

## Supporting Information

# Adsorption of Xyloglucan onto Cellulose Surfaces of Different Morphologies: An Entropy-Driven Process

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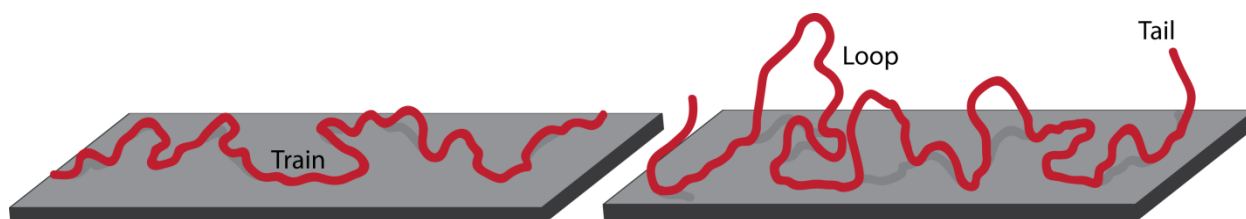
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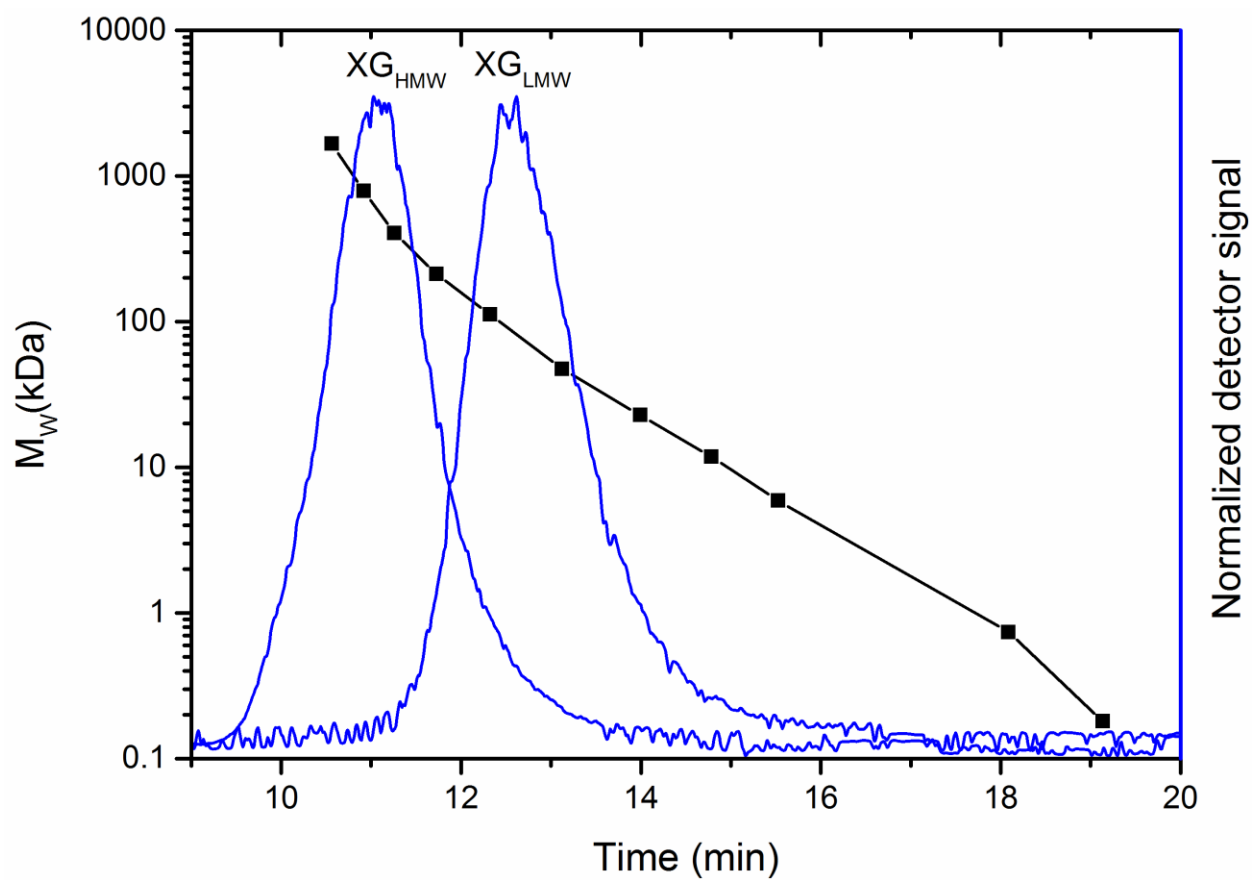
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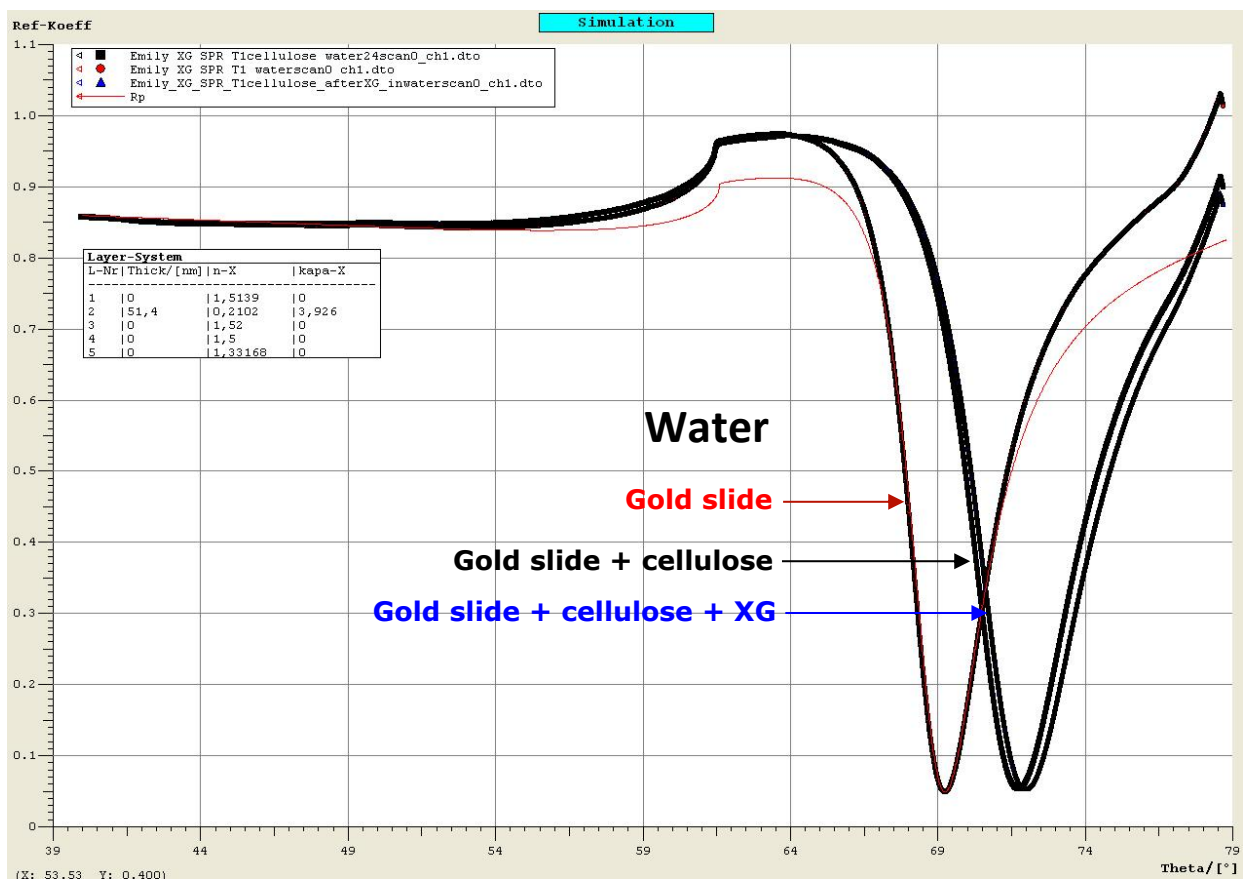
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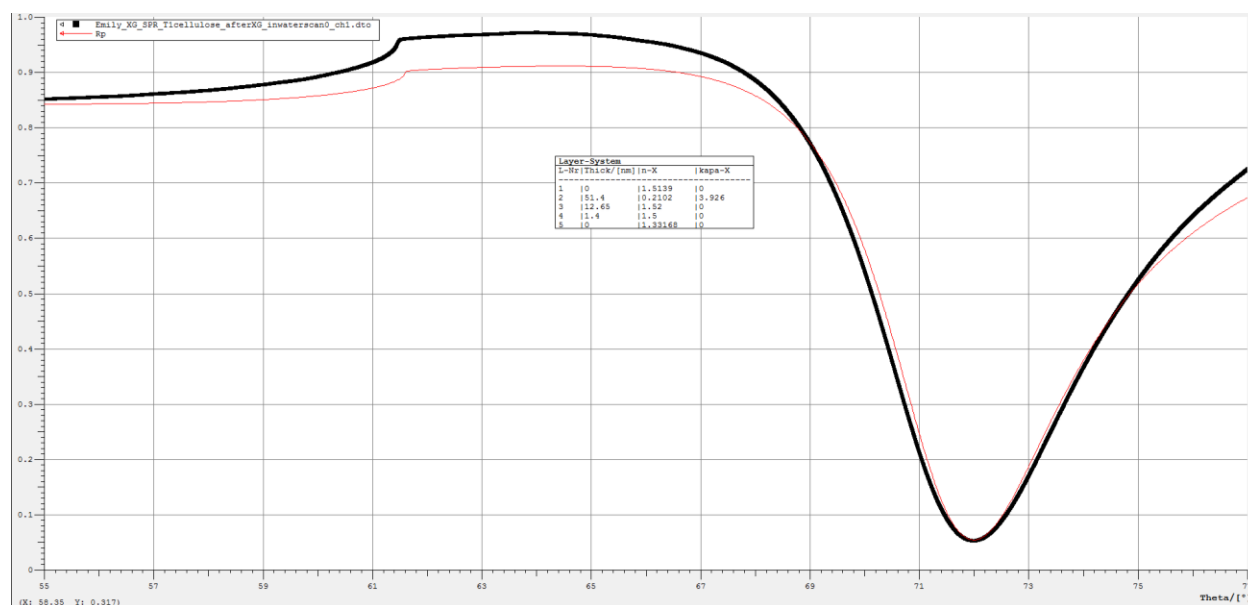
**Figure S1.** Polymers at an interface illustrating the train, loop, and tail configurations.



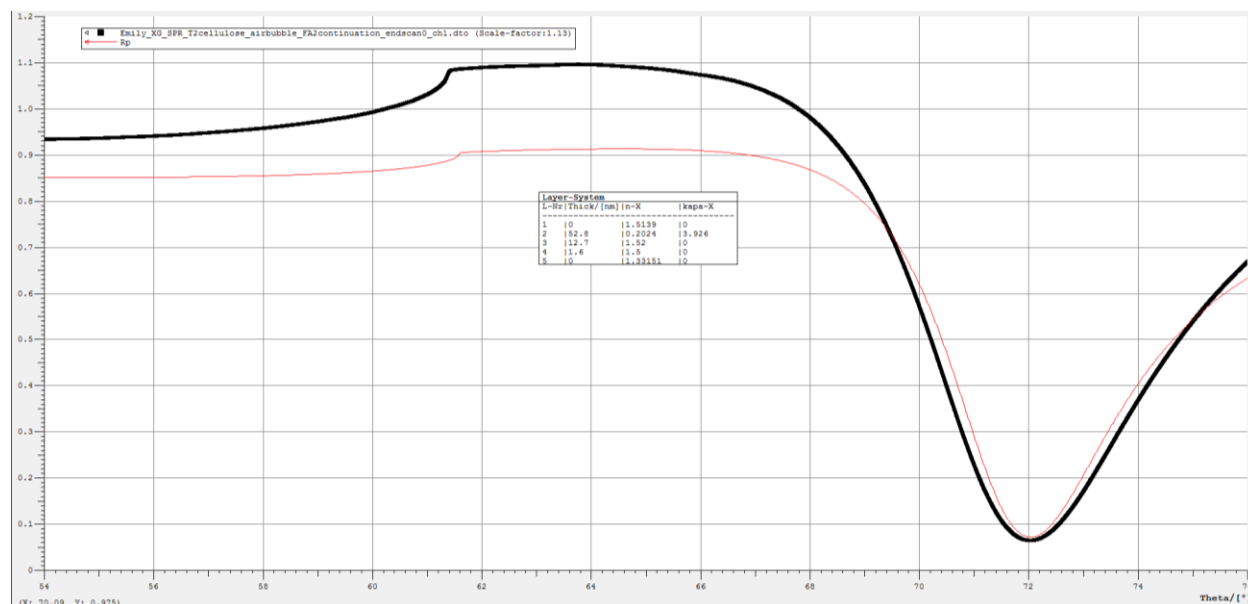
**Figure S2.** Calibration curve with pullulan standards in the range 180 to 1660000 Da and the normalized detector signals from the GPC.



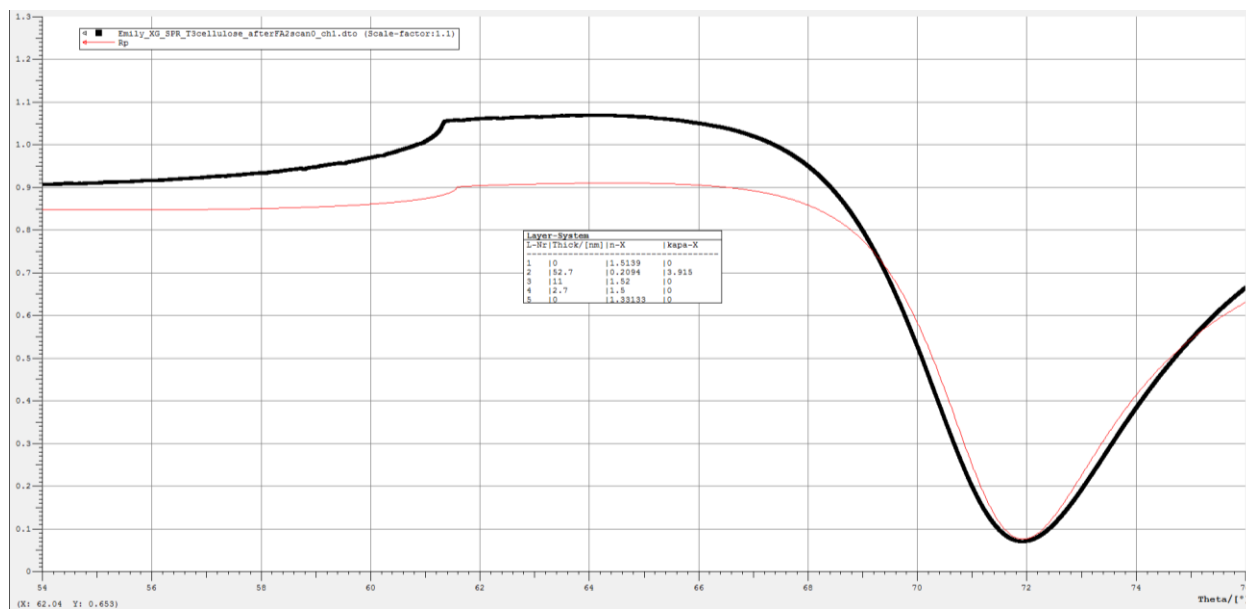
**Figure S3.** Example SPR ‘full angular scans’ in water for a Au substrate, with a spin-coated NMMO cellulose film on Au, and after XG was allowed to adsorb for 200 minutes (50 mg/L, pH  $7 \pm 1$ , flow rate 100  $\mu\text{L}/\text{min}$  at 24°C). Fit (in red) for the Au-Cr layer on BK7 glass is shown and the other fitting parameters are described in Table S1. The ‘best fit’ came from a least-squares fitting routine that fits the curve minimum in the x-axis (i.e. the SPR angle) and converges at 0.01%. The intensity (y-axis) at the SPR angle varied due to surface roughness and film/substrate uniformity.



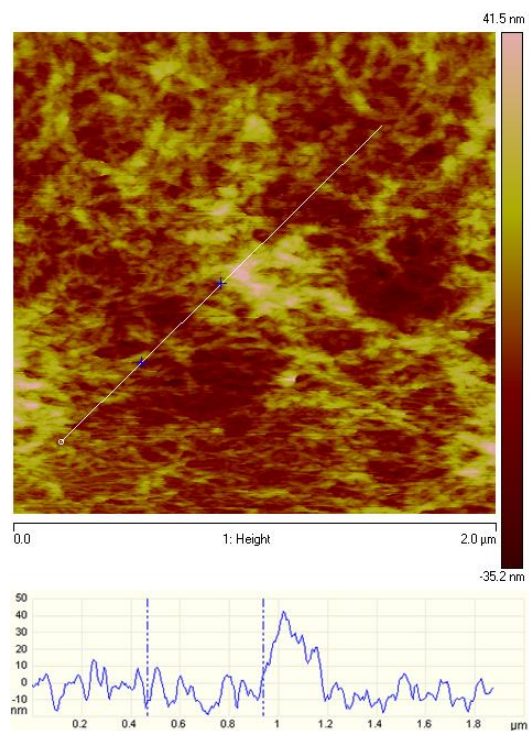
**Figure S4.** Fit for SPR curve of XG Adsorption on NMMO-Regenerated Cellulose in Water at 24°C. Black is experimental data and red is simulated curve. Iterative fitting routine converges at 0.01% leading to peak angle matching to the third decimal place.



**Figure S5.** Fit for SPR curve of XG Adsorption on NMMO-Regenerated Cellulose in Water at 32°C. Black is experimental data and red is simulated curve. Iterative fitting routine converges at 0.01% leading to peak angle matching to the third decimal place.



**Figure S6.** Fit for SPR curve of XG Adsorption on NMMO-Regenerated Cellulose in Water at 40°C. Black is experimental data and red is simulated curve. Iterative fitting routine converges at 0.01% leading to peak angle matching to the third decimal place.



**Figure S7.** Tapping mode AFM image ( $2\ \mu\text{m} \times 2\ \mu\text{m}$ ) of a thin film of cellulose regenerated from NMMO on a gold SPR sensor.

**Table S1.** Refractive Indices<sup>§</sup> used to Fit SPR Data.

Layer description	Layer #	d (nm)	n	imaginary n
Prism and glass slide	1	Infinite (0 in software)	1.5139	0
Au and Cr layer	2	FP=48-56 nm	FP=0.17-0.21	FP=3.7-4.0
Cellulose	3	FP=0-20 nm	1.52	0
XG	4	FP=0-10 nm	1.50	0
Media (H <sub>2</sub> O)	5	Infinite (0 in software)	1.33168- 1.33133	0

FP=fitting parameter, <sup>§</sup> assumed to be temperature independent in the range studied, d= thickness

**Table S2.** Layer Parameter Fits for XG Adsorption on NMMO-Regenerated Cellulose in Water at Various Temperatures.

	T=24°C			T=32°C			T=40°C		
	d (nm)	n	Imaginary n	d (nm)	n	Imaginary n	d (nm)	n	Imaginary n
Prism/glass slide	0(0)	1.5139(0)	0(0)	0(0)	1.5139(0)	0(0)	0(0)	1.5139(0)	0(0)
Au and Cr layer	50(1)	0.205(0.007)	3.94(0.02)	52.8(0)	0.2024(0)	3.94(0.02)	53.1(0.6)	0.204(0.007)	3.92(0.01)
Cellulose	12.8(0.3)	1.52(0)	0(0)	12.8(0.1)	1.52(0)	0(0)	11.05(0.07)	1.52(0)	0(0)
XG	1.4(0)	1.5(0)	0(0)	2.05(0.6)	1.5(0)	0(0)	2.6(0.1)	1.5(0)	0(0)
Media	0(0)	1.33168(0)	0(0)	0(0)	1.33151(0)	0(0)	0(0)	1.33133(0)	0(0)

d = thickness. Average values are shown with standard deviation of the two measurements in brackets.