Supplementary Information for

Rock-on-a-chip: "Seeing" the association/disassociation of an adaptive polymer in solutions flowing through porous media

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Measurement of the porosity and permeability of a three-dimensional porous medium

A 3D porous medium with a granular packing of 38- μ m-diameter borosilicate glass beads (Mo-Sci, USA) was used in this study. The grains were packed into a quartz tube (VitroCom, USA) with a square cross-sectional area ($A_{tube} = 3 \text{ mm x } 3 \text{ mm}$) and tapped for five minutes for densification. Subsequently, the medium was lightly sintered in a furnace at 875 °C for 3 min.

The porosity of packing, ϕ , was calculated using the following equation:

$$\phi_0 = \frac{A_{\text{tube}} \cdot I_{\text{tube}} - \left(\frac{w_1 - w_0}{\rho_b}\right)}{A_{\text{tube}} \cdot I_{\text{tube}}} \times 100\%$$
(S1)

where l_{tube} is the length of the quartz tube, w_1 and w_0 indicate the weight of the tube after and before glass-bead filling, respectively, and $\rho_b=2.2 \text{ g} \cdot \text{cm}^{-3}$ is the glass-bead density. As summarized in Table S2, the six media used here exhibited similar porosities (~37%), confirming the reproducibility of our protocol. Pore-structure analysis using confocal images (Fig. S5) verified this further. The pore spaces of the six groups of models were distributed uniformly, and the local porosity values, calculated according to their area, were in the range of 36–38% (similar to the values calculated by the weighting method).

To measure the water-phase permeability of the medium, the ends of the packing were sealed by cementing the inlet and outlet tubing with valves for pressure taps. Subsequently, saline water (4500 mg/L NaCl) was injected into the medium at various volumetric flow rates (Q_w), and the ΔP was recorded using an Omega PX409 differential pressure transducer. As shown in Fig. S6, ΔP (as a function of Q_w) was fitted according to Darcy's law, $\Delta P = \eta_w Q_w l_{tube} / (A_{tube} k)$. From the slope, $\eta_w l_{tube} / (A_{tube} k)$, $k \approx 1.4 \,\mu\text{m}^2$ for the six media, in good agreement with previous measurements of similar porous media (1,2).

Oil recovery in the three-dimensional porous medium

During multiphase flow within a 3D porous medium, the polymer-induced velocity distribution change (i.e., the displacement efficiency) can be used to evaluate the capacity of the polymer solution for enhanced oil recovery. Here, the oil recovery factors of polymer flooding for the three polymer solutions were compared to evaluate the potential of the adaptive polymer for oil recovery.

Crude oil ($\eta_s \approx 13 \text{ mPa} \cdot \text{s}$, Fig. S7) was injected into the medium at various flow rates for full saturation, followed by water injection, polymer solution flooding, and chase water flushing of the medium. In each sequence, the pressure drop across the medium was measured, and the configurations of oil and displacing fluid in the medium were monitored using a confocal microscope (10× lens, *NA*=3, Leica SP5, USA). The water and polymer solutions were not dyed; thus, they were identified by their contrast with crude oil, showing intensive fluorescence over a broad range of excitation wavelengths.

To determine the exact amount of displaced oil (the oil concentration in the effluent), the effluent was collected and dissolved in a specific volume of toluene, its light absorbance was measured with a UV-vis spectrometer (Agilent, USA) and compared to a calibration curve (Fig. S8).

The oil recovery was evaluated as the mass ratio of accumulated oil production to the initial saturation, and expressed as a percentage. The incremental oil recovery factor of the polymer solution, E_p , was calculated as follows (3):

$$E_{\rm p} = E_{\rm t} - E_{\rm w} \tag{S2}$$

where E_t denotes the total oil recovery factor in the entire flooding process, and E_w indicates the initial water flooding recovery factor prior to polymer injection.

As shown in Fig. S10*A*, the index-matched fluid containing fluorescein (Sigma-Aldrich, USA), with 87.5 vol% dimethyl sulfoxide (Sigma-Aldrich, USA) and 12.5 vol% water, enabled a visualization of the disordered pore structure (green images). In contrast, the glass beads in the oil-saturated medium (red images) were indistinct; crude oil, being non-transparent, hindered the passage of light to the image planes. Nevertheless, the images could be used to identify the remaining oil distribution. A notable reduction in trapped oil was observed for the SAP-solution-flooding case (Fig. S10*B*), particularly after chase water flushing, while oil was only partially displaced by the HPAM solutions (Fig. S10*C* and S10*D*). Thus, using a 5.0 PV SAP solution followed by chase water flushing increased the oil recovery factor to 19.5%; this is higher than the oil recovery factors of the HPAM-1 (17.7%) and HPAM-2 (13.5%) solutions.

The difference in oil recovery between the three polymer solutions could be related to their properties of 3D-porous-medium flow. Here, the polymer solutions, injected at 200 μ l·h⁻¹, yielded an average interstitial velocity, $u_{int}=Q/(A\cdot\phi_0)$, of 16.7 μ m·s⁻¹. Hence, the shear rate of the pore throat within the medium was 12.7 s⁻¹ according to the equation: $\dot{\gamma}_{PT} = 4\alpha u_{int}(8k/\phi)^{-0.5}$, where α stands for the tortuosity of the pore throat and is approximately 1.05 for the spherical-glass-bead pack (4–6). The η_{eff} , $\dot{\gamma}_{W}$ curves in the 2D pore-throat model indicated that the three polymer solutions at this shear rate were in the shear thinning range. The effective viscosity of the HPAM-2 solution was the lowest and closest to that of crude oil, as shown in Fig. S7; thus, it exhibited low oil recovery, despite its high molecular weight.

In the MW-equivalent SAP and HPAM-1 solutions, the propagation pattern played an important role in oil displacement. As elucidated in the main text, the SAP molecules were transported individually and could sweep large areas, while the HPAM solutions clogged large pores and changed the direction of flow. The pressure drops in the polymer-injection regions (shown in Fig. S10*E*) indicated that the former generated more flow resistance, as shown by the delayed onset of pressure breakthrough (at 3.5 PV) for the SAP solution compared to that exhibited by the HPAM solutions (at 2.0 PV). Moreover, the HPAM solutions exhibited a more pronounced pressure decline than the SAP solution after breakthrough. Consequently, despite having a lower effective viscosity than the HPAM-1 solution, the SAP solution facilitated better oil recovery.



Fig. S1 Fluorescence spectra of the (A) SAP, (B) HPAM-1, and (C) HPAM-2 solutions at different polymer concentrations. The SAP solution exhibited an emission-maxima blue shift and an increase in

fluorescence intensity on increasing the polymer concentration. Fluorescence images (scale bar, 200 μ m) for the (D) SAP, (E) HPAM-1, and (F) HPAM-2 solutions (with a concentration of 1000 mg·L⁻¹) containing ANS. The excitation wavelength is 405 nm, C_{ANS} =400 mg·L⁻¹, and T=22 °C. An NaCl solution (4500 mg·L⁻¹) was used as the solvent.



Fig. S2 Stress-relaxation characterization of the (A) SAP, (B) HPAM-1, and (C) HPAM-2 solutions using a rotational rheometer at 22 °C with a strain of 10%. The shear stress (σ S) plotted as a function of time is described by the standard linear solid model indicated by the full lines (Materials and Methods in the main text). CSAP=1000 mg·L-1, CHPAM-1=1300 mg·L-1, and CHPAM-2=525 mg·L-1 in an NaCl solution (4500 mg·L-1), to maintain similar initial viscosities.



Fig. S3 Flow pressure drop data at different injection volumetric rates (indicated by solid symbols), corresponding to Figure 4A in the main text. Dashed lines indicate the predictions of Darcy's Law (using the shear viscosity of the bulk solution).



Fig. S4 2D-plane heat maps of the in-situ shear rate (\hat{Y}) in a sample converging-diverging section within the 2D pore-throat model for the (1) SAP, (2) HPAM-1, and (3) HPAM-2 solutions in NaCl (4500 mg·L-1). The flow rate is 2.88 µl·h-1. CSAP=1000 mg·L-1, CHPAM-1=1300 mg·L-1, and CHPAM-2=525 mg·L-1, to maintain similar initial viscosities. T=22 ° C.



Fig. S5 Confocal images (using an excitation wavelength of 488 nm) of six 3D model samples in a 2D plane showing the pore structure; the area fraction (representing the local porosity) was measured using the ImageJ software. The medium was filled with a fluorescein-dyed index-matching solvent (87.5 vol%)

DMSO and 12.5 vol% water). The black circles indicate glass beads, while the green areas in the lefthand-side image and white regions in the right-hand-side image indicate pore space. The scale bar is 200 µm.



Fig. S6 Steady-state pressure drops plotted as a function of the volumetric flow rates of injecting an NaCl solution (4500 mg·L-1) into different similarly-prepared porous media (indicated by different symbols). The permeabilities (evaluated from the slope, η wItube/kAtube, of the fitting lines based on Darcy's law) of the six media are similar, as shown in Table S2. T=22 °C.



Fig. S7 Bulk shear viscosity (η S) vs. shear rate ($\dot{\gamma}$) for the three polymer solutions and crude oil; the latter exhibits a Newtonian-like feature, with η S \approx 13 mPa·s. Crude oil is diluted using kerosene at a mass

ratio of woil:wker=3:2. CSAP=1000 mg·L-1, CHPAM-1=1300 mg·L-1, and CHPAM-2=525 mg·L-1,

to keep the initial viscosities similar, using an NaCl solution (4500 mg·L-1) as the solvent. T=22° C.



Fig. S8 UV-visible spectra of the crude oil and toluene mixture using different mass mixing ratios at 22 °C (e.g., 1/2400 in the legend represents crude oil/toluene by mass). The inset image, indicating the absorbance plotted as a function of the concentration of crude oil, indicates a linear relationship; A=30.12· C_{oil} .



Fig. S9 Probability density functions (PDF) plotted as a function of the magnitude of the normalized velocity $u \cdot \sqrt{k}$ for the (A) SAP, (B) HPAM-1, and (C) HPAM-2 solutions, after water flooding (indicated by black squares), polymer flooding (indicated by red circles), and chase water flooding (indicated by blue triangles). C_{SAP} =1000 mg·L⁻¹, $C_{\text{HPAM-1}}$ =1300 mg·L⁻¹, and $C_{\text{HPAM-2}}$ =525 mg·L⁻¹, to maintain similar initial viscosities in an NaCl solution (4500 mg·L⁻¹). T=22 °C.



Fig. S10 (A) Images of a sample 3D micromodel in a 2D plane consisting of an empty device filled with the index-matched fluid containing fluorescein before (top) and after (bottom) oil saturation. Areas (1) and (2) are magnified and shown on the right-hand side. (B, C, D) A portion of the remaining oil distribution in a 2D plane within the 3D porous media after water flooding (B(1), C(1), D(1)), polymer flooding (B(2) SAP, C(2) HPAM-1, and D(2) HPAM-2), and chase water flooding (B(3), C(3), D(3)). The red regions indicate crude oil, the black circles represent the beads constituting the medium, while the additional black regions show the invading undyed water and polymer solution. All scale bars are 200 μ m. (E) The pressure drop across the medium as a function of the injected pore volume for water flooding, polymer injection, and chase water flushing. $C_{SAP}=1000 \text{ mg} \cdot \text{L}^{-1}$, $C_{HPAM-1}=1300 \text{ mg} \cdot \text{L}^{-1}$, and $C_{HPAM-2}=525 \text{ mg} \cdot \text{L}^{-1}$ to maintain similar initial viscosities in an NaCl solution (4500 mg $\cdot \text{L}^{-1}$). T=22 °C.

Table S1 Fitting parameters of the Carreau model for SAP, HPAM-1, and HPAM-2 in an NaCl solution $(4500 \text{ mg} \cdot \text{L}^{-1})$ at 22 °C.

Sample	$C_{\rm p} (\rm mg \cdot L^{-1})$	η_0 (mPa·s)	п	$\dot{\gamma}_{c}$ (s ⁻¹)	λ (ms)
SAP	1000	55.3	0.70	0.56	228
HPAM-1	1300	53.9	0.68	2.00	184
HPAM-2	525	54.9	0.64	0.34	437

Table S2 Basic parameters of the 3D porous medium and oil recovery factors.

Medium sample	Polymer	$C_{\rm p}$ (mg·L ⁻¹)	Porosity (%)	Permeability (µm ²)	Oil saturation (%)	Oil recovery factor (%)		
						$E_{\rm w}$	$E_{\rm t}$	Ep
1	SAP	1000	37.1	1.34	81.1	/	/	/
2	HPAM-1	1300	38.0	1.43	82.1	/	/	/
3	HPAM-2	525	36.8	1.48	83.8	/	/	/
4	SAP	1000	37.4	1.41	80.3	64.5	84.0	19.5
5	HPAM-1	1300	36.1	1.49	88.3	67.1	84.8	17.7
6	HPAM-2	525	35.6	1.40	89.8	59.6	73.1	13.5

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