



Title	Modulation and Characterization of the Double Network Hydrogel Surface-Bulk Transition
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Supporting Information

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

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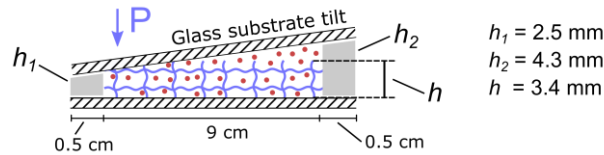
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 714 **Scheme S1: Polymerization mold assembly to synthesize a DN hydrogel with surface layer thickness**
 715 **gradient.** This cross-sectional view demonstrates how the 1st network PAMPS hydrogel (blue lines,
 716 PAMPS 1-3-1) soaked in 2nd network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

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

Linear fit parameters	1 st network	2 nd 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

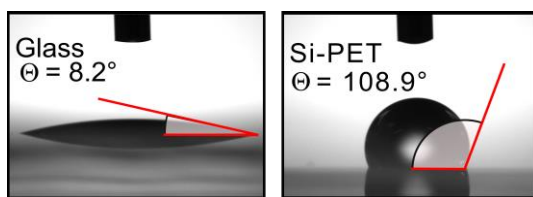
727 y : W_{M1} or W_{M2} , x : $A_{max} \times Q_r$

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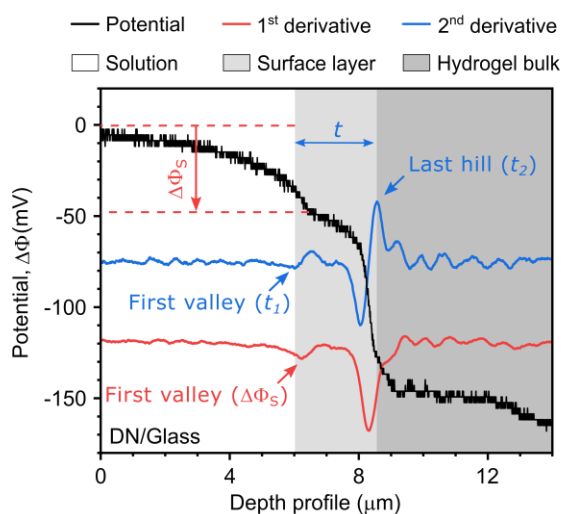


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733 **Figure S1: Molding substrate surface energy.** The water contact angles of $8.5^\circ \pm 1.5^\circ$ and $109.4^\circ \pm 0.8^\circ$
734 (mean \pm SD, $n = 10$) demonstrate the high and low surface energy of borosilicate glass and Si-PET used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

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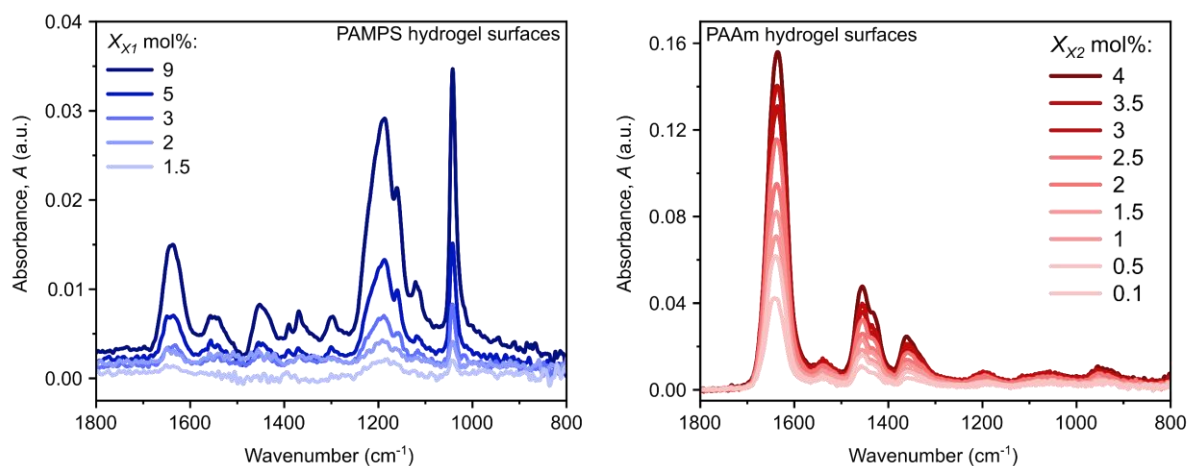
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739 **Figure S2: Analysis of electric potential depth profiles.** The electric surface potential ($\Delta\Phi_s$) is defined
740 as the difference in potential between the initial relative potential (0 mV) and the electric potential at
741 the first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

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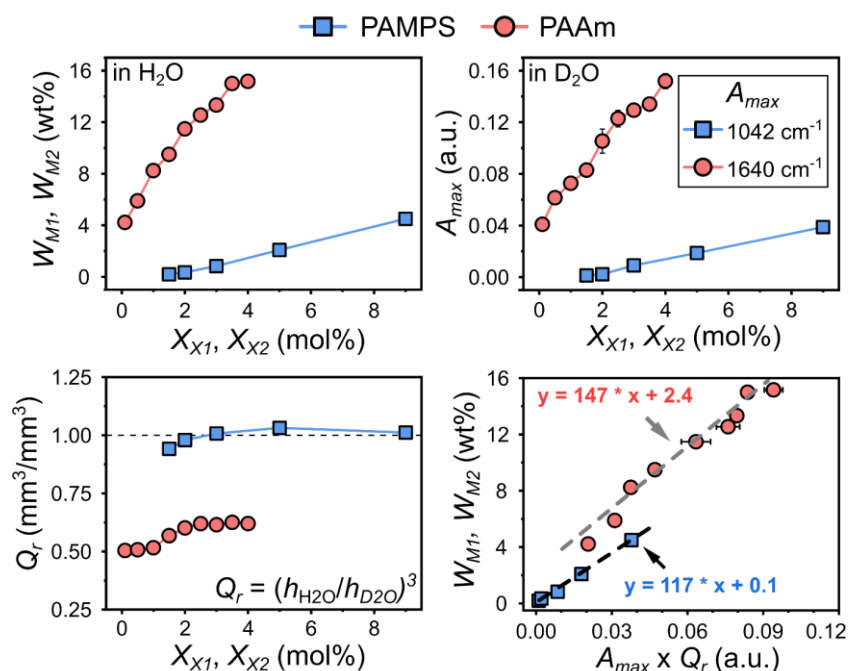


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748 **Figure S3: Infrared absorption spectra and signal intensity of SN hydrogel surfaces.** The variation of
 749 crosslinking degree in PAMPS (X_{X1} : 1.5 – 9 mol%) and PAAm hydrogels (X_{X2} : 0.1 – 4 mol%) swollen in
 750 D_2O increases peak heights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

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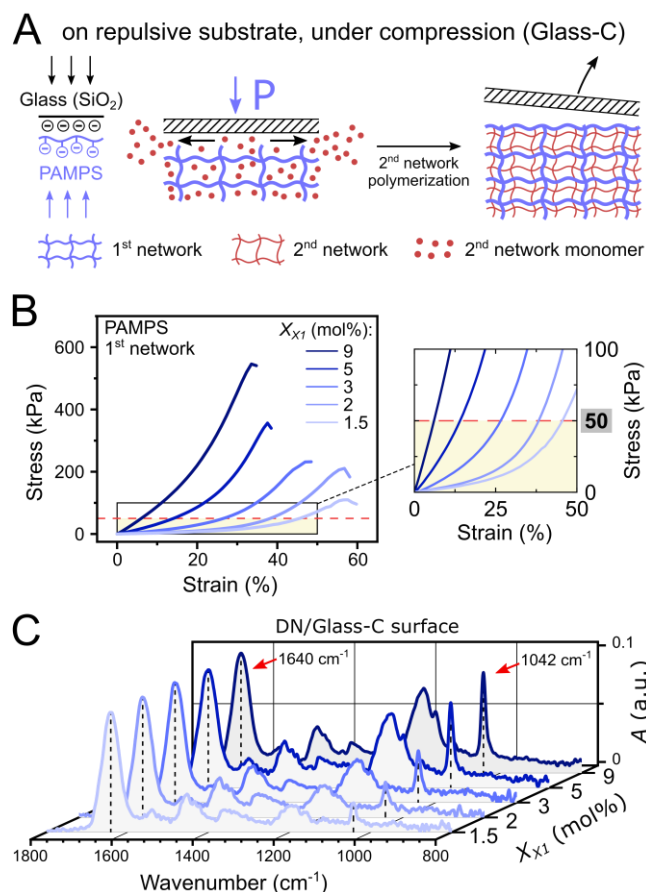


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Figure S4: Calibration curves to analyze PAMPS and PAAm densities at the DN hydrogel surface. To construct the calibration curves from SN PAMPS and PAAm hydrogel of PAMPS, the gravimetric polymer weight fractions of hydrogels swollen in water (W_{M1}, 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 \pm 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, $Q_r = (h_{H_2O}/h_{D_2O})^3$ was determined by the hydrogel thickness after swelling in ddH₂O (h_{H_2O}) relative to swelling thickness in deuterium oxide (h_{D_2O}). 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.

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 772 **Figure S5: Applying compression to the PAMPS hydrogel ($P = 50$ kPa) during synthesis of the 2nd**
 773 **network to prevent the formation of a surface layer.** (A) Applying normal pressure to counteract the
 774 osmotic repulsion at the hydrogel-glass interface during the 2nd network synthesis (DN/Glass-C). (B)
 775 The compressive stress-strain curves of the PAMPS hydrogel (1- X_{X1} -1) immersed in the AAm solution
 776 (2-0.1-0.1) to determining the normal pressure. The compressive stress-strain curves (Figure S5) of the
 777 1st network hydrogel swollen in 2nd network precursor solution was performed on hydrogel discs of 1
 778 cm in diameter and 2 – 3 mm in thickness at a loading strain of 10 %/min using a tensile-compressive
 779 mechanical tester (Tensilon RTC-1310A, Orientic Co.). (C) The ATR/FT-IR spectra of the DN/Glass-C
 780 hydrogels (1- X_{X1} -1/2-0.1-0.1) with varied 1st network crosslinker concentration X_{X1} . The peak intensity
 781 ratio between the PAMPS (1042 cm⁻¹) and the PAAm (1640 cm⁻¹) reveals the surface polymer
 782 composition of the DN/Glass-C hydrogels. To choose a proper compressive pressure, the compressive
 783 stress-strain behavior of PAMPS hydrogels, immersed in AAm solution, was studied for various
 784 crosslinking degrees (X_{X1}) of the PAMPS hydrogels. The compressive stress and fracture stress
 785 increased but the fracture strain decreased with increasing 1st network crosslinking (B). The weakest
 786 PAMPS hydrogel, with 1.5 mol% crosslinker, fractured at around 120 kPa. To make sure that the 1st
 787 network is compressed but does not fracture during the 2nd network polymerization, we applied to
 788 each differently crosslinked PAMPS hydrogel a compression of 50 kPa. This overall compression of 50
 789 kPa is low compared to the bulk modulus of these highly crosslinked SN hydrogels which is in the range
 790 of 100 ~ 1000 kPa but in each ATR/FT-IR spectrum both peaks at 1042 and 1640 cm⁻¹, representing the
 791 1st and the 2nd network respectively, are observable (C).

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