Supporting Information

Modulation and characterization of the double network hydrogel surface-bulk transition

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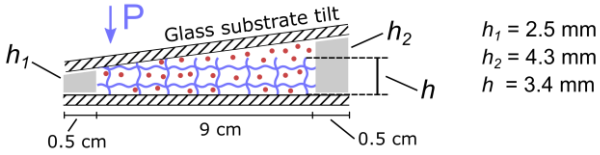
Table of content



Scheme S1: Polymerization mold assembly to synthesize a DN hydrogel with surface layer thickness gradient. This cross-sectional view demonstrates how the 1st network PAMPS hydrogel (blue lines, PAMPS 1-3-1) soaked in 2nd network precursor solution (red dots, AAm 2-0.1-0.1) is sandwiched between two glass plates (length: 10 cm, width: 10 cm). To form the surface layer thickness gradient, the hydrogel is surrounded by a 3D printed spacer (grey) with a height starting from 2.5 mm (h_1) on the left and gradually increasing up to 4.3 mm (h_2) on the right. Because h_1 is thinner than the hydrogel (h = 3.4 mm), the left part of the PAMPS hydrogel is partially compressed, with a maximum compression of 50 kPa close to spacer of height h_1. Close to the spacer of height h_2 the excess 2nd network precursor solution forms a PAAm layer in the as-prepared state of 0.9 mm-thick at maximum ($t = h_2 - h$).

Table S1: Linear fit parameters of the PAMPS and PAAm surface density calibration curves.

Linear fit parameters	1st network	2nd network
(y = d + kx)	PAMPS	PAAm
Intercept (d)	0.084 ± 0.014	2.366 ± 1.046
Slope (k)	116.8 ± 4.5	146.5 ± 13.9
r^2	0.9956	0.9401

y: W_{M1} or W_{M2} , x: $A_{max} \times Q_r$

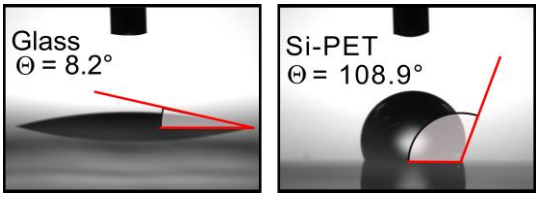


Figure S1: Molding substrate surface energy. The water contact angles of 8.5° ± 1.5° and 109.4° ± 0.8° (mean ± SD, n = 10) demonstrate the high and low surface energy of borosilicate glass and Si-PET used as molding substrates in the 2nd network synthesis, respectively.

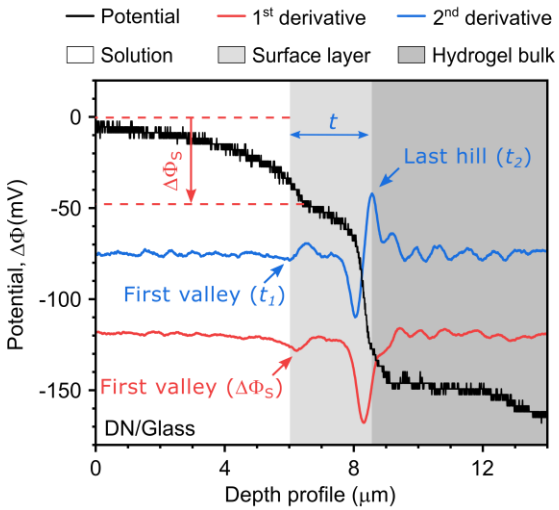


Figure S2: Analysis of electric potential depth profiles. The electric surface potential ($\Delta\Phi_S$) is defined as the difference in potential between the initial relative potential (0 mV) and the electric potential at the first valley of the 1st derivative at the hydrogel surface. The surface layer thickness (t) corresponds to the distance between the first valley (t_1) and the last hill (t_2) of the 2nd derivative in the hydrogel depth profile (Sample: DN/Glass 1-3-1/2-0.1-0.1).

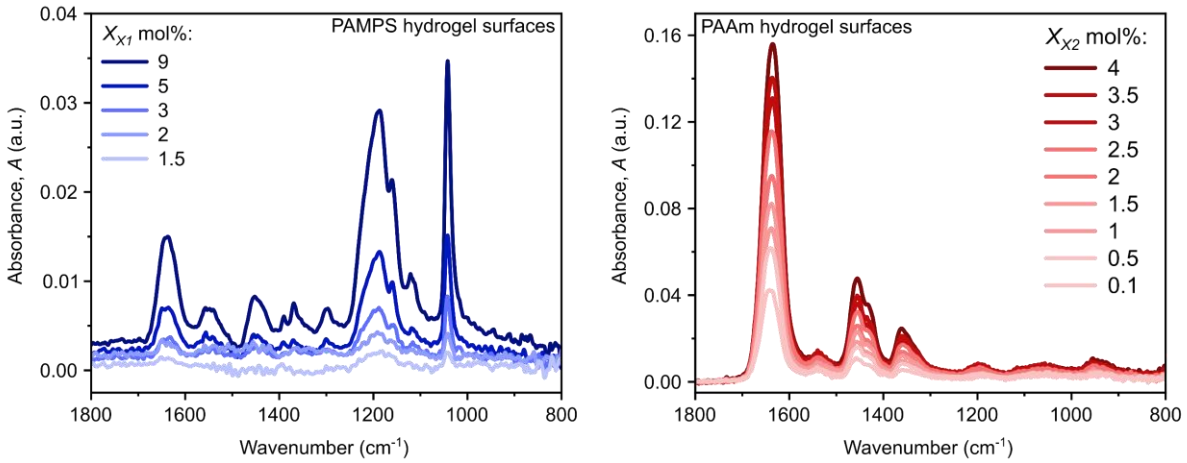


Figure S3: Infrared absorption spectra and signal intensity of SN hydrogel surfaces. The variation of crosslinking degree in PAMPS (X_{X1}: 1.5 – 9 mol%) and PAAm hydrogels (X_{X2}: 0.1 – 4 mol%) swollen in D_2O increases peak heights of spectra obtained by ATR/FT-IR, demonstrating the relation between polymer density at the surface and X_{X1} and X_{X2}. With a PAMPS weight fraction (W_{M1}, Figure S) of ~0.2 wt% (corresponding to a molar concentration C_{M1} of 9.4×10^{-4} M), the detection limit for PAMPS is almost reached for the weakly crosslinked PAMPS hydrogel (1-1.5-1), since the peaks have intensities similar to the background signal.

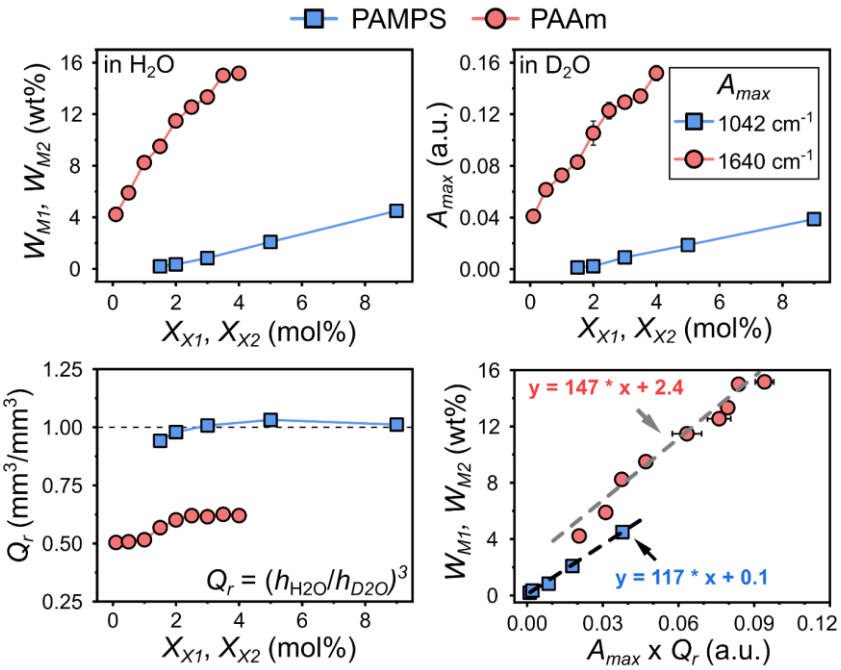


Figure S4: Calibration curves to analyze PAMPS and PAAm densities at the DN hydrogel surface. To construct the calibration curves from SN PAMPS and PAAm hydrogel of PAMPS, the gravimetric polymer weight fractions of hydrogels swollen in water (W_{M1}, W_{M2}), the absorption peak heights of hydrogels immersed in D_2O (A_{max}) and the relative swelling ratio, (Q_r) were related to the crosslinking degree (X_{X1}, X_{X2}), (mean ± SD, n = 3 hydrogels per symbol). To correlate the polymer weight fractions with the absorption peak height, the ATR/FT-IR data need to be corrected by Q_r because of the swelling discrepancy between water and D_2O. The relative swelling ratio, $Q_r = (h_{H2O}/h_{D2O})^3$ was determined by the hydrogel thickness after swelling in ddH2O (h_{H2O}) relative to swelling thickness in deuterium oxide (h_{D2O}). The resulting calibration curves for PAMPS and PAAm surface density based on the relation of the corrected absorbance maxima (x = $A_{max} \times Q_r$) to the corresponding polymer weight fraction (y = W_{M1}, W_{M2}) were used to quantify the polymer surface density of DN hydrogels in the main manuscript. The linear fit parameters for the calibration curve, y = kx + d (slope - k, intercept - d), are displayed in Table S1.

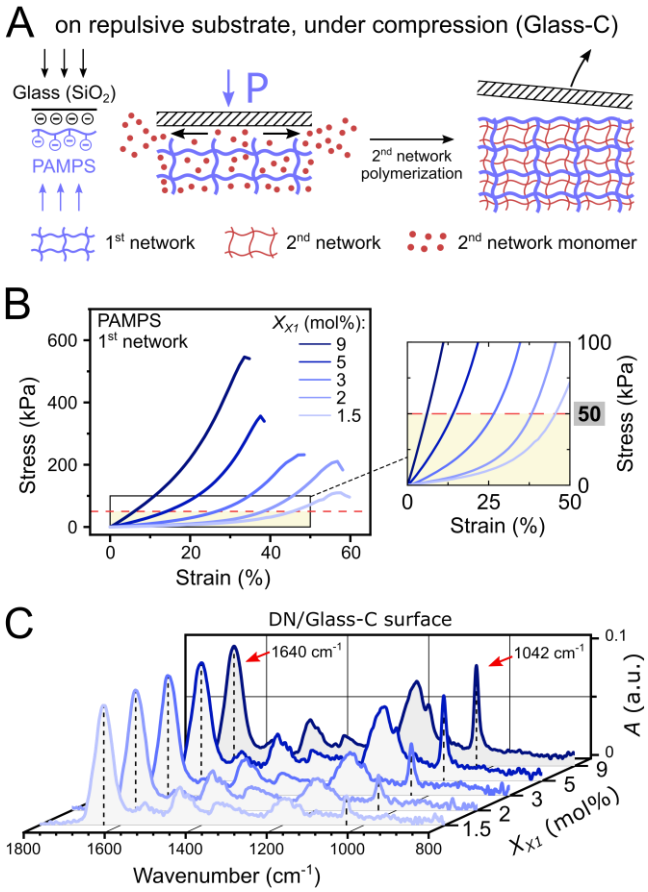


Figure S5: Applying compression to the PAMPS hydrogel (P = 50 kPa) during synthesis of the 2nd network to prevent the formation of a surface layer. (A) Applying normal pressure to counteract the osmotic repulsion at the hydrogel-glass interface during the 2nd network synthesis (DN/Glass-C). (B) The compressive stress-strain curves of the PAMPS hydrogel (1-X_{X1}-1) immersed in the AAm solution (2-0.1-0.1) to determining the normal pressure. The compressive stress-strain curves (Figure S5) of the 1st network hydrogel swollen in 2nd network precursor solution was performed on hydrogel discs of 1 cm in diameter and 2 – 3 mm in thickness at a loading strain of 10 %/min using a tensile-compressive mechanical tester (Tensilon RTC-1310A, Orientic Co.). (C) The ATR/FT-IR spectra of the DN/Glass-C hydrogels (1- X_{X1}-1/2-0.1-0.1) with varied 1st network crosslinker concentration X_{X1}. The peak intensity ratio between the PAMPS (1042 cm^{-1}) and the PAAm (1640 cm^{-1}) reveals the surface polymer composition of the DN/Glass-C hydrogels. To choose a proper compressive pressure, the compressive stress-strain behavior of PAMPS hydrogels, immersed in AAm solution, was studied for various crosslinking degrees (X_{X1}) of the PAMPS hydrogels. The compressive stress and fracture stress increased but the fracture strain decreased with increasing 1st network crosslinking (B). The weakest PAMPS hydrogel, with 1.5 mol% crosslinker, fractured at around 120 kPa. To make sure that the 1st network is compressed but does not fracture during the 2nd network polymerization, we applied to each differently crosslinked PAMPS hydrogel a compression of 50 kPa. This overall compression of 50 kPa is low compared to the bulk modulus of these highly crosslinked SN hydrogels which is in the range of 100 ~ 1000 kPa but in each ATR/FT-IR spectrum both peaks at 1042 and 1640 cm^{-1}, representing the 1st and the 2nd network respectively, are observable (C).