

Chemical Modification of Polyethersulfone Nanofiltration Membranes: A Review

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ABSTRACT: Polysulfone (PS) and poly(ether)sulfone (PES) are often used for synthesis of nanofiltration membranes, due to their chemical, thermal, and mechanical stability. The disadvantage for applying PS/PES is their high hydrophobicity, which increases membrane fouling. To optimize the performance of PS/PES nanofiltration membranes, membranes can be modified. An increase in membrane hydrophilicity is a good method to improve membrane performance. This article reviews chemical (and physicochemical) modification methods applied to increase the hydrophilicity of PS/PES nanofiltration membranes. Modification of poly(ether)sulfone membranes in view of increasing hydrophilicity can be carried out in several ways. Physical or chemical membrane modification processes after formation of the membrane create more hydrophilic surfaces. Such modification processes are (1) graft polymerization that chemically attaches hydrophilic monomers to the membrane surface; (2) plasma treatment, that introduces

different functional groups to the membrane surface; and (3) physical preadsorption of hydrophilic components to the membrane surface. Surfactant modification, self-assembly of hydrophilic nanoparticles and membrane nitrification are also such membrane modification processes. Another approach is based on modification of polymers before membrane formation. This bulk modification implies the modification of membrane materials before membrane synthesis or the incorporation of hydrophilic additives in the membrane matrix during membrane synthesis. Sulfonation, carboxylation, and nitration are such techniques. To conclude, polymer blending also results in membranes with improved surface characteristics. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 630–642, 2009

Key words: polysulfone; poly(ether)sulfone; nanofiltration; membranes; modification; hydrophilicity; surface characteristics; grafting; plasma treatment; blending

INTRODUCTION

Pressure driven membrane processes, and nanofiltration (NF) in particular, traditionally make use of polymeric membranes. Dominant membrane materials in NF are polymers such as cellulose acetate, polyamide, polyimide, and poly(ether)sulfon.¹ These may be symmetric (e.g., cellulose acetate and polyimide membranes typically have a symmetric structure) or asymmetric (thin film composites, made of polyamides or poly(ether)sulfone). Thin film composites combine a high selectivity with a high permeability; the overall structure should have a good resistance to acids, bases, oxidantia and reductantia, high pressures, and sometimes also to high temperatures.² Polysulfone (PS) and poly(ether)sulfone (PES) are attractive materials for NF membranes because of their good mechanical, thermal, and chemical stability. The main disadvantage is related to the relatively hydrophobic character of PS/PES. Several

studies have concluded that membrane fouling is directly related to hydrophobicity,^{3–5} although the opposite has also been reported.⁶ This is mainly caused by adsorption of nonpolar solutes, hydrophobic particles or bacteria.⁷ Membrane fouling is an important problem in NF, resulting in a higher energy demand, shorter membrane lifetime, and unpredictable separation performance.⁸ The current trend is to develop new membrane materials and structures specifically in view of reducing fouling effects. However, alternative materials often prove more vulnerable in terms of stability and are often (unrealistically) expensive. Hydrophilic membranes have a tendency to swell in water, which results in a loss of mechanical strength and often a reduction of rejections that can be attained.

A different approach is the use of common polymers (such as PS/PES) with modifications that increase the membrane's hydrophilicity. It is generally accepted that this would lead to membranes less prone to fouling.⁹ Modification procedures allow finding a compromise between hydrophobicity and hydrophilicity, and localize the hydrophilic material specifically in the membrane pores, where they have a positive effect on flux and fouling reduction

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without compromising mechanical stability. In this way, modified membranes combine the superior bulk properties of hydrophobic polymers with good surface characteristics of hydrophilic polymers. Copolymerization of monomers with hydrophilic groups and monomers with hydrophobic groups is a possibility that allows developing new materials. In contrast, many efforts have been made to use an existing polymer as a starting point and add hydrophilic functional groups specifically on the membrane surface.^{2,10} This article reviews methods to increase the hydrophilicity of PS/PES membranes in view of fouling reduction. Chemical and physico-chemical modifications after membrane formation will be described. These comprise preadsorption, plasma treatment, grafting methods based on UV irradiation, plasma treatment, ion beam irradiation, and redox initiation, and several other methods. Hydrophilic functional groups introduced in this way can be hydroxyl, amine, carboxyl, and sulfone groups.²

Bulk modification methods are often more straightforward because they can be applied to a polymer solution, and not on a membrane surface. However, the entire membrane is modified in this way, thus yielding a lower net effect (and, possibly, an enhanced effect of swelling in the resulting membrane structure).¹¹ Sulfonation and carboxylation are among the most frequently reported methods, which will be described in this article.

The disadvantages of bulk modifications can be solved by applying polymer blending, which is similar to the use of copolymers but using a physical pathway. This also allows the use of "simple" polymers.

Characteristics of PS/PES

Polysulfone and poly(ether)sulfone used in NF membranes is usually aromatic,¹² as generally depicted in

Figure 1. Different variations in the chemical structure of polysulfone exist, as found in, e.g., bisphenol-A polysulfone and tetramethyl bisphenol-A polysulfone.¹³ Commercially available polymers include the Udel type (PS), Victrex (PES), and Cardo (PES).¹⁴ The presence of aromatic groups is an important factor that determines the chemical and mechanical stability, because they limit chain mobility.¹⁵ Oxidative, thermal, and hydrolytic stability is also improved in this way.⁹ Chlorine resistance is, evidently, a key issue for water treatment applications. The stability of both polymers is reflected by the high glass transition temperatures (ca., 190°C for PS and 230°C for PES). PS is an amorphous, transparent, rigid polymer with high molar mass. It is soluble in some organic solvents, such as methylene chloride, dimethylformamide (DMF), and *N*-methylpyrrolidone (NMP).¹⁶ PS is an attractive material because of the low cost and commercial availability.^{17,18}

Disadvantages of PS/PES are the relatively hydrophobic character of the membranes after synthesis, which leads to a high sensitivity to membrane fouling. In addition, PS/PES NF membranes are known to have a broad pore size distribution, which makes a sharp separation of solutes to a challenge; fractionation has a limited applicability.¹⁹

Bulk modification

Sulfonation

Sulfonation is the addition of sulfonic groups to the (aromatic) backbone of PS/PES. This is an electrophilic aromatic substitution reaction, in which a hydrogen atom is replaced by sulfonic acid. The sulfonic groups introduced in this way are usually localized in the ortho positions on the aromatic rings, relative to the ether oxygen atom of the main chain. This is due to the fact that this electron donating

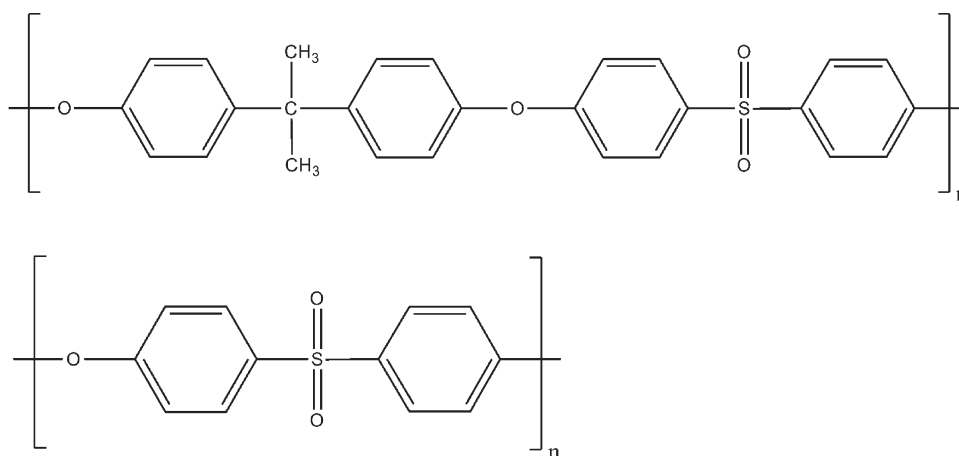


Figure 1 General structure of polysulfone and poly(ether)sulfone used in NF membranes.

oxygen atom activates the ortho position.^{14,20} Because sulfonation is an aromatic electrophilic substitution reaction, electron donating substituents enhance sulfonation, whereas electron repulsing substituents have the opposite effect. With that respect, PES is difficult to sulfonate because of the electron repulsing effect of the sulfonic group (see Fig. 2), which deactivates the aromatic rings for substitution.

Sulfonation is carried out before membrane synthesis, using a sulfonating agents such as sulfuric acid (H_2SO_4),^{2,14} trimethyl silylchlorosulfate ($(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$),^{16-18,21,22} sulfur trioxide (SO_3),^{21,23} sulfur trioxide-triethylphosphate complex ($\text{SO}_3\text{-TEP}$),^{9,24,25} chlorosulfonic acid (ClSO_3H),^{12,26-30} and oleum (SO_3 in H_2SO_4).²⁴ The sulfonation method is similar for most reagents. Starting from a (stirred) polymer solution, the reagent is added drop by drop at constant temperature; after reaction, the polymer is precipitated in a cold liquid, separated by filtration, washed with deionized water, and dried.^{2,21} A typical procedure is described by Pedicini et al.¹⁷ PS was dissolved in chloroform; trimethyl silylchlorosulfate was added for production of a silylsulfonate PS intermediate and HCl. In the next step, sodium methoxide is added to split the intermediate so that the final sodium PS product is obtained. Isopropyl alcohol is used for precipitation, followed by washing, filtering, and drying in an oven. Slight variations were reported by other researchers.^{16,18,22} Figure 3 gives a generalized overview of this method.

Chlorosulfonic acid is used in concentrated sulfuric acid; precipitation occurs in ice-cold deionized water.²⁷ The precipitate was obtained by filtration; afterward, the product was washed with deionized water to pH 6–7. Nabe et al.²⁴ dissolved PS in a TEP-oleum mixture; oleum is a solution of SO_3 in concentrated sulfuric acid. Sulfuric acid can also be applied as such; this was shown by Blanco et al.² for sulfonation of PES-Cardo (PES-C). Li et al.³¹ showed the reaction mechanism for this direct sulfonation.

Sulfuric acid is the cheapest sulfonating agents but has the disadvantage that degradation of the main polymer chain can occur when the reaction tempera-

ture is too high or the reaction time is too long. This degradation may alter the mechanical resistance of the membrane, thus compromising its use in industrial applications.

Among the other reagents, SO_3 is very reactive and inexpensive. This sulfonating agents has the disadvantage that side reactions may occur, and that the reaction is heterogeneous.²¹ This is due to the fact that when a part of the polymer reacts with SO_3 , this part becomes insoluble in an apolar solvent. The rest of the reaction then has to be carried out in a disperse system and not in a homogeneous solution. Trimethyl silylchlorosulfate ($(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$) may solve this heterogeneity problem.²¹ A better control of the reaction can be obtained, because the sulfonated polymer (which still contains silylated groups) remains in solution until the end of the sulfonation reaction, at mild reaction conditions. In this way, it is possible to maintain the backbone structure of the polymer; no degradation phenomena such as breaking of polymer chains and crosslinks occur. The relatively high cost and the slow reaction are mentioned as problems.^{20,22} A possible alternative is the use of the SO_3/TEP complex. This should allow to decrease the SO_3 concentration and control the high SO_3 reactivity. Too high concentrations of TEP, however, make the sulfonation too mild.^{21,32} Reactions with TEP are also exothermic, which makes it use quite challenging.²⁰

Chlorosulfonic acid (ClSO_3H) is also inexpensive but chain degradation, branching, or crosslinking reactions may occur.^{21,27,33} However, these should not pose any problems under controlled conditions.¹² Chlorosulfonic acid allows a homogeneous electrophilic substitution, so that no additional preparation is needed for its use, in contrast to the previous reagents.

For bulk modifications, sulfonation is expressed by DS, the degree of sulfonation. DS is determined by the sulfonating agents, the reaction time, the reaction temperature, and the molar ratio of sulfonating agents and polymer.^{2,17} The reaction temperature has a positive influence on DS: a higher reaction temperature leads to a higher DS²; however, chain degradation should be considered. A longer reaction time leads to an initially fast increase of DS, followed by a slow increase.¹²

DS can be quantified by measuring the ion-exchange capacity (IEC) of the sulfonated polymer.^{2,28} The IEC can be determined by a back titration of the acidic form of the sulfonated polymeric film using sodium hydroxide. IEC is defined as the ratio of the amount of H^+ exchanged to the weight of the dried polymer film after ion exchange. Assuming that all sulfonic groups in the film are accessible, the average degree of sulfonation can be calculated from IEC.^{2,28}

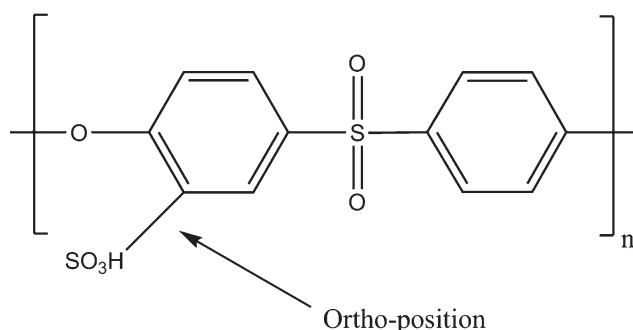


Figure 2 Sulfonation of PES.

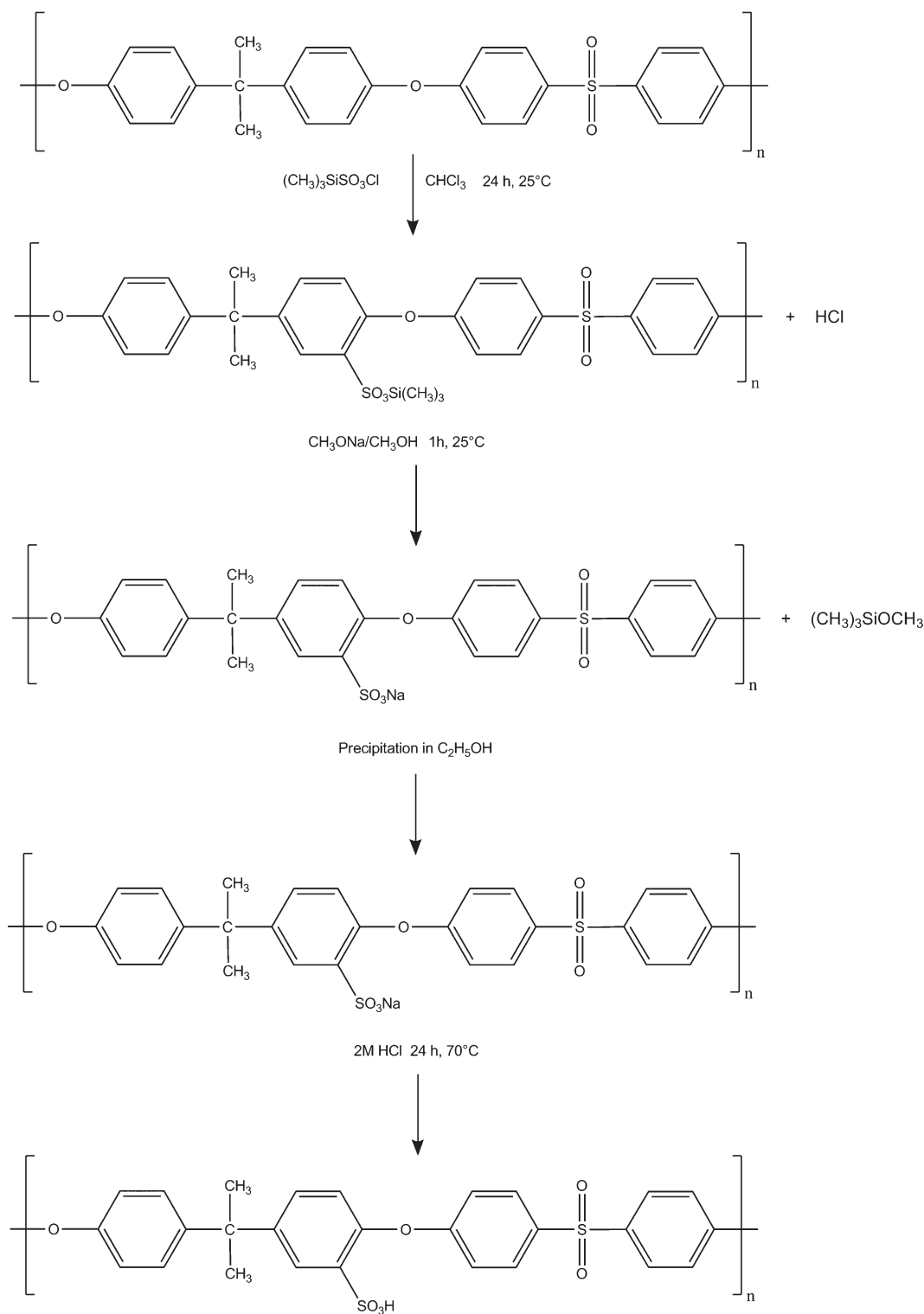


Figure 3 Sulfonation of PS with trimethyl silyl chloro sulfonate.²²

An alternative method to measure DS, or to prove sulfonation, is through proton nuclear magnetic resonance (¹H NMR)^{12,27} or infrared (IR) spectroscopy.^{2,12,27} Boussu et al.³⁴ used ATR-FTIR spectroscopy to determine the chemical structure of PES and SPES membranes; Blanco et al.² studied FTIR spectra

to determine sulfonation of PES-C. However, quantification is difficult by using these techniques.

After sulfonation of the polymer, a membrane can be synthesized with the classical phase inversion technique. This requires dissolution of the polymer in a suitable solvent, such as dimethylacetamide

(DMA), dimethyl formamide (DMF), or N-methylpyrrolidone (NMP).³⁵ It was shown that the solvent used to dissolve the polymer has an influence on the morphology and performance of the membranes^{28,35}; DMF was found to yield a higher contact angle with water, i.e., a less hydrophilic surface.

An additional effect of sulfonation is the increase of the glass transition temperature for the sulfonated polymer in comparison with the virgin polymer. Lufrano et al.²² measured an increase of the glass transition temperature from 187°C for the PS used to 205°C for sulfonated PS. This can be explained by the increased sterical hindrance when a hydrogen atom in an aromatic ring is replaced by a sulfonic group, leading to an increase in the glass transition temperature.

Carboxylation

Similar to sulfonic groups, the presence of carboxylic groups can increase the hydrophilicity of the mem-

brane. This requires a similar substitution reaction but with carboxylic groups as substituents. PS can be easily lithiated to almost two Li atoms per reproductive unit, because the sulfonic group has a strong activating effect for lithiation. Lithiated intermediates are reactive for many electrophiles, including carboxylic groups. Guiver et al.³⁶ used a two-step method for carboxylation of PS (Fig. 4). In a first step, lithiation of PS occurs by using *n*-butyllithium, which results in Li atoms in the ortho position. In the second step, the intermediate is carboxylated by using dry ice. This procedure was also applied by other researchers.^{9,37}

Carboxylated polymer synthesis involves dissolution of PS in THF and cooling to -50°C by immersion in a dry ice/alcohol bath, the low temperature being necessary to avoid crosslinking of the intermediate product. Subsequently, *n*-butyllithium is injected under a mixing regime, in a dry and inert environment. The lithiated intermediate is a viscous,

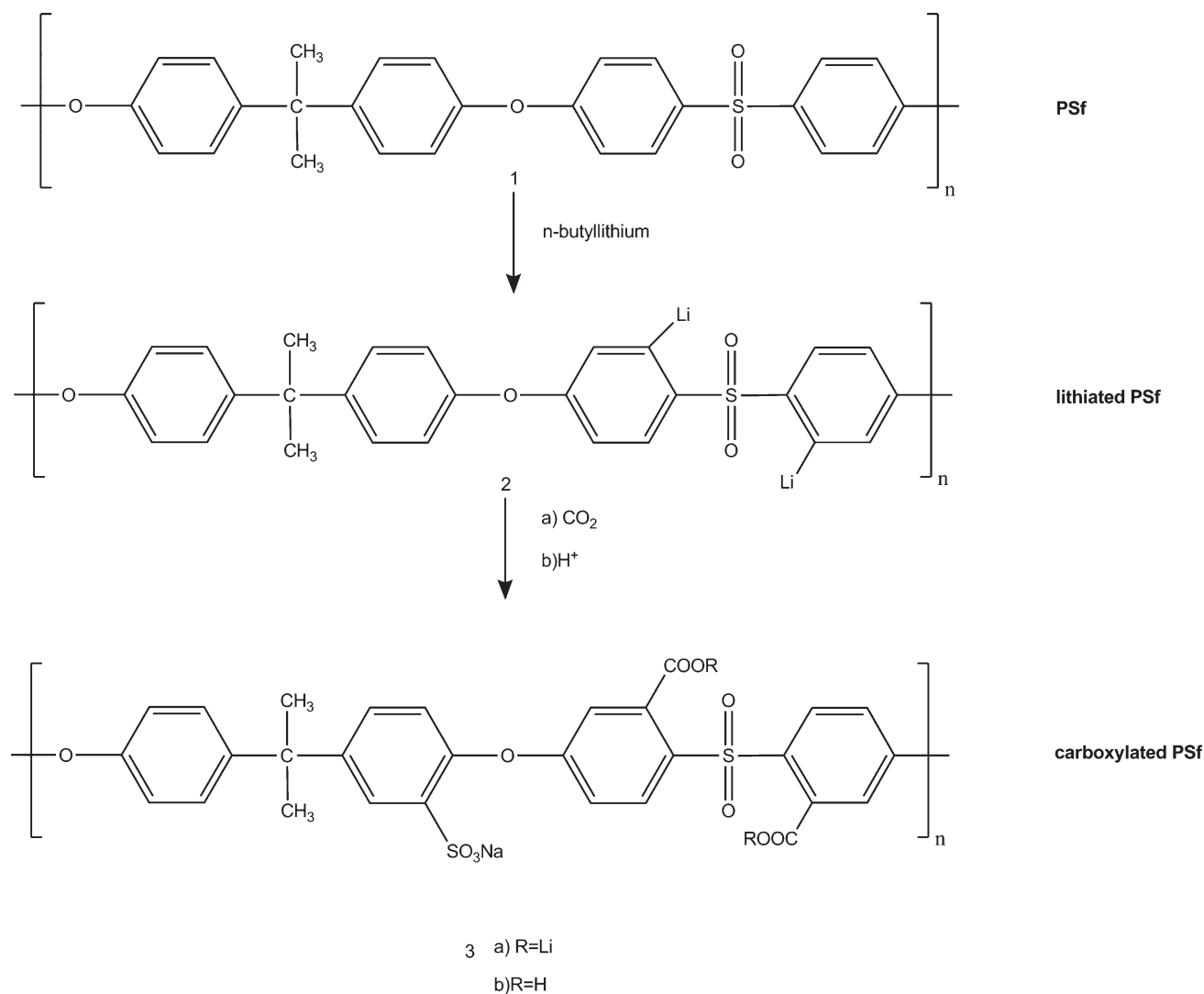


Figure 4 Method for carboxylation of PES.³⁶

homogeneous liquid that needs good mixing to maintain uniformity. Dry ice is added to the solution, which is a lithium carboxylate derivative of the polymer, insoluble in THF. The carboxylate polymer is kept at room temperature; THF is gradually removed. The lithium form of the polymer is obtained through mixing with ethanol and drying in an oven; the acid form can be obtained through reaction with hydrogen chloride.³⁶

The introduction of carboxylic groups has a positive effect on the hydrophilicity of the polymer, which has been shown by water absorption measurements.^{9,36}

Surface modification

Preadsorption

Physical adsorption of hydrophilic compounds is a method to modify membrane surfaces after synthesis, referred to as preadsorption.³⁸ In this method, a thin hydrophilic layer is attached to the membrane surface to increase hydrophilicity.

An example is the adsorption of poly(sodium 4-styrene sulfonate) (PSS) on PES membranes, by permeation of an aqueous solution of PSS through the membrane during 100 min. Physical adsorption can occur on the surface and inside the pores on the pore walls. Depending on the molar mass of the polymer in comparison with the pore size of the membrane, the polymer that is to be adsorbed can enter the inner membrane structure. As a general rule, the molar mass is to be compared with the MWCO ("molecular weight cut-off") of the membrane. In this way, preadsorption can be controlled by selecting an appropriate reagent. Other tested adsorbents include carrageenan crosslinked with isophthaloylchloride and trimesoylchloride.

Adsorption is a result of electrostatic interactions, hydrophobic bonding of nonpolar segments, hydrogen bonding, and chemical reactions with functional groups on the surface.³⁹ IR spectra can be used to show the effect of preadsorption.³⁸

It was shown that PSS-modified membranes have a better resistance against membrane fouling.³⁸ In addition, the rejection characteristics of these membranes were improved, with the same water flux. This is remarkable, given the fact that the pore size should be reduced after adsorption. A possible explanation is that hydrophobic sites on the membrane surface are shielded by preferential adsorption of PSS. However, no information is available about the long-term stability of these modified membranes.

Plasma treatment

PS/PES membranes can be modified via a plasma generated by ionization of a gas or water.⁴⁰ Plasma treatment can also be used as a source of radicals that act as active sites for graft polymerization; this will be described later.

Ionization of a gas can occur by means of an electrical discharge at high frequencies. This can be done by using microwaves and radio frequency waves.

The active components generated in the plasma can activate the upper molecular layers of the membrane surface to increase the hydrophilicity, without affecting the bulk of the polymer.⁴¹ Plasma treatment introduces functional groups on the membrane surface; by variation of plasma treatment parameters, surfaces with different properties can be obtained. Possible gases include CF_4 , Ar, O_2 , H_2 , He, Ne, N_2 , and CO_2 , in addition to H_2O . The surface is bombarded with ionized plasma components to generate radical sites. Bonds that can be attacked by radicals are C—C, C—H, and C—S bonds, with exclusion of the aromatic C—H and C—C bonds. This is similar to photodegradation. The generated radicals can subsequently react with gas molecules (depending on the plasma), schematically shown for O_2 in Figure 5. Remaining radical sites bind with oxygen or nitrogen after contact with the air.

CO_2 -plasma treatment leads to the incorporation of oxygen in the membrane surface in the form of carbonyl, acid, and ester groups, yielding an

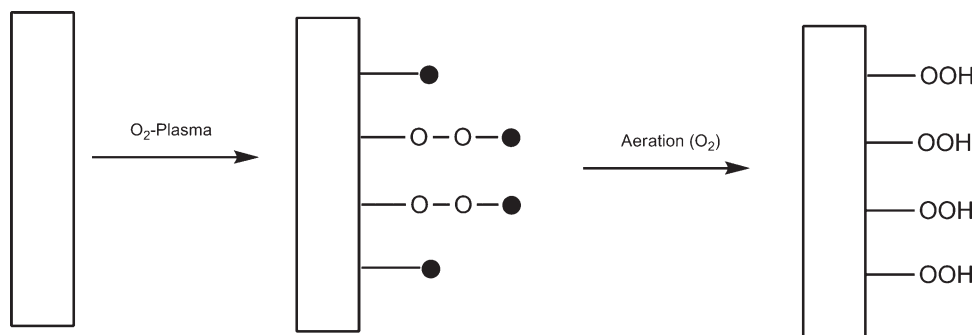


Figure 5 Schematic representation of O_2 plasma treatment of a membrane.⁴²

increase in hydrophilicity. Modification of polymer surfaces with CO₂ plasmas in general leads to surface oxidation and the formation of hydrophilic surfaces.⁴³ A fast reaction was observed; the treated membranes had a better fouling resistance. Continued plasma treatment, however, resulted in membrane degradation.⁴⁰ H₂O plasma treatment also leads to the incorporation of oxygen containing functional groups on the surface.⁴⁴ O₂ plasmas have a similar effect, with reported functional groups mainly being hydroxyl, carbonyl, and carboxyl groups.^{42,45} Nitrogen-containing plasma systems, on the other hand, yield amine, imine, amide, and nitrile functional groups on the membrane surface.⁴⁶ Through postreactions after contact with air, oxygen compounds can also be present.^{47,48} The presence of functional groups can be detected with XPS.^{43,44,45}

A reported disadvantage of plasma modification is the time dependency of the induced changes. Chain migration in the membrane surface can result in a gradual loss of surface properties, referred to as aging or hydrophobic recovery.^{46,49} Possible causes of aging include (1) migration of polar groups on the surface to internal regions of the polymer, whereas untreated polymer chains move in the reverse direction; (2) structural rearrangement that covers chemical groups introduced at the surface; and (3) chemical reactions by contact with atmospheric oxygen and moisture. This was also observed by Gancarz et al.,⁴⁰ although Wavhal et al.⁴³ reported a membrane stability of several months for CO₂ plasma treatment. A combination with graft polymerization (described further) may improve the outcome.

UV-induced grafting

Grafting involves the chemical attachment of hydrophilic compounds to the membrane surface, in view of increasing its hydrophilicity. Grafting occurs at reactive ionic or radical positions, which have to be generated in a preparatory phase. The reactive sites can be generated in many ways among which UV irradiation.⁵⁰

UV-induced grafting is often used because of its simplicity and low cost. Further advantages are the fact that grafting can be applied on existing membranes, the possibility of using various monomers in the grafting procedure, and the possibility for further functionalizing through postreactions.⁵¹⁻⁵⁴ PS and PES membranes can be treated without photoinitiators, because these materials are intrinsically photosensitive, which is not the case for most other materials. For example, for UV grafting of polyimide membranes, benzophenon is used as photoinitiator⁵⁵; also for UV grafting of vinyl monomers on polyacrylonitrile, the membrane surface was covered with benzophenon, upon which UV grafting could take

place.⁵⁶ This is not necessary for PS/PES. The selection of an appropriate wavelength for excitation, however, is of high importance.

The mechanism of UV-induced graft polymerization is schematically given in Figure 6.⁵¹ In the first step, light absorption by the phenoxy-phenyl chromophores in the backbone of the PES polymeric chain takes place. Photoexcitation results in a homolytic cleavage of a C—S bond at the position of a sulfonic group in the polymeric chain. This results in a split of the polymer backbone, which yields two radical positions at the end of the polymeric chains. Both the generated aryl radical and the sulfonyl radical are reactive places on which polymerization can occur. In addition, the sulfonyl radical may lose its sulfonyl group and produce an additional aryl radical.

UV irradiation can occur directly in the presence of water or methanol soluble monomers, by using the immersion technique. With this method, the membrane is immersed in a solution containing, e.g., vinyl monomers.⁵¹ Radical sites are generated by UV irradiation in the solution; these react with monomers; the presence of free radicals results in a degree of polymerization of the monomers that are finally covalently bound to the membrane. After irradiation, the remaining (unreacted) solution is removed by washing with deionized water. Yamagishi et al.⁵¹ used 1-hydroxyethylmethacrylate (HEMA), glycidylmethacrylate (GMA), and methacrylic acid (MAA) as monomers; Ulbricht et al.⁵⁸ applied photo-induced grafting of polyacrylic acid (PAA); Béquet et al.⁵⁹ also used acrylic acid. Kilduff et al.⁶⁰ modified PES membranes using UV-induced grafting of *N*-vinyl-2-pyrrolidone (NVP) to reduce NOM (natural organic matter) fouling on the membrane.

In the dip technique, the membrane is first dipped in a monomer solution, after which UV irradiation occurs in an inert N₂ atmosphere.⁶⁰ This method was also used by Kaeselev et al.,⁶¹ who used a solution containing NVP, 2-acrylamidoglycol acid, or 2-acrylamido-2-methyl-1-propane sulfonic acid (AAP). The dipping technique is faster than the immersion technique, because the latter requires longer reaction times to obtain the same degree of grafting. This is due to the fact that UV radiation has to penetrate through the liquid solution, which shields the membrane.⁶² Pieracci et al.⁶³ obtained hydrophilic membranes with good rejections by using the dipping technique. However, the permeability was lower because of blocking of the membrane pores by grafted polymer chains. A high-grafting density and long grafted chains result in loss of permeability. The choice for shorter chains can be a solution; a compromise between increasing the hydrophilicity and keeping the permeability has to be found. Chain-transfer agents can help controlling the degree of

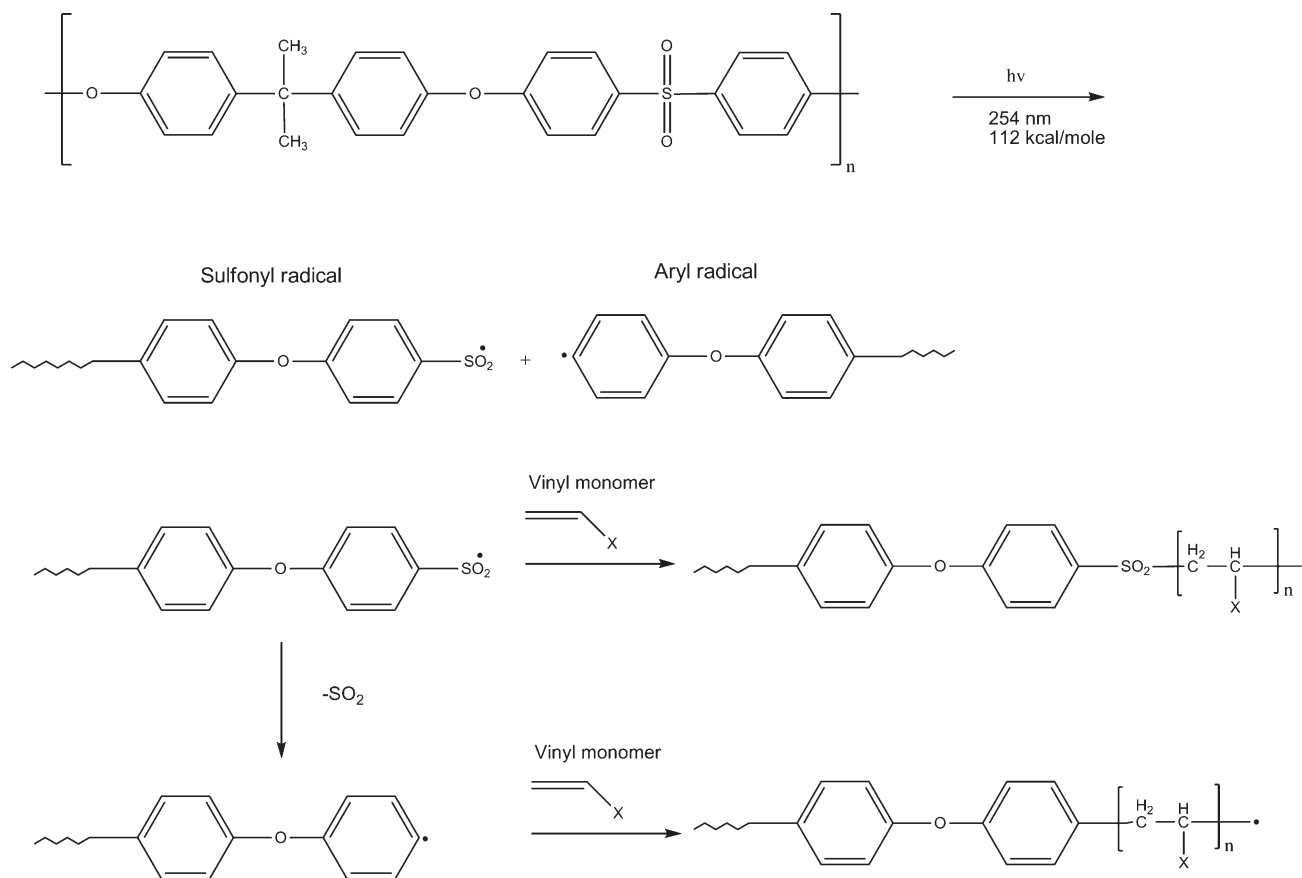


Figure 6 Mechanism of UV-induced grafting of a PES membrane.^{54,57}

polymerization by ending growing polymer chains and inducing new radical sites, leading to a higher chain density and a lower average chain length. 2-mercaptoethanol is an example of such a chain transfer agent.⁶³ However, other examples can be found.⁶⁴

Grafting can be verified by using ATR-FTIR.^{50,58,60,61} Similar to bulk modification, the degree of grafting can be calculated as⁵¹:

$$DG = \frac{W_b - W_a}{M_W}$$

where W_a = weight of membrane before modification (g); W_b = weight of membrane after modification, in the presence of grafted monomers (g); M_W = molar mass of monomer (g/mol)

Or, alternatively, as⁵³:

$$DG = \frac{m_{gr} - m_0}{A}$$

where m_{gr} = membrane weight after modification (μg); m_0 = initial weight of the membrane (μg); A = membrane surface area (cm^2).

Factors influencing the grafting procedure are the monomer type, the monomer concentration, irradiation duration, and UV wavelength.⁶⁰ Ulbricht et al.⁵⁸

observed a higher degree of modification when the reaction time or the monomer concentration increased. A short duration and high concentration yields a limited number of long chains, resulting in an open structure; a short duration and low concentration yield shorter chains; and a long duration and high concentration yields longer, crosslinked chains. Yamagishi et al.⁵¹ showed that the number of HEMA groups grafted on the surface of PS membranes is proportional to the square root of the duration of the irradiation. They also observed⁵⁷ that the longer the reaction time, the larger the number of HEMA polymer segments attached to the surface. However, fluxes decreased as well. Higher monomer concentration led to a higher density of the grafted HEMA polymer blocks. Again, lower fluxes were obtained, but rejections increased. Yamasighi et al.⁵⁷ also compared HEMA with GMA and MAA as monomers and found the highest fluxes with HEMA modified membranes, the highest rejections with MAA modified membranes.

Plasma-induced grafting

A method to avoid the loss of surface characteristics after plasma modification is the combination with

graft polymerization of hydrophilic monomers. Covalent bonds result in a more stable structure not subject to aging. This was observed by Wavhal et al.,⁴⁹ who compared aging of membranes treated with Ar plasma to the same membranes treated with Ar plasma followed by postplasma grafting of AA, and observed a longer effect of hydrophilization.

Plasma treatment produces free radicals or peroxides on the membrane surface. Pore enlargements occur in this phase. This can be considered an induced oxidation and degradation of the chain material through chain cleavage. Radicals and peroxides are used in a subsequent second phase for grafting of hydrophilic groups,⁶⁵ which again reduces the pore size and increases hydrophilicity. The creation of a plasma can be carried out in a microwave plasma generator or an induction-coupled radiofrequency plasma generator.⁶⁶ Ulbricht et al.⁶⁷ used a He plasma, or a He/H₂O plasma, followed by contact with air. Grafting of monomers was induced by using aqueous solutions at 50°C, through thermal decomposition of peroxides generated during plasma treatment. Tyszler et al.⁴² used a similar procedure, starting from Ar plasma to graft membranes with HEMA and PAA, in view of reduction of fouling in membrane bioreactors. The Ar treated membranes were brought in contact with air, after which they were immersed in a HEMA or PAA solution (see Fig. 7). This approach corresponds to the grafting-in-solution approach. Gancarz et al.⁶⁸ also describe two alternatives: grafting in the gas phase, where after completion of plasma treatment, the plasma flow is interrupted, and the mono-

mer gas is introduced in the reaction room. In the plasma polymerization procedure, both plasma and monomer gas are introduced at the same time. Grafting in the gas phase proved to yield superior results.⁶⁸

The yield of grafting can be determined by^{49,68,11}:

$$GY = \frac{W_b - W_a}{A}$$

where W_a = weight membrane before grafting (μg); W_b = weight membrane after grafting (μg); A = surface area of the membrane (cm^2)

ATR-FTIR spectra are used to evaluate the effect of grafting^{49,67,69}; XPS has also been reported.⁴⁹

Grafting by ion beam irradiation

Ion beam irradiation is an alternative method to induce grafting, by the creation of active sites on the membrane surface onto which monomers can be grafted. This can be applied for obtaining cationic and anionic membranes.⁷⁰ A high-energy irradiation source is used to activate the membrane surface chemically (radicals are induced). The membrane is bombarded with ions; when these penetrate through the membrane they lose energy to the polymer structure. This invokes bond breakage, crosslinking, and the formation of volatile components, which change the microstructure of the polymer and the morphology of the membrane surface; some sulfonic and C—H bonds can be broken and new C—S bonds can be formed after irradiation.^{71,7} One result is the

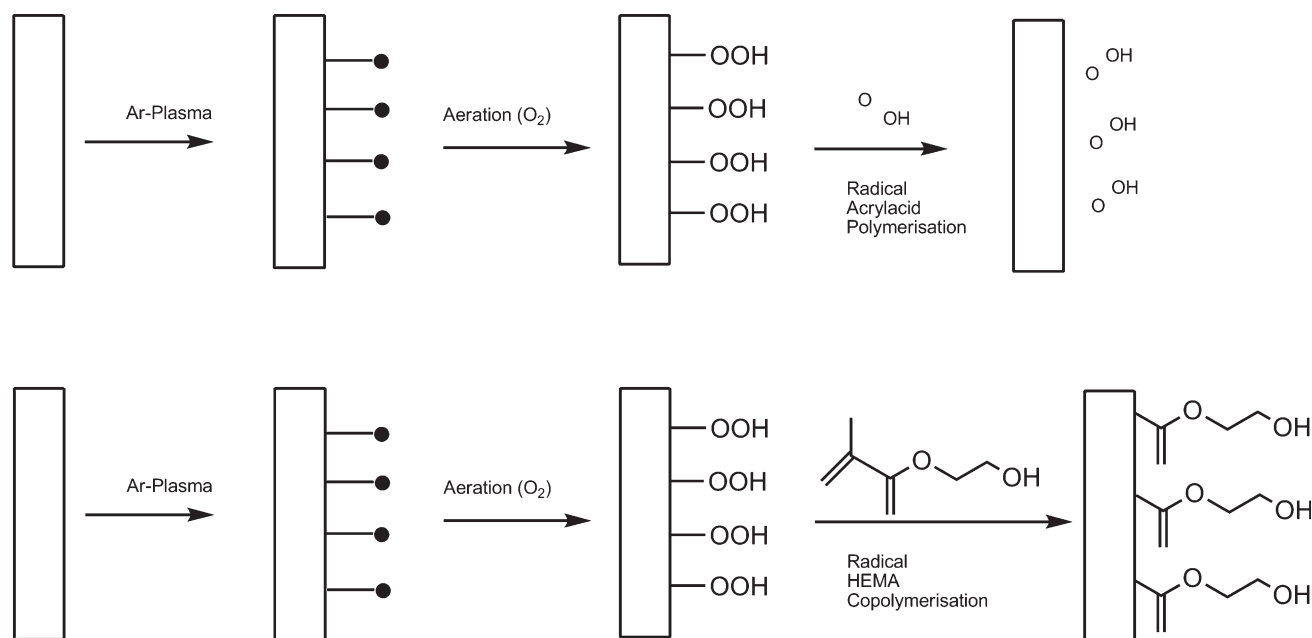


Figure 7 Plasma-induced grafting of AA and HEMA.⁴²

reduction of surface roughness, as was proven for two nanofiltration membranes, one of which having a sulfonated polysulfone selective layer.⁷² Subsequently, the grafting reaction of a monomer in solution occurs.⁷³ The use of gamma rays has also been reported¹; H⁺ irradiation is another possibility.⁷⁴

Keszler et al.⁷⁵ modified PES membranes with electron-induced grafting, in a solution of AA and AAm monomers. This had a positive effect on the water flux through the membrane; however, rejections increased after irradiation. Upon grafting, rejections increased again.

Grafting after redox initiation

A very effective method to generate radicals under mild conditions is the use of redox initiators. This method is often used for the initiation of polymerization reactions.⁷⁶ One of the advantages is that modification of an existing membrane can be carried out in aqueous solutions at room temperature, without oxygen removal.^{77,78}

Redox initiation takes place when an oxidants, such as persulfate, and a reductants, such as sulfite, are present in the reaction mixture. Redox initiation is not limited by temperature, so that it can be used for polymerizations below 50°C. Fast radicals production is obtained.⁷⁹ An often used redox system is K₂S₂O₈/Na₂S₂O₅, which generates radicals on the membrane surface for subsequent grafting. K₂S₂O₈ is the oxidants, Na₂S₂O₅ or K₂S₂O₅ is the reductants.

Redox-induced radical grafting of hydrophilic monomers on membranes is usually carried out on PA membranes.⁸⁰⁻⁸² However, some attempts on PES membranes have also been reported.^{77,83} In these studies, methacrylate-based monomers (MAA, PEGMA and SPMA or sulfopropylmethacrylate) were used. Grafting was evaluated by using ATR-FTIR.^{8,80-82}

Other surface modification methods

A wide variety of other surface modification methods can be found in the literature. Self-assembling nanoparticles,⁸⁴ and the use of various nanoparticles or nanotubes in membranes, have been proposed by many researchers. However, this is outside the scope of this review and will not be further considered here. Surfactant modification has been reported for PA membranes using adsorption of the nonionic surfactant Triton X-100.¹ No attempts have been made for PES membranes; however, an unexpected flux increase was observed by Boussu et al.⁸⁵ when studying nanofiltration of wastewater containing surfactants.

Hydrogen fluoride was used by González Muñoz et al.,⁸⁶ in view of improving the performance of

commercial nanofiltration membranes. After 14 days of immersion in a hydrogen fluoride solution, a higher permeability was obtained without any loss of rejection capacities.

Chowdhury et al.⁸⁷ used a gas phase nitration method based on a mixture of NO and NO₂, followed by a reduction of the nitrated functional groups with hydrazine hydrate. A higher rejection of nonionic slutes (PEGs) in water was obtained. The reaction was carried out in a glass reactor in which the membrane was positioned; subsequent reduction (amination) is followed by washing with deionized water.

Corona induced grafting was described by Zhu et al.¹¹ and is in fact a special form of plasma grafting. This method is also referred to as air plasma grafting. A corona discharge in a medium, usually air, results in ionization of the fluidum. The membrane is brought in contact with the electrode; the electrode induces microscopic defects and ionizes the air around the membrane. This method was applied for activation of AA grafting on PES membranes.¹¹ The increased hydrophilicity was shown by a decrease in water contact angles.

Polymer blending

Polymer blending is a simple and efficient technique to improve polymer properties; it can be considered a modification method in comparison with pure PS/PES because the performance might change significantly. Blending requires that two polymers are dissolved in the same solvent, e.g., NMP or DMF. The mixed solution can be further processed in the usual way.^{88,89} Polymer blending allows to obtain a product with superior properties compared with the pure materials. The limiting factor is usually the miscibility of the polymers.^{13,90} Typical blends combine hydrophobic materials with good mechanical and chemical stability with hydrophilic polymers. In case of PS/PES, blends usually aim at increased hydrophilicity.

Kim et al.¹³ made blends of PES with poly(1-vinyl pyrrolidone co-styrene) in view of obtaining an increased hydrophilicity. They observed that miscibility is limited to a narrow concentration range of vinyl pyrrolidone, confirming the challenges of polymer blends. Higher water permeabilities were found, along with higher rejections; the latter was explained by smaller pore sizes. Blanco et al.¹⁴ solved the miscibility problem by blending sulfonated PES with the original PES. Hydrophilicity can be varied by adapting the ratio in the blend.

Wang et al.⁹¹ blended PES with DMMSA-BMA (*N,N*-dimethyl-*N*-methacryloxyethyl-*N*-(3-sulfopropyl)-butylmethacrylate) copolymer to obtain antifouling membranes and found that hydrophilic groups preferentially concentrated at the membrane surface.

PES polymer was blended with soy bean phosphatidylcholine (SPC).⁸⁸ Through two hydrophobic alkyl chains, SPC is attached to the PES matrix, whereas the zwitterionic part of the polymer gradually segregates to the surface. This has been shown by XPS and water contact angles. They found a better resistance against protein adsorption. For the same purpose, Ma et al.⁸⁹ used an amphiphilic copolymer with polystyrene as the hydrophobic component. Again, XPS and water contact angles showed the increased hydrophilicity. Similar observations were made by Rahimpour et al.,⁹² who blended PES with polyamide-imide (PAI) and found an increase of hydrophilicity with PAI concentration. Protein rejection and antifouling properties improved.

Bowen et al.¹⁵ successfully blended PS and SPEEK (sulfonated poly(ether ether)keton) using NMP as solvent, with positive effects on hydrophilicity and fouling reduction. Roux et al.⁹³ used a branched polyethylene oxide (PEO) block PS polymer to obtain a higher hydrophilicity, another approach to come to the same result.

Influence of modifications on membrane fouling

It is obvious that modifications of the membrane polymer are aimed at an improvement of the performance of the membrane when applied in (mainly) water filtration. Thus, all modifications have very practical objectives, which are often related to fouling. It is assumed that when the polymer is made more hydrophilic, less fouling (both organic fouling and biofouling) will occur. It is well known from the literature^{94,95} that hydrophobic membranes tend to foul more when e.g., surface waters containing NOM are filtered. This is attributed to hydrophobic-hydrophobic interactions between (the hydrophobic fraction of) NOM and the membrane material. A more hydrophilic membrane surface can easily be reflected by a decrease in the contact angle between the membrane and water; therefore, most researchers use contact angle measurements as an assessment of their modification procedure. In many studies, however, membrane fouling is also measured as a decline in water flux compared with pure solutions. For example, Nabe et al.²⁴ found that after sulfonation, membranes were less prone to protein fouling. Other studies also report on protein fouling^{43,46}; however, conditions during the experiments are rather difficult to compare. Reddy et al.³⁸ measured fluxes for poly ethylene glycol (PEG) and dextran solutions and found a positive effect of pre-adsorption. Fouling caused by NOM was also studied in some cases^{60,62}; in these cases, an improved performance was observed, in the sense that fluxes remained more stable after modification of the membrane. NOM fouling is of practical interest for the

application of nanofiltration membranes; several studies show the effect of NOM on the membrane's performance.⁹⁶⁻⁹⁸ However, fouling mitigation studies are rather specific and cannot be used to evaluate the effect of chemical modifications in general. Apart from contact angle measurements, no generally applicable test protocol is available, so that it is difficult, if not impossible, to estimate the effect of modifications in practical applications.

CONCLUSIONS

Many attempts have been made to hydrophilize PS/PES membranes in view of fouling reduction. Three approaches can be distinguished: bulk modification, surface modification, and blending. Bulk modification can be carboxylation, but the most often used method is sulfonation. This is a specific approach, which can be used for improving characteristics during membrane synthesis. Commercial membranes often make use of bulk modification procedures at the point of synthesis. Membrane stability is good.

When existing membranes are to be improved, surface modifications can be carried out by plasma treatment, grafting, and other methods. Good results were reported from numerous studies; nevertheless, long-term stability remains to be seen. Blending is by far the simplest method but has limited applicability due to limited miscibility of hydrophobic and hydrophilic polymers.

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