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Solvent-Resistant Nanofiltration Membranes Based on Multilayered Polyelectrolyte Complexes

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Alternating deposition of oppositely charged polyelectrolyte (PEs) can create stable solvent-resistant nanofiltration (SRNF) membranes with very high flux and selectivity. A new combination of PEs (poly(diallyldimethylammonium chloride) and sulfonated poly(ether ether ketone) is reported from which supported membranes consisting of 5, 10, 15, and 20 bilayers are prepared via the layer-by-layer method. The morphology of the membranes was studied in detail by SEM and AFM, showing rougher membrane surfaces with increasing bilayer number. For the first time, polyelectrolyte complex (PEC) based membranes were also applied in the filtration of organic solvents, where they form an excellent new tool to study the role of charges in solvent filtrations. Due to Donnan exclusion, the multilayered PEC membranes showed very good retentions up to 99% for charged solutes in the pressure-driven filtration of isopropanol solutions. Moreover, they were found to show excellent prospective use in polar aprotic solvents, like dimethylformamide and tetrahydrofuran, which have been extremely troublesome so far for most existing SRNF membranes.

1. Introduction

The layer-by-layer (LBL) deposition of polyelectrolytes (PE) has emerged as a versatile and inexpensive method for the construction of polymeric thin films, often with nanometer-scale control over the spatial distribution of ionized species within the film. This is normally done via the alternating exposure of a charged substrate to solutions of positively or negatively charged PEs.[1–4] Provided that each adsorption step leads to charge inversion of the surface, the subsequent deposition finally results in a layered complex, stabilized by strong electrostatic forces, so-called self-assembled PECs. PECs have unique properties due to their strong internal Coulomb interactions and the possibility to tune their electrostatic nature by the composition and the characteristics of the individual PEC constituents. The LBL electrostatic self-assembly technique has been extended to a wide variety of materials, including proteins, clay minerals, semiconductor colloidal particles, dyes, redox systems, etc.[5–10] The resulting films have been explored in a wide variety of applications such as sensors, selective patterning, and nonlinear optics.[11–14]

Films prepared via this method are in particular attractive materials for membrane separation for several reasons: (1) film thickness can be controlled to the nanometer scale simply by varying the number of deposited bilayers and (2) nearly any PE can form these films, enabling easy tuning for a given separation through proper selection of the bilayer constituents. One of the most studied systems is poly(allylamine), combined with poly(styrene sulfonate) or poly(vinyl sulfonate).[15]

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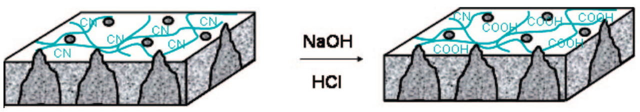
Nanofiltration (NF) is a process in which liquid feeds are separated over a membrane by means of pressures between 5 and 20 bar. Permeation takes place through the very small pores present in the membranes, or sometimes even through the available polymer free volume only.[16] Large-scale applications currently exist in wastewater treatment and drinking water production.[17–19] A major challenge these days is to broaden the range of NF applications to organic feeds, the so-called solvent-resistant nanofiltration (SRNF).[16–20] A more widespread use requires solvent-resistant membranes that preserve their separation characteristics under more aggressive conditions of strongly swelling solvents and elevated temperatures. Solvent-stable polymers mostly contain aromatic structures and hardly possess functional groups. Since some affinity between membrane polymer and permeating solvent is needed, the few commercial SRNF membranes currently available are limited to applications in apolar solvents. Moreover, being un-cross-linked, the existing polymeric membranes dissolve in aprotic solvents.

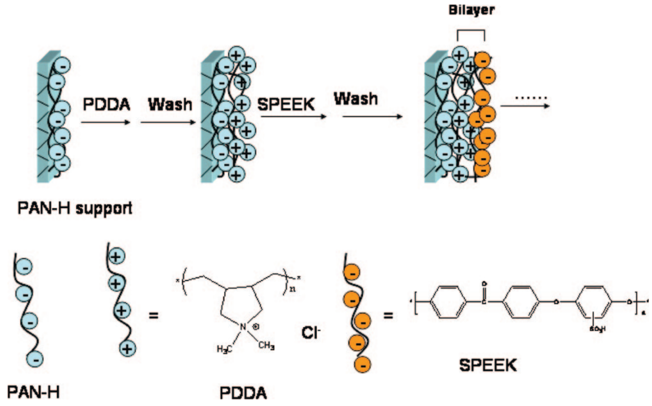
Supported PEC-based membranes have been tested already in pervaporation and aqueous NF.[21–25] Due to the electrostatic repulsion forces, PEs possess the ability to reject ions with a charge opposite that of the last deposited layer. Because of the high charge density, this repulsion is even maintained in very open structures.

This paper describes the first use of PEC-based membranes organic medium, more in particular as SRNF membranes. PECs are the perfect materials to assess more fundamentally the quite controversial influence of membrane charge on the transport mechanism in SRNF. Due to the lower dielectric constant of organic solvents as compared to that of water, such influence has hardly been considered before,[26] but should be far from negligible. Due to their extremely thin top layers, PEC-based membranes can then be expected to combine very high permeabilities in relatively polar organic solvents with high selectivities for charged molecules.

Scheme 1. Preparation of the PAN-H Support



Scheme 2. Preparation of Multilayered PEC Membranes



Negatively charged hydrolyzed polyacrylonitrile membranes (PAN-H) were selected as support materials for the preparation of multilayered PECs via the LBL method to ensure good adhesion between the top layer and the support, thanks to electrostatic interactions. Poly(diallyldimethylammonium, chloride) (PDDA) was used as the positively charged PE. Considering its excellent thermal and mechanical stability reported earlier in the membrane field,[27,28] sulfonated poly(ether ether ketone) (SPEEK) was selected as the negatively charged component. This polymer is introduced for the first time in PEC preparation. The morphology changes as a function of bilayer coating sequence, as well as the performance of the membranes in actual SRNF applications, are studied in detail.

2. Experimental Section

2.1. Materials. Polyacrylonitrile (PAN) was purchased from Scientific Polymer Product. PDDA ($M_w = 200000-350000$) was obtained from Aldrich as a 20 wt % aqueous solution. SPEEK was prepared by direct sulfonation of PEEK (VICTREX) with sulfuric acid at 80 °C for 3 h. The degree of sulfonation (the number of SO_3H groups per repeating unit), as obtained by ^{1}H NMR, is 0.9.[28]

2.2. Preparation of the Hydrolyzed PAN (PAN-H) Support. The PAN support was prepared by the phase-inversion technique with solutions containing 15 wt % PAN in DMSO. The polymer solution was cast on a polypropylene support (FO 2471, Viledon) and then immersed in deionized water. The PAN-H support was obtained by immersing the PAN support in 10 wt % NaOH at 50 °C for 40 min. The remaining NaOH was removed by washing with water. Before preparation of multilayered PEC membranes, the PAN-H support was first immersed in 2 M HCl for 1 h to convert the −COONa into −COOH groups (Scheme 1).

2.3. Layer-by-Layer Deposition. PEs were dissolved in an aqueous medium with a concentration of 0.2 wt %. For adsorption of each layer, the PAN-H support was immersed in the solution of the cationic PE (PDDA), rinsed with water, then immersed in the solution of the anionic PE (SPEEK), and rinsed again with water. The described procedure was repeated until a maximum of 20 pairs of polycation/polyanion bilayers was adsorbed (Scheme 2). Immersion time in the individual solutions was 5 min. For the reference systems prepared on glass plates, a similar method was used for deposition.

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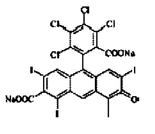
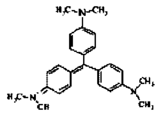
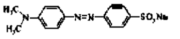
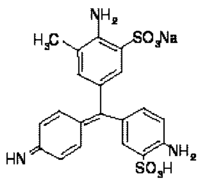
Table 1. Some of the Main Solute Properties

Component (MW, g/mol)	Structure	Charge	Molar volume (cm^3/mol)
Rose Bengale [RB] (1017)		-2	273
Crystal Violet [CV] (408)		+	231
Methyl Orange [MO] (327)		-	160
Acid Fuchsine [AF] (585)		-2	246

2.4. Measurements. *2.4.1. Attenuated Total Reflectance Infrared (ATR-IR) and UV−Vis Spectroscopy.* ATR-IR spectra were acquired using a Bruker IFS66V/S spectrophotometer. A UV−vis spectrum was recorded on a Perkin-Elmer Lambda 12 double-beam spectrophotometer.

2.4.2. X-ray Photoelectron Spectroscopy (XPS). The surface chemical composition of the PAN-H was determined with a VGESCALABMKII spectrometer with a Mg X-ray source. An energy of 20 eV was used to obtain the high resolution, and the takeoff angle of the X-ray source was 90°. The main chamber of the XPS instrument was maintained at 2.0×10^{-7} Pa during the spectral measurements. The relative photoelectron intensities of the C_{1s} and O_{1s} peaks were used to determine the composition of the upper layer of the PAN-H support.

2.4.3. Stability of Multilayered PEC Films in Solvents. The multilayered films prepared on the glass plates were immersed in isopropanol (IPA), dimethylformamide (DMF), or tetrahydrofuran (THF) for about 6 h and rinsed with water after removal. UV−vis measurement was carried out to assess the film stability in the solvents.

2.4.4. Scanning Electron Microscope (SEM). SEM (Philips XL FEG30) was carried out to study the cross section and surface structure of the membranes. The cross section was obtained after breaking the membranes in liquid nitrogen. The SEM samples were first gold-coated before use.

2.4.5. Atomic Force Microscope (AFM). AFM experiments were performed by using a Multimode AFM with a Nanoscope IV controller (Veeco/Digital Instruments, Santa Barbara, CA). Samples were imaged in air in tapping mode with a drive frequency of 200−300 kHz. Silicon nitride oxide-sharpened tips (NCHR, Nanosensors, Germany) were used. The average roughness R_a and the root-mean-square value (R_{MS}) were calculated by eq 1.

$$R_a = \frac{1}{N}\sum_{i=l}^{N} |Z_i - Z| \quad \text{and} \quad R_{ms} = \sqrt{\frac{1}{N}\sum_{i=l}^{N} |Z_i - Z|^2} \qquad (1)$$

The multilayered films for thickness measurement were prepared under the same conditions but on a silicon wafer. The film thickness was determined by measuring the depth of a scratch after indentation of the film with a sharp knife. The imaging was performed after adjusting the tip to the scratch edge.

2.4.6. Filtration Test. Filtrations were done in a stainless steel dead-end pressure cell with 15.2 cm^2 membrane area. The feed solution was poured in the cell, and the cell was pressurized with nitrogen to 20×10^5 Pa (20 bar). During filtration, the feed solution was stirred at 11.66 Hz (700 rpm) to avoid concentration polarization. Permeate samples were collected in cooled flasks as a function of time, weighed, and analyzed. The retention values were calculated with the permeate concentration and the concentration of the original feed solution according to formula 2:

$$R(\%) = (1 - C_p/C_f) \times 100 \qquad (2)$$

The permeation was stopped when the retention reached a constant value. All the measurements were based on at least three samples, and the average values were used. The standard deviation on the measurements is about 5%. The characteristics of the solutes used in this paper are listed in Table 1. All were used in a 35 μM concentration.

3. Results and Discussion

3.1. Multilayered PEC Membranes on a Glass Plate. Multilayered PEC membranes were first prepared on a glass plate to study the interaction between SPEEK and PDDA. With use of the LBL method, 1, 3, 5, 10, 15, and 20 bilayers of PDDA/SPEEK were prepared. The UV absorbance of the membranes at 321 nm for SPEEK increases with increasing bilayer number, which is strong evidence for the layer-by-layer growth (Supporting Information Figure 1). The absorbance at 321 nm and the number of bilayers show a linear relationship. The slope of the line, or the absorbance of one bilayer, is about 0.007. The result proves that PDDA and SPEEK can interact efficiently to form multilayered PEC films.

To test the stability of the multilayers in different solvents, the films were immersed in IPA, THF, or DMF for 6 h. None of the solvents induced a change in the UV−vis spectrum of the films, proving the excellent stability of the multilayered PEC in these solvents (Supporting Information Figure 2). The result shows that the PDDA/SPEEK bilayers are stable in the different solvents and that multilayered PEC membranes can potentially be applied in SRNF applications, even in solvents like THF and DMF, which are really challenging for most polymeric SRNF membranes.

3.2. Multilayered PEC Membranes on a PAN-H Support. *3.2.1. Preparation.* Hydrolysis of PAN under basic conditions is a powerful method for preparation of excellent membranes or membrane supports.[29,30] Many reports exist on the PAN hydrolysis mechanism. Under alkaline circumstances, part of the −CN groups is converted into COO^-.[31] In the reported system, the membranes were first immersed in NaOH for hydrolysis, and then immersed in HCl to convert the formed COONa groups to COOH. The XPS results in Figure 1 confirm the existence of COO^- groups on the surface of the PAN-H membranes. Figure 1a gives the peaks of C_{1s} for C−C and COO^- groups at 285 and 287 eV,

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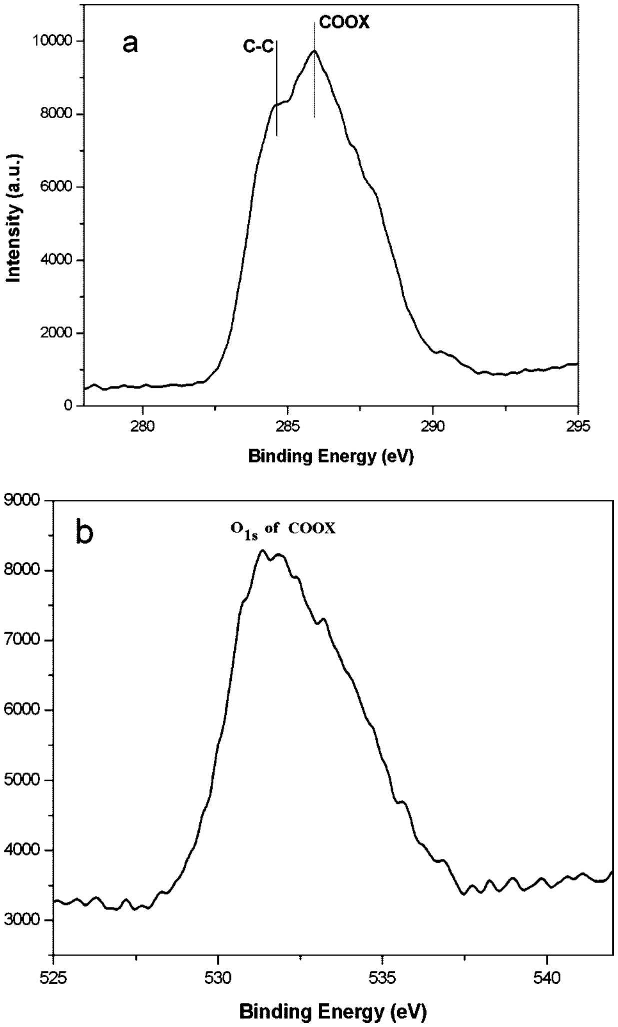

Figure 1. XPS of PAN-H membrane: (a) C_{1s} signal and (b) O_{1s} signal.

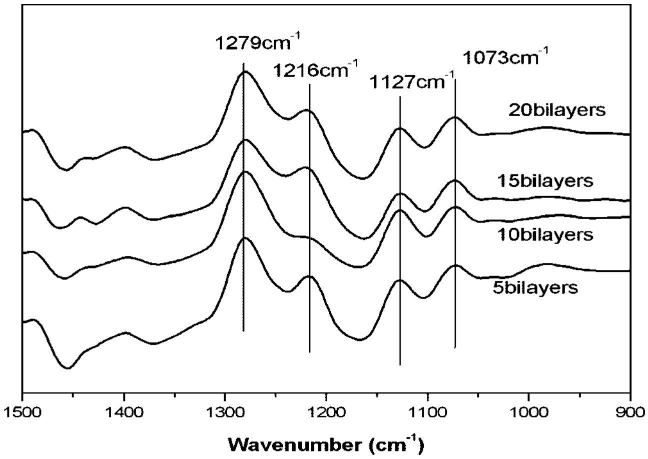

Figure 2. FTIR-ATR of multilayered membranes as a function of the number of bilayers.

respectively. Figure 1b shows the peaks of O_{1s} corresponding to the COOH groups since there is no oxygen present in PAN before hydrolysis.

Different numbers of PDDA/SPEEK bilayers were introduced on the PAN-H support. ATR-IR spectra (Figure 2) were used to confirm the LBL deposition of PDDA/SPEEK on the PAN-H support. The stretching peaks at 1073 and 1216 cm^{-1} are attributed to the SO_3H groups in SPEEK. The stretching at 1127 cm^{-1} is attributed to the $-O-$ in the SPEEK backbone, confirming the incorporation of both PEs into the multilayered structure.[32]

3.2.2. SEM. The cross section and surface structure of the PAN-H support and the multilayered PEC membrane with the thickest coating were obtained with SEM (Figure 3). The support shows a very open pore structure and finger-like pores. After introduction of PDDA/SPEEK bilayers on the support, a very thin dense layer is formed on top of the porous skin layer, which evidences the successful deposition of the PDDA/SPEEK bilayers on the PAN-H support. The distinction between the top layer and the support is rather blurry, indicating good contact between both, but also preventing the accurate measurement of the top layer thickness. Figure 4 shows the surface structure of PAN-H and multilayered PEC membranes. The PAN-H support shows a smooth surface, while the membranes with multilayered PEC show much rougher surface structures. This increased surface roughness with increasing number of bilayers is common for multilayered PECs.[33]

3.2.3. AFM. Tapping mode AFM experiments were performed on the different multilayered PEC membranes. The thickness of the multilayered membranes was measured by AFM after scratching the samples with a metal knife.[34] For this purpose, samples were deposited on negatively charged silicon wafers instead of polymer supports, following exactly the same dipping procedure. Figure 5 shows the typical picture of a scratched film, from which the thickness can be calculated. According to this method, the membranes with 5, 10, 15, and 20 bilayers of PDDA/SPEEK have a thickness of 13 ± 1, 20 ± 1, 25 ± 1, and 34 ± 2 nm, respectively. The thickness of LBL membranes is affected by many factors including the conformation of the adsorbed PE, the density of the electrostatic charge, the rigidity or flexibility properties of PE, etc. Therefore, the thickness strongly depends on the preparation condition such as pH and salt concentration of the PE solutions. The film thickness of (poly(allylamine hydrochloride) + Neutral Red/poly(acrylic acid))$_{25}$, for instance, changed from about 15 to 60 nm as the pH of the PE solution was varied from 2 to 9.5.[35] The thickness of 10 bilayers of PDDA/poly(styrenesulfonate) changed from15 to 300 nm, upon changing the NaCl concentration from 0 to 1 M.[36] Compared with PDDA/PSS multilayered films, the PDDA/SPEEK mutilayered films show a similar thickness when prepared under similar conditions.

Figure 6 gives the height images of the multilayered PEC membranes deposited on PAN-H support for a 1 × 1 μm scale. Some kind of connected spherical nanoparticles can be observed on the surface of the membrane containing 5 PDDA/SPEEK bilayers. With increasing number of bilayers,

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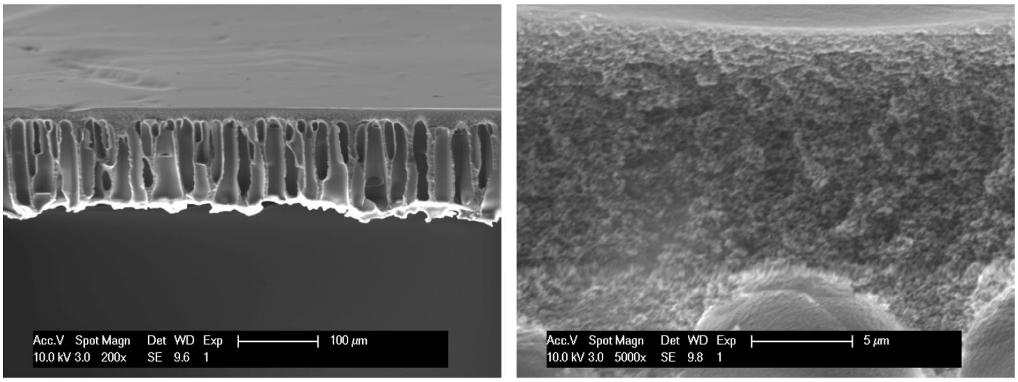
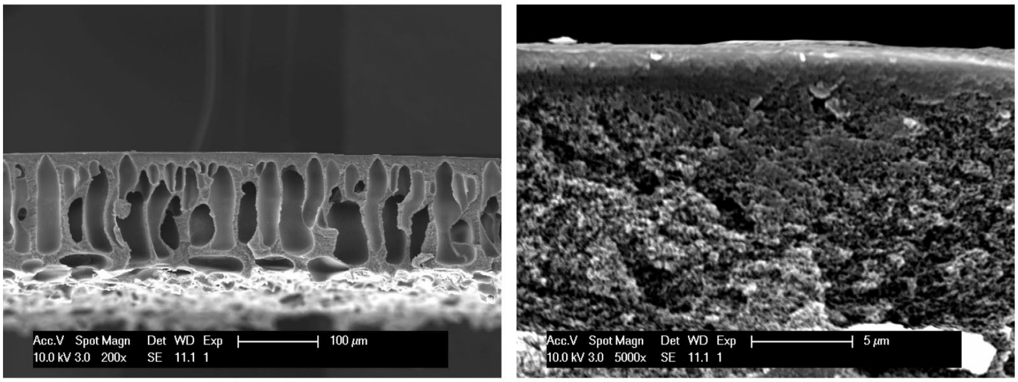


PAN-H



20 bilayers

Figure 3. SEM cross section of (a) the PAN-H support and (b) a multilayered PEC membrane composed of 20 bilayers at different magnifications.

the size of the particles increases. Table 2 gives the calculated surface roughness of the membranes. The average roughness of the membranes (R_a), measured on 1×1 μm scans, increases from 2.5 to 7.6 nm, respectively, as the bilayer number increases from 5 to 20. The maximum depth obtained from AFM analysis of the membranes with 5−20 bilayers is 9, 18, 23, and 27 nm, respectively, which shows the increased thickness of the aggregates with layer growth.

3.2.4. Filtration Performance of the Membranes. Table 3 illustrates the filtration performance of membranes with different numbers of PDDA/SPEEK bilayers. Three different dyes with negative (Bengal Rose B (RB), Acid Fuchsine (AF), and Methyl Orange (MO)) and positive charge (Crystal Violet (CV), all dissolved in IPA, were selected for the filtration test to study the solute charge influence on the membrane separation properties in IPA. After introduction of multilayered PDDA/SPEEK, the retention of the negatively bicharged RB and AF increases significantly respectively from 50 and 72 to more than 90%, with the maximum retention reached already after 5 to 10 bilayer depositions. For the positively charged CV, the retention is much lower as the last deposited layer on the membrane has a negative charge and thus does not repel the dye. To confirm that both charge and molecular size influence the membrane selectivity (CV (231 cm^3/mol) has a much smaller molar volume than RB (273 cm^3/mol)), another dye with negative charge (MO) but much smaller than that of RB (160 cm^3/mol) was selected. The retention of MO also increases drastically after the introduction of PDDA/SPEEK layers on the support, but never really reaches such high values as those for RB and AF. Probably, the bilayer charge density is too low to prevent the smaller MO molecule to permeate. Although MO has a smaller molar volume than CV, the retention of the negatively charged MO is much higher than that of the positively charged CV, clearly proving the important role of the charge of the ultimately deposited PEC. The negatively charged surface of the composite membranes, due to the SPEEK on the surface, creates Donnan exclusion or repulsive forces between the sulfonic acid groups and the negative solute charges leading to the high retentions of the negatively charged dyes.[37]

Solvent permeation seems to be drastically affected by the kind of solute present in the feed. All the membranes show the highest permeability with CV-containing feeds and lowest with RB- and AF-based feeds. Transport of solutes through membranes is a complicated process, including different factors like molecular size of the solute, molar volume of the solvent, charges, solute mobility, etc.[38,39] RB and AF are bicharged molecules, which possibly densify the polycation layers in the membranes by cross-linking PDDA. The membranes show much lower permeability on AF as well compared to the single-charged MO. Another tentative explanation might also be the uptake of the smaller solutes CV and MO within the active layer (very low retention), leading to weaker attractive interactions in the PEC and hence more swelling, and thus higher fluxes.

Table 4 shows the filtration data of the membranes with RB as solute in different organic solvents. All the multilay-

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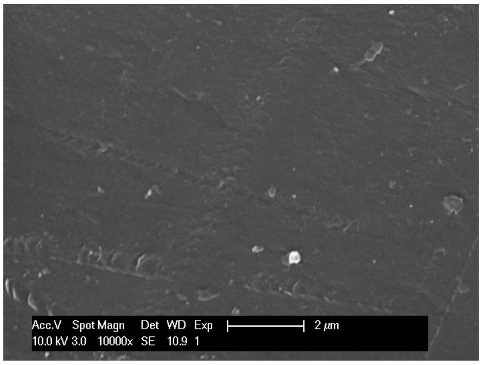
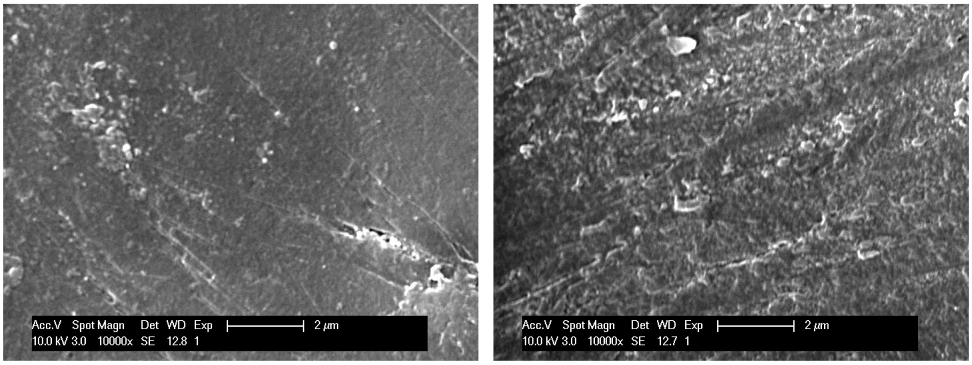
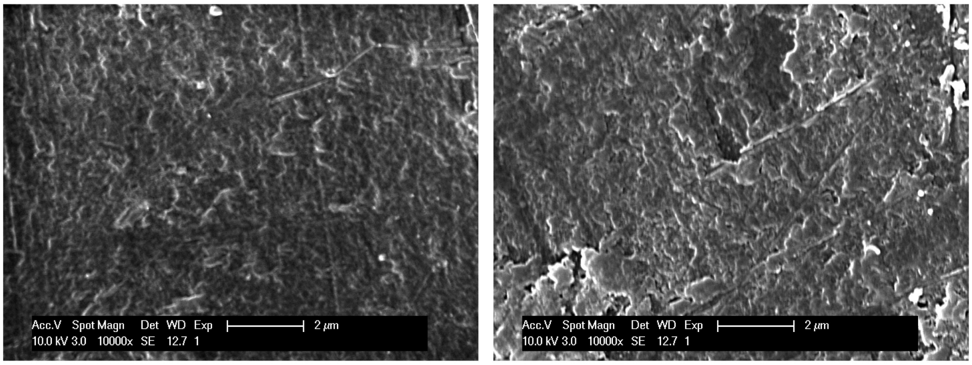


PAN-H



5 bilayers 10 bilayers



15 bilayers 20 bilayers

Figure 4. Surface of multilayered PEC membranes on a PAN-H support as observed by SEM.

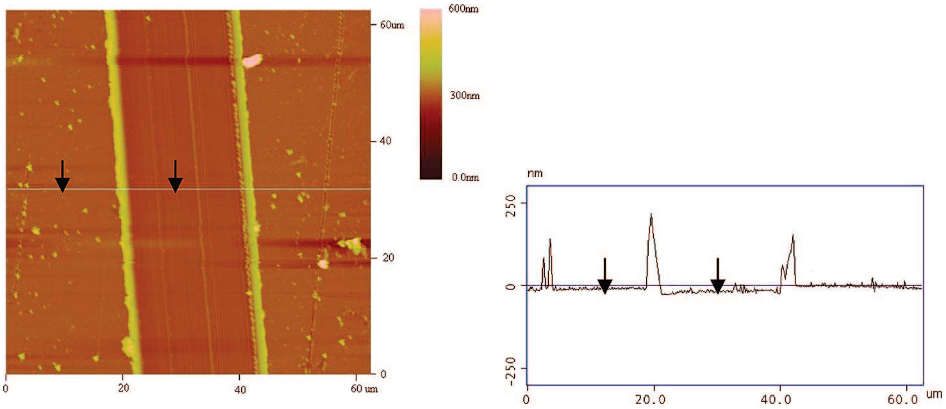


Figure 5. AFM obtained height image of a scratched PEC membrane (15 bilayers) coated on a silicon wafer.

ered PEC membranes show good or excellent retentions for RB in THF, DMF, and IPA. The solvent fluxes differ greatly for the different systems. All the membranes show the highest flux for THF, and the lowest for DMF, which may be due to the different physical properties of solvents or the interaction between the membrane and solvent. As quantified by Bhanushali et al. with the MV/η parameter, the most important physical properties of the solvents are viscosity

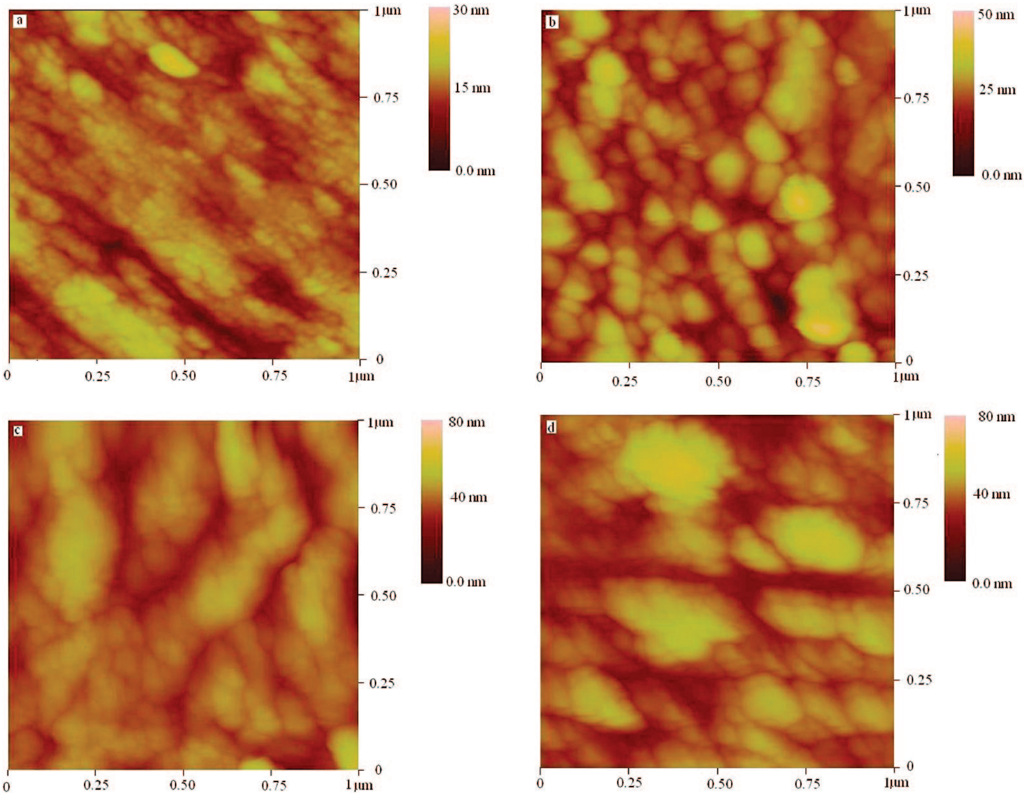


Figure 6. Topography images of multilayered membranes recorded by AFM (a = 5 bilayers, b = 10 bilayers, c = 15 bilayers, d = 20 bilayers).

Table 2. Calculated Surface Roughness of Multilayered Membranes as Obtained by AFM

	5 bilayers	10 bilayers	15 bilayers	20 bilayers
R_{ms} (nm)	2.54	4.45	5.37	7.59
R_a (nm)	1.95	3.49	4.25	6.01

Table 3. SRNF Properties of Multilayered PEC Membranes for Differently Charged Solutes from IPA Solutions

	permeability (L/m^2·bar·h)					retention (%)				
bilayer number	0	5	10	15	20	0	5	10	15	20
RB	6.81	2.92	0.40	0.33	0.50	72	91	99	99	99
AF	11.8	1.98	0.27	0.21	0.40	49	98	99	99	99
CV	47.6	12.9	7.99	4.76	5.46	11	17	17	34	24
MO	46.7	12.5	6.90	3.60	4.50	42	50	58	71	68

Table 4. SRNF Properties of Multilayered PEC Membranes for RB from Different Organic Solvents

	permeability (L/(m^2·bar·h))					retention (%)				
solvent	0	5	10	15	20	0	5	10	15	20
IPA	6.81	2.92	0.40	0.33	0.50	72	91	99	99	99
THF	218	28.0	8.82	4.77	7.89	87	97	98	97	97
DMF	0.07	0.06	0.05	0.06	0.05	78	82	92	85	92
MPF-50 (IPA)				0.72					98	

Table 5. SRNF Properties of Multilayered PEC Membranes with Different Surface Charges for RB from IPA Solutions

	permeability (L/(m^2·bar·h))				retention (%)			
bilayer number	4.5	9.5	14.5	19.5	4.5	9.5	14.5	19.5
RB	1.13	0.32	2.09	0.59	93	93	93	96
MO	8.40	8.30	5.80	2.80	16	21	36	19

(η) and molar volume (MV).[39] THF has a much higher MV/η than IPA (X compared to Y) due to its very low viscosity, which explains well the higher THF flux. For the strongly polar DMF with a MV/η value of Z, however, the explanation is less straightforward. Strong interactions between DMF and membrane can be assumed since, during the filtration of RB/DMF, the flux of the solutes decreases drastically over the first hour of permeation. In addition, all membrane surfaces were noticed to have roughened significantly after DMF filtration, an effect that had never been observed with other systems. The true explanation on a molecular level for the DMF behavior surely requires further investigation.

In IPA, the membrane performance is comparable to that of the commercial MPF-50 membrane.[40,41] Having no DMF or THF resistant membranes commercially available yet, the comparison in these solvents can not be established.

Table 5 shows the filtration results of membranes in IPA with different charges of the finally deposited PE. Membranes with a PDDA top layer thus show a positively charged surface. These membranes (obtained after 4.5, 9.5, 14.5, and 19.5 bilayers) still show the highest retention for RB due to pure steric reasons. For the smaller MO, the membranes with a negatively charged surface show much higher retentions than these positively charged ones. For example, the membranes with 4.5 bilayers of PDDA/SPEEK show a 16% retention of MO, while the membrane with 5 bilayers shows a 50% retention of negatively charged MO, due to the Donnan exclusion.

To confirm the stability of the multilayered PEC membranes in the aprotic solvents, a filtration experiment over an extended period (about 30 h) was carried out on the PAN-H with 15 PDDA/SPEEK bilayers in the RB/DMF

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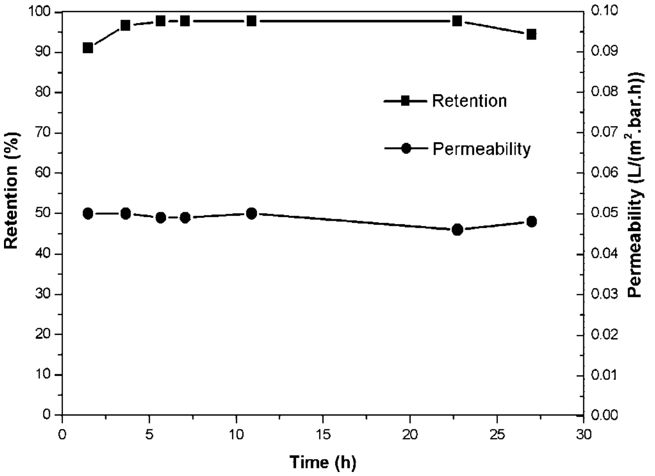

Figure 7. Extended filtration performance of mutilayered PEC membranes with 15 bilayers of PDDA/SPEEK in DMF dissolved RB.

system. The results in Figure 7 show both a stable permeability and retention (around 95%) of the membranes as a function of time, which indicates the excellent stability of multilayered PEC membranes in the solvents.

4. Conclusions

Multilayered PEC membranes were successfully prepared from PDDA and SPEEK PEs by the LBL method. They proved to be very useful for filtrations in organic solvents, including aprotic solvents like THF and DMF, for which they showed excellent solvent stability. SEM and AFM results showed rougher structures as the number of deposited layers increased. The surface charge had a great influence on the retention of charged solutes. Due to Donnan exclusion, the membrane showed the highest selectivity for solutes with the same charge as the last deposited layer on the surface of the multilayered PEC membranes. Solute size also played a role but to a lesser extent. The study shows that alternative PE deposition is a convenient method for preparing excellent SRNF membranes.

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Supporting Information Available: UV−vis spectra of multilayered PEC membranes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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