# Novel negatively charged membrane adsorbers made using a combination of photopolymerization and immersion precipitation

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*Abstract*: A novel method combining a traditional immersion precipitation process for making membranes with photopolymerization and crosslinking of functional monomers included in the casting solution was used to prepare asymmetric polyethersulfone membranes with submicron particles incorporating glycidyl methacrylate copolymer. In order to introduce sulfonic groups, the epoxide rings of glycidyl methacrylate were opened using two methods. The first method was functionalization with sodium sulfite, and the second was functionalization with sulfuric acid and then grafting with 2-acrylamido-2--methylpropanesulfonic acid. The obtained membranes were characterized using infrared spectroscopy, conductometric titration and water permeability measurements. Scanning electron microscopy and atomic force microscopy were used to investigate the surface morphology and topology of the membranes. Dynamic adsorption of rhodamine B as a model dye was used to demonstrate the suitability of these novel membranes for membrane adsorption since the adsorption capacity for dye cations was much better for the membranes functionalized with sodium sulfite and the membranes grafted with 2-acrylamido-2-methylpropanesulfonic acid compared to the non-functionalized membranes.

*Keywords*: membrane formation; grafting; sulfonic acid; epoxide opening; polyethersulfone; glycidyl methacrylate.

## INTRODUCTION

Phase inversion techniques are the most important and commonly used processes for preparing membranes from a large number of polymers.[1] Among these

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techniques, immersion precipitation is the preferred membrane formation method because it allows the preparation of a wide range of membranes by varying the composition and properties of the initial polymer solution. In order to obtain a flat membrane sheet, a thin film of solution comprising at least one polymer, one good solvent, and additives is cast on a suitable support and immersed into a non-solvent coagulation bath where it undergoes phase separation into a polymer-rich and a polymer-lean phase.[2,3]

Polyethersulfone (PES), and PES-based membranes, shows outstanding chemical, thermal, and mechanical stability as indicated by its high glass transition temperature ($T_g$ = 230 °C), which leads to its frequent use for the preparation of asymmetric membranes by immersion precipitation.[1] The main disadvantage of PES membranes is related to their relatively hydrophobic character and these membranes are prone to easy fouling by adsorption of non-polar solutes, hydrophobic particles or bacteria.[4] In order to improve membrane wettability and performance in the filtration of aqueous solutions used for bio-separations, or for more efficient ultrafiltration, various methods were used for modification of PES membranes.[5,6] These methods include modification of the bulk material prior to membrane preparation, surface modification of prepared membranes, and blending of PES membranes with another material to introduce the desired functionalities.[4,7] Surface modification of polymeric membranes can be performed by surface coating and grafting induced by electron beam or gamma ray irradiation, plasma-induced grafting, ozone-induced grafting, thermal-induced grafting, redox-grafting techniques, surface-initiated atom transfer radical polymerization, *etc*. Membranes can also be prepared and modified using the photo-irradiation method.[8] A combination of an immersion precipitation process and photopolymerization was used to make asymmetric PES membranes with adsorbent particles incorporating crosslinked glycidyl methacrylate (GMA) copolymer.[9,10] This method was also used for the preparation of asymmetric membranes with an interpenetrating proton-conducting morphology.[11]

The strong interest in polymers based on GMA is mainly due to the ability of the epoxide groups to enter into a large number of chemical reactions leading to numerous possible chemical modifications, which enables a broad range of applications for these polymers.[12] GMA represents a very attractive platform for the introduction of complex functional groups,[13] due to the easy transformation of the epoxy group under mild reaction conditions into various functionalities.[14] There are numerous publications on ring-opening of the epoxy groups with various reagents, such as amines and hydroxylamine, sulfuric acid, phosphoric acid, iminodiacetic acid, sodium sulfite, and others.[15] The high reactivity of the epoxy group is due to the considerable strain in the three-membered ring, which is also affected by its position, the presence of other polar groups, the type of solvent,

and temperature.[12] Macroporous copolymers based on GMA are very attractive as adsorbents in biochemical and chemical separations.

Sulfonic group (SO₃H) is a strongly acidic ion-exchange group that can be introduced into polymeric materials in several ways, *e.g.*, sulfonation with concentrated sulfuric acid, copolymerization with monomers containing the SO₃H group, ring opening of epoxides with sodium sulfite, or using different grafting procedures.[16] A grafting method catalyzed with cerium(IV) has often been used for surface modification providing that the substrate onto which the grafting occurs contains hydroxyl groups that are transformed into free radicals.[17] A single radical is formed on the oxygen atom of the hydroxyl group leading to surface-initiated polymerization while undesirable competing reactions in the bulk solution are largely suppressed.

$$Ce(IV) + RCH_2OH \rightarrow Ce(III) + H^+ + RCH_2O\cdot$$
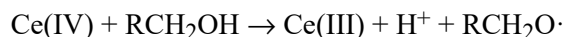
In this study, a combination of photopolymerization and liquid phase inversion was used to prepare negatively charged membrane adsorbers. A polymerized methacrylate network in a PES solution was created by photo-irradiation, and then it was converted into a porous asymmetric membrane with embedded particles by immersion in a water bath. In a previous work, epoxide groups were transformed into amine groups by functionalization with diethylenetriamine and the dynamic adsorption of orange G[9] or copper[10] from dilute aqueous solutions was used to show the efficient capturing of these species by the amine groups. In this work, the epoxide groups were transformed into sulfonic groups by functionalization with sodium sulfite (SS) or by grafting with 2-acrylamido-2-methyl-propanesulfonic acid (AMPS). The dynamic adsorption of rhodamine B from a dilute aqueous solution was used to demonstrate the efficient capturing of basic species by the negatively charged sulfonic groups.

## EXPERIMENTAL

*Chemicals and reagents*

PES (Ultrason E 7020P, $\bar{M}_w$ 92,000 g mol⁻¹, polydispersity index 3) was kindly provided by BASF. GMA (reagent grade), trimethylolpropane trimethacrylate (TMPTMA), *N*-methyl--2-pyrrolidone (NMP, 99 % purity), poly(vinylpyrrolidone) (PVP, $\bar{M}_w$ 25,000 g mol⁻¹), SS (reagent grade), 2-propanol (2-PA), sulfuric acid (H₂SO₄), nitric acid (HNO₃), ammonium cerium(IV) nitrate (ACN), AMPS (99 %), rhodamine B, sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium chloride (NaCl), and phenolphthalein were received from Sigma––Aldrich. The photoinitiator (PI), bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (Irgacure 819), was kindly gifted by Ciba SC. All chemicals were used as received without further purification. Tap water was used in the coagulation bath for precipitation of the membranes. Milli-Q deionized water was used for pure water permeability tests.

*Membrane preparation*

Membranes were prepared using the following procedure. A 25 wt. % solution of PES in NMP was made by mixing at 80 °C overnight. A 25 wt. % solution of PVP was prepared by

dissolving PVP in NMP at 80 °C. A solution of 1.27 g GMA and 0.45 g TMPTMA in 8.39 g NMP was made by mixing components in an amber vial cooled with ice and protected from ambient light. The solution for making membranes was prepared by mixing 1.25 g PES and 0.23 g PVP solutions with a freshly prepared solution of the monomers. Before the casting, 1 % of PI based on the total weight of monomers was added to the solution. The initial concentration of PES in all solutions was 11 wt. % excluding the PVP additive. The concentration of GMA was calculated to be 3 mmol g$^{-1}$ of the final dry membrane at a theoretical 100 % conversion of the reactants. The concentration of crosslinker (TMPTMA) in the solution was 15 mol % based on the GMA concentration. In a previous work,[9] it was found that this composition provided the optimal balance of membrane strength and pure water permeability. The prepared solution was transparent, thereby confirming complete miscibility of the components.

Prepared solution was cast on a glass plate using a 7.62 cm-wide film applicator with a 200 μm gap (BYK-Gardner), then put in an experimental enclosure blanketed with nitrogen gas and exposed to UV irradiation through a glass window on the top of the enclosure for 10 min. The exposure dose, mainly in the UVA region, was 4.5 J cm$^{-2}$, as measured by a YK--35UV light meter. UV exposure initiated photopolymerization and crosslinking of GMA to create a gel in the cast film. Finally, after UV curing, the cast film was immersed in a water bath whereby phase separation occurred by the instantaneous liquid–liquid demixing mechanism. After allowing at least 10 min to complete the phase separation and solidification, the obtained membrane was further extracted in distilled water overnight.

*Opening of the epoxide rings*

Two methods to open the epoxide rings were used. In the first method, functionalization of membranes with SS was performed by immersing the membrane in a solution containing SS, 2-PA, and distilled water under reflux conditions. In the second method, the epoxide groups of membranes comprising crosslinked polyGMA particles were hydrolyzed using sulfuric acid to produce diol groups before grafting the membranes with AMPS. The reaction conditions are given in Table I. The chemical reactions of the functionalizations of the given membranes using SS and $H_2SO_4$ are presented in Figs. 1 and 2.

TABLE I. Reaction conditions of the ring opening reactions

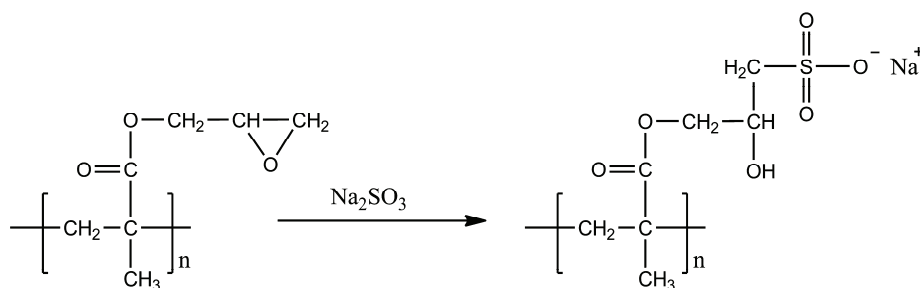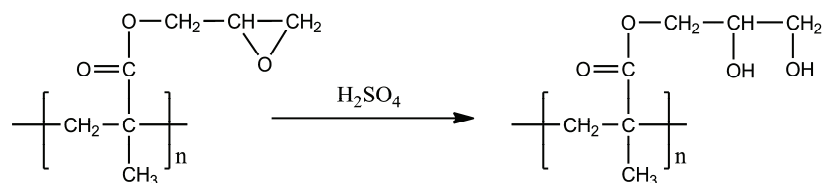| Reactant | Medium | Temperature, °C | Reaction time, h |
|---|---|---|---|
| SS | SS:2-PA:water mass ratio 10/15/75 | 80 | 6 |
| $H_2SO_4$ | 0.5 M solution | 60 | 4 |



Fig. 1. Ring opening using SS.

Fig. 2. Ring opening using sulfuric acid.

*Grafting of AMPS*

In order to graft the membranes with AMPS, 0.137 g of ACN was dissolved in 25 mL of water. Then, 0.116 g of 25 mmol L$^{-1}$ nitric acid was added followed immediately by the addition of 5.175 g of AMPS dissolved in 25 mL of water. The membranes previously converted into the diol form were immersed in the freshly prepared solution of ACN and AMPS. This mixture was purged with nitrogen and the polymerization was allowed to proceed for 5 h at 60 °C under reflux conditions. A schematic overview of AMPS-grafting is presented in Fig. 3.
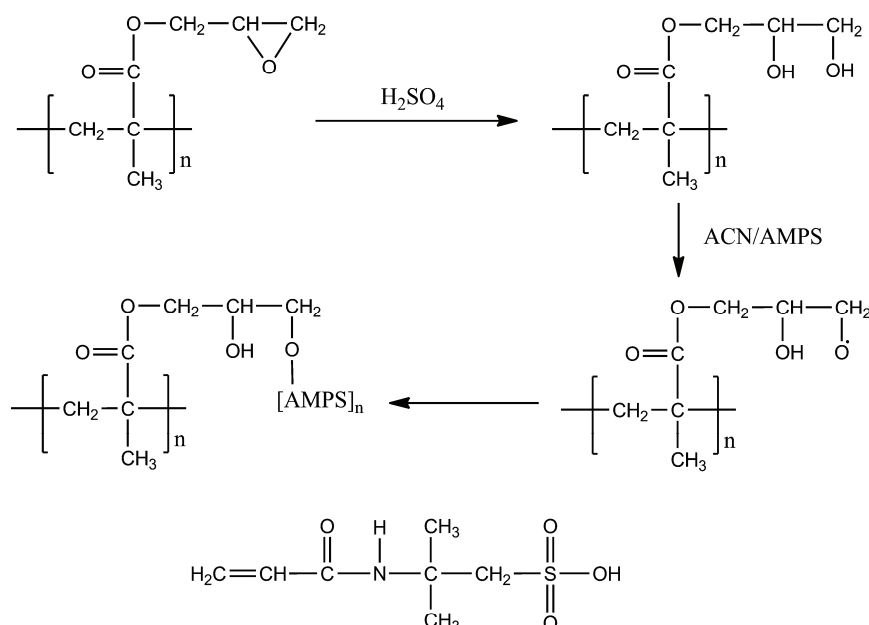
2-acrylamido-2-methylpropanesulfonic acid (AMPS)

Fig. 3. Schematic overview of AMPS-grafting.

*Membrane characterization*

The pure water permeability of the membrane samples was measured with a stirred Millipore cell, model 8050 (13.4 cm$^2$ effective membrane area), using deionized water at 1 bar pressure difference.

Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) analysis was conducted with Thermo Scientific Nicolet 6700 instrument equipped with a Smart ATR diamond accessory.

Scanning electron microscopy (SEM) analysis was performed on a JEOL JSM-6610 L instrument using a W filament as the electron source. Air-dried membrane samples were fractured after cooling in liquid nitrogen and sputtered with gold.

Atomic force microscopy (AFM) analysis was conducted with AFM instrument (Auto-Probe CP Research, TM microscopes) in the noncontact mode. The root mean squared ($R_a$) roughness values were calculated by applying the software package Veeco SPMLab NT ver.6.0.2 on 2D pictures (0.8 μm×0.8 μm).

The conductometric titration method was used to determine the concentration of sulfonic groups. A membrane sample weighing around 0.1 g was cut into small pieces, then immersed in 10 mL of 0.1 M HCl and mixed for 30 min. After thorough rinsing with deionized water until the conductivity was reduced to 1–2 μS cm$^{-1}$, 50 ml of 0.001 M NaCl was added and the solution was stirred for 10 min before measuring the initial pH value. A NaOH solution (0.01 M) was added slowly from a burette under stirring and the conductivity was measured 15–30 s after each addition. The sulfonic groups in the membrane sample gradually changed from acidic to the sodium form reducing the solution conductivity until the minimum was reached at neutral pH. Then, the concentration of sulfonic groups was calculated from the volume of NaOH solution used for the titration and the weight of the dried membrane sample.

The separation performance of the membranes functionalized with SS and grafted with AMPS was determined by filtration of a 50 mg L$^{-1}$ aqueous solution of Rhodamine B using a stirred Millipore cell, Model 8050. For the non-functionalized membrane and the membrane functionalized with SS, the transmembrane pressure was 0.5 bar, and for the membrane grafted with AMPS, the pressure was 1 bar. Membrane samples were placed in the cell with the bottom side facing the feed solution. The concentration of dye in the filtrate was determined using a Thermo Scientific Evolution 60 UV–Vis spectrometer at 550 nm, where a maximum in light absorption was observed.

<div align="center">RESULTS AND DISCUSSION</div>

*SEM analysis*

The SEM image of a cross-section of the PES membrane made with an initial concentration of 3 mmol g$^{-1}$ GMA and 15 mol % TMPTMA in shown in Fig. 4 (left), from which a typical asymmetric structure with a thin selective skin layer on top over a much thicker porous support can be seen. Based on the results of elemental analysis reported earlier,[9] the degree of conversion (polymerization yield) for the reaction between GMA and TMPTMA for this membrane was 80 %. Fig. 4 (right) reveals clusters of submicron particles incorporated within the PES membrane structure in the middle section. The structures seen in this figure result from the complex interplay of phenomena occurring during membrane fabrication, which was discussed previously.[9,10] Photo-irradiation led to GMA polymerization and crosslinking with TMPTMA, and as a result, an organogel was formed. During this step, phase separation between polymer-rich (PES) and methacrylate-rich phases was likely to occur. As a result, the irradiated films were hazy, indicating some degree of localized phase separation between the macromolecular species. All the irradiated films turned immediately white upon immersion into a water bath, indicating that the membranes were formed by an instantaneous liquid–liquid demixing mechanism.
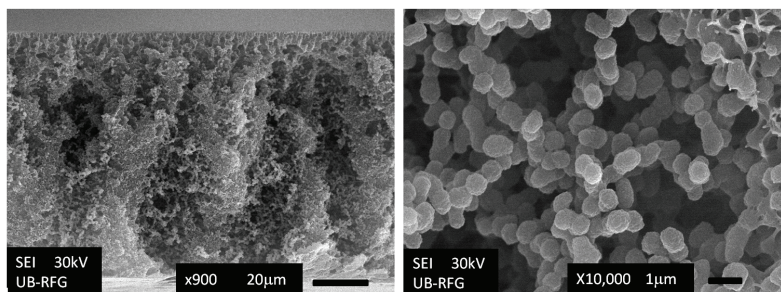
Fig. 4. SEM images of the cross-section of an asymmetric PES membrane with initial concentrations of 3 mmol g$^{-1}$ GMA and 15 mol % TMPTMA: full view (left) and middle section (right).[9]

The submicron particles visible in the SEM image are actually agglomerates of nodules, which were formed by coalescence prior to solidification.[18] The formation of nodular structures could be explained as follows. As discussed in the literature,[19] diffusional exchange between solvent and non-solvent, driven by large chemical potential gradients, leads to the formation of macrovoids when the polymer concentration is low and the composition in front of the formed nuclei remains stable for a relatively long period. When the composition of the casting solution is located in the metastable region or close to the bimodal curve, macro-voids will not be formed and hence the composition in front of the formed nuclei immediately enters the metastable region.[20,21]

Another phenomenon that affects the creation of nodules is caused by the presence of an additional polymeric component (PVP) in the casting solution. The presence of PVP retards the relaxation of the polymer chains that leads to phase separation of the polymeric species by a spinodal decomposition mechanism forming a submicron nodular structure in the top surface layer.[20] In the case of the membranes described in this work, UV curing creates a network of crosslinked polyGMA mixed with PES molecules, and after immersion in the water bath, which creates thermodynamically unstable conditions, these polymeric species also separate by spinodal decomposition. As Radovanovic *et al.* explained,[9] the formed nodules are probably mixtures of polymeric species with compositions dependent on the extent of phase separation during the UV curing step, because the spinodal decomposition process is faster than diffusion of polymer molecules. In the middle section of the membrane, the molecules had more time to diffuse prior to solidification and the nodules coalesced to form agglomerates. These nodules were connected to the pore walls by polymer chains, which are formed during an incomplete demixing of polymers throughout the phase separation.

*Water permeability measurements*

The pure water permeability of the non-functionalized membrane composed of 11 wt. % PES, 3 mmol g$^{-1}$ GMA, 15 mol % TMPTMA, and 2 wt. % PVP was 988 L h$^{-1}$ m$^{-2}$ bar$^{-1}$. After functionalization with SS, the pure water permeability was 462 and 403 L h$^{-1}$ m$^{-2}$ bar$^{-1}$ for membranes grafted with AMPS. These values are typical for ultrafiltration membranes. Previous experiments on the filtration of bovine serum albumin using the non-functionalized membrane showed that the selective skin layer of this membrane has an effective pore radius of 4.85 nm.[9] As can be seen, water permeability was significantly reduced after SS functionalization and grafting with AMPS. This might be related to the swelling of nodules containing relatively high concentrations of negatively charged sulfonic groups, which could reduce the flow to a certain extent due to a reduction in the effective pore size.

*FTIR-ATR analysis*

The FTIR-ATR spectra of the non-functionalized membrane and the membrane functionalized with SS are presented in Fig. 5. The strong carbonyl peaks at 1724 cm$^{-1}$ originate from both GMA and TMPTMA, while the epoxide peaks at 907 cm$^{-1}$ come from GMA. Both spectra exhibit the following peaks characteristic for PES: 1147 cm$^{-1}$ for symmetric SO$_2$ stretching and the aromatic bands at 1238, 1485 and 1577 cm$^{-1}$. After functionalization with SS, sulfonic groups were introduced as shown by the corresponding peak at 1043 cm$^{-1}$.
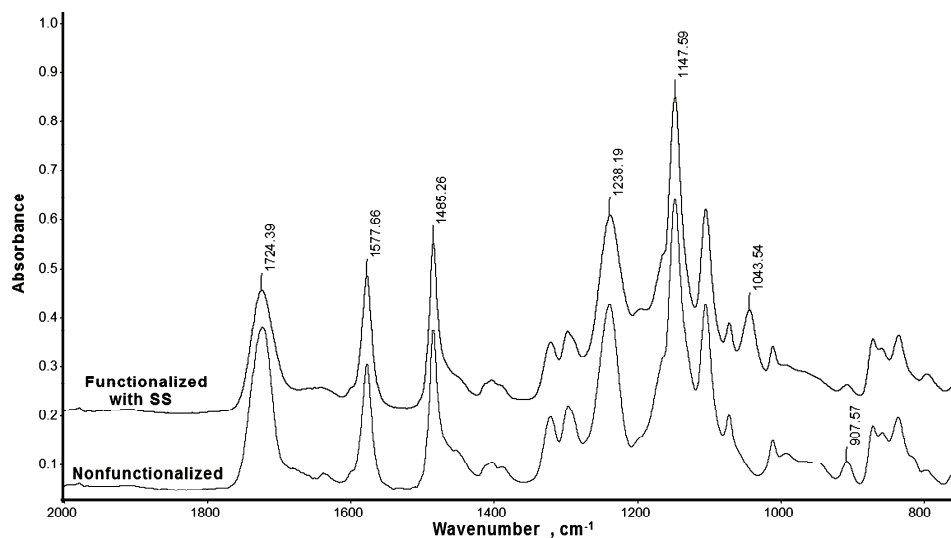


Fig. 5. The effects of functionalization with SS on FTIR-ATR spectra of PES membrane with embedded GMA particles: non-functionalized membrane (bottom), functionalized with SS (top).

FTIR-ATR spectra of PES membranes before and after treatment with $H_2SO_4$ and after grafting with AMPS are shown in Fig. 6. Characteristic carbonyl peaks at 1723 cm$^{-1}$ originating from both GMA and TMPTMA and epoxide peaks at 907 cm$^{-1}$ coming only from GMA were present. In addition, broad peaks at 3400 cm$^{-1}$ characteristic for hydroxyl groups could be seen for both treated membranes in the inset to Fig. 6. All spectra also contained peaks characteristic for PES: 1149 cm$^{-1}$ for symmetric $SO_2$ stretching, and 1238, 1485, and 1577 cm$^{-1}$ for aromatic bands. In addition, there was a peak at 1043 cm$^{-1}$ resulting from the sulfonic group introduced by grafting with AMPS.
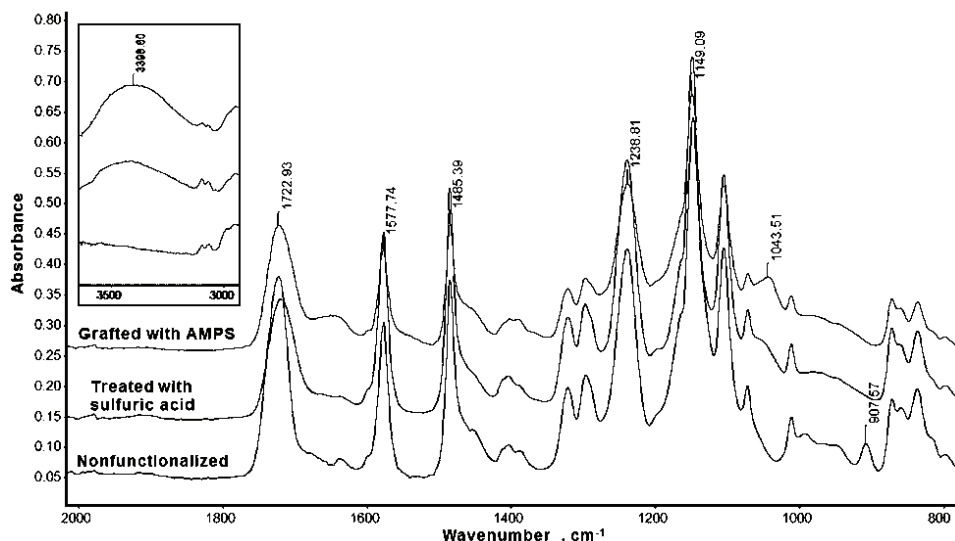


Fig. 6. FTIR-ATR spectra for the non-functionalized membrane (bottom), the membrane after functionalization with $H_2SO_4$ (middle) and after grafting with AMPS (top).

*AFM analysis*

The AFM images of the top membrane surfaces were used to investigate the surface topology of the membranes. The AFM images obtained for the non-functionalized PES membrane and the membrane functionalized with SS showed that the surface topographies were quite similar. Membranes before and after grafting with AMPS are presented in Fig. 7. The surface topographies of these membranes were also very similar with nodules ranging from 20 to 50 nm and a slight increase in surface roughness from 5.36 to 8.23 nm after grafting. This increase in surface roughness might be a result of additional sulfonic groups grafted on the surface of the membrane.
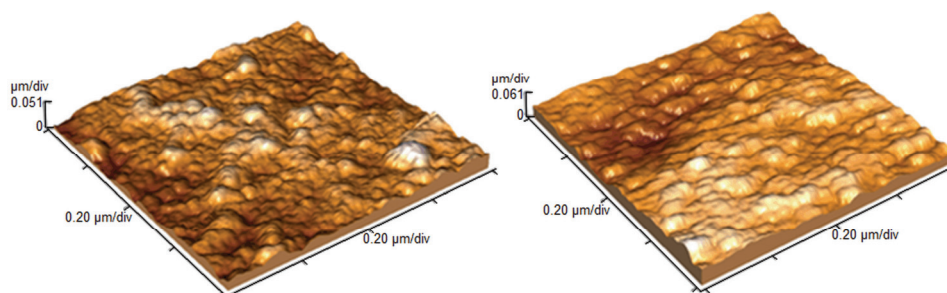
Fig. 7. AFM images of the top surface of PES membranes with initial concentrations of 3 mmol g$^{-1}$ GMA and 15 mol % TMPTMA: non-functionalized (left)[10] and after grafting with AMPS (right).

## Conductometric titration

The conductometric titration method was used to determine the concentration of sulfonic groups in the PES membranes functionalized with SS and grafted with AMPS. The results are listed in Table II and compared to the theoretical value of 2.4 mmol g$^{-1}$ (80 % polymerization yield starting from an initial GMA concentration of 3.0 mmol g$^{-1}$). Both concentrations were significantly lower than the theoretical value, which indicates that the epoxide groups buried inside the nodules were not easily accessible for reaction. The relatively low value for the membrane grafted with AMPS compared to the membrane functionalized with SS might have been the result of differences in molecular sizes of reactants. Lower conversions due to steric effects are often observed in polymer functionalization with larger molecules.[22]

TABLE II. Concentration of sulfonic acid groups from conductometric titration

| Membrane | Sulfonic group concentration, mmol g$^{-1}$ |
|---|---|
| Non-functionalized PES membrane | 0.00 |
| Membrane functionalized with SS | 0.79 |
| Membrane grafted with AMPS | 0.29 |
| Theoretical concentration of sulfonic groups | 2.40 |

## Dynamic adsorption of a cationic dye

In order to investigate the separation performances of non-functionalized PES membranes, membranes functionalized with SS and membranes grafted with AMPS, a series of screening experiments using rhodamine B as a model adsorbate was conducted and the results are shown in Fig. 8. Rhodamine B is a cationic dye that has been used in the fields of pharmaceutics and cosmetics, and the textile industry. The molecular weight of its chloride form is 479 g mol$^{-1}$ and it has one ammonium group per molecule that can bind electrostatically with sulfonic groups. The longest dimension of the rhodamine B molecule was reported

to be 1.77 nm.[23] Due to its smaller molecular size than the pores present in the selective top surface of the membrane, dye adsorption occurs primarily by electrostatic binding between the dye ammonium groups and sulfonic groups in the functionalized membrane and not by a sieving mechanism. Dynamic adsorption experiments were conducted using transmembrane pressures ranging from 0.5 to 1 bar. As can be seen in Fig. 8, instantaneous dye breakthrough occurred with the non-functionalized membrane. This membrane captured only a minor fraction of the dye by nonspecific adsorption on the membrane material itself. PES membranes exhibit slightly negative charges in dilute aqueous solutions,[24] which might explain the adsorption of rhodamine B by the non-functionalized membrane. The lowest concentrations of rhodamine B in the permeate were observed for a membrane grafted with AMPS. Both the membrane functionalized with SS and the membrane grafted with AMPS had much greater adsorption capacity for dye cations compared to the non-functionalized membrane.
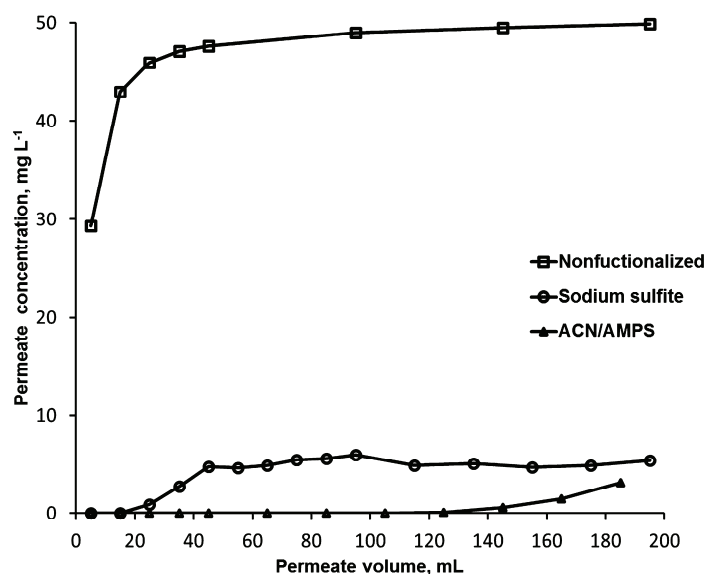


Fig 8. Filtration of rhodamine B solution (feed concentration 50 mg L$^{-1}$, transmembrane pressure 0.5–1 bar) through non-functionalized PES membrane, PES membrane functionalized with SS and PES membrane grafted with AMPS.

CONCLUSIONS

A combination of traditional liquid phase inversion process for fabricating asymmetric membranes and photopolymerization was used for the preparation of asymmetric PES membranes with submicron particles comprised of GMA. The casting solution was exposed to a source of UV irradiation to polymerize the monomers and after immersion of the irradiated film into a water bath, phase

separation between polymer-rich and polymer-lean phases was induced. This novel process led to the creation of asymmetric PES membranes with adsorbent particles comprised of crosslinked GMA copolymer. Two methods were used in order to open the epoxide rings and introduce sulfonic groups. In the first method, the obtained membranes were functionalized with SS and in the second, the membranes were hydrolyzed using sulfuric acid to produce diol groups and then grafted with AMPS.

SEM images of the membrane cross-section revealed clusters of submicron particles embedded within the PES support matrix. Functionalization with SS and grafting with AMPS converted these submicron particles into microadsorbers by introducing sulfonic groups *via* epoxide ring opening. The FTIR-ATR spectra demonstrated the presence of characteristic peaks originating from GMA, AMPS, SS and PES in final membranes. AFM images showed that the surface topographies of the initial and grafted membranes were quite similar. The conductometric titration method was used to determine the concentration of sulfonic groups in the PES membranes functionalized with SS and grafted with AMPS. The separation performance of the obtained membranes was examined by a series of experiments using rhodamine B as a model dye. Dye retention in these dynamic adsorption experiments was the highest for the PES membranes grafted with AMPS.

И З В О Д

НОВИ НЕГАТИВНО НАЕЛЕКТРИСАНИ МЕМБРАНСКИ АДСОРБЕРИ НАПРАВЉЕНИ КОМБИНАЦИЈОМ ФОТОПОЛИМЕРИЗАЦИЈЕ И ПОТАПАЊА У ВОДЕНО КУПАТИЛО

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Нови поступак прављења мембрана заснован на комбинацији традиционалног поступка потапања у водено купатило и фотополимеризације и умрежавања функционалних мономера у почетном раствору примењен је за прављење асиметричних мембрана од полиетарсулфона са уграђеним субмикронским честицама које садрже кополимер глицидил-метакрилата. У циљу уградње сулфонских група примењене су две методе отварања епоксидних прстенова: функционализација натријум-сулфитом и функционализација сумпорном киселином праћена калемљењем 2-акриламидо-2-метилпропансулфонском киселином. Добијене мембране су карактерисане помоћу инфрацрвене спектроскопије, кондуктометријске титрације и мерењем пропустљивости воде. Површинска морфологија и топологија мембрана је испитана скенирајућом електронском микроскопијом и микроскопијом атомских сила. Динамичка адсорпција боје родамин Б показала је да се овај нови тип мембрана може користити за мембранску адсорпцију

пошто је капацитет адсорпције за катјоне боје био знатно већи за мембрану функцио-
наклизовану натријум-сулфитом и за мембрану калемљену 2-акриламидо-2-метилпро-
пансулфонском киселином него за нефункционализовану мембрану.

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