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CHEMICAL MODIFICATION AND CHARACTERIZATION OF THE SURFACE OF POLYSULFONE MEMBRANES

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Abstract

Asymmetric porous membranes were prepared from polysulfone by a wet-phase separation procedure. Different chemical modifications were applied to the upper membrane surface, i.e. the surface which was exposed to interaction with nonsolvent (water) in the coagulation bath during the membrane formation. The membrane surface was modified by the series of Friedel-Crafts electrophilic substitutions of aromatic rings in the polysulfone molecules. As a reagent 1-chlorodecane or propylene oxide dissolved in hexane and $AlCl_3$ as a catalyst were used. In the former case a hydrophobic and in the latter one a hydrophilic coating was achieved, respectively. The membrane surface was also modified by sulfonization with sulfuric (VI) acid water solution; in this way negative charges were introduced at the membrane surface. The membranes, unmodified and chemically modified, were characterized by measuring the membrane thickness, the deionized water flux through the membrane, the zeta potential and contact angle. The specific chemical modifications of the membrane surface affect the water flux, the zeta potential and contact angle values whereas the membrane thickness remains unchanged. These effects are interpreted in terms of hydrophilicity and hydrophobicity, changes of the membrane surface charge and the thickness of shear layer at the membrane surface, all with respect to the particular modification applied. Reaction with 1-chlorodecane gave a hydrophobic surface by nonpolar $–(CH_2)_9\text{-}CH_3$ groups and reaction with propylene oxide gave a hydrophilic surface with polar group $–CH(CH_3)\text{-}CH_2\text{-}OH$. The surface of sulfonized polysulfone membranes contained ionizable ($- SO_3H$) functional groups.

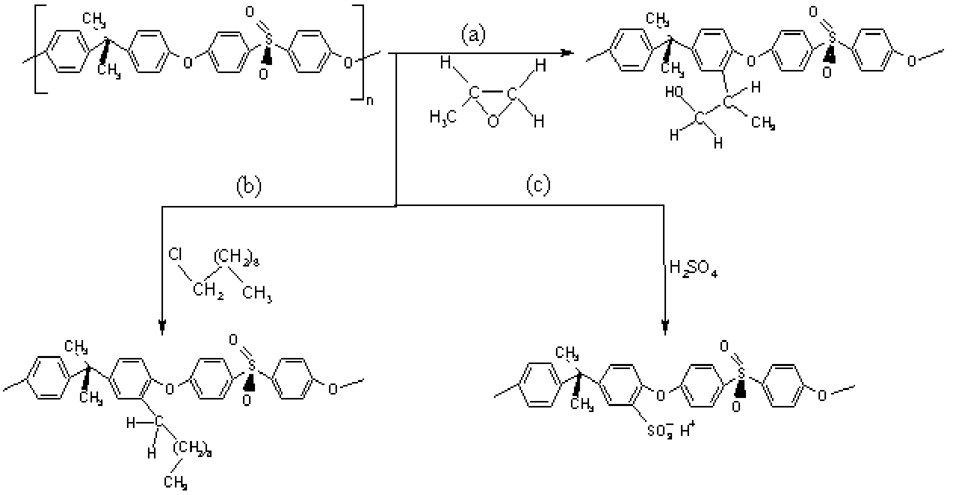
Introduction

Numerous technological applications of polymeric membranes in various kinds of separation are well established. Modification of the membrane surface can affect separation abilities of the membranes and lead to controlling the membrane fouling. In this paper we present a study of some chemical modifications of the polysulfone membrane surface in order to change its physical properties with respect to the surface charge density and surface hydrophilicity/hydrophobicity. In particular, the polysulfone membrane surface was modified by the Friedel-Crafts electrophilic substitution of aromatic rings in polysulfone molecules either with propylene oxide or 1-chlorodecane as well as by sulfonization with sulfuric (VI) acid water solution. We applied the measurements of the membrane thickness, deionized water flux measurements through the membrane, the tangential measurement of the zeta potential and contact angle measurements as characterization methods of chemical modifications of the membrane surface. We demonstrated that the zeta potential, the water flux through the membrane and the contact angles are relevant indicators of the chemical modification of the membrane surface. Measurements of zeta potential, the contact angle and water flux are in a qualitative agreement with the physical and chemical properties of the membrane surface changed by application of the specific chemical modification.

The objects of this study are asymmetric porous membranes prepared by a wet-phase separation process from polysulfone.[1,2] A variety of morphologically very different polymeric membranes can be prepared by changing the parameters of this formation procedure such as composition of polymer solution, additives and temperature. This gives appealing possibilities to further applications of chemical modification of the membrane surface. Studies of the membrane surface can also provide additional information on elementary processes of membrane formation mechanisms.[1,2]

Materials and Methods

Asymmetric porous membranes were prepared from polysulfone by the wet-phase separation. 15 wt.% solution of polysulfone in *N,N*-dimethylacetamide with the nominal thickness 300 μm was immersed in coagulation bath of pure water at the room temperature. Further details are given elsewhere.[1,2]



Scheme 1. Chemical modifications of the surface of polysulfone membranes. The Friedel-Crafts electrophilic substitution of aromatic rings in polysulfone molecule (a) with propylene oxide and (b) with 1-chlorodecane, (c) sulfonization with sulfuric (VI) acid water solution.

Three types of chemical modification of the membrane surface were used in this work. In all cases the modification was applied to the upper membrane surface, i.e. a surface which was exposed to interaction with nonsolvent (water) in the coagulation bath during the membrane formation. The polysulfone membranes were modified by the Friedel-Crafts electrophilic substitution[3] of aromatic rings in polysulfone molecules with propylene oxide or 1-chlorodecane. Reagents were dissolved in hexane, and $AlCl_3$ was used as a catalyst. The membrane surface was previously conditioned in different solvents as water, methanol, butanol and hexane, i.e. a sequence of a polar to a less polar and finally a nonpolar solvent. Exposition time to the chemical reaction was in both cases 60 minutes or 180 minutes (and 120 minutes in the case of modification with propylene oxide) and the volume ratio of the reagent (1-chlorodecane or propylene oxide) and hexane was in all cases 1:5. Sulfonization with the sulfuric (VI) acid of the membrane surface[4] was applied as a third modification. Exposition time of the reaction was 30 minutes. The concentration of sulfuric (VI) acid used for sulfonization was 45 wt.% and 50 wt.%. All modifications were done at the room temperature. The three modifications are schematically represented in Scheme 1.

The membrane thickness was measured by magnetic probe MINIMER HD1. The deionized water flux through the membranes was measured in AMICON 8400 cell under the ultrafiltration pressure of nitrogen.

The streaming potential measurements were carried out using an Elektrokinetic Analyser EKA (manufactured by A. Paar K.G., Graz, Austria)[5] and the zeta potential was calculated according to the method of Fairbrother and Mastin:[6]

$$\zeta = \frac{\lambda\eta}{\varepsilon\varepsilon_0}\left(\frac{\Delta U}{\Delta P}\right)$$

where ΔU is the measured streaming potential, ΔP is the corresponding pressure difference applied to electrolyte flow, λ is the electric conductance of the electrolyte solution, η is the viscosity, ε is the dielectric constant of the electrolyte solution, and ε_o is the influence constant. Each value of the zeta potential at a given pH value is obtained as an average value from four measured linear dependencies of streaming potential upon changing the pressure between 25-750 mbar; at each pressure sweep a direction of electrolyte solution flow was changed.[5] The streaming potential of each sample was measured in 0,001 M KCl; pH changes were achieved by addition of 0,1 M NaOH and 0,1 M HCl. Streaming potential was measured by the so-called tangential method, i.e. the method in which the electrolyte solution flows parallel to the membrane surface.

For measuring contact angle the direct measurement of the angle from sessile drops was used. Using this technique the angle was measured by alignment a tangent with the profile at the point of contact with the solid surface. For the angle measurement the equipment G1 of Krüss (Hamburg, Germany) with an adjustable goniometer was applied. Both angles of either side of a droplet were determined.

Drops of a volume of 20 μl leading to a liquid covered area of 3-4 min diameter were deposited with a micrometer syringe. The following liquid served as probe liquids: α-bromonaphthalene, formamide, glycerol and water. All liquids were Merck products of analytical grade purity > 99 %. Water was distilled twice using crude potassium permanganate. The surface tension of water was measured with the Wilhelmy plate method (tensiometer K12 Krüss, Hamburg, Germany). At 30 °C the measured surface tension of water runs to 71,8 till 72,4 mN/m.

According to theory of van Oss[7] from measured contact angles the values of the proton donor and proton acceptor parameters of surface tension as well as the total free energy of adhesion and the total free energy of interaction of the solid polymeric surface in water can be calculated.

Results

Asymmetric porous polysulfone membranes were chemically modified at their upper surface by three different modifications: the Friedel-Crafts electrophilic substitution of aromatic rings in polysulfone molecules either with propylene oxide or 1-chlorodecane as well as by sulfonization with sulfuric (VI) acid water solution, leading to changes of the membrane surface charge and to changes of hydrophilicity/hydrophobicity of the membrane surface (see Scheme 1). Measurements of the membrane thickness, the deionized water flux through the membrane, the pH-dependence of the zeta potential and the contact angle measurements characterized these modifications. The results are presented in Tables 1-2 and Schemes 2 – 4.

Table 1. Membrane thickness and deionized water flux through the membrane of unmodified and modified polysulfone membranes

time of reaction (min)	thickness		deionized water flux	
	before reaction (μm)	after reaction (μm)	before reaction (l/hm^2)	after reaction (l/hm^2)
reagent: propylene oxide:hexane = 1:5 (volume ratio)				
60	110	114	13,2	39,4
120	111	112	16,3	17,8
180	118	114	25,8	24,4
reagent: 1-chlorodecane:hexane = 1:5 (volume ratio)				
60	119	122	20,4*	10,9*
180	112	105	40,7	13,6**
reagent: H_2SO_4				
a) 30	134	132	7,5	9,8
b) 30	112	107	11,5	27,2

*Δp = 3 bar, ** Δp = 4 bar, other values were measured at Δp = 2 bar,
[a)] 45 wt.% H_2SO_4, [b)]50 wt.% H_2SO_4

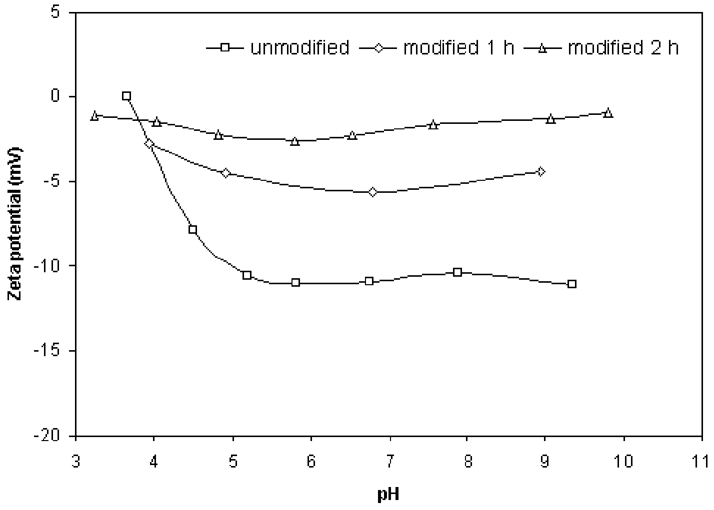
Table 2: Contact angles in degrees and their standard deviations

	1	2	3
water	79,5 ± 4,2	71,1 ± 2,9	85,7 ± 4,4
formamide	56,0 ± 3,2	56,8 ± 2,3	63,6 ± 3,2
glycerol	73,5 ± 3,1	69,8 ± 2,7	75,3 ± 3,6
α-bromonaphthalene	22,3 ± 2,9	16,8 ± 1,8	14,9 ± 1,4

1 polysulfone, modified with propylene oxide, t = 2 h
2 polysulfone, modified with sulfuric acid 50 wt %, t = 30 min.
3 polysulfone, unmodified

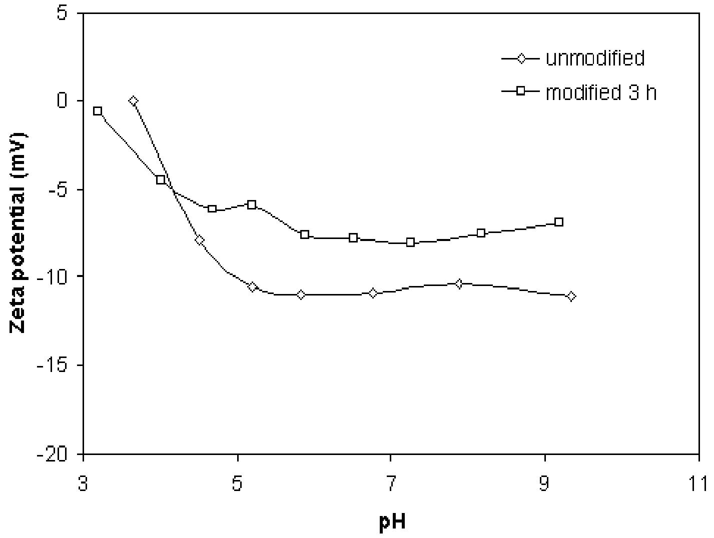
Scheme 2 gives results of the zeta potential measured on chemically modified polysulfone membrane surface; modification was induced by the Friedel-Crafts reaction with propylene oxide. The modified membranes have lower absolute value of the zeta potential than the unmodified ones. Due to the spatial dependence of electric potential in the electrolyte solution close to the membrane surface and due to the related definition of the zeta potential one can expect that the thickness of stagnant layer of the solution strongly affects the measured value of the zeta potential. Therefor the lower zeta potential absolute values obtained can be explained by an appearance of hydrophilic polar group $–CH(CH_3)-CH_2-OH$ at the membrane surface as a consequence of the polysulfone reaction with propylene oxide (see Scheme 1a) and a concomitant increase of the thickness of a stagnant layer of electrolyte water solution at the membrane surface whereby the membrane surface charge remains unchanged. On the other hand, the modification of the polysulfone membrane surface with propylene oxide influences the deionized water flux (Table 1). After testing several different conditions of this reaction the most suitable reaction conditions for a significant enhancement of water flux proved to be the volume ratio of propylene oxide: hexane = 1:5, temperature 20 ^{0}C and the reaction duration of 1 hour. In accord with observations of zeta potential the contact angle measurements show that chemical modification with propylene oxide increases hydrophilicity of membrane surface compared to unmodified membrane (Table 2).

Scheme 3 presents dependencies of the zeta potential on pH for polysulfone membranes, which upper surface was chemically modified by the Friedel-Crafts reaction with 1-chlorodecane. Difference between the modified and unmodified membranes could be observed. The chemical modification with 1-chlorodecane which brings nonpolar groups $–(CH_2)_9-CH_3$ (see Scheme 1b) to the membrane surface does not



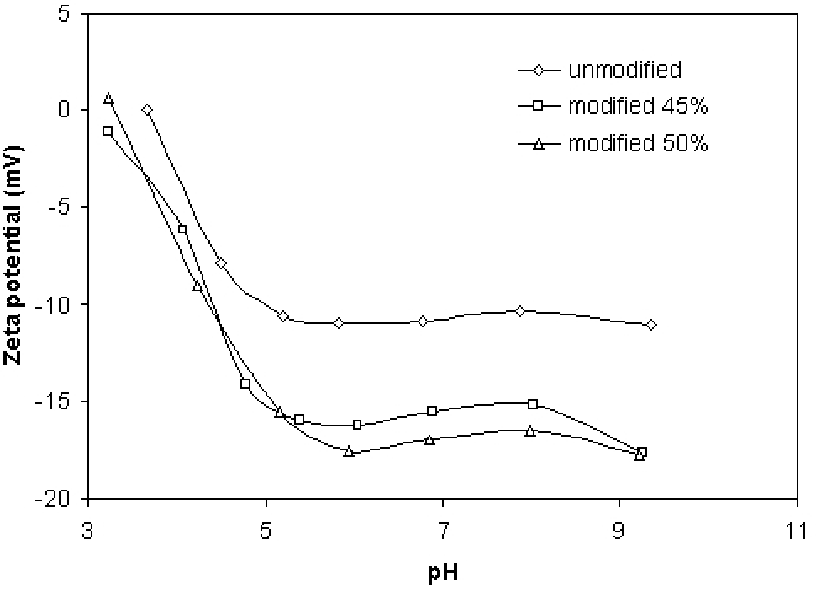
Scheme 2. Dependencies of the zeta potential on pH for polysulfone membranes modified by the Friedel-Crafts reaction with propylene oxide.

affect the charge on the surface. Lower absolute values of zeta potential of modified membranes can be understood by the presence of long decyl groups bounded to the membrane surface. These groups sterically hinder the water flux along the membrane surface which results in increased thickness of immobile water layer at the membrane surface. Reduction of the water flux through the membrane observed upon modification (Table 1) is in accord with the modification reaction between polysulfone and 1-chlorodecane which gives the hydrophobic membrane surface.



Scheme 3. Dependencies of the zeta potential on pH for polysulfone membranes modified by Friedel-Crafts reaction with 1-chlorodecane.

The sulfonized surfaces of polysulfone membranes are characterized by greater negative values of the zeta potential as they are the control values of the unmodified membranes (Scheme 4). This finding can easily be understood by the presence of negative charges of ionizable functional groups –SO_3H (see Scheme 1c) which appear at the membrane surface after reaction between polysulfone and sulfuric acid. Increased hydrophilicity of the membrane surface is consistent with the increased water flux (Table 1) with respect to the case of the unmodified membranes. The contact angle measurements (Table 2) also show that the surface of sulfonized membrane is hydrophilic. We believe that the increase of surface charge prevails the effect of increased thickness of stagnant water layer because of greater hydrophilicity.



Scheme 4. Dependencies of the zeta potential on pH for sulfonized polysulfone membranes.

Unchanged thickness of membranes after modifications indicates that modification do not mechanically change the membrane. (Table 1). The membrane thickness may therefor not be a relevant system parameter for characterization of the chemical modifications applied to the polysulfone membrane surface.

In summary, this work shows that the water flux through the membrane, the zeta potential measured tangentially and the contact angle characterize the chemical modification of the polysulfone membrane surface and that their changes can be interpreted qualitatively in terms of membrane surface charge changes as well as in terms of changed membrane surface hydrophilicity/hydrophobicity.

References and Notes

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Povzetek

Površino asimetričnih poroznih membran iz polisulfona, pripravljenih po postopku mokre fazne separacije, smo kemijsko modificirali s Friedel-Crafts-ovo elektrofilno substitucijo aromatskih delov molekule polisulfona, kjer smo kot reagent uporabili 1-klorodekan in propilen oksid ob prisotnosti $AlCl_3$ kot katalizatorja. Na površino smo vezali nepolarne in polarne skupine, ki tvorijo hidrofobno oziroma hidrofilno oblogo. Površino membrane smo kemijsko modificirali tudi s sulfoniranjem z žveplovo(VI) kislino in s tem vezali na površino negativni naboj. Nemodificirane in kemijsko modificirane membrane smo karakterizirali z merjenjem debelin, pretokov za deionizirano vodo, potenciala zeta in omočitvenega kota. Kemijske modifikacije površine membrane so vplivale na pretok za deionizirano vodo, na potencial zeta in omočitveni kot, debelina pa je ostala nespremenjena. Te spremembe smo kvalitativno pojasnili s spremembami hidrofilnosti in hidrofobnosti ter spremembami naboja na površini in debeline mejnega sloja ob površini membrane. Pri reakciji z 1-klorodekanom tvorijo nepolarne $–(CH_2)_9$-CH_3 skupine hidrofobno površino, pri reakciji s propilen oksidom pa tvorijo polarne $–CH(CH_3)$-CH_2-OH skupine hidrofilno površino. Površina membrane, modificirana z žveplovo(VI) kislino, pa vsebuje ionizabilne $–SO_3H$ funkcionalne skupine.