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Electronic Supporting Information

2 **One-step fabrication of polyamide 6 hollow fibre membrane using non-**

3 **toxic diluents for organic solvent nanofiltration**

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1 Table of contents

2

3 1. Materials and Methods

4

5 2. Figures and Tables

6

7 3. References

8

1 **1. Materials and methods**

2 **Materials:** Polyamide 6 (Mw = 90,000 measured by GPC) was kindly provided by Unitika Ltd.
3 (Kyoto, Japan). Dimethyl sulfone (DMSO₂) and sulfolane (Wako Pure Chemical Industries,
4 Japan) were used as diluents in this study. Polyethylene glycol (PEG) with molecular weights
5 of 300 (PEG300), 400 (PEG400), and 600 g mol⁻¹ (PEG600) (Wako Pure Chemical Industries)
6 were used as bore solutions separately. Propylene glycol (PG) (Wako Pure Chemical
7 Industries) was used as a mixing component in quenching bath to obtain porous outer surfaces.
8 Ethanol, Methanol, dimethyl sulfoxide (DMSO), *N*-methylpyrrolidone (NMP),
9 dimethylformamide (DMF), and dimethylacetamide (DMAc) (Wako Pure Chemical
10 Industries) were used for the solvent stability tests. Cobalamin (vitamin B₁₂, VB₁₂, Mw =
11 1,355) (Sigma-Aldrich, USA) was used for the rejection tests. Milli-Q water (Millipore, USA)
12 was used in these experiments. All chemicals were used as received without further
13 purification.

14

15 **Preparation of polyamide 6 hollow fibre membranes:** Hollow fiber membranes were
16 fabricated by the thermally induced phase separation (TIPS) method using a twin-screw
17 extruder (TW05, ULTnano, Japan) (Fig. S1).¹ After the extruder was heated to a decided
18 temperature of 220 °C, certain amounts of polyamide 6 and mixed diluent (DMSO₂ and
19 sulfolane) were continuously fed into the first zone via pumps, respectively, to maintain
20 constant composition, and then continuously mixed in the second zone by the twin screws.
21 After releasing air bubbles in the third zone at the same temperature, the homogeneous
22 polyamide 6 dope solution was transported to a gear pump under a pressure of 1.0 MPa. The
23 dope solution was flowed by a gear pump (Kawasaki Heavy Industry LTD, Japan) through the
24 polymer channel of an orifice spinneret purchased from Kasen Nozzle Mfg. Co. Ltd. The

1 spinneret consisted of outer and inner tubes with diameters of 1.58 and 0.83 mm, respectively.
2 The bore solution (PEG300, 400 or PEG600) was introduced into the inner orifice to produce
3 a hollow fibre membrane. The hollow fibre was extruded from the spinneret and wound on a
4 take-up winder through a quenching bath kept at room temperature to induce the phase
5 separation and solidify the membrane. The remaining solvent in the hollow fibre membranes
6 was replaced with ethanol, which was then removed by immersing the membrane in Milli-Q
7 water just before use.

8

9 **Characterization:** Field emission scanning electron microscopy (FE-SEM, JSF-7500F, JEOL
10 Co. Ltd., Tokyo, Japan) was employed to observe the morphologies of the hollow fibre
11 membranes. Inner and outer surface images and the cross-section image were obtained. The
12 membranes were fractured in liquid nitrogen in order to obtain a clear cross-section, and then
13 dried overnight in a freeze dryer (FDU-1200 EYELA, Tokyo Rikakikai Co. Ltd., Tokyo,
14 Japan). The dried samples were coated with osmium tetroxide (OsO_4) using an osmium coater
15 (Neoc-STB, Meiwafosis Co. Ltd., Tokyo, Japan) before FE-SEM observation.

16 The tensile strengths and elongations of polyamide 6 hollow fibre membranes were
17 evaluated using a tensile test apparatus (AGS-J, Shimadzu Co., Japan). The membrane
18 was fastened vertically between a pair of tweezers 50 mm apart. The membrane was
19 extended at 50 mm/min until it was broken. Each result was the average of three parallel
20 experiments.

21

22 **Solvent resistance test:** In order to investigate the solvent resistance of membranes, we carried
23 out an immersion test with various organic solvents such as ethanol, methanol, DMSO, NMP,
24 DMF, and DMAc. Each hollow fiber membrane was rinsed with pure water and dried in an

1 oven at 50 °C for 18 hours. The weights of the membranes were fixed to be 1 g (length = 15
2 cm). Each sample was weighed after 1, 2, 4, 8, and 16 weeks. Before the measurement, the
3 membranes were rinsed sufficiently with pure water, dried in an oven, and then weighed. Three
4 specimens were tested for each sample.

5

6 **Solvent permeability:** Methanol permeabilities of the hollow fibre membranes were
7 measured using cross-flow filtration equipment (flow rate of feed solution: 2 ml/min).
8 Prior to the permeability measurement, the hollow fibre membranes (length: 15 cm,
9 membrane area: 2.59 cm²) were rinsed again with pure water. The solvent permeability
10 was calculated on the basis of the inner surface area of the membrane. Solvent was
11 forced to permeate from the lumen side to the shell side of the hollow fibre membrane.
12 The solvent permeability, J_s (Lm⁻²h⁻¹bar⁻¹), was measured for several pieces of the
13 prepared membranes and the average values were recorded. J_s was calculated using the
14 following equation:

$$15 \quad J_s = \frac{V}{A \times \Delta t \times \Delta P} \quad (1)$$

16 where V is the volume of permeated solvent (L), A is the inner membrane area (m²), Δt
17 is the permeation time (h), and ΔP is the pressure (bar).

18

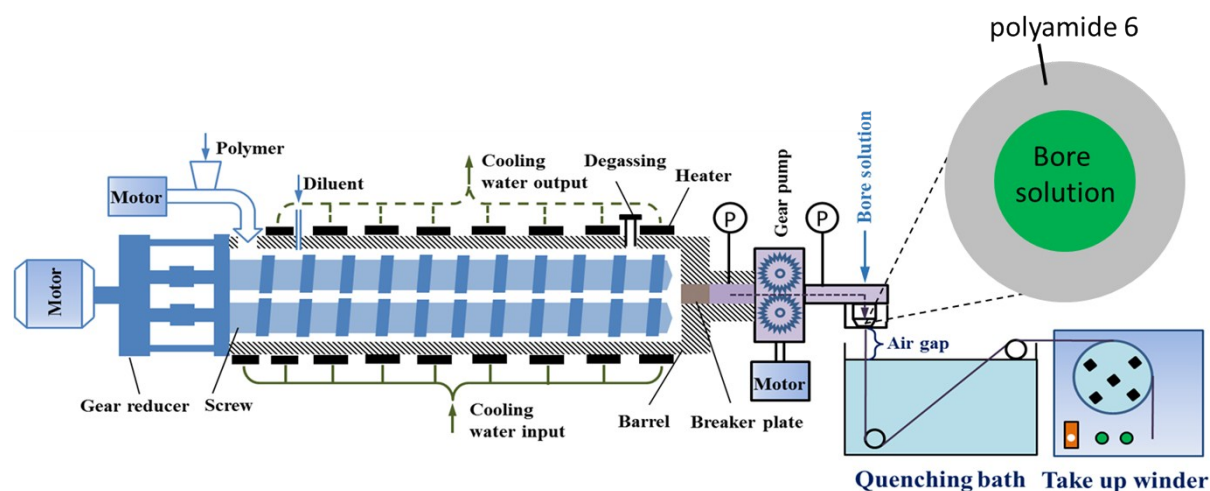
19 **VB₁₂ rejection:** In this study, VB₁₂ (Mw=1,355) was used for rejection tests to
20 determine membrane performance as OSN. VB₁₂ was dissolved in ethanol and methanol
21 (100 mgL⁻¹), respectively, then used as feed solution for rejection test. The
22 concentrations of VB₁₂ in the permeate and feed solutions were measured with a U-200
23 UV spectrophotometer (Hitachi Co., Japan) at a wavelength of 361 nm. The VB₁₂
24 rejection, R (%), was defined as follows:

$$R = \left(1 - \frac{C_P}{C_F}\right) \times 100\% \quad (2)$$

where C_P and C_F are the concentrations of VB₁₂ in the permeate and feed solutions, respectively. The reported values are the average values of three consecutive measurements.

5

1 **2. Figures and Tables**



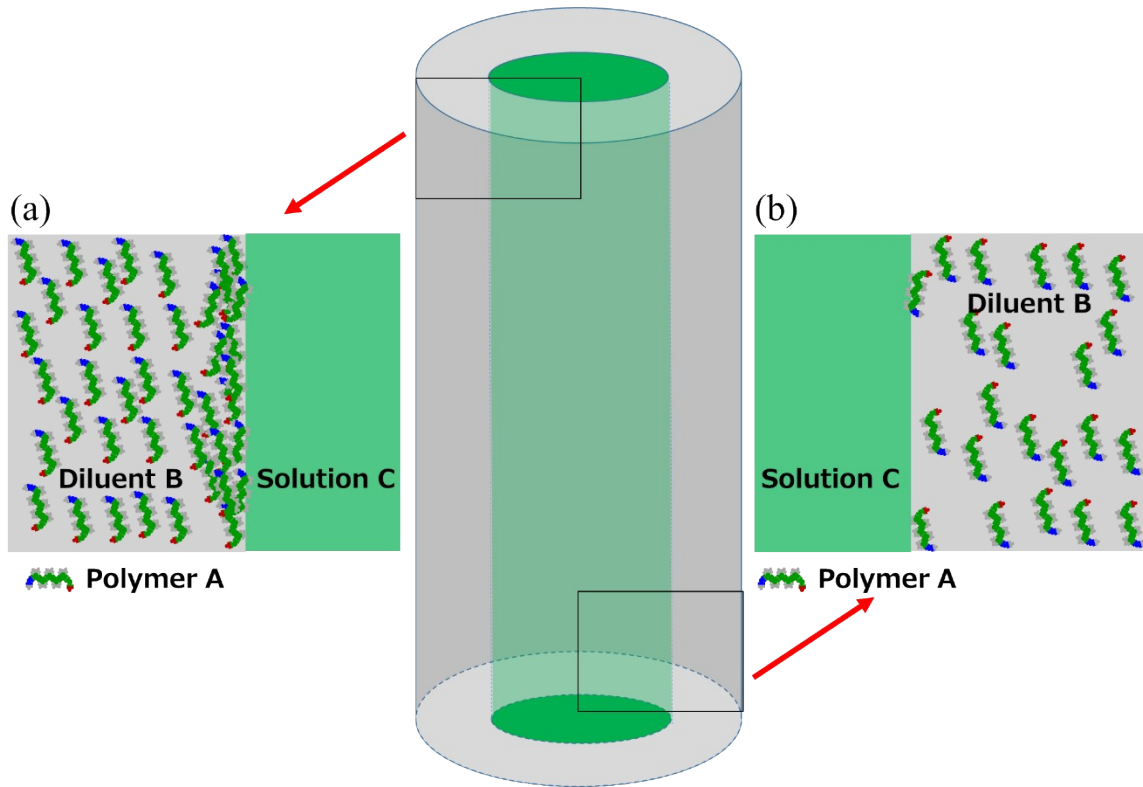
Preparation conditions	Parameters
Polyamide 6 concentration (wt%)	25, 30, 35
Polyamide 6 flow rate (g/min)	2.5, 3, 3.5
Diluent concentration (DMSO ₂ :sulfolane=74:26) (wt%)	75, 70, 65
Diluent flow rate (g/min)	7.5, 7, 6.5
Screw temperature (°C)	220
Screw speed (rpm)	150
Air gap (cm)	0.5
Quenching bath temperature (°C)	Room temperature
Bore liquid	PEG300, PEG400, PEG600
Bore liquid flow rate (g/min)	4
Take-up speed (m/min)	20

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2 Figure S2. Schematic of polymer membrane formation behavior in TIPS process at
 3 interface between polymer dope solution and bore solution. (a) interfacial segregation
 4 of polymer A having a better compatibility with the solution C than the diluent B does.
 5 (b) interfacial segregation of diluent B having a better compatibility with solution C
 6 than the polymer A does.

7

1 Table S2 Solubility parameters of polyamide 6 and diluents.²

Preparation conditions	δ_d (MPa) ^{0.5}	δ_p (MPa) ^{0.5}	δ_h (MPa) ^{0.5}	δ (MPa) ^{0.5}	R_a (MPa) ^{0.5} (distance from polyamide 6)	R_a (MPa) ^{0.5} (distance from mixed diluent)
Polyamide 6	17.0	10.6	3.4	20.32	-	
DMSO ₂ :sulfolane (73:27) ^a	18.8	18.6	10.9	28.60		-
PEG200	16.7	5.6	16.7	24.27	14.22	14.84
PEG300	16.6	4.4	14.5	22.47	12.74	15.29
PEG400	16.6	3.7	13.3	21.59	12.09	15.72
PEG600	16.6	3.2	12.1	20.80	11.45	16.06

2 ^a The δ value was according to the mathematical method for solvent mixtures in eq. (4).

3

4 The total solubility parameter, δ , is given by Eq. (3), where subscripts d , p , and h
5 indicate dispersion, polar-polar interaction, and hydrogen bonding forces, respectively.

$$6 \quad \delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

7

8 Also, the solubility parameter of a solvent mixture can be obtained by calculating the
9 volume-wise contributions of the solubility parameters of the individual components of
10 the mixture³. The solubility parameter of the solvent mixture, δ_M , is given by Eq. (4),
11 where A and B indicate solvents A and B, respectively, and X_A is the weight fraction of
12 solvent A.

$$13 \quad \delta_M = X_A \delta_A + (1 - X_A) \delta_B$$

$$14 \quad = X_A (\delta_{Ad} + \delta_{Ap} + \delta_{Ah}) + (1 - X_A) (\delta_{Bd} + \delta_{Bp} + \delta_{Bh})$$

$$15 \quad = X_A \delta_{Ad} + (1 - X_A) \delta_{Bd} + X_A \delta_{Ap} + (1 - X_A) \delta_{Bp} + X_A \delta_{Ah} + (1 - X_A) \delta_{Bh} \quad (4)$$

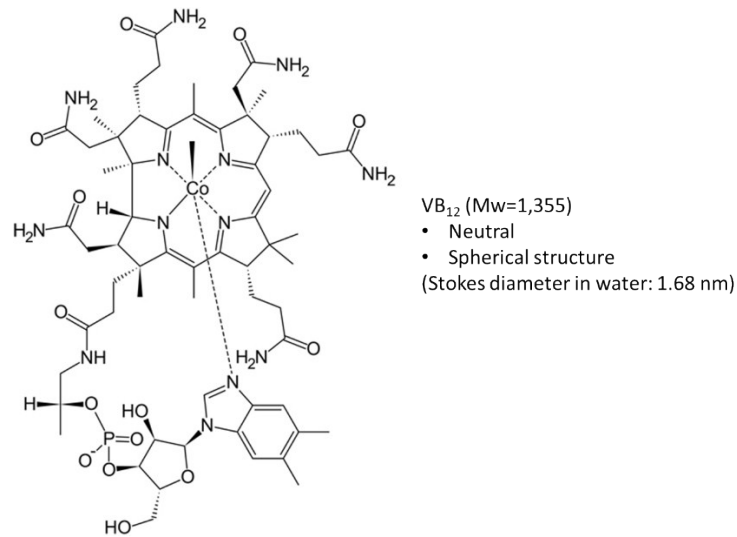
16

17 The solubility parameter distance, R_a is obtained using the following equation:

$$18 \quad (R_a)^2 = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 \quad (5)$$

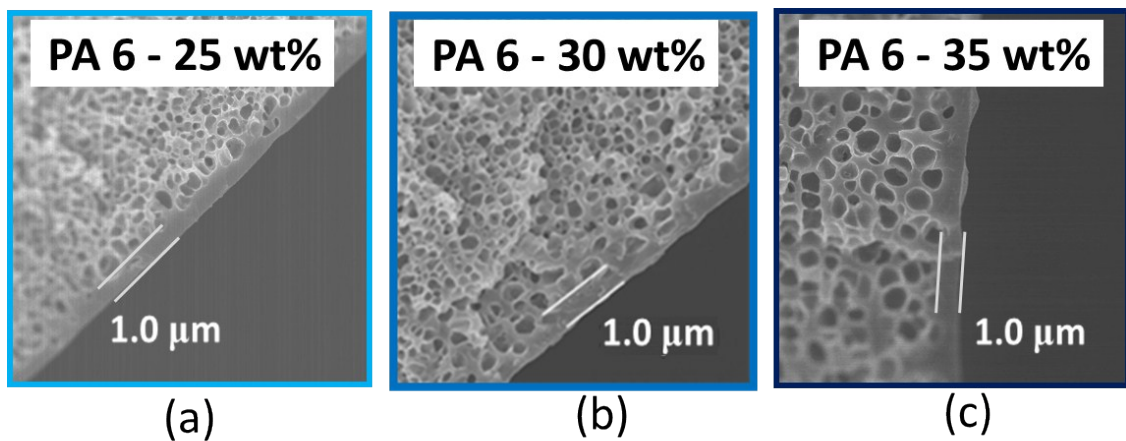
1 where subscripts 1 and 2 refer to polyamide 6 and the bore solution or diluent and the
2 bore solution, respectively.

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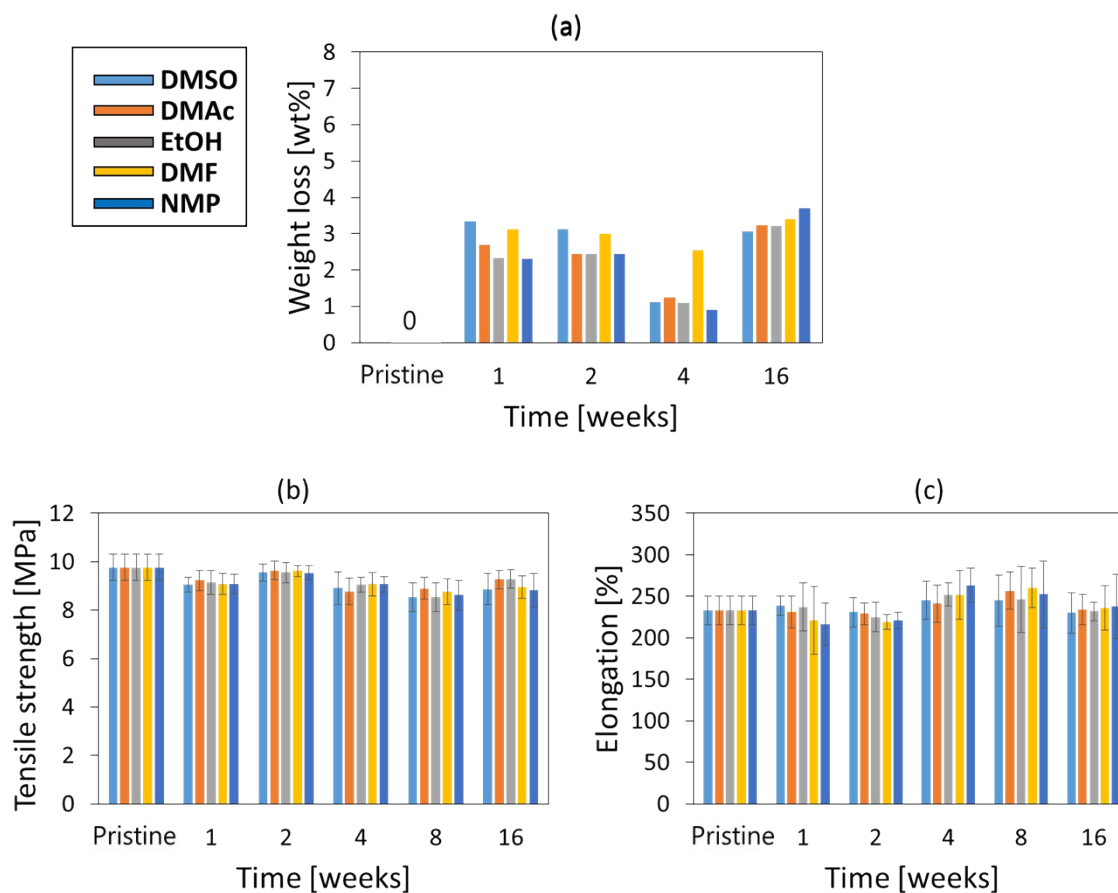
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6 Figure S3. Structure and physical properties of Vitamin B₁₂.



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10 Figure S4. Cross-section SEM images of polyamide 6 hollow fibre membranes
11 fabricated with different polymer concentration



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2 Figure S5. Hollow fibre membranes immersed in various solvents such as ethanol,
3 DMSO, NMP, DMF, and DMAc, and evaluated for long-term mechanical stability
4 through (a) weight loss, (b) tensile strength, and (c) elongation of polyamide 6 hollow
5 fibre membranes.

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1 **3. References**

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