

**Special Issue: Microfiltration and Ultrafiltration
Membrane Science and Technology**

Guest Editors: Prof. Isabel C. Escobar (University of Toledo) and
Prof. Bart Van der Bruggen (University of Leuven)

EDITORIAL

Microfiltration and Ultrafiltration Membrane Science and Technology

I. C. Escobar and B. Van der Bruggen, *J. Appl. Polym. Sci.* 2015,
DOI: [10.1002/app.42002](https://doi.org/10.1002/app.42002)

REVIEWS

Nanoporous membranes generated from self-assembled block polymer precursors: *Quo Vadis?*

Y. Zhang, J. L. Sargent, B. W. Boudouris and W. A. Phillip, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41683](https://doi.org/10.1002/app.41683)

Making polymeric membranes anti-fouling via "grafting from" polymerization of zwitterions

Q. Li, J. Imbrogno, G. Belfort and X.-L. Wang, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41781](https://doi.org/10.1002/app.41781)

Fouling control on MF/ UF membranes: Effect of morphology, hydrophilicity and charge

R. Kumar and A. F. Ismail, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42042](https://doi.org/10.1002/app.42042)

EMERGING MATERIALS AND FABRICATION

Preparation of a poly(phthalazine ether sulfone ketone) membrane with propanedioic acid as an additive and the prediction of its structure

P. Qin, A. Liu and C. Chen, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41621](https://doi.org/10.1002/app.41621)

Preparation and characterization of MOF-PES ultrafiltration membranes

L. Zhai, G. Li, Y. Xu, M. Xiao, S. Wang and Y. Meng, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41663](https://doi.org/10.1002/app.41663)

Tailoring of structures and permeation properties of asymmetric nanocomposite cellulose acetate/silver membranes

A. S. Figueiredo, M. G. Sánchez-Loredo, A. Mauricio, M. F. C. Pereira, M. Minhalma and M. N. de Pinho, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41796](https://doi.org/10.1002/app.41796)

LOW-FOULING POLYMERS

Low fouling polysulfone ultrafiltration membrane via click chemistry

Y. Xie, R. Tayouo and S. P. Nunes, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41549](https://doi.org/10.1002/app.41549)

Elucidating membrane surface properties for preventing fouling of bioreactor membranes by surfactin

N. Behary, D. Lecouturier, A. Perwuelz and P. Dhulster, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41622](https://doi.org/10.1002/app.41622)

PVC and PES-g-PEGMA blend membranes with improved ultrafiltration performance and fouling resistance

S. Jiang, J. Wang, J. Wu and Y. Chen, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41726](https://doi.org/10.1002/app.41726)

Improved antifouling properties of TiO₂/PVDF nanocomposite membranes in UV coupled ultrafiltration

M. T. Moghadam, G. Lesage, T. Mohammadi, J.-P. Mericq, J. Mendret, M. Heran, C. Faur, S. Brosillon, M. Hemmati and F. Naeimpoor, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41731](https://doi.org/10.1002/app.41731)

Development of functionalized doped carbon nanotube/polysulfone nanofiltration membranes for fouling control

P. Xie, Y. Li and J. Qiu, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41835](https://doi.org/10.1002/app.41835)



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SURFACE MODIFICATION OF POLYMER MEMBRANES

Highly chlorine and oily fouling tolerant membrane surface modifications by *in situ* polymerization of dopamine and poly(ethylene glycol) diacrylate for water treatment

K. Yokwana, N. Gumbi, F. Adams, S. Mhlanga, E. Nxumalo and B. Mamba, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41661](https://doi.org/10.1002/app.41661)

Fouling control through the hydrophilic surface modification of poly(vinylidene fluoride) membranes

H. Jang, D.-H. Song, I.-C. Kim, and Y.-N. Kwon, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41712](https://doi.org/10.1002/app.41712)

Hydroxyl functionalized PVDF-TiO₂ ultrafiltration membrane and its antifouling properties

Y. H. Teow, A. A. Latif, J. K. Lim, H. P. Ngang, L. Y. Susan and B. S. Ooi, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41844](https://doi.org/10.1002/app.41844)

Enhancing the antifouling properties of polysulfone ultrafiltration membranes by the grafting of poly(ethylene glycol) derivatives via surface amidation reactions

H. Yu, Y. Cao, G. Kang, Z. Liu, W. Kuang, J. Liu and M. Zhou, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41870](https://doi.org/10.1002/app.41870)

SEPARATION APPLICATIONS

Experiment and simulation of the simultaneous removal of organic and inorganic contaminants by micellar enhanced ultrafiltration with mixed micelles

A. D. Vibhandik, S. Pawar and K. V. Marathe, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41435](https://doi.org/10.1002/app.41435)

Polymeric membrane modification using SPEEK and bentonite for ultrafiltration of dairy wastewater

A. Pagidi, Y. Lukka Thuyavan, G. Arthanareeswaran, A. F. Ismail, J. Jaafar and D. Paul, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41651](https://doi.org/10.1002/app.41651)

Forensic analysis of degraded polypropylene hollow fibers utilized in microfiltration

X. Lu, P. Shah, S. Maruf, S. Ortiz, T. Hoffard and J. Pellegrino, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41553](https://doi.org/10.1002/app.41553)

A surface-renewal model for constant flux cross-flow microfiltration

S. Jiang and S. G. Chatterjee, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41778](https://doi.org/10.1002/app.41778)

Ultrafiltration of aquatic humic substances through magnetically responsive polysulfone membranes

N. A. Azmi, Q. H. Ng and S. C. Low, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41874](https://doi.org/10.1002/app.41874)

BIOSEPARATIONS APPLICATIONS

Analysis of the effects of electrostatic interactions on protein transport through zwitterionic ultrafiltration membranes using protein charge ladders

M. Hadidi and A. L. Zydney, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41540](https://doi.org/10.1002/app.41540)

Modification of microfiltration membranes by hydrogel impregnation for pDNA purification

P. H. Castilho, T. R. Correia, M. T. Pessoa de Amorim, I. C. Escobar, J. A. Queiroz, I. J. Correia and A. M. Morão, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41610](https://doi.org/10.1002/app.41610)

Hemodialysis membrane surface chemistry as a barrier to lipopolysaccharide transfer

B. Madsen, D. W. Britt, C.-H. Ho, M. Henrie, C. Ford, E. Stroup, B. Maltby, D. Olmstead and M. Andersen, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41550](https://doi.org/10.1002/app.41550)

Membrane adsorbers comprising grafted glycopolymers for targeted lectin binding

H. C. S. Chenette and S. M. Husson, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41437](https://doi.org/10.1002/app.41437)



Making polymeric membranes antifouling via “grafting from” polymerization of zwitterions

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ABSTRACT: Protein-fouling of membranes has negative effects on the wide applications of membrane materials, such as poly(vinylidene fluoride) (PVDF), poly(ether sulfone) (PES)/polysulfone (PSf). Zwitterionic materials have recently been used and identified from high throughput screens of large libraries of monomers to modify membranes due to their stable anti-protein-fouling properties. “Grafting from” polymerization is a technique involving monomers that are polymerized using an initiation reaction on the membrane surface. It is regarded as a simple, useful, and versatile modification approach to increase the anti-fouling properties of a membrane. This strategy provides controllable introduction of graft chains with a high density and a long-term chemical stability due to covalent attachment of graft chains. Graft density, chemistry, chain length, and conformation are all important parameters that need to be considered. This article presents a mini-review of recent progress on the “grafting from” polymerization of zwitterionic monomers on the surfaces of PVDF and PES/PSf membranes, including an introduction of zwitterions and methods of graft polymerization. Various approaches such as free radical graft polymerization, photo-induced graft polymerization, and plasma-induced graft polymerization were compared based on uniformity and amount of grafted zwitterionic polymer, relative flux of modified membranes, simplicity and environment pollution of operation, and cost of technique. The application of different approaches and the performance of poly(zwitterion)-grafted PVDF and PES/PSf membranes are summarized according to recent research. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41781.

KEYWORDS: anti-protein-fouling property; “grafting from” polymerization; polymeric membranes; zwitterion

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INTRODUCTION

It has been acknowledged that membrane separations have low energy consumption, easy operation in continuous flow, have environmentally friendly properties, and are a technology of significant note, not only for wastewater treatment but also for agro-food, biotechnological, and biomedical markets.^{1–4} Microfiltration (MF) and ultrafiltration (UF) are pressure-driven membrane processes that retain macromolecules or high molecular-weight compounds, excluding bacteria and viruses.^{5,6} The most attractive polymers in the MF or UF membrane industry include poly(vinylidene fluoride) (PVDF) and poly(ether sulfone) (PES)/polysulfone (PSf) due to their extraordinary mechanical property, high chemical resistance, and good thermal stability.

There are four critical aspects to successful application of pressure-driven membrane processes. Each—selectivity, capacity, concentration polarization (CP), and fouling—need to be addressed. First,

one needs to obtain the desired selectivity and once that has been satisfied, an economically attractive capacity is essential and this is different for various industries (i.e. water treatment vs. biotechnology). Then CP, the build-up near the membrane during filtration of non-interacting solutes, and fouling, the build-up on/in the membrane during filtration of interacting solutes, need to be considered. Several approaches are used to minimize CP and fouling including those based on modifying the solution properties, the hydrodynamics of crossflow and the membrane morphology and surface chemistry. We focus on the latter in this mini-review and specifically on protein resistant zwitterionic membrane surfaces.

Studies on fouling with blood have shown that human serum albumin (HSA) adsorption on a membrane surface is often followed by platelet adhesion or bacterial biofilm formation.^{7,8} This results in deterioration of membrane performance.⁹ Thus, protein adsorption is one of the most important phenomena in determination of the anti-protein-fouling performance of a membrane.¹⁰ In general,

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proteins adsorb onto a surface of a membrane within a few minutes when the membrane contacts protein-containing liquids such as blood, plasma, bio-medical wastewater, and so on.¹⁰ One of the crucial factors impacting protein adsorption is the surface properties of membranes because it determines the interaction between a protein molecule and the membrane material, which plays an important role in the extent of membrane fouling.⁹ Therefore, the primary target for inhibiting or preventing protein adsorption is to develop super-low fouling or anti-fouling surfaces.¹¹

The construction of a hydrophilic surface has been believed to reduce protein adsorption effectively, due to the fact that the hydrophilic surface attracts so much water that adsorption of proteins is reduced and even prevented.⁹ Therefore, surface modification of PVDF and PES/PSf membranes with hydrophilic or a water-soluble polymer chains has been investigated, such as polyethylene glycol, polyvinyl pyrrolidone (PVP), and so on.^{3,12,13} Seminal studies by the Whitesides group at Harvard University using a variety of functionalities created using self-assembled monolayers of alkanethiolates on gold as a model

substrate have identified general features of surfaces having low affinity for proteins. They should be (i) hydrophilic (wetttable), (ii) contain hydrogen bond acceptors, (iii) lack hydrogen bond donors, and (iv) electrically neutral.^{14–16} These results together with earlier work by Harris and Zalipsky allowed membrane and other scientists interested in protein resistance to search rationally for attractive surface chemistries.¹⁷

In the past decades, a promising zwitterionic non-fouling material has been found.¹⁸ Materials containing zwitterionic phosphorylcholine (PC) head-groups have become the representatives to create non-bio-fouling surfaces since the 1990s, but PC based monomers, such as 2-methacryloyloxyethyl phosphorylcholine (MPC), are moisture sensitive and not easily synthesized.¹⁹ Recently, sulfobetaine, which has a similar structure to PC, has been shown to be a biocompatible material with excellent protein adsorption-resistant properties. Sulfobetaine surfaces are capable of binding a significant amount of water molecules because of the formation of a hydration layer via electrostatic interaction and hydrogen bonding.²⁰ Therefore, it can bind a significant amount of water,

which can lead to a strong repulsive force to protein at specific separation distances.^{8,19} That is, the strong hydration of sulfobetaine surfaces prevents protein from contacting with the surface and makes a significant conformational change of the protein near the surface almost impossible.

In order to substantially increase the chances of finding surfaces with superior anti-fouling characteristics, the Belfort Group has developed an inexpensive, fast, simple, reproducible, and scalable modification procedure for testing hundreds if not thousands of surfaces in relatively short periods (hours to days).^{21–23}

The method combines a high throughput platform (HTP) with their patented photo-induced graft polymerization (PGP) or atmospheric plasma polymerization (APP) techniques. Of interest in this mini-summary on zwitterionic functional groups with synthetic membranes is that the HTP-PGP or -APP approaches have “blindly” selected several zwitterionic groups as superior protein resistant surfaces.²³ Their results showed that two zwitterions, [3-(methacryloylamino)propyl]dimethyl (3-sulfopropyl) ammonium hydroxide and [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl) ammonium hydroxide, were among the top performers for the single solute lysozyme feed, and first listed monomer also yielded surfaces that resisted immunoglobulin G fouling in the presence and absence of bovine serum albumin (BSA). Zwitterions also performed well for single solute BSA feeds.²²

Due to its unique structure and functionalities, sulfobetaine has been widely used in the chemical modification of solid substrates and surfaces.^{20,24} During the past 5 years, researchers have confirmed the ability of sulfobetaine coatings on the surfaces of polymer membranes to resist protein adsorption and then significantly retard bacterial biofilm formation.^{2,4,19,20,24} Among the surface modification techniques developed to date, “grafting from” polymerization (monomers are polymerized using an initiation reaction on the surface) has emerged as a simple, useful, and versatile approach. This is due to the controllable introduction of graft chains with a high density and exact localization to the surface without affecting the bulk properties and the long-term chemical stability which is assured by covalent attachment of graft chains.⁹

In this article, zwitterionic materials such as phosphobetaine, sulfobetaine, and carboxybetaine, will be focused on to enhance the anti-protein-fouling performance of PVDF and PES/PSf membranes. Illustrative examples of “grafting from” polymerization of zwitterions on the formed membranes will be discussed. Although multiple parameters influence the performance of membranes, we will mainly focus on decrease in protein adsorption of PVDF and PES/PSf membranes. The methods are compared and rated on their applicability for surface modification of PVDF and PES/PSf membranes.

ZWITTERIONS

Zwitterions, which bear both cationic and anionic groups in the same monomer unit, have proved promising materials for membrane separations.²⁵ The typical anionic group for zwitterion is a quaternary ammonium group, while the cationic groups include sulfonic, carboxylic, and phosphoric groups. In the past 20 years,

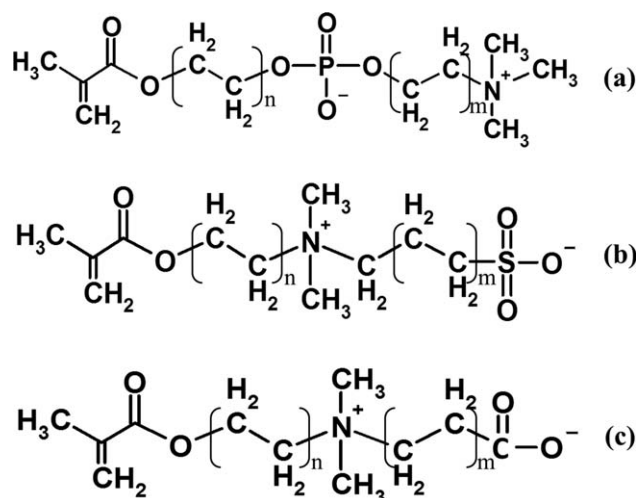


Figure 1. Chemical structural formula of zwitterions used in the anti-fouling modification of polymer membrane surfaces (a) $n = 1$, $m = 1$, 2-Methacryloyloxyethyl phosphorylcholine, (b) $n = 1$, $m = 1$, sulfobetaine-methacrylate (SBMA), and (c) $n = 1$, $m = 1$, carboxybetaine methacrylate.

zwitterions such as phosphobetaine and sulfobetaine were widely applied in the modification of polymer membranes, which not only facilitate water transport through the membranes, but also improve their antifouling properties.^{8,26–28} The monomers of phosphobetaine, sulfobetaine, and carboxybetaine, such as MPC, sulfobetaine methacrylate (SBMA), and carboxybetaine methacrylate (CBMA), respectively, have similar structures, as shown in Figure 1.

It is regarded that biomembrane surfaces are the best for smooth interaction with proteins and cells.^{20,29} In 1972, Singer and Nicolson proposed a model of the structure of a biomembrane, which is well-known as the fluid-mosaic model.³⁰ The negatively charged phospholipids, such as phosphatidylserine, are predominantly on the inner cytoplasmic side of the membrane, whereas the neutral zwitterionic MPC lipids, such as phosphatidylcholines, are located in the outer leaflet. The MPC surface provides an inert surface for biological interactions of proteins to occur smoothly on the membrane.^{20,31} This shows that phosphobetaine with MPC headgroups is naturally protein resistant on the outside layer of cell membranes.^{32–34}

Poly(sulfobetaine) is reported to exhibit a zwitterionic structure and electrically net neutral charge, similar to that of poly(phosphobetaine)-based materials, which results in similar protein resistance.^{35–39} Liu's group reported that poly(sulfobetaine) modified surfaces were as effective as poly(phosphobetaine) modified surfaces at preventing protein adsorption and platelet adhesion.⁸ There are only a few differences of anti-fouling properties between PC polymers and SBMA polymers, while the main difference between phosphobetaine monomer and sulfobetaine monomer is the synthetic facility. According to past results, sulfobetaine monomer is easier to synthesize and handle than PC polymers.^{40–43} Moreover, poly(sulfobetaine) has a very small disruptive effect on the structure of the hydrogen-bonding network of water molecules in dilute solutions because of the intra- and inter-tether proximity between the oppositely charged groups.^{34,40–42} In the past 10 years, preparation and characterization of sulfobetaine polymers have been extensively studied.^{19,27,35,36,44–55}

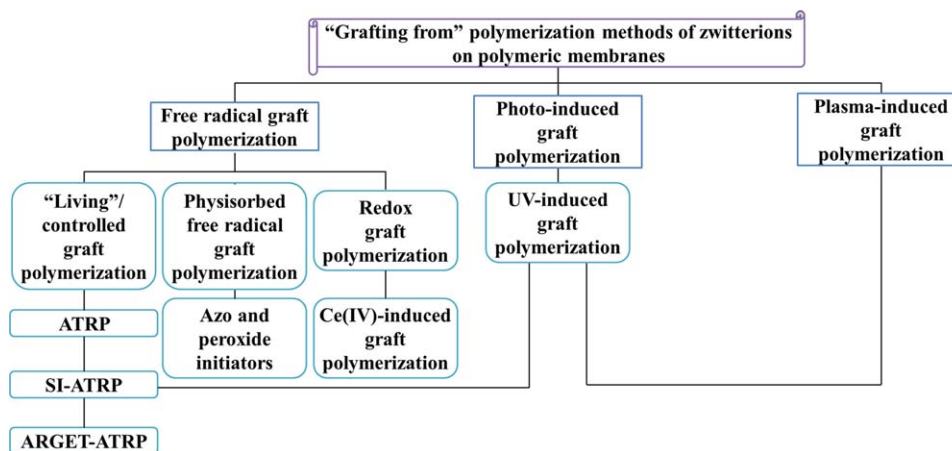


Figure 2. Common methods of “grafting from” polymerization of zwitterions on poly(vinylidene fluoride) (PVDF), poly(ether sulfone) (PES)/polysulfone (PSf) membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Additionally, zwitterionic polymers based on the carboxybetaine monomer not only demonstrate good resistance to nonspecific protein adsorption and short-term bacterial adhesion, but also has abundant functional groups convenient for the immobilization of ligands.^{56,57} It has been found that zwitterions in the sulfobetaine polymers remain in their di-ionic form over a broader pH range than the carboxybetaine polymers.^{36,56–60}

“GRAFTING FROM” POLYMERIZATION OF ZWITTERIONS ON PVDF AND PES/PSF MEMBRANES

Surface modification has been considered as a useful method to improve the anti-fouling performance of membranes without destroying bulk properties.⁶¹ Among various methods, graft polymerization is regarded as one of the most promising methods to modify a membrane surface through covalent bonding interactions between the grafted chains and the membrane.⁶² The process of “grafting from” polymerization consists of two steps: (i) attachment of initiators onto surfaces and (ii) polymer growth from initiator sites.⁶³ Versatile initiation methods for “grafting from” polymerization of zwitterionic monomers onto the surface of a membrane include free radical graft polymerization, photo-induced graft polymerization, plasma-induced graft polymerization, and combined methods, as shown in Figure 2.

Free Radical Graft Polymerization

“Living”/Controlled Graft Polymerization. Recently, “living”/controlled graft polymerization has been used to graft zwitterionic polymer onto a membrane surface.^{64–66} This method shows the ease of polymerization without the stringent reaction conditions required for ionic polymerizations, such as complete absence of water (anhydrous). It combines the advantages of living ionic polymerization with better control and the versatility of free radical polymerization.^{62,67} The development of “living”/controlled graft polymerization in aqueous systems has enabled its application to surface grafting onto membranes using water as the reaction medium.⁶²

The atom transfer radical polymerization (ATRP) process developed by Prof. Krzysztof Matyjaszewski in 1994, is well-known as one kind of “living”/controlled graft polymerization for its versatility with monomers, mild polymerization conditions, toler-

ance for impurities, and the ability to synthesize well defined polymers in a controlled manner.^{4,36,63,65} In recent years, surface-initiated ATRP (SI-ATRP) has been most widely used to graft zwitterionic chains or brushes onto a membrane surface.⁶² This method is able to design and tailor the graft density, chain length, and chemical composition of zwitterionic polymer onto a membrane surface. As a result, the morphology and properties of the membrane surface can be fine-tuned based on application.^{8,64} Moreover, compared with conventional radical polymerization, SI-ATRP can produce more uniform and smooth poly(zwitterion) membrane surfaces, which is of great significance for the anti-protein-fouling performance of membranes.⁶² It is crucial to choose a suitable solvent for the poly(zwitterion) grafting onto membrane surfaces: (i) it should promote the successful controlled polymerization of grafted zwitterionic chains; (ii) it should maintain the integrity of the bulk membrane without damage or dissociation; and (iii) it should be environmentally friendly.⁶²

For inert membranes lacking active groups (such as fluoropolymer and polypropylene membranes), surface modification using SI-ATRP often involves organic solvents and multi-step strategies.⁶⁸ Activator regenerated by electron transfer ATRP (ARGET-ATRP), a new ATRP initiating system, was developed to facilitate solution and emulsion ATRP in aqueous media.⁶⁹ This process can tolerate excess reducing agent so that Cu(II) can be reduced to Cu(I) rapidly in the polymerization system to catalyze the polymerization of ATRP monomer.⁷⁰ Thus, the reaction can be conducted in the presence of limited amounts of air.⁶³ For example, water/methanol and CuBr/Bpy complex can be used as the solvent and catalyst, respectively, to graft the poly(sulfobetaine) from the surface of PVDF-Br membrane.⁴ In aqueous media, the structure of the catalytic species is a mono-cationic complex $[\text{Cu}(\text{I})(\text{Bpy})_2]^+$ with a halide counter ion. The ionic catalyst species in aqueous media are active enough; as a result, the addition of water in the solvent will increase the polymerization rate.³⁶

Physisorbed Free Radical Graft Polymerization. Azo and peroxide initiators, such as azo-bis-isobutyronitrile, can be used as a source of radicals for graft polymerization of vinyl and acrylic monomers onto the surface of polymer membranes since they

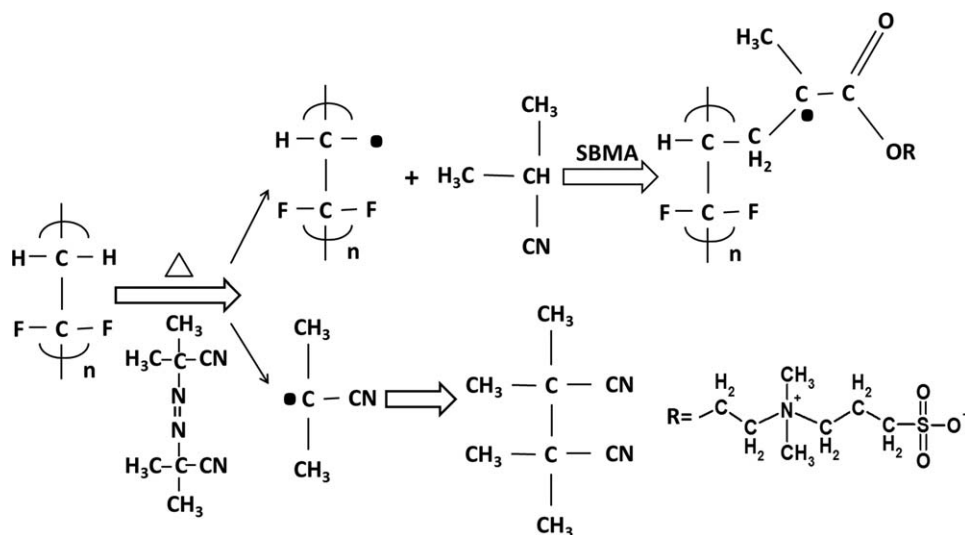


Figure 3. Mechanism of physisorbed free radical polymerization.⁷¹

are able to attach and be decomposed into radicals at moderate temperatures.^{47,71,72} The mechanism of physisorbed free radical polymerization is shown in Figure 3. Hu *et al.* proposed a physisorbed free radical grafting technique to create radicals on polymer surfaces and then react with hydrophilic polymers.⁷³ Using this technique, the sulfobetaine monomers can be covalently attached onto both the surface and the inside of membrane. The graft polymerization can be carried out without limitations or more complicated procedures, such as high-energy reactors or intense light sources.

Redox Graft Polymerization. Redox graft polymerization using cerium ion (Ce(IV)) as an initiator is another well-known method for the polymerization of zwitterionic monomers.⁷⁴ This process can be performed at moderate temperatures and results in minimal side reactions, thus, the Ce(IV)-induced graft polymerization has a minimal extent of ungrafted homopolymer and a high grafting efficiency of initiator.^{65,75,76} During the graft copolymerization, the Ce(IV) is reduced to cerous ion (Ce(III)), and free radical sites are created on the membrane surface. The radical sites initiate graft copolymerization of the vinyl group in zwitterionic monomers which are present in the reaction solution.

Photo-Induced Graft Polymerization

Photo (UV)-induced “grafting-from” polymerization method is another common technique for anti-fouling modification of membrane surfaces due to the mild reaction conditions, simplicity, and versatile operation.^{19,53,77,78} This process occurs at the membrane skin and effectively improves the surface performance of the membrane without affecting the bulk properties because of the relatively low energy of the UV source.⁵⁴ The grafting amount and permeate performance of the modified membrane can be controlled conveniently in UV-induced grafting processes.^{79,80}

Using membranes made from the photo-sensitive base polymer (photo-reactive side group or part of polymer backbone), this approach involves the direct generation of free radicals from the membrane surface under UV irradiation.^{77,81} PES is an intrinsically photo-active polymer and PES hollow fiber membranes

can be modified by photo-grafting of MPC and SBMA to improve their anti-bio-fouling properties.^{21–23,53}

For the membranes with less electro-active property, such as PVDF membranes, initiating radical sites should be generated at the membrane surface by the introduction of an initiator.⁸¹ Benzophenone (BP) and its derivatives are usually needed for the initiation of UV-assisted graft polymerization of zwitterionic monomers at the surface of such membranes.⁶² In this case, BP is decomposed to radicals that then transfer to the membrane and abstract hydrogen atoms from surrounding chemical species, contributing to the generation of initiating radicals.^{62,81} BP can be coated onto the membrane surface by adsorption methods which can minimize the homopolymerization of monomer and enhance the grafting efficiency.^{62,82}

Plasma-Induced Graft Polymerization

To increase the hydrophilicity in order to obtain low-fouling membrane surfaces, treatment using plasma has been extensively studied over the last two decades to anchor the zwitterionic graft chains on the surface of membranes efficiently.^{23,62,81,83} Surface zwitterionization by plasma-induced graft polymerization is easy to operate and especially suitable for biomedical membrane modification using a dry and clean process.⁸⁴ It has been reported that low-temperature plasma-induced grafting has been performed to improve the permeate flux and antifouling performance of PVDF and PES/PSf membranes.⁸⁵

Plasma-induced grafting of poly(zwitterion) chains on the membrane surface includes two main processes: (i) activation of the polymer support via plasma (generation of radicals) and (ii) deposition of a new zwitterionic layer on the membrane surface by polymerization.⁸¹ They can be balanced by altering the plasma gas composition and the applied process parameters. Thus, the grafting amount and the length of zwitterionic chains can be controlled by plasma parameters, such as pressure, power, sample disposition, treatment time, polymerization conditions (such as monomer concentration), solvent choice, and grafting time. As a result, the thickness of the poly(zwitterionic) layer can be controlled down to the angstrom level.^{62,81} Moreover, the dynamic plasma flow not only presents a longer glow distance than the static plasma but also

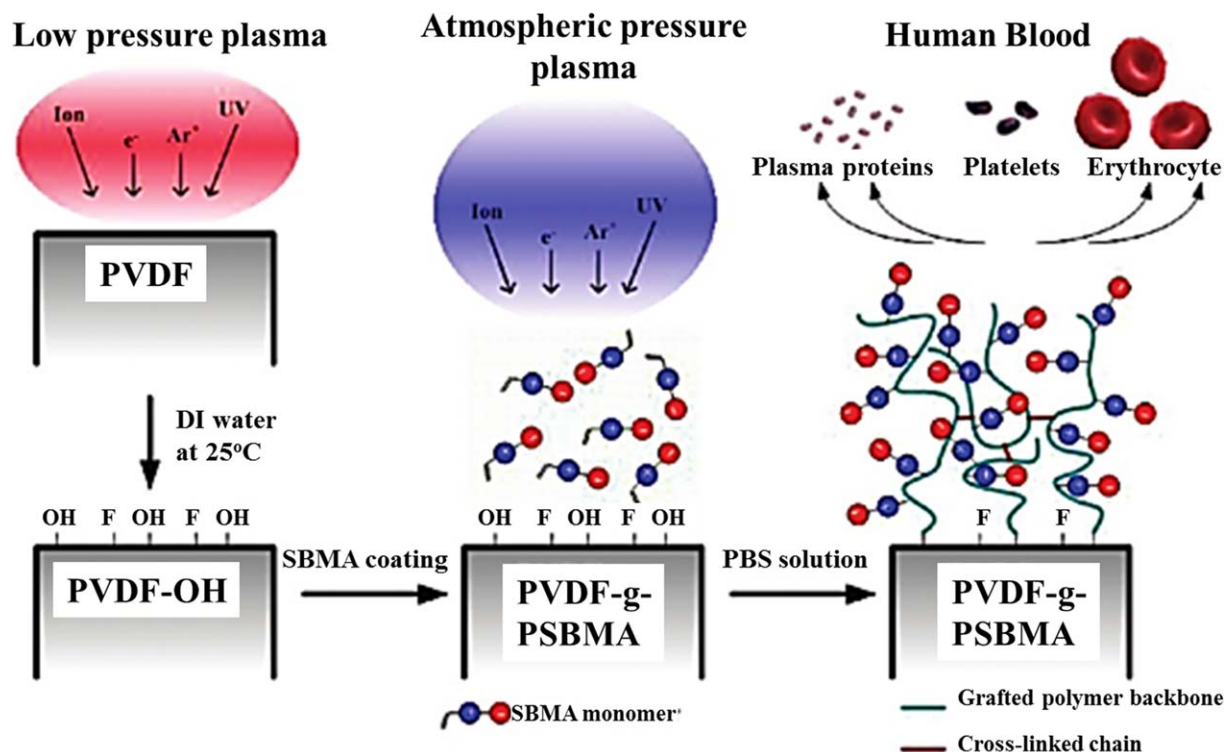


Figure 4. Schematic illustration of the preparation process of the zwitterionic PVDF-g-PSBMA membranes via atmospheric plasma-induced surface copolymerization.⁴⁴ [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

produces larger quantities of peroxides on the membrane, and even excites the underlying membrane layer.⁸⁵ Schematic illustration of the preparation process of the zwitterionic PVDF-g-PSBMA membranes via atmospheric plasma-induced surface copolymerization is shown in Figure 4.

Comparison of Different Graft Polymerizations

Recent results showing application of the “grafting from” polymerization methods on PVDF and PES/PSf membranes is listed in Table I. Table II presents a qualitative comparison between graft polymerization methods. Here we only attempt to give a high level overview based on the presented results in literature because one method may be influenced by many parameters simultaneously.

Free radical graft polymerization, such as the “living” polymerization method, can be used to graft polymers onto surfaces in a controlled manner, including graft amount or density, chain length, chemical composition, and so on.^{4,47,64,74} Therefore, the structure of zwitterionic polymers grafted on the membrane surfaces is easily regulated and controlled by adjusting the operating parameters during graft polymerization. However, this method may lead to undesirable surface changes and contamination due to the multi-step process, which results in a relatively low uniformity of poly(zwitterionic) layer on the membrane surface.

Membrane modification via UV-grafting shows easy and controllable introduction of high density graft chains and exact

Table I. Application of the “Grafting From” Polymerization Methods on PVDF and PES/PSf Membranes

Methods	Monomer	Free radical graft polymerization	Photo-induced graft polymerization	Plasma-induced graft polymerization
PVDF	SBMA	√		√
	MPDSAH			
	CBMA			
PES	MPC	√	√	
	SBMA			
PSf	SBMA	√		

Abbreviations: CBMA, carboxybetaine methacrylate; MPC, 2-methacryloyl-oxethyl phosphorylcholine; MPDSAH, 3-(methacryloylamino) propyl-dimethyl- (3-sulfopropyl) ammonium hydroxide; PES, poly(ether sulfone); PSf, polysulfone; PVDF, poly(vinylidene fluoride); SBMA, sulfobetaine methacrylate.

Table II. Advantages and Disadvantages of Modification Methods

Methods	Uniformity	Grafting amount	Relative flux	Simplicity	Environment pollution	Cost
Free radical graft polymerization	Low	Low	Low	Medium	Medium	Low
Photo-induced graft polymerization	Medium	High	Low	High	Low	High
Plasma-induced graft polymerization	High	Medium	Low	High	Low	High

localization to the membrane surface. The attractive feature of plasma-grafting is the short modification time with the possibility of adjusting the surface properties without affecting the bulk properties of the membrane.⁸¹ The graft polymerization induced by photo or plasma provides simple operation, low surface roughness, and low environmental pollution. However, some problems such as continuity and reproducibility of the modification procedure lead to drawbacks for large-scale application of photo-induced or plasma-induced graft polymerization.

In addition, most of the graft polymerization methods resulted in a reduction of pure water flux due to pore plugging. Since all of the graft polymerization methods can be applied to graft zwitterionic polymer on the membrane surface to improve the hydrophilicity and fouling resistance of proteins, we can compensate for the flux reduction by increasing operating pressure and temperature.

ANTI-PROTEIN-FOULING PERFORMANCE OF POLY(ZWITTERION)-GRAFTED MEMBRANES

Whitesides rules support the hypothesis that the interaction of the surface with water is of great importance to the resistance to adsorption of proteins.^{14,86} Zwitterionic polymers form a hydration layer via electrostatic interactions and do not significantly disturb the H-bonded network structure of the water molecules.^{34,86} It is expected that zwitterions are capable of binding a significant amount of water molecules and form a hydration layer near the surface which forms a physical and energetic barrier to prevent the adsorption of protein.^{87,88} The amount of free water and the change in structure of proteins near the surface of zwitterionic polymers represents its water binding capacity, which plays an essential role in its resistance against adsorption of proteins.^{10,24} The resistance of poly(zwitterionic) materials to protein adsorption is tightly correlated with the uniformity of charge distribution and the charge neutrality of two opposite charge moieties.^{14,87,88} By using both molecular mechanics and molecular dynamics simulation techniques, it can be found that balanced charge, minimized dipole interactions, and close packing density are the key factors for the non-fouling behavior of zwitterions.^{34,86} The properties of zwitterions contributed to the anti-fouling performances of the poly(zwitterion)-grafted PVDF and PES/PSf membranes. Table III lists the performances of PVDF and PES/PSf membranes modified by zwitterions according to research in the past 3 years.

Liu's study confirmed that the poly(sulfobetaine) modified membrane surface was as effective as the poly(phosphobetaine) modified membrane surface for resisting adsorption of protein and adhesion of platelets.⁸ PolySBMA could be grafted from the surface of PVDF membranes via physisorbed free radical grafting

techniques and decrease the water contact angle from 59° to 17° within 120 s at the surface of membrane with 608 $\mu\text{g}/\text{cm}^2$ of grafting surface density.⁴⁷ Liu's study reported on the graft polymerization of zwitterionic monomer, MPC, on the membrane surface by redox graft polymerization using the same initiator [i.e. ceric ammonium nitrate (CAN)], which only required a one-step reaction and avoided the complex and unfavorable pretreatment process and hydroxylated treatment.⁷⁴ Recently, Chang's group employed atmospheric plasma-induced surface copolymerization method to prepare polySBMA-grafted PVDF membranes.⁴⁴ The results suggested that the hemocompatible nature of grafted polySBMA via atmospheric plasma treatment shows great potential in the surface zwitterionization of hydrophobic membranes for use in human whole blood. All other properties of the modified membrane are listed in Table III.

OUR WORK

Preparation of Poly(sulfobetaine)-Grafted PVDF Hollow Fiber MF Membrane

Our group immobilized the zwitterionic sulfobetaine polymers on PVDF hollow fiber MF membranes via a graft polymerization process, which brings some new functions.

A hydrophilic and anti-fouling PVDF hollow fiber MF membrane was first synthesized via the surface alkaline treatment initiated—ATRP with zwitterionic sulfobetaine. Based on the results of stability tests on the prepared membrane, the PVDF hollow fiber MF membrane prepared by the sulfobetaine monomer with the amide group showed more stable anti-protein fouling performance.⁴

The alkaline treatment degrades the PVDF membrane and lowers its mechanical strength, therefore, a two-step graft polymerization method, which can be seen in Figure 5, was proposed in order to enhance the mechanical property of the PVDF hollow fiber MF membrane and increase the surface grafting amount of sulfobetaine polymer simultaneously. The reaction kinetics of the two-step graft polymerization were investigated further and the conditions of the preparation process were adjusted to elucidate the internal relationship between kinetic chain length and grafting amount of the sulfobetaine polymer. As a result, the poly(sulfobetaine)-grafted PVDF hollow fiber MF membrane with the optimal hydrophilicity, anti-fouling, and permeating performance was obtained.⁶⁵

Anti-Fouling Performance of Poly(sulfobetaine)-Grafted PVDF Hollow Fiber MF Membrane

The gravimetry results indicated the grafting amount increased to $520 \pm 12 \mu\text{g}/\text{cm}^2$ for a copolymerization time of more than 3 h via the two-step graft polymerization. Static and dynamic

Table III. Graft Polymerization of Zwitterions from Membrane to Enhance Their Anti-Fouling Performance in the Past 3 Years

Methods	Nascent membrane	Zwitterionic monomer	Grafting amount ($\mu\text{g}/\text{cm}^2$)	Contact angle ($^\circ$)	Pure water flux ($\text{L}/\text{m}^2\text{h}$)	Protein/bio- system	Flux recovery ratio/protein adsorption
Free radical graft polymerization	PES flat membrane ⁷⁴	MPC	-	82.90 ± 2.37 (Nascent ^a)	156.3 (Nascent)	1.0 g/L of BSA	60.6% (Nascent)
				46.43 ± 1.93 (Modified ^b)	107.8 (Modified)		87.0% (Modified)
				after 3 s	at 0.1 MPa		(Flux recovery ratio)
	PSf flat membrane ⁶⁴	SBMA	≈ 1800	≈ 75 (Nascent)	0.02012 (Nascent)	1.0 g/L of BSA	42.37% (Nascent)
				≈ 30 (Modified)	0.04672 (Modified)		98.01% (Modified)
					at 1 mm Hg		(Flux recovery ratio)
	PVDF flat membrane ⁴⁷	SBMA	608	90 (Nascent)	≈ 130 (Nascent)	1.0 g/L of BSA	47.6% (Nascent)
				59 (Modified)	≈ 115 (Modified)		85.1% (Modified)
					at 0.25 MPa		(Flux recovery ratio)
	PVDF hollow fiber membrane ⁴	MPD/SAH; SBMA	247	75.9 (Nascent)	1592 (Nascent)	1.0 g/L of BSA	52.0% (Nascent)
				15 (Modified)	1482 (Modified)		93.4% (Modified)
				40 (Modified)	1365 (Modified)		92.8% (Modified)
				after 100 s	at 0.1 MPa		(Flux recovery ratio)
	PVDF hollow fiber membrane ⁶⁵	MPD/SAH	513	87.5 ± 2.1 (Nascent)	1592 (Nascent)	1.0 g/L of BSA	52.0% (Nascent)
				22.1 ± 2.0 (Modified)	1319 (Modified)		97.8% (Modified)
				after 5.5 s	at 0.1 MPa		(Flux recovery ratio)
	PVDF flat membrane ⁷¹	CBMA	500	91.35 (Nascent)	≈ 170 (Nascent)	1.0 g/L of BSA	$\approx 50\%$ (Nascent)
				70.24 (Modified)	≈ 120 (Modified)		$>90\%$ (Modified)
					at 0.1 MPa		(Flux recovery ratio)

Table III. Continued

Methods	Nascent membrane	Zwitterionic monomer	Grafting amount ($\mu\text{g}/\text{cm}^2$)	Contact angle ($^\circ$)	Pure water flux ($\text{L}/\text{m}^2\text{h}$)	Protein/bio- system	Flux recovery ratio/protein adsorption
Photo-initiated graft polymerization	PES hollow fiber membrane ⁵³	SBMA; MPC	≈ 1700	≈ 90 (Nascent)	≈ 550 (Nascent)	10^6 cells/ml of <i>Pseudomonas putida</i>	≈ 0.4 (Nascent)
			≈ 1670	≈ 40 (Modified)	≈ 350 (Modified)		≈ 0.8 (Modified)
				≈ 30 (Modified)	≈ 400 (Modified)		≈ 0.9 (Modified)
Plasma-induced graft polymerization	PVDF flat membrane ⁴⁴	SBMA	≈ 900	105 (Nascent)	at 0.1 MPa	1.0 g/L of human fibrinogen	(Flux recovery ratio) 100% (Nascent)
				≈ 30 (Modified)			10% (Modified) (Protein adsorption)

Abbreviations: CBMA, carboxybetaine methacrylate; MPC, 2-methacryloyl-oxethyl phosphorylcholine; MPDSA, 3-(methacryloylamino) propyl-dimethyl- (3-sulfopropyl) ammonium hydroxide; PES, poly(ether sulfone); PSf, polysulfone; PVDF, poly(vinylidene fluoride); SBMA, sulfobetaine methacrylate.

^aThe polymer membrane without modification.
^bThe polymer membrane grafted by zwitterions.

water contact angle measurements showed that the surface hydrophilicity of the PVDF membranes was significantly enhanced. As the grafting amount reached $513 \pm 10 \mu\text{g}/\text{cm}^2$, the value of contact angle dropped to $22.1 \pm 2.0^\circ$ and the amount of protein adsorption decreased to zero. The cyclic experiments for BSA solution filtration demonstrated that the extent of protein fouling was significantly reduced and most of the fouling was reversible.⁶⁵

Sulfobetaine polymers have been regarded as a special class of zwitterionic polyelectrolytes.⁸⁹ The presence of inorganic electrolytes can shield the intra- and/or inter-chain associations of sulfobetaine polymer caused by electrostatic attraction among the opposite charges, which is called the “anti-polyelectrolyte effect”.³⁶ It allows the sulfobetaine polymer chains to adopt an extended conformation, thus transforming their surface morphology. Therefore, an excellent permeation performance and a super-low fouling property of sulfobetaine surface would be obtained by varying the concentration of inorganic salts. Our study demonstrated that based on the electrolyte-responsive behavior of poly(sulfobetaine)-grafted PVDF hollow fiber MF membrane, addition of the electrolyte into protein solution and oil-in-water emulsion contributed to the increased anti-protein fouling and oil-fouling resistance properties of the membrane.⁹⁰ In the presence of 0.05 M NaCl, the sulfobetaine-grafted PVDF hollow fiber membrane showed excellent protein-fouling resistance and oil-fouling resistance performance with relative flux recovery values of about 1.4 and 2 times greater than those of the nascent PVDF membrane, respectively.

Formation of a Novel Hollow Fiber UF Membrane with Poly(sulfobetaine) Layer

The PVP immobilized on/in the PVDF membrane attracted more sulfobetaine monomer into the membrane interior for subsequent graft polymerization onto the membrane surface and subsurface, and a thick poly(sulfobetaine) grafting layer was formed.¹ The grafting amount was as high as $721 \pm 13 \mu\text{g}/\text{cm}^2$. The shielding effect of type 1-1 electrolytes on the intra- and/or inter-chain associations of poly(sulfobetaine) chains was superior to that of other electrolytes, which contributed to the completely stretched structure of sulfobetaine polymer chains and a thick poly(sulfobetaine) layer with a thickness of $4.8 \pm 0.2 \mu\text{m}$. As a result, a novel hollow fiber UF membrane with good performance was obtained. Protein separation by the novel membrane could be effectively achieved by isoelectric focusing of one component, as shown in Figure 6. The novel membrane with controllable selective separation for proteins and steady permeate capacity was obtained by means of the immersion/washing method, which is an attractive candidate for the batch separation of protein mixtures.

CONCLUSIONS AND PROSPECTS

Protein fouling is one of the serious problems of synthetic membranes including hydrophobic PVDF and PES/PSf membranes, which often leads to platelet adhesion, bacterial biofilm formation, and other bio-fouling phenomena. Therefore, the growth of anti-protein-fouling materials and associated membrane modification (“grafting-from” polymerization) is critically

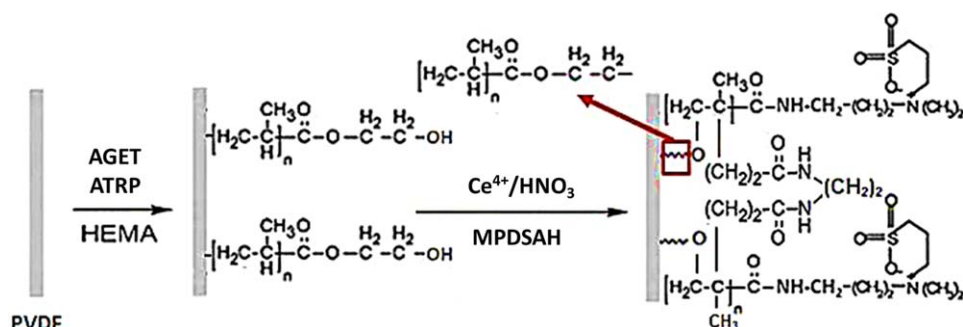


Figure 5. Schematic diagram for the modification of PVDF MF membrane with sulfobetaine 3-(methacryloylamino) propyl-dimethyl- (3-sulfopropyl) ammonium hydroxide via a two-step graft polymerization.⁶⁵ [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

significant, especially for membrane applications in bioseparations, biotechnology, medicine, (surgical instruments) artificial organs, and water/wastewater treatment. Zwitterionic materials are extremely hydrophilic and exhibit stable anti-protein-fouling properties according to the four Whitesides protein resistant criteria. Thus, they have been applied to the modification of polymer membranes. With the understanding of anti-protein fouling mechanisms and graft polymerization principles of zwitterions on the membrane surface, future research should focus on the mechanism of protein zwitterionic interactions and the development of novel zwitterionic monomers that possess various functional groups. Using HT-PGP or -APP we have identified particular zwitterionic monomers that exhibit very low

fouling with particular solutions. The combined graft polymerization methods that render the zwitterionic polymer more efficient and durable on the membrane surface could be investigated to meet the challenge of excellent membrane uniformity and long-term stable performance. Based on these, the cost of techniques and operations could be reduced appropriately by designing the optimal means to synthesize zwitterionic monomers and improve graft polymerization on the membrane surface. Our work demonstrated that zwitterionic sulfobetaine immobilized on PVDF membranes via the graft polymerization process can form a thick poly(sulfobetaine) layer and bring some new functions: not only anti-protein fouling and oil-fouling resistance, but also electrolyte-responsive behavior and

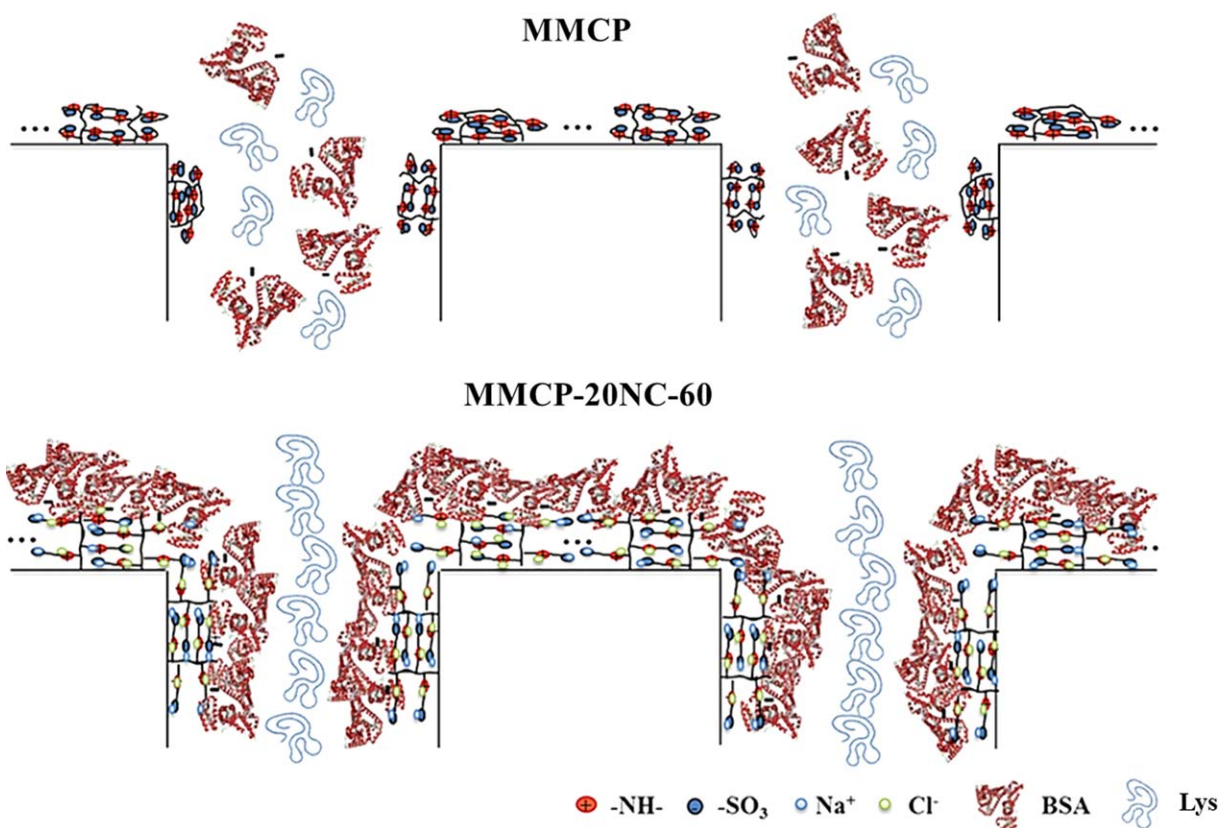


Figure 6. Schematic models of BSA and lysozyme (Lys) transport through the MF membrane (MMCP) and UF membrane (MMCP-20NC-60) at pH = 10.¹ [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

controllable selective separation. In short, the poly(zwitterion)-grafted membrane would be of great interest to the anti-fouling strategies in PVDF and PES/PSf membranes, which helps to expand membrane applications in the fields of agro-food, biomedicine, biotechnology, and water treatment, including water contaminated with oil. Although we have shown that the surface chemistry is critical in repelling proteins, we have only tested a few proteins and different zwitterions behave differently with different proteins. Thus, in addition to chemistry, chain length, density, and chain conformation are all important parameters that need to be considered.

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