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1 **Stepwise synthesis of oligoamide coating on a porous support: Fabrication**
2 **of a membrane with controllable transport properties**

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4 Paramita Manna¹, Alberto Tiraferri², Marco Sangermano³, Roy Bernstein^{1,*}, and Roni
5 Kasher^{1,*}
6

7 ¹Department of Desalination and Water Treatment, Zuckerberg Institute for Water Research,
8 Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev,
9 Midreshet Ben-Gurion, 8499000, Israel

10 ²Department of Environment, Land and Infrastructure Engineering (DIATI), Politecnico di
11 Torino, Corso Duca degli Abruzzi 24, 10129, Torino, Italy

12 ³Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso
13 Duca degli Abruzzi 24, 10129, Torino, Italy

14
15 *Corresponding authors; royber@bgu.ac.il (R.B.); kasher@bgu.ac.il (R.K.)

16 **ABSTRACT**

17 Porous polymeric membranes are widely used in potable water purification, wastewater
18 treatment, the food and pharmaceutical industries, and haemodialysis. However, producing
19 specialized membranes with diverse transport properties is challenging. A method for
20 fabricating membranes with controllable transport properties is described here by stepwise
21 synthesis of aromatic oligoamide on a porous polymeric support. The use of aromatic
22 oligoamide affords good water permeance due to its hydrophilic character. Alternate
23 couplings of trimesoyl chloride and meta-phenylenediamine yielded an oligoamide dendrimer
24 that was covalently bonded to the support. The water permeance and molecular weight cutoff
25 (MWCO) of the synthesized membranes were controlled (with values of 4.6 to 543
26 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and 22.6 to 332 kDa, respectively) by adjusting the number of oligoamide
27 synthesis cycles in the range of 2.5 – 20.5. The oligoamide membrane with 5.5 synthetic
28 cycles showed a high rejection of the negatively charged rose bengal dye (95% rejection)
29 with high flux ($126.4 \pm 4.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 5.2 bar), as compared with other membranes reported
30 in the literature. The fabricated membranes are potentially highly useful for the separation of
31 macromolecules with specific ranges of molecular weight, for industrial separations that
32 require membranes with tunable MWCO ranges, or for the separation of charged
33 macromolecules.

34

35

36 **Keywords:** Stepwise synthesis; oligoamide; polyacrylonitrile; molecular weight cutoff; rose
37 bengal separation.

38 1. Introduction

39

40 Water scarcity is a serious problem, and the shortage of fresh water worldwide is only
41 expected to worsen in the coming decades [1]. Membrane processes are key technologies for
42 wastewater treatment, desalination, and reduction of industrial waste, as well as for
43 improving water-based industrial processes [2]. Methods to prepare porous membranes
44 include phase inversion [3, 4], track-etching, stretching, and sintering [5-7], with phase
45 inversion being the most widely applied and investigated. Dense nanofiltration (NF) and
46 reverse osmosis (RO) membranes can either be prepared by phase inversion (asymmetric
47 membranes), or by interfacial polymerization producing thin-film composite (TFC)
48 membranes [8]. Other methods for producing TFC membranes include coating, grafting, and
49 layer-by-layer deposition [9-13].

50 Nevertheless, new methods for fabricating advanced membranes with diverse transport
51 properties and specialized performance are highly needed, and are a target of extensive
52 research. For example, the self-assembly of block-polymers and template leaching have been
53 used to prepare membranes with very narrow pore-size distributions and advanced
54 performance [14]. The incorporation of organic and inorganic additives (such as
55 nanoparticles) into the polymer casting solution during the phase inversion process may tune
56 the pore size and morphology, and can alter the hydrophilic/hydrophobic properties of the
57 membrane [15-18]. The surface charge of the membrane which can enhance the selectivity of
58 charged solutes, can be varied by using chemically modified polymers (e.g., sulfonated
59 polyphenyl sulfone) [19] or through surface grafting using charged monomers [20-22].

60 Aromatic polyamide is used successfully as a barrier film for reverse osmosis (RO) and
61 nanofiltration (NF) dense membranes due to its hydrophilic character, which enables high
62 water permeance, and due to its crosslinking propensity [23]. Nevertheless, its conventional
63 preparation by interfacial polymerization limits the control of its thickness and crosslinking
64 degree and hence its transport properties. Therefore, strategies of preparing polyamide films
65 with controlled properties are explored. Karan *et al.* performed interfacial polymerization on
66 a substrate having a sacrificial – intermediate layer obtaining a sub-10 nm polyamide film
67 that was installed on ceramic support to obtain organic solvent nanofiltration composite
68 membrane with high solvent permeances [24]. Chowdhury *et al.* used electro-spraying to
69 deposit small droplet sizes of acid chloride and diamine monomers directly on a support and
70 obtained reverse osmosis membranes with very thin polyamide films and controllable
71 thicknesses [25].

72 A different approach was demonstrated by Steiner *et al.* (2011) [26] who synthesized an
73 aromatic oligoamide on gold by a stepwise series of coupling reactions, where unlike the
74 interfacial polymerization, a very thin oligoamide layer was formed and its thickness could
75 be varied by the number of synthetic cycles. The stepwise approach of synthesizing aromatic
76 oligoamide has recently been used by several research groups to fabricate novel polyamide
77 membranes on porous supports. For example, Wu *et al.* used repeated layer-by-layer
78 couplings of polyethyleneimine and trimesoyl chloride (TMC) on a polyethersulfone
79 substrate [27] to make a membrane with permeability in the range of NF membranes. In
80 another study, polyelectrolytes were pre-deposited on porous poly(acrylonitrile) membranes,
81 then a stepwise preparation of aromatic polyamide barrier layer was successfully introduced
82 [28, 29]. The resulting membranes performed similarly to aromatic polyamide NF
83 membranes fabricated by conventional interfacial polymerization.

84 The recent studies described above used anchoring polymers between the porous substrate
85 and the synthesized polyamide. Amelio *et al.* [30] recently used stepwise synthesis [26] to
86 prepare an oligoamide layer covalently attached to an inorganic porous support. The
87 synthesis was initiated by functionalization of alumina support with amino-silane groups,
88 followed by stepwise assembly of TMC and meta-phenylenediamine (mPD); the water
89 permeance and salt rejection of the resulting membrane were in the range of NF membranes.

90 Here, direct stepwise synthesis of aromatic oligoamide films on a porous polymeric support
91 was studied for developing membranes with variable properties, which can be tuned through
92 the preparation conditions. The choice of oligoamide was based on its hydrophilic character,
93 which enables high water permeance, and its high stability. The oligoamide was covalently
94 bonded to the support without an anchoring polymeric layer; as such, this type of membrane
95 is expected to have high mechanical stability, which can be advantageous during backwash or
96 operation under extreme conditions. To the best of our knowledge, this is the first report of
97 stepwise synthesis of oligoamide film directly onto an organic porous support.
98 Polyacrylonitrile (PAN) was chosen as the material of the support membrane because its
99 functionalization with amine groups, which was needed for initiating the oligoamide
100 synthesis, was feasible. A key challenge of developing the synthetic method was finding
101 conditions compatible with the polymeric support; e.g., the correct choice of solvents. A
102 series of membranes was prepared with different numbers of synthetic cycles, the physico-
103 chemical properties of the membranes were characterized, and the water permeance, MWCO,
104 and selectivity of the resulting membranes were determined.

105

106 **2. Experimental Section**

107 *2.1. Materials*

108 Powdered polyacrylonitrile (PAN; 150 kDa) and N-methyl-2-pyrrolidone (NMP) were
109 supplied by Scientific Polymer Products (Ontario, NY, USA) and Bio lab (Jerusalem, Israel),
110 respectively. Diethylenetriamine (DETA), polyethylene glycol (PEG), polyethylene oxide
111 (PEO), mPD, TMC, sucrose, glucose, orange-II, rose bengal, triethanolamine, and 1,4-
112 dioxane were purchased from Sigma Aldrich (St Louis, MO, USA). Sodium carbonate and
113 sodium sulfate were purchased from Frutarom (Haifa, Israel). Except PEG and PEO, all
114 chemicals were used as received. A dialysis tube (Sigma Aldrich, St Louis, MO; MWCO
115 14,000 Da) was used to purify the PEG of molecular weight higher than 35 kDa and PEO.
116 Magnesium sulfate (MgSO₄) was purchased from Carlo Erba (Rodano, Italy). Commercial,
117 flat-sheet, PAN membranes (UlturaTM brand, Long Beach, CA, USA; MWCO 75 kDa) were
118 mainly used as the supports for the fabrication of oligoamide membranes; otherwise, PAN
119 membranes were cast in-house using non-solvent induced phase separation (see details
120 below).

121 *2.2. Membrane fabrication*

122 *2.2.1. Preparation of PAN membranes*

123 A solution of 12% (w/w) PAN in NMP was prepared by stirring for 12 h with subsequent
124 standing for 12 h to remove air bubbles. The membranes were cast on a poly(propylene)
125 support by phase inversion, where double distilled water was used as the non-solvent in the
126 coagulation bath. Membranes were stored in double-distilled water for 24 h before use.

127 *2.2.2. Amination of the PAN membranes*

128 PAN membranes were aminated using DETA (31%) as the amine in an aqueous solution
129 (**Scheme 1**, Step 1) with 1% sodium carbonate [31]. The reaction was continued at a fixed
130 temperature of 60 °C for different times (2–10 h). The degree of amination of the membranes
131 was measured using orange-II staining (see below).

132 *2.2.3. Stepwise synthesis of oligoamide membranes*

133 Oligoamide membranes were synthesized as depicted in Scheme 1 (Steps II–IV), using
134 aminated PAN membranes as the support for coupling alternately mPD and TMC [26]. The
135 aminated PAN membranes were installed in a metallic dead-end filtration cell (porous disc of
136 38 mm diameter) and washed once with 1,4-dioxane for 10 min. The first cycle of synthesis
137 was initiated by adding 40 mM solution of TMC in dioxane, and the reaction proceeded for 2
138 min with shaking on an orbital platform shaker (Heidolph Unimax 1010, Germany) at room
139 temperature. Excess unreacted monomers were washed once for 2 min with dioxane on an
140 orbital shaker; then, 5 mL 1,4-dioxane were filtered through the membranes by applying N₂
141 pressure, and the membranes were again washed for 1 min with 1,4-dioxane on the orbital
142 shaker. Subsequently, 50 mM of mPD in dioxane was added into the cell, which was shaken
143 for 2 min, and the membrane was subsequently washed again thoroughly with dioxane as
144 described above. The successive TMC and mPD couplings (Steps II and III, Scheme 1) were
145 repeated 1.5 (i.e., one time each, plus an additional Step II), 4.5 times, 9.5 times, 14.5 times,
146 or 19.5 times, to perform 2.5, 5.5, 10.5, 15.5, and 20.5 reaction cycles, respectively, leading
147 to membranes designated as OL-2.5, OL-5.5, OL-10.5, OL-15.5, and OL-20.5. Finally, the
148 reaction was completed, including hydrolysis of the residual acyl chloride groups, by
149 treatment in water at 50 °C for 15 min (IV, Scheme 1) and washing with water. The
150 membranes were stored in water prior to use.

151 2.3. Chemical characterization

152 The degree of amination of the aminated PAN membranes was calculated by staining with
153 orange-II dye [32]. The membranes were stained with 0.05 mM orange-II solution in HCl
154 (pH 3) for 3 h, and rinsed with the HCl solution until the rinsing solution became colorless.
155 Then, the adsorbed dye was eluted with a minimal volume of 30% (v/v) triethanolamine in
156 water for 2 h. The absorbance of the dye was measured at 468 nm (UV-1800
157 spectrophotometer, Shimadzu) with reference to a 30% (v/v) triethanolamine solution. The
158 concentration of the eluting solution was determined by using a calibration curve of orange-II
159 dye in 30% (v/v) triethanolamine solution. The calculation of degree of amination was based
160 on the membrane area, the volume of eluate, and the dye concentration of the eluting
161 solution.

162 Surface functional groups of the oligoamide membranes were characterized by ATR-FTIR
163 spectroscopy with a VERTEX 70-FTIR spectrometer (Bruker Optics, Ettlingen, Germany) at
164 4 cm⁻¹ resolution. The system was equipped with a Miracle ATR attachment with a reflection

165 diamond-coated KRS-5 crystal (Pike, Madison, WI, USA). Before analyses, the membranes
166 were dried in a vacuum oven at 40 °C. The IR analyses were performed in 3-4 different
167 locations on each membrane sample, and the average spectra are reported.

168 Scanning electron microscopy (SEM) of surface topography and cross-sections of the
169 membranes were performed with a Quanta 200 microscope (Field Electron and Ion
170 Company, Thermo Fisher Scientific, USA). Cross-sectional SEM analyses were performed
171 using OL-15.5 membranes synthesized on PAN supports cast in the lab (as described in
172 Section 2.2.1), because the commercial PAN membranes did not allow cross-sectional
173 analysis owing to their mechanical reinforcement. Surface topography SEM was performed
174 using oligoamide membranes fabricated on commercial PAN membranes.

175 *2.4. Membrane performance*

176 Membrane performance tests were conducted using a dead-end filtration system with an
177 effective membrane area of 11.34 cm² equipped with a magnetic stirrer.

178 *Membrane permeability:* The permeance of the membranes, L_p , was determined by
179 measuring the permeate volume, divided by the time of collection of the permeate, the area of
180 the membrane, and the pressure at which the measurement was carried out.

181 *Rose Bengal separation:* Separation of rose bengal dye (MW 973.67 g/mol; 1017.65 g/mol of
182 the di-sodium salt) from water was conducted using the OL-2.5 and OL-5.5 membranes.
183 Prior to dye filtration, the membranes were compressed by filtration with water at a constant
184 pressure. Then, the filtration of rose bengal solution (20 μM) was conducted for 50 min with
185 constant stirring. The concentration of rose bengal in the permeate and in the feed solutions
186 was measured at 548 nm using UV-spectrophotometer (UV-1800, Shimadzu) and the
187 rejection of rose bengal was calculated using Eq. (1), where C_p and C_f are the concentrations
188 of permeate and feed, respectively. All the rejection and permeability data are the average of
189 three different measurements.

$$190 \text{ Rejection, } R (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (1)$$

191 *Salt separation:* The salt selectivity, expressed as the rejection rate (R), was evaluated by
192 filtering 1 g/L solutions of Na₂SO₄ or MgSO₄, and measuring the feed and permeate
193 conductivities upon reaching steady-state. The rejection rate was calculated by Eq. (2),

194 Rejection, R (%) = $\left(1 - \frac{\kappa_p}{\kappa_f}\right) \times 100$ (2)

195 where κ_f and κ_p are the specific conductivities of the feed and permeate solutions,
196 respectively.
197

198 *Molecular weight cut-off (MWCO)*: The MWCO of each membrane was determined using
199 glucose, sucrose, PEG (M_n 6 and 35 kDa), and PEO (M_n 100, 200, and 400 kDa) as
200 molecular markers. Solutions of 100 mg/L of the molecular markers in Milli-Q water were
201 prepared separately. The membranes were initially compacted with water. The solutions were
202 then filtered through the membranes using a dead-end filtration system at pressures of 5–20
203 bar and under continuous stirring (500 rpm) to minimize the effect of concentration
204 polarization. The concentrations of the molecular markers were determined in the feed and in
205 the permeate upon reaching steady-state conditions. The concentration of the glucose and
206 sucrose were determined by refractive index and Brix number measurements using a
207 refractometer (Schmidt Haensch High Performance Refractometer, Texas, USA), whereas the
208 concentrations of the macromolecules were determined by measuring the total organic carbon
209 (TOC) concentrations of the feed and permeate solutions using a TOC analyzer (Multi N/C,
210 2100S, Analytikjena, Germany). For all markers, percentages of rejection were calculated
211 according to Eq. (1) and plotted against the molecular weight of the marker. The MWCO for
212 each membrane was determined from the resulting graph by extracting the molecular weight
213 for 90% rejection.

214 2.5. Mean pore size calculation

215 The mean pore size of the membranes was estimated according to the study of S. Singh *et al.*
216 [33]. Initially, the Stokes radii of the molecular markers were calculated using Eq. (3) for
217 PEG and Eq. (4) for PEO

218 $a = 16.73 \times 10^{-3} M_w^{0.557}$ (3)

219 $a = 10.44 \times 10^{-3} M_w^{0.587}$ (4)

220 where a is the Stokes radius (nm) of the PEG or PEO, and M_w is the molecular weight
221 (g/mol). The radius of glucose and sucrose molecules were taken as 0.38 and 0.5 nm,
222 respectively.

223 By ignoring the steric and hydrodynamic interactions between the solute and membrane
224 during separation [34, 35], the mean pore size and the geometric standard deviation of the
225 membrane can be considered the same as the mean solute size and the solute geometric
226 standard deviation. The solute rejection of each membrane was plotted against the solute

227 diameter, and the solute diameter that corresponded to 50% rejection was determined from
228 the graph. The geometric standard deviation about the mean diameter was determined from
229 the ratio of solute diameter at $R = 84.13\%$ to solute diameter at $R = 50\%$.

230

231 **3. Results and discussion**

232 The oligoamide material was chosen for the stepwise synthesis coating due to its hydrophilic
233 character, which enables high water permeance, and its stability. The stepwise synthesis was
234 performed according to the procedure described in our previous study [26] of oligoamide
235 synthesis on gold, where amine groups were used for the initial coupling stage. Hence, the
236 fabrication of oligoamide on a porous support requires the substrate to have amine
237 functionality. The porous supports used here were PAN ultrafiltration (UF) membranes,
238 because they can be functionalized easily with primary amino groups through their reaction
239 with polyamine compounds in a basic catalysis [31].

240 *3.1. Amination of the PAN support*

241 Amination was performed on the PAN membranes using DETA as the polyamine in aqueous
242 sodium carbonate at elevated temperatures (Scheme S1, Supporting Information, and Scheme
243 1, Step 1). The reaction conditions were optimized by evaluating both the amine content and
244 the permeance of the resulting aminated membranes. Comparing amination at 40, 60, and 80
245 °C showed that 60 °C resulted in similar amounts of amine groups as 80 °C, while the
246 reaction at 40 °C yielded substantially lower amine density. The degree of amination of
247 membranes prepared at 60 °C for different durations was also investigated, and is
248 summarized in Table 1. The amine content after 2 h reaction (A2H, Table 1) was lower
249 (1.094×10^{-4} mmol/cm²) than after 5 or 10 h (1.501 and 1.561×10^{-4} mmol/cm², respectively).
250 The 10 h-reaction membrane was substantially less permeable to water than all the others.
251 Therefore, reaction at 60 °C for 5 h was chosen for the subsequent experiments, as it gave the
252 most suitable combination of water permeance and degree of amination. The amination of
253 PAN membranes reported earlier by Neghlani *et al.* [31, 36] used reactions at 90 °C. In the
254 present study, we optimized the amination procedure to minimize membrane deterioration,
255 finding that the reaction at 60 °C for 5 h yielded amine densities that were comparable to
256 those formed at higher temperatures with 10 h reaction time.

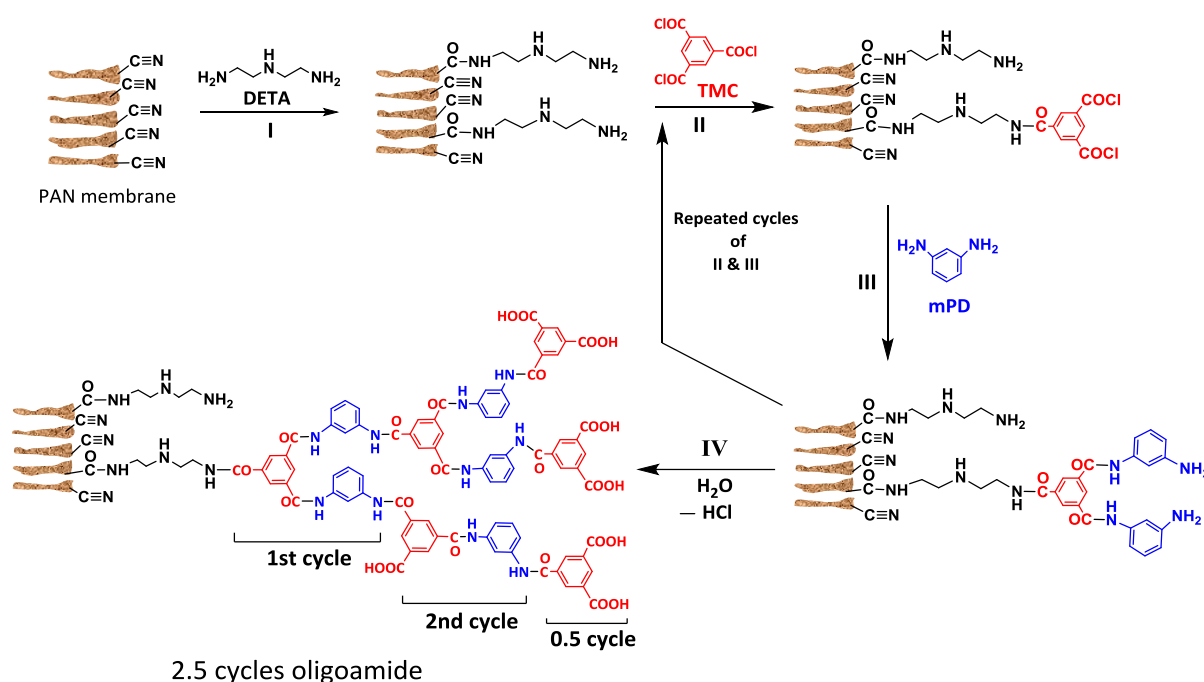
257

258 **Table 1.** Water permeance and surface density of amine groups of PAN membranes aminated
 259 for different reaction times at 60 °C in the presence of DETA.

Support membrane	Reaction time (h)	Amine content ^a (mmole/cm ²)	Water permeance (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)
PAN (Pristine)	0	3.86×10 ⁻⁶	534.6±15.9
Aminated PAN (A2H)	2	1.094×10 ⁻⁴	481.3±14.3
Aminated PAN (A5H)	5	1.501×10 ⁻⁴	436.2±27.3
Aminated PAN (A10H)	10	1.561×10 ⁻⁴	223.7±7.4

260 ^aMeasured by orange-II adsorption assay.

261



262

263 **Scheme 1.** Stepwise preparation of oligoamide on an amine functionalized porous PAN
 264 membrane, with detailed structure of oligoamide after 2.5 cycles. Step I: 31%
 265 diethylenetriamine (DETA) and 1% Na₂CO₃ in water at 60 °C. Step II: 40 mM trimesoyl
 266 chloride (TMC) in 1,4-dioxane, 2 min. III: 50 mM meta-phenylenediamine (mPD) in 1,4-
 267 dioxane, 2 min. Step IV: H₂O at 50 °C, 15 min.

268

269

270 3.2. Selection of suitable solvents for oligoamide synthesis on PAN

271 The choice of appropriate solvents for the oligoamide synthesis (Steps II and III, Scheme 1)
 272 was crucial: the solvent or solvents had to dissolve the monomers (TMC, mPD) while not
 273 degrading the membrane. The stepwise synthesis of oligoamide on gold reported by Steiner

274 *et al.* [26] and the recent work of coating oligoamide on alumina by Amelio *et al.* [30] used
 275 dimethylformamide (DMF) and dichloromethane (DCM) as the solvents for mPD and TMC,
 276 respectively. However, these solvents cannot be used here, as DMF and DCM dissolve most
 277 common polymers that are used for porous membranes preparation, including PAN
 278 membranes. The following solvents were identified as being compatible with PAN: toluene,
 279 hexane, water, and 1,4-dioxane. Table 2 lists the solubility of the monomers and the stability
 280 of PAN membrane in the four solvents, and thus shows that possible solvents for oligoamide
 281 synthesis are a combination of hexane or toluene for TMC, water for mPD, and toluene or
 282 1,4-dioxane for both TMC and mPD. As washing between each step is important, a single
 283 solvent for both monomers is preferable with respect to synthesis with two immiscible
 284 solvents. Previous studies of molecular layer-by-layer approaches have used toluene [28, 29,
 285 37], which does not dissolve TMC or mPD well. Given that the monomers were more soluble
 286 in 1,4-dioxane than in toluene (Table 2), 1,4-dioxane was chosen as the most suitable solvent
 287 for oligoamide synthesis in the present study.

288 **Table 2.** Comparison of solvents for oligoamide synthesis on PAN.

Solvent	mPD solubility ^a	TMC solubility	Permeance of PAN membrane (L·m ⁻² h ⁻¹ bar ⁻¹)	
			Before immersion	After immersion ^b
Hexane	NS	S	ND	ND
Toluene	PS	PS	ND	ND
Water	S	NS	ND	ND
1,4- dioxane/water solution	3:7 6:4 1:0	S S S	507.8 500.5 575.9	555.0 540.9 597.3

289 ^{a)} PS, partially soluble; S, soluble; ND, not determined; NS, non-soluble.

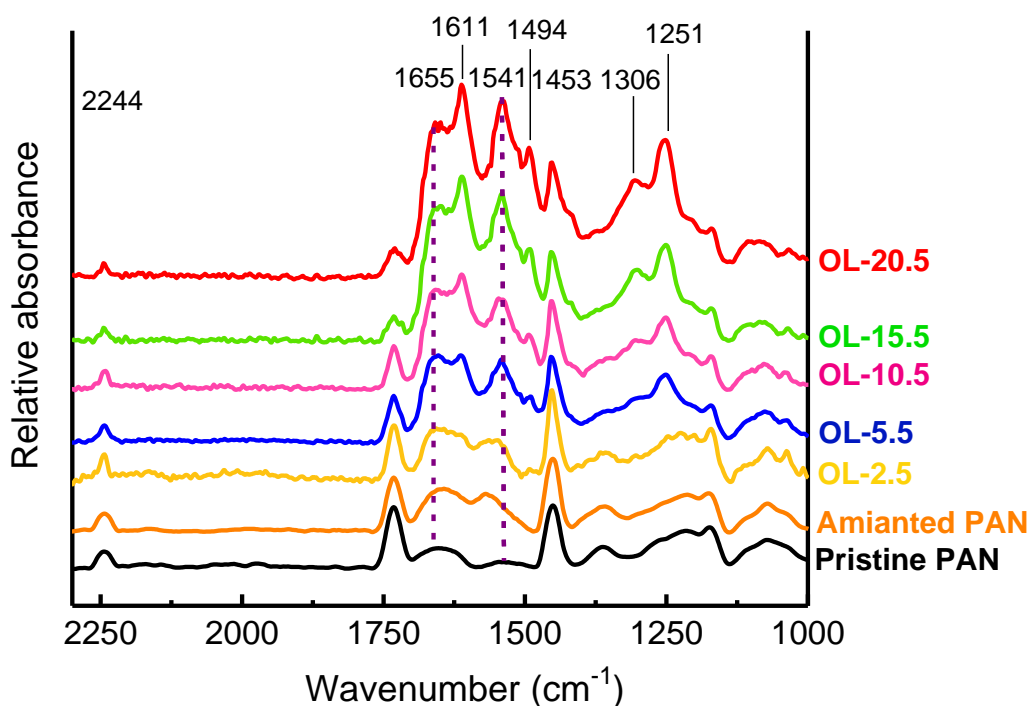
290 ^{b)} Immersion of the PAN membrane overnight in the solvent.

291 3.3. Oligoamide synthesis

292 Oligoamide synthesis was performed on the 5 h aminated PAN membrane as illustrated in
 293 Scheme 1, with both TMC and mPD dissolved in 1,4-dioxane. Successive TMC and mPD
 294 couplings (II and III, Scheme 1) were repeated to obtain oligoamide with 2.5, 5.5, 10.5, 15.5,
 295 and 20.5 synthesis cycles, including final hydrolysis (IV, Scheme 1) and extensive washing,
 296 and the membranes were designated as OL-2.5, OL-5.5, OL-10.5, OL-15.5, and OL-20.5.
 297 Although Steiner *et al.* [26] reported that their oligoamide synthesis on gold required organic
 298 base in the TMC reaction to neutralize the hydrochloric acid formed, we found that a base

299 was not essential for successful oligoamide synthesis on PAN membranes (see Table S1,
300 Supporting Information). All the syntheses ended with TMC coupling (half a cycle), as
301 carboxylic acid surface moieties make the membranes more hydrophilic than a typical
302 amine-terminated surface. A possible structure for an oligoamide membrane with 2.5
303 synthetic cycles is shown in Scheme 1.

304 Surface functional groups on the membranes were characterized using ATR-FTIR
305 spectroscopy (Fig. 1). All the vibrational spectra include a peak at 2244 cm^{-1} , which is
306 characteristic of the nitrile stretching vibration of the PAN membrane. The aminated
307 membranes displayed two new peaks at 1606 and 1572 cm^{-1} that are not shown by the
308 pristine membrane; these peaks are characteristic of amine -N-H bending (see Supporting
309 Information for the IR peaks of DETA). All the oligoamide membranes (2.5, 5.5, 10.5, 15.5,
310 and 20.5 synthetic cycles) show new IR bands at 1655 (amide-I, C=O stretching vibration)
311 and 1541 cm^{-1} (amide-II, N-H in-plane bending) that are attributed to the amide functionality
312 of oligoamide [38]. Notably, the relative intensities of the amide-I and amide-II peaks
313 increased with the number of synthetic cycles, as expected, owing to the increased size of the
314 oligoamide. The peak at 1611 cm^{-1} is assigned to aromatic ring breathing, and both peaks at
315 1494 and 1453 cm^{-1} result from aromatic C=C stretching. The peak at 1306 cm^{-1} and the
316 strong peak at 1251 cm^{-1} may be assigned to the C-N of amine and C-O stretching of
317 carboxylic acid, respectively. No characteristic peak of acyl halide functionality (at
318 1770 cm^{-1}) was observed, indicating the negligible presence of unreacted acyl chloride
319 groups. A peak at 1732 cm^{-1} was shown by the commercial PAN membranes (but those cast
320 in the lab); this peak is characteristic of -C=O stretching in carboxylic acids or esters, and
321 was probably due to additives present in the commercial membranes. Overall, the FTIR
322 spectra show peaks typical of oligoamide on PAN, and the oligoamide peak intensities
323 increased with increasing number of synthetic cycles as was expected from the stepwise
324 synthesis.



325

326 **Figure 1.** ATR-FTIR spectra of PAN-oligoamide membranes made by 2.5, 5.5, 10.5, 15.5,
 327 and 20.5 synthetic cycles (Scheme 1) alongside those of pristine PAN and aminated PAN
 328 membranes (A5H, Table 1).

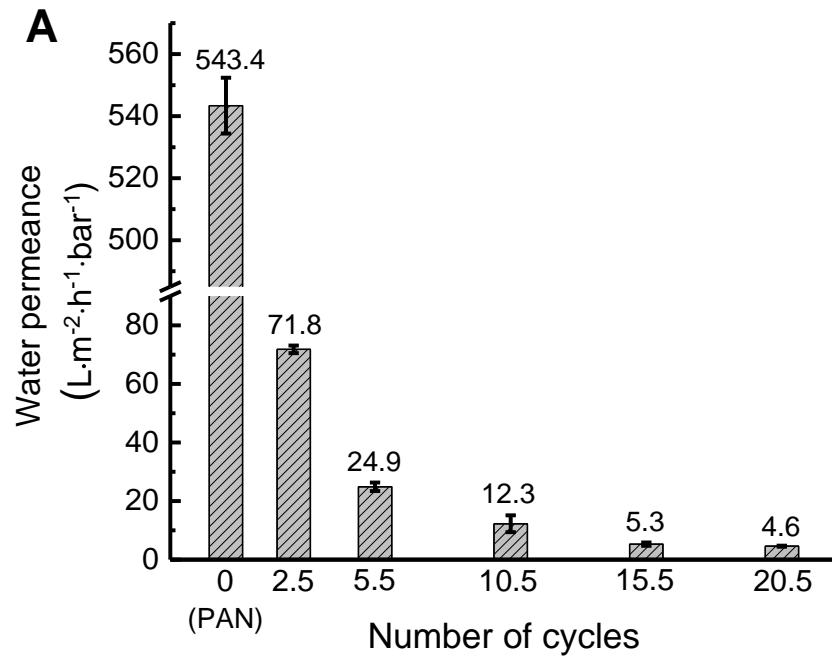
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330 3.4. Membrane transport properties

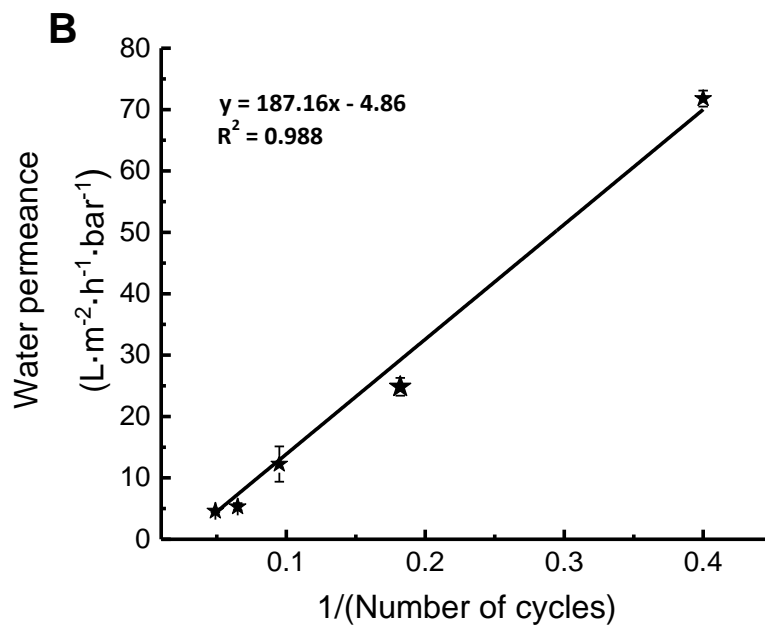
331 The synthesis of oligoamide on a porous PAN support is expected to produce membranes
 332 with diverse transport properties by reducing its permeability and pore size; therefore, the
 333 permeance was evaluated for membranes made with different numbers of oligoamide
 334 synthesis cycles (Fig. 2A). The pristine PAN membrane showed a water permeance of
 335 $543.4 \pm 9.0 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, which was indeed greater than any permeance shown by the
 336 oligoamide membranes, whose values decreased with the number of cycles of oligoamide
 337 synthesis. The permeance significantly decreased after 2.5 cycles (OL-2.5 membrane) to
 338 $71.8 \pm 1.3 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ and it decreased yet further to $4.6 \pm 0.2 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for the thickest
 339 membrane (OL-20.5). Fig. 2A also shows that the correlation between L_p and the number of
 340 synthetic cycles was not linear, e.g., membrane OL-15.5 showed an L_p value of 5.3 ± 0.6
 341 $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, which is close to that of membrane OL-20.5.

342 The permeance was inversely correlated with the number of oligoamide synthetic cycles (Fig.
 343 2B); this correlation is in agreement with the inverse relation between the permeance of a
 344 membrane and the thickness of its barrier layer [39]. Hence, it implies that increased number
 345 of synthetic cycles led to higher oligoamide thickness, as observed in our previous study of

346 oligoamide synthesis on gold [40]. Additionally, the reduced permeance can be explained by
347 the reduction in membrane pore volume and the subsequent increase in hydraulic resistance
348 due to the oligoamide coating of the pores.



349

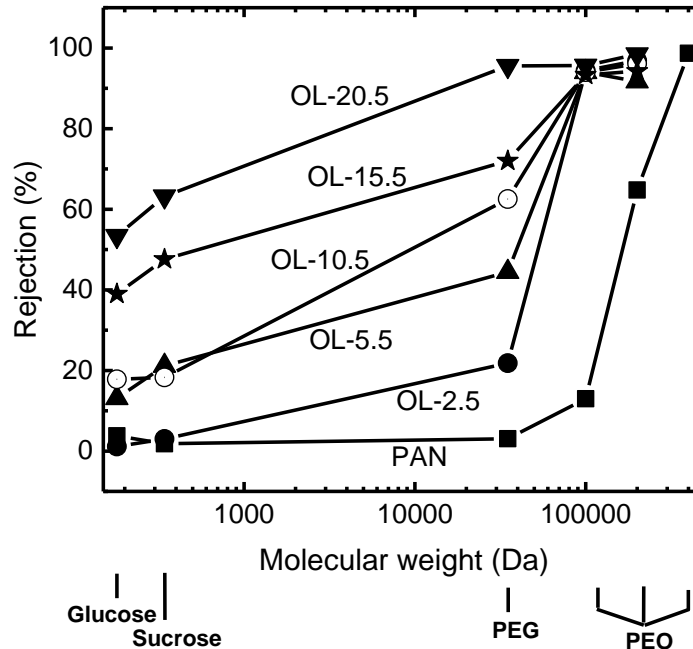


350

351 **Figure 2.** A) Water permeance (L_p) of membranes synthesized with 2.5, 5.5, 10.5, 15.5, and
352 20.5 cycles of oligoamide on aminated PAN support (5 h of amination), compared with
353 pristine PAN membrane, and (B) the correlation between the water permeance and the
354 inverse of number of synthetic cycles of oligoamide membranes.

355

356 To investigate the effect of the number of oligoamide synthetic cycles on the mean pore size
 357 of the membranes, MWCO values of the membranes were determined by filtration
 358 experiments using glucose, sucrose, PEG, and PEO as molecular markers. The solute
 359 rejection results are summarized in Fig. 3; it can be seen that higher number of oligoamide
 360 synthetic cycles resulted in higher solute rejection in all the range of molecular weights that
 361 were analyzed. Pristine PAN membrane showed the highest MWCO value of 332.0 kDa.
 362 Values for the OL-2.5, OL-5.5, OL-10.5, and OL-15.5 membranes were much lower (93.3,
 363 92.0, 87.0, and 84.2 kDa, respectively), and the value for the OL-20.5 membrane was lower
 364 still (22.6 kDa). Note that the OL-15.5 and OL-20.5 membranes showed significant rejection
 365 of glucose and sucrose (MW of 180 and 342 g/mol, respectively; Fig. 3), which are small
 366 molecules. The mean pore sizes for all the membranes were calculated from the MWCO data
 367 according to the literature [33] and are presented in Fig. S1, Supporting Information. The
 368 pristine PAN membrane had the largest pores (24.1 nm), and the pores of the oligoamide
 369 membranes narrowed with the number of synthetic cycles to 0.4 nm for membrane OL-20.5
 370 It should be noted that the standard deviations for membranes with high number of cycles
 371 were high (see Table S2 and Fig. S1, Supporting Information).



372

373 **Figure 3.** Rejection of polyethylene glycol (PEG), polyethylene oxide (PEO), glucose, and
 374 sucrose (solutions at 100 mg/L) by the oligoamide membranes in comparison with the
 375 pristine PAN membrane.

376

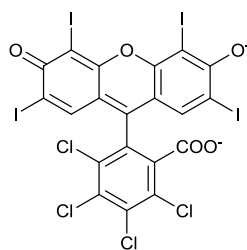
377 The separation performance of the oligoamide membranes was further tested by filtration
 378 experiments of rose bengal dye solutions. Filtration of 20 μM rose bengal solutions by the
 379 OL-2.5 and OL-5.5 membranes showed high rejection with good flux (Table 3). The OL-2.5
 380 membrane showed a reasonable rose bengal retention of $78.6 \pm 3.7\%$ with a high flux of 194
 381 $\pm 19.3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (at 3.5 bar) while the OL-5.5 membrane had a high rejection of $94.7 \pm 0.5\%$
 382 and a flux of $126 \pm 4.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (at 5.2 bar). The high retention for the negatively charged
 383 rose bengal with the OL-2.5 and OL-5.5 membranes having MWCO more than 90 kDa
 384 implies for the Donnan exclusion, probably due to the presence of charged carboxyl groups
 385 on the oligoamide surface which repels the negatively charged dye. Zeta potential analysis
 386 showed that OL-5.5 membrane is negatively charged in pH range of 4-9 (Fig. S2, Supporting
 387 Information). When comparing the rose bengal separation by the two oligoamide membranes,
 388 the higher rejection by the OL-5.5 membrane (compared to OL-2.5) can be explained by the
 389 increasing steric hindrance effect due to more synthetic cycles which is also evident in the
 390 water permeance data of the two membranes. The rose bengal dye separation performances
 391 obtained in this study for the oligoamide membranes were compared with other membranes
 392 that were recently published, and are summarized in Table S3 (Supporting Information). The
 393 permeability of OL-5.5 membrane is very high compared to most of the other membranes
 394 while maintaining a high retention of rose bengal (94.7%).

395 **Table 3.** Separation performance of rose bengal dye from water by OL-2.5 and OL-5.5
 396 membranes.

Membrane	Rose bengal rejection ^{a,b} (%)	Flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)
PAN	14.7 ± 1.0	1158.8 ± 64.6 at 0.5 bar
OL-2.5	78.6 ± 3.7	194.9 ± 19.3 at 3.5 bar
OL-5.5	94.7 ± 0.5	126.4 ± 4.2 at 5.2 bar

397 ^{a)} Rose bengal molecular weight (of the di anion) is 973.67 g/mol.

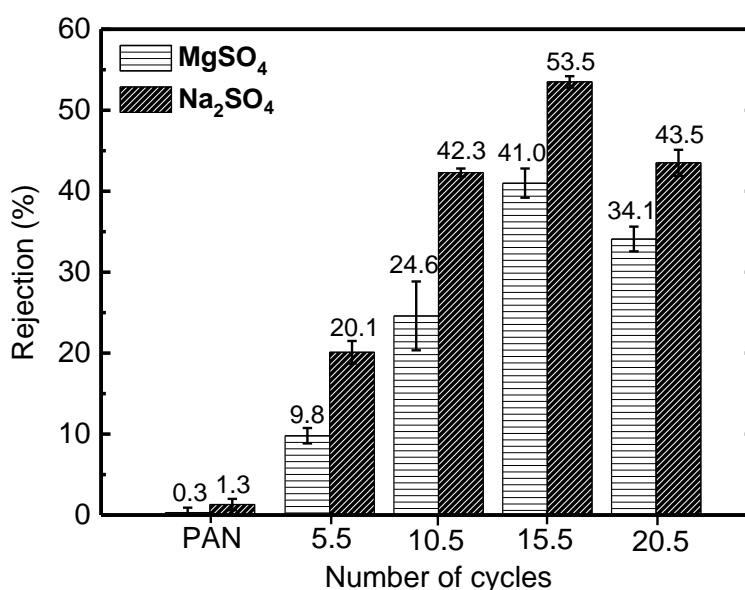
398 ^{b)}



Rose bengal

399

400 The membranes were also examined for salt rejection (Fig. 4). All the oligoamide membranes
 401 rejected Na_2SO_4 at a higher rate than MgSO_4 , suggesting the Donnan exclusion is an
 402 important mechanism of salt rejection by the membranes. Their salt rejection rates increased
 403 with increasing number of oligoamide synthesis cycles up to 15.5 cycles. Membrane OL-15.5
 404 showed the highest rejection rates for both MgSO_4 and Na_2SO_4 (41.0% and 53.5%,
 405 respectively). Rejection rates then decreased in OL-20.5 to 34.1% and 43.5% for MgSO_4 and
 406 Na_2SO_4 , respectively. The increased salt rejection with increasing number of oligoamide
 407 cycles may be explained by the smaller pores. Hence, the mechanism of salt rejection of the
 408 oligoamide membranes is a combination of both the Donnan exclusion, and the reduced pore
 409 size (size exclusion). Substantial ion rejection which was evident in the oligoamide
 410 membranes is not common for porous membranes, and this could represent a great advantage
 411 for the oligoamide membranes in the reclamation of wastewater for irrigation and in the
 412 separation of charged macromolecules. A small decrease in salt rejection for membrane OL-
 413 20.5 was noticed as compared with OL-15.5; however due to the very low permeance of OL-
 414 20.5 this membrane was not explored further.



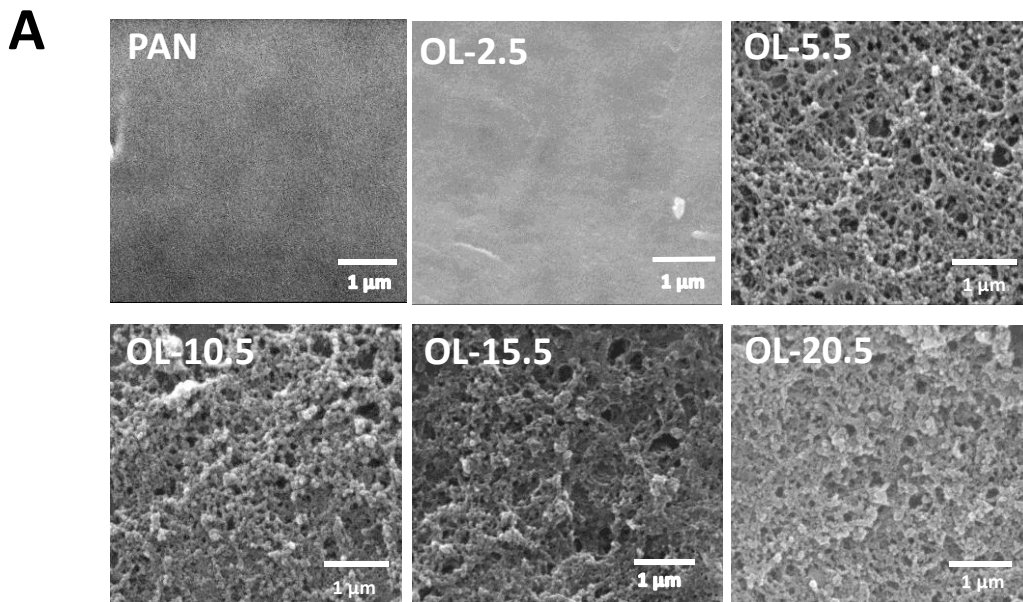
415

416 **Figure 4.** Rejection of Na_2SO_4 and MgSO_4 (1 g/L solutions) by oligoamide membranes and a
417 pristine PAN membrane.

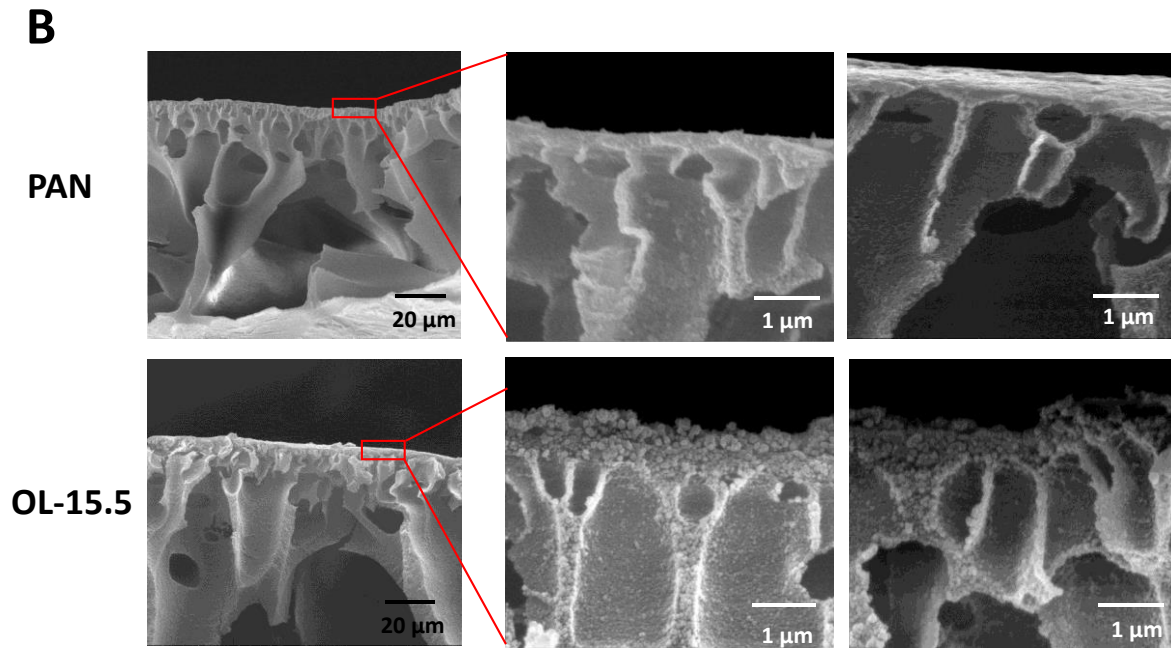
418

419 *3.5. Microscopic characterization of membranes*

420 The surface morphology of the various membranes was analyzed by SEM and is shown in
421 Fig. 5A. The oligoamide membranes OL-5.5, OL-10.5, OL-15.5, and OL-20.5 appeared
422 rough and porous, whereas the OL-2.5 membrane and the pristine PAN membrane had a
423 smooth top surface. Hence, it is assumed that the fabricated oligoamide induces a rough-
424 porous structure at the top surface, except for membrane OL-2.5 which had only 2.5 synthetic
425 cycles.



426



427

428 **Figure 5.** (A) SEM top surface images of a pristine PAN membrane and oligoamide
 429 membranes OL-2.5, OL-5.5, OL-10.5, OL-15.5, and OL-20.5. (B) Cross-sectional SEM
 430 images of the pristine PAN membrane (top) and oligoamide membrane OL-15.5 (bottom).
 431 Membranes shown in (A) were synthesized on commercial PAN supports, whereas those in
 432 (B) were synthesized on supports cast in the lab.

433

434 Cross-sectional SEM images were obtained for the OL-15.5 membrane and a pristine PAN
 435 membrane (Fig. 5B). Membrane OL-15.5 was chosen due to its interesting separation
 436 properties. Its synthesized oligoamide material appears as rounded features on top of the
 437 PAN support, as well as inside the membrane pores (Fig. 5B, high magnification). Based on
 438 that observation it is assumed that similar growth of oligoamide might also partly occur
 439 inside the small pores in the separating layer of the membrane, leading to decreased
 440 permeance and lower MWCO. There were no significant changes in the surface topology of
 441 the synthesized oligoamide membranes with the number of synthesis cycles. Overall, SEM
 442 analysis suggested that the oligoamide formed arbitrarily on the porous PAN support as
 443 rounded features on top of the surface, as well as inside the pores.

444

445 **4. Conclusions**

446 In this study, membranes with controllable MWCO and pore size were obtained by the
 447 stepwise synthesis of oligoamide on porous PAN supports. The technique relied on finding

448 an appropriate solvent (1,4-dioxane) for both coupling steps and washing steps, which was
449 advantageous over the use of two different solvents. Another improvement in this synthesis
450 was avoiding the use of a base in the TMC coupling stage. The formation of oligoamide on
451 the membrane surface and the consequential control of its properties were demonstrated by
452 different analysis techniques: Infrared spectroscopy showed the characteristic peaks of the
453 amide functionality on the PAN support which increased with increasing number of synthesis
454 cycles of oligoamide. In addition, the water permeance was inversely correlated with the
455 number of oligoamide synthetic cycles. Furthermore, SEM analysis showed that the
456 oligoamide formed as rounded features on the porous PAN support, at the surface and partly
457 inside the pores.

458 Performance tests showed that the membranes' MWCO was controllable by varying the
459 number of oligoamide synthetic cycles, from 332.0 kDa for the pristine membrane to 22.6 for
460 the OL-20.5 membrane. Water permeance values ranged from $4.6 \pm 0.2 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for OL-
461 20.5 membrane to $543.4 \pm 9.0 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for the pristine PAN membrane. The changes in
462 MWCO and in the permeance may be explained by variations of the mean pore size, which
463 varied from 0.4 nm of the OL-20.5 membrane to 23.5 nm for the pristine membrane. OL-2.5
464 and OL-5.5 membranes showed good separation of the charged rose bengal dye from water,
465 with high water permeance ($71.8 \pm 1.3 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for OL-2.5 and $24.9 \pm 0.8 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$
466 for OL-5.5) compared to some recently published membranes. Additionally, the
467 oligoamide membranes could reject salts, showing maximum rejection rates of 41.0% for
468 MgSO_4 and 53.5% for Na_2SO_4 . As the oligoamide is covalently bonded to the support porous
469 membrane, these membranes are expected to be more stable than other composite membranes
470 (e.g., TFC nanofiltration or RO membranes) during membrane backwashing; therefore, they
471 are expected to be more efficient and more durable in practice. The stepwise synthesis
472 approach of oligoamide can be applied with organic porous supports other than PAN, given
473 that an appropriate amination method and compatible solvents are found.

474 The oligoamide membranes described in this study may be used in applications that require
475 control of the membrane transport properties, including the separation of charged
476 macromolecules such as proteins with specific MWCO ranges, filtration of streams in the
477 whey industry and in the pulp and paper industry, pharmaceutical separations, and
478 hemodialysis.

479

480 **Supporting Information** contains the use of an organic base in oligoamide synthesis; details
481 of PAN amination reaction; IR data of diethylenetriamine; the mean pore size and MWCO
482 values of oligoamide membranes; zeta potential analysis of OL-5.5 and PAN membrane; and
483 a comparison of the rose bengal separation performance of the oligoamide membranes with
484 other membranes reported previously.

485

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494

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