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Low-biofouling membranes prepared by liquid-induced phase separation of the PVDF/polystyrene-*b*-poly (ethylene glycol) methacrylate blend

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ABSTRACT

In the present work, the focus is laid on the formation, and low-biofouling properties of polyvinylidene fluoride (PVDF) membranes modified using an amphiphilic copolymer additive: polystyrene-*b*-poly (ethylene glycol) methacrylate (PS-*b*-PEGMA). PVDF was blended with PS-*b*-PEGMA and membranes were prepared by liquid-induced phase separation. The additive played a significant role on membrane formation, slightly decreasing surface porosity, reducing the shrinkage during phase separation, and increasing both the size and porosity of macrovoids. Owing to its numerous hydrophilic moieties, the copolymer was believed to promote solvent and nonsolvent exchanges during phase inversion. In addition, it significantly enhanced surface hydrophilicity and matrix hydration capability. Indeed, water was easily trapped by the PEGylated chains spread onto the surface and within the matrix, and then stored in the larger macrovoids. It led to an important reduction of protein adsorption, including bovine serum albumin (65%) and lysozyme (89%). Bacterial attachment tests revealed that adhesion of *Escherichia coli* and *Staphylococcus epidermidis* was almost totally prevented (over 99% reduction of attachment), which demonstrates the excellent efficiency of PS-*b*-PEGMA copolymer to provide PVDF membranes with low-biofouling properties.

1. Introduction

Formation and application of low-biofouling membranes have been widely investigated over the past 10 years [1–6]. Still, it remains challenging to find both an appropriate formulation and a preparation method that would be cost-effective, quick to carry out, and efficient regarding the desired properties. Existing methods can be classified into three categories. The first one gathers methods aiming at modifying the surface top-layer using a surface chemical reaction [7–9], induced for instance by plasma, UV, or ozone treatment. These methods are efficient, since they permit to achieve very low-biofouling properties. However, their scale-up is difficult to control and expensive. The second type of methods concerns the modification by coating [10,11]. Coating is readily preformed and only requires immersing the membrane in a

solution containing the copolymer additive. Physical interactions occur, but they are less strong than covalent bonds, which may lead to stability issues. Supplementary disadvantages of coating methods concern the scale-up of membranes too. In addition, to ensure a high coating density, an important amount of additive must be used. So, the process becomes expensive at larger scale. Furthermore, modification of the physical structure, especially the surface porosity, may be responsible for permeability decline. Finally, the third type of method involves the blending method associated to a phase separation process [12–14]. These methods are convenient and readily carried out. Also, the scaling of membranes is facile, since only one unit operation is involved. Nonetheless, issues concern (i) potential modification of porous structure and, most of all, (ii) lack of stability: the additive may leach out of the matrix since it is often very hydrophilic and solubilized in the aqueous nonsolvent used during membrane formation, or in the feed during membrane filtration. But despite these disadvantages explaining why few results are reported using the blending method, compared to other techniques, it is believed to be a very promising path.

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When a phase separation process is chosen in the design of antifouling membranes, the additive may affect their final structure, phenomenon that cannot be neglected. In this respect, works need to be carried out to fully understand the impact of polymer additives on membrane formation. Several investigations were performed in the past with common additives such as PVP or PEG systems, which led to important results [14–16]. Indeed, they were often shown to act as pore formers, therefore increasing membrane permeability. Consequently, additives have both a chemical influence and a physical effect on membranes' properties. However, it is hard to predict the real impact of a polymer additive, since it may also depend on its concentration in the casting solution. Therefore, a systematic study should be carried out each time a new formulation is tested.

As aforementioned, PEG-like systems are commonly employed to prepare low-biofouling membranes. But if used in blend with a polymer, part of the additive is washed out of the matrix during membrane formation by wet-immersion process (or liquid-induced phase separation – LIPS). Indeed, the non-solvent is almost always water, which solubilizes many PEG systems. From this consideration, if one wants to keep investigating this direction, there are two possible choices: either using another phase separation process, vapor-induced phase separation for instance, or employing an additive copolymer water insoluble. Changing the preparation process leads to membranes with different morphologies and this is not always suitable as far as the final application is concerned. Therefore, the focus is now laid on the development of appropriate amphiphilic additives possessing anchoring groups totally insoluble in water, able to interact with common hydrophobic membrane polymers and containing hydrophilic moieties [18–21].

Among the popular hydrophobic polymers used in membrane technology, polyvinylidene fluoride (PVDF) exhibits good chemical, thermal and mechanical properties. But its use as a membrane material is limited by its hydrophobic nature. Indeed, water does not wet spontaneously PVDF membrane. Consequently, this material shows adsorption tendency, which has a highly negative influence on the flux through the creation of a supplementary resistance to mass transfers. Therefore, hydrophilic polymers are sometimes more interesting for the design of porous membranes. Yet, PVDF offers very good bulk properties, which makes it an ideal polymer material for application of membranes in water treatment. So, efforts need to be made to successfully modify PVDF membranes with a suitable additive and results of major investigations using various additives among which amphiphilic copolymers have been summarized in Liu et al.'s review paper [22]. Despite all of these extensive works and studies performed till then, there is still a need for the preparation of stable anti-biofouling PVDF matrices, considering their potential wide range of applications – from water treatment to blood filtration – in which biofoulants of various natures (proteins, cells or bacteria) can be found. Recently, Li et al. reported the preparation of anti-fouling PVDF membranes, by grafting sulfobetaine-based zwitterionic polymers [23]. Their process – a two-step polymerization process – led to very good results concerning antifouling properties, but it is a time-consuming process which appears to be complicated to scale up. A promising set of results was also published very recently by Pezeshk et al. They prepared PVDF ultrafiltration flat-sheet membranes by blending the polymer with hydrophilic polyurethane additive that they named L2MM [24]. Results highlighted that L2MM additive acted both as a pore former and a surface modifier, eventually leading to an increase of water permeability. The wetting of PVDF membranes was dramatically improved and it is accepted that increasing hydration capability of membranes usually leads to a decreasing of fouling tendency. Then, Pezeshk and coworkers presented a second work on the potential fouling resistance of these modified PVDF ultrafiltration membranes in water treatment applications [25]. Fouling was assessed by filtration/fouling tests, and results suggested that modified L2MM helped improving the

fluxes, but (i) a decreasing of fouling was only reported in some cases and (ii) a significant cake formation of NOM was observed for all membranes. This study is very promising since the method is easy to carry out, and the additive is water-insoluble: no removal occurs during phase inversion. However it still remains challenging to try to further decrease the fouling tendency of PVDF membranes. Especially, water contains lots of proteins and bacteria that can easily interact with membrane material. There is clearly a lack of investigation on the development of low-biofouling PVDF membranes intended to resist bacteria adhesion. In addition, the type of bacteria, whether gram-positive or gram-negative, can also affect the fouling tendency. Consequently, extensive research is still needed to obtain a membrane combining the very good bulk properties of PVDF and a reduced fouling/biofouling tendency, whatever the nature of the proteins/bacteria.

In our group, we have synthesized polystyrene-*b*-poly (ethylene glycol) methacrylate copolymer block [26]. This molecule is made of a strong anchorage group – polystyrene (PS) – that may easily interact with hydrophobic membrane materials such as PVDF, and a hydrophilic segment – poly (ethylene glycol) methacrylate (PEGMA) – able to bind water molecules and therefore increase the wettability and membrane resistance to fouling. What is more, the PS to PEGMA ratio can be controlled, that is, the hydrophilic-lipophilic balance can be tuned. This additive is soluble in solvent for PVDF such as *N*-methylpyrrolidone (NMP) and water-insoluble. Also, preliminary experiments showed that homogeneous solution was obtained when blending this amphiphilic copolymer with PVDF in NMP. Therefore, it might be an appropriate copolymer to form low-biofouling membrane by LIPS process. The scope of this manuscript is to present our first results concerning the elaboration of low-biofouling membrane with this type of additive. After fully characterizing the membranes using physical and chemical tools, and carefully investigating its role on PVDF membrane formation during phase separation, a special attention will be given to its effect on membranes' low-biofouling properties. Especially, adsorption of protein will be tested using several proteins, and attachment of bacteria assessed with micro-organisms of different nature.

2. Experimental

2.1. Materials

Polyvinylidene fluoride (PVDF) ($M_w = 150,000 \text{ g mol}^{-1}$) was supplied by Kynar[®]. It was washed with methanol and deionised water before use. PS-*b*-PEGMA copolymer was synthesized in our group. It contains 30 repeat units of hydrophobic anchorage group, polystyrene (PS), and 68 repeat units of hydrophilic segment, poly (ethylene glycol) methacrylate (PEGMA). Its molecular weight and polydispersity index are $35,656 \text{ g mol}^{-1}$ and 1.28, respectively. *N*-methylpyrrolidone (NMP), purchased from Tedia, was used as solvent without further purification. Deionized water used in the experiments was purified using a Millipore water purification system with a minimum resistivity of $18.0 \text{ M}\Omega \text{ cm}$.

2.2. Methods

2.2.1. Preparation of solutions

Solutions were prepared blending PVDF and PS-*b*-PEGMA in NMP solvent at $40 \text{ }^\circ\text{C}$. Total weight of solutions was kept constant to 20 g. Solvent content was always 75 wt%. PVDF concentration varied between 20 wt% and 25 wt% while PS-*b*-PEGMA was in the range 0–5 wt%. Solutions were stirred for at least 24 h, until homogeneous blend was obtained, and then allowed to rest until they stopped bubbling.

2.2.2. Preparation of membranes

Membranes were prepared using the liquid-induced phase separation process (sometimes referred as wet-immersion process or nonsolvent-induced phase separation process) as presented by Fig. 1. Solutions were cast on a glass plate, using an appropriate metal casting knife allowing to control the initial thickness of the film to 300 μm . Afterwards, glass plates were immersed in DI water, to induce phase separation of the system. The newly-formed membranes were kept in water for 24 h, and water was changed once during that period of time, to ensure a total removal of residual solvent. Thereafter, membranes were dried at ambient temperature for at least 24 h before use.

In solution, it is expected that PEGMA segments of copolymer molecules located at the upper interface will be oriented toward the liquid, which provides a more hydrophilic environment. Hydrophobic PS groups should be in contact with air. But once phase separation has been initiated, copolymer molecules are turned up-side down. Indeed, the polymer system becomes more hydrophobic owing to a solvent outflow. In the end, PS groups interact with PVDF while PEGMA segments should be oriented toward the upper interface. Also, additive molecules initially in the bulk solution may migrate toward the interface during phase separation, which would ensure a more stable configuration [24]. However, one should note that this motion is limited because phase separation occurs quickly in LIPS process.

2.2.3. Surface characterization

Chemical composition of membranes was assessed using two methods. In a first time, ATR FT-IR spectrophotometry (Perkin-Elmer Spectrum One) with ZnSe as an internal reflection element was used. Measurements were realized perpendicular to the surface of the membranes. Each spectrum was captured by averaging 16 scans at a resolution of 4 cm^{-1} . In addition, X-ray photoelectron spectroscopy (XPS) was performed using a PHI Quantera SXM/Auger spectrometer with a monochromated Al KR X-ray source (1486.6 eV photons). The energy of emitted electrons was measured with a hemispherical energy analyzer at pass energies ranging from 50 to 150 eV. All the data were collected at photoelectron take off angles of 45° with respect to the sample surface. The binding energy (BE) scale was referenced by setting the peak maximum in the C1s spectrum to 284.6 eV. A high-resolution C1s spectrum was fitted using a Shirley background subtraction and a series of Gaussian peaks. The data analysis software was from Service Physics, Inc.

Porous structure of virgin PVDF membrane and modified PVDF membranes was characterized using microscopy techniques. Scanning electronic microscopy (SEM) analysis was performed using a Hitachi S-3000 instrument. Accelerating voltage varied in the range 7 keV–10 keV, depending on the observation carried out. Prior to observation, membranes were mounted on sample stages, using double-sided adhesive tape, and sputter-coated with gold for 150 s. Furthermore, membranes were examined by atomic force microscopy (AFM). The AFM images were acquired with a JPK Instruments AG multimode NanoWizard (Germany). The instrument is equipped

with a NanoWizard scanner and operated in air. For tapping-mode AFM, a commercial Si cantilever (TESP tip) of ~ 320 kHz resonant frequency from the JPK instrument was used. The relative humidity was less than 40%.

2.2.4. Assessment of wettability and low-biofouling properties

Water contact angles were measured with an angle-meter (Automatic Contact Angle Meter, Model CA-VP, Kyowa Interface Science Co., Ltd. Japan) at 25 °C. The DI water was dropped on the sample surface at 10 different sites and the average of the measured values was taken as the membrane water contact angle. Hydration capabilities (mg/cm^3) of membranes were also determined. Dry weights of 0.85 cm diameter membranes were first recorded using a 10^{-5} g precision balance (Mettler, Toledo Pac Rim AG, Taiwan Branch). Afterwards, membranes were immersed in deionized water for 24 h. Then, water was gently wiped out with tissue, and membranes weighed. Hydration capability was evaluated taking the difference of dry and wet weights per unit volume. The volume considered was calculated after measuring the thickness of the membranes at 10 different positions. For each membrane, five independent measurements were performed and the average of the obtained values was taken as the final value for membrane hydration capability.

The adsorption of bovine-serum-albumin (BSA, $M_w \approx 66,000$ g mol^{-1} ; Sigma®) was performed. Membranes were placed in a 24-well plate and immersed in 1 mL of pure ethanol for 30 min. Subsequently, membranes were soaked in phosphate-buffered saline (PBS) for 2 h at 25 °C. PBS was removed and membranes were incubated with 1 mL of 1 mg mL^{-1} BSA for 2 h at 25 °C. The absorbance at 280 nm was measured using a UV-vis spectrophotometer (PowerWave XS, Biotec). Each test was performed three times on each membrane. A similar method was used for adsorption of lysozyme from chicken egg white ($M_w = 14,300$ g mol^{-1}) provided by Sigma®. After immersing membranes in ethanol (30 min) and in PBS (2 h), they were incubated with 1 mL of 1 mg mL^{-1} lysozyme for 2 h at 25 °C and absorbance was measured at 280 nm. A control test was performed on membrane containing 5 wt% additive to ensure that there was no release of additive that would interfere with the reading of absorbance.

Staphylococcus epidermidis (Gram-positive) and *Escherichia coli* (Gram-negative) were used to investigate bacterial adhesion behavior on the surface of membranes. *S. epidermidis* and *E. coli* were cultured in a medium containing 3.0 mg mL^{-1} beef extract and with 5.0 mg mL^{-1} peptone. Cultures were incubated at 37 °C and shaken at 100 rpm until the stationary phase was reached. For *S. epidermidis*, final concentration was 109 cells/ml after 15 h of incubation whereas for *E. coli*, it reached a concentration of about 106 cells/ml after 12 h. Membranes were washed three times with PBS in a 24-well plate. Afterward, one milliliter of bacteria suspension was added to each well, and incubation at 37 °C lasted for 3 h. Bacterial solution was then removed and membranes were washed with PBS three times at 37 °C. Bacteria adhering to the

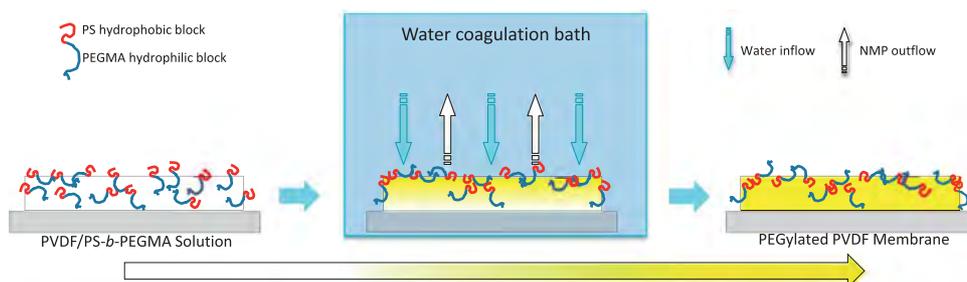


Fig. 1. Schematic of the preparation of PEGylated PVDF membranes from the liquid-induced phase inversion of PVDF/PS-b-PEGMA solution.

sample surfaces were observed by SEM (Hitachi S-3000 instrument) using an accelerating voltage of 7 keV, and after sputter-coating surfaces with gold for 150 s.

3. Results and discussion

3.1. Chemico-physical characterization of membranes – effect of PS-*b*-PEGMA on PVDF membrane formation

Chemical state of virgin and PEGylated membranes were first investigated using FT-IR, and related spectra are displayed on Fig. 2. Spectrum of a PVDF-PS membrane prepared from a blend containing 20 wt% PVDF and 5 wt% polystyrene (PS) is also displayed and referred as P20.00-PS5.00. Characteristic absorption bands of PVDF membranes are provided in literature and will not be reminded herein [27–29]. Our purpose concerned absorption bands attributed to PS-*b*-PEGMA copolymer. Spectra of virgin PVDF membrane (P25.00-PSPEGMA0.00) and of P20.00-PS5.00 do not show major differences. Many characteristic absorption bands due to the benzene rings of polystyrene should be located in the range 1450–3060 cm^{-1} [30] while main absorption bands of PVDF are found in the range 700–1400 cm^{-1} . Herein, the

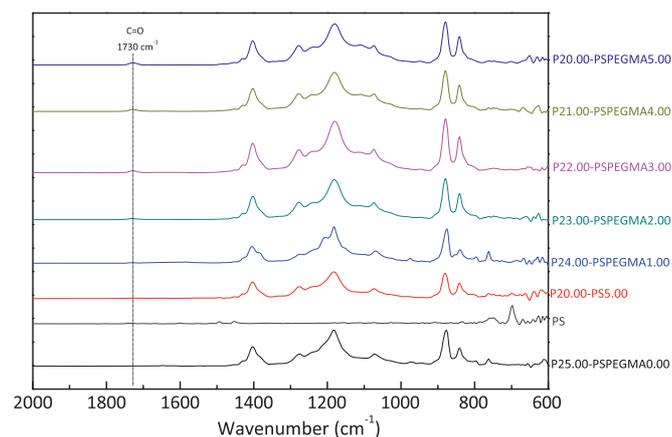


Fig. 2. FT-IR chemical analysis of virgin PVDF membrane, polystyrene, PVDF/PS membrane and PEGylated PVDF membranes.

concentration of additive was low (5 wt%) compared to that of PVDF (20 wt%). In addition, as all PS groups were probably not all found at the surface, but dispersed within the whole matrix, it may explain why stretching bands of PS could not be detected and major difference not found between two spectra. Similarly, absorption bands attributed to PEGMA segments were difficult to identify, especially at very low additive concentration. Nonetheless, it could be seen that when increasing PS-PEGMA concentration, a broad signal appeared at about 1730 cm^{-1} . It was attributed to the stretching of carbonyl function, as mentioned in literature in the preparation of heparinized polypropylene films grafted with PEGMA [31], or in the preparation of poly(phthalazinone ether sulfone ketone) (PPESK) backbones containing poly-(poly(ethylene glycol) methyl ether methacrylate) (P(PEGMA)) side chains [32]. The increasing of this signal intensity with additive content tended to prove the presence of copolymer at the surfaces of membranes.

XPS was subsequently used and related spectra are shown on Fig. 3. As for the virgin membrane, literature is very complete, permitting to identify the peaks of the curve-fitted C1s core-level spectrum [20,23,33–36]. Quickly, the peak at binding energy (BE) of 284.6 eV corresponds to neutral CH species, that at BE of 286.2 eV is associated to CH_2 species while the final large peak at BE of 290.6 eV is due to CF_2 bonds. One should note that the presence of the shoulder at 284.6 eV is not always reported. As for the spectrum of the PEGylated membrane, it also evidenced two main peaks and one shoulder. If the peak at 290.3 eV and that at 284.4 eV are owed to CF_2 and CH bonds, respectively, the large peak observed at 285.9 eV is due to both CH_2 and C–O function contributions. Indeed, Li and coworkers prepared membranes by blending PVDF with PVDF-*g*-PSBMA and PEG, and clearly showed that the peak due to C–O bonds was overlapped by that of CH_2 [23]. Furthermore, as shown by Fig. 4 when adding PS-*b*-PEGMA, the relative oxygen content slightly increases with the additive content, due to C–O functions carried by PS-*b*-PEGMA backbone. On the other hand, fluoride content logically decreased since PS-*b*-PEGMA does not contain fluoride atoms.

Trends obtained from chemical analyses were very slight. Owing to a fast phase separation, polymer additive is rapidly entrapped when matrix solidifies, which prevents possible motion toward the upper interface and the complete change of orientation of additive molecules initially located at the surface. Consequently, probably not all hydrophilic moieties could be found at the surface. However, they

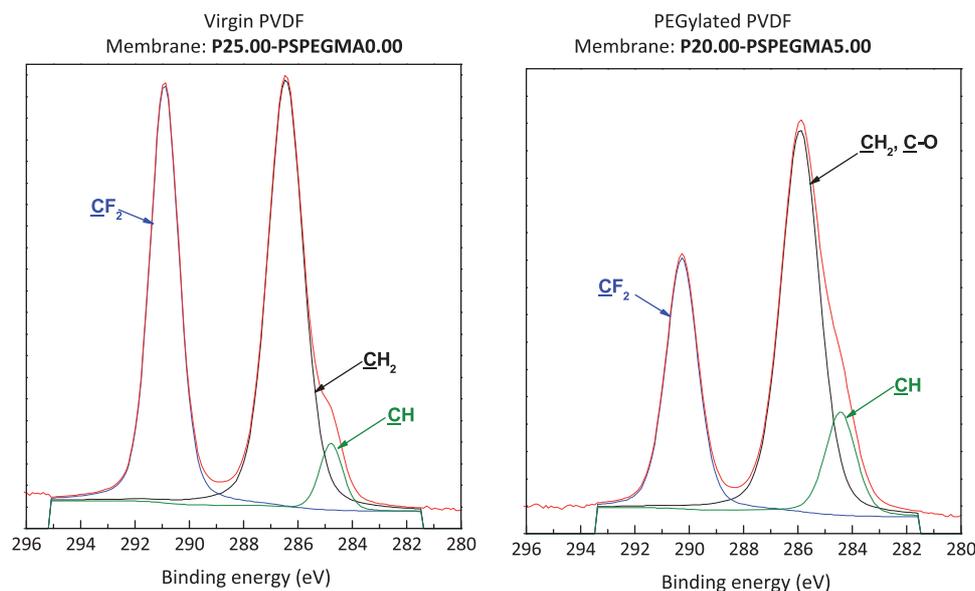


Fig. 3. C1s core-level spectra of virgin PVDF and PEGylated PVDF membranes.

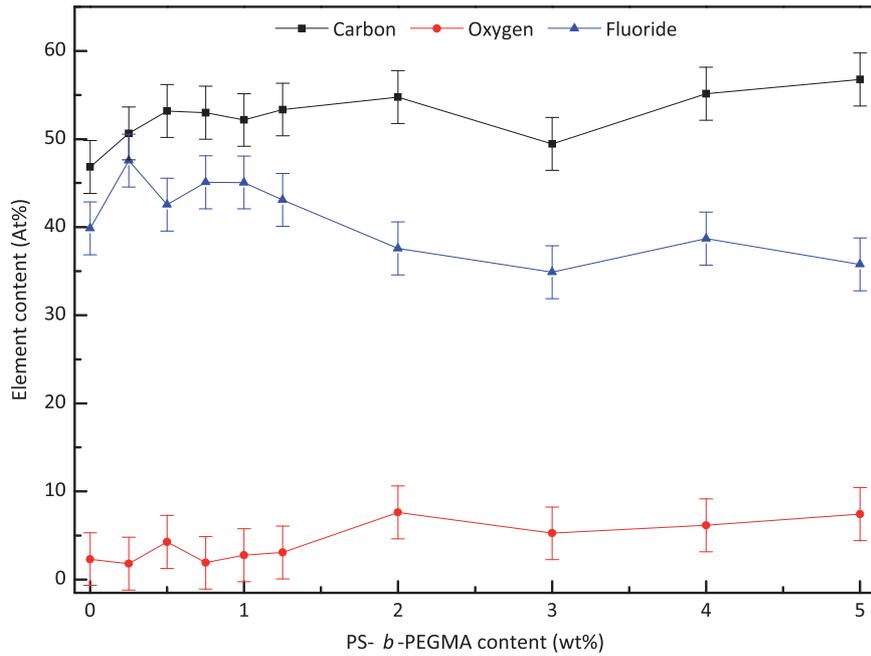


Fig. 4. XPS chemical analysis of virgin PVDF membrane and PEGylated PVDF membranes.

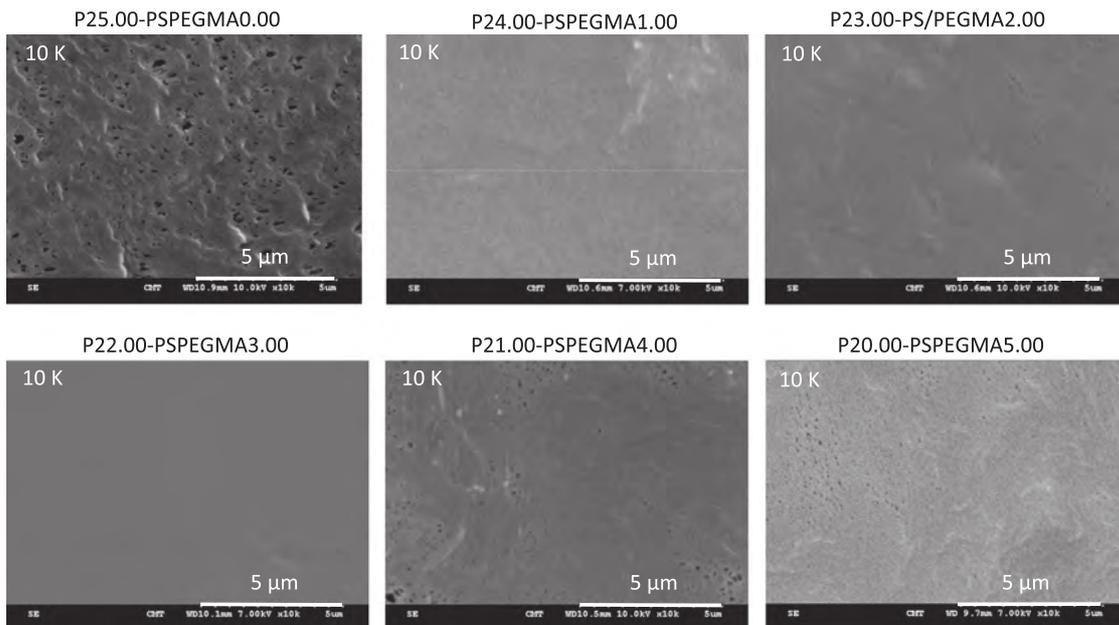


Fig. 5. SEM characterization of the surfaces of virgin PVDF membrane and PEGylated PVDF membranes.

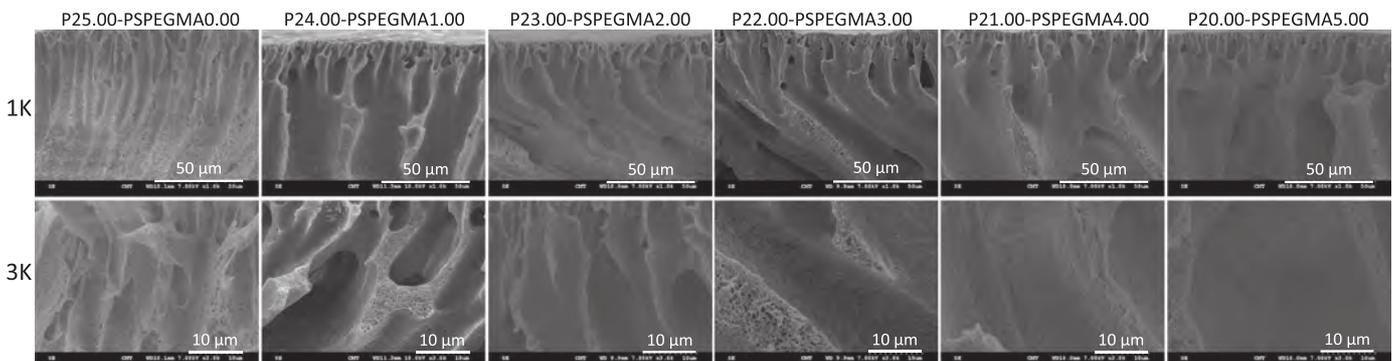


Fig. 6. SEM characterization of the cross-sections of virgin PVDF membrane and PEGylated PVDF membranes.

at least remained in the membrane matrix, since PS-*b*-PEGMA copolymer is totally water insoluble.

Structures were then investigated by performing SEM observations. Images obtained related to surfaces and cross-sections are presented by Figs. 5 and 6, respectively. First, images highlight typical structures obtained by LIPS process, that is, finger-like structures with a porous skin top-layer. Such morphologies arise from fast phase separation rate. Indeed, systems exhibiting instantaneous demixing usually show macrovoids whereas when phase separation is delayed, these formations are usually absent. Second, results evidenced that PS-*b*-PEGMA affected membrane formation mechanisms. Concerning the surfaces, they tended to be denser when adding copolymer. According to fundamentals related to the formation of phase inversion membranes, a decreasing of surface porosity occurs when polymer concentration in the upper layer is increased. In the present case, amphiphilic copolymer additive was added in the casting solution. For thermodynamic considerations, migration of this additive toward the surface could be expected, to ensure equilibrium of the system. Therefore, a polymer concentration gradient may have been created in the system. If this assumption is verified, then the total polymer concentration (PVDF+PS-*b*-PEGMA) should be higher at the surface than in the deeper layers, arising in a denser surface, compared to the virgin membrane for which there is no copolymer, and therefore not a similar concentration gradient. The fact that the trend was not clear could be explained by the fast phase inversion rates involved in LIPS process inhibiting optimal motion of the copolymer. Moreover, expansion of polymer-lean phase in the bulk when adding copolymer was evidenced by cross-section images. Indeed, PEGylated membranes exhibited larger finger-like structures. In addition, Fig. 7, reporting the evolution of membrane's thickness as a function of additive content, evidenced that shrinkage during membrane formation tended to be prevented for PEGylated membranes. Undoubtedly, the additive has an important impact on membrane formation: from SEM pictures of Fig. 6, it can be seen that to the width of the largest macrovoids is increased from about 10 μm for virgin PVDF membrane to about 45 μm for PEGylated PVDF membrane containing 5 wt% additive. Assuming a same trend in the three dimensions of the space, the polymer-lean phase leading to the final membrane porosity had been greatly expanded, which was also supported by the thickness evolution.

When phase separation is instantaneous, Mulder reminds that first droplets of polymer-lean phase are formed underneath the surface [37]. Their growth depends on concomitant solvent flow, coming from the polymer-rich phase right underneath the nuclei, and non-solvent diffusion from the top-layer. Growth of macrovoids stops when the polymer concentration at the interface between the polymer-lean phase and the polymer solution below is so high that solvent/nonsolvent contribution to the expansion of the macrovoids cannot balance forces responsible for polymer solidification. Adding PS-*b*-PEGMA in the casting solution clearly contributed to expand the polymer-lean phase domains, which meant that growth of nuclei was favored. It was possible either because copolymer contributed to better solvent/nonsolvent exchanges or because no new nuclei were formed, below the first set of growing nuclei from the upper interface, that could have inhibited macrovoids growth. The effect of polymer-additive on membrane formation has been reported many times, but is not clearly elucidated. The fast phase separation involved makes on-line experimental analyses complicated and challenging and there seems to be no general rule. Indeed, Guillen and coworkers recently presented a review on membranes formed by nonsolvent induced phase separation (termed LIPS in the present paper) [38]. They reported that PEG additives mostly acted as a pore-forming agent but it also depended on the additive molecular weight since small molecular weight PEG additives tended to work as

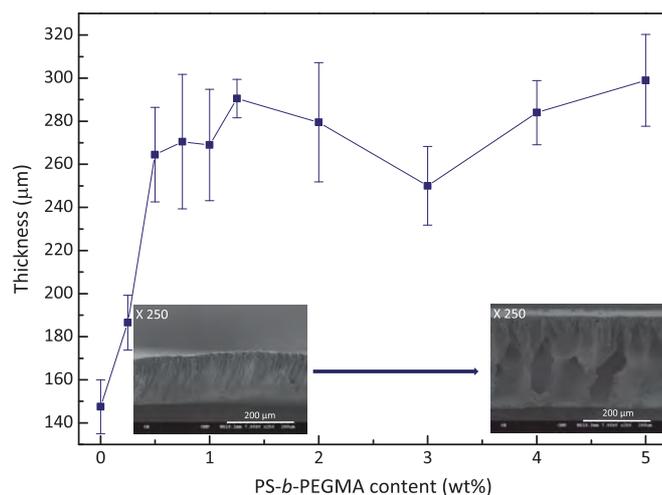


Fig. 7. Influence of PS-*b*-PEGMA content on PVDF membrane thickness.

pore-reducing agent. Still, mechanisms could be proposed by considering PS-*b*-PEGMA nature. It is an amphiphilic copolymer, soluble in NMP solvent, and insoluble in water. PEGMA blocks did entrap water molecules (this is the main goal of this work) while solubility in NMP was due to both blocks (PS and PEGMA). Therefore, it was reasonable to assume that inflows of solvent and nonsolvent in the nucleus were enhanced, compared to those occurring in a totally hydrophobic matrix. Especially supplementary hydrogen bonds were formed between additive and water, compared to PVDF and water, owing to the presence of polyethylene glycol groups, leading to improved mass transfers and in the end, to larger macrovoids. There was also an impact on the wall of these macrovoids, as shown by the 3 K magnification of the cross-sections in Fig. 6. If virgin membrane exhibits rough dense walls, those of PEGylated PVDF membranes present many small pores. Thus, PS-*b*-PEGMA favored pore-formation in the system studied.

AFM characterization was performed to obtain further information concerning the potential effect of copolymer additive on the surface structuring. In addition, the roughness (RMS) coefficient can be related to the homogeneity and surface coverage of top-surfaces [39]. Images are displayed on Fig. 8, and RMS coefficients are reminded in Table 1. Relatively smooth surfaces were obtained, owing to the preparation process and to the nature of nonsolvent. Indeed, LIPS using water as a nonsolvent favors the obtaining of dense smooth top-layers. It was worth noting that in each case, the roughness coefficient was in a similar range. The change observed was not important enough to be attributed to a major effect of additive on membrane surface structuring. This also confirmed SEM results that mainly showed an important effect of the additive on the macrovoids morphology while only a slight change of surface porosity was evidenced. Globally, the change of structure may have two consequences on the membranes properties: (i) mechanical properties should be reduced in terms of tensile strength or Young's modulus (ii) permeability should be increased. As for the mechanical properties, they will be assessed in subsequent works prior to applying the membranes in filtration processes. A priori, it was not noticed any reduction of mechanical properties of the modified membranes compared to those of virgin PVDF matrix. None of them was torn apart upon handling.

To conclude, contrary to water soluble PEG-system additives also acting as pore-formers [40], PS-*b*-PEGMA is not washed out of the membrane during phase inversion. Chemical analyses did not evidence important changes when comparing virgin PVDF membrane to PEGylated PVDF membranes, but this additive, water-insoluble, did affect both surface chemistry and morphology of membranes. In this

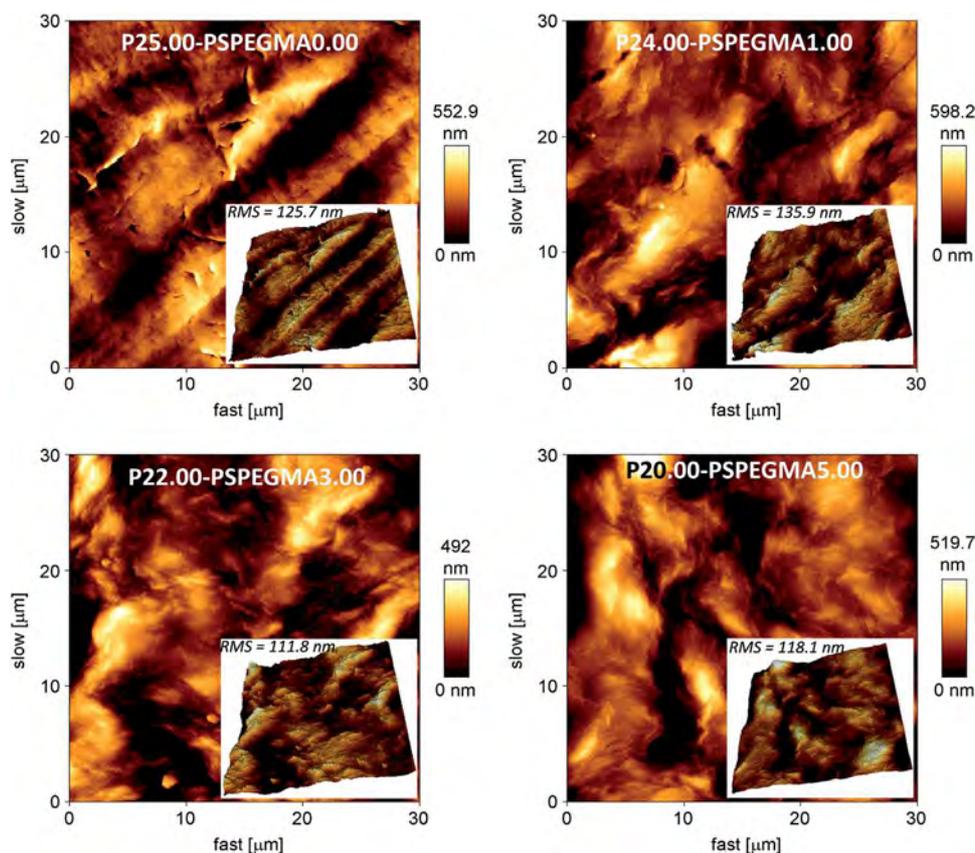


Fig. 8. AFM characterization of virgin PVDF membrane and PEGylated PVDF membranes.

Table 1

Preparation of membranes and their physicochemical characterization.

Membrane ID	PVDF (wt%)	PS (wt%)	PS- <i>b</i> -PEGMA (wt%)	NMP (wt%)	Atom content			Water contact angle (deg)	Hydration capability (mg/cm ³)	Thickness (μm)	RMS coefficient (nm)
					C (%)	O (%)	F (%)				
P25.00-PSPEGMA0.00	25.00	–	–	75	55.37	4.47	40.16	85 ± 1	0	148 ± 12	125.7
P20.00-PS5.00	20.00	5.00	–	75	–	–	–	–	–	180 ± 5	–
P24.75-PSPEGMA0.25	24.75	–	0.25	75	50.63	1.80	47.56	80 ± 1	51.9 ± 6.6	187 ± 13	–
P24.50-PSPEGMA0.50	24.50	–	0.50	75	53.19	4.27	42.55	80 ± 1	56.3 ± 30.5	265 ± 22	–
P24.25-PSPEGMA0.75	24.25	–	0.75	75	53.00	1.91	45.09	80 ± 1	83.1 ± 16.2	271 ± 31	–
P24.00-PSPEGMA1.00	24.00	–	1.00	75	52.16	2.46	45.07	79 ± 1	106.7 ± 46.1	269 ± 26	135.9
P23.75-PSPEGMA1.25	23.75	–	1.25	75	53.35	3.07	43.08	78 ± 1	107.0 ± 27.8	291 ± 9	–
P23.00-PSPEGMA2.00	23.00	–	2.00	75	54.77	7.64	37.59	73 ± 1	112.1 ± 30.0	280 ± 28	–
P22.00-PSPEGMA3.00	24.00	–	3.00	75	49.45	5.26	34.88	72 ± 1	233.0 ± 35.2	250 ± 18	111.8
P21.00-PSPEGMA4.00	21.00	–	4.00	75	55.14	6.15	38.71	59 ± 3	233.1 ± 35.4	284 ± 15	–
P20.00-PSPEGMA5.00	20.00	–	5.00	75	56.77	7.44	35.78	59 ± 2	226.7 ± 27.1	299 ± 21	118.1

respect, it was expected to influence membranes hydrophilic properties via both physical and chemical contributions.

3.2. Effect of PS-*b*-PEGMA on hydration properties of PVDF membranes

The additive was used to increase the hydrophilicity of PVDF membranes. Indeed, it is currently admitted that adsorption of biofouling compounds (proteins, bacteria) is often facilitated on rough and hydrophobic surfaces. As membranes were prepared by LIPS, they are quite smooth (see also RMS coefficients). So, the chemical effect is expected to be the major parameter affecting protein adsorption and bacterial attachment. Hydrophilicity of virgin and PEGylated membranes were measured by evaluating their water contact angle and hydration capacity, and results are

presented in Fig. 9 and in Table 1. As for the water contact angle, it is about 85 ± 1° for virgin PVDF membrane, evidencing a quite hydrophobic surface. By adding amphiphilic copolymer additive, it decreased until reaching a plateau at about 59°. This result proves that hydrophilicity of surfaces is enhanced by incorporating additive copolymer. In the meantime, hydration capacity of polymer matrices was increased from 0 to 226.7 ± 27.1 mg/cm³ when adding 5 wt% copolymer additive. In this respect, the whole wettability of membranes was improved. Entrapment of water inside the polymer structure became possible owed to the presence of ethylene-glycol groups dispersed in the bulk and establishing hydrogen bonds with water molecules. Furthermore, it was shown in Fig. 7 that the thickness was expanded when adding copolymer and Fig. 6 evidenced that the polymer-lean phase, that is the overall porosity of the membranes, was more

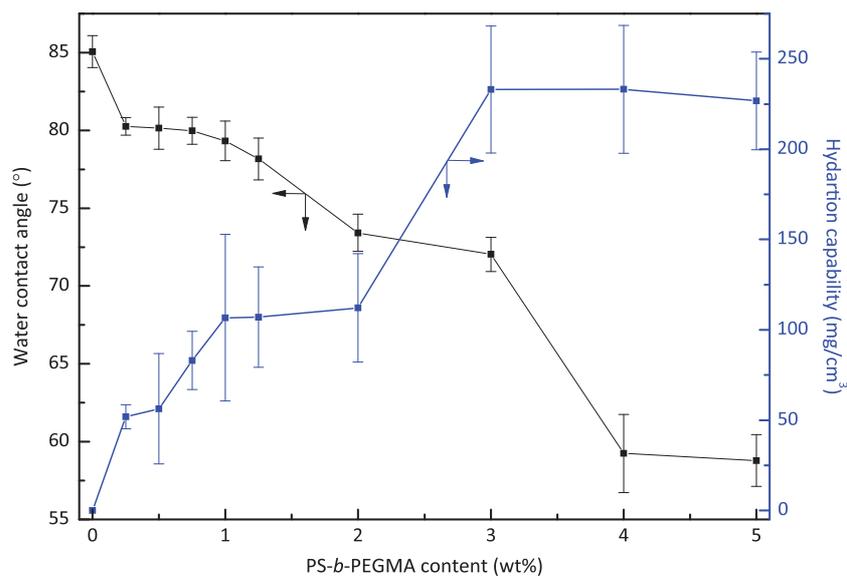


Fig. 9. Hydrophilic properties of virgin PVDF membrane and PEGylated PVDF membranes.

important for PEGylated membranes. This physical effect of the additive also contributed to allow the entrapment of more water molecules within the matrix. Also, a plateau is reached, possibly due to (i) saturation of membranes' surfaces with PS-*b*-PEGMA copolymer, and to (ii) a maximum thickness obtained from a 1 wt% additive content. Hence, no more water molecules could be entrapped within the structure using the LIPS process, and wettability (swelling) of membranes was optimum from a 3 wt% additive content.

This result supports the efficient modification of PVDF membrane. In previous section, it was pointed the difficulty to ascertain an effective change of surface chemistry. But water contact angles were reduced, mostly attributed to a change of surface chemistry. Combined to the results of hydration capability measurements, the new membranes are clearly more hydrophilic and may possibly reduce biofouling, which is to be investigated in next section.

3.3. Effect of PS-*b*-PEGMA on resistance of PVDF membranes to protein adsorption

In membrane applications such as water or blood treatment, feed often contains numerous proteins, able to interact with hydrophobic membrane material. Adsorption of proteins leads to biofouling, but also favors adsorption of micro-organisms such as bacteria, via hydrophobic-hydrophobic interactions with proteins constituting their outer cell wall. In this respect, it is of major concern to design membranes able to resist protein adsorption. BSA is a common protein tested to evaluate membrane resistance to biofouling by carrying out typical adsorption tests [41] or filtration experiments [42]. Therefore, it was used in the present study, as well as lysozyme, found in many secretions and that may contribute to biofouling in biological applications of membranes.

Fig. 10 presents the adsorption of BSA and LY as a function of the copolymer additive content. The amphiphilic additive permits to reduce BSA adsorption from about 0.087 mg/cm² for the virgin membrane to 0.024 mg/cm² for the PEGylated membrane containing 5 wt% additive, while LY attachment was reduced from 0.104 mg/cm² to 0.012 mg/cm². Hence, more than 65% and about 89% of BSA and LY adsorption, respectively, was prevented thanks to the amphiphilic copolymer, showing its efficiency in the preparation of low-biofouling surface. Binding water around ethylene glycol groups and favoring water entrapment within the very porous matrix led to a sharp decrease of protein adsorption. As reported earlier, better

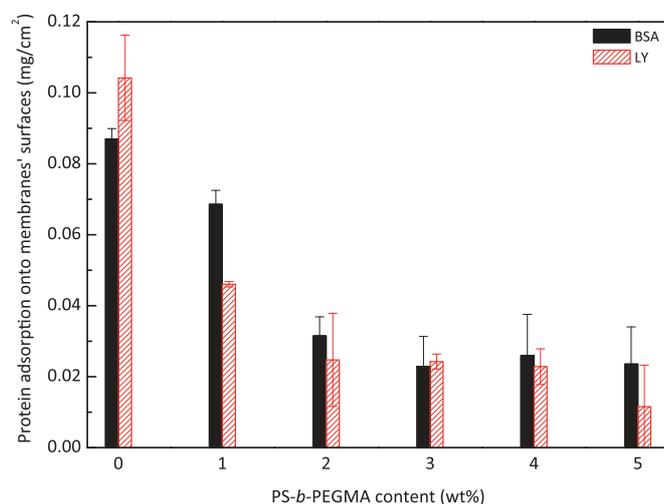


Fig. 10. Protein adsorption tests performed onto virgin PVDF membrane and PEGylated PVDF membranes.

results were obtained with LY, probably due to the fact that it possesses a molecular weight lower than that of BSA (66,000 vs. 14,300 g mol⁻¹). Therefore, it contains less hydrophobic segments on its backbone able to interact with hydrophobic sites available on membrane surface and within the matrix [43].

It was also important to compare these results with previously published data. Wang et al. used a membrane prepared by similar process as that in our study, but blending polyethersulfone (PES) (18 wt%), PEG 2000 (15 wt%) and P123-*b*-PEG copolymer (prepared from Pluronic[®] 123 and PEG by substitution reaction) (0.8 wt%) in DMF solvent [17]. For this initial formulation, BSA adsorption was about 2 µg/cm². Compared to their control membrane prepared using PES (18 wt%) and PEG 2000 (15 wt%) for which BSA adsorption was 6.8 µg/cm², protein adsorption was reduced to about 70%, which compares to the present work. Wang and coworkers managed to obtain even better results, but they actually used two additives, including one (PEG 2000) in large amount compared to the main polymer content. Furthermore, Boributh and coworkers modified PVDF membranes by introducing chitosan into the casting solution in the range 0.5–2 wt% [44]. Indeed, chitosan is a hydrophilic polymer which can be efficient to inhibit protein adsorption.

BSA adsorption tests at neutral pH (our conditions) revealed that chitosan permitted to reduce protein adsorption from about $58 \mu\text{g}/\text{cm}^2$ to $22 \mu\text{g}/\text{cm}^2$, that is, a decreasing of 62% was reported. We also compared these results to those we previously reported. Using vapor-induced phase separation (VIPS) process applied to a PVDF/Pluronic[®] (poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide)) blend, BSA and LY adsorption were reduced to about 65% and 95% the limitation of the virgin membrane [43]. In that study, VIPS process was applied, which means that more additive copolymer was found onto the surface, owing to a facilitated motion during phase separation, compared to LIPS. Indeed, protein adsorption tests using fibrinogen as a model protein, polysulfone as a bulk polymer and Pluronic[®] F108 as an additive, have shown that VIPS process allowed preparing better low-biofouling membranes than LIPS process [45]. One may wonder why LIPS was chosen in this study and not VIPS. Actually, the present research work aimed at preparing microfiltration membranes. Applying VIPS to a PVDF solution system will more likely lead to a nodular morphology, which will not present optimum mechanical properties, from our knowledge. In addition, using this polymer system, it seems rather difficult to obtain a bi-continuous structure by VIPS suitable for MF applications. Indeed, low dissolution temperature (32°C) is required to obtain a bi-continuous PVDF membrane by VIPS [46], but for such a temperature, it is not possible to totally solubilize the PVDF/PS-*b*-PEGMA system in a reasonable period of time. Therefore LIPS was used rather than VIPS, process that is not believed to lead to a copolymer surface density as high as that obtainable in VIPS, but still good enough to permit an important decrease of protein adsorption, as demonstrated herein.

Globally, and even though comparisons cannot always be accurately performed between research studies, present data show that PEGylated PVDF membranes were very efficient to resist BSA and LY adsorption.

3.4. Effect of PS-*b*-PEGMA on resistance of PVDF membranes to bacterial adhesion

Proteins adsorption usually favors bacteria adhesion. Once the first microorganisms have stuck to a membrane's surface, this surface may undergo bacteria colonization, phenomenon responsible for biofouling. Our target is to limit biofouling of membranes by creating a hydrophilic interface. It was shown in previous sections that results regarding protein adhesion tests were encouraging, with an important decreasing of BSA and LY adsorption. Therefore, further biofouling tests were conducted, using

Escherichia coli and *Staphylococcus epidermidis* incubated with the membranes for 3 h. These two bacteria have different nature, size and shape. Moreover, EC is regularly used to assess low-biofouling properties of membranes [3,4,47–49]. The use of fluorescence technique and confocal microscope technique are reported to analyze adhesion of bacteria onto surfaces [43,45]. In this work, noise attributed to the PVDF surface background was too important. So, we made use of SEM to analyze bacterial attachment on membranes, as displayed in Fig. 11. Each test was performed five times. To obtain quantitative data for each condition, bacteria were counted on five SEM images obtained at a 5 K magnification. It corresponded to the scan of a $437.5 \mu\text{m}^2$ surface area. The average number of bacteria per unit surface area, obtained from five different membranes, was then reported in Fig. 12.

Both *E. coli* and *S. epidermidis* easily attached to virgin PVDF membranes. Indeed, hydrophobic surfaces favor interactions with bacteria hydrophobic outer cell-wall. Despite smooth surfaces earlier evidenced by AFM images, and therefore preventing bacterial attachment by physical interaction as with rough interfaces, the number of bacteria onto virgin membranes was important (about 350,000 bacteria/ mm^2 in each case). As shown

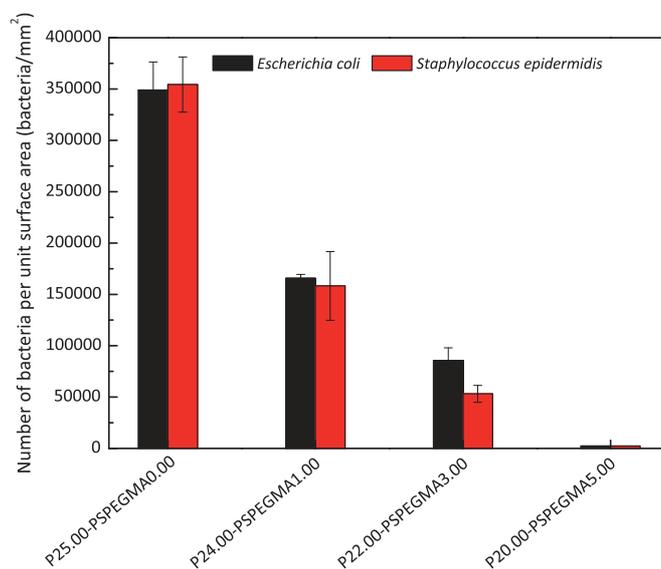


Fig. 12. Quantitative attachment of bacteria onto virgin PVDF membrane and PEGylated PVDF membranes after a 3-h incubation time in bacteria solution.

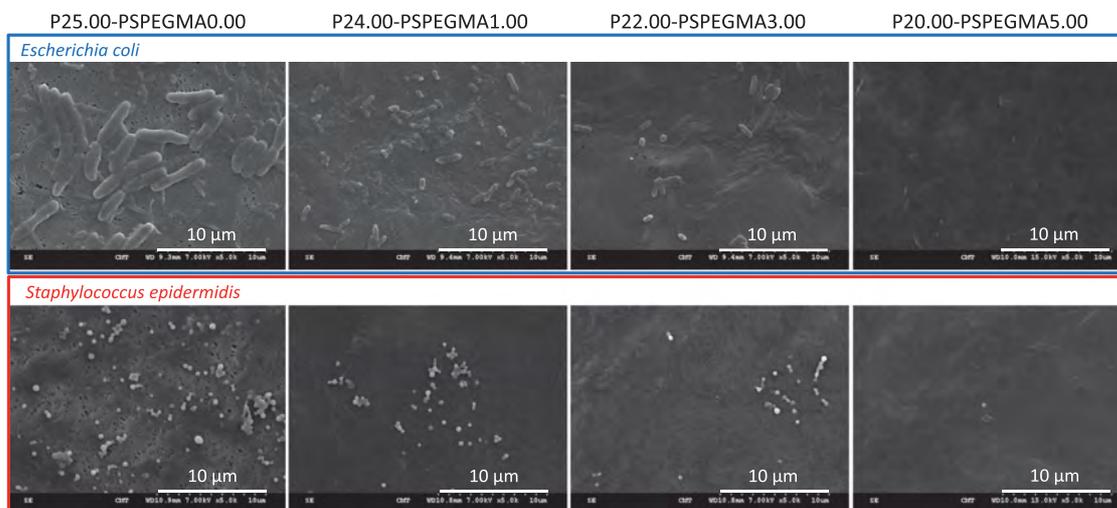


Fig. 11. Bacterial attachment tests performed onto virgin PVDF membrane and PEGylated PVDF membranes.

earlier, the surface morphology was not drastically affected by PS-*b*-PEGMA copolymer and the surface roughness was in the same range. In this respect, the surface chemistry is the key point permitting to explain the results. SEM images presented on Fig. 11, and related quantitative data displayed on Fig. 12, showed that copolymer tested in this study allowed providing an efficient chemical modification of the surface in order to resist bacterial adhesion. From a 5 wt% additive, almost no bacteria remained onto the surface (adhesion was reduced by 99%, compared to the virgin surfaces), whether from EC tests or SE ones, which was a good indication of low-biofouling properties of the membranes prepared in this work.

Literature also provides interesting data on the efficiency of PEG-like systems to resist bacteria. For instance, Miller and coworkers recently reported on the use of polydopamine-*g*-poly(ethylene glycol) surface coatings to control biofouling of membranes and feed spacers. Their short-term static adhesion tests ran for 1 h evidenced that the PEG-like systems permitted reducing adhesion of *P. aeruginosa* to about 75% the limitation of the virgin polysulfone membrane [50]. Recently, we also reported on the potential low-biofouling properties of membranes prepared by LIPS or VIPS process [43,45]. The additive used was Pluronic® F108 which is water-soluble. Reduction of bacterial attachment (EC and SE) was only observed when membranes were prepared by VIPS. Indeed, during membrane formation by LIPS process, part of F108 was washed out of the matrix, therefore reducing the potential low-biofouling properties of the membranes. Herein, we obtained as good results as those early presented with membranes prepared by VIPS, but using LIPS and a PEG additive water insoluble. Moreover, regardless the intended application, one can find that literature is well provided concerning PEGylation of surfaces aiming at resisting bacterial attachment. Indeed, it is a challenge in many fields to design anti-biofouling surfaces. For instance, Li et al. designed silicone films grafted with both PEG-derivative polymer to improve their hemocompatibility [51]. They showed that grafted silicone substrates reduced the adhesion of bacteria including *Staphylococcus aureus*, *Escherichia coli*, and *Staphylococcus epidermidis* by over 90%, showing the efficiency of PEG-systems, further supporting the results of the present work. Furthermore, Weber et al. recently presented their study on the effect of PEGylation of aminopropylated surfaces on bacteria adhesion and evidenced that EC adhesion was inhibited [52]. Of course, it is again hard to compare data of other authors with those presented in this work, since the polymer matrix, the bacteria tested or the additive copolymer are different, but it is important noting that PEG-systems in general, and the present system in particular, have excellent low-biofouling properties. To the best of our knowledge, the results presented in this study constitute among the best reported on the design of PVDF membranes resisting bacterial attachment.

4. Conclusions

In this manuscript, we reported the use of PS-*b*-PEGMA amphiphilic additive in the preparation of PVDF membrane by LIPS process. The main goal was to decrease biofouling of PVDF membranes, and the major conclusions are listed as follows:

- Membrane structure was drastically affected by the copolymer additive, with a decreasing of surface porosity, probably owed to the establishment of a polymer concentration gradient during membrane formation, and an expansion of the polymer lean-phase, due to an improvement of solvent outflow and non-solvent inflow during membrane formation. The walls of the characteristic macrovoids tended to be more porous with the additive content, and the shrinkage usually occurring during PVDF membrane formation was inhibited by the copolymer additive;
- Membrane surface hydrophilicity was improved, thanks to the presence of PEGMA segments onto membranes' surface;
- Membrane hydration capability was importantly enhanced, attributed to both chemical and physical effects of the copolymer additive;
- Protein adsorption including BSA and LY, was decreased in an important extent;
- Bacterial attachment onto the surfaces was inhibited using two model bacteria, *Escherichia coli* and *Staphylococcus epidermidis*.

Subsequent studies will concern filtration tests using membranes presented in this work. Indeed, evaluation of low-biofouling properties in practical filtration operation is now a major priority.

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References

- [1] H. Ivnitsky, I. Katz, D. Minz, E. Shimoni, Y. Chen, J. Tarchitzky, R. Semiat, C. G. Dosoretz, Characterization of membrane biofouling in nanofiltration processes of wastewater treatment, *Desalination* 185 (2005) 255–268.
- [2] X. Ma, Y. Su, Q. Sun, Y. Wang, Z. Jiang, Preparation of protein-adsorption-resistant polyethersulfone ultrafiltration membranes through surface segregation of amphiphilic comb copolymer, *J. Membr. Sci.* 292 (2007) 116–124.
- [3] C.X. Liu, D.R. Zhang, Y. He, X.S. Zhao, R. Bai, Modification of membrane surface for anti-biofouling performance: effect of anti-adhesion and anti-bacteria approaches, *J. Membr. Sci.* 346 (2010) 121–130.
- [4] Y.F. Yang, Y. Li, Q.L. Li, L.S. Wan, Z.K. Xu, Surface hydrophilization of micro-porous polypropylene membrane by grafting zwitterionic polymer for anti-biofouling, *J. Membr. Sci.* 362 (2010) 255–264.
- [5] C.H. Worthley, K.T. Constantopoulos, M. Ginic-Markovic, R.J. Pillar, J.G. Matisons, S. Clarke, Surface modification of commercial cellulose acetate membranes using surface-initiated polymerization of 2-hydroxyethyl methacrylate to improve membrane surface biofouling resistance, *J. Membr. Sci.* 385–386 (2011) 30–39.
- [6] M. Zhang, K. Zhang, B. De Gussene, W. Verstraete, Biogenic silver nanoparticles (bio-Ag⁺) decrease biofouling of bio-Ag⁺/PES nanocomposite membranes, *Water Res.* 46 (2012) 2077–2087.
- [7] Z. Zhang, Z. Wang, J. Wang, S. Wang, Enhancing chlorine resistances and anti-biofouling properties of commercial aromatic polyamide reverse osmosis membranes by grafting 3-allyl-5,5-dimethylhydantoin and N,N'-Methylenebis(acrylamide), *Desalination* 309 (2013) 187–196.
- [8] Y. Chang, T.Y. Cheng, Y.J. Shi, K.R. Lee, J.Y. Lai, Biofouling-resistance expanded poly(tetrafluoroethylene) membrane with a hydrogel-like layer of surface-immobilized poly(ethylene glycol) methacrylate for human plasma protein repulsions, *J. Membr. Sci.* 323 (2008) 77–84.
- [9] F. Razi, I. Sawada, Y. Ohmukai, T. Maruyama, H. Matsuyama, The improvement of antibiofouling efficiency of polyethersulfone membrane by functionalization with zwitterionic monomers, *J. Membr. Sci.* 401–402 (2012) 292–299.
- [10] A. Nguyen, S. Azari, L. Zou, Coating zwitterionic amino acid l-DOPA to increase fouling resistance of forward osmosis membrane, *Desalination* 312 (2013) 82–87.
- [11] Y.C. Chiang, Y. Chang, C.J. Chuang, R.C. Ruaan, A facile zwitterionization in the interfacial modification of low bio-fouling nanofiltration membranes, *J. Membr. Sci.* 389 (2012) 76–82.
- [12] H.D.W. Roesink, M.A.M. Beerlage, W. Potman, Th. van den Boomgaard, M.H.V. Mulder, C.A. Smolders, Characterization of new membrane materials by means of fouling experiments adsorption of BSA on polyetherimide–polyvinylpyrrolidone membranes, *Colloids Surf.* 55 (1991) 231.
- [13] Y.Q. Wang, T. Wang, Y.L. Su, F.B. Peng, H. Wu, Z. Jiang, Remarkable reduction of irreversible fouling and improvement of the permeation properties of poly(ether sulfone) ultrafiltration membranes by blending with Pluronic F127, *Langmuir* 21 (2005) 11856–11862.

- [14] W. Zhao, Y. Su, C. Li, Q. Shi, X. Ning, Z. Jiang, Fabrication of antifouling polyethersulfone ultrafiltration membranes using Pluronic F127 as both surface modifier and pore-forming agent, *J. Membr. Sci.* 318 (2008) 405–412.
- [15] H.J. Li, Y.M. Cao, J.J. Qin, X.M. Jie, T.H. Wang, J.H. Liu, Q. Yuan, Development and characterization of anti-fouling cellulose hollow fiber UF membranes for oil-water separation, *J. Membr. Sci.* 279 (2006) 328–335.
- [16] A. Higuchi, K. Shirano, M. Harashima, B.O. Yoon, M. Hara, M. Hattori, K. Imamura, Chemically modified polysulfone hollow fibers with vinylpyrrolidone having improved blood compatibility, *Biomater* 23 (2002) 2659–2666.
- [17] Y.Q. Wang, Y.L. Su, Q. Sun, X.L. Ma, Z.Y. Jiang, Y. Chang, S. Chen, Q. Yu, Z. Zhang, Generation of anti-biofouling ultrafiltration membrane surface by blending novel branched amphiphilic polymers with polyethersulfone, *J. Membr. Sci.* 286 (2006) 228–236.
- [18] F. Ran, S. Nie, W. Zhao, J. Li, B. Su, S. Sun, C. Zhao, Biocompatibility of modified polyethersulfone membranes by blending an amphiphilic triblock co-polymer of poly(vinyl pyrrolidone)-*b*-poly(methyl methacrylate)-*b*-poly(vinyl pyrrolidone), *Acta Biomater.* 7 (2011) 3370–3381.
- [19] Y.H. Zhao, Y.L. Qian, B.K. Zhu, Y.Y. Xu, Modification of porous poly(vinylidene fluoride) membrane using amphiphilic polymers with different structures in phase inversion process, *J. Membr. Sci.* 310 (2008) 567–576.
- [20] F. Liu, Y.Y. Xu, B.K. Zhu, F. Zhang, L.P. Zhu, Preparation of hydrophilic and fouling resistant poly(vinylidene fluoride) hollow fiber membranes, *J. Membr. Sci.* 345 (2009) 331–339.
- [21] C. Zhang, Y. Bai, Y. Sun, J. Gu, Y. Xu, Preparation of hydrophilic HDPE porous membranes via thermally induced phase separation by blending of amphiphilic PE-*b*-PEG copolymer, *J. Membr. Sci.* 365 (2010) 216–224.
- [22] F. Liu, N. Awanis Hashim, Y. Liu, M.R. Moghaeh Abed, K. Li, Progress in the production and modification of PVDF membranes, *J. Membr. Sci.* 375 (2011) 1–27.
- [23] Q. Li, Q.Y. Bi, B. Zhou, X.L. Wang, Zwitterionic sulfobetaine-grafted poly(vinylidene fluoride) membrane surface with stably anti-protein-fouling performance via a two-step surface polymerization, *Appl. Surf. Sci.* 10 (2012) 4707–4717.
- [24] N. Pezeshk, D. Rana, R.M. Narbaitz, T. Matsuura, Novel modified PVDF ultrafiltration flat-sheet membranes, *J. Membr. Sci.* 389 (2012) 280–286.
- [25] N. Pezeshk, R.M. Narbaitz, More fouling resistant modified PVDF ultrafiltration membranes for water treatment, *Desalination* 287 (2012) 247–254.
- [26] Y.C. Chiag., Y. Chang, W.Y. Chen, R.C. Ruaan, Biofouling resistance of ultrafiltration membranes controlled by surface self-assembled coating with PEGylated copolymers, *Langmuir* 28 (2012) 1399–1407.
- [27] T. Boccaccio, A. Bottino, G. Capannelli, P. Piaggio, Characterization of PVDF membranes by vibrational spectroscopy, *J. Membr. Sci.* 210 (2002) 315–329.
- [28] A. Salimi, A.A. Yousefi, Conformational changes and phase transformation mechanisms in PVDF solution-cast films, *J. Polym. Sci. Part B: Polym. Phys.* 42 (2004) 3487–3495.
- [29] R. Gregorio Jr., Determination of the α , β , and γ crystalline phases of poly(vinylidene fluoride) films prepared at different conditions, *J. Appl. Polym. Sci.* 100 (2006) 3272–3279.
- [30] A. Siri, C. Alkan, A. Biçer, A. Karaipekli, Synthesis and thermal energy storage characteristics of polystyrene-graft-palmitic acid copolymers as solid–solid phase change materials, *Sol. Energy Mater. Sol. Cells* 95 (2011) 3195–3201.
- [31] J. Jin, W. Jiang, Q. Shi, J. Zhao, J. Yin, P. Stagnaro, Fabrication of *PP-g-PEGMA-g-heparin* and its hemocompatibility: from protein adsorption to anticoagulant tendency, *Appl. Surf. Sci.* 258 (2012) 5841–5849.
- [32] L.P. Zhu, Y.Y. Xu, H.B. Dong, Z. Yi, B.K. Zhu, Amphiphilic PPESK-graft-P(PEGMA) copolymer for surface modification of PPESK membranes, *Mater. Chem. Phys.* 115 (2009) 223–228.
- [33] J.F. Hester, A.M. Mayes, Design and performance of foul-resistant poly(vinylidene fluoride) membranes prepared in a single-step by surface segregation, *J. Membr. Sci.* 202 (2002) 119–135.
- [34] G.M. Qiu, L.P. Zhu, B.K. Zhu, Y.Y. Xu, G.L. Qiu, Grafting of styrene/maleic anhydride copolymer onto PVDF membrane by supercritical carbon dioxide: preparation, characterization and biocompatibility, *J. Supercrit. Fluids* 45 (2008) 374–383.
- [35] Y. Sui, X. Gao, Z. Wang, C. Gao, Antifouling and antibacterial improvement of surface-functionalized poly(vinylidene fluoride) membrane prepared via dihydroxyphenylalanine-initiated atom transfer radical graft polymerizations, *J. Membr. Sci.* 394–395 (2012) 107–119.
- [36] Y. Sui, Z. Wang, X. Gao, C. Gao, Antifouling PVDF ultrafiltration membranes incorporating PVDF-*g*-PHEMA additive via atom transfer radical graft polymerizations, *J. Membr. Sci.* 413–414 (2012) 38–47.
- [37] M. Mulder, *Basic Principles of Membrane Technology*, 2nd Edition, Kluwer Academic Publishers, Dordrecht, the Netherlands, 1997.
- [38] G.R. Guillen, Y. Pan, M. Li, E.M.V. Hoek, Preparation and characterization of membranes formed by nonsolvent induced phase separation: a review, *Ind. Eng. Chem. Res.* 50 (2011) 3798–3817.
- [39] Y. Chang, Y.J. Shih, R.C. Ruaan, A. Higuchi, W.Y. Chen, J.Y. Lai, Preparation of poly(vinylidene fluoride) microfiltration membrane with uniform surface-copolymerized poly(ethylene glycol) methacrylate and improvement of blood compatibility, *J. Membr. Sci.* 309 (2008) 165–174.
- [40] J.H. Kim, K.H. Lee, Effect of PEG additive on membrane formation by phase inversion, *J. Membr. Sci.* 138 (1998) 153–163.
- [41] Y. Zhou, Z. Wang, Q. Zhang, X. Xi, J. Zhang, W. Yang, Equilibrium and thermodynamic studies on adsorption of BSA using PVDF microfiltration membrane, *Desalination* 307 (2012) 61–67.
- [42] M. Hashino, K. Hirami, T. Ishigami, Y. Ohmukai, T. Maruyama, N. Kubota, H. Matsuyama, Effect of kinds of membrane materials on membrane fouling with BSA, *J. Membr. Sci.* 384 (2011) 157–165.
- [43] A. Venault, Y. Chang, D.M. Wang, J.Y. Lai, Surface anti-biofouling control of PEGylated poly(vinylidene fluoride) membranes via vapor-induced phase separation processing, *J. Membr. Sci.* 423–424 (2012) 53–64.
- [44] S. Boributh, A. Chanachai, R. Jiratananon, Modification of PVDF membrane by chitosan solution for reducing protein fouling, *J. Membr. Sci.* 342 (2009) 97–104.
- [45] A. Venault, Y. Chang, D.M. Wang, D. Bouyer, A. Higuchi, J.Y. Lai, PEGylation of anti-biofouling polysulfone membranes via liquid- and vapor-induced phase separation processing, *J. Membr. Sci.* 403–404 (2012) 47–57.
- [46] C.L. Li, D.M. Wang, A. Deratani, D. Quemener, D. Bouyer, J.Y. Lai, Insight into the preparation of poly(vinylidene fluoride) membranes by vapor-induced phase separation, *J. Membr. Sci.* 361 (2010) 154–166.
- [47] E. Lee, H.K. Shon, J. Cho, Biofouling characteristics using flow field-flow fractionation: effect of bacteria and membrane properties, *Bioresour. Technol.* 101 (2010) 1487–1493.
- [48] K. Zdrow, L. Brunet, S. Mahendra, D. Li, A. Zhang, Q. Li, P.J.J. Alvarez, Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal, *Water Res.* 43 (2009) 715–723.
- [49] R. Malaisamy, D. Berry, D. Holder, L. Raskin, L. Lepak, K.L. Jones, Development of reactive thin film polymer brush membranes to prevent biofouling, *J. Membr. Sci.* 350 (2010) 361–370.
- [50] D.J. Miller, P.A. Araújo, P.B. Correia, M.M. Ramsey, J.C. Kruithof, M.C.M. von Loosdrecht, B.D. Freeman, D.R. Paul, M. Whiteley, J.S. Vrouwenvelder, Short-term adhesion and long-term biofouling testing of polydopamine and poly(ethylene glycol) surface modifications of membranes and feed spacers for biofouling control, *Water Res.* 46 (2012) 3737–3753.
- [51] M. Li, K.G. Neoh, L.Q. Xu, R. Wang, E.T. Kang, T. Lau, D.P. Olszyna, E. Chiong, Surface modification of silicone for biomedical applications requiring long-term antibacterial, antifouling, and hemocompatible properties, *Langmuir* 28 (2012) 16408–16422.
- [52] T. Weber, Y. Gies, A. Terfort, Bacteria-repulsive polyglycerol surfaces by grafting polymerization onto aminopropylated surfaces, *Langmuir* 28 (2012) 15916–15921.