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Support information for: Time-Dependent FTIR Microscopy for Mechanism Investigations and Kinetic Measurements in Interfacial Polymerisation: A Microporous Polymer Film Study

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Contents

- 1 Materials
- 2 ATR-FTIR Devices
- 3 FTIR Spectra of Reactants
- 4 Dienol-Diketone Tautomerism
- 5 Enlarged Figures of FTIR Curves
- 6 The Relationship Between Absorption Peak Areas and Concentrations
- 7 Partition Coefficient
- 8 Diffusivity of RES and BHPF
- 9 Calculation of Reaction Kinetics

References

1 Materials

9,9-bis(4-hydroxyphenyl)fluorene (BHPF, 99%, Sigma-Aldrich Co., Ltd., USA), 1,3benzenediol (resorcinol, RES, 99%, Sigma-Aldrich Co., Ltd., USA) and trimesoyl chloride (TMC, 99%, Beijing Bailingwei Technology Co., Ltd., China) were used as monomers for the interfacial polymerization (IP) process to form TFC membranes. Hexane (>99%), phenolphthalein (99%) and sodium hydroxide (NaOH, 99%) (Sinopharm Chemical Reagent China Co., Ltd.) were used as solvents for the monomers. All chemicals were of analytical grade and used without further purification. Deionized (DI) water (conductivity $< 6 \ \mu S \ cm^{-1}$) was prepared in the laboratory. To prepare the aqueous solutions, BHPF and RES phenol monomers were first dissolved in dilute sodium hydroxide aqueous solution (pH 13) with molar ratios of 4:1 (NaOH: BHPF) and 2:1 (NaOH: RES). The resulting concentrations of BHPF and RES aqueous solutions were both 1 w/v%. A small quantity of phenolphtalein was then added into the aqueous solution to make up a molar ratio of 1000:1 (BHPF or RES:phenolphthalein). Phenolphthalein was used as an indicator to turn the basic aqueous solutions from colourless to magneta to aid visualisation. The organic solution was prepared by dissolving TMC in hexane (1 w/v%) under rigorous stirring for 2 min. The aqueous solutions of phenol monomers and organic solution of TMC monomer were reacted interfacially to form thin film layers.¹

2 ATR-FTIR Devices

2.1 Microscope to observe the IP process

A optical microscope (Olympus BX51) was used to observe the IP process. The objective lens was set to 20 x magnification.

2.2 ATR-FTIR spectroscopy

Attenuated total reflectance (ATR)-Fourier transform infrared (FTIR) spectrometer (Nicolet 6700 Continuum, USA) was used to measure the interfacial reaction and monitor the changes of functional groups at the thin film layer. Zinc selenide (ZnSe) was used as ATR internal reflection element and each spectrum was in average captured by 16 scans at a 4 cm⁻¹ resolution.

2.3 Experimental details

To prepare FTIR spectrometer, fixed quantity of liquid nitrogen was first added into the vacuum bottle. Then, a KBr window was placed on the loading platform (a gold mirror plate) of the spectrometer and secured stably. The X, Y and Z axes of the microscope were initialized. After that, the platform was adjusted until its center aligned with the infrared light and the light source was tuned to brighten the field of view. Once the spectrometer was ready, organic solution of TMC and aqueous solutions of phenols were loaded separately into 1 μ L syringe injectors. Firstly, the aqueous solution (0.1 μ L), was instilled into the gap between the platform and the KBr window. The KBr window was used to press gently against the droplet to form a thin aqueous layer with boundary underneath the window (Fig. 1). Secondly, the organic solution (0.1 μ L), was instilled into the gap from the other side of the window which was opposite to the aqueous solution. Then, the KBr window was squeezed gently to move the organic solution towards the boundary of the aqueous layer. The thickness of the encounter boundary formed when the organic and aqueous layers first contacted was about 10 μ m. The encounter boundary area is estimated to be about 10⁻⁷ cm² (10 μ m × 1 cm). At the same time, the mapping of spectrometer was initiated to scan along the direction starting from the aqueous phase to the organic phase. Infrared data of the aqueous solution were first collected, and then the changes in functional groups were detected at the boundary where aqueous and organic layers met and IP occurred (Fig. S1). Lastly, infrared data of the TMC hexane solution were collected when the scan reached the organic layer. By taking the time intervals and the distances between each consecutive measurement, film thickness and dynamics were observed at real-time.



Fig. S1: The picture of FTIR-microscope area. The scanning is along the red line and the scanning distance (μ m) is from the aqueous (Y=0 μ m) to the organic phase in an interval of 10 μ m per 6.72 s.

3 FTIR Spectra of Reactants

Pure TMC, 1 w/v % TMC solution in hexane, PAR-RES, 1 w/v % RES in NaOH aqueous solution, and 1 w/v % BHPF in NaOH aqueous solution were characterised by FTIR. The doublet around the region close to 1000 cm⁻¹ are C-O/C-H absorption peak. The absorption peak at 1780 cm⁻¹ is the Cl-C=O of an acyl chloride of pure TMC in solid state, as indicated by green line in Fig. S2. After dissolving pure TMC in hexane, the Cl-C=O absorption peak shifted slightly to 1790 cm⁻¹ due to the homophilic interaction with nonpolar solvent. After dissolving in the hexane, the peaks of Cl-C=O and C-H of the aromatics diminished significantly. As expected, the alkyl (CH₃/CH₂) absorption peaks appeared due to hexane. The stretching vibration of CH₃/CH₂ is around 2900 cm⁻¹ and the bending vibration is around 1450 cm⁻¹.

The PAR-RES was synthesized on a watch glass using the equal molar concentrations of RES and TMC. The aromatics (Ar) absorption peaks were found at around 1450 and 1600 cm⁻¹. The C-O-C absorption peak was split into multiple peaks around 1150 cm⁻¹, while O-C=O absorption peak appeared at 1770 cm⁻¹. Both C-O-C and O-C=O are from the functional groups of PAR crosslinked network used to distinguish the occurance of IP. As expected, for both aqueous solutions of RES and BHPF, strong and broad O-H absorption peak appeared at 3000-3500 cm⁻¹ and the peaks at 1600 cm⁻¹ is aromatics (Ar). The small peaks at 2150 cm⁻¹ are the absorption

peaks of diketone counterparts of RES and BHPF. Due to low concentration, the absorption peaks of other functional groups were overwhelmed by O-H absorption peak from NaOH solution. With high resolution of FTIR among these groups, the absorbance of each peak could be quantitatively isolated for real-time chemical transformation of the IP process.



Fig. S2: The FTIR spectrums of pure TMC, 1 w/v % TMC dissolved in hexane, PAR-RES, 1 w/v % RES in NaOH aqueous solution and 1 w/v % BHPF in NaOH aqueous solution.

4 Dienol-Diketone Tautomerism

Between C=C-C=O and C=C-C=C, oxygen is more electronegative than carbon. The area of bonding orbitals of C=C-C=O overlap more so the bond length is shorter and the bond energy is higher. Hence, the C=C-C=O is more stable and phenol exists as ketone rather than enol type. The tautomerism is reversible so phenol can react either in the form of dienols (*e.g.* acylation) or diketones (*e.g.* dioxime). With the consumption of RES, the RES-DK continues to proceed towards RES formation, which can be completed instantly (<1 s), far faster than the PAR polymerisation.²⁻⁶



Fig. S3: Dienol-diketone tautomerism of RES and BHPF.

5 Enlarged Figures of FTIR Curves

TMC in hexane was added 20 s after the aqueous solution, and then the area of C=C-C=O absorption peak at 2150 cm⁻¹ decreased with reaction time indicating that the RES being consumed (Fig. S4). The small peaks appeared at 1150 cm⁻¹, are the C-O-C absorption peaks of the PAR. At 1450 cm⁻¹, the absorption peak area of aromatics increased with reaction time. This indicates higher reactant concentrations, both the RES and TMC. TMC and RES diffused to interface and participated in the reaction in the organic phase. After 20 s, the absorption peaks of O-C=O of PAR started to appear at 1770 cm⁻¹ until 100 s which indicates film formation. The results also show that the IP is very fast and can complete within 60 s.^{7,8}



Fig. S4: Enlarged FTIR curves from 1000 to 1900 cm⁻¹. (a) RES. (b) BHPF.

6 The Relationship between Absorption Peak Areas and Concentrations

FTIR absorption peak areas of known concentrations: RES-DK, BHPF-DK, C=C-C=O of PAR-RES were measured. RES and BHPF of various concentrations dissolved in dilute sodium hydroxide aqueous solution. For PAR-RES, the solution was stirred and PAR was wrapped around a glass rod then dried in vacuum more than 24 h. The dried PAR was dissolved in aqueous solution at various concentrations for measurement.⁹⁻¹¹



Fig. S5: The relationship between absorption peaks areas and concentrations. (a) RES-DK. (b) BHPF-DK. (c) PAR-RES.

7 Partition Coefficient

The oil/water partition coefficient *K* was measured using the method similar to ref S12. 1 mL of aqueous MPD solution are mixed with equal volume of hexane, and then stirred at 1000 rpm for 5 h to allow equilibration.¹² UV absorbance of oil samples at different concentrations were measured over a range of wavelength to determine the specific wavelength with maximum absorption (Fig. S6 a and d). The absorbance at 296 nm is then converted to concentration by measuring the absorbance of known concentrations (Fig. S6 b and e). Fig. S6 shows concentrations in the oil versus the water after equilibration. Samples are measured at different aqueous concentrations. The slope indicates a partition coefficient of *K* = 0.002 for RES and *K*=0.0016 for BHPF.



Fig. S6: (a) Absorbance spectra for RES in hexane over a range of wavelength under various concentrations. (b) Absorbance at 296 nm for RES in hexane under various concentrations. (c) RES concentrations in oil against in water after equilibration with the slope represents the oil/water partition coefficient. (d) Absorbance spectra for BHPF in hexane over a range of wavelength under various concentrations. (e) Absorbance at 296 nm for BHPF in hexane under various concentrations. (f) BHPF concentrations in oil against in water after equilibration with slope represents the oil water after equilibration with slope represents the slope represents the oil water after equilibration with slope represents the oil water after equilibration with slope represents the slope represents the slope represents the oil water after equilibration with slope represents the slope

oil/water partition coefficient.

8 Diffusivity of RES and BHPF

The diffusive flux of RES or BHPF was determined by the concentration gradient as shown below,

$$J = -D_{\rm w} \frac{\partial [RES]}{\partial \mathbf{r}} \bigg|_{r=R}$$
(1)

$$J = -D_{\rm w} \frac{\partial [BHPF]}{\partial \mathbf{r}} \bigg|_{r=R}$$
⁽²⁾

J is the diffusive flux of RES or BHPF into the organic phase, D_w is the diffusivity of RES or BHPF in aqueous phase), *r* is the radial coordinate, and *R* is the distance.

The diffusivity of RES and BHPF in D₂O (D_w) was obtained using pulsed field gradient nuclear magnetic resonance (PFG NMR).¹³ Experiments were performed at 20°C on a 600M hydrogen (H-NMR) (JNM-ECA600, Japan). As Fig. S7 shows, Log(D_w)=2.35 for RES and Log(D_w)=2.07 for BHPF in D₂O were obtained. So D_w =223.87 µm²/s for RES and D_w =117.25 µm²/s for BHPF in water. The solubilities of RES and BHPF in hexane are too low and outside the detection limit of NMR, so the diffusivity in hexane (D_o) was estimated according to Eqn (3) and (4).¹⁴

$$D_{\rm o} = 7.4 \times 10^{-8} \times \frac{T(xM)^{1/2}}{\eta V^{0.6}}$$
(3)

$$\frac{D_{o}}{D_{w}} = \sqrt{\frac{x_{Hexane}M_{Hexane}}{x_{Water}M_{Water}}} \frac{\eta_{Water}}{\eta_{Hexane}} = \sqrt{\frac{86 \times 1}{18 \times 2.6}} \times \frac{0.8937}{0.307}$$
(4)

where T is temperature (K); M is the molecular mass of the solvent (g/mol); η is the viscosity of the solution (mPa·s); V is molar volume of solute at normal boiling point

(mL/g·mol); x is the constant with a value equal to 1.0 for hexane and 2.6 for H₂O, respectively.¹⁴ Due to low solute concentrations, the solute viscosity can be approximated as solution viscosity. The absolute viscosity of water is 0.8937 mPa·s and that of hexane is 0.307 mPa·s at 25 °C. The diffusivities were calculated to be 883.48 μ m²/s for RES in hexane and 462.69 μ m²/s for BHPF in hexane.



Fig. S7: The source file of ¹H PFG NMR spectra for (a) RES and (b) BHPF in the water. The ordinate is Log(D).



Fig. S8: The diffusivities of RES and BHPF in the water and hexane.

9 Calculation of Reaction Kinetics

The equations used to determine the reaction kinetics are below:¹⁵

$$J_0 = K[RES]_0 \sqrt{6k[TMC]_0 D_0}$$
⁽⁵⁾

$$J_0 = K[BHPF]_0 \sqrt{6k[TMC]_0 D_0}$$
(6)

where J_0 is the initial diffusive flux of RES or BHPF. *K* is the oil/water partition coefficient of RES, which was measured by UV spectrophotometer as shown in Fig. S6. [*RES*]₀, [*BHPF*]₀ and [*TMC*]₀ are the initial concentrations of RES, BHPF in aqueous solution and TMC in hexane, respectively. The factor 6 reflects bifunctional RES or BHPF and trifunctional TMC. *k* is the unknown reaction rate constant and D_0 is the diffusivity in oil. Based on Eqn (5) or (6), the reaction rate constant *k* could be calculated as showed below:



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