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Stepwise synthesis of oligoamide coating on a porous support: Fabrication of a membrane with controllable transport properties / Manna, Paramita; Tiraferri, Alberto; Sangermano, Marco; Bernstein, Roy; Kasher, Roni. - In: SEPARATION AND PURIFICATION TECHNOLOGY. - ISSN 1383-5866. - 213:(2019), pp. 11-18. [10.1016/j.seppur.2018.12.014]

Availability: This version is available at: 11583/2720639 since: 2018-12-14T11:08:43Z

Publisher: Elsevier

Published DOI:10.1016/j.seppur.2018.12.014

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# Stepwise synthesis of oligoamide coating on a porous support: Fabrication of a membrane with controllable transport properties Paramita Manna<sup>1</sup>, Alberto Tiraferri<sup>2</sup>, Marco Sangermano<sup>3</sup>, Roy Bernstein<sup>1,\*</sup>, and Roni

Paramita Manna<sup>1</sup>, Alberto Tiraferri<sup>2</sup>, Marco Sangermano<sup>3</sup>, Roy Bernstein<sup>1,\*</sup>, and Roni Kasher<sup>1,\*</sup>

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<sup>7</sup> <sup>1</sup>Department 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
- <sup>10</sup> <sup>2</sup>Department of Environment, Land and Infrastructure Engineering (DIATI), Politecnico di
- 11 Torino, Corso Duca degli Abruzzi 24, 10129, Torino, Italy

<sup>12</sup> <sup>3</sup>Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso

- 13 Duca degli Abruzzi 24, 10129, Torino, Italy
- 14

<sup>\*</sup>Corresponding authors; royber@bgu.ac.il (R.B.); kasher@bgu.ac.il (R.K.)

#### 16 ABSTRACT

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

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

#### 38 **1. Introduction**

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

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

Aromatic polyamide is used successfully as a barrier film for reverse osmosis (RO) and 60 61 nanofiltration (NF) dense membranes due to its hydrophilic character, which enables high water permeance, and due to its crosslinking propensity [23]. Nevertheless, its conventional 62 preparation by interfacial polymerization limits the control of its thickness and crosslinking 63 degree and hence its transport properties. Therefore, strategies of preparing polyamide films 64 with controlled properties are explored. Karan et al. performed interfacial polymerization on 65 a substrate having a sacrificial – intermediate layer obtaining a sub-10 nm polyamide film 66 that was installed on ceramic support to obtain organic solvent nanofiltration composite 67 membrane with high solvent permeances [24]. Chowdhury et al. used electro-spraying to 68 deposit small droplet sizes of acid chloride and diamine monomers directly on a support and 69 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 aromatic oligoamide on gold by a stepwise series of coupling reactions, where unlike the 73 interfacial polymerization, a very thin oligoamide layer was formed and its thickness could 74 be varied by the number of synthetic cycles. The stepwise approach of synthesizing aromatic 75 oligoamide has recently been used by several research groups to fabricate novel polyamide 76 membranes on porous supports. For example, Wu et al. used repeated layer-by-layer 77 couplings of polyethyleneimine and trimesoyl chloride (TMC) on a polyethersulfone 78 substrate [27] to make a membrane with permeability in the range of NF membranes. In 79 80 another study, polyelectrolytes were pre-deposited on porous poly(acrylonitrile) membranes, then a stepwise preparation of aromatic polyamide barrier layer was successfully introduced 81 [28, 29]. The resulting membranes performed similarly to aromatic polyamide NF 82 membranes fabricated by conventional interfacial polymerization. 83

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

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

#### 106 2. Experimental Section

#### 107 *2.1. Materials*

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

#### 121 2.2. Membrane fabrication

# 122 2.2.1. Preparation of PAN membranes

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

127 2.2.2. Amination of the PAN membranes

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

#### 132 2.2.3. Stepwise synthesis of oligoamide membranes

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

# 151 2.3. Chemical characterization

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

Surface functional groups of the oligoamide membranes were characterized by ATR-FTIR spectroscopy with a VERTEX 70-FTIR spectrometer (Bruker Optics, Ettlingen, Germany) at  $4 \text{ cm}^{-1}$  resolution. The system was equipped with a Miracle ATR attachment with a reflection diamond-coated KRS-5 crystal (Pike, Madison, WI, USA). Before analyses, the membranes
were dried in a vacuum oven at 40 °C. The IR analyses were performed in 3-4 different
locations on each membrane sample, and the average spectra are reported.

Scanning electron microscopy (SEM) of surface topography and cross-sections of the membranes were performed with a Quanta 200 microscope (Field Electron and Ion Company, Thermo Fisher Scientific, USA). Cross-sectional SEM analyses were performed using OL-15.5 membranes synthesized on PAN supports cast in the lab (as described in Section 2.2.1), because the commercial PAN membranes did not allow cross-sectional analysis owing to their mechanical reinforcement. Surface topography SEM was performed 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  $11.34 \text{ cm}^2$  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.

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

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

Salt separation: The salt selectivity, expressed as the rejection rate (R), was evaluated by filtering 1 g/L solutions of  $Na_2SO_4$  or MgSO<sub>4</sub>, and measuring the feed and permeate 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)

where  $\kappa_f$  and  $\kappa_p$  are the specific conductivities of the feed and permeate solutions, respectively.

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

- 214 2.5. Mean pore size calculation
- The mean pore size of the membranes was estimated according to the study of S. Singh *et al.* [33]. Initially, the Stokes radii of the molecular markers were calculated using Eq. (3) for PEG and Eq. (4) for PEO
- 218  $a = 16.73 \times 10^{-3} M_w^{0.557}$  (3)
- 219  $a = 10.44 \times 10^{-3} M_w^{0.587}$
- where *a* is the Stokes radius (nm) of the PEG or PEO, and  $M_w$  is the molecular weight (g/mol). The radius of glucose and sucrose molecules were taken as 0.38 and 0.5 nm, respectively.

(4)

By ignoring the steric and hydrodynamic interactions between the solute and membrane during separation [34, 35], the mean pore size and the geometric standard deviation of the membrane can be considered the same as the mean solute size and the solute geometric standard deviation. The solute rejection of each membrane was plotted against the solute diameter, and the solute diameter that corresponded to 50% rejection was determined from the graph. The geometric standard deviation about the mean diameter was determined from the ratio of solute diameter at R = 84.13% to solute diameter at R = 50%.

230

### **3. Results and discussion**

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

240 3.1. Amination of the PAN support

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

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

Support membrane	Reaction time (h)	Amine content <sup>a</sup> (mmole/cm <sup>2</sup> )	Water permeance $(\mathbf{L} \cdot \mathbf{m}^{-2} \mathbf{h}^{-1} \mathbf{bar}^{-1})$
PAN (Pristine)	0	3.86×10 <sup>-6</sup>	534.6±15.9
Aminated PAN (A2H)	2	$1.094 \times 10^{-4}$	481.3±14.3
Aminated PAN (A5H)	5	$1.501 \times 10^{-4}$	436.2±27.3
Aminated PAN (A10H)	10	$1.561 \times 10^{-4}$	223.7±7.4

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<sup>a)</sup>Measured by orange-II adsorption assay.

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Scheme 1. Stepwise preparation of oligoamide on an amine functionalized porous PAN membrane, with detailed structure of oligoamide after 2.5 cycles. Step I: 31% diethylenetriamine (DETA) and 1% Na<sub>2</sub>CO<sub>3</sub> in water at 60 °C. Step II: 40 mM trimesoyl chloride (TMC) in 1,4-dioxane, 2 min. III: 50 mM meta-phenylenediamine (mPD) in 1,4dioxane, 2 min. Step IV:  $H_2O$  at 50 °C, 15 min.

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

The choice of appropriate solvents for the oligoamide synthesis (Steps II and III, Scheme 1) 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

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

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

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

<sup>a)</sup> PS, partially soluble; S, soluble; ND, not determined; NS, non-soluble.

<sup>b)</sup>Immersion of the PAN membrane overnight in the solvent.

#### 291 *3.3. Oligoamide synthesis*

Oligoamide synthesis was performed on the 5 h aminated PAN membrane as illustrated in Scheme 1, with both TMC and mPD dissolved in 1,4-dioxane. Successive TMC and mPD couplings (II and III, Scheme 1) were repeated to obtain oligoamide with 2.5, 5.5, 10.5, 15.5, and 20.5 synthesis cycles, including final hydrolysis (IV, Scheme 1) and extensive washing, and the membranes were designated as OL-2.5, OL-5.5, OL-10.5, OL-15.5, and OL-20.5. Although Steiner *et al.* [26] reported that their oligoamide synthesis on gold required organic base in the TMC reaction to neutralize the hydrochloric acid formed, we found that a base was not essential for successful oligoamide synthesis on PAN membranes (see Table S1, Supporting Information). All the syntheses ended with TMC coupling (half a cycle), as carboxylic acid surface moieties make the membranes more hydrophilic than a typical amine-terminated surface. A possible structure for an oligoamide membrane with 2.5 synthetic cycles is shown in Scheme 1.

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





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

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# 330 *3.4. Membrane transport properties*

The synthesis of oligoamide on a porous PAN support is expected to produce membranes 331 with diverse transport properties by reducing its permeability and pore size; therefore, the 332 permeance was evaluated for membranes made with different numbers of oligoamide 333 synthesis cycles (Fig. 2A). The pristine PAN membrane showed a water permeance of 334 543.4 $\pm$ 9.0 L·m<sup>-2</sup>h<sup>-1</sup>bar<sup>-1</sup>, which was indeed greater than any permeance shown by the 335 oligoamide membranes, whose values decreased with the number of cycles of oligoamide 336 synthesis. The permeance significantly decreased after 2.5 cycles (OL-2.5 membrane) to 337 71.8±1.3 L·m<sup>-2</sup>h<sup>-1</sup>bar<sup>-1</sup> and it decreased yet further to 4.6±0.2 L·m<sup>-2</sup>h<sup>-1</sup>bar<sup>-1</sup> for the thickest 338 membrane (OL-20.5). Fig. 2A also shows that the correlation between  $L_p$  and the number of 339 synthetic cycles was not linear, e.g., membrane OL-15.5 showed an  $L_p$  value of  $5.3\pm0.6$ 340  $L \cdot m^{-2}h^{-1}bar^{-1}$ , which is close to that of membrane OL-20.5. 341

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

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



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

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



372

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

377 The separation performance of the oligoamide membranes was further tested by filtration experiments of rose bengal dye solutions. Filtration of 20 µM rose bengal solutions by the 378 OL-2.5 and OL-5.5 membranes showed high rejection with good flux (Table 3). The OL-2.5 379 membrane showed a reasonable rose bengal retention of  $78.6 \pm 3.7\%$  with a high flux of 194 380  $\pm$  19.3 L·m<sup>-2</sup>h<sup>-1</sup> (at 3.5 bar) while the OL-5.5 membrane had a high rejection of 94.7  $\pm$  0.5% 381 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 382 rose bengal with the OL-2.5 and OL-5.5 membranes having MWCO more than 90 kDa 383 implies for the Donnan exclusion, probably due to the presence of charged carboxyl groups 384 on the oligoamide surface which repels the negatively charged dye. Zeta potential analysis 385 showed that OL-5.5 membrane is negatively charged in pH range of 4-9 (Fig. S2, Supporting 386 Information). When comparing the rose bengal separation by the two oligoamide membranes, 387 the higher rejection by the OL-5.5 membrane (compared to OL-2.5) can be explained by the 388 increasing steric hindrance effect due to more synthetic cycles which is also evident in the 389 water permeance data of the two membranes. The rose bengal dye separation performances 390 obtained in this study for the oligoamide membranes were compared with other membranes 391 that were recently published, and are summarized in Table S3 (Supporting Information). The 392 permeability of OL-5.5 membrane is very high compared to most of the other membranes 393 394 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 <sup>a,b</sup> (%)	Flux (L·m <sup>-2</sup> ·h <sup>-1</sup> )
PAN	$14.7 \pm 1.0$	$1158.8 \pm 64.6$ at 0.5 bar
OL-2.5	$78.6\pm3.7$	$194.9 \pm 19.3$ at 3.5 bar
OL-5.5	$94.7\pm0.5$	$126.4 \pm 4.2$ at 5.2 bar

<sup>a)</sup> Rose bengal molecular weight (of the di anion) is 973.67 g/mol.

398 <sup>b)</sup>



The membranes were also examined for salt rejection (Fig. 4). All the oligoamide membranes 400 rejected Na<sub>2</sub>SO<sub>4</sub> at a higher rate than MgSO<sub>4</sub>, suggesting the Donnan exclusion is an 401 important mechanism of salt rejection by the membranes. Their salt rejection rates increased 402 with increasing number of oligoamide synthesis cycles up to 15.5 cycles. Membrane OL-15.5 403 showed the highest rejection rates for both MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> (41.0% and 53.5%, 404 respectively). Rejection rates then decreased in OL-20.5 to 34.1% and 43.5% for MgSO<sub>4</sub> and 405 Na<sub>2</sub>SO<sub>4</sub>, respectively. The increased salt rejection with increasing number of oligoamide 406 cycles may be explained by the smaller pores. Hence, the mechanism of salt rejection of the 407 oligoamide membranes is a combination of both the Donnan exclusion, and the reduced pore 408 size (size exclusion). Substantial ion rejection which was evident in the oligoamide 409 membranes is not common for porous membranes, and this could represent a great advantage 410 for the oligoamide membranes in the reclamation of wastewater for irrigation and in the 411 separation of charged macromolecules. A small decrease in salt rejection for membrane OL-412 20.5 was noticed as compared with OL-15.5; however due to the very low permeance of OL-413 20.5 this membrane was not explored further. 414



Figure 4. Rejection of Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> (1 g/L solutions) by oligoamide membranes and a
 pristine PAN membrane.

418

# 419 *3.5. Microscopic characterization of membranes*

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





427

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

433

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

444

#### 445 **4. Conclusions**

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

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

Performance tests showed that the membranes' MWCO was controllable by varying the 458 number of oligoamide synthetic cycles, from 332.0 kDa for the pristine membrane to 22.6 for 459 the OL-20.5 membrane. Water permeance values ranged from  $4.6\pm0.2 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}$  for OL-460 20.5 membrane to  $543.4\pm9.0 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}$  for the pristine PAN membrane. The changes in 461 MWCO and in the permeance may be explained by variations of the mean pore size, which 462 varied from 0.4 nm of the OL-20.5 membrane to 23.5 nm for the pristine membrane. OL-2.5 463 and OL-5.5 membranes showed good separation of the charged rose bengal dye from water, 464 with high water permeance  $(71.8 \pm 1.3 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1} \text{ for OL-2.5 and } 24.9 \pm 0.8 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ 465 <sup>1</sup>·bar<sup>-1</sup> for OL-5.5) compared to some recently published membranes. Additionally, the 466 oligoamide membranes could reject salts, showing maximum rejection rates of 41.0% for 467 MgSO<sub>4</sub> and 53.5% for Na<sub>2</sub>SO<sub>4</sub>. As the oligoamide is covalently bonded to the support porous 468 membrane, these membranes are expected to be more stable than other composite membranes 469 (e.g., TFC nanofiltration or RO membranes) during membrane backwashing; therefore, they 470 are expected to be more efficient and more durable in practice. The stepwise synthesis 471 approach of oligoamide can be applied with organic porous supports other than PAN, given 472 473 that an appropriate amination method and compatible solvents are found.

The oligoamide membranes described in this study may be used in applications that require control of the membrane transport properties, including the separation of charged macromolecules such as proteins with specific MWCO ranges, filtration of streams in the whey industry and in the pulp and paper industry, pharmaceutical separations, and hemodialysis. Supporting Information contains the use of an organic base in oligoamide synthesis; details of PAN amination reaction; IR data of diethylenetriamine; the mean pore size and MWCO values of oligoamide membranes; zeta potential analysis of OL-5.5 and PAN membrane; and a comparison of the rose bengal separation performance of the oligoamide membranes with other membranes reported previously.

485

# 486 Acknowledgements

- 487 This work was supported by project "StepPolyMem" within the Italy-Israel Scientific and
- 488 Technological Cooperation funded by the Ministry of Science, Technology and Space of the
- 489 State of Israel and the Italian Ministry of Foreign Affairs and International Cooperation. We
- 490 thank Yelena Logek (Ben-Gurion University of the Negev) for assisting with the lab work and
- 491 Dr. Anya Milionchic and Roxana Golan (Ilse Katz Institute for Nanoscale Science, Ben-Gurion
- 492 University of the Negev) for SEM analysis of the membranes. We thank professor Viacheslav
- 493 (Slava) Freger (Technion Israel Institute of Technology) for fruitful discussions.

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