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# The Art of Surface Modification of Synthetic Polymeric Membranes

K. C. Khulbe, C. Feng, T. Matsuura

*Industrial Membrane Research Laboratory, Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada*

Received 3 December 2008; accepted 13 July 2009

DOI 10.1002/app.31108

Published online 14 September 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The development in the area of surface modification of polymeric synthetic membranes since 2000 is reviewed. Many patents, articles, and reviews have been written on the development in the area of surface modification of polymeric synthetic membranes subjected to RO, UF, NF, gas separation (GS), and biomedical applications, mainly since 2000, but recently more attention has been given to the modification of their surfaces to obtain desirable results. In particular, most emphasis has been given to plasma treatment, grafting of polymers on the surface, and modifying the surfaces by adding SMMs (surface-modifying molecules). New additives are synthesized to make the

polymeric membrane surfaces either to be more hydrophilic or hydrophobic, aimed at improvement in selectivity and permeability of the membranes for GS, NF, and RO. Improvement in antifouling by surface modification is also a popular topic in the membrane industries. In the last 8 years, tremendous research efforts have been made on the development of antifouling membranes. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 855–895, 2010

**Key words:** synthetic membrane; surface modification; filtration; liquid separation; water treatment; gas separation

## INTRODUCTION

At present the demand of membrane technology in the field of gas separation (GS), medicine, waste water treatment, production of drinking water by desalination, and other methods is increasing day-by-day. The use of synthetic materials in biomedical applications has increased dramatically during the past few decades.

Surface properties of polymers are of fundamental importance in many branches of industrial applications (e.g., separation of gasses, liquid mixtures, bonding, coating, adhesion, etc.). Performances of membranes also depend on the properties of their surfaces, since membrane may be considered as one of the surface phenomena. Hence, it is very natural that much attention has been paid to the membrane surface modification. Surface contamination which may lead to deterioration in membrane performance is also known to be governed by the membrane surface properties.

According to Zeman and Zydney,<sup>1</sup> almost 50% of all MF and UF membranes marketed by 1996 were surface modified. However, the additive used and procedures followed in commercial membrane manufacture are industrial secret. It is well known that,

in polymer blends, thermodynamic incompatibility usually causes demixing of polymers. Polymer blend surfaces have been studied by many different groups using theoretical calculations<sup>2–5</sup> and various surface-sensitive techniques, including X-ray photoelectron spectroscopy (XPS),<sup>6–8</sup> secondary ion mass spectroscopy (SIMS),<sup>5,6,9</sup> atomic force microscopy (AFM),<sup>6,7,9</sup> contact angle goniometry,<sup>10</sup> Sum-Frequency spectroscopy,<sup>11</sup> and neutron reflectivity.<sup>12</sup>

There are many articles that are related to membrane surface modification in the literature. Some of the examples are: Mittal<sup>13</sup> edited a book entitled "Polymer surface modification: relevance to adhesion." Kang and Zhang<sup>14</sup> in 2000 wrote a review on the surface modification of fluoropolymers via molecular design. Pinnau and Freeman<sup>15</sup> edited a book (Conference papers) named Membrane Formation and Modification in 2000. The chapters in this book are mainly related to novel membrane materials, membrane fabrication methods, and membrane modification techniques. Hilal et al.<sup>16</sup> wrote a review on the enhanced membrane pretreatment process using macromolecular adsorption and coagulation in desalination plants. Nunes and Peinemann<sup>17</sup> wrote an article on surface modification of membranes via chemical oxidation, plasma treatment, classical organic reactions, and polymer grafting. A review concerning the separation of liquid mixtures by pervaporation and vapor permeation was presented by Kujawski<sup>18</sup> in 2000. Li et al.<sup>19</sup> reported that the membrane morphology strongly depends on the

Correspondence to: K. C. Khulbe (khulbe@eng.uottawa.ca).

membrane thickness during the phase-inversion process of asymmetric membranes.

In his article with more than 400 references, Ulbricht<sup>20</sup> wrote a comprehensive overview on the development of polymeric membranes or novel functions in various membrane separation processes for liquid and gaseous mixtures (GS, RO, pervaporation, NF, UF, and MF) and in other important applications of membranes such as biomaterials, catalysis (including fuel cell systems), or lab-on-chip technologies. In his article, Ulbricht<sup>20</sup> discussed novel processing technologies of polymers for membranes, the synthesis of novel polymers with well-defined structure as “designed” membrane materials, advanced surface functionalization of membranes, the use of templates for creating “tailored” barrier or surface structures of membranes and preparation of composite membranes for the synergistic combination of different functions by different (mainly polymeric) materials, and the developments for the future of membrane technology.

Many of the surface modifications were done to improve the selectivity and permeability. Plasma treatment, grafting reaction, etc.,<sup>21</sup> were applied for this purpose.

For example, surface oxidation by plasma treatment (e.g., O<sub>2</sub> and water) improved the wettability of polymers such as polyethylene (PE), polysulfone (PSf), poly(methyl methacrylate), etc.<sup>22,23</sup> Many new methods have also been developed such as the introduction of active additives<sup>24,25</sup> and ion implantation on the surface, either physically or chemically. Hutchings et al.<sup>26</sup> wrote a mini-review entitled “Modifying and managing the surface properties of polymers” in which they demonstrated the possibilities of modifying the surface properties of polymers by the addition of relatively small quantities of multi end-functionalized polymers (26 references). In 2002, Ismail et al.<sup>27</sup> wrote an article entitled “Latest development of the membrane formation for GS” and have given the references in or before 2002. Wallac et al.<sup>28</sup> discussed the importance for developing first-generation asymmetric hollow-fiber GS membranes using small amounts of novel, experimental polymers. A case study using crosslinkable polyimide is discussed to illustrate the method.

The most important purpose of membrane surface treatment is, however, the improvement in fouling reduction, since in spite of its remarkable achievement, membrane separation technology suffers from a serious problem: the membrane fouling.<sup>29</sup> Membrane fouling is caused mainly by two following reasons.<sup>30–32</sup>

- i. Plugging the pore openings at the porous membrane surface by the suspended solid particles or large solutes in the feed.

- ii. The attachment of bacteria and subsequently colonization on the membrane surface (biofouling).

Generally, proteins are adsorbed more strongly at hydrophobic surfaces than hydrophilic surfaces.<sup>31,32</sup> Initial biofilm is achieved by bacteria attachment through exopolymer synthesis at the membrane surface, and this would be avoided if the membrane surface be hydrophilic in nature. Most of the hydrophilic UF membranes have fixed negative charges at the membrane surface; this negative surface charge prevents the negatively charged colloidal particles to settle on the membrane surface, and, therefore, it slows down the membrane fouling process.<sup>31</sup> The reduction in membrane fouling can be done by increasing the negative surface density of the membrane and the hydrophilic nature of the neutral membrane.

The membranes with the hydrophilic surface are less susceptible to fouling than hydrophobic membranes, whereas the ability to recover the performance upon washing is higher for the membrane with a chemically neutral surface than the charged membranes.

It was also reported that the susceptibility of membranes of microbiological fouling decreases with a decrease in the roughness of the membrane surface.<sup>33</sup> Thus, surface charge, hydrophilicity, and roughness were identified as three important factors that govern the membrane fouling, and attempts are made to control these factors by surface modification. It is well known that casting solvent affects the surface properties of the membrane.<sup>34</sup>

#### MODIFICATION OF POLYMERIC MEMBRANE SURFACES BY ADDITIVES

A number of factors have been noticed to affect surface composition of a homopolymer blend system. Clarke et al.,<sup>35</sup> studied poly( $\epsilon$ -caprolactone)/poly(vinyl chloride) (PCL/PVC) blends and found that the surface composition was dependent on molecular weight and degree of crystallinity. It was noticed that the surface behavior of poly(propylene oxide)/polystyrene (PPO/PS) blends was strongly dependent on the casting solvent used.<sup>36</sup> In fact, solvent-cast films may not be equilibrated thermodynamically due to the rapid solvent evaporation during the film formation process, and the resulting surface could be predominantly due to solvent effect.<sup>36</sup> PVC/PMMA {poly(methyl methacrylate)} blends were found that the surface was enriched with PMMA if blends were cast from tetrahydrofuran (THF), whereas surface composition was equivalent to bulk if blends were cast from

methylethylketone.<sup>37</sup> Moreover, it has been shown that the phase morphology depends on polymer molecular structure, composition, and the method of blend preparation. Surface morphology can also be influenced by a suitable choice of the substrate surface free energy.<sup>37</sup> The film surface segregation and morphology may also be modified by film thickness.<sup>6,38</sup> Moreover, annealing at a temperature higher than the glass transition temperatures ( $T_g$ ) of the polymer components of the blend films is believed to produce a different structure than that prepared at temperatures below the  $T_g$  of the polymer components.<sup>7,39,40</sup>

Wang et al.<sup>41</sup> modified the surface of phenolphthalein poly(ether sulfone) UF membranes by blending with acrylonitrile based copolymer containing ionic groups for imparting surface electrical properties.

It is hence interesting to use the phenomena of polymer demixing for the surface modification. In this context, the simplest method seems blending hydrophilic polyvinyl pyrrolidone (PVP) or poly(ethylene glycol) (PEG) into polysulfone (PSf) or polyethersulfone (PES) host polymers, which have been exercised for a long time for casting flat sheet (FS) membranes or hollow fibers, without knowing that the additives were indeed modifying the surface.

For example, Lafrenière et al.<sup>42</sup> made a thorough study of PVP blended PES membranes revealing the effect of PVP content on the pore size and pore size distribution. The highest product permeation rate was obtained at a PVP/PES weight ratio of unity when the PES concentration in the casting solution was 15–30 wt %.

It was later found by Miyano et al.<sup>43</sup> that PVP, although soluble in water, remained in the polysulfone (PSf) membrane for a long time under the UF operating conditions. As well, PVP molecules were more concentrated at the surface than in the bulk. Therefore, addition of PVP can make the surface of the membrane made of PSf or other polymers more hydrophilic. Much attention was paid therefore the surface properties of PVP blended PES or PSf membrane.

A small amount of PVP in the casting solution of PES resulted in an increase in permeability without significant changes in selectivity.<sup>44</sup> From AFM parameters it was concluded that the addition of PVP changed mainly the surface porous structure, along with little change in bulk parameters such as porosity, thickness, and/or tortuosity. These changes gave increasing permeability's without changing the manufacturing process. Hollow fibers subjected to removal of natural organic matter (NOM) prepared from PES/PVP exhibited a much lower fouling tendency than the commercial PSf membrane.<sup>45</sup>

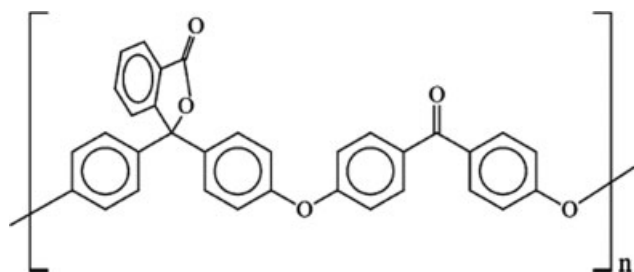
Xu and Xu<sup>46</sup> prepared PVC hollow-fiber UF membranes by using PVP or PEG with different molecular weight as additive and DMAc as a solvent. It was found that using PVP or PEG as additives can increase the membrane porosity and enhance the permeation flux by changing the membrane morphology.

Wang et al.<sup>47</sup> demonstrated asymmetric polyetherimide (PEI) hollow-fiber membrane (HFM) with high gas selectivity by introducing volatile organic compounds as additives into the dope. The additives used were methanol, acetone, a mixture of methanol/acetone, and THF. Asymmetric PEI HFMs with high He/N<sub>2</sub> separation ratio was prepared by using volatile nonsolvent additives and NMP as the solvent at a suitable length of the air gap. Wang et al.<sup>48</sup> prepared a highly permeable PES hollow-fiber GS membrane by using water as nonsolvent additive. Wang et al.<sup>49</sup> also prepared high-flux PSf hollow-fiber GS membranes by using *N*-methyl-2-pyrrolidone (NMP)/water and NMP/ethanol solvent system. The separation performance of the membranes prepared from the NMP/water solvent system was better than the membranes spun from NMP/ETOH solvent system. It was reported that proper selection of internal coagulant such as the mixture of water and C<sub>1</sub>–C<sub>3</sub> aliphatic alcohols could alter membrane structure with the maintenance of good permeability and selectivity.

Fu et al.<sup>50</sup> prepared polymer blend HFMs via thermally induced phase separation (TIPS). Poly(vinyl butyral) (PVB) and poly(ethylene-co-vinyl alcohol) (EVOH) were used as polymers, and the diluents was PEG. The addition of EVOH had an eminent effect on the HFM structure and membrane performance. With the increase of EVOH content in the polymer blend system, the membrane became more hydrophilic, and water permeability became higher due to the enlargement of the pores. The addition of EVOH was also effective to improve the mechanical property of HFM.

Hollow fibers prepared by dry-wet phase-inversion technique from modified poly(ether ether ketone) (PEEKWC)/DMAc or DMF solutions blended with PVP demonstrated that increasing the concentration of PVP in the spinning solvent led to an overall porosity reduction and suppression of macrovoids. PEEKWC is a modified poly(ether ether ketone) with a cardo group in the backbone (Fig. 1) (Scheme 1), having excellent chemical and mechanical properties.<sup>51</sup> In terms of the membrane performance, addition of PVP to the spinning solution resulted in a very steep increase of the dextran rejection (i.e., selectivity) with only a limited reduction of the water permeability. This phenomenon could be due to densification of the outer surface and also to the presence of residues of PVP in the final





**Figure 1** Modified poly(ether ether ketone) with a cardo group in the backbone.

membrane. The suppression of macrovoids and the reduction of the overall porosity lead to improvement of the mechanical properties of the HFMs. Such membranes may find application typically in the field of ultrafiltration.<sup>51</sup>

HFMs prepared from spinning solutions composed of polymer (PAN : PVDF = 10 : 0, 9 : 1, 7 : 3), additive (PVP, PEG 600) and solvent (DMAc) possessed much higher fluxes than PAN membrane and fairly good retention ratios especially for the membrane made by PAN: PVDF = 9 : 1.<sup>52</sup> It is believed that the membrane surface becomes more hydrophilic in the presence of the hydrophilic additives.

Yeow et al.<sup>53</sup> prepared a porous PVDF HFM via a phase-inversion method using lithium perchlorate ( $\text{LiClO}_4$ ) as an additive. The results from the gas permeation data revealed an increase in the mean pore size, coupled with a more uniform pore size distribution as the amount of  $\text{LiClO}_4$  added was increased from 1 to 3 wt %. An increase in coagulation temperature was found to be advantageous in the production of a network membrane pore structure with higher permeation performance with aid of a sufficient amount additive up to a certain limit.

Polyethylene glycol (PEG) additive in the PEI spinning dopes suppresses the growth of macrovoids and produces a membrane morphology having a more porous skin surface and more compact substructure, which provides a lower skin resistance and a higher substructure resistance for gas permeation.<sup>54</sup> Gas permeation data suggested that the skin layer resistance decreases while the substructure resistance increases with increasing the PEG content in the spinning dope. Although there are many evidences that PVP or PEG make the membrane surface more hydrophilic, the effects are temporally since they are water soluble and will eventually leach out from the membrane into the aqueous solutions.

An addition of pegylated polyethersulfone (PEG) (obtained via a reaction of chlorosulfonated PES with oligomeric PEG to PES/DMAc solution for the preparation of UF membranes showed superior resistance to bovine serum albumin (BSA) adsorption compared with the unmodified counterparts. Furthermore, UF experiments revealed that both

pegylated PES and sulfonated PES could enhance the permeation properties.<sup>55</sup>

The surface film properties of the homopolymers polystyrene (PS), PMMA, poly(butyl methacrylate) (PBMA), and the copolymer poly(methyl methacrylate)-*co*-poly(butyl methacrylate) (PMMA-*co*-PBMA), and their blends with PS were examined by AFM and contact angle measurement.<sup>56</sup> It was noticed that PBMA migrated to the air/film surface of the PS/PBMA film. In PS/PMMA-*co*-PBMA blend surfaces islands (nodules or nodule aggregates) were found by AFM. Those islands were composed of PS-rich phase, which was completely covered by an over-layer of the copolymer. The surface of the films prepared from PS/PMMA blends was found to be heterogeneous.

Yang et al.<sup>57</sup> prepared asymmetric annular HFMs by coextrusion of PES/PVP polymer blend and PVDF with a triple-orifice spinneret. The successful formation of annular HFM was due to the use of two partially immiscible polymer solutions and different shrinkage ratio of the two layers. Addition of a small amount of PVP increases not only the hydrophilicity and water flux of the outer layer but also changes the morphology of the outer layer of the annular HFM. With addition of PVP, the outer layer prepared showed a very open structure facing the annular gap.

Wu et al.<sup>58,59</sup> by using vacuum membrane distillation operation, removed volatile organic compounds (1,1,1-trichloroethane, benzene, toluene) from water through PVDF HFM module. PVDF HFMs with an asymmetric structure was prepared by the phase-inversion method using DMAc as solvent and  $\text{LiCl-H}_2\text{O}$  as additives.

Xu et al.<sup>60</sup> prepared UF HFMs from PEI with a wet-spinning method. Effects of DMAc as a solvent additive in internal coagulant and acetic acid as a nonsolvent additive in spinning dope on the morphologies and performances of the membranes were investigated, respectively. Addition of DMAc into the internal coagulant changed the inner fiber surface from dense skin layer to porous structure. However, the pure water flux of the membrane decreased with the increase of DMAc content. With the increase of acetic acid ratio into the casting solution, the pure water flux of the membrane increased about four times, and the solute retention showed slight decrease. The mechanical properties also improved slightly by this additive.

Ye et al.<sup>61</sup> fabricated cellulose acetate (CA) hollow fibers, subjected to hemopurification, by blending phospholipid polymer (PMB30). The structure and permeability of HFMs could be controlled by changing preparation conditions. The CA/PMB30-blend HFMs had good permeability, low protein adsorption, and low-fouling property during the

permeability experiment in comparison with unblended CA HFMs, because the hydrophilic and hemo-compatible copolymer (PMB30) existed on the HFM surface.

Polyacrylonitrile-*graft*-poly(ethylene oxide) (PAN-*g*-PEO), an amphiphilic comb copolymer with a water insoluble PAN backbone and hydrophilic PEO side chains, was used as an additive in the manufacture of novel PAN UF membranes.<sup>62</sup> This PAN UF membrane showed complete resistance against irreversible fouling by BSA, sodium alginate, and humic acid at 1 g/L.

Polymeric additives carrying multiple fluoroalkyl groups prepared by both atom transfer radical polymerization (ATRP) and lactide by ring-opening polymerization (ROP), have been shown to be highly surface active and in some cases 0.2% by weight of additive is required near PTFE (1 poly(tetrafluoroethylene) or poly(tetrafluoroethylene)-like surface properties.<sup>26</sup>

To make the modified surface properties more permanent, surface-modifying macromolecules (SMMs) were developed. SMM has an amphiphatic structure consisting theoretically of a main polyurethane chain terminated with two low polarity polymer chains (i.e., fluorine segments) (Fig. 2).<sup>63</sup>

Because of the low polarity and high hydrophobicity of the fluorine segments, this type of SMM is called hydrophobic surface modification molecule (BSMM). When BSMM is added to a solution of a more hydrophilic host polymer, for example, PSf or PES, and a solution film is cast, BSMM will migrate to the air/solution interface to reduce the system's surface tension (Fig. 3).<sup>63</sup> The migration of BSMM onto surface was confirmed by the change of contact angle and surface fluorine content as a function of evaporation time<sup>64</sup> (Figs. 4 and 5). The preferential adsorption of a polymer of lower surface tension at the surface was confirmed by a number of researchers for a miscible blend of two different polymers,<sup>65,66</sup> as well.

Later, hydrophilic SMMs (LSMM) and charged SMMs (CSMM) were developed by replacing the fluorocarbon end caps of BSMM with polyols. One of a typical BSMM's structures is shown in Figure 6.<sup>65</sup>

Depending on whether SMM is BSMM or LMSS, the membrane surface becomes either more hydrophobic or more hydrophilic than the host polymer.<sup>24,63,66</sup>

One of the most important features of SMMs is, however, that the central polyurethane part is miscible with the host PSf or PES polymer and holds the SMM secure to the membrane surface. Thus, SMMs stay at the membrane surface semipermanently.<sup>63,67,68</sup>

Several works of surface modification by SMMs are highlighted below.

Pham et al.<sup>68</sup> blended eight types of BSMMs into PES membranes and characterized the membranes

for surface and physical properties. The BSMMs were synthesized with a diisocyanate, polypropylene oxide (PPO), and a fluoro alcohol as the reactants. Water droplet contact angle measurements and X-ray photoelectron spectroscopy data revealed that BSMMs migrated to the surface and rendered the PES material more hydrophobic. Although advancing contact angle data were equivalent to those of pure Teflon<sup>TM</sup>, the highest average values of receding angles of these systems were less than those of commercial Teflon<sup>TM</sup>. The opaqueness of PES/BSMMs films and data from differential scanning calorimetric experiments showed that the BSMMs were either immiscible or only partially miscible with PES.<sup>69</sup>

The modified PES/BSMMs UF membranes had a superior performance, reflected in their higher flux when treating oil/water emulsions, than the control unmodified membrane.<sup>69</sup> Both the mean pore size and pore size distribution and MWCO of the BSMM-modified membranes were lower than those of the corresponding unmodified ones.<sup>70</sup> Membrane fouling tests with humic acid as the foulant indicated that the permeate flux reduction of the BSMM-modified membranes was much less than that of the unmodified ones. In pervaporation, PES-BSMM membranes showed that it is water selective as a significant depletion of chloroform in the permeate was observed.<sup>70</sup>

Suk et al.<sup>63</sup> studied the kinetics of surface migration of surface-modifying macromolecules in membrane (subjected to UF) preparation. BSMMs were blended into the casting solution of PSf. The cast films were placed in an oven with a forced air circulation for 3–2000 min range to remove the solvent before being immersed in water at 4°C for gelation. According to the XPS analysis, after an initial time lag the surface fluorine content increased as the evaporation time increased and finally leveled off. During the process of casting the polymer solution into a film and the removal of solvent by evaporation, BSMMs migrate to the membrane surface, rendering the surface of the membrane ultimately obtained more hydrophobic than the bulk membrane.

Similar migration of BSMMs toward the surface of the membrane is reported in the PEI/BSMMs, and PES/BSMMs membrane preparation.<sup>25,71,72</sup> On evaporation of the modified membranes, it was noticed that more of BSMMs migrated toward the membrane surface as the evaporation time increased.

The mean pore size and the MWCO of the BSMM-modified PEI membranes were lower than those corresponding to the unmodified membranes, whereas the sizes of the macromolecular nodules observed by AFM were larger. The membrane surface became

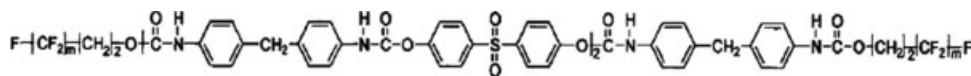


Figure 2 Molecular structure of a hydrophobic BSMM.<sup>63</sup>

smoother by the addition of the BSMM in the PEI polymer casting solution and with an increase in the PEI polymer concentration. The mean roughness of the unmodified membrane was higher than that of the PEI/BSMM membranes and decreased as the solvent evaporation time increased. The reduction in surface roughness may be attributed in part to the reduction of the pore size due to migration of BSMM toward the PEI membrane surface.<sup>71</sup>

Modified with LSMMs, PES membranes were used for water treatment (concentrated Ottawa River water). The addition of LSMM significantly affected the membrane performance.<sup>66</sup> TOC removal was higher when compared with the results reported in the literature for UF membranes. Mosqueda-Jimenez et al.<sup>73</sup> modified the PES UF membranes by adjusting three membrane manufacturing variables: addition of LSMMs, the solvent evaporation time and PES concentration in casting solution. The impact of membrane surface modification with hydrophilic LSMMs was not as high as expected. The performance of these membranes was exceptionally good in terms of NOM (natural organic matter) removal, and their permeate flux was within the range of tight commercial membranes. The use of 18 wt % PES and PPOX (LSMM synthesized using polypropylene diol as polyol) in the casting solution proved to be the most suitable combination of manufacturing conditions to maximize the TOC (total organic carbon) removal and final flux, and to minimize fouling.<sup>66</sup>

It was reported that LSMM blended membrane showed higher fouling resistance and long-term stability than the PES membrane without LSMM.<sup>70</sup> However, Nguyen et al.<sup>74</sup> studied PES/UF membranes modified by three different tailor-made

hydrophilic surface-modifying macromolecules, and reported that no clear correlation between membrane hydrophilicity and fouling reduction was observed.

Khulbe et al.<sup>75</sup> modified the surfaces of hollow fibers prepared at different air gaps, by adding SMM to the dope (PES in DMAc). From the AFM, XPS, and UF results, it was observed that the membranes could be put into two groups: i) the membranes fabricated between 10 and 10 cm air gap and ii) fabricated at higher than 50 cm air gap.

Suk et al.<sup>76</sup> designed and synthesized a new type of surface-modifying macromolecules (nSMM) by incorporating polydimethylsiloxane (PDMS) component in its structure. Membranes of nSMM+PES were prepared with different compositions, evaporation temperature and evaporation period. It was reported that nSMM migrated to the surface and effectively increased the surface hydrophobicity of PES membrane when blended. The cast film was kept at room temperature for a designated period before immersion in water. Figure 7 shows that the contact angle decreased as the evaporation period increased. The hydrophobicity of nSMM blended PES membranes changed depending on the conditions of membrane preparation.

Barsema et al.<sup>77</sup> reported the preparation and characterization of highly selective dense and hollow-fiber asymmetric membranes based on BTDA-TDI/MDI copolyimide. The copolyimide BTDA-TDI/MDI is a commercial polymer produced by Lenzing with the trade name P84. P84 copolyimide proved to be one of the most selective glassy polymers. Figure 8 shows the ideal selectivity factors for He, CO<sub>2</sub>, and O<sub>2</sub> over N<sub>2</sub> vs. the temperature for dense P84 membranes at 4 bar.

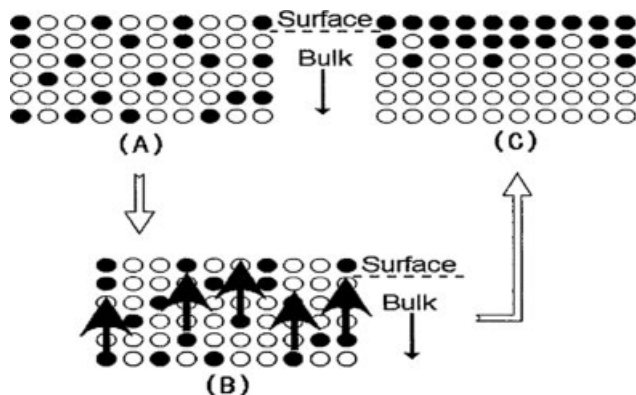


Figure 3 Schematic diagram illustrating BSMM migration: • BSMM; ○ host polymer (PSf, PES) Case A: time zero; Case B: time in between; Case C: time infinite.<sup>63</sup>

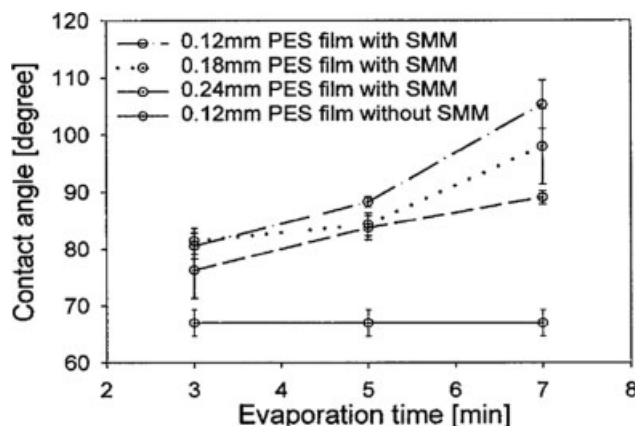
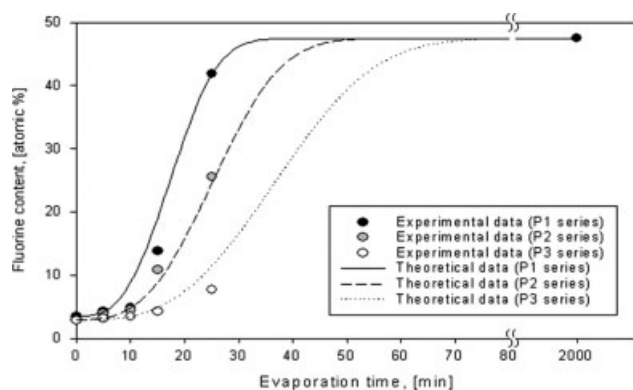


Figure 4 Contact angle versus evaporation time.<sup>63</sup>





**Figure 5** Surface fluorine content versus evaporation time.<sup>64</sup>

The achieved ideal selectivity coefficients are 285–300 for  $\text{He}/\text{N}_2$ , 45–50 for  $\text{CO}_2/\text{N}_2$ , and 8.3–10 for  $\text{O}_2/\text{N}_2$ , which are in the range of the highest values reported ever for polymeric membranes. Thus, P84 copolyimide is a promising material for the preparation of GS membranes with extremely high selective coefficients.

Kapantaidakis et al.<sup>78,79</sup> prepared and characterized the GS membranes based on PES Sumikaexcel (PES) and polyimide Matrimid 5238(PI) blend and suggested that PES/PI hollow fibers as excellent candidate membranes for the separation of gaseous mixtures in industrial level.

Kazama and Sakashita<sup>80</sup> prepared asymmetric HFMs from a cardo polyamide by using a wet phase-inversion process. Polymer dope contained the cardo polyamide (20 wt parts), LiCl (5 wt parts) and NMP (100 wt parts), and coagulant was water both for bore fluid and the coagulation bath. The membrane showed the selectivity of oxygen over nitrogen of 6.0, which was similar to that of a dense film, and oxygen permeation rate of  $12 \times 10^{-6} \text{ cm}^3 (\text{STP})/(\text{cm}^2 \text{ s cmHg})$  (12 GPU and  $9.0 \times 10^{-11} \text{ m}^3/\text{m}^2 \text{ s Pa}$ ) at  $25^\circ\text{C}$ . The membrane was stable up to  $240^\circ\text{C}$  with an  $\text{O}_2/\text{N}_2$  selectivity of 2.3. It was observed that the cardo polyamide HFM had the skin layer at the inside surface, whereas it was porous on the outside surface.

Kwak et al.<sup>81</sup> explored the role of dimethyl sulfoxide (DMSO) used as an additive to modify the morphological as well as the molecular nature of aromatic polyamide during the formation of thin-film-composite (TFC) membranes. DMSO enhanced the flux in RO. The combined results of AFM, XPS

and solid-state NMR provided a robust explanation for the mechanism of flux enhancement of the aromatic polyamide.

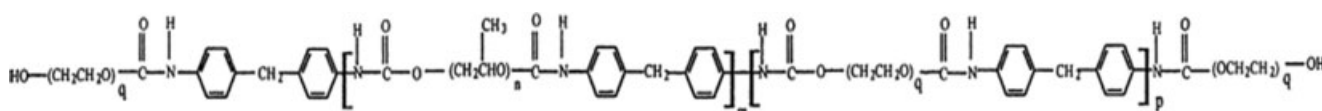
It is well known that PS dialysis membranes hydrophilized by blending PVP have excellent biocompatibility in clinical use. Hayama et al.<sup>82</sup> clarified how PVP improves biocompatibility of PS membranes.

Khayet et al.<sup>83</sup> studied the effect of concentration of ethylene glycol (EG) in the PVDF spinning solution as well as the effect of ethanol either in the internal or the external coagulant on the morphology of the hollow fibers subjected to UF. Pore sizes increased as the concentration of EG in the spinning solution increased and when ethanol was added to either the internal or the external coagulant or both. The effective porosity decreased with the addition of ethanol in either the bore liquid or in the coagulation bath or both. Similar effect was observed on the surface porosity.

Espinoza-Gomez and Lin<sup>84</sup> prepared negatively charged hydrophilic UF membranes from acrylonitrile-vinyl acetate (CP16)/acrylonitrile-vinyl acetate-sodium *p*-sulfophenylmethallyl ether (CP24). It was demonstrated by them that the basic characteristics of CP16/CP24 membranes like water content, “A-value,” molecular weight cut-off, surface hydrophilicity, surface charge density, and surface roughness can be altered by addition of the desired copolymer in the membrane casting solution.

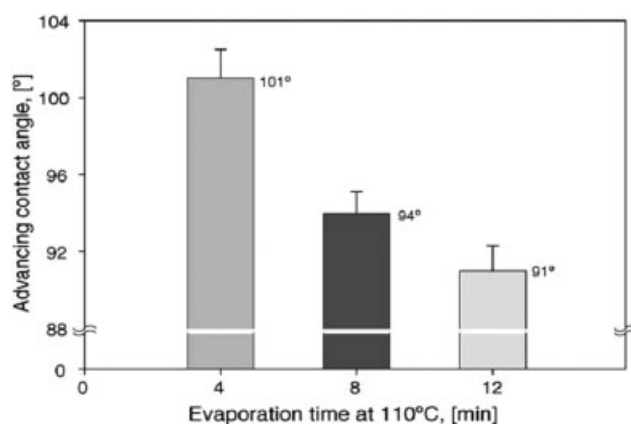
Qiu and Pinemann<sup>85</sup> reported that on adding small amount of organic filler trimethylsilyl glucose (TMSG) into glassy polymers affects the gas-transport through the membrane. With poly(trimethylsilyl-propyne) (PTMSP) the permeability of gasses ( $\text{He}$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ ) decreased, whereas strong increase in permeability observed when TMSG was added to the ethyl cellulose.

Zeolite particles were incorporated into polyetherimide (PEI, Ultem). Zeolites with hydrophilic surfaces, however, do not interact well with the hydrophobic polymer used in fiber spinning. This requires that the surface of the zeolite particles be modified to change the level of interaction between polymer and zeolite. In the modified zeolite, surface hydrophobicity was increased by capping surface hydroxyls with hydrophobic organic molecules. Husain and Koros<sup>86</sup> modified the zeolite surface by treating zeolite with Grignard reagent (zeolite was first treated with a mixture of toluene and thionyl chloride and



**Figure 6** Molecular structure of a hydrophilic SMM.<sup>65</sup>





**Figure 7** Contact angle vs. evaporation time. Evaporation temperature, 100°C; Composition of casting solution, PES/nSMM1/NMP = 15/0.9/84.1.<sup>76</sup>

then with methyl magnesium bromide) to increase the hydrophobicity of the zeolite surface. Modified zeolite was mixed with Ultem<sup>®</sup> 1000 PEI in a solvent mixture of NMP and THF and then the hollow fibers were spun via dry-jet-wet quench procedure. Hollow fibers incorporating Grignard treated zeolite showed a selectivity enhancement of 10, 29, and 17% for O<sub>2</sub>/N<sub>2</sub>, He/N<sub>2</sub>, and CO/CH<sub>4</sub> pure gas pairs, respectively, 25% for mixed gas CO<sub>2</sub>/CH<sub>4</sub> when compared with nonzeolite hollow fibers.

Chung et al.<sup>87</sup> blended a series of a benzylamine-modified fullerene, C<sub>60</sub> with pure Matrimid 5218. Gas permeabilities of He, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> showed a monotonous decrease with increasing benzylamine-modified C<sub>60</sub> content. The selectivity for He/N<sub>2</sub> increased, whereas the selectivity for O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> remained unchanged. Therefore, the inclusion of benzylamine-modified fullerene as the mixed matrix phase in Matrimid seems to be more favorable in the separation of He/N<sub>2</sub>.

Yoshino et al.<sup>88</sup> studied the gas permeation properties of asymmetric HFM of copolyimide prepared from equimolecular portion of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) with 3,7-diamino-2,8(6)-dimethyldibenzothiophene sulfone (DDBT) for single component light gasses, olefins and paraffins and for mixed components of C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>6</sub>/C<sub>4</sub>H<sub>10</sub>. The gas permeability of the copolyimidefilm was close to that of 6FDA-DDBT polyimide and much larger than that of BPDA-DDBT. Gas permeance of the asymmetric copolyimide HFMs decreased significantly in the first several months and leveled off after about 10 months of aging. The skin layer thickness calculated from the gas permeability and permeance was in the range of 0.6 (for H<sub>2</sub>) to 1.7 μm (for C<sub>3</sub>H<sub>6</sub>) and about 10 times larger than the thickness estimated from the SEM data. These results indicated that the signif-

icant densification of the skin layer was caused by physical aging. The silicone rubber coating hardly changed the selectivity for light gas pairs such as H<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub>, but enhanced that for C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>6</sub>/C<sub>4</sub>H<sub>10</sub> significantly at low temperatures.

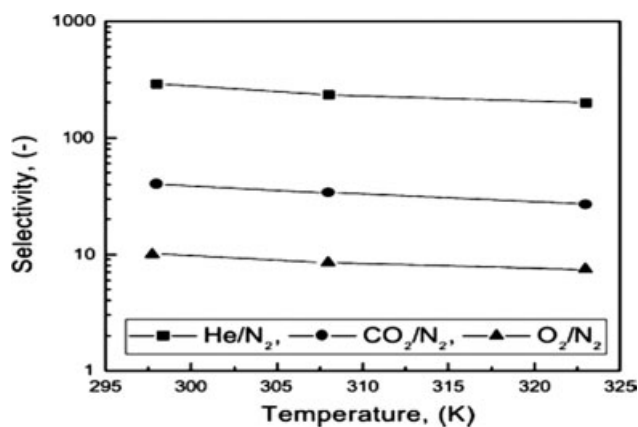
Ye et al.<sup>89</sup> prepared CA HFMs modified with poly(2-methacryloyloxyethyl phosphorylcholine (MPC)-*co-n*-butyl methacrylate) (PMB30 and PMB80) by the dry-jet wet-spinning process. It was claimed that these membranes have high potential for application in high performance plasmaphoresis and hemofilter device because of their good permeability and hemocompatibility.

The surface modifications reported in this section are summarized in Table I.

## COATING

The membrane surface can be modified by contacting the surface of one side of the polymeric (A) membrane with a solution of a different polymer (B). A thin layer of polymer (B) is left on top of the membrane of polymer (A) after solvent evaporation. Some post-treatment can also be applied. The following reports are based on these techniques.

The Hilal School<sup>93</sup> investigated the surface structure of molecularly imprinted (MIP) PES (UF) membrane by AFM. Molecularly imprinted polymeric membranes were developed using photoinitiated copolymerization of 2-hydroxyethyl methacrylate (HEMA) as functional monomer and trimethylpropane trimethacrylate as crosslinker in presence of adenosine 3'/5'-cyclic monophosphate as template, followed by deposition of a MIP layer on the surface of PES microfiltration membranes. For producing the MIP layer, membranes were coated with photo initiator by soaking in a 0.25 M solution of benzoin ethyl ether/methanol and then immersing in a



**Figure 8** Ideal selectivity factors for He, CO<sub>2</sub>, and O<sub>2</sub> over N<sub>2</sub> vs. the temperature for dense P84 membranes at 4 bar.

**TABLE I**  
**Surface Modification by Additives and SMMs**

Membrane		Additive	Reference	
Polyethersulfone	Flat sheet (FS)	PVP	UF	42
Polyethersulfone	FS	PVP	UF	43
Polyethersulfone	FS	PVP	UF	44
Polyetheretherketone modified	Hollow fibere	PVP	UF (transport properties)	51
Polyacrylonitrile/polyvinylidene fluoride	Hollow fiber	PVP, PEG	UF	52
PAN	FS	PAN-g-PEO	UF	62
PVP/PEI	Hollow fiber	PEG	GS	54
Polyethersulfone	FS	BSMM	PV	68
Polyethersulfone	FS	BSMMs	UF	69
			PV	70
			UF	90
Polyethersulfone	FS	BSMMs	UF	72
Polysulfone	FS	BSMMs	UF	63
Polyetherimide	FS	BSMMs	UF	71,91
Polyethersulfone	FS	LSMMs	UF	73,74
Polyethersulfone	FS	Pegylated polyethersulfone (PEG)	Antifouling UF	55
Polystyrene	FS	PMMA, PBMA, PMMA-co-PBMA	UF	56
Cellulose acetate	Hollow fiber	PMB	Hemofilter	61
CP-16	FS	CP-24	UF	84
Glassy polymer	FS	TMSG	GS	85
PEI	Hollow fiber	Zeolite particles	GS	86
Matrimid	FS	Benzylamine-modified fullerene, C <sub>60</sub>	GS	87
PVC	Hollow fiber	PVP or PEG	UF	46
PEI	Hollow fiber	Volatile organic compounds	GS	47
PEG	Hollow fiber	PVB or EVOH	UF	50
PVDF	Hollow fiber	LiClO <sub>4</sub>	UF	56
PESf	Hollow fiber	PVP	Bioreactor	57
PVDF		PEG		
PVDF	Hollow fiber	LiCl-H <sub>2</sub> O	MD	58,59
PVDF	Hollow fiber	PVP, LiCl, organic acids	Removal of H <sub>2</sub> S and SO <sub>2</sub> from waste gas stream	92
PEI	Hollow fiber	DMAC (internal coagulant)	UF	60
6FDA/BPDA	Hollow fiber	DDBT	GS	88
PES	Hollow fiber	SMM	UF	75
PES	Hollow fiber	Polyimide (Matrimid)	GS	78,79
Cardo polyimide	Hollow fiber	LiCl	GS	80
Aromatic polyamide	FS	DMSO	RO	81
PVDF	Hollow fiber	EG	UF	83
PEI	FS	Zeolite particles and treated with Grignard reagent	GS	86
Matrimid	FS	Benzylamine-modified fullerene	GS	87
CA	Hollow fiber	MPC and PMB30, PMB80	Hemofilter	89

solution of 80 mM TRIM (trimethylpropane trimethacrylate), 40 mM HEMA, and 2 mM Adenosine 3', 5'-cyclic monophosphate (cAMP) (adenosine 3'/0.5'-cyclic monophosphate) in an ethanol water mixture (70 : 30 vol %). Thereafter, samples were exposed to B-100 lamp of relative radiation intensity 21.7 mW cm<sup>-2</sup> at 355 nm. Membranes with different modification were obtained using various UV exposure time. AFM images of these membranes revealed that a consistent increase in the degree of modification led to a systematic decrease in pore size and an increase in surface roughness. The AFM characteristics of

imprinted membranes were in good correlation with the filtration data.

PES UF membrane surface was modified by self-assembly of TiO<sub>2</sub> nanoparticles (40 nm or less) via dip coating. The neat PES membrane was dipped in the transparent TiO<sub>2</sub> colloidal solution, stirred for 1 minute by ultrasonic method and placed for 1 h to deposit TiO<sub>2</sub> nanoparticles. The contact angle test of the composite membrane showed that the hydrophilicity of the membrane surface improved remarkably. The fouling experiment verified a substantial prevention of the dip-coated membrane against the

fouling by hydrophobic substances, suggesting a possible use as a new type of antifouling composite membrane.<sup>94</sup>

The performances for CO<sub>2</sub> separation of membranes prepared from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA)-based polyimides with a polar group of hydroxyl or carboxyl such as 6FDA-BAPAF {2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane}, 6FDA-DAP (2,4-diaminophenyl dihydroxychloride), and 6FDA-DABA (3,4-diaminobenzoic acid) were studied. The corresponding composite membranes were then prepared by the dip coating using a poly(ether sulfone) (PES) membrane as a supporting layer. CO<sub>2</sub> permeances of these composite membranes were measured in comparison with those for other gasses such as H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>. The membrane performances were affected considerably by the preparation conditions such as the kinds of diamine moiety, coating solvent, and coating polymer concentration. CO<sub>2</sub> permeances were obtained in the range of 20–38 GPU depending on the preparation condition, and the selectivities for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation were good enough compared with other dense or asymmetric 6FDA-based polyimide membranes.<sup>95</sup>

Basheer et al.<sup>96</sup> synthesized amphiphilic polyhydroxylated polyparaphenylene (PH-PPP) and coated on the surface of a porous polypropylene HFM. The polymer coated HFM was used for the extraction of 15 organic chlorine pesticides (OCPs) from water, and the extraction efficiency was compared with emerging and established methods such as liquid-phase microextraction (LPME), solid-phase microextraction (SPME), and stir bar sorptive extraction (SBSE) techniques. It was noticed that the polymer coated hollow fiber showed good selectivity and sensitivity. The sensitivity and selectivity of the coated HFM could be adjusted by changing the characteristics of the coated PH-PPP film.

The HFM surface coating was also attempted by spinning dual-layer hollow fibers. There are new techniques to coat the hollow fiber's inner surface. Widjojo et al.<sup>97</sup> coated aluminum oxide nanoparticles in the inner layer of Ultem/P84 copolyimide hollow fiber. dual-layer Ultem/P84 copolyimide HFMs with various morphologies by using dual coagulation baths and different spinneret designs have been reported. It was observed that dual-layer HFMs spun with a longer air-gap showed a larger size closed-cell structure compared with those spun at a shorter air gap. Delamination-free dual-layer HFMs can be obtained by two approaches: (i) incorporating aluminum oxide particles into the inner layer followed by heat treatment; (ii) introducing an early convective premixing with the aid of an indented and heated dual-layer spinneret. The first method reduced the degree of shrinkage of the inner layer

during the heat treatment and thus lowered the heat-treatment temperature to mitigate the delamination, whereas the second method eliminated delamination during the spinning process without any post-treatment.<sup>97</sup>

The substructure resistance of copoly(4,4'-diphenyleneoxide/1,5-naphthalene-2-2'-bis(3-4-dicarboxyphenyl)hexafluoropropane diimide (6FDA-ODA-NDA)/PSf dual-layer HFMs subjected to GS can be reduced by the addition of Al<sub>2</sub>O<sub>3</sub> nanoparticles in the inner layer dope solution. A combination of the incorporation of Al<sub>2</sub>O<sub>3</sub> nanoparticles in the inner layer dope solution with an indented dual-layer spinneret was the preferred method to effectively minimize the substructure resistance as well as to enhance membrane separation performance.<sup>98</sup>

Zhen et al.<sup>99</sup> prepared polydimethylsiloxane-PVDF (PDMS-PVDF) composite membranes subjected to vapor permeation using asymmetric PVDF HFMs as the substrate where a very thin layer of silicone-based coating material was deposited via a developed dip-coating method. In the optimal coating procedure, homogeneous and stable oligo-PDMS coating layers as thin as 1–2 μm were successfully deposited on the surface of PVDF membrane. The developed PDMS-PVDF composite membranes were applied for separation of a wide variety of volatile organic compounds (benzene, chloroform, acetone, ethyl acetate, and toluene). The results showed that the PDMS-PVDF hollow-fiber composite membranes that had been developed exhibited very high removal efficiency (>90%) for all the VOCs examined under favorable operating conditions.

Hamad et al.<sup>100</sup> reported the composite membranes, prepared by coating PPO on top of a 12 kDa MWCO UF membrane (Osmonics-HO51), enhanced the gas permeability ratio and separation for CO<sub>2</sub>/CH<sub>4</sub> gas system. However, permeability of CO<sub>2</sub> gas decreased in comparison to the dense homogeneous PPO membrane. Average permeability ratio, CO<sub>2</sub>/CH<sub>4</sub> being reported 37 for composite membranes, and 17 for homogeneous membranes. The CO<sub>2</sub> permeability obtained for composite and homogeneous membranes were 80 and 92 Barrer, respectively.

Divinyl-polydimethylsiloxane (divinyl-PDMS) layer with the thickness of a few microns was successfully coated on a PVDF HFM by Yeow et al.<sup>101</sup> The coating thickness was approximately 5–7 μm. The ability of the divinyl-PDMS/DVDF composite membrane in selectivity separating the BTX (benzene, toluene, and xylene) from nitrogen was clearly demonstrated with recovery greater than 95%.

Song et al.<sup>102</sup> used hydrophobic PP hollow fibers with a porous fluoro-silicone coating on the outside surface for the direct contact membrane distillation (DCMD)-based desalination. As the brine temperature was increased from 40 to 90°C, water-vapor

**TABLE II**  
**Surface Modification by Coating (Composite Membranes)**

Membrane		Coated material	Application	Reference
Polyethersulfone	FS	MIP layer	UF	93
Polyethersulfone	FS	TiO <sub>2</sub> nano-particle	UF	94
Polyethersulfone	FS	6FDA based polyimide	GS	95
Polypropylene	Hollow fiber	Polyhydroxylated polyparaphenylene	Filtration, LPME, SBSE	96
Utem/P84 copolyimide (dual-layer hollow fiber)	Hollow fiber	Al <sub>2</sub> O <sub>3</sub>	GS	97
6FDA-ODA-NDA/ Polysulfone (dual-layer hollow fiber)	Hollow fiber	Al <sub>2</sub> O <sub>3</sub> particles in the inner layer	GS	98
PVDF (composite membrane)	Hollow fiber	PDMS	VP (Separation of VOCs)	99
Osmonic-HO51 UF	FS	PPO	GS	100
PVDF hollow fiber	Hollow fiber	Divinyl-PDMS	VP	101
PP	Hollow fiber	fluorosilicone	DCMD	102

flux increased almost exponentially. Increasing the distillate temperature to 60 from 32°C yielded reasonable fluxes. The surface modification works by coating are summarized in Table II.

#### INTERFACIAL POLYMERIZATION/ COPOLYMERIZATION

When reactive monomers are dissolved in two different solvent phases and these two phases are brought into contact, rapid reaction occurs only at the interface between the two phases, creating a thin polymer film. This is a technique well established for the fabrication of RO and NF membrane. Some of recent studies are for the through understanding of this technique and also the application of the technique for fouling reduction.

Nano filtration (NF) composite membranes were prepared by the interfacial polymerization (IP) technique. The membrane support was made from a mixture of polysulfone (PSf) and PVP. The top active layer was obtained through IP between trimesoyl chlorides (TMC) in hexane with aqueous phase containing bisphenol.<sup>103</sup> The variation of reaction time as well as monomer concentrations could affect the properties of the membrane produced. Increasing the reaction time resulted in decreasing water permeabilities. However, based on AFM data, the pore sizes were of similar values. Increasing the monomer concentration also resulted in decreasing water permeabilities. Based on AFM imaging the pore sizes differed considerably.

Zhang et al.<sup>104</sup> prepared composite NF membranes subjected to concentration of antibiotics, by IP of piperazine and trimesoyl chloride. Some of the membranes were coated with a thin layer of PVA. The base support material was PSf UF membranes. The coated surfaces were found to be smoother and more hydrophilic, which could reduce membrane

fouling. The experimental results showed that the nano filtration was effective in concentrating antibiotics with proper molecular mass.

Chu et al.<sup>105</sup> reported a simple and effective route for the hydrophilic surface modification of ceramic-supported PES membranes by synthesizing a poly (vinyl alcohol)/polyamide composite thin surface layer with an IP method. The fabricated membranes were characterized with XPS, SEM, and contact angle measurements, and the effects of hydrophilic surface modification on the membrane flux and oil rejection in the treatment of oil-in-water (O/W) microemulsions were experimentally studied. All the characterizations and filtration results showed that, the hydrophilic surface modification was achieved successfully and consequently reduced the membrane fouling effectively. The route of modification presented by Chu et al.<sup>104</sup> is valuable for developing robust membranes with a low level of membrane fouling in the separation of Oil/Water microemulsions.

Susanto et al.<sup>106</sup> prepared low-fouling UF membranes by simultaneous photograft copolymerization of PEG methacrylate (PEGMA) onto a PES UF membrane with a nominal cut-off of 50 kg/mol. The effects of UV irradiation and monomer concentration on membrane characteristics as well as performance were studied. The results showed that UV irradiation time was the most important parameter to adjust the degree of functionalization. All modified membranes showed more resistance to fouling and higher rejection than unmodified membrane for both BSA solution and sugarcane juice. This study provides valuable information for the development of low-fouling UF membranes for sugarcane juice clarification.

Kim and Lee<sup>107</sup> fabricated organic inorganic hybrids of poly(amide-6-b-ethylene oxide) (PEBAX<sup>®</sup>) and silica via *in situ* polymerization of tetraethoxysilane (TEOS)



**TABLE III**  
**Surface Modification by Interfacial Polymerization**

Membrane	Membrane type	Surface layer	Application	Reference
PSf and PVP mixture	FS	Polyester	NF	103
PSf UF	FS	Polyvinyl alcohol	NF	104
Ceramic-supported polyethersulfone	FS	Poly(vinyl alcohol) polyamide	Oil/water microemulsions	105
PES UF	FS	PEGMA	UF	106
PEBAX <sup>®</sup>	FS	TEOS	GS	107
SPES and PVDF	FS	BPA, amine/piperzine	NF	108

using the sol-gel process, and their gas-transport properties were studied. Gas permeation measurements were accomplished at various temperatures with He, CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>. These hybrid membranes exhibited higher gas permeability coefficients and permselectivities than PEBAX<sup>®</sup>, particularly at an elevated temperature.

Lu et al.<sup>108</sup> reported high performance NF membranes prepared by IP, using UF membranes (SPES and PVDF UF membranes). Bisphenol-A (BPA) and iso-phthaloyl chloride, amine, and/or piperazine were used to form three reaction systems for IP. The results showed that NF series membranes all exhibited high rejection of electrolytes including divalent ions. The works reported in this section are summarized in Table III.

### PLASMA TREATMENT

Plasma polymerization process is a technique that allows us to obtain highly crosslinked polymers from nonfunctional monomers that are not utilized in conventional polymer synthesis. Plasma surface modification can improve biocompatibility and biofunctionality. In the plasma surface modification process, glow-discharge plasma is created by evacuating a plasma reactor, usually made of quartz because of its inertness, and then refilling it with a low pressure gas. The gas is then energized using techniques such as radio-frequency energy, microwaves, alternating current, or direct current. The energetic species in gas plasma include ions, electrons, radicals, metastables, and photons in the shortwave ultraviolet (UV) range. When membrane surfaces are brought into contact with gas plasmas the surfaces are bombarded by these energetic species, and their energy is transferred from the plasma to the solid. As a result, the surface of the membrane is etched leaving many reactive sites (mostly radicals) on the surface. When an organic vapor or a monomer is introduced into the plasma reactor, polymerization takes place at the reactive sites. This is called plasma polymerization.

Plasma polymers were prepared from three different organosilicon monomers: diethoxydimethyl silane, hexamethyldisiloxane (HMDSO), and octamethyltrisilox-

ane (OMTSO). Films were deposited upon silicon wafers and different porous substrates. Silicon-containing polymers are well known as polymers excelling in gas permeation. When they are synthesized by the plasma process, they also exhibit high selectivities because of high cross-linking compared with conventional polymers.<sup>109</sup> Roualdes et al.<sup>109</sup> studied the gas (N<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>) separation properties of organosilicon plasma polymerized membranes.

Acrylamide (AAm)-plasma graft-aromatic polyamide (AAm-*p*-aramide) membrane was prepared by plasma polymerization. The membrane was subjected to pervaporation (water/ethanol mixtures).<sup>110</sup> The effects of degree of grafting, feed composition, feed temperature, and surface properties on the pervaporation performances were studied. The separation factor and permeation rate of AAm-*p*-aramide membranes were higher than those of the unmodified aramide membrane. Optimum pervaporation was obtained by a AAm-*p*-aramide membrane with a degree of grafting of 20.5% for a 90 wt % ethanol feed concentration, giving a separation factor of 200 and permeation rate of 325 g/m<sup>2</sup> h.

A commercial PSf membrane was modified by grafting a positively-charged polymer onto it using low plasma treatment.<sup>111</sup> The effects of the plasma treatment time, plasma generating power, and polymerization time on the pore structure, chemical composition, and  $\zeta$ -potential of the membrane surface were examined. The static adsorption of BSA and lysozyme on a DMAEMA {2-(dimethylamino) ethyl methacrylate}- or C<sub>4</sub> monomer- modified HT (commercial hydrophilic PSf membrane) and filtration of BSA through an acrylic acid modified HT membrane showed that the enhancement of the repulsive electrostatic force was effective in reducing protein adsorption on the membrane surface. The results show the role of electrostatic forces in membrane fouling and can be used to guide membrane synthesis and membrane surface modification.

Cyclohexane plasma was also used to modify the poly(ethylene terephthalate) track-etched membrane (Particle track-etched membrane, PTM, applications as in sensors, virus detection or removal, high quality water production).<sup>112</sup>

Surface of polypropylene (PP) membrane was modified by dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) plasma to induce hydrophilic and hydrophobic modifications. It was revealed that the surface had a thin cross-linked network, which was verified by solubility test. On the other hand, film treated in  $\text{CCl}_4$  and  $\text{CHCl}_3$  plasma gave greater hydrophilic modifications. Modification of PP film in  $\text{CH}_2\text{Cl}_2$  plasma showed good durability and bondability when compared with that in  $\text{CCl}_4$  and  $\text{CHCl}_3$  plasmas.<sup>113</sup>

Chitosan membranes were modified by alkane (petroleum ether) vapor plasma technique.<sup>114</sup> Water contact angles of chitosan surface increased from  $13^\circ$  to  $23^\circ$  after plasma treatment at 93 W for 60 min and from  $13^\circ$  to  $26^\circ$  after plasma treatment at 119 W for 30 min. It indicated that the hydrophilicity of the membrane surface decreased. Mechanical properties such as tensile strength and elongation-at-break of the chitosan membranes were also improved. Permeation coefficients through the chitosan membrane plasma treated at 93 W for 30 min for urea, creatinine, uric acid, and *cis*-DDP decreased by 54.0, 83.3, 64.7 and 47.6%, respectively.

### Inorganic plasma treatment

Inorganic gas plasma is known to promote the implantation of atoms, radical generation, and etching reactions, and is called a nonpolymer forming plasma. It is reported that highly reactive particles from gas plasma can etch a surface very gradually.<sup>115,116</sup> Van't Hoff et al.<sup>115</sup>, Fritzsche et al.<sup>116-118</sup> and Weigel et al.<sup>119</sup> performed etching experiments with oxygen plasma on PES GS HFMs and on asymmetric PSf hollow fibers, respectively. They noticed that it was possible to determine the sublayer resistance after etching the fiber.

Plasma etching is a technique that also allows the measurement of the thickness of the top layer in asymmetric and composite membranes. The uniformity of the structure in the top layer as well as the properties of the layer just beneath the top layer and those of the sublayer can also be determined. By measuring the gas-transport properties as a function of the etching time, information can be obtained about the morphology and the thickness of the thin nonporous top layer.<sup>120</sup>

Mühlen et al.<sup>121</sup> deposited a  $-\text{C} : \text{H}(\text{N})$  thin film onto Si(100) wafers using a 13.46 MHz radio-frequency (rf) glow-discharge, in 1-butene/nitrogen atmosphere. After deposition, film surfaces were treated in a  $\text{N}_2$  or  $\text{O}_2$  plasma for 1–3 min. It was observed that the treatment led to a decrease on the measured contact angle, meaning an improvement on the surface wettability. For the untreated film the contact angle value obtained was about  $80^\circ$ . After treatment with oxygen plasma for 3 min at  $V_b =$

$-30$  V this value reduced to less than  $40^\circ$ . Measured contact angles increased with  $V_b$  values, being about  $75^\circ$  at  $V_b = -240$  V. This behavior was similar to that observed for surfaces treated with  $\text{N}_2$  plasma. However, in this case the measured angles were about 20% higher than the ones observed for oxygen treated films. XPS spectra revealed that significant oxygen incorporation occurred on the film surface even for low  $V_b$  values. Nitrogen incorporation could also be observed after treatment with nitrogen plasma. It was concluded that the high reactive species present in plasma phase led to a coupled effect of chemical and morphological modifications of the surface of the thin a  $-\text{C} : \text{H}(\text{N})$  film, that caused a decrease in contact angle, mainly at low  $V_b$  ( $-30$  V) treatment, meaning an increasing of surface hydrophilicity.

Polyether sulfone (PES) and polysulfone (PSf) membranes were plasma treated by several researchers.

In PES membranes,  $\text{CO}_2$ -plasma (at low temperature) introduced several oxygen functional groups, including carboxylic acid, ketone/aldehyde, and ester groups and the membranes became highly hydrophilic. The wettability of these membranes did not change even after storage in air for 6 months.<sup>122</sup> Hydrophobic surfaces of PSf membranes also can be changed to hydrophilic by  $\text{CO}_2$  plasma treatment.<sup>123</sup>

PES UF membrane was treated by Argon-plasma, and it was found that the plasma treatment had no physical damage under moderate plasma conditions and rendered a complete hydrophilicity to the PES membrane. However, the hydrophilicity was not permanent. The Ar-plasma treatment of PES UF membrane significantly reduced protein fouling and increased water flux. Moreover, the adsorbed protein layer was found to be completely reversible, with nearly 100% recovery after gentle washing with water.<sup>124</sup>

Hydrophilic modification of porous PES membranes was achieved by Ar-plasma treatment followed by graft copolymerization with acrylamide (AAm) in the vapor phase. Both surfaces of the modified membranes were found to be highly hydrophilic (ungrafted and grafted).<sup>125</sup>

Microporous polyethersulfone membranes were modified by nitrogen based plasma systems such as  $\text{N}_2$ ,  $\text{NH}_3$ , Ar/ $\text{NH}_3$ , and  $\text{O}_2/\text{NH}_3$ .<sup>126</sup> Treatments were designed to alter the surface chemistry of the membranes to create permanently hydrophilic surfaces. Analyses by FTIR and XPS established the incorporation of  $\text{NH}_x$  and OH species in the PES membrane. The plasma treatment modified the entire cross-section of the membrane as the plasma penetrated the thickness of the membrane. Optical emission spectroscopy revealed the presence of  $\text{OH}^*$  when the membrane was modified with gaseous plasma,

which was not in 100% ammonia plasma, suggesting OH<sup>\*</sup> must play a critical role in the membrane modification process. The usefulness of plasma treatment was revealed by increased water flux, reduced protein fouling, and greater flux recovery after gentle cleaning when compared with an untreated membrane.

Chen and Belfort<sup>127</sup> modified commercial PES UF membranes (Millipore Corp., Lot No. 042,897 AGC 2A) via low-temperature helium plasma treatment followed by grafting of *N*-vinyl-2-pyrrolidone (NVP). Helium plasma treatment alone and post-NVP grafting substantially increased the surface hydrophilicity compared with the unmodified virgin PES membranes. The degree of modification can be adjusted by plasma treatment time and polymerization conditions (temperature, NVP concentration, and graft density). Plasma treatment roughened the membrane as measured by AFM. Using an ultrafiltration protocol to simulate protein fouling and cleaning potential, the surface modified membranes were notably less susceptible to BSA fouling than the virgin PES membrane or a commercial low protein binding PES membrane. In addition, the modified membranes were easier to clean and required little caustic to recover permeation flux. The absolute and relative permeation flux values were quite similar for the plasma-treated and NVP-grafted membranes and notably higher than the virgin membrane.

Ultrafiltration PSf membrane was treated with glow discharge created by nonpolymerizable gases, with low power radio-frequency (rf) plasma. Asymmetric porous substrates of PSf were used, and their surfaces were modified with inorganic gas plasma (ammonia). Detailed studies of the plasma degradation process of PSf membranes submitted to the NH<sub>3</sub> plasma treatment were made by AFM, SEM, and XPS. No substantial decrease in the permeability properties of the used PSf membranes for both N<sub>2</sub> and CO<sub>2</sub> gases was observed. The ammonia plasma treatment was very aggressive to the PSf surface and cracks developed in the membrane.<sup>128</sup> The hydrophilic character of the hydrophobic PSf membrane increased after Ar plasma-treated membrane was exposed to the atmosphere due to the oxygen incorporation.<sup>129</sup>

It was observed that the contact angle decreased by increasing the oxygen plasma treatment time of PSf membrane until it leveled off after 20 s of oxygen plasma-treated time. The ratio of O/C on the surface increased from 33–50% and isoelectric point (IEP) of membrane surface increased from pH 3 to 4.5. The permeation rates of pure water and gelatine solution increased over the entire pH range, and the plasma-treated membrane surface showed less fouling.<sup>130</sup> Cho et al.<sup>131</sup> modified PES UF membrane by

treating with low-temperature plasma of oxygen, acrylic acid (AA), acetylene, diaminocyclohexane (DACH), and HMDSO. The effects of these modifications on the filtration efficiency of a membrane in waste water treatment been investigated. The oxygen, AA and DACH plasma-treated membranes become more hydrophilic. Acetylene and HMDSO plasma-treated membranes became more hydrophobic and displayed both lower initial flux and lower fouling resistance.

Plasma modification of polymeric membranes with water is a logical extension of technological and industrial utility of plasmas to improve wetting properties of polymers.<sup>132,133</sup> There are few main works in the literature that focus on using H<sub>2</sub>O based plasmas to modify PSf membranes. One of them entails H<sub>2</sub>O and air plasma treatment of polyetherimide and PSf plane and HFMs for hydrophilic modification.<sup>134,135</sup> The other describes H<sub>2</sub>O/He plasma treatment of polyacrylonitrile and PSf UF membranes to promote antifouling properties.<sup>131</sup>

The H<sub>2</sub>O plasma-treated asymmetric polysulfone (PSf) membranes (completely hydrophobic) become permanently hydrophilic. Treated membranes remain wettable for a minimum of 16 months after plasma treatment. XPS analysis of the treated membrane confirmed that the change in wettability was a result of chemical changes in the membrane induced by plasma treatment. The membrane modification can be complete across the cross-section as plasma penetrates through the entire cross-section of the membrane.<sup>134</sup>

Plasma treatment of polymeric membranes other than PES and PSf membranes is also reported.

The selectivity and permeability for GS of polyphenylene oxide (PPO) dense membranes could be improved by short time plasma etching.<sup>120</sup> Oxygen plasma etching on the membrane may result in some chemical modification of the polymer material. Based on AFM pictures morphological changes were observed toward the depth direction.

CF<sub>4</sub> and CO<sub>2</sub> plasma were used to modify a polyamide (PA) membrane, resulting in different surfaces: one is rather hydrophobic (with CF<sub>4</sub>), whereas the other is more hydrophilic (with CO<sub>2</sub>). The effect of this modification on permeometric properties was investigated by liquid water and liquid toluene permeation measurements. The results showed two opposite effects of the two different treatments. CF<sub>4</sub> plasma treatment led to a reduction of water and toluene permeability. With CO<sub>2</sub> plasma treatment, in terms of permeation, two different behaviors were observed, an increase and a decrease of permeance for water and toluene, respectively. The results were in full agreement with those obtained for the surface characterization (contact angle measurement, XPS and AFM), and confirmed the change in the

**TABLE IV**  
**Surface Modification by Plasma Treatment**

Substrate	Membrane type	Organics and monomers	Application	Reference
Organic plasma treatment				
Silicon wafers	FS	Organo-silicon monomer	GS	109
Polyamide	FS	Acrylamide	PV	110
Hydrophilic polysulfone	FS	Acrylic acid	UF	111
Poly(ethylene terephthalate)	FS	Cyclohexane	UF, water treatment)	112
Polypropylene	FS	CH <sub>2</sub> Cl <sub>2</sub> , CCl <sub>4</sub> , CHCl <sub>3</sub>	UF	113
Chitosan	FS	Petroleum ether	UF or MF	114
Inorganic plasma treatment				
		Inorganic gasses		
PPO	FS	O <sub>2</sub>	GC	120
C:H (N) thin layer	FS	N <sub>2</sub> , O <sub>2</sub>	UF	121
Polyether sulfone	FS	CO <sub>2</sub>	UF	122
	FS	Ar	UF	124,125
	FS	N <sub>2</sub> , NH <sub>3</sub> , Ar/NH <sub>3</sub> , O <sub>2</sub> /NH <sub>3</sub>	UF	126
	FS	He (NVP post-treatment)	UF	127
Polysulfone	FS	NH <sub>3</sub> , Ar, CO <sub>2</sub>	GS	123,128,129
	FS	O <sub>2</sub>	Water treatment	118,131
	FS	H <sub>2</sub> O	UF	134
Polysulfone, Polyetherimide	FS	H <sub>2</sub> O, Air	UF	134,135
Polysulfone, polyacrylonitrile	FS	H <sub>2</sub> O/He	UF	143
Polyphenylene oxide	FS	Oxygen	GS	120
Polyamide	FS	CF <sub>4</sub> , CO <sub>2</sub>	Pervaporation	136
Polytetrafluoroethylene	FS	Acetylene/N <sub>2</sub>	Vapour permeation	137
Siloxane-containing copolyimides	FS	UV/ozone	Gas transport	140
PAA/TPX	FS	Air (residual)	Pervaporation	138
P2ClAn	FS	ECR plasma	Increasing pore diameters and number of pores for better anion or molecule transportation.	139
PU	FS	He plasma /Ar <sup>+</sup> implantation.	Improve the biocompatibility	141

polymeric surface affinity for the permeant leading to a variation of materials permeancy.<sup>136</sup>

The surface of poly(tetrafluoroethylene) (e-PTTE) membrane was modified by using acetylene/nitrogen plasma. The variation in surface morphology of e-PTTE membranes was confirmed by FTIR-ATR, SEM, and contact angle measurements. It was noticed that the surface hydrophilicity increased with increasing nitrogen content in the feed gas mixture, RF power, and plasma treatment time. The surface pore size decreased with increasing RF power and plasma treatment time. The water contact angles of modified e-PTTE membrane decreased from 125.8 to 34.1° through the acetylene/nitrogen plasma treatment. The vapor permeation results were obtained using a plasma modified membrane, giving a permeation rate of 666 g/m<sup>2</sup> h and water concentration in the permeate of 72 wt % from the feed solution containing 90 wt % of ethanol.<sup>137</sup>

Wang et al.<sup>138</sup> demonstrated a composite membrane (subjected to pervaporation) of PAA dip-coated asymmetric poly(4-methyl-1-pentene) (TPX) membrane. To improve the interface peeling of the PAA/TPX composite membranes, the surface of the TPX membranes was modified by residual air

plasma. The plasma treatments were effective in rendering the asymmetric TPX membrane hydrophilic.

Kir et al.<sup>139</sup> prepared poly(2-chloroaniline) (P2ClAn) membranes from chemically synthesized P2ClAn by casting method. P2ClAn membranes were treated by electron cyclotron resonance (ECR) plasma for surface modification. Plasma treatment resulted in increasing pore diameters and number of pores for better anion or molecule transportation.

Park et al.<sup>140</sup> studied the effect of UV/ozone treatment on siloxane-containing copolyimides membranes. Gas permeation experiments on nonUV/ozone-treated and on UV/ozone-treated PIS films were carried out using He, oxygen, and nitrogen and CO<sub>2</sub> penetrants. It was observed that poly(imide siloxane) (PIS) films having a high siloxane content (i.e., a volume fraction of 0.457), the UV/ozone treatment decreased the gas permeabilities, but increased the selectivity of several gas pairs owing to the formation of a dense layer, which increased with increasing treatment time.

Meling et al.<sup>141</sup> improved biocompatibility of PU surface by treatment with He plasma and Ar<sup>+</sup> ion implantation.



It is suggested that low-temperature plasma treatment is an effective method for the modification of polymeric materials.<sup>142</sup> This method is very effective for the enhancement of adhesive properties of a wide range of polymeric materials used in different fields of technology, as well as in the manufacture of membranes for different designations.

Table IV summarizes various plasma treatments reported in this section.

### SURFACE MODIFICATION BY IRRADIATION OF HIGH ENERGY PARTICLES

It is known that the polymer surfaces can be modified both chemically and physically when they are exposed to high energy particles. This method has been applied for the membrane surface modification.

#### UV irradiation

Treatment with UV-ozone has been used as a means of removing organic contaminants from different polymer surfaces.<sup>144</sup> However, UV/ozone treatment has also been used to increase the wettability of poly (ethylene terephthalate) (PET), polyethylene (PE), polypropylene, different rubbers (vulcanized styrene-butadiene-SBR, unvulcanized styrene-butadiene-SBS).<sup>140-151</sup> This UV/ozone treatment results in an increase in the surface energy<sup>152</sup> of the polymer through oxidation of the polymer.<sup>153,154</sup> The photons produced by UV/ozone irradiation have sufficient energy to break most C—C bonds and also can induce chain scission and cross-linking on polymer surface.<sup>146,155</sup> Both ozone and atomic oxygen radicals can react with polymer surfaces to remove low weight contaminants and to modify surfaces.<sup>156</sup> Recently, Landete-Ruiz and Martin-Martínez<sup>157</sup> reported that the UV treatment for 5 min gave the highest increase in the adhesion of ethylene vinyl acetate (EVA) copolymer to polychloroprene adhesive due to improved wettability, the creation of surface roughness (cracks), and the formation of carbon-oxygen moieties.

Exposing PP to ozone in the presence of UV light is simple and effective way of modifying its surface to improve its wettability and adhesion.<sup>158,153</sup>

Vijay et al.<sup>159</sup> modified the PC membrane (40–50  $\mu\text{m}$  thick) (subjected to gas permeation) by etching process ( $\alpha$  particles). The permeability of  $\text{CO}_2$  and  $\text{H}_2$  increased rapidly after different etching time.

Nie et al.<sup>158</sup> studied the UV/ozone-treated polypropylene films by AFM. It was clearly observed that UV/ozone-treated film had different morphology of the surface and also adhesion force increased. The increase in adhesion force indicated the increase in the surface energy.

Puro et al.<sup>160</sup> modified nano filtration membrane {NF45 (Dow Chemical Co.), NF270 (Dow chemical Co.), and NTR7450 (Nitto Denko)} by UV irradiation in water or in lactic acid solution with stirring for 20 min. The modification was characterized by octanoic acid filtration and FTIR analysis. It was reported that the modification depended on the membrane material. The flux of the NF270 membrane was almost unchanged and octanoic acid fouled the membrane permanently after modification. However, modification of the NF45 and NTR7450 membranes increased the water fluxes considerably. The best fluxes were obtained after the filtration of octanoic acid with UV irradiated membranes. The flux was almost two-fold and eight-fold for NF45 and NTR7450 membranes, respectively. It is speculated that octanoic acid either adsorbs on the NF45 and NTR7450 membranes or influences the orientation of the membrane structure, especially after UV irradiation. FTIR spectra revealed that every membrane contained a layer of PSf similar to Udel PSf. After UV irradiation all the membranes had changed in their chemical structure. The binding of octanoic acid was different for the tested modified membranes: for all the membranes methyl groups were involved in the interaction of membrane and octanoic acid while for NF270 membrane octanoic acid also binds to the sulfonic group.

Berdichevsky et al.<sup>161</sup> investigated the conversion of bulk poly(dimethylsiloxane) by deep penetration and complete oxidation of thick-film by UV/ozone treatment. UV/ozone treatment resulted, improved wettability, enhanced electro-osmotic flow, and reduced adsorption properties in the modified PDMS channels.

#### Ion-beam irradiation

Xu and Coleman<sup>162</sup> modified the 6FDA-pMDA (polyimide) films by irradiating ion-beam and studied the structure and morphology by AFM. Detailed roughness and bearing analyses of the AFM images indicated that free-standing polyimide films have deep surface valleys which could extend to a depth of several micrometers. Ion-beam irradiation, even at a small dose, alters the microstructure of the surface layer of the polymer, and high fluence irradiation resulted in a large number of small-size microvoids in the surface. All of these changes had effects on the gas permeation properties as well as on iodine diffusion.

Surfaces of polyimide and PSf membranes were modified by carbonization using ion-beam.<sup>163</sup> To control the structure of membrane skin and to improve gas-transport properties, the irradiation conditions, such as the dosage and the source of ion beams, have been varied. The ideal separation factor

**TABLE V**  
**Membrane Modification by Irradiation of High Energy Particles**

Membrane	Membrane type	Energy source	Application	Reference
Polypropylene	FS	UV/ozone irradiation	Surface study, wettability improvement	158
PC	FS	$\alpha$ particles	Gas permeation	159
NF 45, NF270, NTR 7450 membranes	FS	UV in water	NF (surface study)	153
Polyimide (6FDA-pMDA) membrane	FS	Ion-beam	Gas permeation properties	163
Polyimide and polysulfone membrane	FS	Ion-beam	GS	163
Sulfonated polysulfone membrane	FS	Ion-beam	Water treatment	164
PC, PET, PS, PI	FS	Ion, electron, neutron beam, swift heavy ion	Enhance the bacterial growth.	166
Polysulfone, composite RO and activated membranes	FS	X-ray	Chemical and morphological characterization	167
Polysiloxane	FS	CF <sub>4</sub> and Ar	Morphological study.	168
Poly(dimethylsiloxane)	FS	UV/ozone	Filtration	161
Commercial membranes	FS	Ion-beam	Improve the abiotic and biofouling resistance.	165

of CO<sub>2</sub> over N<sub>2</sub> through the surface modified PI and PSf membranes increased three-fold compared with those of the untreated, pristine membranes, whereas the permeability decreased by almost two orders of magnitude. This could be due to the fact that the structure of the membrane skin had changed to a barrier layer.

Chennaamsetty et al.<sup>164</sup> modified a commercial sulfonated PSf water treatment membrane by ion-beam irradiation. During modification some of the sulfonic groups on the surface of the membrane were broken, which resulted in cross-linking of the polymer. These changes modified the surface morphology of the membrane, and also decreased the negative charge of the membrane. It was observed that fouling of the modified membrane was significantly less severe than that of the virgin membrane.

Good et al.<sup>165</sup> modified the water treatment commercial membranes by ion-beam irradiation. They reported that the irradiation induced structure modification had positive impact on the membranes application to waste water treatment. Not only did the irradiation improve both abiotic and biofouling resistance, it also doubled the membrane solvent mass transfer coefficient (MTC). Water quality testing revealed removal of contaminants, whereas fouling tests indicated an improvement in the membrane's resistance to fouling, especially in the case of biofouling.

Different types of treatment such as electron, ion, neutron beam, and swift heavy ion (SHI) at different energy and dose can modify the polymeric membrane surface and its characteristics. It was reported that the permeability and selectivity of these membranes depend upon thickness, ion dose, etching time, and chemical nature. The electron irradiation changes the cross-linking density in the polymer at

the surface as well as bulk. The SHI generated tracks can be etched further in a controlled manner to generate the nanoscale filter. The electron irradiated active site enhances the bacterial growth.<sup>166</sup>

Ariza et al.<sup>167</sup> studied the X-ray irradiation effect on six polymeric membranes; two PSf membranes, two composite RO polyamide/polysulfone membranes having polyamide as the active layer and two activated membranes containing di-2-ethylhexylphosphoric acid and di-2-ethylhexyldithiophosphoric acid carriers, respectively. The membranes were characterized before and after irradiation with an X-ray source, both chemically and topographically by XPS and AFM, respectively. Chemical modifications were observed on the membrane surfaces. The most significant changes were observed for PSf, which was reduced by X-ray action: this fact also indicated the inhomogeneity of the surface of the di-2-ethylhexyldithiophosphoric-activated membrane. In contrast, polyamide top layers of composite membranes had been shown to be the most stable. Chemical modifications were not related directly to changes in membrane roughness because for all membranes only small changes were observed for AFM images recorded before and after membrane irradiation.

Finot et al.<sup>168</sup> performed fluorination treatment on polysiloxane membranes using a plasma glow discharge of gaseous mixture CF<sub>4</sub> and argon (plasma enhanced chemical vapor deposition.). Fluorination increases the hydrophobic character of membranes. This effect, found to be more pronounced on amorphous silica-like membranes than on polymer-like ones, was explained by the chemical composition of the topmost surface.

Table V summarizes the irradiation techniques quoted in this section.

## SURFACE MODIFICATION BY HEAT TREATMENT

Membrane surfaces can also be modified by heat treatment. The PES HFMs were prepared by dry-wet-spinning method and heated in an oven at 120, 150, and 180°C. The membrane shrank by heating. It was noticed that pore size decreased from 8.16 nm for untreated hollow fiber to 3.8 nm with 1 minute heating and then increased to about 6 nm with 5 min heating at 150°C. With an increase in heating temperature, the pore size of the membrane decreases.<sup>169,170</sup>

By using a coextrusion and dry jet wet spinning phase-inversion technique with the aid of heat treatment at 75°C, Li et al.<sup>171</sup> fabricated a dual-layer PES HFMs (GS) with an ultra-thin dense-selective layer of 407 Å. The dual-layer hollow fibers had an O<sub>2</sub> permeance of 10.8 GPU and O<sub>2</sub>/N<sub>2</sub> selectivity of 6.0 at 25°C. It was observed that heat treatment at 75°C improved the gas permeation and ideal selectivity, whereas heat treatment at 150°C resulted in a significant reduction in both permeation and selectivity due to enhanced substructure resistance. SEM pictures confirmed that higher heat-treatment temperature can significantly reduce pore sizes and the amount of pores in substructure immediately underneath the dense-selective layer.

Ton-That et al.<sup>172</sup> studied the effects of annealing on the surface composition and morphology of PS (polystyrene)/PMMA blend. The PS/PMMA film was annealed at a temperature above their glass transition temperatures for up to 48 h. The polymer with a lower surface free energy, PS, was shown to aggregate to the surface upon annealing. The surface enrichment and morphology changes upon annealing were explained by dewetting of PMMA relative to PS.

Maya et al.<sup>173</sup> reported that the thermally treated copolyimides consisting of flexible PEO segments and rigid polyimide segments are very attractive as CO<sub>2</sub>/N<sub>2</sub> separation membranes. After a thermal treatment of these membranes under an inert atmosphere, a large improvement in CO<sub>2</sub> permeability was observed, yielding a more productive membrane.

Pyrolysis temperature was found to significantly change the structure and properties of carbon membrane based on PAN.<sup>174</sup> Tsai et al.<sup>175</sup> studied the effect of heat treatment on the morphology and pervaporation performances of asymmetric PAN HFMs. Compared with the precursor HFMs, the pervaporation performances of heat-treated PAN HFMs effectively improved. The porous structure of PAN precursor HFMs became denser after heat treatment. The pervaporation results of permeation rate and water content in permeate for a 90 wt % aqueous

isopropanol solution through a 120°C and 12 h heat-treated PAN HFM were 186 g/m<sup>2</sup> h and 99.2 wt %, respectively, whereas in PAN precursor the permeate rate and water content were 4801 g/m<sup>2</sup> h and 13.6 wt % respectively.

Koros and Wood<sup>176</sup> studied the effect of elevated temperatures on three asymmetric HFMs (polyaramide, polyimide, and composite polyimide on a polyimide/polyetherimide blend support). Polyaramide membranes were shown to exhibit good stability at elevated temperatures and good separation properties after silicon rubber post-treatment. The hydrogen permeance of 300 GPU at 175°C is acceptable for industrial application. The polyimide-containing membranes had superior room-temperature properties; however, the thin skin aged at elevated temperatures. This aging effect decreased the permeance of the membranes approximately 40% at 175°C and slightly increased the permselectivity; however, the effects of aging leveled out over 200–250 h at 175°C and the membrane properties became constant. At this level, the polyimide membranes exhibited ~ 400 GPU of hydrogen permeance with 660 selectivity to *n*-butane.

Charkoudian et al.<sup>177</sup> revealed that increased levels of protein adsorbed to thermally treated polyacrylamide-modified PVDF microporous membranes in comparison to polyacrylate-modified membranes

## GRAFT POLYMERIZATION/GRAFTING

Grafting can also be applied for the surface modification of the membrane. Although the method should work for any polymeric materials, most of the recent works on membrane surface graft polymerization were on polyamide thin-film composite (TFC) membranes or porous polypropylene membranes.

The reports on the grafting on the surface of polyamide TFC membranes are as follows.

Hydrophilic PEG chains were grafted onto the surface of a thin-film composite (TFC) polyamide RO membrane.<sup>178</sup> Aminopolyethylene glycol monomethylether (MPEG-NH<sub>2</sub>) was used as the grafting monomer. The membranes were characterized by ATR-FTIR, XPS, and AFM. A preliminary experiment confirmed that the grafting of PEG chains improved membrane antifouling property.

Gilron et al.<sup>179</sup> modified the commercial RO polyamide membranes, ranging from ultra low pressure to seawater desalination membrane, using redox generation of monomer radicals. Base membranes were thin-film composite aromatic polyamides membranes. A redox system composed of potassium persulfate and potassium metabisulfate was used to generate radicals. These attack the polymer backbone, thus initiating the graft polymerization by

attachment of monomers to the membrane surface. The following monomers were used to generate grafted polymers on the membrane surface: glycol ester of methacrylic acid (PEGMA)—uncharged, sulfopropyl methacrylate (SPM)—anionic, and 2 acrylamido-2-methyl propane sulfonate (AMPS)—anionic. Modification of membrane significantly reduced both receding and advancing contact angles. Modified membranes adsorbed less organic material and were more easily cleaned than unmodified membranes. Specific fluxes were not changed by more than 0–25%, and NaCl rejection was unchanged or increased slightly.

Ferger et al.<sup>180</sup> modified TFC-PA membranes using graft polymerization of acrylic acid (AA) monomers. FTIR, AFM, and TEM (transmission electron microscopy) revealed that AA polymer was formed on the PA surface, which could be accompanied by a change of the surface morphology.

Saito<sup>181</sup> reported that the charged polymer brush grafted onto porous HFM (polyethylene) improves separation and reaction in biotechnology.

The reports on the surface modification of polypropylene (PP) membranes are as follows.

The surface of microporous PP HFM was modified by radical-induced graft polymerization of *N,N*-dimethylaminoethyl methacrylate (DMAEMA).<sup>182</sup> It was found that the appropriate graft temperature was 75°C, at which the grafting degree was the highest and the hydrolytic decomposition of DMAEMA was lowest. Contact angle and water swelling experiments showed that a moderate grafting degree could improve the hydrophilicity of the membranes. Xu et al.<sup>183</sup> described a novel method for the surface modification of a microporous membrane by tethering phospholipid analogous polymers (PAPs), which included the photo-induced graft polymerization of DMAEMA and the ring-opening reaction of grafted poly(DMAEMA) with 2-alkyloxy-2-oxo-1,3,2-dioxaphospholanes (AOP). Xu et al.<sup>183</sup> used five AOP, containing octyloxy, dodecyloxy, tetradecyloxy hexadecyloxy, and octadecyloxy groups in the molecular structure, to fabricate the phospholipid analogous polymers (PAPs)-modified polypropylene membranes. The influences of temperature, monomer concentration, and pre-adsorbed amount of benzoyl peroxide on grafting degree were studied. Contact angle and water swelling experiments showed that moderate grafting degree could improve the hydrophilicity of the membranes. Platelets adhesion experiment indicated that PP membrane with excellent blood compatible surface could be fabricated by this method. BSA adsorption experiments indicated that the five PAP-modified membranes had a much better protein-resistant property than the original PP membrane and the poly(DMAEMA)-grafted membranes.

Ma et al.<sup>184</sup> induced hydrophilic surface from a hydrophobic surface of PP membrane by grafting monomers of poly(ethylene glycol 200) monomethacrylate, or acrylic acid (AA), to produce a neutral surface or a surface with positive or negative charge. Using both unmodified and modified PP membranes, the effects of back-pulsing for waste water treatment and surface chemistries on membrane fouling were investigated for cross-flow microfiltration of bentonite clay suspensions and crude oil emulsions. Five-fold and six-fold permeate enhancements were obtained by back-pulsing alone and by a combination of back-pulsing and surface modification, respectively, for clay filtration.

A novel synergist immobilization photo-graft polymerization method has been developed to functionalize polymer materials in polar organic solutions. This two-step method, based on the immobilization of tertiary amine groups as synergists for the photoinitiator benzophenone, has been evaluated for commercial hydrophilized PP microfiltration membranes.<sup>185</sup> It was observed that the hydrophilization of the PP membrane was due to a thin layer of a polyacrylate. Reaction conditions for the introduction of tertiary amino groups via an aminolysis reaction with *N,N*-diethylethylenediamine have been optimized. Compared with the original membrane, aminolysed membranes demonstrated high-surface selectivity for photo-grafting of polyacrylamide from methanol solution. Grafting density and polymer chain length can be well controlled by adjusting the main functionalization parameters (synergist surface concentration, UV irradiation time, benzophenone concentration, and monomer concentration). He and Ulbricht<sup>185</sup> predicted that the primary functionalization via aminolysis should be applicable to all polymers with ester groups on their surfaces.

Another method was developed by Qi and Lee<sup>186</sup> for the modification of PP hollow fibers using graft copolymerization of PMMA. The unsaturated residues in PP were reacted with borane-dimethylsulfide, and PMMA graft polymerized on the surface to form a stable coating which reduced the electro-osmotic flow and adsorption of biomolecules. The PMMA modified PP membrane exhibited a lower electro-osmotic flow (EOF, which is dependent on the surface charge) than fused silica and propylene, close to that of bulk PMMA.

The surface of polypropylene membranes was modified by  $\gamma$ -ray induced graft copolymerization with hydrophilic HEMA. The modified membranes showed a decrease in deionized water flux due to the narrowed and plugged pores. On the other hand, maximum two-fold increase in a BSA solution flux was noticed due to the increased hydrophilicity of membrane. The amount of BSA adsorbed on the modified membrane was smaller than that of the



unmodified membrane because the hydrophobic interactions between BSA molecules and membrane surface were prevented by grafted HEMA chains. The modified membrane showed better antifouling capabilities and washing effects than that of the unmodified membrane due to an induced hydrophilicity.<sup>187</sup>

A sugar containing monomer, D-gluconamidoethyl methacrylate (GAMA), was grafted on polypropylene microporous membrane (PPMM) with an UV-induced polymerization to improve both the surface hydrophilicity and hemocompatibility.<sup>188</sup> The decrease of the water contact angles and the increase of the pure water flux for the modified PPMMs indicated the improvement of the surface hydrophilicity by the grafting of GAMA. Platelet adhesion experiment revealed that a more hemo-compatible interface can be obtained between the membrane and the biomolecules.

Pore-filled membranes were made by plasma-graft polymerization in the pores of porous high density polyethylene (HDPE) hollow fiber and FS for the removal of chlorinated organics from water.<sup>189</sup> The hollow-fiber-type laurylacrylate (LA)-grafted membranes (pervaporation) showed extremely high separation properties: a 0.09 wt % TCE (1,1,2-trichloroethane) aqueous solution was condensed to 99 wt % in the permeate. The membrane could remove TCE from a water stream, and at the same time the membrane could purify the TCE for reuse. The membrane also showed high separation performance for an aqueous dichloromethane (DM) solution.

Surface grafting was also applied for other polymers as the following examples show.

The surfaces of PES UF membranes were modified via simultaneous photografted polymerization of the hydrophilic monomer poly(ethylene glycol) methacrylate (PEGMA) onto the membrane surface to prepare low-fouling UF membranes. This study provided valuable information for the development of low-fouling UF membranes especially for sugar-cane juice clarification.<sup>190</sup>

Taniguchi et al.<sup>191</sup> described a photochemical graft polymerization technique to produce modified PES UF membranes that exhibit reduced interaction with natural organic matter (NOM), as a route to reduce the fouling caused by NOM. Six different hydrophilic monomers were evaluated for their ability to reduce fouling by NOM: two are neutral monomers, *N*-vinyl-2-pyrrolidone (NVP) and HEMA; two are weakly acidic (carboxylic) monomers, acrylic acid (AA) and 2-acrylamidoglycolic acid (AAG); and two strongly acidic (sulfonic) monomers, 3-sulfopropyl methacrylate (SPMA) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS). Grafting increased membrane surface wettability and shifted the membrane pore size distribution to smaller sizes, which

increased natural organic matter rejection (except in the case of NVP). Total fouling depended primarily on solute rejection, and varied in a complex way that could be interpreted in the context of the NOM molecular weight distribution. Taniguchi et al.<sup>191</sup> concluded that wettability (or hydrophilicity) is not an appropriate parameter for estimating reduced fouling potential for NOM feeds, as it is for feed containing protein. However, this is a consequence of the structural and chemical heterogeneity of NOM.

The surface of hydrophobic poly(vinyl chloride) (PVC) membrane was modified with *N*-vinyl-2-pyrrolidone (NVP) monomer by the ultraviolet-assisted graft polymerization to increase the surface wettability and to decrease the adsorptive fouling. The flux of the modified membrane was higher than that of unmodified membrane due to the increase of hydrophilicity on the membrane surface and the more or less dilution of protein concentration in the sludge solution at NVP layer.<sup>192</sup> The results obtained by Kim et al.<sup>191</sup> suggested that the adhesive interactions of the mixed liquor-suspended solid (MLSS) with the hydrophilic membrane surfaces were weaker than those with a hydrophobic surface. The average permeate flux of surface modified membrane with back-pulsing (5.6-fold) was higher than with cross-pulsing (2.8-fold), indicating that the deposition of MLSS in the interior of the membrane pore was the dominant fouling mechanism. The trans-membrane pressure (TMP) of modified membrane was lower than that of unmodified membrane.

A new method was developed for surface-initiated ATRP on the technical polymer poly(ethylene terephthalate) (PET).<sup>193</sup> It allows controlling and estimating the layer thickness of the grafted polymeric iso-cylindrical pores of track-etched membranes. After PET surface treatment by oxidative hydrolysis, the bromoalkyl initiator was immobilized on the PET surface in a two-step solid-phase reaction; the isoporous membrane structure was preserved, and the pore diameter was increased from 760 to 790 nm. Poly(*N*-isopropylacrylamide) (PNIPAAm) was grafted under ATRP conditions from a methanol/water mixture at room temperature. Both monomer concentration and reaction time could be used as parameters to adjust the degree of grafting. Salam and Ulbricht<sup>194</sup> studied the effect of surface modification on synthesis of pore-filling polymeric monoliths in microfiltration membranes made from poly(propylene) and poly(ethylene terephthalate). Premodification of the entire pore surface of PP microfiltration membrane and PET track-etched membranes by UV-initiated grafting with PEGMA (poly(ethylene glycol) monomethacrylate) was performed using well established methods. Then the membranes were functionalized with poly(MAA-co-

EDMA) {poly(methacrylic acid)-*co*-(ethylene glycol dimethacrylate)}.

Cen et al.<sup>195</sup> developed a surface modification technique to impart antibacterial properties on poly(ethylene terephthalate) (PET) films and PVDF membranes. Both film and membrane were first graft-copolymerized with 4-vinylpyridine (4VP) and subsequently quaternized with hexylbromide. Both these substrates can be functionalized with varying amounts of pyridinium groups and these groups possess antibacterial properties. This surface modification method has the advantages of simplicity in processing, good control over the surface concentration of pyridinium groups, long-term stability as well as wide applicability.

Commercial CA UF membrane was modified by using a simple experimental procedure that might be used to perform *in situ* modification.<sup>196</sup> An oxidant agent, a highly hydrophilic macromolecule, and a chain-transfer agent were used to modify the membrane. The oxidizing agent was sodium persulfate and the macromolecular monomer was poly(ethylene glycol). To control the grafting process, 2-mercapto-ethanol was used as a moderate reducing agent. 2-Mercapto-ethanol may also act as a chain-transfer agent. On modification surface roughness was increased. It was observed that the modification may have some effect in increasing the rejection of the organic compound (humic acid). Despite the increase in rejections, the fluxes seemed to have been unaffected by the modification. And this may be attributed to an increase in the hydrophilicity of the membrane which enhanced water transport.

Park et al.<sup>197</sup> synthesized amphiphilic graft copolymers having polysulfone (PSf) backbones and PEG side chains via reaction of an alkoxide formed from PEG and a base (NaOH) with chloromethylated PSf. The resulting polysulfone-*graft*-PEG, (PSf-*g*-PEG) materials were hydrophilic but water insoluble, rendering them potentially useful as biomaterial coating. When used as an additive in PSf membranes prepared by immersion precipitation, the graft copolymer preferentially segregates to the membrane surface, delivering enhanced wettability, porosity, and protein resistance compared with unmodified PSf membranes. The surface properties of PSf-*g*-PEG membranes render them desirable candidates for haemodialysis.

Hester et al.<sup>198</sup> demonstrated a direct preparation of amphiphilic graft copolymers from commercial PVDF using ATRP. Graft polymers were used as membrane additive in PVDF. The membrane displayed substantial resistance to BSA fouling compared with pure PVDF membranes and wetted spontaneously when placed in contact with water.

Korikov et al.<sup>199</sup> prepared interfacially polymerized hydrophilic microporous thin-film composite membranes on porous polypropylene hollow fibers and flat films. Flat Celgard 2400 films and X-20 hollow fibers of PP were used as a support for TFC membranes. Monomer reactants for this reaction were diacyl chlorides such as sebacoyl chloride or *iso*-phthaloyl dichloride and diamines such as hexanedimines or polyethyleneimine (PEI). These TFC membranes had substantial solvent stability. Their interfacially polymerized (IP) layer, and the membrane were also hydrophilic. These membranes were characterized by the permeance of a gas (N<sub>2</sub>), permeability of water and ethanol, SEM, and UF of protein, Zein, from an ethanolic solution. The HFMs developed successfully were capable of 97% zein rejection from an ethanolic solution. It was noticed that when the monomer system of PEI and *iso*-phthaloyl dichloride was used, the support was additionally hydrophilized with the self crosslinked PEI which was forming the selective layer. On the other hand, the support remained completely hydrophobic when 1,6-hexanediamine and sebacoyl chloride were used as monomers.

Taniguchi et al.<sup>200</sup> modified PES UF membranes surface via UV-assisted graft polymerization of NVP and reported that the modified membrane effectively reduced the irreversible membrane fouling.

Liu et al.<sup>201</sup> tethered two kinds of polypeptides onto the surface of PP microporous membrane (PPMM) through a ring-opening polymerization of L-glutamate *N*-carboxyanhydride initiated by amino groups which were introduced by ammonia plasma and  $\gamma$ -aminopropyl triethoxysilane treatments. The wettability of the membrane surface increases at first and then decreases with the increase in degrees of grafting on polypeptide. It was reported that polypeptide grafting can simultaneously improve the hemocompatibility as well as reserve the hydrophobicity for the membrane, which will provide a potential approach to improve the performance of PP hollow-fiber microporous membrane used in artificial oxygenator.

Kou et al.<sup>202</sup> modified the surface property of microporous polypropylene HFMs, from hydrophobic to hydrophilic, to improve the antifouling property by the N<sub>2</sub> plasma-induced graft polymerization of sugar-containing monomer ( $\alpha$ -allyl glucoside, AG). It was revealed that the hydrophilicity was permanent, and no hydrophobic recovery was observed. Furthermore, modification by AG grafting made the membrane surface less susceptible to the adsorption of BSA.

Schnyder and Rager<sup>203</sup> reported that the surface composition of radiation-grafted poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)-*g*-polystyrene films and FEP-*g*-poly(styrenesulfonic acid)

membranes was strongly influenced by the degree of cross-linking of the polystyrene phase. While high-surface concentrations of the grafting component were observed in the absence of crosslinker, the surface was almost exclusively composed of FEP at high crosslinker concentrations.

Yoshida and Cohen<sup>204</sup> removed methyl *tert*-butyl ether from water by pervaporation using ceramic-supported polymer membranes. These membranes were created by the free radical graft polymerization of vinyl acetate onto a trimethoxysilane-activated porous silica substrate having native average pore size of 500 Å. The resulting membranes consisted of poly(vinyl acetate) chains terminally and covalently anchored to the membrane surface.

Goma-Bilongo et al.<sup>205</sup> developed a numerical model to represent the process by which HFMs can undergo continuous surface modification by UV photo-grafting. It gives approximately correct values for the mass of polymer grafted, but attempt was made to relate this quantity with permeability or retention.

Liu et al.<sup>206</sup> studied the effect of polymer surface modification on polymer-protein interaction via hydrophilic polymer grafting. It was reported that the grafting of hydrophilic polymers onto UV/ozone-treated PES resulted in the improvement in the hydrophilicity of the commercial PES membrane. Hydrophilic polymers, that is, PVA, PEG, and chitosan, were employed to graft onto PES membrane surface because of their excellent hydrophilic property. It was concluded that grafting of PVA, PEG, or chitosan onto UV/ozone-treated PES membranes increases hydrophilicity and lowers protein adsorption by 20–60% compared with the virgin PES membrane. Among the three hydrophilic polymers studied, PEG showed the most favorable result in terms of contact angle and protein adsorption.

Gawenda et al.<sup>207</sup> prepared nanoporous membranes with tailored block copolymers as selective layer. The support membranes were track-etched PET membranes and commercial UF membranes with barrier pore diameters ranging from ~ 5 to 3000 nm. The tailored diblock or triblock copolymers were synthesized by living ionic or controlled radical polymerization. They claimed that such work will give important information with respect to the feasibility of the original approach and about the potential of the prepared composite membranes.

Taniguchi and Belfort<sup>208</sup> studied low protein fouling synthetic membranes. The surfaces of membranes were modified by varying monomers using UV-assisted surface grafting technique. The sensitivity of photo-induced grafting and polymerization and the filtration performance of six different grafted monomers {2 neutral, *N*-2-vinyl pyrrolidone (NVP), HEMA; 2 weak (carboxylic) acids,

acrylic acid (AA), 2-acrylamidoglycolic acid (AAG); and 2 strong (sulfonic) acids, SPMA, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS)} on poly(ether sulfone) (PES) membranes were measured. Although all the grafted and polymerized monomers increased the surface wettability of the PES grafted membranes over that for the unmodified PES membranes, their effect of filtration performance was different. Using the 50 kDa PES membrane for grafting, membranes with superior performance (high protein retention, high protein solution flux, and low irreversible fouling) were obtained with NVP, AMPS, and AA monomers. For larger pore size membranes (70 and 100 kDa), however, PES-*g*-AMPS and PES-*g*-AA membrane exhibited reasonably high BSA rejection and protein solution fluxes with excellent cleaning capability (with projected high long-term performance) as compared with the control membranes. Grafting of NVP and HEMA resulted in an initial substantial decrease in BSA rejection due to their tendency to dissolve PES, but with further grafting rejection was recovered.

Voznyakovskii et al.<sup>209</sup> modified the surface of polyethylene terephthalate (PETP) (Dacron) track membranes by ultra-thin films of polysiloxane block copolymers to get a hydrophobic surface and retained pore space. It was demonstrated that a uniform distribution of a nanodimensional modifier (fullerene) in a polymer matrix can be achieved, which ensures a high strength of the composite layer.

Wei et al.<sup>210</sup> developed a novel electrophoresis-UV grafting technique for the modification of PES UF membranes used for NOM removal. A novel technique which combines controlled deposition by electrophoresis of charged moieties, with UV grafting on the membrane surface had been applied to modify PES membranes with several different monomers. The monomers included three strong polyelectrolytes, {methacrylic acid (MA), acrylic acid (AA), and 2-acrylamido glycolic acid (AAG)} and two weak polyelectrolytes, HEMA, and *N*-vinyl formamide (NVF)}. It was found that the modified membrane surfaces exhibited more hydrophilic and negative-charged features after the electrophoresis\UV grafting technique was applied.

Table VI represents the surface modification by grafting or polymerization.

## SURFACE MODIFICATION BY CHEMICAL REACTION

The membrane surface can also be modified by chemical reaction.

Maekawa et al.<sup>212</sup> examined the chemical modification of the internal surface of the pores of poly(ethylene terephthalate) (PET) membranes using the

**TABLE VI**  
**Surface Modification by Grafting or Polymerization**

Membrane	Membrane type	Grafted polymer or monomer	Application	Reference
Polyamide TFC	FS	MPEG-NH <sub>2</sub>	RO	178
Polyamide RO	FS	Glycol ester of methacrylic acid (PEGMA), sulfopropyl methacrylate (SPM) and 2-acrylamido-2-methyl propane sulfonate (AMPS)	RO	179
Polypropylene	Hollow fiber	Acrylic acid	RO	180
		<i>N,N</i> -dimethylaminoethyl methacrylate, followed by ring-opening reaction	Water treatment (improve the biocompatibility)	182
	Hollow fiber	AG-N <sub>2</sub> plasma treatment	Water treatment	211
	FS	2-alkyloxy-2-oxide-1,3, 2-dioxaphospholanes	Improve the hydrophilicity of the membrane	183
	FS	Poly(ethylene glycol 200) monomethacrylate, acrylic acid	Waste water treatment. to produce a neutral surface or a surface with positive or negative charge	184
	FS	Aminolyzed polyacrylate	(MF)	185
	Hollow fibers	PMMA	Capillary electrophoresis(to reduce the EOF)	186
	FS	2-Hydroxyethyl methacrylate (HEMA)	antifouling	187
	FS	GAMA	Improve the surface hydrophilicity and hemocompatibility	188
	FS and hollow fibers (TFC)	Monomers (diacyl chloride and diamines)	UF	199
HDPE PES	Hollow fibers	Ring-opening polymerization of L-glutamate <i>N</i> -carboxyanhydride initiated by amino groups	Improve the hemocompatibility	201
	FS	LA or BA	Pervaporation	189
	FS	Poly(ethylene glycol) methacrylate (PEGMA)	Low-fouling UF membrane	190
	FS	HEMA, NVP, AA, AAG, SPMA, AMPS	Increase surface wettability	191,208,210
Polyvinyl chloride	FS	NVP	UF (reduced irreversible fouling)	210
		<i>N</i> -vinyl-2-pyrrolidone	UF, cross-flow filtration, back-pulsing	192
Polyethylene terephthalate	FS	NVP	UF (reduced irreversible fouling)	210
		Poly( <i>N</i> -isopropylacrylamide)	Microfluidic system or other application	192
		4-Vinylpyridine	Water filtration (anti bacterial, long-term stability of membrane)	195
CA	FS	Ultra-thin films of polysiloxane copolymer	To get a hydrophobic surface	209
Trimethoxysilane-activated on porous silica	FS	Poly(ethylene glycol)	UF (rejection of organic compounds )	196
PSf	FS	Vinyl acetate	Pervaporation	204
PVDF	FS	PSf/PEG	Haemodialysis	197
PPMM	Hollow fiber	Atom transfer radical polymerization (ATRP)	Wettable and fouling resistant.	198
PEI	Hollow fiber	Polypeptides	Artificial oxygenator	201
UV/ozone-treated PES	Hollow fiber	UV photo-grafting	GS	205
Polyethylene	Hollow fiber	PVA and PEG	Increase the hydrophilicity	206
PETP	FS	Charged polymer brush	Highly efficient protein recovery, chiral separation, and enzymatic reaction	181
PS	FS	Polysiloxane block copolymers	To get hydrophobic surface.	209
	FS	FEP	Fuel cell	203



alkylation reaction of the carboxylic acids on the surfaces. The chemical incorporation of the reagent on the surfaces was confirmed by the fluorescence microscope images of the membranes reacting with the alkylation reagent bearing a pyrene fluorophore.

Reid et al.<sup>213</sup> modified the surface of poly(3-(2-acetoxyethyl) thiophene) (P3AcET) membranes. Modified membranes were produced through surface hydrolysis under both basic and acidic conditions, yielding poly(3-(2-hydroxyethyl)thiophene) (P3HET), a highly permselective conducting polymer. Base hydrolyzed P3AcET membranes were prepared by treating the top surface with 4 M methanolic KOH for 30 min at room temperature. Acid hydrolyzed P3AcET membranes were prepared in a similar way using a solution of CH<sub>3</sub>OH : CHCl<sub>3</sub> : H<sub>2</sub>SO<sub>4</sub> 10 : 3 : 4 (v/v) for 15 min at room temperature. Microscopic (AFM, SEM) and spectroscopic (ATR-FTIR) characterization of the thin-film composites confirmed the surface specificity of the hydrolysis reaction. The gas transporting properties of these modified membranes were dramatically improved.

Polyacrylonitrile (PAN) membranes with an MWCO of 35,000 subjected as supports to NF composite membranes were prepared by the phase-inversion process of the PAN/NMP solutions, followed by the modification with NaOH. The modification with NaOH not only changed the hydrophilicity of membrane but also changed the morphology such as pore size. By the modification, both the flux and rejection of the PAN membrane can be increased due to the increased hydrophilicity and decreased pore size compared with the unmodified one.<sup>214</sup>

Composite polymer membranes with chemically different surfaces were prepared by the photochemical modification of Millipore microfiltration poly(vinylidene fluoride) (PVDF) and PSf membranes using 2-acrylamido-2-methyl-1-propanesulfonic acid, 2-hydroxyethylmethacrylate, and 2-(dimethylamino)ethyl methacrylate quaternized with methyl chloride. These membranes proved to be the most efficient in the filtration of natural surface water in a noncontiguous regime. That is explained by the ability of membranes to prevent the formation of a biofilm on their surfaces.<sup>33</sup>

Polyimide membranes were modified by immersing the films in the diamine/methanol solution for a stipulated period of time (cross-linking). A series of linear aliphatic cross-linking diamines reagents (ethylenediamine, propane-1,3-diamine, and butane-1,4-diamine) were used. This study demonstrated for the first time that diamine crosslinked membranes possess high separation performance and provide impressive separation efficiency for H<sub>2</sub>/CO<sub>2</sub> separation. Both pure gas and mixed gas data were better

than other polymeric membranes and above the Robeson's upper bound curve.<sup>215</sup>

The grafting of polyamide (PA) RO membrane was done by immersing the pieces or disks of the membrane in the reaction medium (mixture of monomer {methacrylic acid (MA), and 3-sulfopropyl methacrylate, K salt} and initiators (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> in aqueous medium) for appropriate time intervals. Comparison with the unmodified membrane showed that surface modification of the membranes resulted in drastic decrease in contaminant adsorption for some polymer grafts and increased ease in rinsing the contaminated surface.<sup>216</sup>

Phospholipid moieties were induced on the surface of poly(acrylonitrile-co-2-hydroxyethyl methacrylate) (PANCHEMA) based membranes via reaction of the hydroxyl groups on the membrane surface with 2-chloro-2-oxo-1,3,2-dioxaphospholane (COP) followed by the ring-opening reaction of COP with trimethylamine.<sup>210</sup> The chemical changes of phospholipid-modified acrylonitrile-based copolymers (PMANCP) were characterized by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The surface properties of PMANCP membranes were evaluated by pure water contact angle, protein adsorption, and platelet adhesion measurements. Pure water contact angles were obviously lower than those measured on the PANCHEMA membranes and decreased with the increase of the content of phospholipid moieties on the membrane surface. It was noticed that the BSA albumin adsorption and platelet adhesion were suppressed significantly with the introduction of phospholipid moieties on the membrane surface. These results suggested that the described process was an efficient way to improve the surface biocompatibility for the acrylonitrile-based copolymer membrane. Huang et al.'s<sup>217,218</sup> work also revealed that the antifouling property of PANCHEMA membrane could be enhanced along with the biocompatibility by the introduction of phospholipid moieties on the membrane surface.

Tan et al.<sup>219</sup> prepared PVDF HFMs with asymmetric structure and good hydrophobicity by a phase-inversion method and applied them for the removal of ammonia from water. Experimental results indicated that the post-treatment with ethanol was useful to improve both the hydrophobicity and the effective surface porosity of the resulting PVDF HFMs, and thus favor the ammonia removal.

PAN hollow-fiber UF membranes have been made from a new dope solution containing PAN/DMF/PVP 360K/1,2-propanediol.<sup>220</sup> The as-spun fibers were post-treated by means of hypochlorite solutions under different concentrations. The experimental results showed that water flux of a membrane decreased but retention for the same solute

increased with increasing air gap. The flux of a treated membrane was about twice higher than that of an untreated membrane. Retentions of an untreated membrane and a treated membrane for PEG 35K were 94 and 1%, respectively. There was an optimum hypochlorite concentration for the treatment to achieve a PAN membrane with a pure water flux of over  $200 \times 10^{-5} \text{ l m}^{-2} \text{ h}^{-1} \text{ Pa}^{-1}$ . The treated membranes experienced higher fouling tendencies than the untreated membrane.

The surface of a PSf membrane was modified by a series of Friedel-Crafts electrophilic substitutions of aromatic rings in the PSf molecules using reagent 1-chlorodecane or propylene oxide dissolved in hexane. The membrane surface was also modified by sulfonation with sulphuric acid water solution; in this way, negative charges were introduced at the membrane surface. Reaction with 1-chlorodecane gave a hydrophobic surface by nonpolar  $(\text{CH}_2)_9-\text{CH}_3$  groups and reaction with propylene oxide gave a hydrophilic surface with polar group  $-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{OH}$ . The surface of sulfonised PSf membranes contained ionizable  $-\text{SO}_3$  groups.<sup>221</sup>

Bridge et al.<sup>222</sup> reported that ethanol treatment of PAN-PVC phase-inversion membranes (hollow fibers) alters their morphology and permeability. In particular, hydropermeability and solute diffusive permeability of ethanol treated samples displayed significant increases when compared with that of the untreated controls.

Moloney<sup>223</sup> reported that modification of large range polymeric membranes can be done by direct chemical reactions under mild conditions and using inexpensive reagents. It was reported by Moloney<sup>222</sup> that functionalized diarylcarbenes are excellent reactive intermediates suitable for direct surface modification of a range of organic and inorganic materials.

Cao et al.<sup>224</sup> modified the poly(2,6-toluene-2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane diimide) (6FDA-2,6DAT) HFMs by chemical cross-linking for natural GS. To make fiber more resistant to plasticization, hollowfibers were immersed into a *p*-xylenediamine or *m*-xylenediamine/methanol solution for a short period of time at ambient temperature. FTIR

spectra confirmed that chemical crosslinking reactions took place between xylenediamine and imide groups of 6FDA-2,6DAT and formed amide groups.

Liu et al.<sup>225</sup> studied the effects of amidation on gas permeation properties of polyimide membranes. Using 6FDA-durene and 6FDA-durene/mPDA (50 : 50) as the examples, the amidation was performed by immersing these polyimide dense films in a 10% (w/v) *N,N*-dimethylaminoethyleneamine hexane solution for a certain period of time at ambient temperature. Gas permeabilities of the modified polyimides to He, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> were measured at 35°C, and the results suggested that the amidation lowered the gas permeability of all gasses, whereas it improved the gas permselectivities of He/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub>.

Tin et al.<sup>226</sup> modified Matrimid® 5218 by chemical cross-linking. The cross-linking reaction was conducted by simply immersing the membranes in a *p*-xylenediamine solution at ambient temperature for a stipulated time. The gas permeabilities decreased gradually with immersion time after achieving their maximum values at 1-day immersion time. The following table (Table VII) shows GS properties of original and crosslinked Matrimid® dense films.

The above modifications are summarized in Table VIII.

## OTHER TECHNIQUES FOR MODIFICATION

Several surface modification techniques that do not belong to any of the above methods are summarized below.

Molecular Imprinting Technology (MIT) allows preparing polymeric materials with selectivity toward specific molecules through polymerization or phase inversion in presence of template.<sup>227</sup>

Ion implantation on the surface of the membranes affects the surface properties. The surfaces of a composite polyamide NF membrane (NF 90 Filmetec) and a cellulose acetate NF membrane (SP 28 Osmonics) were modified by implanting with F-ions at two different intensities. Zeta potential measurements of unmodified membranes and modified membranes showed higher negativity with an

TABLE VII  
Gas Separation Properties of Original and Crosslinked Matrimid Dense Film<sup>a</sup>

Immersion time (days)	Permeability (Barrer)					Selectivity			
	He	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	He/N <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /N <sub>2</sub>
0	22.2	1.7	0.25	0.19	6.5	87	6.6	34	25.6
1	26.2	1.9	0.29	0.20	7.4	91	6.5	36	25.6
3	25.0	1.6	0.24	0.18	6.0	105	6.9	34	25.2
7	22.1	1.5	0.21	0.15	5.1	107	7	33	24.6
14	21.7	1.4	0.19	0.14	4.7	112	7	34	24.1
21	19.4	1.1	0.15	0.10	3.4	128	7.4	32	22.2
32	17.5	0.9	0.13	0.07	1.9	140	6.9	28	15.0

<sup>a</sup> 1 Barrer =  $1 \times 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm/cm}^2 \text{ s cmHg}$

**TABLE VIII**  
**Surface Modification by Chemical Reaction**

Membrane	Membrane type	Reaction	Application	Reference
Polyethylene terephthalate		Alkylation		212
Poly(3-(2-acetoxyethyl) thiophene)	FS	Hydrolysis (Base and acid catalysis)	Gas separation	213
Polyacrylonitrile	FS	Hydrolysis with NaOH	NF	214
Polyvinylidene fluoride and polysulfone	FS	Photochemical reaction	Filtration	33
Polyimide	FS	Cross-linking with diamines	H <sub>2</sub> /CO <sub>2</sub> separation	215
Polyamide RO	FS	Grafting MA and 3-sulfopropyl methacrylate with radical initiators	RO (decrease in contamination)	216
Poly(acrylonitrile-co-2-hydroxyethyl methacrylate)	FS	Adding phospholipid moieties	(antifouling)	217,218
PVDF	Hollow fiber	Ethanol	Ammonia removal from water. (improve the hydrophobicity and the effective surface porosity)	219
Polysulfone	FS	Friedel-Crafts reaction	Filtration of water (negative charges introduced on the surface)	221
PAN-PVC	Hollow fiber	Ethanol	Delivery of small molecules using cell encapsulation membranes. (increase in hydropermeability)	222
PAN/DMF/PVP 360K/1,2-propanediol 6FDA-2,6DAT	Hollow fiber	Hypochlorite solutions	UF	220
	Hollow fiber	<i>p</i> -xylenediamine or <i>m</i> -xylenediamine/methanol solution.	CO <sub>2</sub> /CH <sub>4</sub> Separation (natural gas separation).	224
polyimide	FS	<i>N,N</i> -dimethylaminoethyleneamine hexane solution	GS	225
Polyimide (Matrimid®)	FS	<i>p</i> -xylenediamine solution	GS	226

increased intensity of ion implantation. Multi-component salt permeation experiments were performed. A decrease of solute flux for all the ions through the modified membranes was observed when compared with the unmodified membrane. It was suggested that ion implantation on NF surface is a novel technique to increase salt rejection property of membrane.<sup>228</sup>

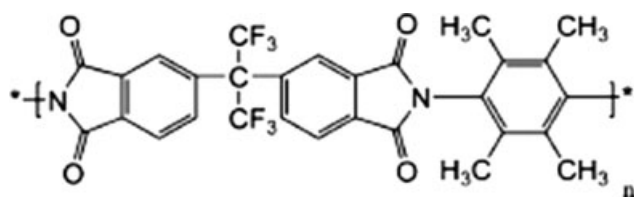
Kochkodan et al.<sup>229</sup> studied composite microfiltration membranes with a thin layer of imprinted polymer (MIP) selective to cAMP (adenosine 3′0.5′-cyclic monophosphate). PVDF microfiltration membrane was used as a porous support for deposition of polymer layer imprinted with cAMP. The surface of the membranes was studied by AFM and SEM. Both PVDF membranes with and without (blank) MIP coating were subjected to UV irradiation for the surface modification. Different degrees of modification were obtained by varying the UV irradiation period to control the binding capacity of the membrane.

The following Table VIII shows sorption and water flux on MIP coated and blank. PVDF membranes with different degrees of modification (degree of modification was calculated from the difference in weight between the modified membrane with deposited MIP layer and the initial membrane sample). The fluxes through MIP membranes were still in the

**TABLE IX**  
**Sorption and Water Flux of MIP and Blank PVDF Membranes with Different Degrees of Modification<sup>229</sup>**

Degree of modification μg cm <sup>-2</sup>	Sorption, %		<i>J<sub>m</sub></i> / <i>J<sub>0</sub></i> *
	MIP	Blank	
0	—	3	1.00
400	22	8	0.82
580	44	12	0.77
1100	72	28	0.48

Note: *J<sub>m</sub>* = water flux in MIP membrane and *J<sub>0</sub>* = water flux in blank PVDF membrane.



**Figure 9** Chemical structure of 6FDA-Durene polyimide.

range for micro-filters, and, thus, are well suited for a fast membrane solid-phase extraction.

Table IX Sorption and water flux of MIP and blank PVDF membranes with different degrees of modification.<sup>229</sup>

Dendrimers or other hyperbranched polymers are a new class of artificial polymers with unique properties, such as high degree of branching units, high density of surface functional groups, nano-scaled size, well-defined molecular weight, and low-dispersity.<sup>230</sup> These features make them attractive materials in the field of membrane science. Wang et al.<sup>230</sup> wrote a small review of current patents on Dendrimers or other hyperbranched polymers in membrane field such as proton exchange, bipolar membranes, GS membranes, and solid-liquid separation membranes, etc.

Xiao et al.<sup>231</sup> reported 6FDA-polyimide films modified by polyamidoamine (PAMAM) dendrimers with generations of 0, 1, and 2.

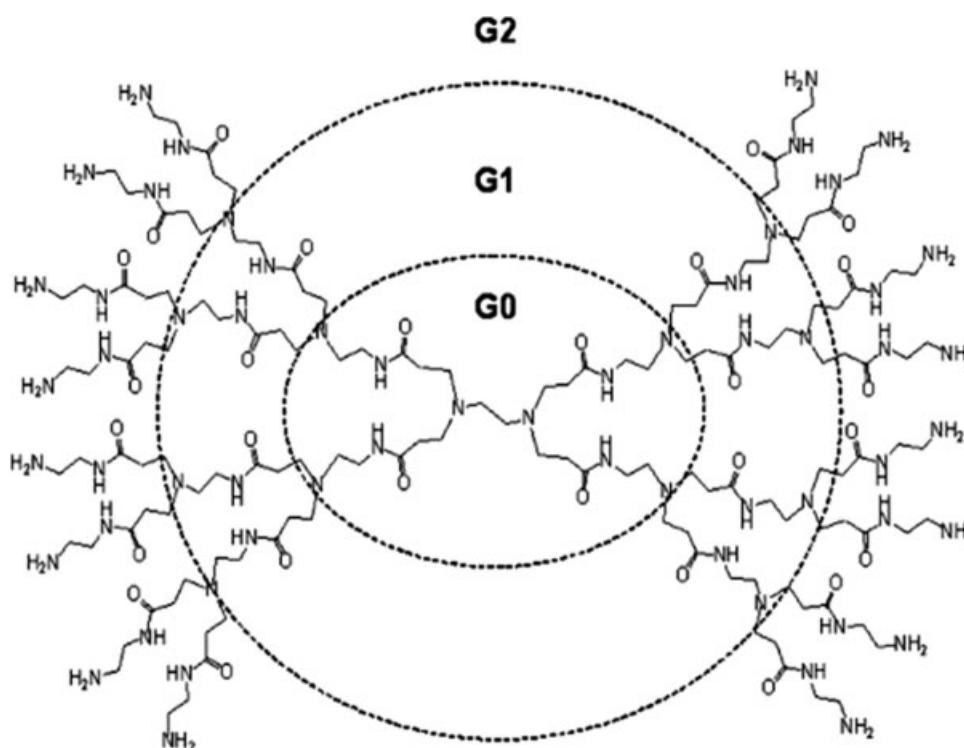
Figure 9 shows the chemical structure of 6FDA-Durene polyimide. The planer schematic structure of these dendrimers is shown in Figures 10 and 11

show the dimension of different generation PAMAM dendrimers.

The films were modified by simple immersion procedure at room temperature and characterized by AFM, XPS, ATR-FTIR spectroscopy, and gas-transport measurements. Compared with simulated results, the morphology and conformation of grafted PAMAM dendrimers on polymer surfaces were disk-shaped molecular clusters. These modified polyimide films exhibited excellent GS performance. Figure 12 shows the immersion time effects on performance of modified polyimide films excluding solvent swelling effects. The ideal selectivity of He/N<sub>2</sub> increases tremendously to about 200% as compared with that of the original polyimide film. Particularly, the separation performance of CO<sub>2</sub>/CH<sub>4</sub> gas pair can be improved beyond the upper bond limit possibly due to the strong interactions of dendrimer molecules with CO<sub>2</sub>, which was verified by sorption tests.

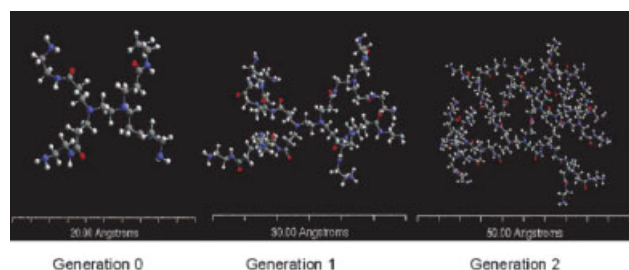
Chung et al.<sup>232</sup> demonstrated the effect of shear rate on the outer surface morphology of PES hollow-fiber UF membranes. The analysis of AFM images showed that the roughness of the outer surface of hollow-fiber UF membranes in terms of  $R_m$ ,  $R_a$ , and  $R_z$  decreased with an increase in shear rate. It was observed that the pure water flux of the membranes was nearly proportional to the mean roughness and higher mean roughness resulted in lower separation of membranes.

Peng and Chung<sup>233</sup> successfully produced defect-free as-spun Torlon® HFMs with an ultra-thin dense



**Figure 10** Planar schematic of the basic PAMAM dendrimer functionality.





**Figure 11** Dimension of different generation PAMAM dendrimers (simulated). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

layer of around 540 Å from a one polymer (Torlon® 4000TF poly(amide imide))/one solvent (NMP) binary system at reasonable take-up speeds of 10–50 m/min. The best O<sub>2</sub>/N<sub>2</sub> permselectivity achieved was much higher than the intrinsic value of Torlon® dense film. Figure 13 shows the comparison of the highest obtained O<sub>2</sub>/N<sub>2</sub> selectivity and the corresponding dense-layer thickness of the hollow fibers versus spinneret dimension.

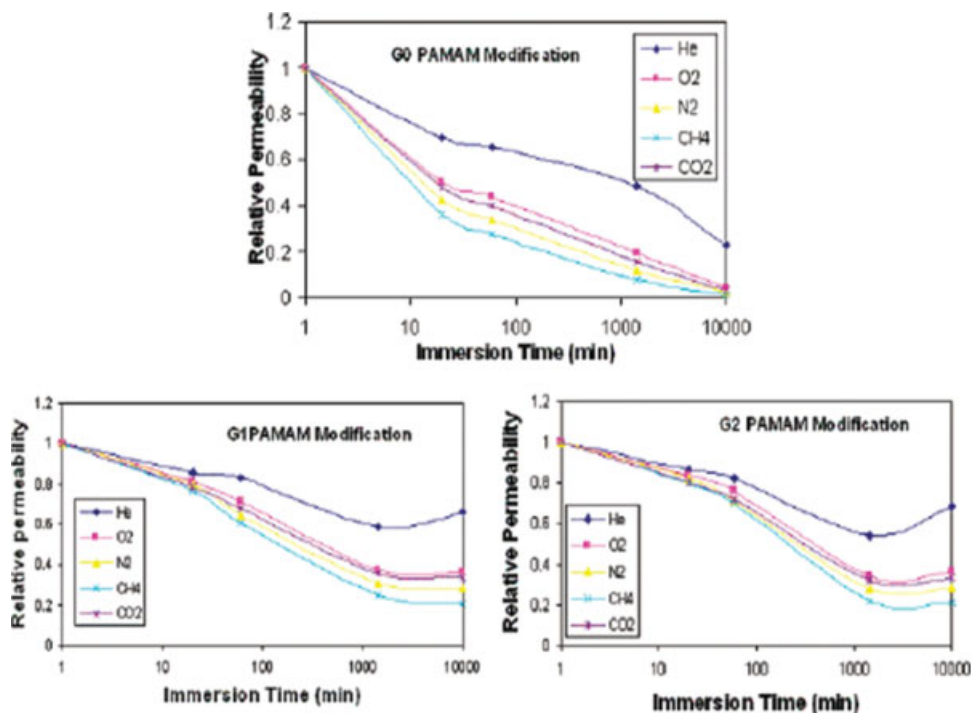
Li<sup>92</sup> employed tailor-made (newly designed) PVDF asymmetric HFMs for soluble gas removal from waste gas stream. It was reported that skin location (by SEM study) was largely dependent on the coagulation medium. Addition of a substantial amount of ethanol in a coagulation medium would largely affect the formation of the skin. Experimental results obtained from the different membrane developed indicated that the PVDF membranes with

much reduced membrane resistance could be prepared by properly selecting internal coagulant and adding an appropriate additive in the polymer-forming solution.

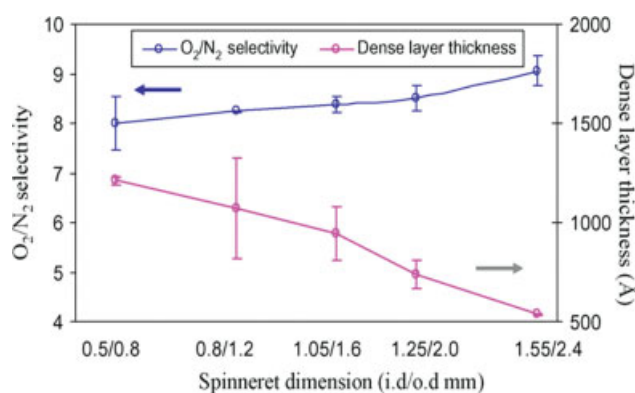
Jin et al.<sup>234</sup> developed a light-responsive permeation membrane modified by an organic azo derivative on a porous glass tube and showed decrease in gas permeation upon simulation with an Xe-lamp, which returns to the starting level upon stopping the irradiation.

A new method for polymer inclusion membrane (PIM) has been developed. In this method, a commercial cellulose triacetate (CTA) HFM was allowed to swell in 2-nitrophenyl-*n*-octyl ether (NPOE) in the presence of chloroform as a solvent for CTA and *N,N,N,N'*-tetraoctyl-3-oxapentane diamide (TODGA) as a carrier. After evaporating chloroform, a hollow-fiber PIM containing NPOE and TODGA was obtained. The result of the transport experiment of Ce+3 ions using the hollow-fiber PIM showed that cerium ions were effectively transported from the feed solution to the strip solution through the hollow-fiber PIM, indicating that the hollow-fiber PIM was successfully prepared using the post-treatment method.<sup>235</sup>

It has been shown that molecularly imprinted polymers (MIPs) have a specific synthetic receptor structure.<sup>236</sup> The preparation of MIPs usually includes copolymerization of a functional and cross-linker monomer in the presence of a template molecule. Subsequent removal of the template molecules



**Figure 12** Immersion time effects on performance of modified polyimide films excluding solvent swelling effects. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 13** Comparison of the highest obtained  $O_2/N_2$  selectivity and the corresponding dense-layer thickness of the hollow fibers vs. spinneret dimension. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

leaves behind receptor sites, which are complementary to the template because of shape and the position of the functional groups. In this way a molecular memory is introduced into the polymer, which becomes capable of selectivity rebinding the template molecule.<sup>237,93</sup>

Yu et al.<sup>238</sup> modified the surface of poly(L-lactic acid) (PLLA) membrane in a layer-by-layer (LBL) self-assembly manner for the improvement of hydrophilicity, antibacterial activity, etc., via polyelectrolyte multilayer (PEM) immobilization. The polysaccharide PEMs, including chitosan (CH) and dextran sulfate (DS)-stabilized silver nanosized colloid (DSS), were successfully deposited on the aminolyzed PLLA membrane in a LBL self-assembly manner. This membrane can be used for applications in haemodialysis devices is useful.

Hamad and Matsuura<sup>239</sup> brominated to three levels of degree of bromination of high molecular weight PPO and studied the transport properties of  $CO_2$ ,  $CH_4$ ,  $O_2$ , and  $N_2$  gases of brominated PPO membranes. The main effect of bromination of PPO was to increase the permeability of gases while maintaining the same permselectivity. The main effect of simultaneous sulfonation and bromination of PPO was: (i) to increase the gas permeability, and to decrease the gas permeability ratio, in comparison to sulfonated PPO (SPPO), while on the other hand, (ii) to decrease the gas permeability, and to increase the gas permeability ratio, in comparison to brominated PPO (PPOBr).

The composite membranes from copolymers of tetrafluoroethylene (TFE) and 2,2,4 trifluoro-5-trifluoromethoxy-1,3-dioxane (TTD) (HYFLON® AD) supported on PA MF membranes were prepared by Gordano et al.<sup>240</sup> The three key properties affecting performance: pore size distribution, surface morphology, and particle adhesion were studied by AFM.

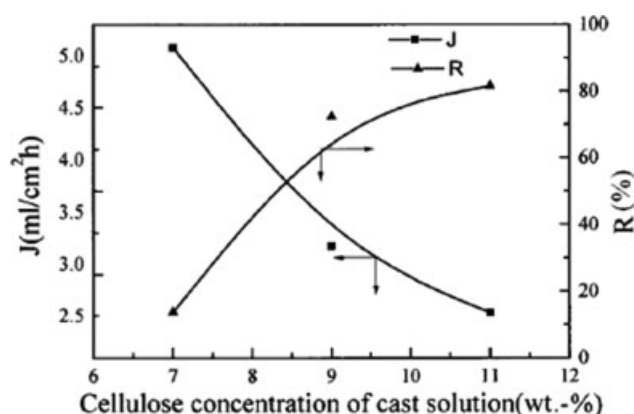
Zhang et al.<sup>241</sup> obtained cellulose membranes by solutions of cellulose being cast into a mixture of *N*-methyl-morpholine-*N*-oxide (NMMO) and water under different processing conditions. The results obtained showed that the surface morphologies were intrinsically associated with permeation properties. For cellulose membranes, increasing the NMMO concentration and the temperature of the coagulation bath led to higher fluxes and lower BSA rejection. The relationship between the cellulose concentration, pure water flux, and rejection of BSA is shown in Figure 14.

Kapantaidakis et al.<sup>242</sup> studied the effects of major spinning parameters, such as polymer concentration, air-gap distance, bore fluid composition, and take-up velocity on the structure and permeation properties of PES-PI GS hollow fibers. The longer the nascent HFM was exposed to a humid air gap, the higher the water content in the top layer before demixing occurred and the higher surface porosity and gas permeance. Suitable selection of the spinning conditions resulted in GS hollow fibers with thin skin layer (0.1  $\mu m$ ), macrovoid-free substructure, and high permeation rates ( $CO_2$ : 40–60 GPU) and selectivity coefficients ( $\alpha_{CO_2/N_2}$ : 40).

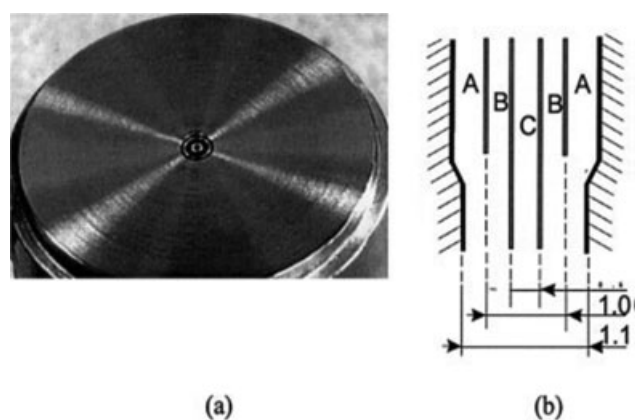
He et al.<sup>243</sup> used a triple-orifice spinneret for the preparation of hollow-fiber PSf microfiltration membranes with a high-surface porosity. Figure 15 shows a schematic of a triple-orifice spinneret.

A simple way to obtain a highly porous top layer independent of polymer solution in spinning process is to apply a good solvent as the external liquid using a triple-orifice spinneret. Table X shows the effect of NMP on the properties of a PSf/PVP blend membranes.

Dilution solvents, i.e., NMP and NMP/Acetone (50/50 wt %), can be used as the external liquids during spinning, but acetone, a mild nonsolvent for PSf, alone can not be used.



**Figure 14** Effect of the concentration of the casting solution on the permeation flux and cut-off performance of membranes.

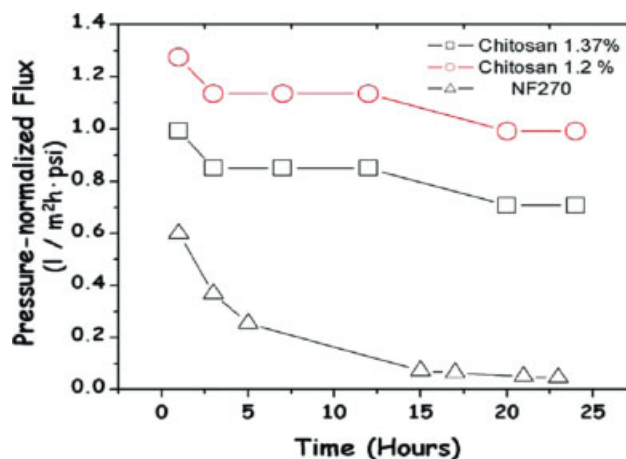


**Figure 15** Schematic of a triple-orifice spinneret. Dimension values are in millimeter. (a) bottom view of a spinneret; (b) cross-section view. A, external fluid; B, polymer solution; C, bore liquid.

Sharp and Escobar<sup>244</sup> tested different coagulation pretreatment techniques to improve membrane filtration in water treatment by UF. These techniques were (i) conventional coagulation, (ii) forming a dynamic, or secondary, coagulant-based layer on the membrane, and (iii) injecting the coagulant into the feed line so that it runs in line with the raw water across the membrane. The favorable best results were obtained from the dynamic membrane's mode of operation. Thus, a coagulant-based dynamic membrane has the potential to be an effective method to improve UF efficiency in water separation application.

Yoon et al.<sup>245</sup> demonstrated a new type of high-flux UF/NF medium based on an electrospun nanofibrous scaffold (PAN) coupled with a thin top layer of hydrophilic, water resistant, but water-permeable coating (e.g., chitosan). Figure 15 shows the flux performance of the three-tier composite membrane with coating of 1.37 and 1.2 wt % solutions on an asymmetric electrospun PAN support as well as the commercial NF filter for filtration of oily waste water. Such nanofibrous composite membranes can replace the conventional porous membranes and exhibit a much higher flux rate for water filtration.

Figure 16 Flux performance of the three-tier composite membrane with coating of 1.37 and 1.2 wt % solutions on an asymmetric electrospun PAN sup-



**Figure 16** Flux performance of the three-tier composite membrane with coating of 1.37 and 1.2 wt % solutions on an asymmetric electrospun PAN support as well as the commercial NF filter (Dow NF270) for filtration of oily waste water (1350 ppm of vegetable oil + 150 ppm of DC 1193 fluid + water). The operation conditions were as follows: the inlet pressure was 130 psi and the temperature was 30–33°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

port as well as the commercial NF filter (Dow NF270) for filtration of oily waste water (1350 ppm of vegetable oil + 150 ppm of DC 1193 fluid + water). The operation conditions were as follows: the inlet pressure was 130 psi and the temperature was 30–33°C.

Li et al.<sup>247</sup> using Matrimid 5218 as the outer-layer material and PES and its blends as the inner layer materials, studied the morphological aspects and structure control of dual-layer asymmetric HFMs formed by a simultaneous coextrusion approach. The science and engineering factors to produce dual-layer HFMs with high integrity have been investigated. Experimental results indicated that the macrovoids in the inner PES dope cannot be easily eliminated by the modification of the inner dope viscosity, but can effectively suppressed by either the addition of PEO in the PES inner dope or spinning fibers at much higher elongational draw ratios.

Taselli et al.<sup>247</sup> produced a series of HFMs by the dry-wet-spinning method from PEEKWC, a modified poly(ether ether ketone) with good mechanical, thermal, and chemical resistance. The fibers were prepared under different spinning conditions, varying the following spinning parameters: polymer concentration in the spinning solution, height of the air gap, and bore liquid composition. The effect of these parameters on the water permeability, the rejection of macromolecules (using dextran with an average molecular weight of 68,800 g/mol, and the morphology of the membrane was studied. Permeability varied from 300 to 1000 L/(h m bar) and rejection to the dextran from 10 to 78%.

**TABLE X**  
Effect of NMP on the Properties of a PSf/PVP Blend Membranes (Dope Composition PSf : PVP : NMP = 15 : 15 : 70 wt %)

External liquid	PWP <sup>a</sup> (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	Pore size (μm)
NMP/Acetone	18	Dense layer
NMP	4700	1.2–1.3

<sup>a</sup> PWP; pure water permeability



Albrecht et al.<sup>248</sup> demonstrated the preparation of highly asymmetric HFMs from poly(ether imide) by a modified dry-wet phase-inversion technique using a triple spinneret. These fibers were characterized by solute rejection technique and gas permeability. These membranes are aimed at a first application in a gas-liquid contactor system.

Tsai et al.<sup>249</sup> indicated that air-gap length and ambient humidity have dramatic effect on the HFM morphology, prepared from PSf/NMP system. Microvoids in the membrane disappeared, reappeared, and redisappeared with increasing air-gap length.

Wang et al.<sup>250</sup> studied the effect of flow angle and shear rate within the spinneret on the separation performance of PES UF HFMs. Experimental results showed that higher dope flow rates (shear rates) in the spinneret produced UF HFMs with smaller pore size and denser skin layers due to molecular orientation. Macrovoids was significantly suppressed and almost disappeared in the 90° (straight) spinneret at high dope flow rates. This phenomenon cannot be observed for the 60° conic spinneret.

Idris et al.<sup>251</sup> used surface force-pore flow model for the deduction of fine structural details of RO HFMs. The modeling results revealed that increased extrusion shear rate would decrease both pore size and thickness of the active layer, thus increasing the separation performance of the RO HFMs.

Qin et al.<sup>252</sup> developed novel hollow-fiber polyimide composite membrane for GS. Five fluorinated polyimide (including 6FDA-durene, 6FDA-Durene-mPDA, 6FDA-pSED, 6FDA-mSED, and 6FDA-ODA) were used for composite membranes with PSf as substrates. Both selectivity and permeance of 6FDA-Durene-mPDA composite membranes increased with increasing concentration of the coating solution. A defect-free multilayer membrane of PSf/6FDA-Durene/silicon rubber was obtained after the 6FDA-Durene composite membrane was repaired by silicon rubber.

Li et al.<sup>253</sup> prepared a composite PU-SiO<sub>2</sub>HFMs via optimizing the technique of dry-jet wet-spinning, and their pressure responsibilities were confirmed by the relationship of pure water flux-trans-membrane pressure (PWF-TP). The effects of SiO<sub>2</sub> content on the structure and the properties of membrane were investigated. The experimental results indicated that SiO<sub>2</sub> in membrane created many interfacial microvoids and played an important role in pressure responsibility, PWF and rejection of membrane: with the increase of SiO<sub>2</sub> content, the ability of membrane recovery weakened, PWF increased, and rejection decreased slightly.

Meng et al.<sup>254</sup> coated an uniform layer (thickness around 5–12 μm) of polyvinyl dimethylsiloxane (PVDMS) on the surface of porous PVDF hollow fibers. Using N<sub>2</sub>/O<sub>2</sub> as the medium, the separation

properties of PVDMS-PVDF composite HFMs were evaluated experimentally. The experimental data of both permeability and selectivity were in good agreement with the theoretical results predicted by the presented pore-distribution model. To obtain the compact composite membrane free of defects by the dip-coating technique, the thickness of PVDMS skin must be higher than 5 μm.

It was observed that on deposition of titanium oxide on the surface of polymeric membranes the biological overgrowth on the membrane surfaces is diminished.<sup>255</sup>

Wang et al.<sup>256</sup> demonstrated a new kind of high-flux UF membrane based on PVA electrospun nanofibrous scaffold support and coated with PVA hydrogel. Results obtained from these membranes indicated that such unique hydrophilic nanofibrous composite membranes exhibited a water flux rate (>130 L/m<sup>2</sup> h) significantly higher than commercial UF membranes but with similar filtration efficiency (rejection rate >99.5%).

Tan et al.<sup>257</sup> removed three triphenylmethane dyes, malachite green (MG), brilliant green (BG), and new fuchsine (NF) from aqueous solution by PSS polymer-enhanced UF using PSf HFMs.

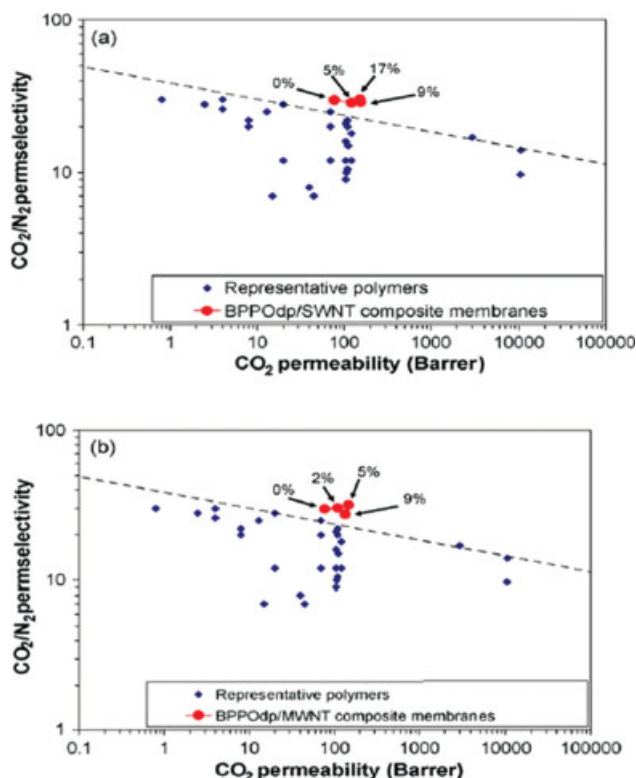
Qin and Wang<sup>258,259</sup> prepared nano-scaled cross-linked PVA fibers by electrospinning and reported its use in filtration process. The filtration efficiency increases sharply when crosslinked PVA nanofibers layers were added to the sublayers.

Li et al.<sup>260</sup> developed delamination-free dual-layer asymmetric composite HFMs (fluoropolyimide/PES) for GS by using coextrusion and dry-jet wet-spinning-phase-inversion technique. Delamination-free is essential for dual-layer membrane. In their study, they used a 6FDA-durene-1,3-phenylenediamine(mPDA) copolyimide with a molar ratio 50 : 50 as the top selective layer material. PES was employed to yield the inner interpenetrated porous supporting layer. Pure gas test results showed that the resultant 6FDA-durene-mPDA/PES membranes had a O<sub>2</sub>/N<sub>2</sub> selectivity which was approaching to the intrinsic ideal selectivity value for 4.7 with a permeance of oxygen around 28 GPU (gas permeation unit) at room temperature, indicating the dual-layerHFMs were apparently defect-free.

Wang et al.<sup>261</sup> developed defect-free asymmetric hexafluoro propane diandhydride (6FDA)-durene polyimide hollow fibers with a selectivity of 4.2 for O<sub>2</sub>/N<sub>2</sub> and a permeance of  $33.1 \times 10^{-6}$  cm<sup>3</sup> (STP)/cm<sup>2</sup> s cmHg for O<sub>2</sub>. These fibers were spun from a high viscosity *in situ* imidization dope consisting of 14.7% 6FDA-durene in NMP solvent and the inherent viscosities (IV) of this 6FDA-durene polymer was 0.84 dL/g.

Ren et al.<sup>262</sup> and Chung et al.<sup>263</sup> developed an asymmetric poly(2,6-toluene-2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane diimide) (6FDA-2,6DAT)





**Figure 17** Separation properties of BPPO<sub>dp</sub>/SWNTs (a) and BPPO<sub>dp</sub>/MWNTs (b) nanocomposite membrane.<sup>246</sup> [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

HfMs with high performance for CO<sub>2</sub>/CH<sub>4</sub> separation. It was noticed that the shear rate within the spinneret plays an important role in determining morphology and separation performance of HfMs.

In recent years, much attention has been given to carbon molecular sieve membranes. A novel method has been demonstrated to produce hollow carbon fibers with excellent separation properties by a special type of precursor. These hollow carbon fibers have been produced from PSf-beta zeolite/Matrimid dual-layer hollow fiber. The outer layer was PSf-beta zeolite mixed matrix, and Matrimid was inner layer. The performance of the resultant dual-layer hollow carbon fibers was much superior over that of single layer hollow carbon fibers. Pure gas permeation measurements, on dual-layer hollow carbon fibers showed selectivity of 9.1 and 150 for O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>, respectively, while the selectivity for the mixed gas CO<sub>2</sub>/CH<sub>4</sub> was 128.<sup>264</sup>

Since the discovery in 1991,<sup>265</sup> carbon nanotubes (CNTs) have been considered the ultimate carbon fiber with unique mechanical, thermal, and electric properties, and thus have been added to so many polymeric materials to improve their properties.<sup>266,267</sup> It is well known that low concentrations of CNTs in polymer matrices can significantly enhance the mechanical strength of the polymeric materials. Kim et al.<sup>266</sup> reported that adding CNTs to poly(i-

mid siloxane) membranes increased the permeability of O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>. Cong et al.<sup>267</sup> revealed that pristine single-wall CNTs (SWNTs) and multiwall CNTs (MWNTs) formed polymeric nano composite membranes with brominated poly (2,6-diphenyl-1,4-phenylene oxide) (BPPO<sub>dp</sub>). These membranes were used for GS. The CO<sub>2</sub> permeability increased with increasing the CNT content and reached a maximum of 551 Barrer at 9 wt % of SWNTs, or 148 Barrer at 5 wt % of MWNTs. As shown in Figure 17, the CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity points of both BPPO<sub>dp</sub>/SWNTs and BPPO<sub>dp</sub>/MWNTs membrane were above a reference line referred to as Robeson's line.<sup>268</sup> It is feasible to add CNTs to polymeric membranes for improved mechanical properties without deteriorating their GS performance.

Pereira et al.<sup>269</sup> prepared HFMs for GS, via simultaneous spinning of two polymer solutions by using a triple-orifice spinneret and presented several benefits such as the possibility of forming each membrane layer by different concepts. However, besides the complexity of the phenomena involved in hollow-fiber formation, mass transfer between the polymer solutions required further investigation.

As delamination-free is essential for dual-layer membranes, Li et al.<sup>260</sup> developed delamination-free dual-layer asymmetric composite HFMs for GS. 6FDA-durene-1,3-phenylenediamine (mPDA) (50%) copolyimide was used to form the outer symmetric separating layer, whereas PES was employed to yield the inner interpenetrated porous supporting layer. Pure gas test results showed that the resultant 6FDA-durene-mPDA/PES dual-layer membranes had an O<sub>2</sub>/N<sub>2</sub> selectivity approached to the intrinsic ideal selectivity value of 4.7 with a permeance of oxygen around 28 GPU at room temperature, indicating that the dual-layer HFMs were apparently defect-free.

Holt et al.<sup>270</sup> used micro-fabricated membranes having aligned carbon nanotubes with diameter of less than 2 nm which served as pores for the molecular transport of water and gas. Two types of carbon nanotubes, i.e., multi-walled (MWNTs) and double-walled (DWNTs) were used. Both types of gasses, i.e., nonhydrocarbon (H<sub>2</sub>, He, Ne, N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub>, and Xe) and hydrocarbon gasses (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>6</sub>, and C<sub>4</sub>H<sub>8</sub>) were studied. It was observed that the absolute gas flux through these membranes exceeded the flux predicted by the Knudsen model by more than an order of magnitude. The measured water flow rates also revealed a flow enhancement that is more than the slip, hydrodynamic flow as calculated from the Hagen-Poiseuille equation. The gas and water permeabilities of those nanotube based membranes were several orders of magnitude higher than commercial polycarbonate membranes, despite having pore sizes an order of magnitude smaller.

Holt et al. predicted that these membranes would enable fundamental studies of mass transport in confined environments, as well as more energy-efficient nanoscale filtration.

Yoshimune et al.<sup>271</sup> fabricated carbon molecular sieve (CMS) HFMs using PPO and its functionalized derivatives (R-PPO). Gas-transport properties were measured for He, H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>. PPO CMS membranes exhibited higher performances than those of polymeric precursors. The highest performance was attained by trimethylsilyl-PPO (TMSPPPO) CMS membrane pyrolyzed at 923 K, of which O<sub>2</sub> permeability was 125 Barrer and O<sub>2</sub>/N<sub>2</sub> permselectivity was 10.0 at 298 K.

Gas separating carbon HFMs based on 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 80% methylphenylene-diamine + 20% methylene diamine copolyimide precursor were studied for their permselective properties.<sup>272</sup> The permeability (Barrer) of He, H<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub> were measured at atmospheric pressure and temperatures 313, 333, and 373 K and were found higher than those of the precursor.

School of Chung<sup>273-276,87</sup> studied the GS on many modified polyimide membranes.

#### RECENT PATENTS ON THE MODIFICATION OF SYNTHETIC MEMBRANES

Since 2000, more than 100 patents have been made/applied on the modification of surfaces or surface related. Mostly the patents are on the medical field and of inorganic membranes. In this section, the matter of the article is limited to synthetic polymeric membrane for filtration and GS.

The main subject of the modification is to change hydrophobic surfaces to hydrophilic or vice versa. To render hydrophobic membranes hydrophilic, a wetting agent, such as a surface-active agent, can be added to a polymeric system being used to cast the membrane. Typically such coatings are only temporary, and the membrane so coated cannot be subjected to repeated wetting and drying procedures without loss of wettability.

Additional method of casting membranes rely on the inclusion of hydrophilic crosslinkable monomers in a casting solution of dissolved hydrophobic polymer. Upon casting, a semicrystalline polymer with hydrophilic surface properties is formed.<sup>277,278</sup>

Another method of preparing hydrophilic membranes involves graft polymerizing a hydrophilic monomer onto the surface of a porous hydrophobic polymeric membrane substrate. A typical example of a photochemical grafting process used to modify a hydrophobic surface with hydrophilic polymers is described in US Patent No. 5,468,390.<sup>279</sup> Many pat-

ents were made on the preparation of hydrophilic surfaces over the hydrophobic surfaces.

Muller<sup>280</sup> fabricated a porous polymeric membrane from a blend of a membrane forming material, such as PVDF or PSf, and a polymeric reactivity modifying agent adapted to modify the surface-active properties of the porous polymeric membrane. The reactivity modifying agent was preferably a linear polymeric anhydride, such as poly(alkyl vinyl ether/maleic anhydride). The surface activity modification included the modification of hydrophilicity/hydrophobicity balance of the membrane, or hydrolysis followed by reaction with a polyamine to form a crosslinked polyamide layer. Such modified membranes can be used as RO membrane.

Rana et al.<sup>281</sup> reported hydrophilic surface-modifying macromolecules (H-phil SMM) and H-phil SMM blended membranes. The membranes include a base polymer, and a hydrophilic surface-modifying macromolecules (H-phil SMM) which impart surface hydrophilic properties to the membrane. The membranes produced with the surface-modifying molecules were useful in the separation of water from a solution containing volatile organic compound and water.

Microfiltration membranes having high pore density and mixed isotropic and anisotropic structure were also patented by Wang et al.<sup>282</sup>

Ditter et al.<sup>283</sup> fabricated elongated HFMs having an outer surface, a plurality of pores and a pore size gradient increasing inwardly in radial direction such that the pores form a substantially hollow passage in the fiber. The HFMs were made by mixing a liquid lumen forming agent with a polymer dope, and the contacting the dope with a quench fluid for a time sufficient for the dope to solidify, wherein the quench fluid is contacted only at an outer surface of the dope corresponding with an outer surface of the hollow fiber.

The invention Muller and Mullette<sup>284</sup> relates to a terpolymer of tetrafluoroethylene (TFE) monomer, PVDF monomer and hexafluoropropylene (HFP) monomer for forming an UF or MF membrane, method of forming said membranes, and to the UF or MF membranes themselves. They claimed the method of preparing polymeric UF or MF of improved structure including the step of adding a nucleating agent to the membrane dope before casting.

Laurencin et al.<sup>285</sup> developed polymeric nanofibers which were useful in a variety of medical and other applications such as filtration devices. Nanofibers were formed from biodegradable and nonbiodegradable polyphosphazene, their blends with other polyphosphazenes or with organic, inorganic/organometallic polymers as well as composite nanofibers of polyphosphazenes with nanosized particles such as hydroxyapatites.

Kriesel et al.<sup>286</sup> described the usefulness of nano film prepared from a mixture of polymeric components (one or more) and amphiphilic species for filtration purposes. The amphiphilic species or components may be oriented on an interface or surface. In some embodiments, the nanofilm composition comprises a reaction product of a polymeric component and an amphiphile.

Moya<sup>287</sup> described the process for coating a polymeric composition having hydrophilic functional group onto a porous or nonporous substrate.

Moya and Kozlov<sup>288</sup> described a process for forming a hydrophobic PSf composite polymeric membrane having its surface rendered hydrophilic with a hydroxyalkyl cellulose and having a throughput greater than about 1000 L/m<sup>2</sup>. They claimed the membrane will be also useful for removing virus from a protein solution.

Witzko et al.<sup>289</sup> invented a permanent hydrophobic and optionally oleophobic thin film for polymer surfaces comprising at least one layer of water-soluble polycation or cationic synthetic resin and optionally a substance selected from the group consisting of long-chain surfactants and alkyl-substituted polyanions. The surfactant may be an aliphatic-unbranched long-chain fluorinated surfactant or an anionic surfactant.

Kurth and Hodgins<sup>290</sup> invented a novel method for modifying the surface of polymeric matrix (as well as other materials). The method is versatile and can be used to prepare polymeric matrix having altered, improved, or specifically engineered properties. Additionally, the method can be used to prepare polymeric matrices that have reactive groups that can be used to immobilize upon the matrices a variety of other "ligand" groups.

Penezina et al.<sup>291</sup> patented a method to make composite porous membranes comprising a porous hydrophobic substrate (such as polyvinylidene fluoride (PVDF)) coated with difunctional surface-modifying molecules. The difunctional surface-modifying molecules provide a hydrophilic surface without forming branches of interconnected polymer molecules in pores. The hydrophilic portion of the surface-modifying molecules comprises at least two crosslinking active groups. One group facilitates polymerization of the molecules, while the other group facilitates crosslinking between polymerized molecules. In one aspect, a crosslinking active group comprises a carbon-carbon double bond or another chemical group capable of free radical formation after hydrogen abstraction. Suitable hydrophilic groups comprise the general formula  $[-X_{n1}-Y-CR=CH_2]_{n2}$  where X is independently selected from the group including, but not limited to,  $X=(-CH_2-CH_2-O-); (-CH_2-O-); (CH_2-CH(COOH)-); (-CH_2-CH(OH)-)$ , Y can

include, but is not limited to  $(-CH_2)_{n3}; (-COO-)$  and  $n1$  is from about 1–50, whereas  $n2$  is from about 1–2, and  $n3$  can be from about 1–50. This method also provides a method for making composite porous membranes, such as a composite hydrophilic membrane with reduced concentration of surface-modifying molecules required to coat a hydrophobic substrate.

Nelson and Dahl<sup>292</sup> described a new technique for modifying at least a portion of a porous polymeric surface. The method includes contacting the porous polymeric surface with at least one polyelectrolyte, resulting in the physical adsorption of at least one polyelectrolyte onto the porous polymeric surface to form a charge modified surface.

Charkoudian<sup>293</sup> reported a method for crosslinked multipolymer coating on the membrane surfaces. These membranes had superior combination of properties (including heat stable biomolecule resistant adsorptive properties, resistance to strong alkaline solutions, and low levels of extractable matter).

Mullette and Muller<sup>294</sup> introduced Halar [poly(ethylene chlorotrifluoroethylene)] and related compounds for the preparation of porous polymeric UF and MF membranes. Preferred solvents, coating agents, and pore forming agents were citric acid ethyl ester or glycerol triacetate. The membranes may be in the form of a hollow fiber or FS and may include other agents to modify the properties of the membrane, such as the hydrophilic and hydrophobic balance.

Moya and Goddard<sup>295</sup> described a method for producing a composite porous article having a porous polymeric substrate and a hydrophobic/oleophobic polymeric surface formed from a crosslinked ethylenically unsaturated monomer containing a fluoroalkyl group. Suitable porous polymeric substrates include microporous or UF membranes, screens, nonwoven or woven fabrics, hollow fibers, or the like.

Raghavan et al.<sup>296</sup> described a filter medium comprising a microporous polyvinylidene fluoride membrane and a polymer containing a positively charged organic phosphonium compound grafted to the membrane in a concentration sufficient to provide a surface of said membrane with a positive charge such that there is minimal susceptibility to the extraction of said polymer. The polymer may also contain an acrylate or methacrylate. The membranes can be used for ultrapurifying a liquid and an ultrapurifying system for water.

Agarwal<sup>297</sup> invented a technique to make NF/RO membranes with superior salt rejection and flux properties by IP. The porous surface treated by a solution of an amine, an organic acid, and a nonamine base, was treated again with a solution containing an acyl halide and an organic solvent immiscible in water.



Emrick et al.<sup>298</sup> synthesized azidoaryl-substituted cyclooctene monomers and used in the preparation of various copolymers. These copolymers were deposited on the surface of a polymer substrate as a thin film. The copolymers were useful in the formation of crosslinked films that reduce fouling of water purification membrane.

Mayes et al.<sup>299</sup> described a method for grafting hydrophilic chains onto hydrophobic polymers such as PVC, PVDF, and chlorinated polypropylene (cPP).

Polyimide HFMs were modified chemically by contacting the fibers in a polyamine solution (in a suitable solvent) at temperature between 5 and 80°C (preferably 15 to 40°C).<sup>211</sup>

Tsou and Pacheco<sup>300</sup> described a method for modifying the pore of a porous membrane. In this method, the membrane surface was treated with a pore modifying agent, wherein the pore modifying agent modifies the pore opening at the first surface of the membrane differently than the pore opening at the second surface of the membrane. This invention also described a porous membrane having a first surface and a second surface, comprising a plurality of pores extending between the first and second surfaces, wherein the pores have been modified by a pore modifying agent such that the pore opening at one membrane surface is distinct for the pore opening of the other membrane surface, or the pore shape is distinct at one or more locations between the first and second surfaces.

Noh<sup>301</sup> disclosed a method for chemically modifying the surface of polytetra fluoroethylene materials, which allows biocompatibility of the materials to be improved.

Johnson<sup>302</sup> described a process for the surface modification of a polymeric substrate. Process was comprised of a contacting a surface of a polymeric substrate with a protic liquid or fluid containing diazonium composition under such conditions that will effectively allow the reaction of diazonium composition with the surface, resulting in the attachment of aromatic groups to the polymeric surface. The polymeric substrate contains aliphatic carbon-hydrogen bonds, whereas the protic composition is comprised of a diazonium complex formed by diazotizing an amino compound comprised of at least one amino group bonded to an aromatic group. Also disclosed the products generated by using aforementioned surface modification. This invention may also be applied in the food industry, the medical, and hospital supply fields, diapers and other liners, e.g., chemical, biological, and other areas where hydrophilic, porous, wettable, or wicking articles are desired.

Kriesel et al.<sup>303</sup> prepared useful nanofilms for filtration from oriented amphiphilic molecules and oriented macrocyclic modules. The amphiphilic species

may be oriented on an interface or surface. The nanofilms may be prepared by depositing or attaching an oriented layer to a substrate. A nanofilm may also be prepared by coupling the oriented macrocyclic modules to provide membranes.

A patent on the fabrication of ultra-thin dense-layer asymmetric HFMs (high performance) with a dense layer of less than 500 Å from a binary solution, comprising a polymer and a solvent was made by Chung et al.<sup>304</sup> In this process, the spinning polymeric solution had a high viscosity and exhibited chain entanglement at the spinning temperature.

Kozlov and Wilson<sup>305</sup> disclosed a method for porous membrane surface modification by radiation-induced polymerization.

Koh et al.<sup>306</sup> reported a method of modifying a surface of polymer membrane by ion assisted reaction. In this process, the pore size on surface of the membrane can be controlled according to the irradiation dose and the kind of the ion beam thereby enabling water penetration or electrolyte transmission.

Guiver et al.<sup>307</sup> separated gas pairs such as H<sub>2</sub>/CO<sub>2</sub> by using PSf-zeolite composite membrane. Zeolite, preferably zeolite 3A particles were covalently bonded to the polymer using an amino functional methoxysilane as a coupling agent to bind the zeolite particles to an aldehyde modified polysulfone matrix.

The invention of Leong et al.<sup>308</sup> provides a method for preparing a surface modified GS membrane, wherein the membrane has improved permselective properties. The method is used to separate oxygen, nitrogen, carbon dioxide, methane, hydrogen, and other gasses from gas mixtures. The surfaces were modified by ozone treatment.

Simonetti<sup>309</sup> described a process for the modification of porous polymeric materials {PVDF, polyvinylidene difluoride/polytetrafluoroethylene (PDF/PTFE) fluorocopolymer, PTFE, PP, PE, and PAN in the form of membranes, films, or porous webs} without the use of a free radical initiator by using acrylate monomers and UV light. The modified polymeric material exhibited new properties such as wettability and advantageous flow characteristics. The modified porous material exhibited hydrophilic properties rather than its original hydrophobic properties, except for PAN, which actually became more hydrophobic.

Tanihara and Kusuki<sup>310</sup> fabricated partially carbonized asymmetric hollow fiber using aromatic polyimide as a base material, for GS.

Sikdar et al.<sup>311</sup> invented adsorbent-filled pervaporation membranes used for removing volatile organic compounds from waste water. These membranes were prepared by dispersing at least one hydrophobic adsorbent such as activated carbon uniformly into a polymer matrix.



**TABLE XI**  
**Recent Patents on the Modification of Polymeric Membrane Surfaces Via Different Procedures**

Patents related to modifying the polymeric membranes	Components	Membrane	Application	References
Additives	(PVDF or PSf) + polymeric anhydride.	FS	RO	280
	Sulfone polymer + hydrophilic polymer	FS	Diagnostic and Filtration	282
	Polymer + lumen forming agent.	Hollow fiber	Filtration	283
	Hydrophilic base polymere/H-philSMM	FS	Separation of water from a solution of VOC + water	281
	Polymer dope/ nucleating agent	FS	UF or MF	284
Coating	Polyphosphazene/ inorganic/ organometallic polymers	Nanofibers	Filtration	285
	Polymer/amphiphilic species	Nanofilm	Filtration	286
	Porous or nonporous membranes coated with a polymer containing hydrophilic functional groups	FS	Filtration	287
	UF membranes rendered hydrophilic by hydroxyalkyl cellulose	FS	UF	288
	Polymer/polycation or cationic synthetic resin	FS	MF	289
	Polymeric surface coated with "ligand groups"	FS	Filtration	290
	Hydrophobic substrate (PVDF)/ difunctional surface-modifying molecule	FS	Filtration (Ultrapurification of water)	291
	Porous polymeric surface/ polyelectrolyte	FS or hollow fiber	To form charge modified surface	292
	PVDF/ cross-lined multipolymer	FS or hollow fiber	Superior combination of properties	293
	Poly(ethylene chlorofluoroethylene)/citric acid, ethyl ester or glycerol triacetate	FS or hollow fiber	UF and Mf	294
	Porous polymeric substrate/ crosslinked ethylenically unsaturated monomer	FS	Hydrophobic/oleophobic surface	295
	Polymeric membrane/positively charged organic phosphonium	FS	Ultrapurifying water etc.	296
	Porous substrate/amine,acyl halide etc.	FS	NF/RO	297
	Plymer substrate/azidoaryl- substituted cyclooctene monomers	FS	Water purification	298
	Hydrophilic chains onto hydrophobic polymers	FS	Water filtration	299
	Polymer/PI/ aliphatic-aromatic polyamine	Dual hollow fiber	GS	210
Graft/interfacial Polymerization/ chemically	Porous membrane/pore modifying agent	FS	Filtration	300
	ePTFE/ sodium hydroborate + anthraquinone.	FS	Hydrophobic surface changed to hydrophilic.	301
	Polymeric surface/protic liquid containing a diazonium composition	FS	Filtration	302
	Polymer surface/amphiphilic molecules and oriented macrocyclic modules	FS (nano films)	Filtration	303
Radiation-induced polymerization	Porous membranes/mixture of monomers etc.	FS	Separation technology	305
Ion assisted reaction	Polymer surface/ion beam	FS	Electrolyte transmission or water penetration	306
Ozone treatment	Coated membrane surface	FS	GS (improved permselectivity)	308
UV light assisted	Porous polymeric material + acrylate monomers	FS	Increase wettability, filtration.	309
Partially carbonised	Aromatic PI	Hollow fiber (HF)	GS	310
Others	Adsorbent-filled membranes	FS	PV	311
	PSf / Zeolite	FS	GS	307
By spinning	Polymer (PES, PI, PSf etc)/solvent	HF	Air and other separation	304

Table XI. Recent Patents on the modification of polymeric membrane surfaces via different procedures.

### SUMMARY

This is a review of the surface modification of synthetic membrane, used in different fields (RO, UF, NF, GS, biomedical application, etc.); especially the report covers the communications on this subject made after the year 2000. Composite UF membrane has good separation performance and offered a strong potential for possible use as a new type of antifouling UF membrane. Many new polymers have been synthesized and tested for their permeation properties. Particular attention is given on the modified membranes which were developed with in past 5 years. New techniques are developed, particularly by plasma treatment (organic and inorganic), grafting of polymers on the membrane, blending different types of polymers, adding functional groups to the surface by exposing to UV or by other methods (irradiation), heat treatment, chemical treatment, ion implantation, dip coating etc. The favorable performances of the membranes can be obtained by choosing right types of functionality on the membrane surface. The hydrophobicity or hydrophilicity of the UF, NF, and MF membrane surfaces can be tailored by using SMMs. More attention has been given to SMMs, graft polymerization and different types of plasma treatment for surface modification of synthetic membranes. Composite HFMs are very interesting and have great potential for future research and in the membrane separation development. The membrane morphology strongly depends on the membrane thickness during the phase-inversion process of asymmetric membranes. The future direction of R and D will be focused more for on development of new methods of surface modification.

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