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Towards permanent hydrophilic PVDF membranes. Amphiphilic PVDF-*b*-PEG-*b*-PVDF triblock copolymer as membrane additive.

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RAFT, Poly(vinylidene fluoride), Block copolymer, Poly(ethylene glycol), NIPS, Hydrophilic membrane

ABSTRACT:

Poly(vinylidene fluoride) (PVDF) ultrafiltration membranes were prepared by NIPS using a blend of a new amphiphilic PVDF-based triblock copolymer (PVDF-*b*-PEG-*b*-PVDF) and high molar mass PVDF. During the phase inversion step, the triblock copolymer acts both as a pore forming and surface modifying agent. Thanks to the presence of the short PVDF blocks in the triblock copolymer, the hydrophilic PEG segment is fixed in the PVDF matrix, thus reducing the gradual loss of hydrophilic additive by leaching of the triblock copolymer out of the membrane matrix. The PVDF-*b*-PEG-*b*-PVDF triblock copolymer additive improved the surface hydrophilicity and significantly increased the pure water flux and permeability of the PVDF membrane. The membrane composition was optimized in terms of additive concentration and compared to membranes prepared with an equivalent amount of commercial PEG of similar molar mass. Pure water filtration tests and contact angle measurements suggested that addition of small amounts of the triblock copolymer additive (2-5% w/w) has a strong impact on the performance and hydrophilic characteristic of the PVDF membranes. The control tests showed that less than 30% w/w of the additive is lost after 9 months, while most commercial PEG (59 % w/w) leached out of the membrane matrix in only two months.

1. Introduction:

1 Membrane technology plays a crucial role in water and energy sustainability.[1] Access to water is one
2 of the keys for economic, social and cultural development. The main reason why membrane technology
3 has become an important separation technology over the past years is the fact that membranes require
4 relatively low energy [1,2], are atom-efficient and are nowadays economically viable.[3]
5
6 Polymer membranes lead the membrane separation industry market because they are very competitive
7 in terms of performance, cost and ease of handling. They can also be relatively easy to functionalize if
8 additional properties are desired. Many polymers are available, and the choice of the material is the
9 most important as it dictates the chemical properties and the final performance of the membrane. A pol-
10 ymer must have appropriate characteristics to be used in micro (MF) and ultrafiltration (UF) membrane

formulations. It has to tolerate the cleaning conditions (i.e. high pressure backwash with sodium hypochlorite solution for example), the driving forces (i.e. pressure) and has to be compatible with the membrane fabrication method (e.g. phase inversion, stretching of semi-crystalline polymer foils or hollow fibers, interfacial polymerization, temperature-induced phase separation (TIPS), non-solvent-induced phase separation (NIPS)...). Significant effort has been devoted to enhancing the permeation flux,[3–7] fouling resistance,[6,8–12] operation stability,[13] and service life of membranes.[3,14,15]

The most common commercial polymers used for fabrication of MF and UF membranes are poly(ether sulfone) (PES),[16] polyethylene (PE),[17] polypropylene (PP),[14] polytetrafluoroethylene (PTFE)[18,19] and poly(vinylidene fluoride) (PVDF).[8,20–23]

Ultrafiltration (UF) and microfiltration (MF) membranes are employed when high separation efficiency is required.[9,12,21,24] Such filtration membranes as water treatment devices are susceptible to low fouling resistance.[14] Membrane fouling affects productivity, and generates additional operating costs, and the need for regular chemical cleaning procedures that shorten the membrane lifetime. Membrane surface hydrophilicity is generally accepted as the main factor affecting fouling. A hydrophilic membrane surface generally has higher fouling resistance compared to hydrophobic membranes.[25–28] To help solve these problems, materials scientists and chemical engineers are working to develop inexpensive, scalable, and sustainable methods to produce hydrophilic membranes for water purification.[8]

Among all the methods that can be employed for the fabrication of polymer membranes, phase inversion method is the most popular technique. The non-solvent-induced phase separation (NIPS) method is the method of choice in industry. In this method, the polymer is dissolved in a suitable solvent, cast into the desired shape (i.e. flat or hollow fiber) and is then immersed into a non-solvent bath (coagulation bath) where the phase inversion process takes place. For this method to work, the polymers (membrane forming polymer and the additives), need to be insoluble in the non-solvent and solvent and non-solvent should be miscible. Phase inversion can also proceed via thermally induced phase separation (TIPS),[23,29] vapor induced phase separation (VIPS),[30] and evaporation-induced phase separation.[31]

PVDF is one of the most widely used polymers in membrane formulations due to its remarkable properties such as wide chemical compatibility, excellent mechanical properties, relatively easy processing and high temperature resistance.[2,8,11] However, PVDF is relatively hydrophobic. This hydrophobicity is a

problem for the efficiency and energy consumption of membranes designed for water purification.[21,24,27] Indeed, ultrafiltration and microfiltration PVDF membranes require high operating pressures resulting in high energy consumption to provide acceptable flux values.

Several studies describe the modification of PVDF membranes with hydrophilic additives such as polymers[3,20] and copolymers[12,32,33] to improve their hydrophilicity. However, most of the added additives (mainly hydrophilic polymers or nanoparticles[14,15,24,26]) is lost during the membrane manufacturing process, and through gradual leaching during operation. This is often because there is no specific interaction between the hydrophilic additive and the PVDF since the two components are simply blended with each other.

Post-fabrication treatment via physical surface modification (e.g. coating with a hydrophilic polymer layer)[6,12,21] or chemical treatment (e.g. plasma grafting of polar groups)[7,27,28] are some of the techniques used to confer hydrophilicity to PVDF membranes. Finding formulations and preparation methods that optimize fabrication costs, ease of implementation, efficiency, and long-term durability remains a challenge. Blending PVDF with hydrophilic polymers (e.g. polyvinyl alcohol (PVA), polyethylene glycol (PEG), polyvinylpyrrolidone (PVP)) via phase separation process is the most used method in membrane industry. This is because; preparing membranes from a mixture of polymers is relatively easy, convenient and adaptable to the industrial membrane fabrication set-up.

Numerous studies report the use of additives such as PVP[3,20,25] and PEG[32,34]. These polymers act as both pore-formers (increasing porosity and hence membrane permeability) and hydrophilic additives. However, assessing the real and final impact of these polymer additives is difficult, since the relationship between the amounts of additive added in the casting solution and their final concentration in the membrane matrix after coagulation bath is hard to establish/calculate by regular analysis methods. A systematic study is required each time a new formulation is tested. Likewise, establishing the rate of migration of the additive retained within the polymer matrix is very difficult.[35,36] For example, when PEG is blended with PVDF, a large part of it is washed out during the phase inversion step (coagulation bath). The non-solvent is often water, which dissolves most of the PEG, promoting the formation of the pores. In consequence only a small amount of the initial added PEG remains in the PVDF membrane matrix.[32,36] To reach higher hydrophilicity, larger quantities of additive should be added. However larger quantities of additives also results into higher membrane porosity. Finding the right compromise between hydrophilicity and porosity is not straightforward.

77

78 Here, we describe the use of an ABA triblock copolymer containing a PEG central block and two PVDF
79 lateral blocks, as a hydrophilic additive for PVDF membranes. This PVDF-*b*-PEG-*b*-PVDF amphiphilic
80 triblock copolymer should increase the wettability of the resulting membrane. In addition, leaching of
81 the PEG should be reduced both at the preparation and filtration steps, since the PEG and the PVDF
82 segments would be connected via covalent bond and the two PVDF segments of the triblock co-
83 crystallize with the high molar mass PVDF membrane matrix. Different proportions of triblock copoly-
84 mer additive (PVDF₅₀-*b*-PEG₁₃₆-*b*-PVDF₅₀, with weight fraction of PEG₆₀₀₀ = 0.47) were used in the
85 casting solution, and the membranes thus prepared via the NIPS process were compared with similar
86 membranes prepared from casting solutions containing an equivalent amount of PEG₆₀₀₀. The prepared
87 membranes were aged over 9 months and their performance as well as the amount of additive left in the
88 membrane matrix was assessed during this period using contact angle, NMR and pure water
89 flux/permeability measurements. The membranes were also characterized using SEM before and after
90 aging.

91

92

93 2. Experimental

94

95 2.1. Materials

96 All reagents were purchased from Sigma-Aldrich and were used as received unless otherwise stated.
97 High molar mass PVDF (Kynar 761; Mw: 441,000 g/mol) was kindly donated by ARKEMA. Deuteri-
98 um oxide (D₂O) and dimethylsulfoxide ((CD₃)₂SO) were purchased from Eurisotop. PVDF-*b*-PEG-*b*-
99 PVDF block copolymer was synthesized as reported previously.[37]

100 2.2. Methods

101 2.2.1. Preparation of high molar mass PVDF mother solution.

102 3.75g of PVDF (Kynar 761) was dissolved in 20g of NMP under magnetic stirring at 80 °C for 24h (fi-
103 nal PVDF concentration = 15.79 % w/w).

104 2.2.2. Preparation of dope solutions containing the triblock copolymer.

105 The dope solutions were prepared by blending 4 g of the PVDF mother solution with different amounts
106 of PVDF-*b*-PEG-*b*-PVDF triblock copolymer solution (1 to 25% w/w) in NMP (see Table 1). To ensure
107 homogeneous mixing, the mixture was stirred for 24h at 80 °C.

108 2.2.2 Preparation of control dope solutions containing PEG homopolymer.

109 A 15% (w/w) high molar mass PVDF solution in NMP was blended with two different concentrations
110 of PEG₁₃₈ for 24h at 80 °C (see Table 1).

111 2.2.3. Blade casting

Membranes of 20 cm in 20 cm were prepared using a blade with a 250 μm clearance using dope solutions stored at 80 $^{\circ}\text{C}$ on a glass plate. 60 seconds after film casting, the substrate was transferred to a water coagulation bath thermostated at 25 $^{\circ}\text{C}$. The membrane was left in this coagulation bath for 24 h, prior to drying at room temperature for another 24h (see Scheme 1).

2.2.4. Water Contact angle (WCA)

The contact angle measurements, which quantify the wettability/hydrophilicity of the membrane surface, were assessed using a monochrome camera B-CAM-21-BW (CCCIR) and a Led R60 lamp purchased from CONRAD. For each sample, 10.0 μL of ultra-pure water was deposited on a polymer-coated silica wafer using a micro needle. The images were recorded using One Touch Graber software and treated using Image J software.

2.2.5. NMR spectroscopy

NMR spectra were acquired in either D_2O or a mixture of D_2O and $(\text{CD}_3)_2\text{SO}$ using a Bruker 300 MHz spectrometer. All chemical shifts are reported in ppm.

2.2.6. Scanning electron microscopy (SEM)

The porous structure of virgin PVDF membrane and modified PVDF membranes were characterized using microscopy techniques. SEM analyses were conducted using a Hitachi S-4500 instrument operating at a spatial resolution of 1.50 nm at 15 kV energy. The samples were dried and coated with an ultrathin layer of electrically conducting platinum deposited by high vacuum evaporation.

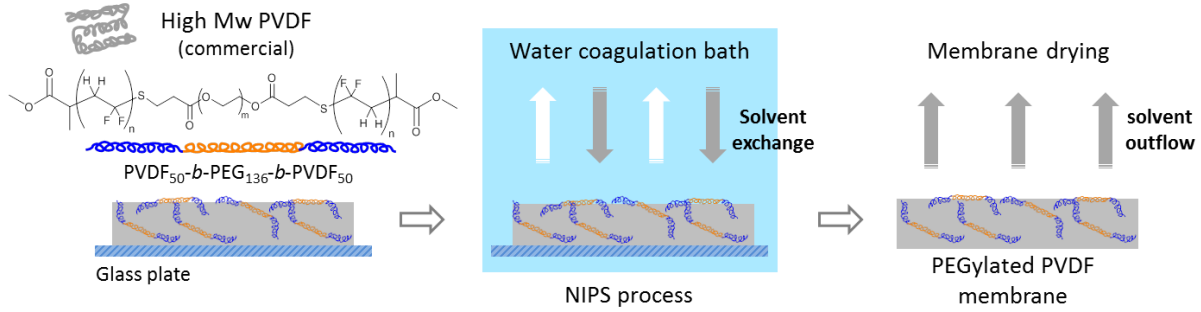
2.2.7. Water filtration experiments

For filtration tests, Circles of 2.5 cm in diameter were cut from each membrane and were placed in sealed petri dishes filled with distilled water. This water was replaced weekly with fresh distilled water during the study period of 9 months. The membrane was fitted in a 10 mL filtration cell (Amicon 8010 stirred cell). Filtration cell was then connected to a water reservoir and compressed air line. The measurements were performed at pressures between 0.1 and 2.0 bar. The mass of the water passing through the membrane (permeate) was recorded by the Sarto Connect software at regular time intervals. All filtration experiments were performed at room temperature with dust free ultrapure water (filtered through a 400- μm filter). Before recording the water flux, the membranes were conditioned for 2h at 2 bar. The flux and permeability of the 4 modified membranes were evaluated during the aging period via three cycles of pure water filtration. The volumetric flux and permeability were calculated according to Darcy's law using equations (1) and (2):

$$\text{Flux } (J_v) = V_p / (t * S) \text{ (L h}^{-1} \text{ m}^{-2}) \quad (1)$$

$$Permeability (L_p) = J_v / \Delta P \text{ (L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}) \quad (2)$$

Where V_p = Permeate volume, t = Time, S = Surface area and ΔP = pressure difference.



Scheme 1. Membrane preparation via NIPS process from a blend of high Mw PVDF and PVDF₅₀-*b*-PEG₁₃₆-*b*-PVDF₅₀ triblock copolymer in NMP.

2.2.8. Porosity and Pore Size Determination

The porosity of the membrane was determined from its dry and wet masses. The membrane was immersed in water for 24 h. After that, the mass of the wet membrane was measured after wiping off excess water using filter paper. Then, the wet membrane was dried in an oven under vacuum for 10 h at 25°C and the mass of this dried membrane was measured. The porosity was calculated using the following equation[38]:

$$\varepsilon(\%) = \frac{\frac{(w_w - w_d)}{\rho_w}}{\frac{(w_w - w_d)}{\rho_w} + \frac{w_d}{\rho_p}} \times 100\% \quad (3)$$

where ε is the membrane porosity, w_w is the wet membrane mass (g), w_d is the dry membrane mass (g), ρ_w is the pure water density while ρ_p is the density of the polymer. The densities of the polymer blends were estimated using the weight fractions of PEG and PVDF. Since $\rho_{PVDF} = 1.78 \text{ g}\cdot\text{cm}^{-3}$ and $\rho_{PEG} = 1.20 \text{ g}\cdot\text{cm}^{-3}$. Thus, the density of the blend containing 2 % w/w of triblock (i.e. 0.81 % w/w of PEG) was estimated to be $1.775 \text{ g}\cdot\text{cm}^{-3}$ while the density of the blend containing 5% w/w of triblock (or 1.95 % w/w of PEG) was $1.769 \text{ g}\cdot\text{cm}^{-3}$.

The mean pore radius (r_m) was calculated from the pure water flux (PWF) value and porosity data obtained previously using the Guereout-Elford-Ferry equation as follows[39]:

$$r_m = \sqrt{\frac{(2.9 - 1.75 \cdot \varepsilon) \cdot 8 \cdot \eta \cdot l \cdot Q}{\varepsilon \cdot A \cdot \Delta P}}$$

(4)

Where η is the viscosity of water (mPa·s) (1.002 at 20°C), l is the membrane thickness (m) (150-200μm), Q is the pure water flux (m³·s⁻¹), A is the area of membrane (m²) ($d = 2.5$ cm) and ΔP is the operating pressure (mPa) (2 bar = 2·10⁸ mPa).

2.2.9. Additive Loss Assessment

$$Additive\ loss(\%) = 100 - \frac{\int_{3.47}^{3.55} CH_2(PEG)_{aged\ membrane}}{\int_{3.47}^{3.55} CH_2(PEG)_{membrane\ t=0}} \times 100$$

(5)

Note: The integral of PVDF signal at 2.8 ppm were used as reference.

1. Results and discussion

The well-defined triblock copolymer PVDF₅₀-*b*-PEG₁₃₆-*b*-PVDF₅₀ was synthesized according to our previously published work.[40] This triblock copolymer was then used as the hydrophilic additive in the preparation of PVDF membranes. A series of dope solutions (composed of high molar mass PVDF and the triblock copolymer) containing different mass fraction of this triblock copolymer was prepared. The mass fraction of the high molar mass PVDF in NMP was fixed at 15 % (w/w). To ensure complete dissolution of PVDF in NMP, the solutions were heated at 80 °C under stirring for 24h. Different amounts of the triblock copolymer PVDF₅₀-*b*-PEG₁₃₆-*b*-PVDF₅₀ (1, 2, 5, 10, 15 and 20 % w/w) were then added to the homogeneous PVDF solution. These mixtures were stirred at 25°C until homogeneous. A series of membranes were prepared via the NIPS process using dope solutions containing different amounts of the triblock copolymer (see Table 1). Additionally, control membranes were made from dope solutions containing commercially available PEG. The quantities of PEG added to the casting solutions were carefully calculated to match the amount of PEG present in the casting solutions containing the triblock copolymer as additive.

1.1.1. Effect of PVDF₅₀-*b*-PEG₁₃₆-*b*-PVDF₅₀ on the membrane formation.

The membranes were prepared via the NIPS process using a water coagulation bath. As mentioned before, different concentrations of the triblock copolymer (1, 2, 5, 10, 15, 20% w/w) were employed to prepare the membrane casting solutions (Table 1). Membranes prepared from triblock copolymer solutions of concentration higher than 5% w/w were very soft and swollen after immersion in the coagulation bath. They seemed to retain large amounts of water that caused the membranes to become unstable and fall apart (Figure S4). For this reason only the membranes prepared with 1, 2 and 5% (w/w) of triblock copolymer were used in the rest of the present study.

SEM images of the stable membranes (Figure 1) showed asymmetric structures with a thin top skin porous layer supported by a finger-like sublayer. Formation of finger-like structure is typical in membranes prepared via a liquid-liquid phase separation process such as NIPS, in which polymer-rich and polymer-poor phases are developed. The surface and cross-section images of the membranes showed that increasing the PVDF-*b*-PEG-*b*-PVDF content in the dope solution led to more porous surfaces. This observation is in agreement with previous reports [34,41–43] and is not surprising as the PEG segment of the triblock copolymer retains water and facilitates the formation of pores. In NIPS process the phase separation happens very fast. This causes the PVDF blocks of the copolymer to precipitate along with the high molar mass PVDF forming the matrix of the membrane. This co-precipitation of the two types of PVDF chains is also likely accompanied by co-crystallization. This combined phenomena likely result in the immobilization of the triblock copolymer in the membranes matrix, reducing the possibility for this copolymer additive to migrate and leach out.

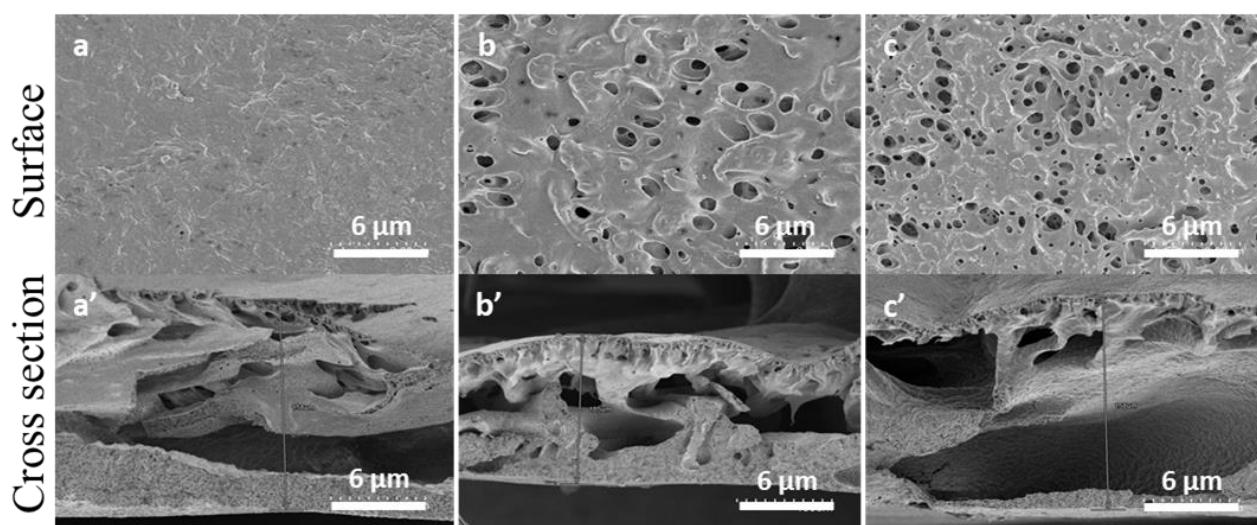


Figure 1. SEM images of the surface and cross-section of PVDF membranes prepared from dope solutions containing (a, a') 0%, (b, b') 2% and (c, c') 5% w/w of PVDF-*b*-PEG-*b*-PVDF triblock copolymer.

The relevant changes in the number and size of the macro voids with the increasing amount of the additive could not be calculated using the SEM cross-section images. All the analyzed membranes presented large macro voids. This may be ascribed to the presence of the hydrophilic PEG segments in the triblock copolymer which enhances the in-flow/out-flow of solvent and non-solvent molecules in the membrane structure resulting in high porosity.

1.1.2. Effect of PVDF₅₀-*b*-PEG₁₃₆-*b*-PVDF₅₀ on the surface hydrophilicity of the PVDF membranes.

As explained above the addition of PEG-containing triblock copolymer resulted in a general higher surface porosity. As observed by SEM (Figure 1), membranes formed from solutions containing larger mass fractions of triblock copolymer displayed higher surface porosity. This porosity was rather irregular which resulted in large pore size distribution as well as increased roughness of the membrane surface. As expected, the hydrophilicity of the surface of the membranes increased with increasing the additive concentration in the dope solutions.

Table 1. Dope solution formulations for the preparation of the hydrophilic PVDF membranes.

Membrane ID	Composition of the casting solution				Copolymer % (w/w)	m _{copolymer} /m _{PVDF}	M _{PEG*} /m _{PVDF}	WCA (°)
	m _{PVDF} (g)	m _{Copolymer} (g)	m _{PEG} (g)	m _{NMP} (g)				
Triblock0	0.750	-	-	4.85	0	-	-	105±18
Triblock1	0.750	0.056	-	4.79	1.00	7.47 10 ⁻²	2.94 10 ⁻²	74±6
Triblock2	0.750	0.112	-	4.74	2.00	14.93 10 ⁻²	5.63 10 ⁻²	54±5
Triblock5	0.750	0.279	-	4.55	5.00	37.20 10 ⁻²	12.51 10 ⁻²	39±6
Triblock10	0.750	0.554	-	4.23	10.00	73.87 10 ⁻²	21.09 10 ⁻²	10±10
Triblock15	0.750	0.814	-	3.86	15.00	108.53 10 ⁻²	27.13 10 ⁻²	-
Triblock25	0.750	1.4	-	3.45	25.00	186.67 10 ⁻²	36.42 10 ⁻²	-
PEG2eq	0.816	-	0.046	4.74	-	-	5.64 10 ⁻²	61±7
PEG5eq	0.920	-	0.115	4.55	-	-	12.50 10 ⁻²	47±5

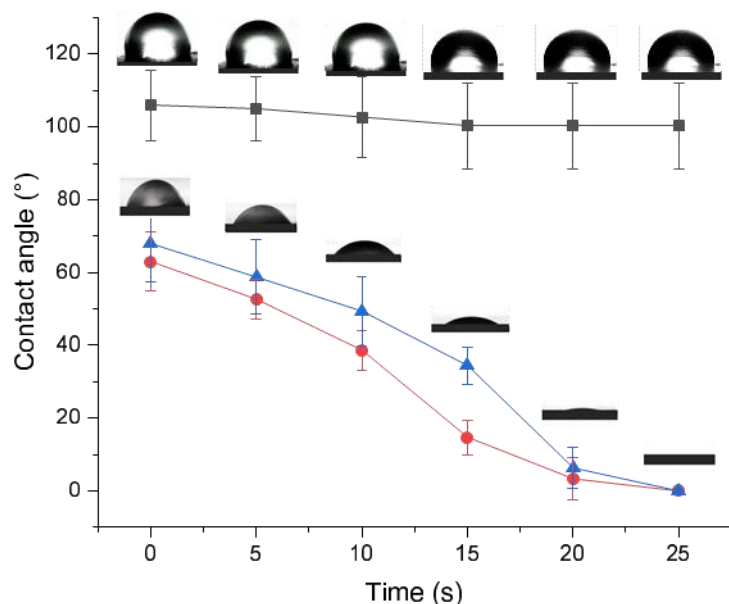
Note: *calculated masses of PEG from copolymer additive or commercial PEG.

Water contact angle (WCA) measurements (Table 1 and Figure 2) were performed to evaluate the membrane surface hydrophilicity/wettability.

WCA of the pure PVDF membrane (Triblock0 in Table 1) at t = 10 s was (105 ± 18°). The PVDF surface of this membrane was thus slightly hydrophobic as expected. The membrane prepared using dope solution containing 1% (w/w) triblock copolymer displayed a much lower water contact angle (74 ± 6°) at t = 10 s. This value decreased to 54±5°, 39±6° and 10±10° at t = 10 s when dope solutions containing 2, 5 and 10% (w/w) triblock copolymer were used respectively. When more concentrated dope solutions

252 were used ($> 5\%$ w/w) the water droplets were rapidly absorbed into the membranes (≤ 10 s). Figure 2
 253 shows the evolution of WCA with time for pure PVDF membrane and those prepared using solutions
 254 containing 2 and 5% triblock copolymer. In the case of the pure PVDF membrane the WCA remained
 255 stable at around 105° for the duration of the monitoring (25 s). In contrast, the WCA decreased drasti-
 256 cally reaching 0° within 25 s for the membranes prepared from dope solutions prepared with 2 and 5%
 257 (w/w) triblock copolymer.

258 These results show that addition of even small amounts (1-5% (w/w) in the dope solution) of triblock
 259 copolymer enhances the hydrophilicity of the PVDF membranes drastically. This is probably due to the
 260 fact that most of the added triblock copolymer stays in the membrane matrix thanks to the presence of
 261 the two short PVDF blocks acting as anchoring points for the PEG segments to the high molar mass
 262 PVDF chains forming the bulk of the membrane. In addition, the presence of this short PVDF blocks
 263 likely promotes a more homogeneous distribution of the PEG segments in the membrane matrix com-
 264 pared to the commercially available PEG used as additive.



276 **Figure 2. Evolution of the WCA versus time: Pure PVDF membrane (black squares), and membranes pre-**
 277 **pared using 2 and 5% (w/w) triblock copolymer solutions (blue triangles and red dots respectively).**

278
 279 To test the hypothesis that the presence of the short PVDF blocks of the triblock copolymer is responsi-
 280 ble for the strong interaction of the triblock copolymer with the high molar mass PVDF leading to im-
 281 mobilization of the PEG segments in the membrane matrix, ageing experiments were carried out over 9
 282 months. For these experiments two 10 cm x 10 cm membranes were prepared using dope solutions with

2 and 5% w/w triblock copolymer (Triblock2 and Triblock5 in Table 1). In addition, two membranes (100 cm²) were prepared from dope solutions containing equivalent amounts of commercial PEG homopolymer. These membranes (PEG2eq and PEG5eq in Table 2) were used as control experiments.

WCA was monitored over 9 months to assess the loss of hydrophilicity with time. The WCA measurements (Table 2) indicate a small loss of hydrophilicity for membranes containing triblock copolymer; the WCA increased by 13° and 14° in 9 months for membranes prepared from the 2 and 5 % (w/w) dope solutions (Triblock2 and Triblock5 in table 2). These membranes remained hydrophilic during the study period with WCA < 70°. In contrast, over the same period of time, the WCA of the membranes prepared with PEG homopolymer increased much more: 29° and 41° respectively (PEG2eq and PEG5eq membranes). At the end of the study period the WCA reached values (90°) close to those observed for pure PVDF membranes (ca. 105°). It is important to note that the PEG2eq and PEG5eq membranes were less hydrophilic (showed higher WCA) than their triblock copolymer counterparts at t=0. This indicates that a significant quantity of the PEG homopolymer is lost during the preparation process (likely in the coagulation bath). In all membrane samples the additives (both the commercial PEG homopolymer and the synthesized triblock copolymer) did leach out of the membrane matrix within the first 60 days. However, the WCA results clearly show that the triblock copolymer loss is marginal (8-9°) compared to that of the PEG homopolymer (17-26°) confirming that the presence of the short PVDF blocks does help in retaining the hydrophilic PEG chains in the membrane matrix.

Table 2. WCA evolution of the membranes during the ageing experiment.

Membrane ID	Mean WCA at 10 s [° of change].		
	0 month	2 month	9 month
Triblock2	54	63 [9]	67 [13]
Triblock5	39	47 [8]	53 [14]
PEGeq2	61	78 [17]	90 [29]
PEGeq5	47	73 [26]	88 [41]

To quantify the amount of the additive (triblock copolymer and PEG homopolymer) loss, ¹H NMR experiments were carried out on the membranes before and after the ageing process. Integrals of the PVDF (2.6-3.0 ppm) and PEG (3.5 ppm) signals were used to determine the percentage of additive loss (see Table 3 and S6). The CH₂ signal of the PVDF ($\int_{2.66}^{3.01} \text{CH}_2(\text{PVDF})$) was taken as reference, and the mass fraction of PEG loss was calculated using equation 5.

311 **Table 3. PEG loss after the ageing process.**

Membrane ID	$M_{\text{PEG}}^*/M_{\text{PVDF}}$	Additive loss after 2 months (%)	Additive loss after 9 months (%)
Triblock2	$5.63 \cdot 10^{-2} *$	9.1	21.4
PEG2eq	$5.64 \cdot 10^{-2}$	41.2	58.8
Triblock5	$12.51 \cdot 10^{-2} *$	21.4	27.3
PEG5eq	$12.50 \cdot 10^{-2}$	41.7	70.8

312 Note: the signals of the high molar mass PVDF and the short PVDF blocks of the triblock copolymer overlap. *PEG from the triblock
313 copolymer additive.

314 The data summarized in Table 3 shows that the loss of triblock copolymer is much lower than that of the
315 PEG homopolymer. For the membrane prepared from the 2 wt % triblock copolymer dope solution
316 (Triblock2), about 21 % of the PEG was lost during the study period (9 months) while about 59 % of the
317 PEG homopolymer was lost over the same time for the membrane prepared using PEG homopolymer
318 (PEG2eq). This loss rose to 27 % and 71 % for the membranes prepared from the 5 wt % triblock co-
319 polymer (Triblock5) or PEG homopolymer (PEG5eq) dope solution respectively. This set of data indi-
320 cates that 2 wt % of triblock copolymer additive is sufficient to confer long-lasting hydrophilicity to the
321 PVDF membranes. Higher triblock copolymer weight fraction leads to higher loss of the additive. These
322 results show that more atom-efficient (and maybe cheaper) PVDF membranes endowed with long last-
323 ing hydrophilicity could be prepared using such $\text{PVDF}_{50}\text{-}b\text{-PEG}_{138}\text{-}b\text{-PVDF}_{50}$ triblock copolymer addi-
324 tive.

325 For the Triblock2 membrane, flux reached up to $1400 \text{ L/h}\cdot\text{m}^2$ at 2 bar right after preparation (t_0). After 9
326 months the flux value halved to around $600 \text{ L/h}\cdot\text{m}^2$. This decrease is mainly due to the loss of hydro-
327 philicity caused by additive leaching (see Table 2 and 3) and water-retaining ability of the membrane,
328 and to a lower extent to fouling (bacteria growth) as shown in Figure S5. The Triblock5 membrane fol-
329 lowed a similar trend although the decrease in flux during the ageing period was lower (it only de-
330 creased by $200 \text{ L/h}\cdot\text{m}^2$). However both membranes present an improvement in terms of flux compared
331 to membranes prepared from PEG homopolymer as additive. The highest flux values obtained for mem-
332 branes prepared using the PEG homopolymer were 100 and $200 \text{ L/h}\cdot\text{m}^2$ (for PEG2eq and PEG5eq
333 membranes during the first filtration experiments) while the membranes containing the triblock copol-
334 ymer reach flux values of 650 and $1400 \text{ L/h}\cdot\text{m}^2$ (for Triblock2 and Triblock5 respectively).

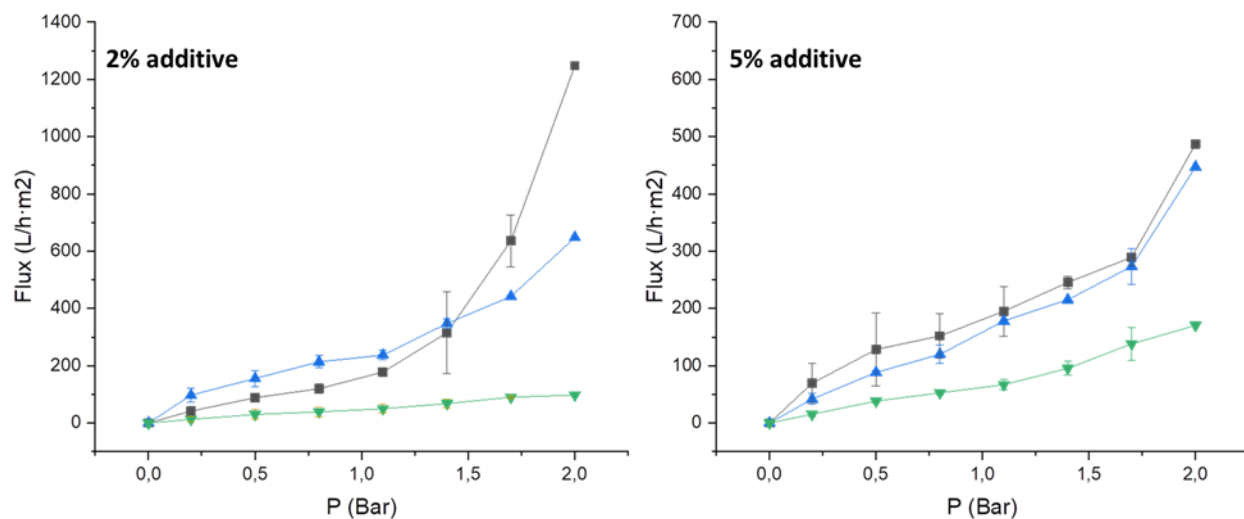


Figure 3. Flux vs. pressure of PVDF membranes prepared using dope solutions containing 2% w/w (left) and 5% w/w (right) PVDF-*b*-PEG-*b*-PVDF block copolymer. The flux measurements were performed right after membrane preparation (black squares), after 9 months (blue triangles) and compared to flux values obtained for membranes prepared using dope solutions containing PEG homopolymer concentrations equivalent to the total PEG concentrations of triblock doped casting solutions (green inverted triangle) just after preparation ($t=0$).

The permeability plots (Figure S7) show that the membranes modified with the PEG homopolymer were almost insensitive to pressure with a low permeability ($110\text{--}150\text{ L h}^{-1}\text{ m}^{-2}\text{ bar}$) over the pressure range tested (0-2 bar). The permeability profile of the membranes prepared using the 2 and 5% (w/w) triblock copolymer dope solution showed moderate fluctuations. This is most probably due to the pore size and pore density of the membrane rather than their degree of hydrophilicity. However, the structural integrity of the membranes prepared using PEG homopolymer as additive was higher than that of the membranes containing the triblock copolymer. This is likely due to the fact that the former effectively do not retain much PEG in their structure compared to the latter. In consequence their pores do not swell as much when in contact with water.

Since the SEM images of the membranes prepared using different triblock copolymer dope solutions (Figure 1) did not show major changes in structure or porosity, water uptake was used as an indirect method to estimate pore size and porosity (Table 4). Membranes prepared from 5 wt. % triblock copolymer dope solution were more porous (76%) than the membranes prepared from the 2 wt. % triblock copolymer dope solution (61%). However, membrane Triblock2 had larger average pore size (62-73 nm) compared to membrane Triblock5 which featured an average pore size of 43 - 50 nm. These data are in agreement with the flux values obtained for each membrane. The Triblock5 membrane had lower flux than the Triblock2 membrane over the entire ageing period. The PEG2eq and PEG5eq membranes had the smallest mean pore radii (ca. 17 nm for PEG2eq and 23 nm for PEG5eq) hence their low flux and permeability values.

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Table 4. Membrane porosity (ϵ) and mean pore size (r_m).

PVDF Membrane	Porosity (%)	Mean pore radii (nm)*
Triblock2	61	62-73
PEG2eq	41	17-19
Triblock5	76	43-50
PEG5eq	48	23-26

**Pore size estimated using two thicknesses (150 and 200 μ m)*

2. Conclusions

In summary, a well-defined PVDF-PEG-PVDF ABA triblock copolymer synthesized using RAFT and thia-Michael addition click chemistry was used as a hydrophilic additive for PVDF water filtration membranes. The triblock copolymer was blended with high molar mass PVDF in different proportions, and membranes were prepared via the NIPS process. The resulting porous membranes were fully characterized using SEM, ^1H NMR, WCA and filtration tests. These tests showed that the hydrophilicity of the membranes increased with increasing additive content. Control experiments performed on PVDF membranes prepared using PEG homopolymer as additive showed that most of the PEG leached out during the first 60 days following membrane preparation. It was also demonstrated that only small amounts of the triblock copolymer (2-5% w/w) were required to confer sufficient and long-lasting hydrophilicity to the PVDF membranes. Larger amounts of triblock copolymer led to membrane swelling and structural instability. This study suggests that migration of the copolymer additive towards the air-polymer interface or water-polymer interface and subsequent leaching still occurs. However, these phenomena are significantly decreased thanks to the presence of the short PVDF segments covalently attached to the PEG. These PVDF segments likely anchors the PEG block in the PVDF matrix by co-precipitation and co-crystallization with the high molar mass PVDF forming the bulk of the membrane. The strategy proposed here, based on the use of amphiphilic PVDF-containing block copolymers as hydrophilic additives, is able to significantly extend the operational lifetime of PVDF membranes for water purification applications.

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392 **Data availability**

393 The raw/processed data required to reproduce these findings cannot be shared at this time as the data
394 also forms part of an ongoing study.

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396 **References**

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- 398 [1] N.L. Le, S.P. Nunes, Materials and membrane technologies for water and energy sustainability,
399 SUSMAT. 7 (2016) 1–28. doi:10.1016/j.susmat.2016.02.001.
- 400 [2] Z. Cui, E. Drioli, Y.M. Lee, Recent progress in fluoropolymers for membranes, Prog. Polym. Sci.
401 39 (2014) 164–198. doi:10.1016/j.progpolymsci.2013.07.008.
- 402 [3] Q. Bi, Q. Li, Y. Tian, Y. Lin, X. Wang, Hydrophilic modification of poly(vinylidene fluoride)
403 membrane with poly(vinyl pyrrolidone) via a cross-linking reaction, J. Appl. Polym. Sci. 127
404 (2013) 394–401. doi:10.1002/app.37629.
- 405 [4] Y.Q. Wang, T. Wang, Y.L. Su, F.B. Peng, H. Wu, Z.Y. Jiang, Remarkable reduction of
406 irreversible fouling and improvement of the permeation properties of poly(ether sulfone)
407 ultrafiltration membranes by blending with pluronic F127, Langmuir. 21 (2005) 11856–11862.
408 doi:10.1021/la052052d.
- 409 [5] A. Kuila, D.P. Chatterjee, N. Maity, A.K. Nandi, Multi-functional poly(vinylidene fluoride) graft
410 copolymers, J. Polym. Sci. Part A Polym. Chem. 55 (2017) 2569–2584. doi:10.1002/pola.28671.
- 411 [6] J.R. Du, S. Peldszus, P.M. Huck, X. Feng, Modification of poly(vinylidene fluoride)
412 ultrafiltration membranes with poly(vinyl alcohol) for fouling control in drinking water
413 treatment, Water Res. 43 (2009) 4559–4568. doi:10.1016/j.watres.2009.08.008.
- 414 [7] M.J. Han, G.N.B. Baroña, B. Jung, Effect of surface charge on hydrophilically modified
415 poly(vinylidene fluoride) membrane for microfiltration, Desalination. 270 (2011) 76–83.
416 doi:10.1016/j.desal.2010.11.024.
- 417 [8] G. dong Kang, Y. ming Cao, Application and modification of poly(vinylidene fluoride) (PVDF)
418 membranes - A review, J. Memb. Sci. 463 (2014) 145–165. doi:10.1016/j.memsci.2014.03.055.
- 419 [9] H.J. Li, Y.M. Cao, J.J. Qin, X.M. Jie, T.H. Wang, J.H. Liu, Q. Yuan, Development and
420 characterization of anti-fouling cellulose hollow fiber UF membranes for oil-water separation, J.
421 Memb. Sci. 279 (2006) 328–335. doi:10.1016/j.memsci.2005.12.025.
- 422 [10] J. Liu, X. Shen, Y. Zhao, L. Chen, Acryloylmorpholine-grafted PVDF membrane with improved
423 protein fouling resistance, Ind. Eng. Chem. Res. 52 (2013) 18392–18400.
424 doi:10.1021/ie403456n.
- 425 [11] F. Liu, N.A. Hashim, Y. Liu, M.R.M. Abed, K. Li, Progress in the production and modification
426 of PVDF membranes, J. Memb. Sci. 375 (2011) 1–27. doi:10.1016/j.memsci.2011.03.014.
- 427 [12] R. Revanur, B. McCloskey, K. Breitenkamp, B.D. Freeman, T. Emrick, Reactive amphiphilic
428 graft copolymer coatings applied to poly(vinylidene fluoride) ultrafiltration membranes,
429 Macromolecules. 40 (2007) 3624–3630. doi:10.1021/ma0701033.
- 430 [13] N. Li, C. Xiao, S. An, X. Hu, Preparation and properties of PVDF/PVA hollow fiber membranes,
431 Desalination. 250 (2010) 530–537. doi:10.1016/j.desal.2008.10.027.
- 432 [14] A. Saffar, P.J. Carreau, M.R. Kamal, A. Ajji, Hydrophilic modification of polypropylene

- microporous membranes by grafting TiO₂ nanoparticles with acrylic acid groups on the surface, *Polymer (Guildf)*. 55 (2014) 6069–6075. doi:10.1016/j.polymer.2014.09.069.
- [15] S. Liang, K. Xiao, Y. Mo, X. Huang, A novel ZnO nanoparticle blended polyvinylidene fluoride membrane for anti-irreversible fouling, *J. Memb. Sci.* 394–395 (2012) 184–192. doi:10.1016/j.memsci.2011.12.040.
- [16] 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. Memb. Sci.* 318 (2008) 405–412. doi:10.1016/j.memsci.2008.03.013.
- [17] A. Akbari, R. Yegani, B. Pourabbas, A. Behboudi, Analysis of antifouling behavior of high dispersible hydrophilic poly (ethylene glycol)/ vinyl functionalized SiO₂ nanoparticles embedded polyethylene membrane, 76 (2017) 20652. doi:10.5004/dwt.2017.20652.
- [18] P. Membranes, N. Dow, N. Milne, J. Zhang, Membrane Distillation Trial on Textile Wastewater Containing Surfactants Using Hydrophobic and Hydrophilic-Coated Polytetrafluoroethylene, (n.d.). doi:10.3390/membranes8020031.
- [19] N. Khumalo, L. Nthunya, S. Derese, M. Motsa, A. Verliefde, Separation and Purification Technology Water recovery from hydrolysed human urine samples via direct contact membrane distillation using PVDF / PTFE membrane, *Sep. Purif. Technol.* 211 (2019) 610–617. doi:10.1016/j.seppur.2018.10.035.
- [20] B.J. Cha, J.M. Yang, Effect of high-temperature spinning and PVP additive on the properties of PVDF hollow fiber membranes for microfiltration, *Macromol. Res.* 14 (2006) 596–602. doi:10.1007/BF03218730.
- [21] X. Wang, C. Chen, H. Liu, J. Ma, Preparation and characterization of PAA/PVDF membrane-immobilized Pd/Fe nanoparticles for dechlorination of trichloroacetic acid, *Water Res.* 42 (2008) 4656–4664. doi:10.1016/j.watres.2008.08.005.
- [22] D. Sun, D. Yue, B. Li, Z. Zheng, X. Meng, Preparation and Performance of the Novel PVDF Ultra filtration Membranes Blending With PVA Modified SiO₂ Hydrophilic Nanoparticles, (2019). doi:10.1002/pen.25002.
- [23] J. Zhao, J. Yi, L. Shi, R. Wang, Explorations of combined nonsolvent and thermally induced phase separation (N-TIPS) method for fabricating novel PVDF hollow fiber membranes using mixed diluents, *J. Memb. Sci.* 572 (2019) 210–222. doi:10.1016/j.memsci.2018.11.015.
- [24] O. Benhabiles, F. Galiano, T. Marino, H. Mahmoudi, Preparation and characterization of TiO₂ - PVDF / PMMA blend membranes using an alternative non-toxic solvent for UF / MF and photocatalytic application, (2018) 1–20.
- [25] 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, *Biomaterials*. 23 (2002) 2659–2666. doi:10.1016/S0142-9612(01)00406-9.
- [26] N. Ghaemi, P. Daraei, S. Palani, Surface Modification of Polysulfone Membranes Using Poly (Acrylic Acid) - Decorated Alumina Nanoparticles, (2018) 261–269. doi:10.1002/ceat.201700124.
- [27] F. Liu, B.K. Zhu, Y.Y. Xu, Improving the hydrophilicity of poly(vinylidene fluoride) porous membranes by electron beam initiated surface grafting of AA/SSS binary monomers, *Appl. Surf. Sci.* 253 (2006) 2096–2101. doi:10.1016/j.apsusc.2006.04.007.
- [28] P. Wang, K.L. Tan, E.T. Kang, K.G. Neoh, Plasma-induced immobilization of poly (ethylene

glycol) onto poly (vinylidene fluoride) microporous membrane, *J. Memb. Sci.* 195 (2002) 103–114.

[29] H. Zhang, X. Lu, Z. Liu, Z. Ma, S. Wu, Z. Li, Study of the dual role mechanism of water-soluble additive in low temperature thermally-induced phase separation, *J. Memb. Sci.* 543 (2017) 1–9. doi:10.1016/j.memsci.2017.08.032.

[30] T. Marino, F. Russo, A. Figoli, H. May, The Formation of Polyvinylidene Fluoride Membranes with Tailored Properties via Vapour / Non-Solvent Induced Phase Separation, (2018) 1–17. doi:10.3390/membranes8030071.

[31] R. Pervin, P. Ghosh, M.G. Basavaraj, Tailoring pore distribution in polymer films via evaporation induced phase separation , *RSC Adv.* 9 (2019) 15593–15605. doi:10.1039/c9ra01331h.

[32] A. Venault, Y.H. Liu, J.R. Wu, H.S. Yang, Y. Chang, J.Y. Lai, P. Aimar, Low-biofouling membranes prepared by liquid-induced phase separation of the PVDF/polystyrene-*b*-poly (ethylene glycol) methacrylate blend, *J. Memb. Sci.* 450 (2014) 340–350. doi:10.1016/j.memsci.2013.09.004.

[33] S. Park, Y. Ahn, M. Jang, H. Kim, K. Yong, Separation and Puri f i cation Technology E ff ects of methacrylate based amphiphilic block copolymer additives on ultra fi ltration PVDF membrane formation, *Sep. Purif. Technol.* 202 (2018) 34–44. doi:10.1016/j.seppur.2018.03.018.

[34] J.H. Kim, K.H. Lee, Effect of PEG Additive on Membrane Formation by Phase Inversion, *J. Memb. Sci.* 138 (1998) 153–163.

[35] Y. Yun, P. Le-Clech, G. Dong, D. Sun, Y. Wang, P. Qin, Z. Chen, J. Li, C. Chen, Formation kinetics and characterization of polyphthalazinone ether ketone hollow fiber ultrafiltration membranes, *J. Memb. Sci.* 389 (2012) 416–423. doi:10.1016/j.memsci.2011.11.007.

[36] J. Liu, Z. Zhong, R. Ma, W. Zhang, J. Li, Development of high-antifouling PPSU ultrafiltration membrane by using compound additives: Preparation, morphologies, and filtration resistant properties, *Membranes (Basel)*. 6 (2016). doi:10.3390/membranes6020035.

[37] E. Folgado, M. Guerre, A. Da Costa, A. Ferri, A. Addad, V. Ladmira, M. Semsarilar, “One-Pot” Aminolysis/Thiol-ene preparation of well-defined amphiphilic PVDF-*b*-PEG-*b*-PVDF triblock copolymers: Self-assembly behaviour in mixed solvents, *Polym. Chem.* (2019).

[38] X. Li, Y. Wang, X. Lu, C. Xiao, Morphology changes of polyvinylidene fluoride membrane under different phase separation mechanisms, 320 (2008) 477–482. doi:10.1016/j.memsci.2008.04.033.

[39] C. Feng, B. Shi, G. Li, Y. Wu, Preparation and properties of microporous membrane from for membrane distillation, 237 (2004) 15–24. doi:10.1016/j.memsci.2004.02.007.

[40] E. Folgado, M. Guerre, A. Da Costa, A. Ferri, A. Addad, V. Ladmira, M. Semsarilar, “One-Pot” Aminolysis/Thia-Michael Addition preparation of well-defined amphiphilic PVDF-*b*-PEG-*b*-PVDF triblock copolymers: Self-assembly behaviour in mixed solvents, *Polym. Chem.* (2019).

[41] D.-M. Wang, J.-Y. Lai, Recent advances in preparation and morphology control of polymeric membranes formed by nonsolvent induced phase separation, *Curr. Opin. Chem. Eng.* 2 (2013) 229–237. doi:10.1016/j.coche.2013.04.003.

[42] M.W. Matsen, Effect of Architecture on the Phase Behavior of AB-Type Block Copolymer Melts, *Macromolecules.* (2012) 2161–2165. doi:10.1021/ma202782s.

518 [43] C. Heng Loh, R. Wang, Effects of Additives and Coagulant Temperature on Fabrication of High
519 Performence PVDF/Pluronic F127 Blend Hollow Fiber Membranes via Nonsolvent Induced
520 Phase Separation, Chinese J. Chem. Eng. 1 (2012) 71–79. doi:10.1016/S1004-9541(12)60365-6.
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