Supporting Information

Polyamide Nanofilms Synthesized via Controllable Interfacial Polymerization on the "Jelly" Surface

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Materials

Piperazine (99%) and 1,3,5-benzenetricarbonyl trichloride (TMC, 98%) were obtained from Sigma-Aldrich, USA. Agar (>95%), benzoyl chloride (>99%) and n-hexane (97%) were supplied by Aladdin Chemical Co. Ltd., China. 1,3,5-Trioxane (>99%) was purchased from TCI Chemical Co., Ltd., China. 1-Benzoylpiperazine (98%) was purchased from J&K Scientific Ltd., China. Other chemicals, such as ethanol (99.7%), tetrahydrofuran (99%), sodium sulfate (Na_2SO_4, 99%), sodium chloride (NaCl, 99.5%), magnesium sulfate ($MgSO_4$, 98%), magnesium chloride ($MgCl_2$, 98%) were procured from Sinopharm Chemical Reagent Co. Ltd., China. Polyethersulfone microfiltration substrate (average pore size: 0.22 μm) was purchased from Haining Xindongfang Technology Co. Ltd., China. All the materials were used as received without further treatment.

Preparation of "jelly" and synthesis of PA nanofilms

Preparation of piperazine-containing agar hydrogel:

A scaled-up synthesis of piperazine-containing agar hydrogel was carried out as follows: 0.015g of agar power and a certain quality of piperazine were dissolved in 10 mL of deionized water. After being stirred and heated to 90 ºC to make the agar dissolved completely, the hot solution was cooled down to room temperature to form a gel substrate in a mould.

Nanofilms formation *via* interfacial polymerization:

An interfacial polymerization process was conducted to obtain PA nanofilms. In this procedure, 3 mL of TMC in n-hexane solution was added onto the hydrogel substrate to react with piperazine in gel for 2 min. Then, the n-hexane solution was removed, leaving a newly formed PA nanofilm on the gel surface. The prepared substrate was cured under 60 ºC for 10 min to allow n-hexane to evaporate completely.

Transfer of the nanofilms to other supports:

The agar hydrogel with PA nanofilm on it was put into water at 90 ºC for a few minutes. The agar gel would melt due to the thermo-sensitive property of it. Then hot water was added several times to replace agar sol adhering to the underside of the nanofilm. A free-standing nanofilm floating on water surface was eventually obtained, and could be easily transferred to another support, like polyethersulfone microfiltration substrates, silicon wafers and glass plates. It is worth noting that a five-minute vacuum filtration process has been applied to enhance the combination between PA nanofilms and polyethersulfone microfiltration substrates for preparing the composite membranes.

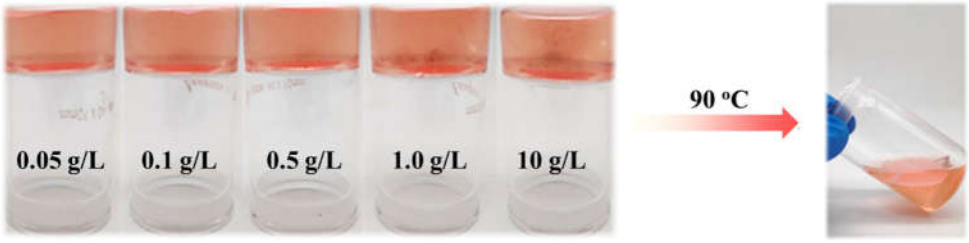


Fig. S1. Formation and transformation of agar hydrogel added different concentrations of piperazine.

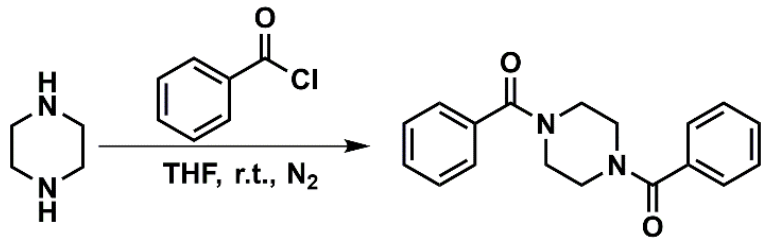
Quantitative ^{1}H NMR experiment

To quantitatively study the reaction products by ^{1}H NMR, we should obtain the standard spectra of reactants and probable products as well as internal standard in order to know the chemical shifts of all substance that may appear in the reaction solution.

Among them, piperazine and benzoyl chloride are the reactants, 1-bnzoylpiperazine and 1,4-dibenzoylpiperazine are probable products. 1,3,5-Tioxane was chosen to be internal standard because its peak position does not overlap with the characteristic peaks of other products.

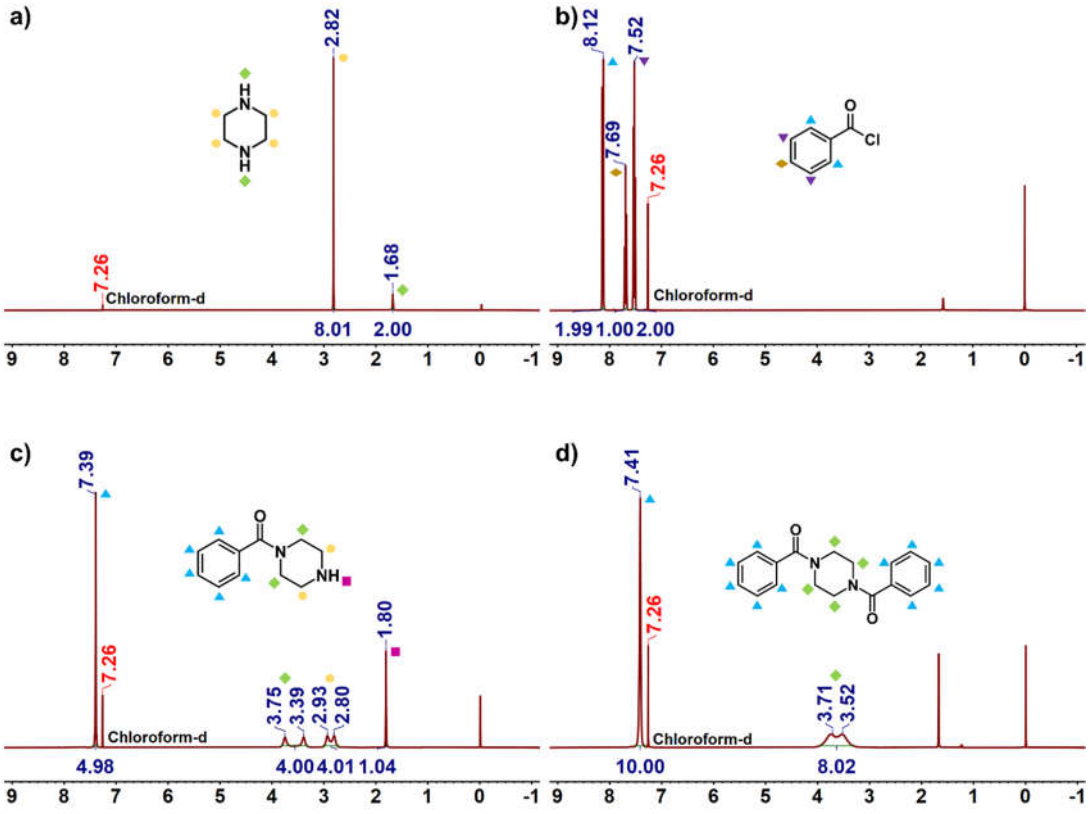
All the chemicals involved here can be purchased as standard instead of 1,4-dibenzoylpiperazine, so we synthesized the substance according to the methods reported in literature and purified it as a standard.

Synthesis of 1,4-dibenzoylpiperazine[1]:



860 mg (10 mmol) of piperazine was dissolved in 15 mL of THF and placed in a round bottom flask. 1.4 g (10 mmol) of benzoyl chloride was dissolved in 10 mL of THF and placed in a dropping funnel. The solution of benzoyl chloride was slowly added dropwise under a nitrogen atmosphere and stirred for 1.5 h. A large of white precipitates were observed. The crude product was filtered and then recrystallized twice from anhydrous ethanol to give title compound (0.85g, 2.89mmol, 46%) as transparent crystal.

Standard spectra of the chemicals involved:



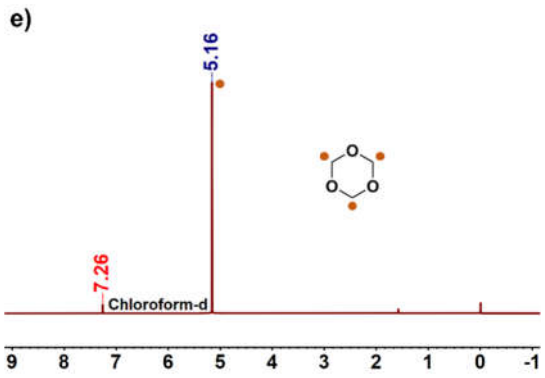


Fig. S2. ^{1}H NMR spectra of a) piperazine, b) benzoyl chloride, c) 1-bnzoylpiperazine, d) 1,4-dibnzoylpiperazine and e) internal standard: 1,3,5-tioxane. The chemical shifts are noted above the peaks, different shapes and colours of marks indicating different active hydrogen.

Comparison of diffusion rates:

0.1 g of piperazine and 15 mg of agar was added to 10 mL of ultrapure water to prepare the "jelly" (0.1g of piperazine added in 10 mL of ultrapure water without agar for control group). 1200 μL of d-chloroform solution containing 9.8 μL of 1-benzoylpiperazine as an organic phase was added to the amine-containing phase to react for 5 min. Then, 600 μl of the reaction solution was extracted with a syringe and injected into a nuclear magnetic tube. 2.0 mg of internal standard was added to the nuclear magnetic tube. Subsequently, the reaction products were analysed using nuclear magnetic resonance spectrometer (Bruker AVANCE III 400, USA) with the same parameter settings.

The weight of product (W_x) in the solution was calculated according to the following equation:

$$W_x = W_s \cdot \frac{A_x}{A_s} \cdot \frac{E_x}{E_s}$$

where W_s is the weight of internal standard; A_x and A_s are the characteristic peak area of product and internal standard, respectively; E_x and E_s are the proton equivalent (ratio of the

molecular weight of a substance to the number of protons of a resonant peak) of product and internal standard, respectively.

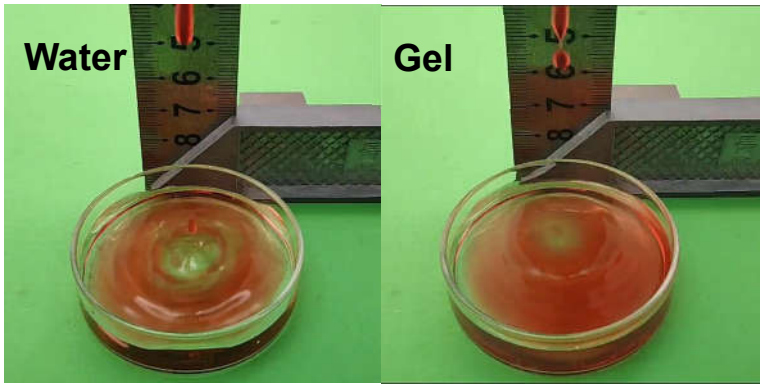


Fig. S3. Fluctuation situations when consecutive droplets landing on the surface of water and agar hydrogel.

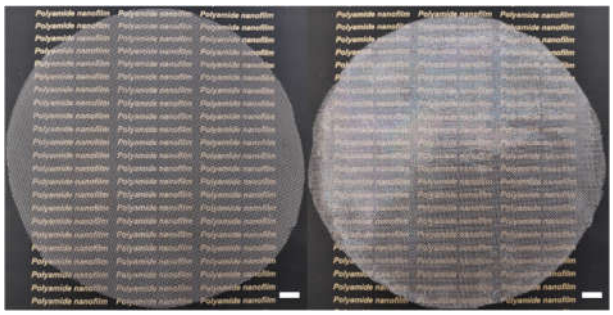


Fig. S4. Synthesizing large-area PA nanofilms (25 ºC, piperazine/TMC = 0.5/0.7 g/L; left: metal mesh, right: metal mesh with a PA nanofilm on it). The scale bars are all 1.0 cm.

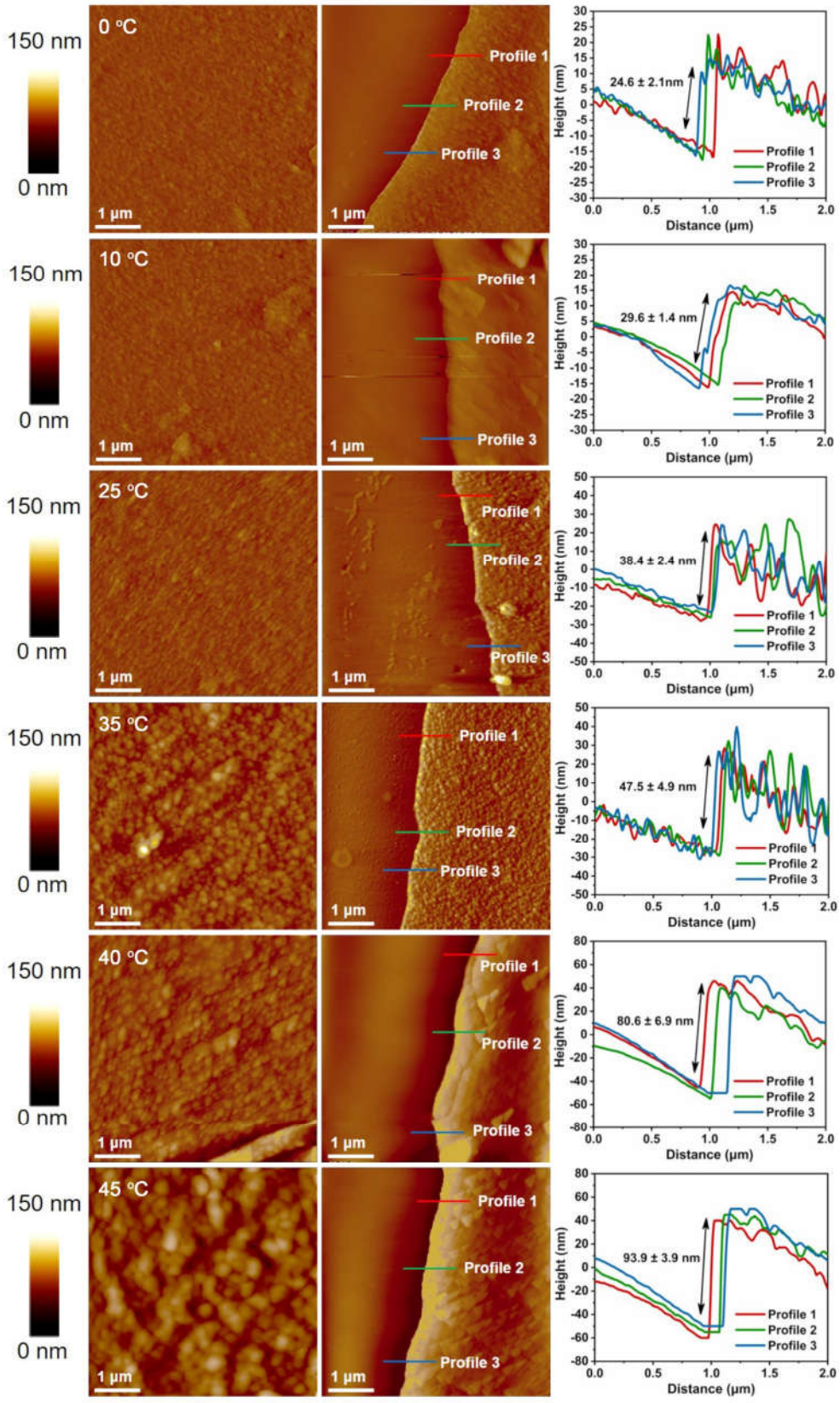


Fig. S5. AFM images of surface (left column) and thickness with height profile (middle column and right column) of PA nanofilms synthesized at different temperatures at free hexane-water interface (piperazine/TMC = 0.2/0.7 g/L).

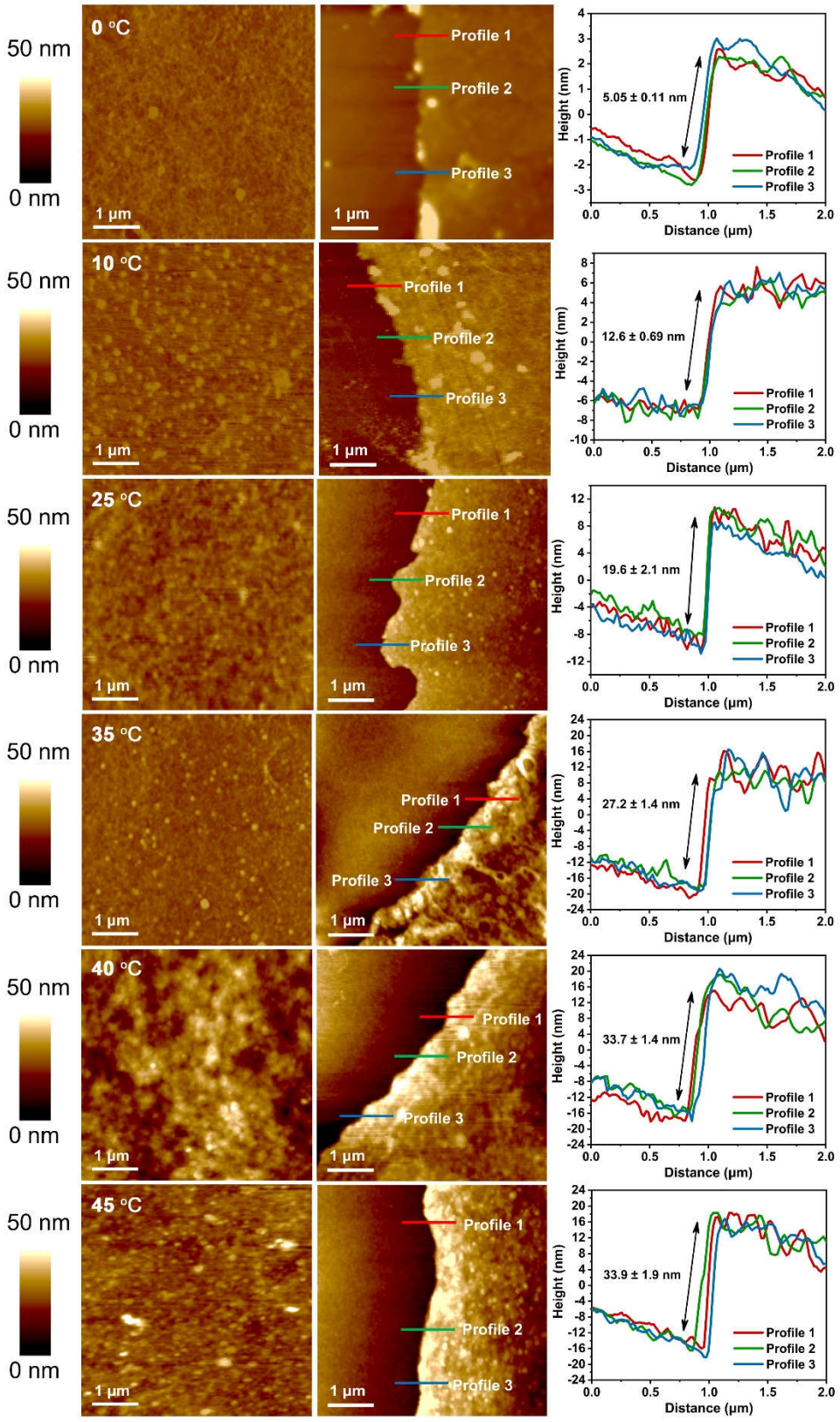


Figure S6 AFM images of surface (left column) and thickness with height profile (middle column and right column) of PA nanofilms synthesized at different temperatures using the "jelly" as storage phase of piperazine (piperazine/TMC = 0.2/0.7 g/L).

Table. S1 AFM height parameters of PA nanofilms synthesized at different temperatures using the "jelly" as storage phase of piperazine (piperazine/TMC = 0.2/0.7 g/L).

Reaction temperature (°C)	Height profile of PA nanofilms synthesized at hexane-"jelly" interface (nm)	Height profile of PA nanofilms synthesized at hexane-water interface (nm)	Average thickness of PA nanofilms synthesized at hexane-"jelly" interface (nm)	Average thickness of PA nanofilms synthesized at hexane-water interface (nm)
0	5.09 5.13 4.92	23.58 23.22 27.19	5.05±0.11	24.6±2.1
10	12.78 11.85 13.19	30.96 28.16 29.79	12.6±0.69	29.6±1.4
25	21.92 17.90 19.03	38.18 37.02 41.17	19.6±2.1	38.4±2.4
35	25.81 27.26 28.5	47.99 42.32 52.14	27.2±1.4	47.5±4.9
40	32.08 34.59 34.53	88.36 78.71 74.80	33.7±1.4	80.6±6.9
45	32.11 35.84 33.62	98.12 93.65 91.17	33.9±1.9	93.9±3.9

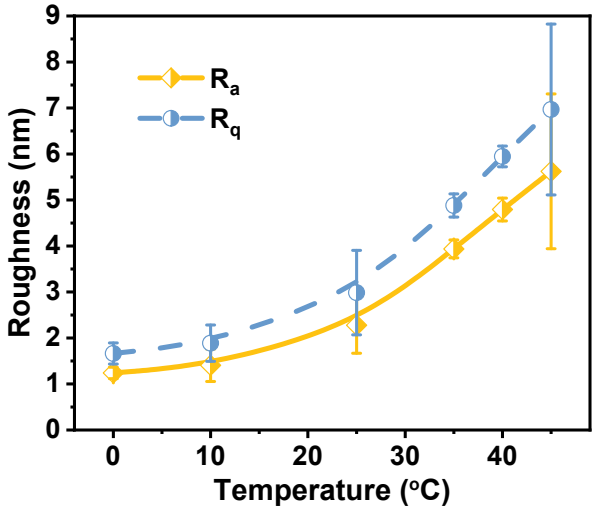


Fig. S7. Surface average roughness (R_a) and root mean square roughness (R_q) of PA nanofilms synthesized at different temperatures (piperazine/TMC = 0.2/0.7 g/L).

Estimation of apparent activation energy

For the whole interfacial polymerization process, the rate constants of reaction and diffusion of the interfacial polymerization are expressed as k_1 and k_2, respectively. Ideally, both two rates satisfy the Arrhenius equation. k_1 and k_2 are combined into k on behalf of the macroscopic rate constant of the entire interfacial polymerization for simplification, and k satisfies the equation:

$$\ln k = \frac{-E_a}{RT} + \ln A_1 \quad (1)$$

where E_a is the apparent activation energy of the interfacial polymerization (kJ·mol^{-1}), R is molar gas constant (8.3145 J·mol^{-1}K^{-1}), T is thermodynamic temperature (K), A_1 is preexponential factor.

Assuming that the thickness is h for the PA nanofilm by the interfacial polymerization for a certain period of time and the density of the nanofilm is uniform, then h has the following relationship with the macroscopic reaction rate constant k,

$$h \propto \frac{\Delta m}{\Delta t} \propto \frac{\Delta C}{\Delta t} \propto k \quad (2)$$

where Δm is the mass loss of monomer during the reaction, ΔC is the change of concentration during the reaction, Δt is the unit reaction time.

Taking the natural logarithm of the film thickness h, the relationship between h and k can be expressed as

$$\ln h = \ln k + A_2 \quad (3)$$

A_2 is an arbitrary constant. Substituting equation (1) into (3) can obtain the following equation,

$$\ln h = \frac{-E_a}{RT} + \ln A_1 + A_2 \quad (4)$$

Let $\ln A_1 + A_2$ be A, then equation (4) can be expressed as

$$\ln h = \frac{-E_a}{RT} + A \quad (5)$$

Taking $1/T$ as the abscissa and $\ln h$ as the ordinate can get the curve depicted in Fig. 3 in the main text.

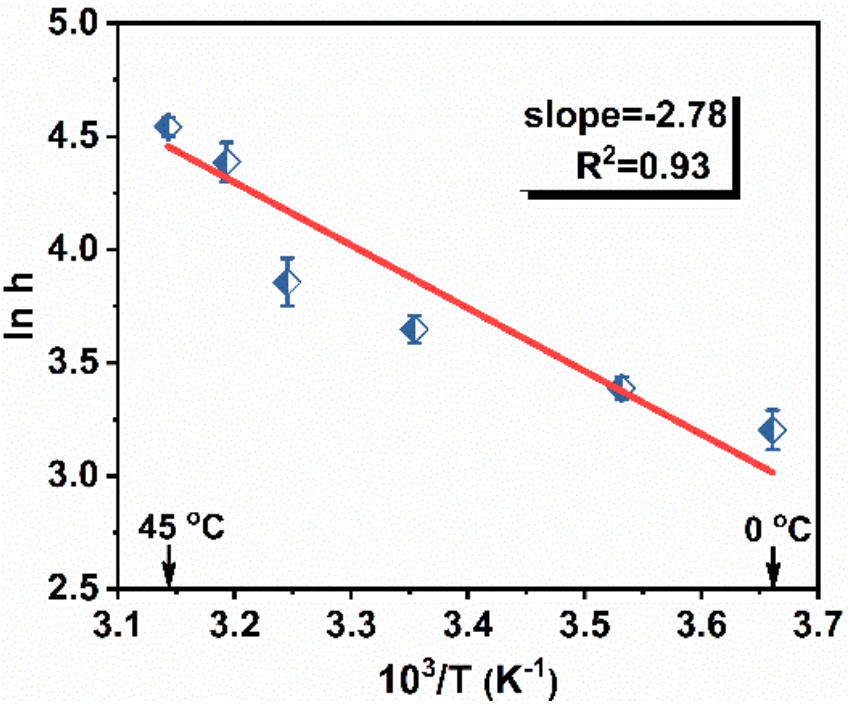


Fig. S8. Estimation of apparent activation energy of free hexane-water interfacial polymerization based on the relation between the reaction temperature and the thickness of the synthesized PA nanofilms.

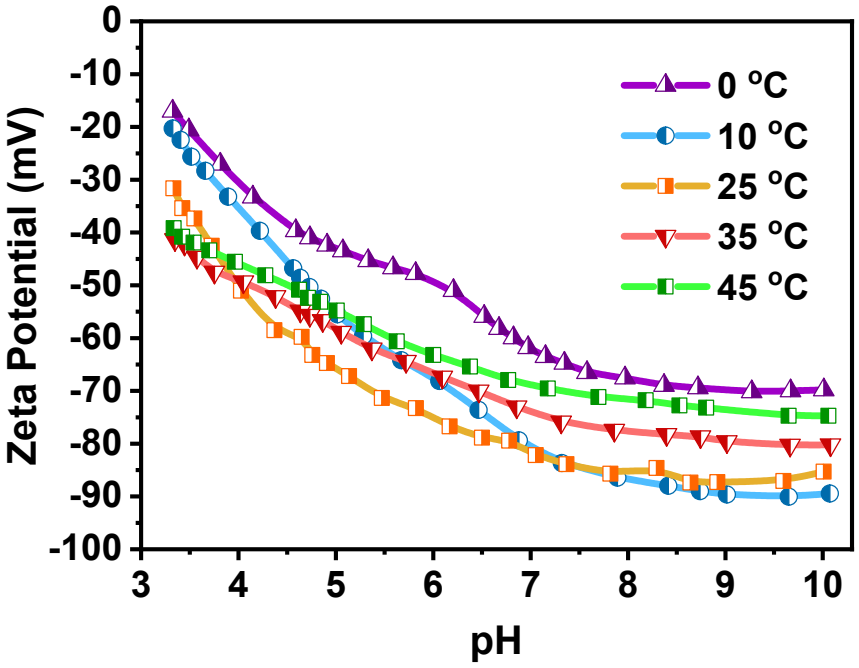


Fig. S9. Surface zeta potential of PA nanofilms synthesized at different temperatures (piperazine/TMC = 0.2/0.7 g/L).

Table S2. Zeta potential and rejection to Na_2SO_4 of some polyamide-based membranes reported in literatures.

Membrane	Zeta potential (mV, pH=7)	Rejection to Na_2SO_4 (%)
This work (piperazine/TMC = 0.2/0.7 g/L, 25 ºC)	-82	97.7
Ref. 8	ca. -8	96.5
Ref. 18	-31.5	99.6
Ref. 19	ca. -17	ca. 95
Ref. 20	-38.2	97
Ref. 31	ca. -54	99.1
Ref. 33	-35.54	94.7
Ref. 36	ca. -30	ca. 97
Ref. 37	ca. -76	98
Ref. 39	ca. -75	ca. 96%
Ref. 43	ca. -35	97.5%

*Reference number corresponds to the citation in the main text.

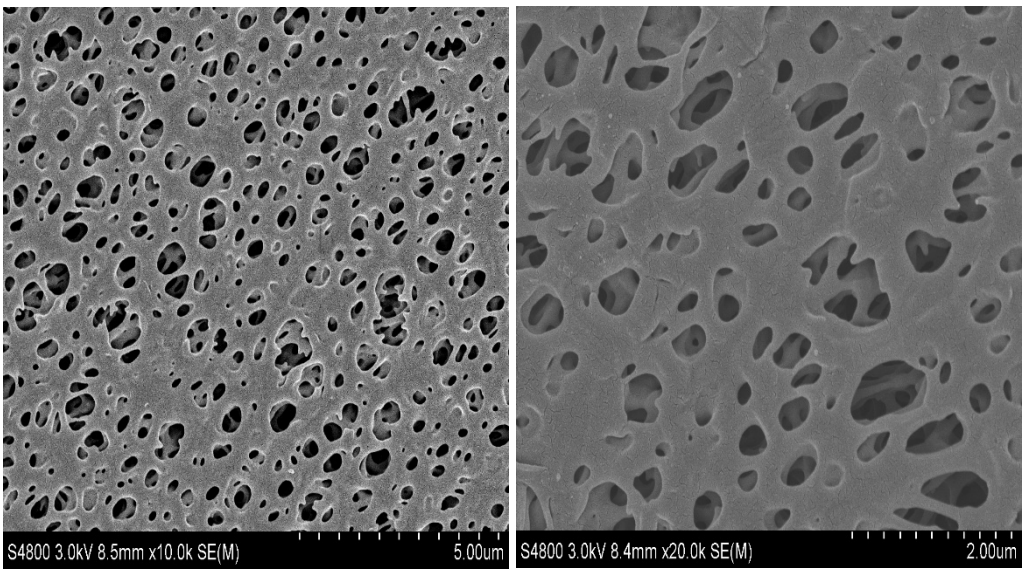


Fig. S10. SEM images of polyether sulfone substrate used to support PA nanofilms.

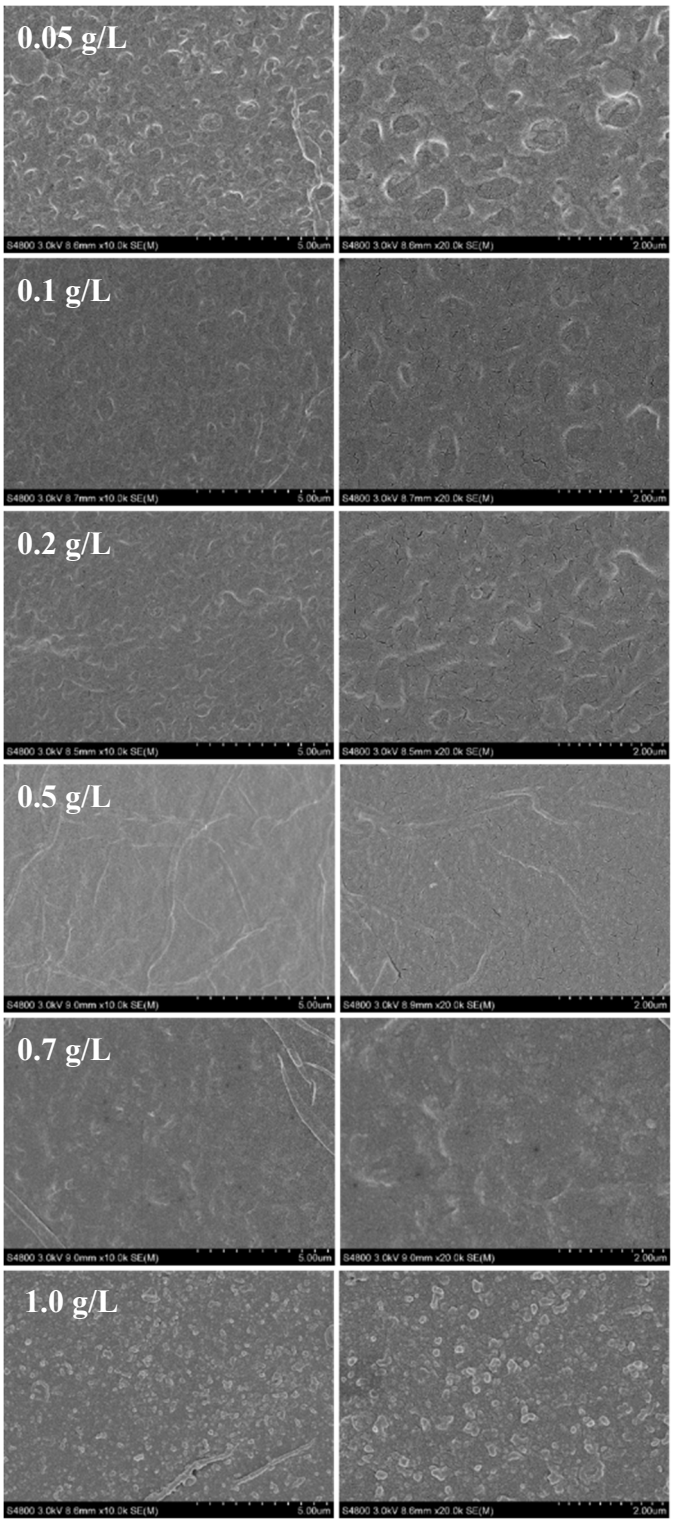


Fig. S11. SEM images of PA nanofilms synthesized with different concentrations of piperazine (TMC in hexane is fixed at 0.7 g/L, 25 ºC). The right side are partially enlarged images.

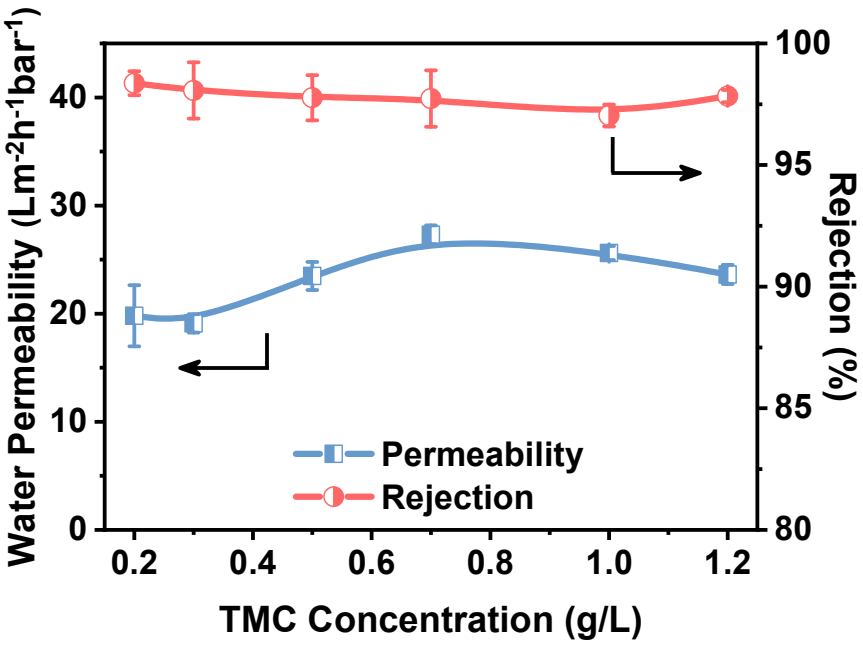


Fig. S12. Water permeability and rejection to Na_2SO_4 of the PA nanofilms synthesized with different concentrations of TMC in hexane (the concentration of piperazine in "jelly" is fixed at 0.2 g/L; Na_2SO_4 concentration: 1000 ppm; applied pressure: 4 bar).

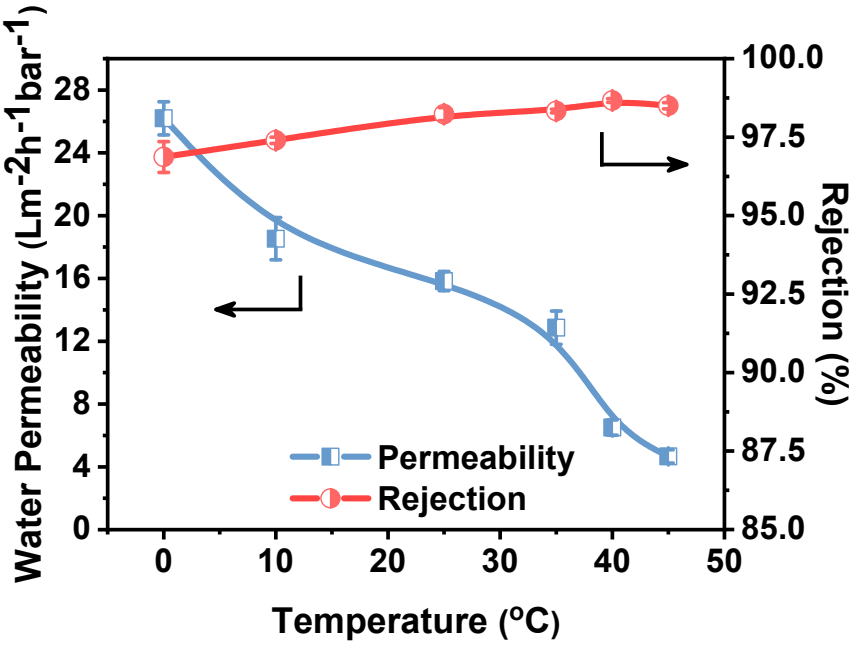


Fig. S13. Nanofiltration property of the PA nanofilms synthesized at free hexane-water interface at different temperature (piperazine/TMC = 0.2/0.7 g/L; Na_2SO_4 concentration: 1000 ppm; applied pressure: 4 bar).

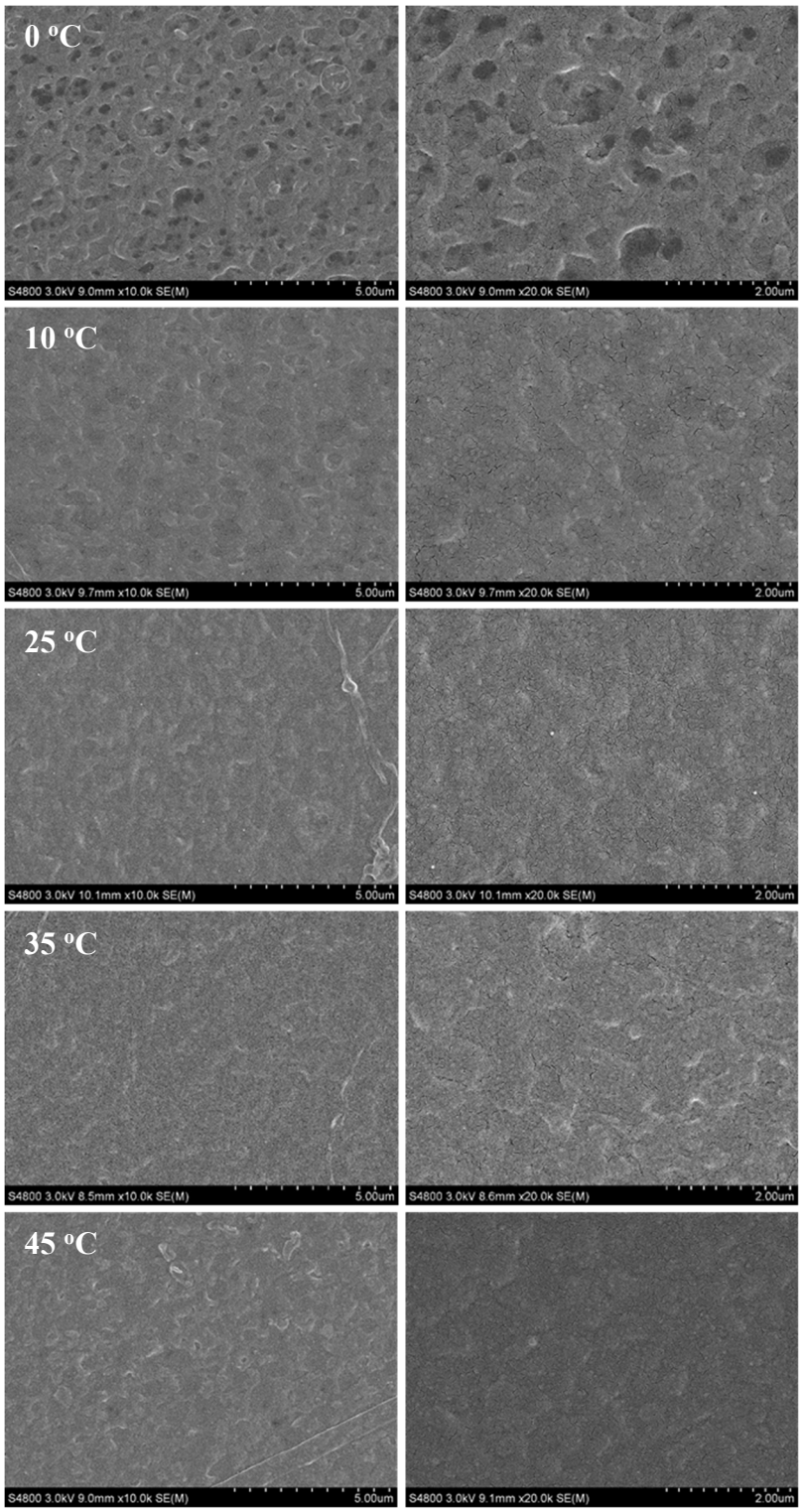


Fig. S14. SEM images of PA nanofilms synthesized at different temperatures (piperazine/ TMC = 0.2/0.7 g/L). The right side are partially enlarged images.

Characterization and measurements

The surface morphologies of PA nanofilms were observed by a field emission scanning electron microscope (SEM, Hitachi, S4800, Japan) and a scanning probe microscope (SPM, Veeco, MultiMode, USA). NanoScope Analysis software V.1.40 was used for collecting thickness and roughness values from the SPM data. The surface zeta potentials of the PA nanofilms were analysed by an electrokinetic analyser (SurPASS AntonPaar, GmbH, Austria) with KCl solution (1 mmol·L^{-1}) as the electrolyte solution, and the pH was tuned by adding HCl or NaOH solutions to titrate the electrolyte solution.

The water permeance and salt rejection properties of the PA nanofilms with PES substrates was assessed by lab-scale cross-flow flat membrane filtration apparatus at a feed flow rate of 30 L·h^{-1} and at a trans-membrane pressure of 4 bar. The testing conditions were maintained at 30 ºC with an agitating speed of 300 rpm. The concentrations of involved salt solutions were all 1 g/L (1000 ppm). All samples were preloaded at 6 bar for 30 min before assessment. The water permeance of the nanofilms was calculated using the following equation:

$$P_{\mathrm{w}}=\frac{V}{A\,t\,P}$$

where V is the volume of permeated solution (L), A is the effective filtration area (m^2), t is the permeation time (h), P is the applied pressure during the measurement (bar).

The salt rejection was calculated by

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

where C_p and C_f are the concentrations of permeated and feed solutions, respectively. The concentrations of solutions were inferred by the conductivity of the solutions using an electrical conductivity meter (METTLER TOLEDO, FE38, China).

REFERENCES

1 H. Petride, C. Drăghici, C. Florea and A. Petride, *Open Chemistry*, 2006, **4**.