Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Oxygen inhibition of free-radical polymerization is the dominant mechanism behind the "mold effect" on hydrogels

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To evaluate the elastic modulus at the surface of the gels, the Hertzian contact model was fitted to the force-indentation data using least-square-error approach. The follow formula was applied:

$$F = \frac{4}{3}\frac{E\sqrt{R}}{1-\nu^2}(d-d_0)^{1.5},$$

where F is the measured force, E is the elastic modulus, R is the probe radius, ν is Poisson ratio, d is the indentation distance and d_0 is a shift along the indentation axis. In our case, E and d_0 were the fitting parameters, where d_0 served as a compensation for small errors in contact point determination. Fitting was performed within the first 1.5 µm of indentation depth. Homogeneous hydrogel surfaces could be very well described with the Hertzian model, Fig. S1.

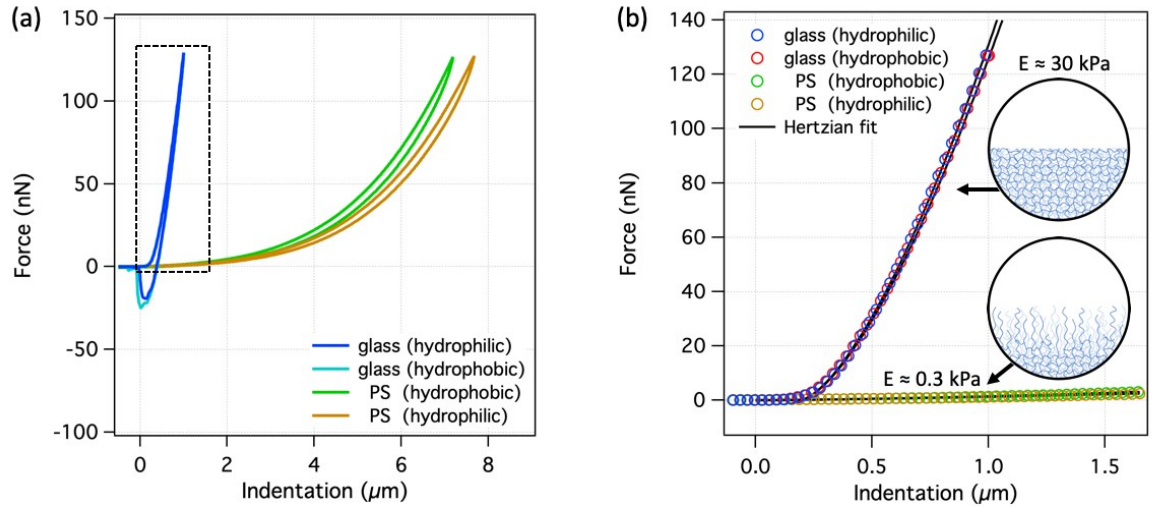

Figure S1: a) Representative force-indentation curves for PAAm hydrogel surfaces synthesized against a hydrophilic glass, OTS-functionalized glass, a PS surface and an acid-treated, hydrophilic PS surface. (b) Inset of the initial indentation zone showing the Hertzian model fitted to the experimental data.

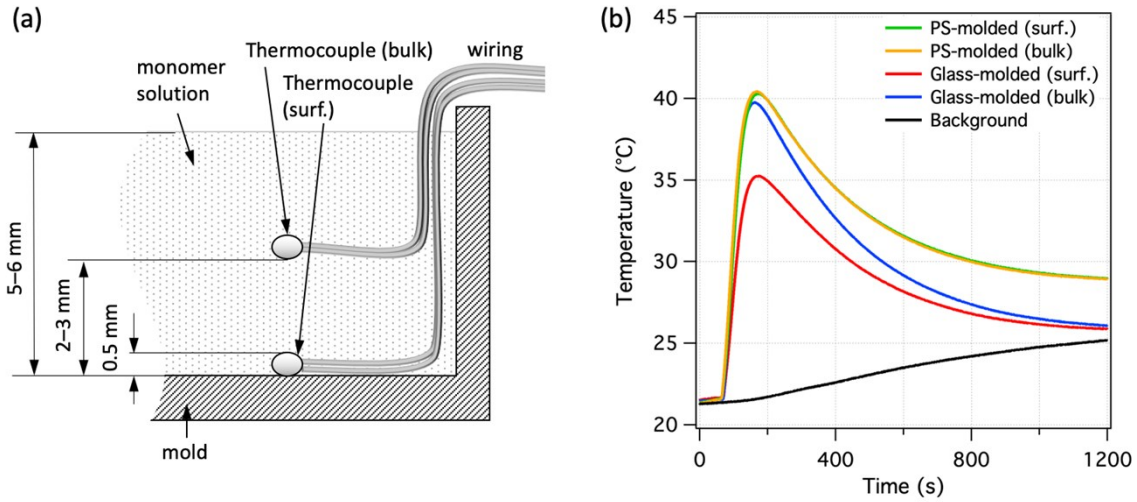

Figure S2: (a) Schematic of the temperature measurement using thermocouples of 0.5 mm in size positioned near the mold-solution interface and in the bulk of the polymerizing solution. (b) Temperature evolution during polymerization of 10 wt.% PAAm hydrogel measured in the bulk of the solution as well as near the interface with the glass and the PS mold. The black line shows the background heating of the UV chamber.

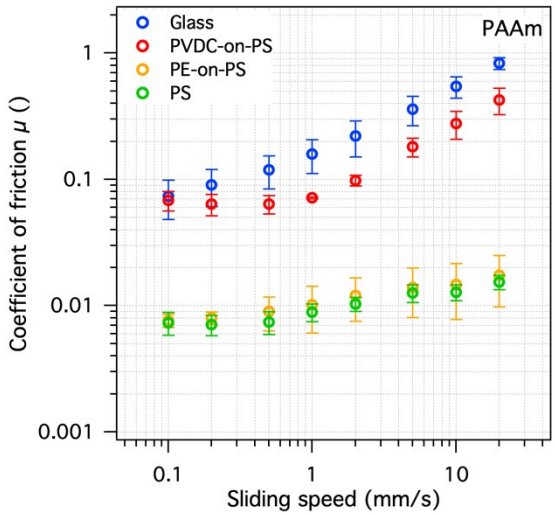

Figure S3: Coefficient of friction as a function of sliding speed for a cross-linked, glass-molded PAAm surface sliding against a glass-molded, PVDC-on-PS-molded, PE-on-PS-molded and PS-molded PAAm hydrogel at a contact pressure of 6 kPa in water. The coefficient of friction agrees with the elastic moduli presented in Fig. 4 of the manuscript, confirming the major influence of oxygen inhibition rather than hydrophobicity of the mold.

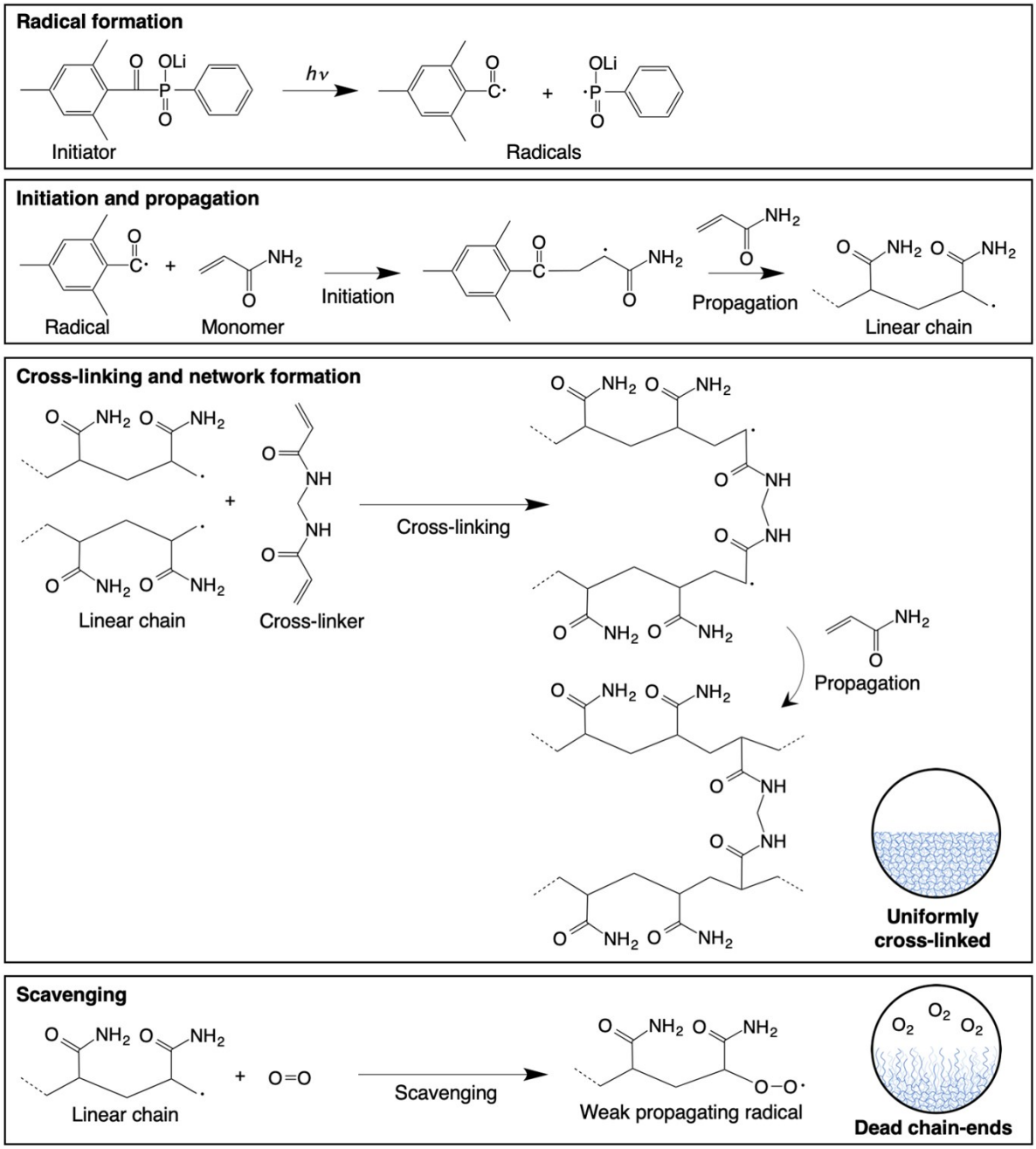

Figure S4: Schematic of the PAAm hydrogel network formation and oxygen-inhibition during free-radical polymerization. In the first step, the initiator absorbs UV light and forms radicals. The radicals initiate the reaction by opening up the monomer double-bond. The newly formed radicals at the monomer propagate the reaction, which results in linear polymer chain formation. The crosslinking of the chains occurs when a bifunctional monomer (crosslinker) enters the reaction. The presence of oxygen can scavenge the radials and thus stop the chain propagation and crosslinking, resulting in formation of dead chain-ends.