

Supplementary text I

Key Considerations in Targeting the Dilute Regime of the Polymer Solution

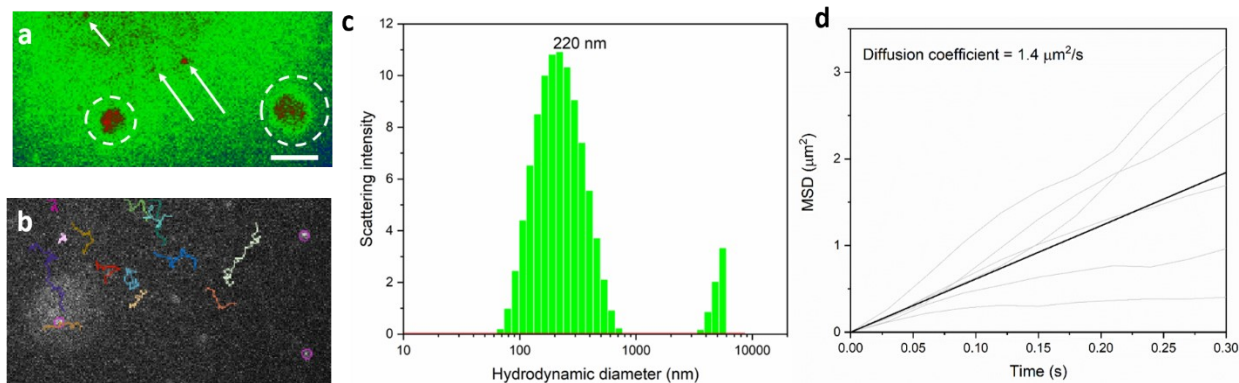
We considered three factors to determine that the 10 $\mu\text{g/mL}$ concentration lies in the dilute regime.

1- Our flow experiment demonstrated the presence of large polymer agglomerates in the solution (Fig. S1a, arrows). These agglomerates have an average hydrodynamic diameter of 220 nm, according to DLS (Supplementary Fig. S1a-c). The average diffusion coefficient (D) of these agglomerates obtained from single-particle tracking is $D = 1.4 \mu\text{m}^2/\text{s}$ (Fig. S1b,d). Viscosity of the polymer solution (η) was then calculated to be $\eta = 1.42 \text{ cp}$ by using the Stokes-Einstein equation (Equation S1). The calculated viscosity is close to that of water, suggesting that the polymer solution is in the dilute regime.

2- In addition, we examined the flow behavior inside the microchannels. With a flow rate of 10 $\mu\text{L}/\text{min}$, we observed a flow speed of up to 0.2 mm/s (Fig. 6d,e). The relatively high flow rate suggests a minimal impact of viscosity, indicating a dilute regime where viscosity effects are limited.

3- It is known that multiple scattering in semi-dilute and concentrated solutions increase the polydispersity index (Ragheb et al., Sci. Rep. 2020, 10, 21768). In our study, the polymer solution's polydispersity index (PDI) measured at 0.1 $\mu\text{g/mL}$ dilution was 0.16 (Fig. 1e,f). The low PDI suggests a relatively narrow distribution of particle size and thus indicates that a major fraction of the polymer molecules are monodispersed (un-entangled).

$$D = \frac{k_B \cdot T}{6 \cdot \pi \cdot \eta \cdot r} \quad (1)$$



Supplementary Fig. 1. Dynamic light scattering and single molecule tracking of polymer particles at 1 $\mu\text{g/mL}$ concentration. a) Fluorescence image of polymer molecules and agglomerates. The images were converted to RGB scale for enhanced visualization. The image illustrates the polymer molecules in green, and the polymer agglomerates in red. The circles indicate large agglomerates whereas the arrows indicate small agglomerates. Scale bar = 5 μm . b) Fluorescence image with overlaid diffusion tracks of small agglomerates. c) Dynamic light scattering histograms showing hydrodynamic diameter versus scattering intensity %. d) Mean squared displacement of small polymer agglomerates.

Supplementary text II

Calculation of the radius of gyration of Poly(fluorescein isothiocyanate allylamine hydrochloride)

The Kuhn length of poly(allylamine hydrochloride) is 2.3 nm² (= 5.8 monomer units; without considering the effect of fluorescein). The molecular weight of one unit of the polymer without and with fluorescein is 93.5 D and 425.5 D respectively. The ratio of polymer units to fluorescein-labeled units is 50:1, therefore the average molecular weight per unit is 100 D. The total molecular weight of the polymer is 56,000 D, thus, the number of units is 560 on average (contour length = 222 nm; monomer length = 0.3976 nm). The radius of gyration ($R_g = 9.25$ nm) of the flexible polymer can be calculated by

$$R_g = \sqrt{\frac{Nl^2}{6}}$$

where l is the length of Kuhn segments in the polymer chain and N is the number of Kuhn segments (97 segments)

Supplementary text III

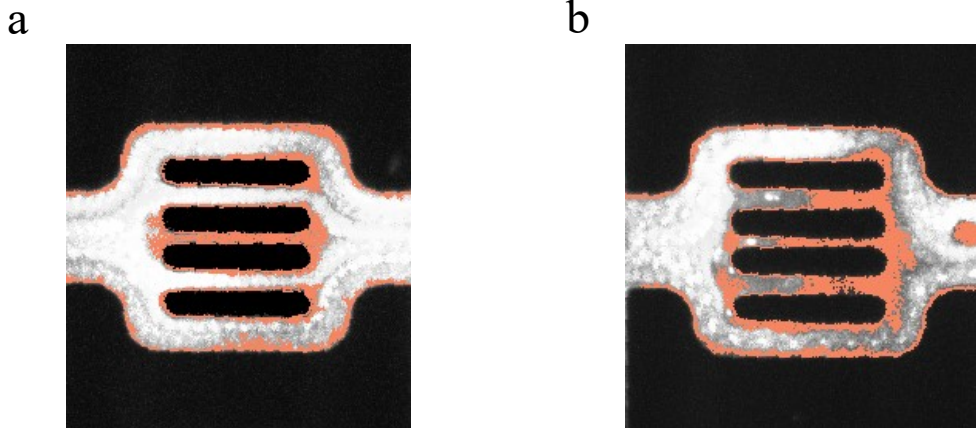
Time Scales of Polymer Entrapment in Porous Media and Their Implications on Flow Dynamics

The time scales linked to the three categories of polymer entrapment in porous media can vary and are contingent upon a multitude of factors, including polymer properties, rock characteristics, and fluid flow conditions. Although specific time scales may fluctuate, the following provides a general understanding of the typical time scales associated with each category:

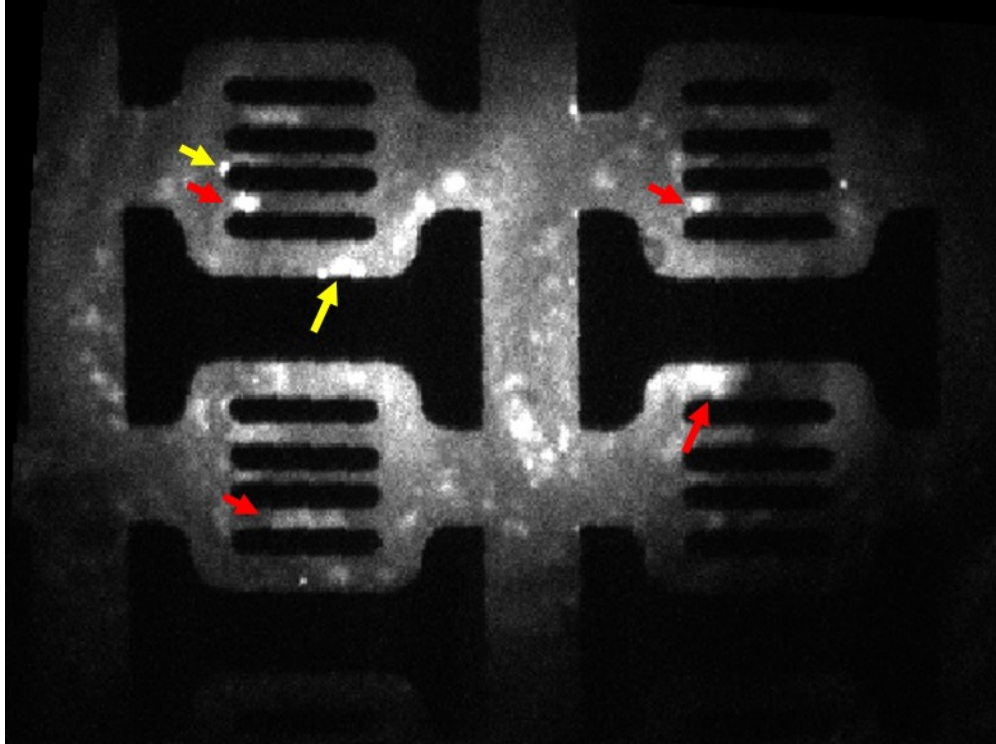
- The initial adsorption process, where polymers adhere to the surface, can happen rapidly, within minutes to hours. This is well observed in static adsorption experiments, used to measure polymer adsorption on crushed rocks (e.g., for sandstone it's typically within the range of 3-8 $\mu\text{g-polymer/g-rock}$).
- The time scale for mechanical entrapment is influenced by the rate of fluid flow and the size of the polymer molecules relative to the pore throats. If the polymers are larger than the pore throats, they can become mechanically trapped almost instantaneously upon entering the smaller pore spaces.
- Hydrodynamic retention occurs as a result of the fluid flow dynamics, and this could be the most complex mechanism. Lab observations showed that the impact of this mechanism can be very slow.³

Additionally, the entrapment mechanisms can occur simultaneously or sequentially, and the overall entrapment process can continue over longer time scales as polymers accumulate and interact with the porous media. Observed dynamic entrapment (i.e. mechanical and hydrodynamic) can be 1 order of magnitude higher than adsorption (i.e., > 50 $\mu\text{g/g}$).

Supplementary figure 2



Supplementary Fig. 2. Temporal color maps showing, the static adsorption of polymer molecules that occurred during the early time of the flow (1-2 hours), in orange, and the area available for fluid flow, in grey, in two different flow units within the microfluidic device. The average adsorption layer thickness on the outer walls is around $2\mu\text{m}$. The trapped polymeric material in the middle channels $2\mu\text{m}$ (a) and $5\mu\text{m}$ (b) is related to both static and dynamic components of retention. However, in this case, a clear distinction between the polymers entrapped by adsorption and by mechanical entrapment cannot be made. To clarify, the term "static" refers to the initial stage of adsorption, where polymer molecules attach to the walls of the PDMS chip and represent the interactions between the polymer and chip materials. This initial adsorption occurs during the early phase of flow when the chip is saturated with the polymer solution. The phenomenon described in the paper, including clogging of the $2\mu\text{m}$ and $5\mu\text{m}$ channels, occurs exclusively under dynamic flow conditions. The flow velocity in Supplementary Fig. 1 is the same as during the experiments, but the difference lies in the time frame: Supplementary Fig. 1 captures the early stage of flow within the first 1-2 hours, when the chip is being saturated with the polymer solution.



Supplementary Fig. 3. Adsorption and mechanical entrapment events occurring at different locations inside the microfluidic units. The yellow arrows indicate adsorption whereas the red arrows indicate mechanical entrapment or a combination of adsorption and mechanical entrapment.

Supplementary references

- 1- Ragheb, R. Multiple scattering effects on intercept, size, polydispersity index, and intensity for parallel (VV) and perpendicular (VH) polarization detection in photon correlation spectroscopy. *Sci. Rep.* 10, 21768 (2020).
- 2- Jachimska, B., Jasinski, T, Warszynski, P. and Adamczyk, Z. Conformations of poly(allylamine hydrochloride) in electrolyte solutions: Experimental measurements and theoretical modeling. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 355, 7–15 (2010).
- 3- Seright, R. S. How Much Polymer Should Be Injected During a Polymer Flood? Review of Previous and Current Practices. *SPE J.* 22, 01, 1–18 (2017). doi.org/10.2118/179543-PA