and UF membranes can be used to filter dissolved macromolecules, such as proteins, from solutions [5]. MF and UF have many applications in a wide range of industries, including plasmaphresis (i.e. separation of plasma from blood) in the medical industry, dairy and beverage processing in the food industry, recovery of electrodeposition paints in the automobile industry, production of ultrapure water for semiconductor processing in the microelectronics industry, and concentration and purification of enzymes and antibiotics in the pharmaceutical industry [4, 6, 7]. Also, they are extensively used in wastewater and drinking water treatments [3, 8, 9] and serve as an important pretreatment step to reverse osmosis (RO) for desalination of seawater and brackish water to provide freshwater supply [10-12]. However, the main limitation of the current membrane technology is fouling, which negatively affects membrane performance by reducing membrane permeability, increasing energy costs and decreasing membrane longevity [13-15].

Polysulfone (PSf) (Figure 1.1) is one of the most widely utilized membrane materials in MF and UF membranes because of its exceptionally high thermal, chemical, and mechanical stabilities [16-18], as well as its excellent film forming properties [19]. It is hydrolytically stable [20] and can be sterilized with various methods such as β-/γ- ray,

e-beam, ethylene-oxide and steam [21], making PSf a suitable material for medical applications [22]. Polysulfone is used in gas separations [23-25] and also used as a porous support layer of thin film composite (TFC) membranes for reverse osmosis (RO) [26, 27], nanofiltration (NF) [28-30], and pervaporation [31, 32]. Some notable examples of polysulfone MF/UF membrane applications are whey protein concentration and fractionation in the dairy industry [33, 34], concentration and clarification in the fruit juice industry [35-38], and wastewater treatment [39]. Moreover, PSf membranes are used as hemodialysis hollow fibers that have high permeability for low-molecular weight proteins [40, 41]. However, because of their hydrophobic nature, polysulfone membranes are susceptible to fouling via nonspecific solute adsorption on the membrane surface and within its pores. Major foulants of concern are organic solutes, such as protein [42-44], polysaccharide [45, 46], and natural organic matter (NOM) [47, 48], since they are commonly encountered in various industrial applications and may cause irreversible fouling [34, 46, 49]. Additionally, the hydrophobic polysulfone surface has a poor blood compatibility and promotes blood coagulation and platelet aggregation, thus requiring injections of anticoagulants during hemodialysis [50-52].

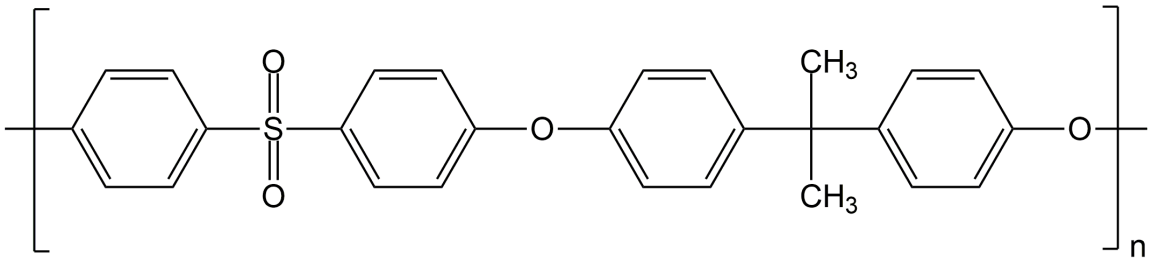


Figure 1.1 Polysulfone (PSf) structure

Currently, various pretreatment and membrane cleaning methods (i.e. physical, chemical, and biological) are employed for fouling minimization and extension of useful membrane life. Pretreatment methods, such as coagulation, flocculation, adsorption, and ozonation, etc., are effective at reducing fouling and improving membrane performance by treating the feed solution before it enters the membrane separation processes [53-55]. However, pretreatment processes involve use of expensive chemicals and produce extra wastes [56, 57], and, in some cases, they may exacerbate membrane fouling [3]. Physical cleaning methods rely on mechanical treatment to dislodge and remove foulants from membrane surfaces; examples include forward/reverse flushing, backwashing, vibration, air sparging, and CO_2 back permeation [58]. These are environmentally benign methods for cleaning reversible membrane fouling; however, they interrupt the continuous filtration process, leading to longer processing times [33]. Chemical cleaning is an effective method for removing irreversible foulant layers and restoring membrane flux. However, chemical cleaning consumes large volumes of expensive chemicals, which can damage membrane materials, reduce useful membrane life, and produce undesirable toxic wastes [33, 59-61].

Surface modification of membranes offers a different approach to solving the fouling problem. Membrane fouling is mainly caused by the interaction between foulants (i.e. organic compounds, microorganisms, etc.) and membrane surfaces via hydrophobic interactions, hydrogen bonding, van der Waals interactions etc. [62, 63]. Therefore, the main strategy of surface modification is to modify the surface properties (i.e. hydrophilicity, charge, etc.) of the membrane in order to minimize undesired adsorption or adhesion interactions between the foulants and membrane surface. Various surface

modification methods have been suggested, including physical adsorption, plasma treatment, and graft polymerization, for improving surface hydrophilicity and endowing antifouling properties to conventional hydrophobic polymeric membranes [64-66]. Physical adsorption of hydrophilic materials on membrane surfaces is a simple way of modifying membrane surfaces. However, adsorbed materials can leach out, and such modified layers lose their functionalities over time. Physical adsorption as a surface modification approach is particularly disfavored in biomedical applications due to the risk of causing cytotoxicity [67]. Plasma treatment is an effective way of introducing hydrophilic functional groups onto the membrane surface, but it has been reported that hydrophilicity may be lost over time may be due to polymer chains reorientation [68, 69]. In surface graft polymerization, on the other hand, polymer chains are covalently tethered to a substrate [70], which suppresses the polymer chain reorientation, retaining hydrophilicity [71]. Surface initiation sites for graft polymerization can be formed by using chemical initiators [72, 73], plasma treatment [74-77], UV-irradiation [78, 79], electron-beam irradiation [80, 81], γ-ray irradiation [82, 83], and ozone treatment [84, 85].

Plasma-induced graft polymerization (PIGP) is an attractive method to graft desired functionalities onto a membrane surface because of its advantages in creating dense, covalently-bound polymer brush layers directly on substrate surfaces without the need for chemical initiators in solution or macroinitiators immobilized on the surface [86]. PIGP utilizes plasma treatment to activate membrane surfaces to create surface initiation sites from which vinyl monomers can be added subsequently. The majority of reported studies on PIGP have relied on low-pressure plasma systems, which cannot be scaled-up for high surface area treatment because of the requirement of ultra-high vacuum

chambers for plasma processing [87, 88]. The above scaling-up challenge can be solved by using atmospheric pressure (AP) plasma systems. AP plasma systems are more feasible for treatment of larger surface areas since they can be operated in open air and do not require an ultra-high vacuum environment. AP plasma sources are particularly effective for surface activation under atmospheric pressure for subsequent graft polymerization. Surface nano-structuring by atmospheric pressure plasma-induced graft polymerization (APPIGP) has proved to be an effective surface modification for reducing mineral scaling and biofouling of RO membranes [89, 90].

PSf membranes are the most widely used membranes for protein separations and dialysis. Therefore, reducing fouling and improving blood compatibility are the most pressing issues for optimizing PSf membrane applications in these areas. Various membrane modification approaches, including surface modification methods, have been reported for polysulfone membranes, but APPIGP has yet to be applied to polysulfone membranes. Successful surface modification of polysulfone membranes via APPIGP can potentially lead to commercial scale production of low fouling membranes for MF/UF operations in food, biomedical industries as well as more efficient water pretreatments to RO for drinking water production. Accordingly, the present study focused on grafting hydrophilic polymer brush layers onto polysulfone membrane surrogate surfaces via APPIGP in order to assess the potential for creating a fouling resistance surface. Methacrylic acid (MAA) and acrylic acid (AA) were chosen as monomer candidates since they are two of the most effective monomers for hydrophilic membrane modifications [74, 79, 91, 92].

1.2 Objectives

The main goal of the present study was to demonstrate that surface nano-structuring of polysulfone membrane surface by APPIGP approach is achievable. The detailed objectives towards this aim are the following:

1. Create a surrogate polysulfone membrane surface via spin-coating an ultrathin (<200 nm thick), smooth polysulfone layer on a silicon wafer. Samples prepared with varying spin coating conditions, including spin speed, polymer solution concentrations, and different solvents are characterized with atomic force microscopy (AFM), contact angle measurement, and ellipsometry to produce a smooth polysulfone surface with low roughness;
2. Investigate the impact of plasma surface treatment parameters (i.e. precursor gas composition, radio frequency (RF) power, plasma treatment time, etc.) on polysulfone membrane surrogate surface by measuring the water contact angles of the plasma treated surfaces, and identify the optimal conditions for the subsequent graft polymerization;
3. Graft polymerize hydrophilic monomers, methacrylic acid (MAA) and acrylic acid (AA), from their aqueous solutions onto polysulfone substrates using various grafting condition parameters including initial monomer concentration and grafting time; and
4. Characterize the grafted polysulfone substrate surfaces by AFM and contact angle measurement to evaluate the effect of grafting condition parameters on the morphology and the wettability of the modified surfaces.

2. BACKGROUND AND LITERATURE REVIEW

Despite the increasing importance of inorganic membranes (i.e. ceramic and metal membranes), the majority of membranes are made of polymers due to their inexpensive cost, ease of manufacture, and wide variability of barrier structures and properties, which can be designed with polymer materials [66, 93]. Many different types of polymeric materials are commercially available for membrane applications including cellulose acetate, polyamide, polyester, polyethylene, polysulfone, etc. However, most polymers that exhibit good bulk properties do not necessarily possess suitable surface properties (and vice versa) for specific applications. For example, membranes that have excellent mechanical properties (e.g. polysulfone) may foul severely due to its hydrophobic nature during water treatment and protein filtration [45, 94, 95]. To solve this dilemma, a membrane modification approach has been suggested to alter the surface properties of a membrane while preserving the bulk properties [66, 96]. Various membrane modification methods can be used to introduce hydrophilic functional groups on the hydrophobic membrane surfaces and minimize undesired interactions between the membrane surface and the foulants [62, 64, 65].

Membrane modification methods can be broadly divided into two different categories depending on whether the modification step takes place before or after the membrane formation (Figure 2.1): (i) *bulk modification* and (ii) *surface modification*. Bulk modification methods involve modifying the bulk polymer system by blending [97], copolymerization [98], nanoparticle incorporation [39], etc. and subsequently preparing the membrane. The above approaches require fine-tuning (i.e. composition of the bulk polymer system, solvent, etc.) in order to ensure proper bulk properties of the membranes

such as the mechanical and thermal stabilities. [99, 100]. On the other hand, surface modification methods involve modifying surfaces of preformed membranes [70]. It is usually preferred over the bulk modification methods because only the membrane surface is modified and the bulk properties of the base membranes are preserved. Surface modification includes greater variety of means than bulk modification, such as physical adsorption, plasma treatment, graft polymerization, etc. Various membrane modification methods performed on polysulfone membranes, including both bulk and surface modifications, are reviewed in Section 2.1 and 2.2.

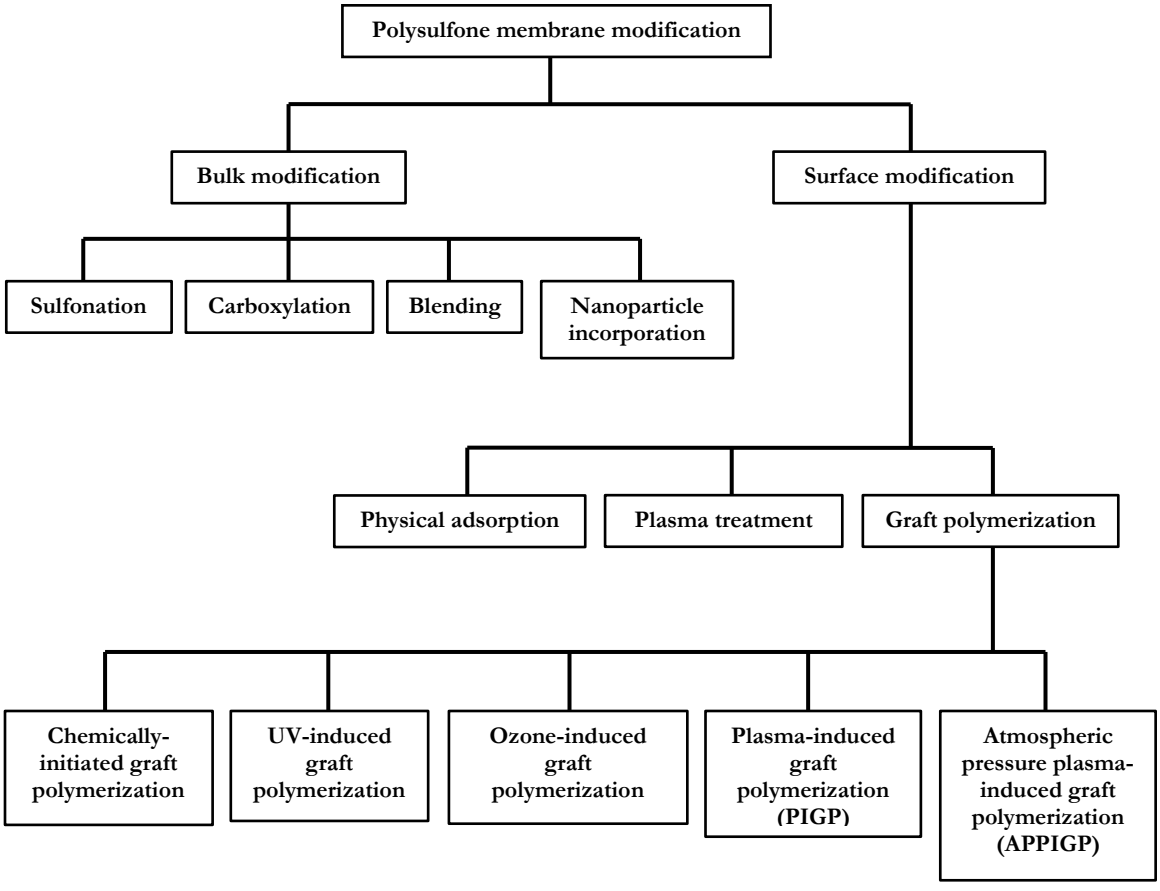


Figure 2.1 Polysulfone membrane modification methods for fouling mitigation

2.1 Bulk Modification of Polysulfone Membranes

2.1.1 Carboxylation and Sulfonation

Two common methods of bulk modification of polysulfone membranes are carboxylation and sulfonation, in which hydrophilic functional groups are added to the polymer chains via organic chemical reactions. Although both carboxylation and sulfonation are usually carried out prior to membrane synthesis, it is possible to perform these modifications on the pre-formed polysulfone membranes by simply dipping them into suitable active reagents [101, 102].

The typical carboxylation and sulfonation processes for polysulfone are shown in Figure 2.2. Carboxylation proceeds via a two-stage process of lithiation, followed with use of dry ice to add carboxylic acid groups (-COOH) to aromatic backbones of polysulfone [95, 103]. Similarly, sulfonation adds sulfonic groups in the form of a free acid ($-SO_3H$), a salt ($-SO_3^-Na^+$) or an ester ($-SO_3R$) [102], using a variety of sulfonating agents such as sulfuric acid (H_2SO_4) [104, 105], sulfur trioxide-triethylphosphate complex (SO_3-TEP) [95, 102, 106], and chlorosulfonic acid ($ClSO_3H$) [107, 108]. The membrane structures are then prepared by phase inversion method using carboxylated/sulfonated PSf or blends of it and other polymers to synthesize unique membranes with functionalities [109-112]. For bulk modifications, carboxylation or sulfonation is expressed by the degree of carboxylation (DC) or sulfonation (DS), which is defined as the number of carboxylic acid or sulfonic group per polysulfone repeat unit. DC and DS depend on the type of modifying agents, the reaction time, the reaction temperature, and the molar ratio of modifying agents and polymer [113].

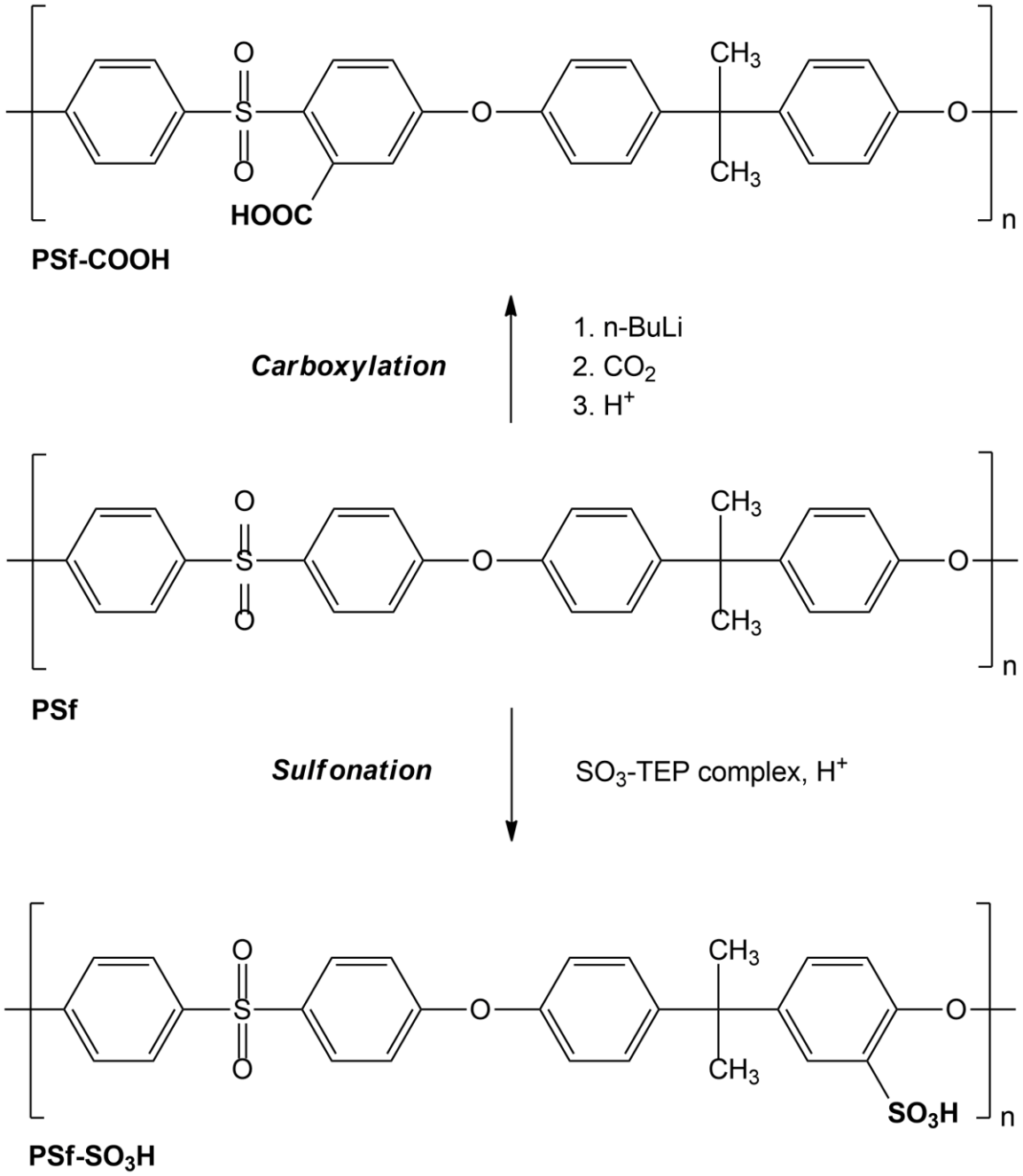


Figure 2.2 Carboxylation and sulfonation of polysulfone (adopted from [95])

PSf membranes that were modified by carboxylation and sulfonation showed improved hydrophilicity and reduced fouling during UF of protein solutions. Möckel et al. [95] compared the UF performance of the carboxylated PSf (PSf-COOH) and sulfonated PSf (PSf-SO_3H) membranes with sulfhydryl modified bovine serum albumin (cys-BSA) solution; both of the modified membranes had lower flux reduction compared to the unmodified PSf UF membrane. Fouling was most severe at the isoelectric point of cys-BSA (pH=4.8), but the modified membranes demonstrated antifouling properties. The flux ratios (J_p/J_0), in which J_p is the flux of protein solution after 2 hours of UF operation and J_0 is the initial electrolyte solution flux prior to protein UF, were 0.53, 0.71, and 0.75 for the unmodified PSf, PSf-COOH (DC= 1.74), and PSf-SO_3H (DS = 0.58), respectively. It was found that a lower degree of sulfonation resulted in greater antifouling propensities than a higher degree of carboxylation. Also, Nabe et al. [106] reported improved hydrophilicity of the sulfonated PSf as quantified by the water contact angle of 34º, which was about ~50% lower than for the unmodified PSf, while the PSf-SOH_3 membrane had ~8% flux reductions compared to the unmodified PSf membrane which had ~29% permeate flux reduction of the BSA solution after filtration period of 200 min. The main drawback of carboxylation and sulfonation is the relatively complex and time consuming modification processes, which involves numerous steps. Also, carboxylation has to be performed at a low temperature (e.g. -50ºC) to prevent crosslinking of the intermediate product [103].

2.1.2 Blending

Blending is a process in which two or more polymers are physically mixed to obtain a product with superior properties relative to the pure materials [96]. For example, polysulfone was blended with various hydrophilic polymers in order to prepare membranes with enhanced antifouling properties as well as blood compatibilities [40, 41, 114]. However, the main issue with the above approach is that it requires two polymers of significant differences in hydrophilicity to be dissolved in the same solvent [113]. Therefore, the approach is limited by the miscibility of the polymers [115, 116].

Phosphorylcholine copolymers (i.e. synthesized copolymer composed of 2-methacryloyloxyethyl phosphorylcholine (MPC) and either *n*-butyl methacrylate (BMA) or *n*-dodecyl methacrylate (DMA)) were blended with polysulfone to prepare membranes with improved blood compatibilities [40, 41]. The blend membranes, prepared with poly(MPC-co-BMA) or poly(MPC-co-DMA), had significantly reduced amounts of plasma protein adsorption on the membrane surface, which were as low as ~0.3 $\mu g/cm^2$ and ~0.5 $\mu g/cm^2$, while that of the neat PSf membrane was nearly ten times higher, ~2.75 $\mu g/cm^2$. Also, the modified membrane effectively suppressed platelet adhesion since the adsorbed plasma proteins promoted platelet adhesion. It was also reported that X-ray photoelectron spectroscopy (XPS) revealed that MPC polymers were concentrated on the membrane surface, and the mechanical properties of the blend membrane were similar to that of the original PSf membrane [40, 41].

Zhao et al. [114] used single-strand DNA as a biomaterial additive to modify PSf membranes for improved blood compatibility. However, due to the interaction between DNA and the proteins, the adsorption capacity of the proteins did not significantly

decrease compared to the neat PSf membrane. Also, high ratios of DNA and PSf were obtained only at low concentrations of PSf in N-methyl pyrrolidone (NMP) since water was used as the solvent of DNA. DNA is costly compared to cheaper polymeric materials such as poly(vinylpyrrolidone) (PVP), and thus the use of DNA is questionable for commercial membrane synthesis.

Sulfonated polysulfone has been used as a hydrophilic modifying agent to blend with PSf for improving antifouling properties of UF membranes. For example, Chen et al. [117] reported on two different kinds of blend membranes, sulfonated PSf/PSf (SPSf/PSf) and aminated PSf/PSf (APSf/PSf). It was reported that upon increasing SPSf/PSf blending ratio from 1:9 to 2:1, the water flux increased and salt rejection decreased. For APSf/PSf, the casting solution with blending ratio of 1:2 was incompatible, and only solutions of lower blending ratios, 1:9 and 1:3, were suitable for preparing the blended membranes. It is noted that the above study did not evaluate the surface hydrophilicity or the antifouling properties of the blend membranes. Poźniak et al. [107] also prepared SPSf/PSf membranes and evaluated their antifouling properties with BSA ultrafiltration. Blend membranes with more than 50 wt% of the SPSf were reported to have antifouling character, which was as effective as that of sulfonated PSf membranes. It was suggested that the above result suggests that sulfonated polysulfone undergoes a phase separation from polysulfone and localizes on the surface during the membrane preparation process [107].

2.1.3 Nanoparticle Incorporation

The use of nanoparticles in membrane modification has received much attention over the last few years in attempts to enhance flux and reduce fouling [66]. Two different methods for preparing membranes with nanoparticles have been reported. The first one is entrapment of nanoparticles in the polymer membrane matrix by adding nanoparticles in the casting solution and make membranes by the phase inversion. The second is deposition of nanoparticles on the membrane surface by dipping the membrane in an aqueous suspension of nanoparticles [118, 119].

Zodrow et al. [120] utilized the antibacterial properties of silver nanoparticles (nAg) in modifying PSf UF membranes for improving biofouling resistance during water treatment. The PSf UF membrane matrix impregnated with the silver nanoparticles (nAg-PSf) exhibited antimicrobial properties towards a variety of bacteria, including *Escherichia coli*, and showed reduced cell attachment and suppressed biofilm growth on the membrane surface. The hydrophilicity and permeability of the nAg-PSf membranes were improved compared to the neat PSf membrane. The water contact angle decreased from 76.8º to 68.8º, and the permeability increased from 408 $L/m^2/h/bar$ to 532.6 $L/m^2/h/bar$, relative to the unmodified PSf membranes. However, it was reported that the impregnated silver nanoparticles in the membrane surface region were depleted after 0.4 L/cm^2 of water filtration, resulting in a loss of the antibacterial and antiviral activity of the membrane. The leaching silver nanoparticles is a severe limitation of this membrane modification method since nanoparticles in the treated effluent may enter the surface water environment, potentially adversely impacting biological ecosystems [121].

In addition to silver nanoparticles, titanium dioxide (TiO_2) nanoparticles were also incorporated into PSf membranes for hydrophilic surface modification and fouling mitigation in water treatment applications because of their high affinity to water [122, 123]. Yang et al. [122] prepared TiO_2-PSf composite membranes using the phase inversion method with varying concentrations of TiO_2 nanoparticles in the casting solution (1 – 5 wt%). They found that the TiO_2-PSf composite membrane prepared from 2 wt% TiO_2 solution had the best hydrophilicity, permeability, mechanical strength, and anti-fouling properties, as well as retention of bovine serum albumin (BSA). The composite membrane had a water contact angle of 41.4º and its initial water flux was 488 L/m^2h, while the PSf membrane had water contact angle of 84.7º and water flux of 289 L/m^2h. After 30 days of BSA solution filtration, the flux for the TiO_2 modified membrane decreased by ~11%, which was much lower than for the PSf membrane (~43%). However, the modified PSf membrane, prepared from a higher TiO_2 concentration ($\geq$ 3 wt%), had reduced porosity and yet larger pores on the membrane surface due to aggregation of nanoparticles, which led to a decrease in permeability and retention of BSA. In another study, Bae et al. [123] compared the performance TiO_2-PSf membranes, prepared from two different approaches (i.e. TiO_2-entrapped and TiO_2-deposited membranes), and found that TiO_2-deposited membranes had greater fouling resistance compared to TiO_2-entrapped membranes due to the larger density of nanoparticles located in the membrane surface region. Neither of the above studies evaluated the long-term stability of the TiO_2-PSf membranes with respect to the potential leaching of nanoparticles.

2.2 Surface Modification of Polysulfone Membranes

2.2.1 Physical Adsorption

Coating membrane surfaces with a thin layer of hydrophilic modifying agents (e.g. polymers, surfactants, etc.) by physical adsorption is a simple way to improve surface hydrophilicity and reduce fouling propensity of a membrane [62, 70, 124]. In this method, the membranes are either immersed in the solutions containing hydrophilic modifying agents [125, 126] or filtered with the solution at a low transmembrane pressure (TMP) [127, 128], and the modifying agents interact with the membrane surface through hydrogen bonding and/or Van der Waals interaction [129].

Modification of polysulfone membrane surfaces has been reported via preadsorption with various hydrophilic polymers such as methyl cellulose (MC) [130], polyaniline (PANI) nanofiber [128], poly(ethyleneimine) (PEI) [131], and poly(vinyl methyl ether) (PVME) [130], as well as chemical cleaning agents, such as citric acid and sodium bisulfite [129]. In all of the above studies, pore narrowing was reported due to pore blockage by the adsorbed materials that resulted in decreased permeate flux albeit with similar or slightly higher solute (e.g. protein) rejection. It was found that the extent of pore narrowing was dependent on the degree of surface adsorption of the modifying agents, which in turn is dependent on the concentration of the modifying agents in the solution and the relative sizes of the membrane surface pores and that of the modifying agent. The PSf UF membranes, which were modified with MC had an overall membrane resistance increase (relative to the unmodified membrane) that was ~40% smaller than the resistance increase for the unmodified membranes after the filtration of a whey solution [130]. However, the same membranes modified with PVME had even higher

membrane resistance than the unmodified membranes, showing that modification with PVME produced greater ‘fouling’ effects. The above was attributed to the fact that PVME is significantly larger than MC and shields or blocks the membrane pores more extensively. A similar pore blocking effect was observed for PSf UF membranes modified by preadsorption of polyethyleneimine (PEI) [131]. Whereas the membrane modified in a relatively low concentration of PEI solution (1 and 5 ppm) had lower flux reduction after ultrafiltration of ovalbumin solution compared to the unmodified membrane, the membranes modified in 10 ppm PEI solution resulted in even higher flux reduction due to pore blocking by the excess PEI molecules.

Leaching of the adsorbed agents over the course of filtration resulted in loss of antifouling properties. For example, Wei et al. [129] evaluated membrane performance for citric acid (CI) and sodium bisulfate (SB) modified PSf membranes and reported percent flux recovery for three cycles of wastewater filtration. Each cycle consisted of 2 hours of wastewater filtration, followed by membrane cleaning by water filtration for 30 minutes. At the end of the first cycle, percent flux recovery was 71.5% and 62.5% for the CI and SB modified PSf membranes, respectively, higher than that for the unmodified membrane (54.7%). However, at the end of the third cycle, percent flux recovery of CI and SB modified membranes were 86.4%, and 79.2%, which were similar or even lower than that for the unmodified membrane (85.1%). The above result suggested the loss of antifouling properties of the modified membranes due to desorption of CI and SB over the course of filtration. Fan et al. [128] also evaluated the long-term stability of PANI nanofibers on PSf membranes by dipping the membranes in water daily and observed minor desorption of nanofibers after 4 months.

2.2.2 Plasma Treatment

Plasma consists of highly excited species that can alter the physicochemical properties of polymeric membrane surfaces. Due to its low penetration depth, of several hundred angstroms [66], plasma can be used to improve polymer surface properties such as wettability, permeability, conductivity, adhesion or biocompatibility while preserving bulk properties of the material. The chemical and topographical modification of membrane surfaces and their extent depend on the plasma system parameters such as type of precursor gas, applied microwave or radiofrequency (RF) power, treatment time, the distance between the plasma source and the surface, system pressure, etc. [132-134]. Plasma treatment generally refers to the process that uses non-polymerizable gases such as Ar, He, N_2, O_2, etc., whereas using polymerizable gases, which usually are vinyl-containing monomers such as allyl alcohol, allyloamine and acrylic acid, is also known as plasma polymerization [69].

Plasma treatment using various precursor gas(es) that have been performed on polysulfone membranes have resulted in the introduction of a variety of hydrophilic functional groups and improvement of protein fouling resistance (Table 2.1). Treatment with plasma of oxygen-containing gases, such as CO_2, H_2O, and O_2 resulted in a higher atomic concentration of oxygen in the polysulfone membrane surfaces such as hydroxyl, carbonyl and carboxyl groups [135-140]. N_2 and NH_3 plasma treated PSf membrane surfaces had nitrogen containing functional groups, but also some degree of O was incorporated into the PSf membrane surfaces [133, 141, 142]. This is due to the surface radical species reacting with oxygen during exposure to ambient air subsequent to the

plasma treatment [133, 141, 142]. The same phenomenon has been observed for plasma treatment with inert gases such as Ar and He [143, 144].

The permeability of plasma treated PSf membranes showed variable results, depending on the plasma system and its operating conditions (i.e. applied power, plasma exposure time, precursor gas, etc.) as well as the pore size of the membranes [135, 136, 140-142, 144]. For example, water flux of PSf membrane treated with CO_2 plasma decreased by up to ~75% after 2 minutes of treatment; however, longer than 2 minutes of treatment resulted in increased water flux, and it increased by more than 200% at 10 min, relative to the original PSf membrane. The above result was presumably due to deposition of etched membrane materials inside the pore of the membrane in the early stage of the treatment (up to ~2 min), and prolonged treatment was accompanied by progressive ablation, which resulted in pore enlargement and increased water flux [135].

The major limitation of plasma treatment is the temporal nature of the modified surface. It has been hypothesized that polar functional groups at the surface can reorient from the topmost layer (or migrate due to segmental diffusion) toward the underlying subsurface region, which results in gradual deterioration of surface hydrophilicity [132]. This process, called “aging” or “hydrophobic recovery”, is driven by minimization of the free energy of the interface between the polymer surface and surrounding medium [68] and is facilitated by the flexibility of polymer chains that allows for rearrangement [145]. Ulbricht et al. [144] reported that a small increase in contact angle ($\Delta\theta_w$ = +6) was measured for membranes treated with either He or He/H_2O plasma and stored in air for 6 weeks. Steen et al. [137] showed that PSf MF/UF membranes treated with H_2O plasma

were completely wettable after storage in ambient air for 16 months; however, membrane performances was not evaluated.

Table 2.1 Summary of plasma treatment methods for polysulfone membranes

Reference	Plasma treatment[a]	Chemical composition of the modified surface[b]	Membrane performance[c]	Surface characterization methods	Comments
[143]	Ar t_{exp} = 1 – 50 min Power = 5 – 15 W Pressure = 60 mTorr	Oxygen content increased	*Gas permeation:* $P_{N2} \downarrow$; $P_{CO2} \downarrow$	AFM and XPS	Oxygen incorporation onto the membrane surface; surface free radicals created during the plasma treatment react with oxygen when the membrane is exposed to the atmosphere post-treatment.
[135]	CO_2 t_{exp} = 0 – 10 min Power = 60 W Pressure = 300 mTorr	C=O and COOH groups were introduced	*BSA filtration:* $L_p \downarrow$ ($t_{exp} \leq 2$ min); $L_p \uparrow$($2 < t_{exp} \leq 10$ min); PFR ↑	ATR-FTIR, contact angle, pore size, and SEM	% flux reductions (of buffer solution) after BSA filtration were 59.9% for PSf and 50.9% for the plasma treated PSf at pH=3; 53.5% for PSf and 22.1% for the plasma treated PSf at pH=9.
[136]	CO_2 t_{exp} = 10 – 300 s Power = 5 – 20 W Pressure = 150 mTorr	C=O, COOH, and O-H groups were introduced	*BSA filtration:* $L_p \uparrow$; PFR ↑	ATR-FTIR contact angle, SEM, % weight loss, and XPS	% flux recovery was 73.8% and 96.5% for PSf and CO_2 plasma treated PSf (10W, t_{exp} = 60s), respectively after BSA filtration and membrane cleaning.

Table 2.1 (Continued)

Reference	Plasma treatment[a]	Chemical composition of the modified surface[b]	Membrane performance[c]	Surface characterization methods	Comments
[137, 138]	H_2O t_{exp} = 2 min Power = 25 W Pressure = 50 mTorr	C-O, C=O, O-C=O, and OH groups were introduced	NR	Bubble point, contact angle, SEM, porometry, and XPS	θ_w of the plasma treated samples stored under ambient air remained completely wettable (i.e. θ_w ~0º) for ~16 months.
[139]	H_2O/air t_{exp} = NR Power = 100 – 200 W Pressure = 8 – 150 mTorr	C-O bond increased and O-C=O group appeared in the plasma treated samples	NR	Contact angle and XPS	The optimal conditions for the maximum contact angle reduction and highest concentration of oxygen at the surface corresponded to plasma conditions that produced the greatest intensity of OH radicals in the plasma.
[144]	He, He/H_2O t_{exp} = 30 s Power = 10, 25 W Pressure: He = 100 mTorr He/H_2O = 100mTorr/100mTorr	Oxygen content increased	*BSA filtration:* L_p ↓; PFR↑; R_p ≈	ATR-FTIR, contact angle, and XPS	PSf UF membrane (PM 10) treated with He/H_2O plasma (10W, 30s) had 49% higher filtrate flux compared to the parent samples.

Table 2.1 (Continued)

Reference	Plasma treatment[a]	Chemical composition of the modified surface[b]	Membrane performance[c]	Surface characterization methods	Comments
[141]	N_2 t_{exp} = 0 – 20 min Power = 60 W Pressure = 300 mTorr	C=O present as aldehyde, ketone, amide, acid and ester groups appeared; but most of the above species disappeared/reduced during first day of storage in the air	*BSA filtration:* L_p ↓; PFR ↑; R_p ≈	ATR-FTIR, contact angle, and pore size	% flux reductions (of buffer solution) after BSA filtration were 59.9% for PSf and 47.5% for plasma treated PSf at pH=3; 53.5% for PSf and 45.5% for plasma treated PSf at pH=9.
[142]	NH_3, NH_3/Ar t_{exp} = 0 – 10 min Power = 60 W Pressure: NH_3 = 750 mTorr; NH_3/Ar = 750/225 mTorr	Atomic concentrations of oxygen and nitrogen were increased; C-N, C=O, N-C=O, N-C=N, O-C=N groups introduced	*BSA filtration:* NH_3 plasma: L_p ↓; PFR(pH=3) ↓; PFR(pH=9)↑; R_p ≈ NH_3/Ar plasma: L_p ↑; PFR(pH=3, 9) ↓; R_p ≈	ATR-FTIR, contact angle, pore size, and XPS	% flux reductions (of buffer solution) after BSA filtration were 59.9% for PSf, 71.1% for NH_3 plasma treated PSf, and 68.0% for NH_3/Ar plasma treated PSf at pH=3; 53.5% for PSf and 45.3% for NH_3 plasma treated PSf, and 72.1% for NH_3/Ar plasma treated PSf at pH=9.

[133]	NH_3 t_{exp} = 1 – 50 min Power =5 – 15 W Pressure = 60 mTorr	Nitrogen incorporation; increase in oxygen content	*Gas permeation:* P_{N2} ↓; P_{CO2} ↓	AFM and XPS	Ammonia plasma treatment on PSf surface resulted in surface etching and surface cracks even at plasma power as low as 5W.
[140]	O_2 t_{exp} = 5 – 120 s Power = 60 W Pressure = 300 – 900 mTorr	C=O, COOH, and OH groups were introduced	*Gelatin filtration:* L_p ↑; PFR ↑	Contact angle, FESEM, XPS, and zeta potential	The IEP of PSf membrane changed from pH=3 to 4.5; the % flux recovery were 50%, 40%, and 52% for untreated PSf and 64%, 68%, 63% for O_2 plasma treated PSf at pH=3, 8, 12, respectively.

Legend: ↑, increased; ↓, decreased; ≈, less than 5% change; NR, not reported; L_p, permeability of pure water (if not specified); P_{gas}, gas permeability; R_p, rejection of protein(s); PFR, protein fouling resistance; and θ_w, water contact angle.

[a] The first line refers to the plasma gas; t_{exp} = plasma exposure time; power and pressure of the plasma system used are reported.

[b] Qualitative description of the chemical compositions of the plasma treated surfaces were reported from ATR-FTIR and/or XPS results(s). Only the functional groups that correspond to the most prominent bands were reported here.

[c] Indicated in italics is the type of membrane filtration study done to evaluate membrane performances. For simplicity, in some cases, only the selected (the best) results from the literatures were cited with specific information regarding that particular sample(s) (see comments)

2.2.3 Graft Polymerization

Surface modification of polymeric membranes by graft polymerization is a technique that has demonstrated its versatility in various applications. It is advantageous in that the introduction of graft chains onto the surface is simple and controllable, and the graft chains are covalently attached to the surface, which provides long-term stability and avoids delamination or leaching of the grafted chains as in physically coated polymer chains [146]. In general, grafting can be achieved in two ways (Figure 2.3): 'grafting-to' (polymer grafting) and 'grafting-from' (graft polymerization). In the 'grafting-to' methods, polymer chains that have reactive groups at the end or on the side chains are covalently coupled to the membrane surface [147]. In the 'grafting-from' method, monomers are polymerized using an active (initiation) site at the membrane surface, and propagation occurs until chain termination. 'Grafting-to' methods have the potential advantages that the structure of the polymer to be used for surface modification can be well controlled by synthesis and also characterized in detail [93]. However, the polymer chains cannot diffuse through previously bound chains to the surface reactive sites due to steric hindrance, thus high grafting densities cannot be achieved. Because of this reason the 'grafting-to' method is seldom used for membrane modification [62].

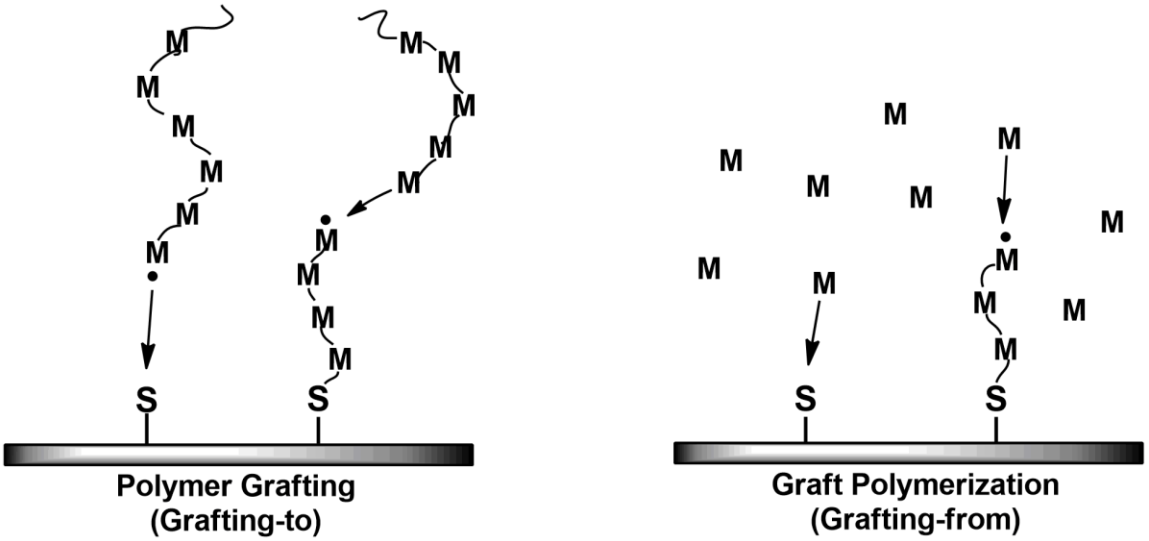


Figure 2.3 Illustration of polymer grafting ('grafting-to') and graft polymerization ('grafting-from') methods (M = monomer, • = monomer radical, S = surface sites)

On the other hand, surface graft polymerization can typically achieve high grafting densities. Although the synthesis of surface-anchored polymers is often less controlled with respect to polymer structure, a wide variation of grafting densities and chain length can be obtained under relatively convenient reaction conditions [93]. Surface graft polymerization has been used to modify polysulfone membrane surfaces, using various surface activation methods including chemical initiator [148-150], UV-irradiation [78, 151-159], plasma treatment [144, 160, 161], and ozone treatment [162].

2.2.3.1 Chemically Initiated Graft Polymerization

In chemically initiated graft polymerization, the grafting can proceed via either free radical graft polymerization or living graft polymerization [70]. In free radical graft polymerization either redox initiators or free radical initiators (i.e. azo compounds, peroxides, etc.) are used in the solution phase, and free radicals are produced from the initiators and transferred to the substrate surface to initiate graft polymerization. It is also possible to bind free radical initiators onto the polymeric membrane surface by grafting, chemisorption, or physisorption [163]. However, in chemically initiated free radical graft polymerization, the chemical initiators can also initiate polymerization in the bulk solution which can lead to homopolymerization and polymer grafting ('grafting-to') [163].

Living polymerization is advantageous in that polymer chains with controlled length and low polydispersity can be grafted [164]. Atom transfer radical polymerization (ATRP) is a polymerization method that mimics living polymerization [165]. In ATRP, dormant chains are capped by halogen atoms, which are reversibly transferred to metal complexes in the lower oxidation state, generating the transient growing radicals and complexes in the higher oxidation state [164]. In particular, surface-initiated ATRP (SI-ATRP) is a 'grafting-from" method that allows the preparation of well-defined polymer bushed with dormant chain ends on various types of substrates [150]. In this method, reactive alkyl halide groups such as C-Cl and C-Br groups on polymer chains on surface are necessary as the initiators of ATRP [148].

Surface grafting of hydrophilic polymer brushes onto polysulfone membranes by SI-ATRP was achieved by introducing chloromethyl ($–CH_2Cl$) groups on the polysulfone

main chain. Chloromethylation was performed prior to membrane formation by phase inversion, and $–CH_2Cl$ groups on PSf membrane surface served to initiate graft polymerization in the monomer containing solution in the presence of the catalyst, which was comprised of copper(I) chloride, copper(II) chloride, and 2,2'-bipyridine ($CuCl/CuCl_2$/bpy). Several different kinds of hydrophilic polymers including polyacrylamide (PAM), poly(poly(ethylene glycol) methyl ether methacrylate) (P(PEGMA)), poly(poly(ethylene glycol) monomethacrylate) (PEGMA), poly(glycidyl methacrylate) (PGMA), and poly(2-hydroxyethyl methacrylate) (PHEMA) were grafted onto chloromethylated PSf membranes, which showed improved hydrophilicity and antifouling properties [148-150]. However, the obvious drawback of this approach is the need for chloromethylation of polysulfone prior to graft polymerization, and the active sites for the initiation of ATRP are limited by the degree of chloromethylation. Moreover, excess chloromethylation may lead to the deterioration of membrane mechanical properties [150].

2.2.3.2 UV-induced Graft Polymerization

UV-light irradiation of polysulfone membrane surfaces was used to activate the membrane surface for subsequent grafting of hydrophilic polymers (Table 2.2). Depending on the UV-light emission wavelength, the polysulfone membrane surface was activated either with or without a photoinitiator. Since polysulfone has an intrinsic photoreactivity and shows strong absorption peaks in the wavelengths range between 250 and 300 nm [155], exposure to UV-light of short wavelengths (approximately $\lambda < 300$ nm) can induce polymer main chain scission and generate radicals on the surface of the polysulfone membranes without a photoinitiator (Figure 2.4) [166]. However, unspecific polymer main chain scission led to strong pore etching of the membrane active layer, and degradation of the polymer was accompanied by yellowing of the samples [167, 168]. Alternatively, a specific bond scission of PSf is possible by using a photoinitiator (e.g. benzophenone (BP), benzophenone carboxylic acid (BPC), etc.), which can be activated at a longer wavelength ($\lambda > 350$ nm) and subsequently abstract H from the methyl groups of PSf and thus avoids its main chain scission [166]. In both cases, the modified PSf membranes (with hydrophilic polymers) had lower fouling propensity relative to the unmodified PSf membranes, though in most cases it was accompanied by permeability reduction. For example, compared to the unmodified PSf UF membranes, 2-acrylamido-2-methyl-1-propanesulfonic acid (AAP) grafted PSf UF membrane had ~31% less reduction in flux after BSA filtration, but the water permeability decreased by ~61% [153]. Similarly, 2-hydroxyethyl methacrylate (HEMA) grafted onto polysulfone UF membranes resulted in ~15% lower flux reduction after BSA filtration, but water flux decreased by ~29% after surface modification [157, 158]. Performance of the modified

membranes in protein solution filtrations improved with a higher degree of grafting, which increased with longer UV exposure time and higher monomer concentration. However, the above approach resulted in severe decrease in permeability and lower rejection of proteins.

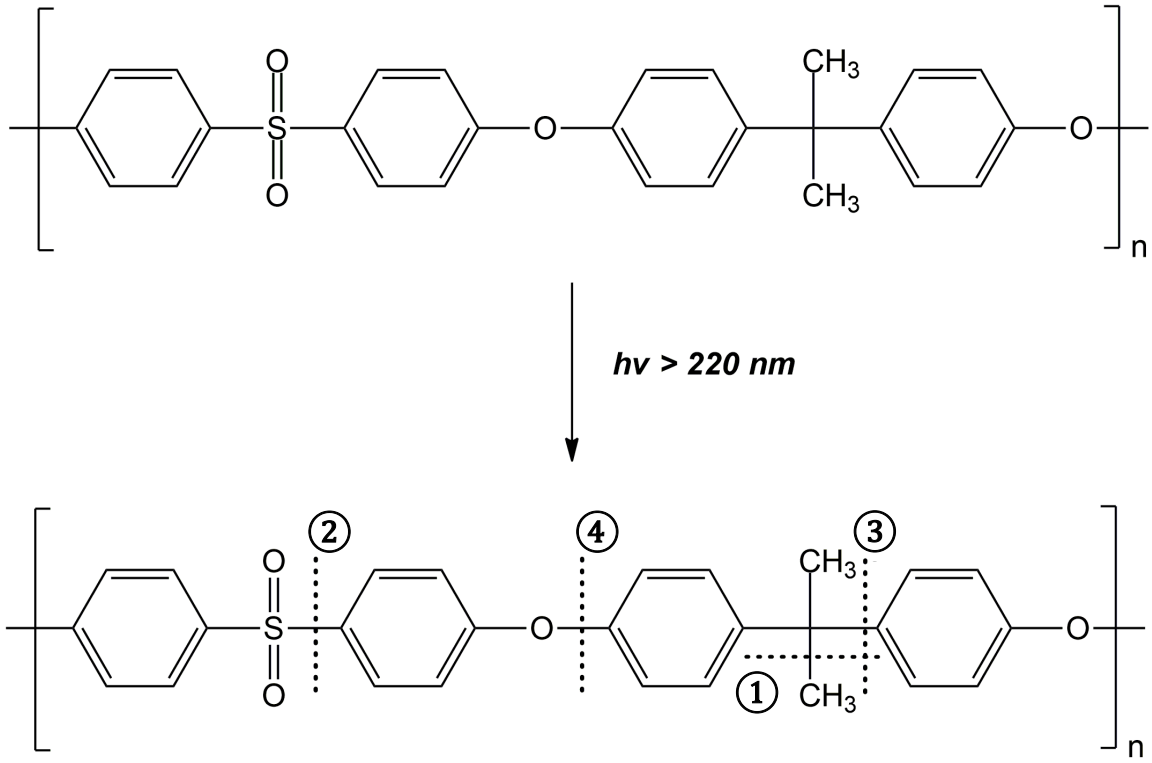


Figure 2.4 **Primary homolytic bond scissions of the major photodegradation pathways (in the order of increasing binding energy) for PSf (figure adapted from [166])**

Table 2.2 Summary of UV-induced graft polymerization methods for polysulfone membranes

Reference	UV-irradiation[a]	Monomer(s)[b]	Graft polymerization[c]	Membrane performance[b,d]	Grafted polymer characterization methods	Comments
[151]	*Photoinitiator:* benzophenone (BP) t_{exp} = 6 – 10 min λ < 365 nm Intensity = 20 mW/cm^2	MA	PSf-*graft*-MA was prepared by UV-irradiation of homogeneous solutions of PSf, MA and BP.	*BSA filtration:* L_p ↑; PFR ↑; R_p ≈	ATR-FTIR, contact angle, DG, and SEM	PSf-*graft*-MA copolymer solutions were used to prepare membranes via phase inversion method.
[152]	*Photoinitiator :* 1-hydroxycyclohexyl phenyl ketone (HCPK) t_{exp} = 90 s λ = 312 nm Intensity = 3.0 mW/cm^2	PEGDA	A monomer solution containing the photoinitiator was spread on the membrane surface and exposed to UV-light.	*Oil/water filtration:* L_p ↓; PFR ↑; R_p ↑	Contact angle, MWCO, and SEM	Crosslinked PEGDA coated PSf membrane for oil/water separation.
[153]	λ = 300 nm Energy = 65 – 5838 mW/cm^2	AAG, AAP, and NVP	UV-irradiation of membranes, which had been dipped in the monomer solution.	*BSA filtration:* L_p ↓; PFR ↑; R_p ≈	Contact angle and DG	The membranes modified with 5 wt% AAP and lowest UV radiation energy had the best performance.

Table 2.2 (Continued)

Reference	UV-irradiation[a]	Monomer(s)[b]	Graft polymerization[c]	Membrane performance[b,d]	Grafted polymer characterization methods	Comments
[155]	t_{exp} = 10 – 180 s	AA	UV-treated PSf membranes were dipped into the monomer solution for 2 h.	*Riboflavin filtration:* L_p(riboflavin) ↓ at pH (3-7)	AFM, ATIR-FTIR, DG, and XPS	The surface radical density and DG increased with a longer UV irradiation time up to 150s and decreased afterwards.
[166]	*Photoinitiators:* benzophenone (BP) and benzoylbenzoic acid (BPC) λ > 300 or >350 nm Intensity: 1.7 mW/cm^2 for λ >300 nm 0.7 mW/cm^2 for λ > 350 nm	AA	Monomer solutions, saturated with BP or BPC and containing BP/BPC coated PSf membranes were subject to UV irradiation.	*Dextran filtration:* L_p ↓; J_p(Dextran)↓; R_p(Dextran)↓ for λ>300 nm; R_p(Dextran)↑ for λ>350 nm	ATR-FTIR and DG	At λ > 300 nm, a less selective excitation induced both PSf degradation and H-abstraction by the photoinitiators; at λ > 350 nm, only the photoinitiator induced process took place.

[157, 158]	λ = 253.7 nm	HEMA	PSf membranes were immersed in the monomer solution (water or methanol), which was subsequently UV-irradiated.	*BSA filtration:* L_p ↓; PFR ↑; R_p ≈	ATR-FTIR and DG	Modified PSf membranes which were irradiated in methanol monomer solutions exhibited higher fluxes compared to aqueous monomer solutions.
[159]	*Photoinitiator:* benzophenone (BP) λ > 300 nm	MPDSAH	PSf membranes were adsorbed with BP and immersed in the monomer solution, which were subsequently UV-irradiated.	*BSA filtration:* L_p ↓; PFR ↑; R_p ≈	ATR-FTIR, contact angle, DG, and SEM	Grafting degree increased with a longer UV-irradiation time and a higher concentration of the monomer and the photoinitiator.

Legend: ↑, increased; ↓, decreased; ≈, less than 5% change; NR, not reported; L_p, permeability of water (if not specified); J_p, permeate flux of protein solution; R_p, rejection of protein(s); PFR, protein fouling resistance; DG, degree of grafting, and θ_w, water contact angle.

[a] The first line refers to the type of photoinitiator (if any); t_{exp} = UV exposure time; wavelength (λ) and intensity of the UV-irradiations are reported.

[b] For the monomers and proteins with acronyms, their full names are as follows:
AA: acrylic acid; AAG: 2-acrylamidoglycolic acid monohydrate; AAP: 2-acrylamido-2-methyl-1-propanesulfonic acid; BSA: bovine serum albumin; DEX: dextran; HEMA: 2-hydroxyethyl methacrylate; MA: Methyl acrylate; MPDSAH: [3-(methacryloylamino) propyl]-dimethyl(3-sulfopropyl) ammonium hydroxide inner salt; NVP: *N*-vinyl-2-pyrrolidone; PEGDA: poly(ethylene glycol) diacrylate.

[c] Detailed description of the UV-induced graft polymerization method of the study is provided in this column.

[d] Indicated in italics is the type of membrane filtration study done to evaluate membrane performances. For simplicity, in some cases, only the selected (the best) results from the literatures are cited with specific information regarding the particular sample(s) (see comments).

2.2.3.3 Ozone-induced graft polymerization

Ozone treatment of polymers can introduce peroxide groups onto polymer surfaces; these peroxide groups can decompose and initiate graft polymerization upon exposure to a monomer solution [84, 85, 169]. Two different approaches for peroxide decomposition have been reported [84, 170], whereby peroxides can be decomposed either by thermal decomposition or by redox reaction to initiate graft polymerization at milder temperatures. It was reported that peroxide concentration on ozone treated membrane surface increased with a longer ozone treatment time; however, at the same time, deterioration of membrane mechanical properties was observed [84, 171]. For example, poly(propylene) (PP) membrane that was subjected to ozone treatment for 5 min had more than double the peroxide surface concentration relative to a membrane that was treated for 3 min. While the PP membrane treated for 3 min had ~20% decreased tensile strength, the membrane treated for 5 min had further decreased tensile strength (~40%) relative to the untreated membrane [171].

Polysulfone membranes grafted with poly(acrylic acid) (PAA) were reported via ozone-induced graft polymerization approach. The grafted PAA was then used for coupling of chitosan oligomer (i.e. chitooligosaccharides (COS)) to endow antimicrobial properties [162]. COS-coupled PSf membranes exhibited a marginal level of biocidal properties whereas neither PSf nor PAA-grafted PSf membrane exhibited any bactericidal activity. The water contact angles for ozone treated PSf (3 min exposure to ozone), PAA-grafted and COS-coupled PAA-PSf membranes were 69º, 58º and 55º, respectively, while that for the unmodified PSf was 79º. The surface peroxide density of the ozone treated PSf membrane increased by up to 14.2 nmol/cm^2 at 3 min treatment time and decreased

to ~9 nmol/cm^2 at 10 minutes of ozone exposure. It was suggested that the above behavior was possibly due to increased degree of crosslinking caused by peroxide groups and free radicals from ozone treatment at a longer ozone treatment time. The change in the mechanical properties of PSf membranes at 3 min ozone treatment time was negligible, and the tearing strength decreased by less than 10% relative to the original PSf.

2.2.3.4 Plasma-induced graft polymerization

In plasma-induced graft polymerization (PIGP), plasma is used to activate the surface, and a monomer in either the liquid or vapor phase is sequentially grafted onto the initiation sites via free radical polymerization [86]. PIGP proceeds via the following three steps: (1) surface plasma treatment to generate free radicals on the base membrane, (2) radicals' exposure to air/oxygen ambient to create peroxide groups on the surface (–O-O or –O-O-H), and (3) graft polymerization of monomers initiated by surface radicals generated from thermal decomposition of peroxide bonds (O-O) (see Figure 2.5). The grafting density can be controlled by plasma treatment parameters such as plasma treatment time and RF power, and subsequent graft polymerization conditions.

PIGP methods using low-pressure plasma sources for hydrophilic surface modification of polysulfone membranes are summarized in Table 2.3. For example, PSf UF membranes have been grafted with acrylic acid (AA) in both the aqueous solution and vapor phase [160]. In both cases, a decrease in permeability was observed with a higher grafting degree due to pore narrowing. BSA UF study revealed that PSf membranes grafted with AA in the vapor phase had 19.3% lower flux reduction from BSA filtration than for unmodified PSf membranes. However, the study did not provide membrane

performance information for the PSf membranes modified in the aqueous solution. HEMA-grafted PSf UF membranes have also been reported to exhibit promising antifouling properties. At pH=12 and pH=6.6, flux reduction from lysozyme (LYS) filtration was 47.3% and 30.8% lower, respectively, than for the unmodified PSf membrane [161]. However, a rejection decrease was observed, as the relative solute flux (of lysozyme) was more than 200% higher than with the unmodified. In another study, PSf UF membranes grafted with HEMA had ~100% higher flux for lysozyme solution and ~31% higher flux for BSA solution filtration compared relative to the unmodified PSf membrane without compromising reduction in protein retention [144].

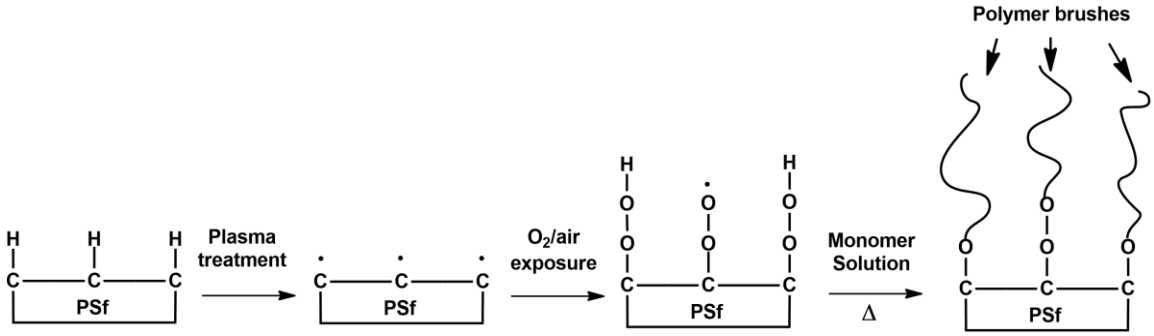


Figure 2.5 Plasma-induced graft polymerization procedure for PSf membranes

Table 2.3 Summary of plasma-induced graft polymerization methods for polysulfone membranes

Reference	Plasma treatment[a]	Monomer[b]	Graft polymerization[c]	Membrane performance[d]	Grafted polymer characterization methods	Comments
[160]	Ar, CO_2, and air t_{exp} = 1- 8.5 min Power = 30-120 W Pressure = 0.45 Torr	AA (liquid)	t_{gp} =1 – 2.5 h; T_{gp} = 70ºC	L_p ↓	ATR-FTIR, contact angle, graft yield and pore size	Ar plasma treatment yielded more peroxides on the surface than air or CO_2 plasma.
[160]	Ar t_{exp} = 30 s Power = 30 W Pressure = 0.45 Torr	AA (vapor)	t_{gp} = 5 – 54,000 s	*BSA filtration:* L_p ↓; R_p ≈; PFR ↑	ATR-FTIR, contact angle, graft yield and pore size	At pH=9, flux reduction from BSA filtration was 19.3% less than that of unmodified PSf membrane.
[161]	He t_{exp} = 1 min Power = 25 W Pressure = 0.175 Torr	HEMA	t_{gp} = 1 h; T_{gp} = 50ºC	*LYS filtration:* R_p ↓; PFR ↑	AFM, ATR-FTIR and contact angle	At pH=12 and pH=6.6, flux reduction from LYS filtration was 47.3% and 30.8% lower than that of unmodified membrane, respectively.

[144]	He t_{exp} = 30 s Power = 25 W Pressure = 0.1 Torr	HEMA	t_{gp} = 1 h; T_{gp} = 50 °C	*BSA, LYS filtration:* L_p ↑; PFR ↑; R_p ≈	ATR-FTIR, contact angle, and DG	The HEMA-grafted PSf membranes had ~100% higher LYS flux and ~31% higher BSA flux than the unmodified PSf membrane.

Legend: ↑, increased; ↓, decreased; ≈, less than 5% change; NR, not reported; L_p, permeability of water (if not specified); J_p, permeate flux of protein solution; R_p, rejection of protein(s); PFR, protein fouling resistance; DG, degree of grafting, and θ_w, water contact angle.

[a] The first line refers to the plasma gas; t_{exp} = plasma exposure time; power and pressure of the plasma system used are reported.

[b] For the monomers and proteins with acronyms, their full names are as follows:
AA: acrylic acid; BSA: bovine serum albumin; HEMA: 2-hydroxyethyl methacrylate; LYS: lysozyme.

[c] t_{gp} refers to grafting time, and T_{gp} refers to the graft polymerization reaction temperature.

[d] Indicated in italics is the type of membrane filtration study done to evaluate membrane performances. For simplicity, in some cases, only the selected (the best) results from the literatures are cited with specific information regarding that particular sample(s) (see comments).

2.2.3.5 Atmospheric Pressure Plasma-Induced Graft Polymerization (APPIGP)

The majority of the plasma treatment and PIGP processes uses low-pressure plasma sources, which requires vacuum systems that are expensive, and the size of the substrates are limited by the size of the vacuum chamber [88, 172, 173]. On the other hand, atmospheric pressure plasma is operated in open air, thus it can be scaled-up for materials processing on relatively large substrates. Various atmospheric plasma sources are available, including plasma transfer arc, corona discharge, dielectric barrier discharge, and the plasma jet [88]. However, plasma transfer arcs generate high temperature plasma that is not suitable for surface modification of polymeric materials due to thermal degradation, and corona discharge and dielectric barrier discharge plasmas are not uniform throughout the volume [88]. AP plasma jet, on the other hand, produces a uniform plasma at low temperature that may be used for material processing on relatively large substrates [174]. Previously, atmospheric pressure plasma, generated with a plasma jet source, has been used to activate surfaces of both inorganic and organic substrates, silicon and polyamide, which were subsequently grafted with hydrophilic polymers [87, 89].

3. EXPERIMENTAL

3.1 Materials and Reagents

Test grade 4" silicon <100> wafers were obtained from Semiconductor Solutions LLC (Alhambra, CA) and used as substrates for polysulfone membrane surrogate surface. Reagent grade sulfuric acid and aqueous hydrogen peroxide, used for silicon wafer cleaning, were purchased from Fisher Scientific (Pittsburgh, PA). Ultra-high purity helium (99.99%) and hydrogen (99.99%), oxygen (99%), and nitrogen (99%) were obtained from Airgas (Long Beach, CA). Polysulfone pellets (PSf, M_w ~35,000) and poly(ethyleneimine) (PEI, M_w ~750,000) solution (50 wt% in H_2O) were obtained from Sigma-Aldrich (St. Louis, MO). The solvents for polysulfone pellets, chloroform (≥99.9%) and *N*-methyl-2-pyrrolidone (99.5%), were both purchased from Sigma-Aldrich (St. Louis, MO). The monomers used in this study, methacrylic acid (99%) and acrylic acid (99%), were also purchased from Sigma-Aldrich (St. Louis, MO). Ultra-pure de-ionized (DI) water was produced using a Milli-Q filtration system from Millipore Corp. (San Jose, CA). All solutions used in the study, including the polymer solutions and monomer solutions, were prepared in Kimble glass screw-thread sample vials (40 mL, 28 x 98 mm) with polytetrafluoroethylene/silicone septa and open-top polypropylene closures purchased from Fisher Scientific (Pittsburgh, PA).

3.2 Preparation of Polysulfone Membrane Surrogate Surfaces

Polysulfone-polyethyleneimine-silicon (PSf-PEI-Si) surrogate membrane surfaces were prepared by using a spin-coater (790 Spinner with PWM32 controller) purchased from Headway Research Inc. (Garland, TX). The silicon wafers were cleaned in a piranha bath (a mixture of 70 vol% sulfuric acid and 30 vol% aqueous hydrogen peroxide) for 10 min at 90°C. They were then triple rinsed with DI water and blow dried with a nitrogen gun. After drying the wafer, it was cut into 1 cm x 1 cm square samples using a carbide wheel glass cutter, which was purchased from Fisher Scientific (Pittsburgh, PA). About 0.1 mL of a 0.3 wt% aqueous solution of PEI was used to spin-coat an adhesion layer on the cleaned silicon surface at 2500 RPM for 30 s. Following the PEI layer casting, 0.1 mL of a 1 wt% PSf solution in chloroform was spin-coated onto the PEI-Si surface at 2500 RPM for 30 s. The spin-coated samples were then dried in a vacuum oven at 75°C for 24 hours prior to further use.

3.3 Preparation of Monomer Solutions

Aqueous solutions of MAA and AA were prepared in glass vials. The total volume of the monomer solutions were 25 mL, and the monomer concentrations were varied for 5 – 20 vol% in DI water. Prior to graft polymerization, the solutions were degassed with bubbling nitrogen for 10 minutes. For detailed experimental protocols, see Appendix A.1.

3.4 Plasma Surface Activation and Graft Polymerization

The atmospheric plasma source used in this study was a cylindrical plasma jet (Figure 3.1) for which a detailed description is provided elsewhere [88]. The plasma controller (Atomflo^{TM} 300 Series), purchased from Surfx Technologies Inc. (Redondo Beach, CA), was used to adjust the RF power output and gas flow rates. Ultra-high purity helium (99.99%) and hydrogen (99.99%) were connected to the plasma controller, from which their mixture was delivered to the AP plasma source (valve ① open and ② closed). The flow rate of helium was constant at 30 L/min and the hydrogen flow rate was varied from 0 – 0.60 L/min. The surface was exposed to plasma for a period of 10 – 60 s at RF power of 40 – 60 W. Following the plasma treatment, valve ① was closed and ② was open immediately, and the substrates were treated with O_2 for 2 min, allowing the surface radicals to form peroxides. After O_2 treatment, the PSf samples were immediately placed in the vials containing degassed monomer solutions. The temperature of the reaction mixture was maintained at 60°C for both MAA and 70ºC for AA solutions by immersing the vials in a temperature controlled water bath. The duration of the polymerization reactions ranged for 0.5 – 2 hr. Upon termination of the graft polymerization reaction, the substrates were triple-rinsed with DI water to remove unreacted species then dried in a vacuum oven for 24 hours at 75°C. The detailed experimental protocols are presented in Appendix A.2.

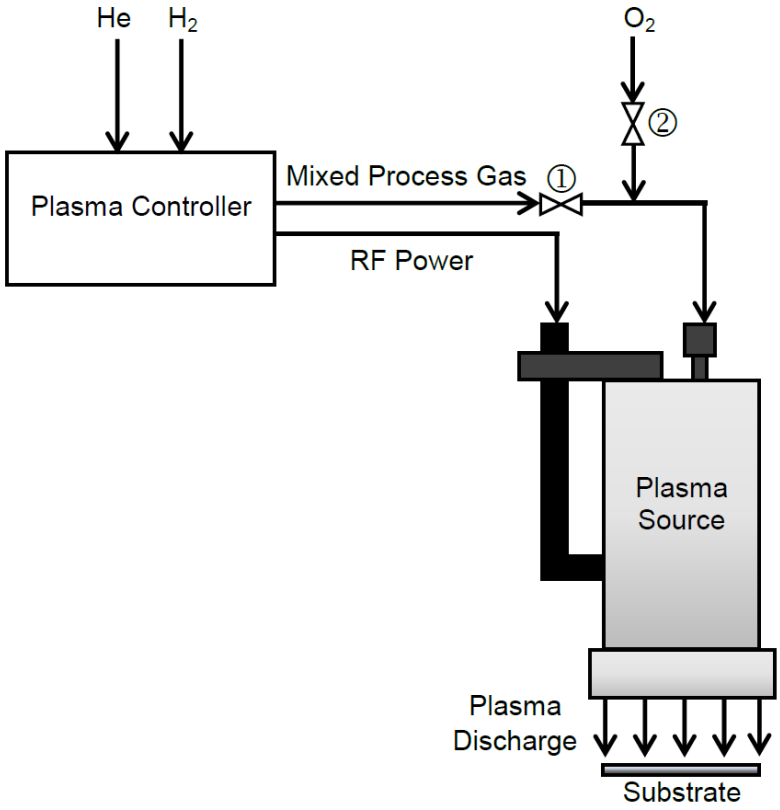


Figure 3.1 Schematic of atmosphere pressure plasma source process configuration

3.5 Surface Characterization

The thickness of the polysulfone layer on the PSf-PEI-Si substrates was determined by ellipsometry using a Stokes ellipsometer LSE (632.8 nm, incident angle = 70º) (Gaertner Scientific Corporation, Skokie, IL). The thickness measurements were taken at ten different locations on the substrate, and averaged values were reported. Water contact angles for the PSf-PEI-Si surrogate membrane surfaces were measured by the sessil-drop method using a Krüss Model G-23 contact angle instrument (Krüss GmbH,

Hamburg, Germany) at 22°C and 40-50% relative humidity. Contact angle measurements were taken at five different locations on the substrate, and averaged values were reported.

Surface topography was evaluated by atomic force microscopy (AFM, Veeco Instruments, Santa Barbara, CA) in tapping mode, in ambient air, using NSC15 silicon nitride probes (MicroMasch USA, Lady's Island, SC) with a typical force constant of 46 N/m. AFM scans of size 2 μm x 2 μm on grafted PSf substrates were taken at a scan rate of 0.803 Hz. Five different locations were sampled for each modified substrate, with two scans at 0° and 90º taken for each location to ensure that images were free of directional errors. Root-mean-square (RMS) surface roughness, R_{rms} , was determined directly from the height data for the 2 μm x 2 μm scans as

$$R_{rms} = \sqrt{\frac{\sum\left(Z_i - Z_{avg}\right)^2}{N}} \tag{3.1}$$

where R_{rms} is the RMS roughness, Z_i is the *i*th height sample out of *N* total number of samples, and Z_{avg} is the mean height. The skewness, S_{skew}, which is a measure of the asymmetry of the height distribution data about the mean, was determined from

$$S_{skew} = \frac{\sum\left(Z_i - Z_{avg}\right)^3}{(N-1)\sigma^3} \tag{3.2}$$

where σ is the standard deviation of the surface feature heights.

4. RESULTS AND DISCUSSION

4.1 Preparation of Polysulfone Membrane Surrogate Surface (PSf-PEI-Si)

The surface roughness of the commercial membranes is relatively high [90]. Therefore, it is difficult to detect changes in topography that are in the order of nanometers post grafting. Thus, relatively smooth polysulfone membrane surrogate surfaces were developed in order to optimize the grafting process. Polysulfone-polyethyleneimine-silicon (PSf-PEI-Si) samples were prepared by spin coating polysulfone solution onto silicon wafer substrates using PEI as an adhesion layer. In order to optimize and produce a smooth, homogeneous polysulfone substrate surface, spin coating parameters and the concentration of the polymer solutions and solvents were varied (Table 4.1), and their effects on the PSf film quality were characterized by measuring the water contact angles and the surface topography via AFM analysis.

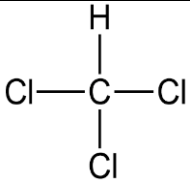
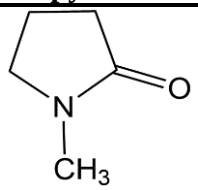
Table 4.1 The spin coating conditions for the preparation of PSf-PEI-Si samples

PSf-PEI-Si	Solvent	Polysulfone concentration (wt%)	Spin speed (rpm)	Spin duration (s)	Contact angle (°)	Film Thickness (nm)
PSf-1	NMP	1	2500	60	44.0	11.7
PSf-2	NMP	3	2500	60	57.3	12.6
PSf-3	NMP	6	2500	60	54.6	13.6
PSf-4	Chloroform	1	2500	30	97.8	120.6
PSf-5	Chloroform	3	2500	30	100.1	294.7
PSf-6	Chloroform	6	2500	30	100.6	362.3

The results provided in Table 4.1 revealed that less polysulfone was coated on the surface when using NMP as a solvent compared to chloroform; this was confirmed by the lower values of the water contact angles and the lower film thickness. The water contact angle of polysulfone films coated using chloroform as the solvent was in agreement with

the values for polysulfone membranes and films [161]. The lower PSf film thickness obtained when using NMP as the PSf solvent can be explained by comparing the vapor pressure of NMP and chloroform (Table 4.2). In spin-coating polymer films, it has been shown that film thickness is controlled by the solvent evaporation rate, which is dependent on the polymer concentration in solution, spin speed, and the viscosity and the vapor pressure of the solvent [175, 176], when external conditions are held constant. When the polymer concentration and the spin speed are the same, the solution viscosity and the vapor pressure of the solvent are the major determinant in the film thickness. It is expected that polymer films, which are spun from a solvent with a higher vapor pressure, would also have a higher film thickness [177]. Since chloroform has vapor pressure that is nearly three orders of magnitude higher than that of NMP, it is expected to evaporate faster (i.e. higher evaporation rate), thus yielding a thicker film. Also, spin coating with NMP required longer spin duration (~ 60 s) to evaporate all the solvent compared to chloroform (~ 30 s).

Table 4.2 Properties of the solvents, chloroform and *N*-methyl-2-pyrrolidone [178]

	Chloroform ($CHCl_3$)	***N*-methyl-2-pyrrolidone (NMP)**
Structure		
Specific gravity	1.479 g/cm^3	1.033 g/cm^3
Vapor pressure	26.266 kPa	0.0455 kPa
Viscosity	0.5357 mPa·s	1.666 mPa·s

Specific gravity, vapor pressure, and viscosity at 25ºC

Solvent effects on the topography of the polysulfone film coated from PSf solutions prepared in NMP (PSf-1, PSf-2, and PSf-3) and chloroform (PSf-4, PSf-5, and PSf-6) are shown in Figure 4.1 and 4.2, respectively. It is apparent from the AFM images that surfaces of the PSf films (PSf-2 and PSf-3) that were spun from NMP are heterogeneous and have higher RMS values relative to the PSf films spun from choloroform. PSf-1, which was casted at the lowest concentration, had a similar roughness compared to the films coated from chloroform, which could be attributed to the more dilute solution. PSf films spin casted from chloroform solutions had similar water contact angles and roughness; however, PSf films casted from 3 wt% and 6 wt% polysulfone solution in chloroform (PSf-5 and PSf-6) delaminated after immersion in water for 2 hours. This is presumably due to their high film thickness. Based on the water contact angles, the film thickness, and the surface topography, the best polysulfone membrane surrogate surface was determined to be PSf film spun from 1 wt% polysulfone solution in chloroform at 2500 rpm for 30s.

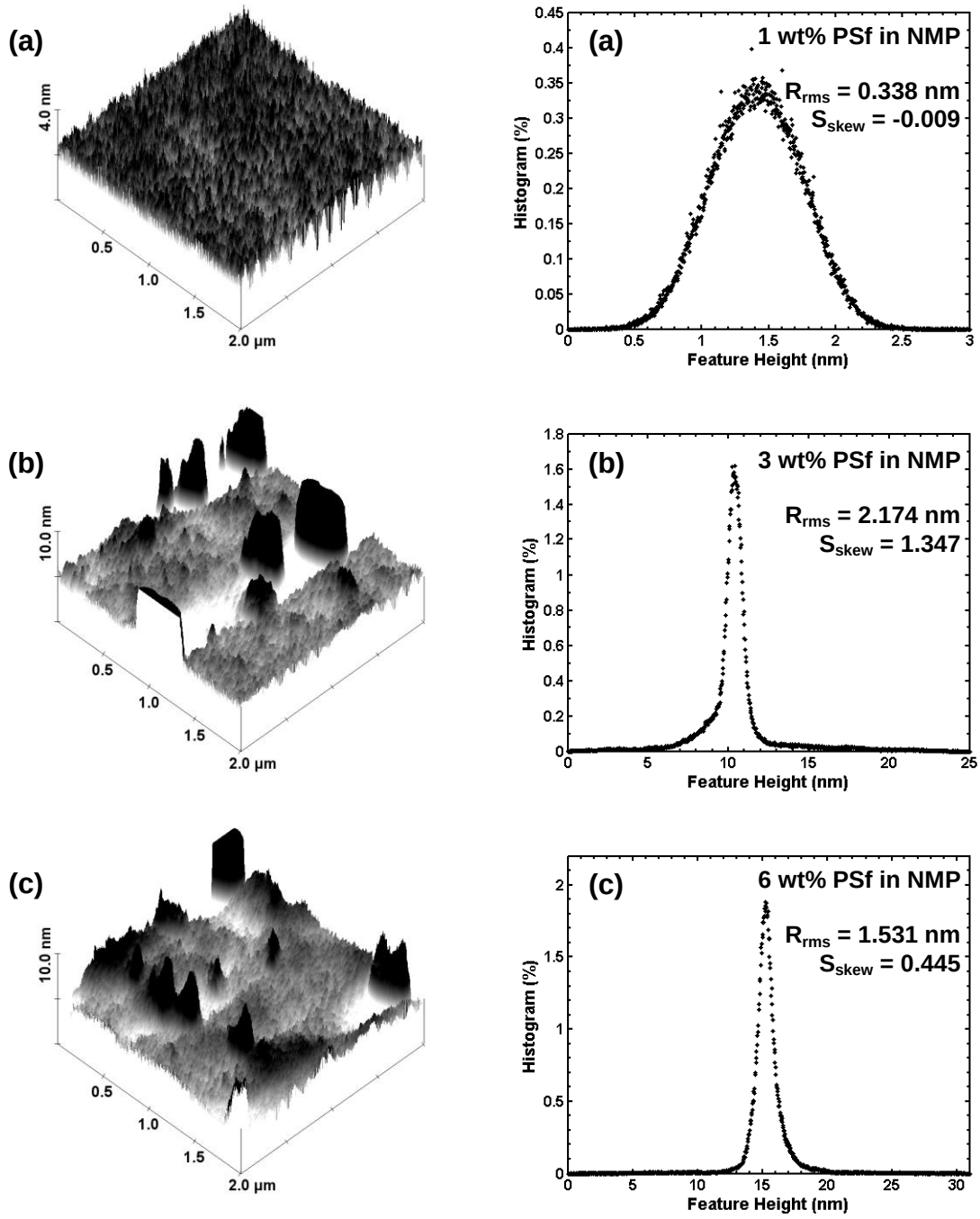


Figure 4.1 **AFM images (*left*) and height distributions (*right*) of PSf-PEI-Si surfaces prepared from spin coating of (a) 1 wt%, (b) 3 wt%, and (c) 6 wt% polysulfone solution in *N*-methyl-2-pyrrolidone**

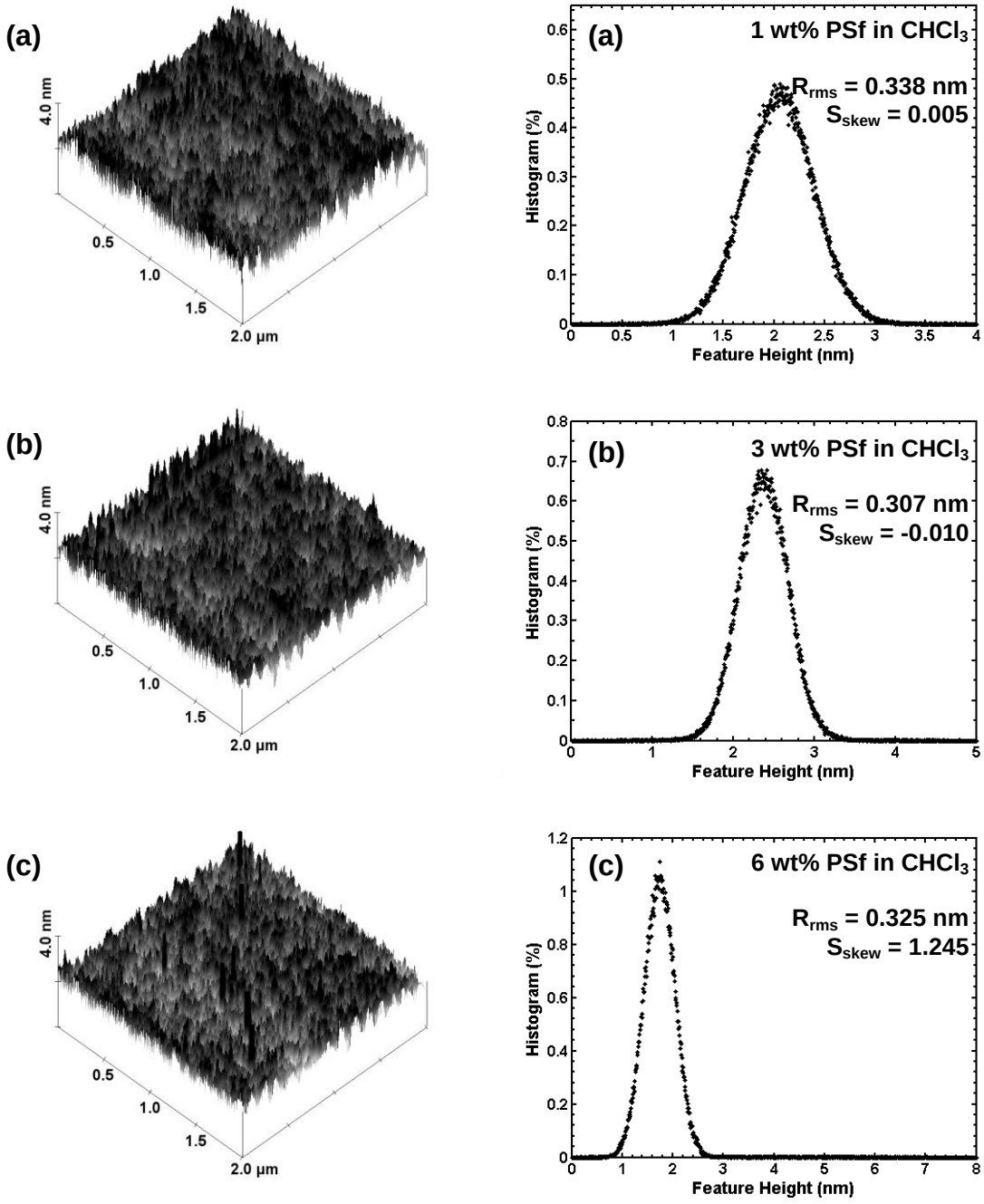


Figure 4.2 **AFM images (*left*) and height distributions (*right*) of PSf-PEI-Si surfaces prepared from spin coating of (a) 1 wt%, (b) 3 wt%, and (c) 6 wt% polysulfone solution in chloroform**

4.2 Plasma Surface Activation of PSf-PEI-Si

In order to arrive at the optimal conditions for the plasma surface activation of PSf-PEI-Si, the effects of plasma treatment parameters, RF power, H_2 flow rate, and plasma treatment time, on surface wettability were studied by measuring water contact angles immediately following plasma treatments. The optimal plasma treatment condition was determined by selecting the combination of the parameters that showed the most decrease in the water contact angles for the PSf surfaces.

4.2.1 Effect of RF Power and Hydrogen Flow Rate

The percentage decrease in water contact angles of the polysulfone substrate, after the plasma treatment of varying RF power and the hydrogen flow rate, is shown in Figure 4.3. Although previous studies have showed an apparent trend that a higher RF power decreases the water contact angles, the RF power did not show appreciable difference with respect to contact angle changes when utilizing hydrogen gas for He plasma system. However, changes in wettability of the polysulfone substrates were significantly affected by the hydrogen flow rate. This is presumably due to hydrogen plasma species passivating surface radicals and re-creating C-H bonds once a threshold concentration of surface radicals was reached. Thus, it is postulated that a higher hydrogen flow rate will confer a higher concentration of hydrogen plasma species, thereby resulting in a greater extent of inactivation of surface radical species, which is reflected in a lower decrease of water contact angles. Helium plasma treatment without hydrogen resulted in the highest percentage decrease in contact angle, ~47%, which was nearly two folds higher relative to that which was obtained with helium with hydrogen additives. Since the plasma was

operated in open air, it is possible that oxygen from ambient air could have diffused into the plasma jet, which may have promoted formation of oxygen containing functional groups on the polysulfone surface.

Similarly, a low impact of RF power (with hydrogen) on wettability changes can be explained by the higher density of reactive species due to increased electron-atom collisions in the gas phase at a higher RF power. Thus, the increased abundance of hydrogen plasma species at the substrate surface can passivate surface radicals, which would then offset reduced surface wettability. It was noted that the plasma system was observed to be most stable at 50 W, exhibiting a uniform glow and lowest reflected power. Therefore, helium plasma without hydrogen at RF power of 50 W was selected as the optimal plasma setting for graft polymerization.

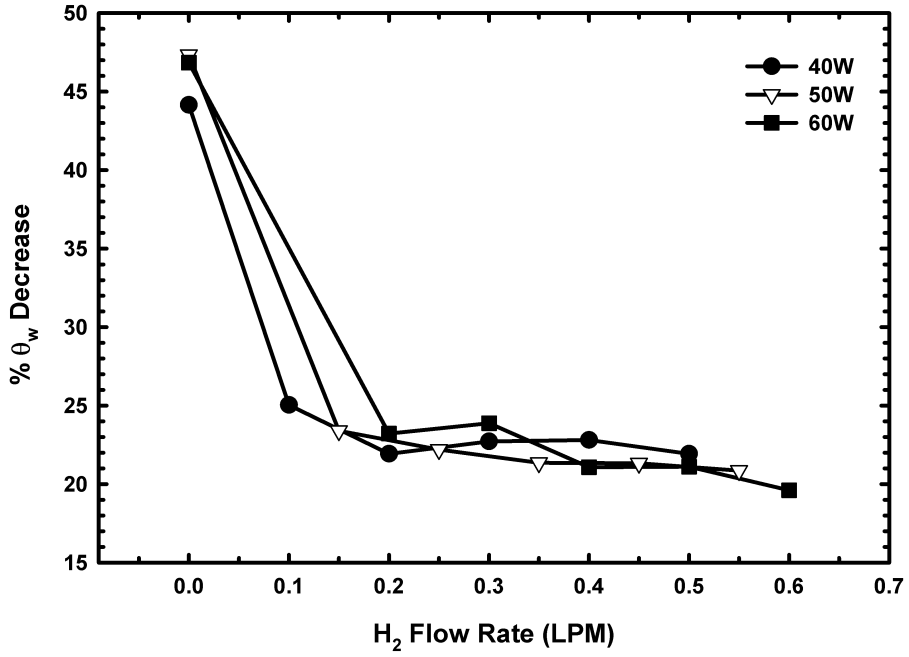


Figure 4.3 Dependency of the percentage decrease of water contact angle on plasma RF power and hydrogen flow rate (helium flow rate = 30 L/min and plasma treatment time = 10 seconds)

$$\%\ \boldsymbol{\theta_w\ decrease} = \left(1 - \frac{\theta_{w,before}}{\theta_{w,after}}\right) \times 100$$

4.2.2 Effect of Plasma Treatment Time

The percentage decrease of water contact angle for the polysulfone substrates, as a function of the plasma treatment time, is shown in Figure 4.4 for helium plasma treatment (He flow rate = 30 L/min) and helium and hydrogen (He/H_2) plasma treatment (He flow rate = 30 L/min and H_2 flow rate = 0.35 L/min). In both cases, the water contact angle decreased with a longer plasma treatment time; however, He plasma treatment resulted in nearly two-fold increase in surface wettability of the polysulfone surface relative to He/H_2 plasma treatment for all treatment times. The percentage water contact angle decrease reached up to 61.4% (θ_w = 38.0º) at 30 seconds of He plasma treatment,

and for He/H_2 plasma treatment up to 29.6% (θ_w = 68.7º) at 40 seconds. Furthermore, the highest changes in surface wettability occurred in a relatively short treatment period, which can be observed from rapid contact angle decrease up to treatment time of ~15 seconds with marginal additional decrease (up to ~5%) at longer times (>15s). Thus, helium plasma treatment time of 15s at RF power of 50 W was chosen as the optima; plasma surface treatment condition for the subsequent grafting study.

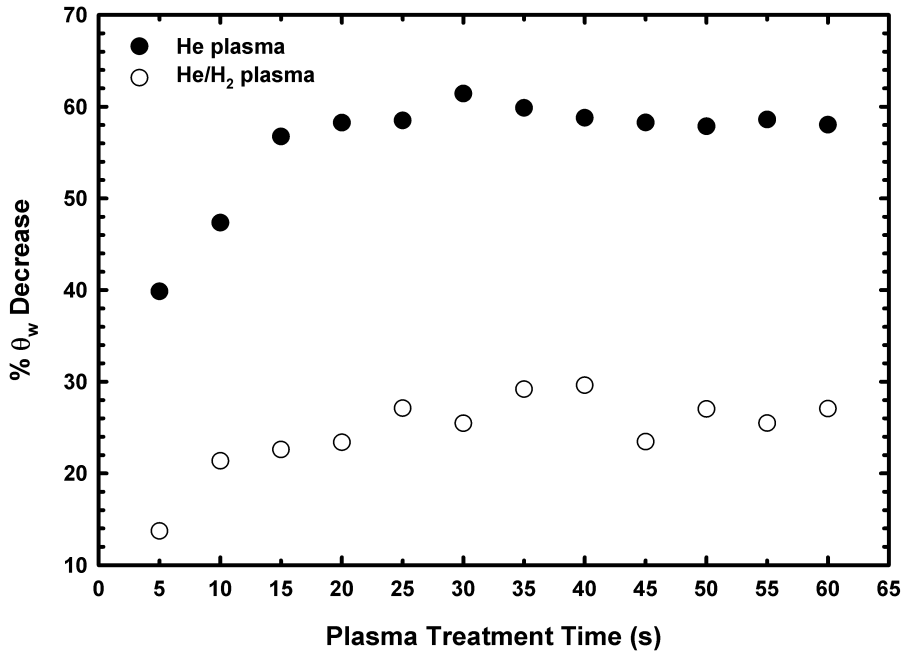


Figure 4.4 **Dependency of the percentage decrease of water contact angle on plasma treatment time (He plasma: He flow rate = 30 L/min, He/H_2 plasma: He flow rate = 30 L/min and H_2 flow rate = 0.35 L/min, RF power = 50 W for both He and He/H_2 plasma)**

4.3 Graft Polymerization

4.3.1 Poly(methacrylic acid)-grafted Polysulfone

Poly(methacrylic acid) (PMAA) was grafted onto PSf-PEI-Si using a two-step APPIGP approach. Surfaces of PSf membrane surrogates were treated by atmospheric pressure helium plasma at the optimal plasma surface activation condition (15 s of plasma treatment time, helium flow rate of 30 L/min without H_2, and RF power of 50 W), followed by graft polymerization of MAA in its aqueous solution. Table 4.3 shows the surface characteristics of the PMAA grafted polysulfone (i.e. PMAA-g-PSf) substrates conducted at various initial monomer solution concentrations (5 – 20 vol%) and the reaction times (0.5 – 2 hr) at 60ºC.

Table 4.3 Characteristics of PMAA-grafted polysulfone in aqueous solvent as a function of initial monomer concentration and reaction time

Reaction conditions[a]		R_{rms} (nm)[b]	Peak number density (peaks/μm^2)[b]	Contact angle (º)[c]	
$[M]_0$ (vol%)	Reaction time (h)			PSf-PEI-Si	PMAA-g-PSf
5	0.5	0.539	890	98.6	75.7
5	1.0	0.594	1101	99.9	74.6
5	2.0	0.545	1182	98.9	70.4
10	0.5	0.592	928	97.9	82.9
10	1.0	0.573	909	99.1	82.0
10	2.0	0.688	1001	98.8	79.3
20	0.5	0.574	1023	97.3	86.0
20	1.0	0.607	865	98.4	83.2
20	2.0	1.119	1473	98.6	82.9

[a] Surface initiation at treatment time = 15 s, helium flow rate = 30 L/min, and RF power = 50 W; grafting temperature = 60ºC

[b] Polymer surface feature properties determined by AFM and averaged over five measurements.

[c] Water contact angle measured by the sessil-drop method

Note: PSf was spin casted from 1 wt% polysulfone solution in chloroform at 2500 rpm for 30 s.

The contact angles of the PMAA-grafted polysulfone substrates revealed that surface hydrophilicity was improved for all samples compared to the unmodified PSf substrates, which had θ_w in the ranges of 97-100°. The percentage decrease in the water contact angle due to graft polymerization is shown in Figure 4.5. It increased with reaction time for all initial monomer concentrations. This trend was expected since a longer reaction time allows more monomers to graft polymerize on the surface, resulting in a higher content of hydrophilic surface groups. However, increasing the initial monomer concentration lowered the percentage decrease in contact angles. The PMAA-grafted surfaces derived from surface modification at 20 vol% initial monomer concentration had a contact angle, which was 12.5° higher than for the samples grafted from 5 vol% monomer solution at 2 h reaction time. This could be explained by comparing the surface topography of the grafted surfaces with different initial monomer concentrations. From Table 4.3, it is seen that the R_{rms}, S_{skew}, and the peak number density increased with the increasing monomer concentration and reaction time. This suggests that there are dense grafted polymers of longer chain length on the surface due to a higher level of monomer initiation. It is also supported by the feature height histograms (Figure 4.6) where the difference in the polymer feature sizes can be seen for different initial monomer concentrations. As the monomer concentration increases, there are larger grafted polymer features, and the polymer features height distribution shifts to a higher range with a longer tail, which accounts for the higher skewness. Also, the width of the distribution slightly increased with initial monomer concentration. At 5 vol%, with the lowest S_{skew}, polymer features are most uniform but composed of shorter polymer chains. On the other hand, sample grafted at 20 vol% MAA had higher skewness (S_{skew} =

3.664) and longer polymer chains, but with a small number of very long chains (up to 30.4 nm), which accounted for the higher observed roughness. The R_{rms} of PMAA-grafted PSf synthesized from 20 vol% monomer concentration was larger by a factor of two relative to the surfaces obtained with the 5 vol% monomer concentration, and the high roughness could have possibly contributed to the higher contact angle values [179].

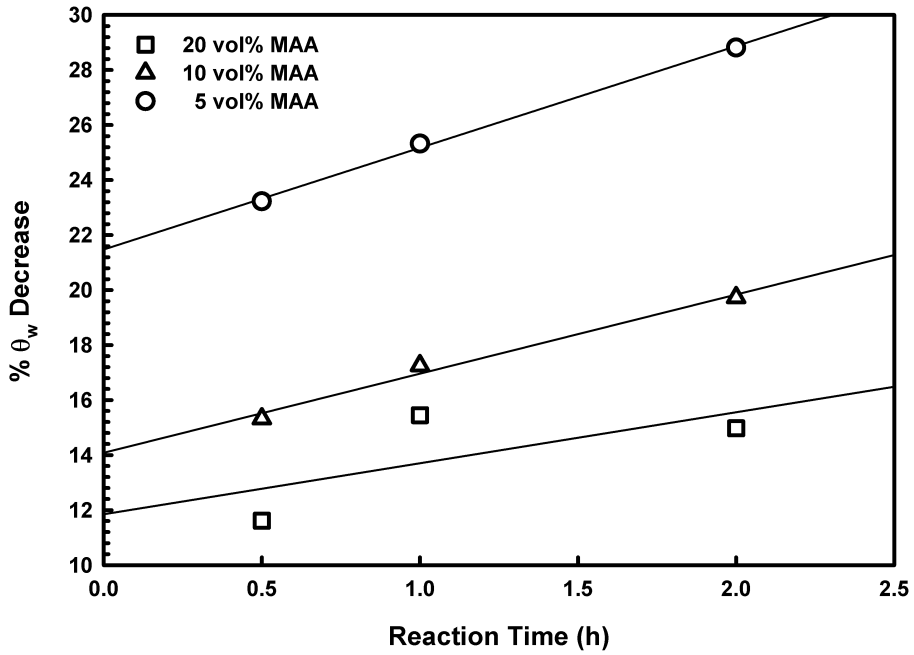


Figure 4.5 Percentage contact angle decrease due to PMAA-grafting onto PSf-PEI-Si at various initial monomer concentrations and reaction times

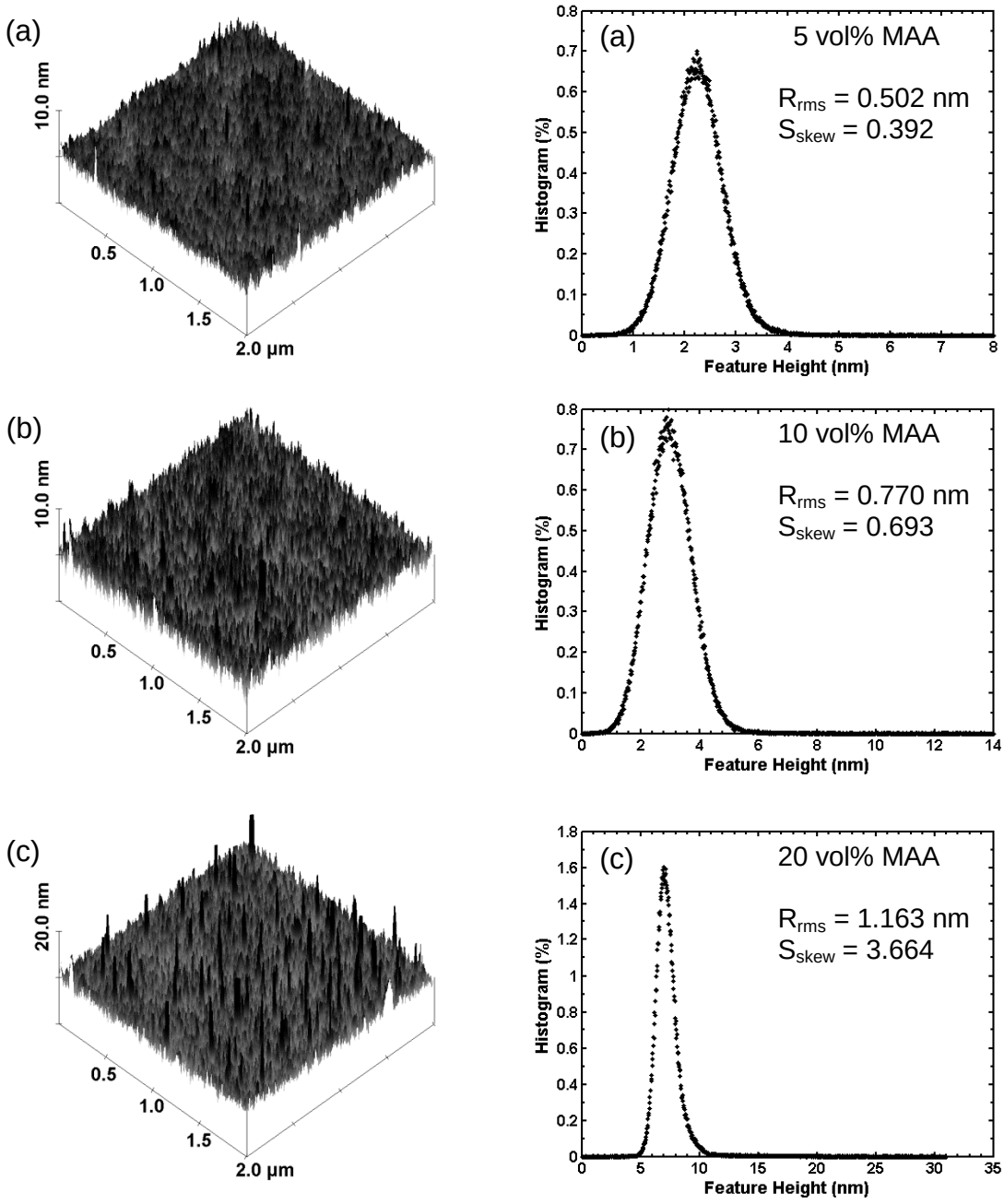


Figure 4.6 **AFM images (*left*) and height distributions (*right*) of PSf-PEI-Si surfaces graft polymerized with poly(methacrylic acid) (at 60ºC and 2 h reaction time) for initial MAA monomer concentration of (a) 5 vol%, (b) 10 vol%, and (c) 20 vol%**

4.3.2 Poly(acrylic acid)-grafted Polysulfone

Poly(acrylic acid) (PAA) was grafted on the surfaces of PSf-PEI-Si substrates using the same procedure for graft polymerization of MAA. Surface characteristics of the PAA-grafted PSf-PEI-Si, prepared from various grafting conditions, are summarized in Table 4.4. The contact angles of the PAA-grafted polysulfone were lower than that of PSf-PEI-Si, suggesting improved hydrophilicity of the modified surfaces. Also, they had slightly lower contact angles relative to the PMAA-grafted polysulfone surface. This trend was expected since MAA has a methyl group that could contribute to a slightly decreased surface hydrophilicity. The percentage decrease in contact angles (Figure 4.7) showed a similar trend as for the PMAA-grafted PSf with a reduced degree of surface hydrophilicity improvement with the increasing initial monomer concentration.

Table 4.4 Characteristics of PAA-grafted polysulfone in aqueous solvent as a function of initial monomer concentration and reaction time

Reaction conditions[a]		R_{rms} (nm)[b]	Peak number density (peaks/μm^2)[b]	Contact angle (°)[c]	
$[M]_0$ (vol%)	Reaction time (h)			PSf-PEI-Si	PAA-g-PSf
5	0.5	0.430	744	98.9	73.3
5	1.0	0.536	564	96.1	65.5
5	2.0	0.440	705	98.5	65.0
10	0.5	0.532	955	97.1	83.0
10	1.0	0.559	751	95.9	81.2
10	2.0	0.662	873	97.9	75.7
20	0.5	0.614	704	97.5	90.5
20	1.0	0.475	564	98.9	87.4
20	2.0	0.685	744	97.3	79.6

[a] Surface initiation at treatment time = 15 s, helium flow rate = 30.0 l/min, and RF power = 50 W; grafting temperature = 70°C

[b] Polymer surface feature properties determined by AFM and averaged over five measurements.

[c] Water contact angle measured by the sessil-drop method

Note: PSf was spin casted from 1 wt% polysulfone solution in chloroform at 2500 rpm for 30 s.

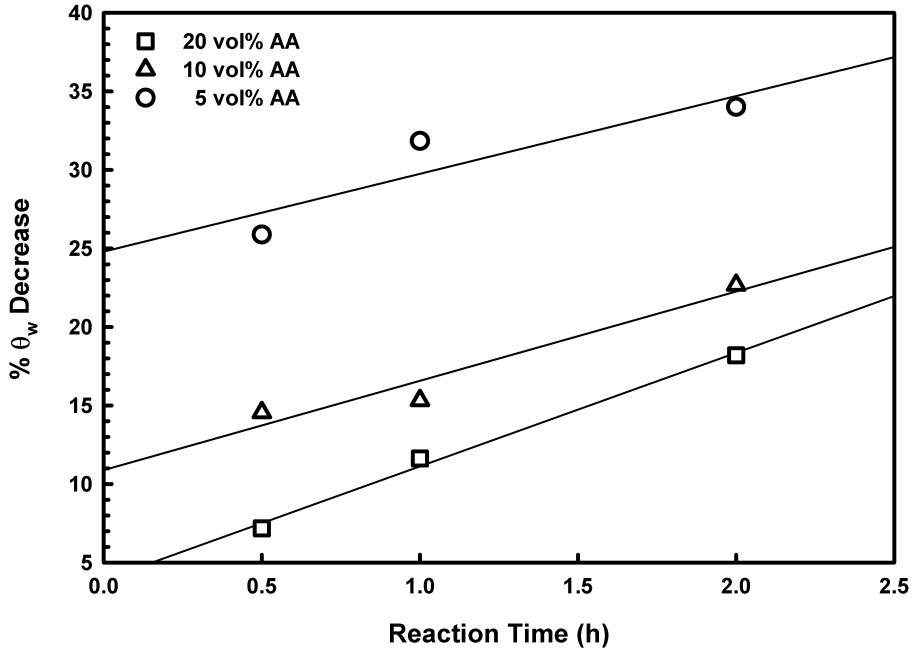


Figure 4.7 **Percentage contact angle decrease due to PAA-grafting onto PSf-PEI-Si at various initial monomer concentrations and reaction times**

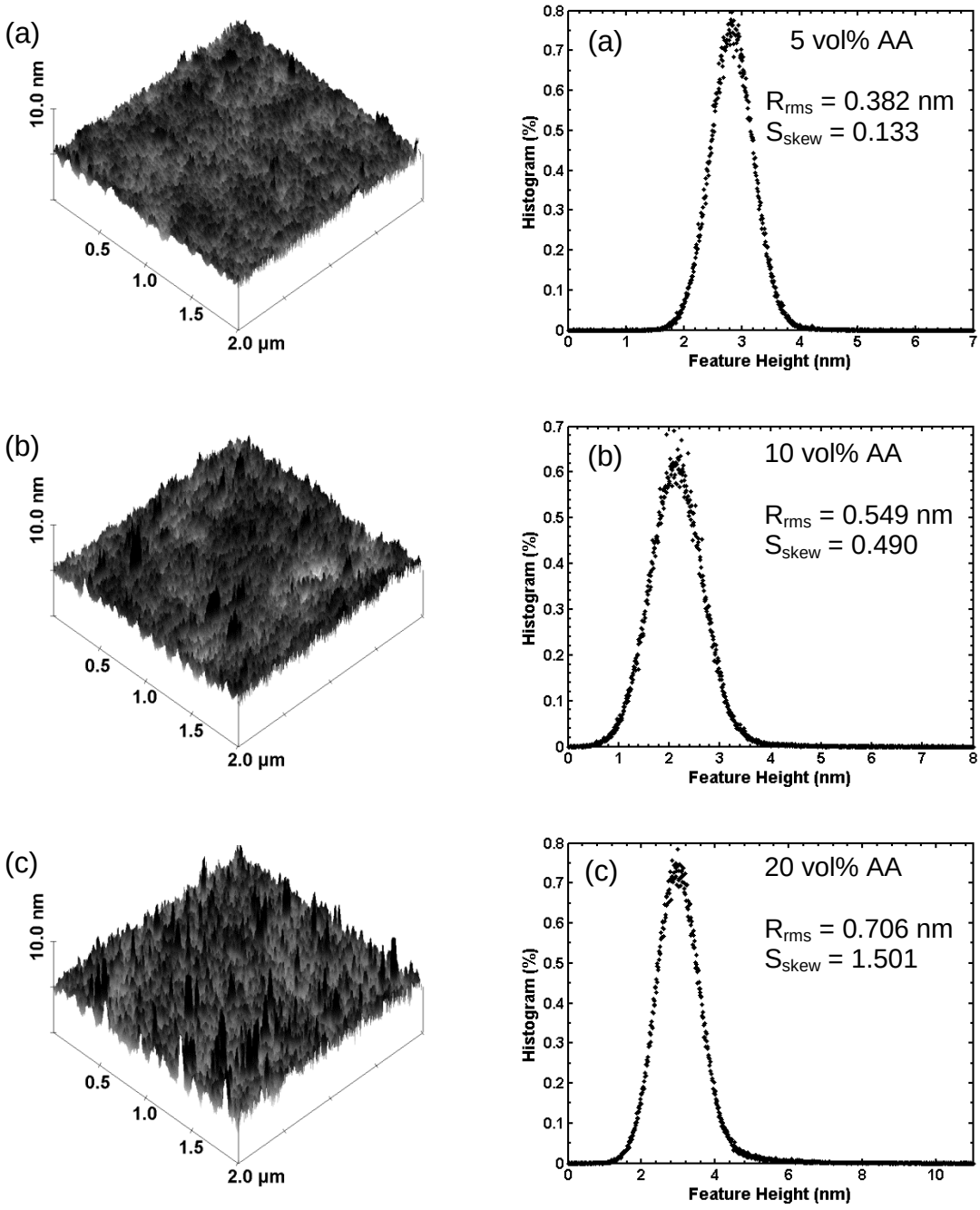


Figure 4.8 **AFM images (*left*) and height distributions (*right*) of PSf-PEI-Si surfaces graft polymerized with poly(acrylic acid) (at 70ºC and 2 h reaction time) for initial AA monomer concentration of (a) 5 vol%, (b) 10 vol%, and (c) 20 vol%**

5. CONCLUSIONS

Using the atmospheric pressure plasma-induced graft polymerization approach, poly(methacrylic acid) and poly(acrylic acid) were grafted onto polysulfone membrane surrogate surfaces. Characterization of the modified polysulfone surfaces revealed that surface hydrophilicity was enhanced upon graft polymerization with methacrylic acid and acrylic acid monomers. The water contact angles were decreased by up to 28.8% and 34.0% for the PMAA- and PAA-grafted PSf, respectively, at 5 vol% of the initial monomer concentration and 2 hours of reaction time. Increasing the initial monomer concentration resulted in a wider distribution of surface polymer feature heights with higher average heights, and increased RMS roughness and skewness. Graft polymerization at the highest monomer concentration of 20 vol% of MAA and AA resulted in contact angle that was a factor of 0.15 and 0.18, respectively, lower relative to the PSf surface. From a practical viewpoint it appears that graft polymerization can be achieved in a relatively short period of ~0.5 h while providing reasonable reduction of contact angle at a low initial monomer concentration of 5 – 20 vol%. However, higher level of improvement could be feasible and is worth exploring via the use of more active plasma.

6. RECOMMENDATIONS

The detailed methodology of the surface nano-structuring of the polysulfone membrane surrogate surface was established using the APPIGP approach. However, additional studies are warranted in order to optimize graft polymerization onto a PSf surface. For example, helium/oxygen combination for the plasma could be more effective for surface activation of aromatic polymers such as polysulfone [180]. Also, the effect of temperature on the graft polymerization process should be evaluated to optimize the grafted polymer layer structure. Moreover, additional surface characterization to determine the chemical composition and elemental analysis of the grafted surfaces could serve to optimize the grafting process. Once the APPIGP is optimized for PSF it would be possible to develop polysulfone with graft polymerized surfaces and evaluate their filtration performance for various solutes of industrial interest.

APPENDIX A: EXPERIMENTAL PROTOCOL

A.1 Preparation of Polysulfone Membrane Surrogate Surface (PSf-PEI-Si)

0.3 wt% polyethyleneimine (PEI) solution in DI water:

1. Add 1.5 grams of 50 wt% PEI gel to a glass vial containing approximately 10 mL of DI water.
2. Using a vortex mixer, mix the solution until the gel is fully dissolved.
3. Place the solution in a 200 mL volumetric flask, then add DI water up to the 200 mL mark. Whirl the solution until the solution is completely mixed.

1 wt% polysulfone (PSf) solution in chloroform:

1. Using a weighing scale, place 0.1 grams of polysulfone pellets in a glass vial, then add chloroform into the vial until the total solution weighs 10 grams.
2. Sonicate the polysulfone solution for about 5 minutes to dissolve all the pellets using a Branson ultrasonic cleaner model 2510.

Cleaning Silicon wafer substrate (UCLA Nanolab):

1. Set the temperature of the piranha bath to 90 °C.
2. Place a 4” silicon test wafer in a wafer carrier securely, and submerge the carrier in the piranha bath for 10 minutes.
3. Place the wafer carrier in the DI water dump rinser for 3 cycles to wash the acid residue.

4. Take out the wafer with a tweezer from the carrier with care and dry off moisture by blowing nitrogen with a N_2 blow gun thoroughly on both sides of the wafer.
5. Cut the wafer into 1 cm x 1 cm square samples with a glass cutter, and place the samples in a petri dish after blowing nitrogen on each sample to make sure the surface is clean.

Spin coating procedure (UCLA Nanolab):

1. Place a silicon wafer sample at the center of the chuck (the smallest chuck with raised center).
2. Using a pipette, drop approximately 0.1 mL of PEI solution on the sample to cover the whole surface, and start the spinner to spin at 2500 rpm for 30 seconds.
3. Immediately after the PEI layer is coated, place approximately 0.1 mL of polysulfone solution on the sample to cover the whole surface, then start the spinner to spin at 2500 rpm for 30s.
4. Store the spin-coated sample in a petri dish and repeat steps 1 – 3 for the remainder of the samples.
5. Place the petri dish containing the samples inside the vacuum oven (without the cover) to dry over a 24 hour period at 75° prior to use.

A.2 Atmospheric Pressure Plasma-induced Graft Polymerization Procedure

Plasma treatment procedure:

1. Turn the plasma controller on 30 minutes prior to use.
2. Open outlet valve of nitrogen tank. Under the fume hood, degas the monomer solutions by bubbling nitrogen into the solution for 10 minutes (Figure A.1, without the sample in the vial).
3. Open outlet valves of the helium, hydrogen, and oxygen gas tanks. Check the delivery pressure gauge for each gas tank: helium (~ 30 psi), hydrogen (~ 30 psi), and oxygen (~ 40 psi).
4. Make sure that valve ① is open and valve ② is closed (see Figure 3.1). Valve ① open/closes the process gas line from the controller to the plasma source, and valve ② open/closes the oxygen line, which joins the process gas line to the plasma source.
5. Select "AtomFlow 250C" by hitting the green button ("Stop/Start").
6. Purge the plasma system by pressing the "purge" button on the back of the controller for about 30 seconds to clear out any moisture or impurities in the gas line.
7. Tune the RF power and the flow rates of helium and hydrogen to the cold start conditions: RF power: 50 W, helium: 30 L/min, and hydrogen (Gas #2): 0.35 L/min.
8. Turn on the plasma by pressing the green button ("Stop/Start"). On the controller display, the topline should read "Tuning" before it changes to "Plasma On" when

the plasma ignites. It takes about 6 seconds for the plasma to turn on after pressing the start button.

9. Leave the plasma on for about a minute. Visually inspect the plasma discharge by checking its reflection on a silicon wafer (Figure A.2). The plasma discharge should be uniform.

10. Turn off the plasma power by pressing the green button on the controller. Place a sample on center of a sample stage (an upside-down Pyrex cylindrical jar), and set it next to the plasma source (Figure A.3 (*left*)).

11. Turn on the plasma power and leave it on for ~30 seconds. With a stopwatch in one hand, place the sample-carrying Pyrex cylindrical jar directly under the plasma source, and start the stopwatch at the same time (Figure A.3 (*right*)).

12. Leave the sample under the source for a desired plasma treatment period, and slide the sample glass container to the side to remove it from the plasma source when the treatment is done.

13. Turn off the plasma controller power (the green button), and close valve ① and open valve ② (Figure 3.1) to purge oxygen from the plasma source. Place the sample under the plasma source for ~2 minutes for oxygen treatment.

Grafting procedure:

14. Immediately after the oxygen treatment, close valve ② and move the sample into a degassed monomer solution in a vial using a tweezer. Close the cap of the vial, and place the vial inside the temperature controlled water bath. Secure a 14 gauge needle (N_2 inlet) in place using the insulated clamps attached to the wooden stand. (Figure A.1). Pierce through the septum top of the vial with the N_2 inlet needle to bubble nitrogen in the monomer solution. Pierce an 18 gauge needle through the septum top to vent air. Leave the sample-containing vial inside the water bath for the duration of the graft polymerization.
15. Reopen valve ① and remain ② closed (Figure 3.1), and repeat step 11 – 14 for the remaining samples.
16. At the termination of graft polymerization, dispose of the remaining monomer solution in a proper waste container, and carefully take out the sample from the vial using a tweezer. Immerse the sample in DI water for ~10 seconds in order to rinse the sample.
17. Dry the sample by blowing nitrogen, and place the dry sample in a petri dish. When the experiment is over, place the petri dish (without cover) in a vacuum oven (w/o heating) for at least 48 hours before surface characterization.

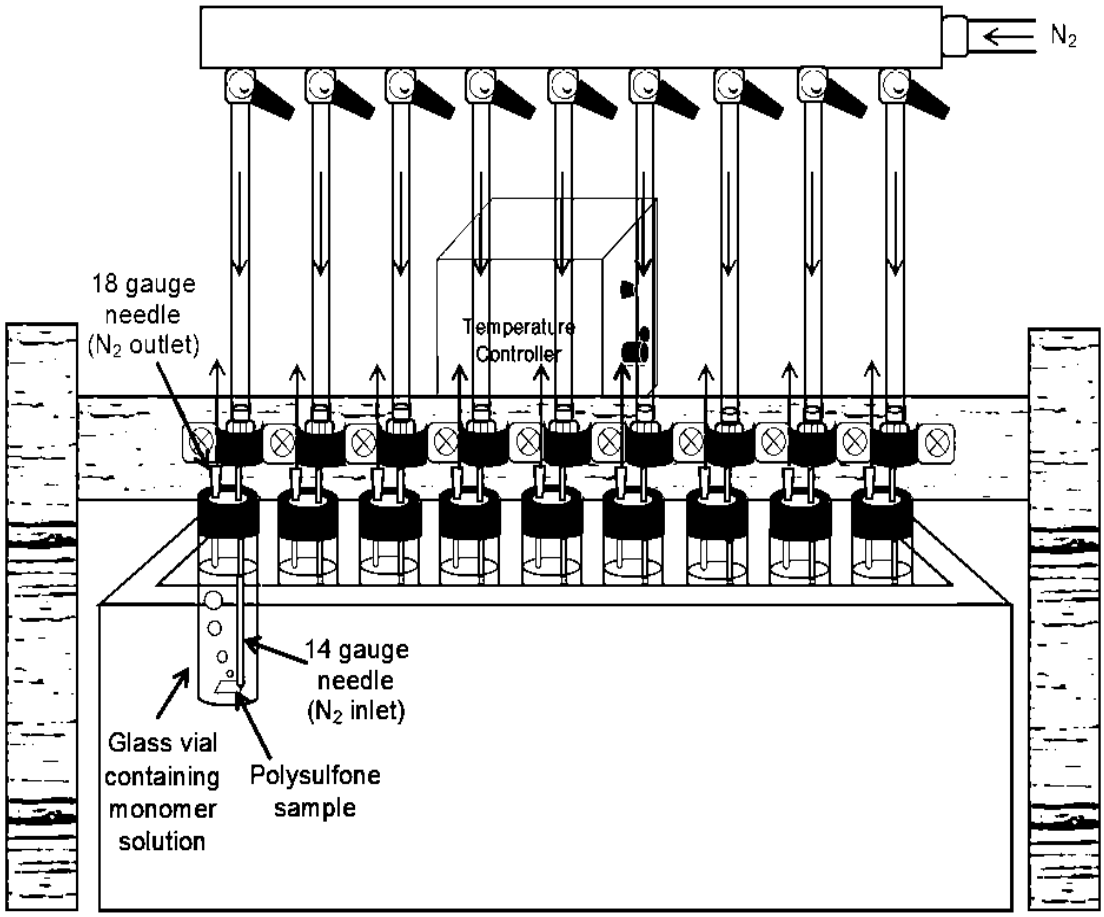


Figure A.1 Graft polymerization experimental setup

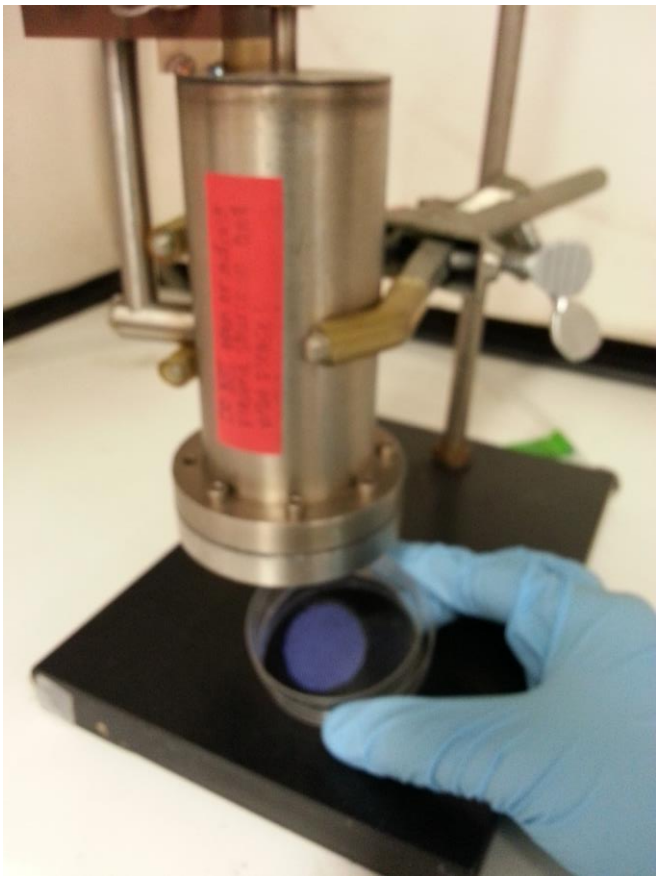


Figure A.2 The AP Plasma source discharge

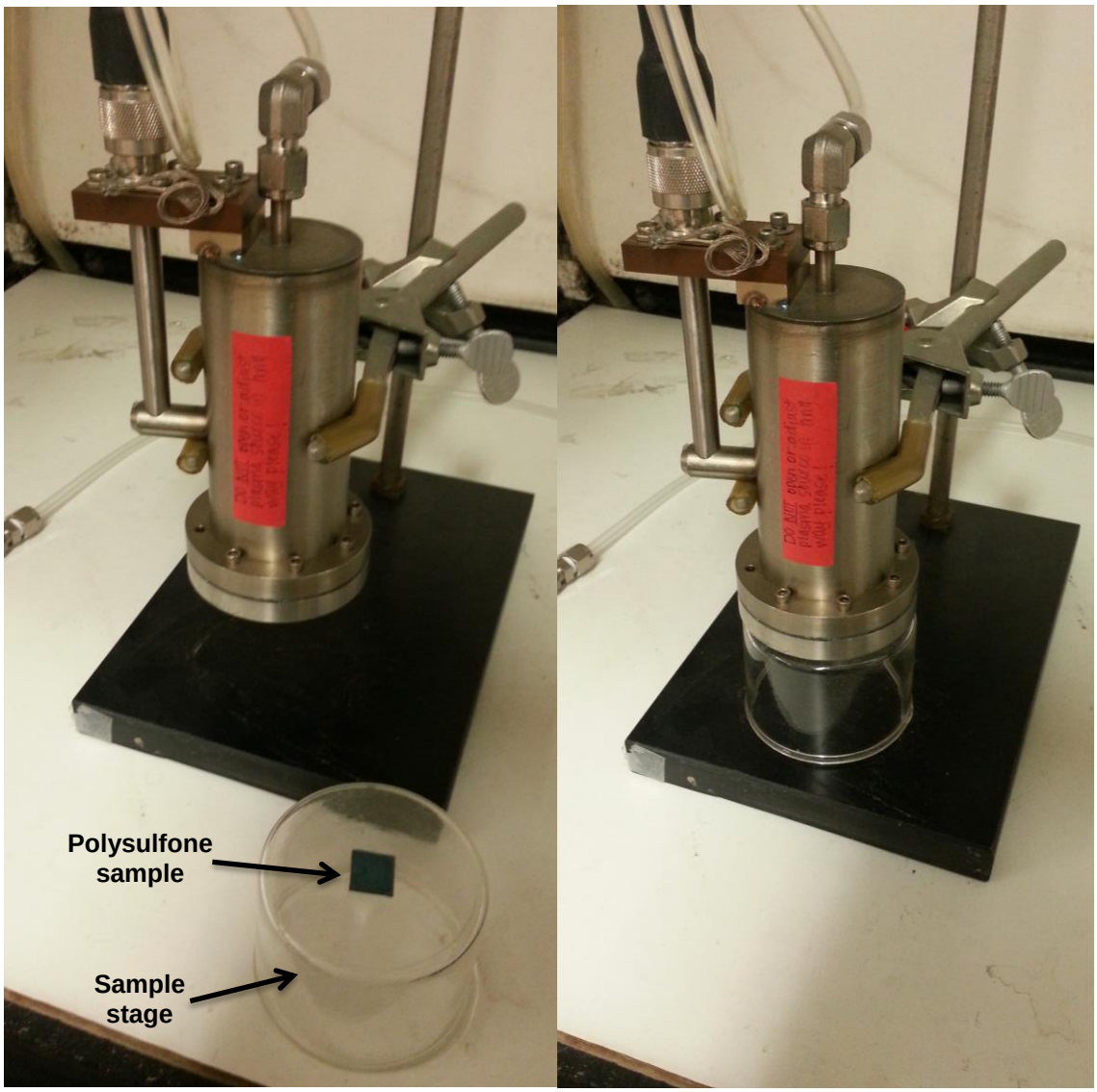


Figure A.3 **Plasma treatment setup: a polysulfone sample placed on center of a sample stage (*left*) and placement of sample stage directly under the plasma source for treatment (*right*)**

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