

Supporting Information

Water desorption from a confined biopolymer

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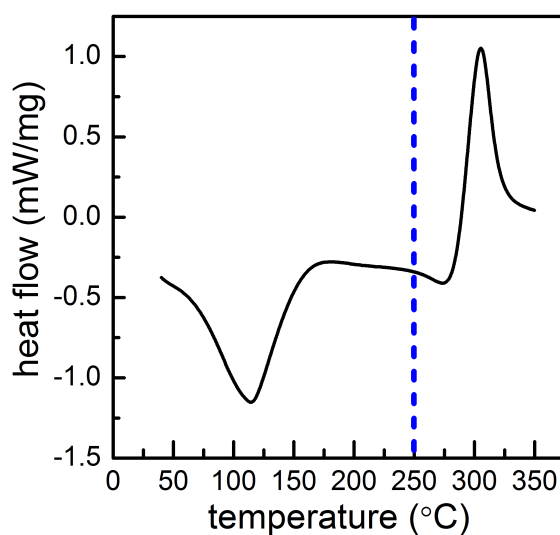


Figure S1: DSC curve of bulk chitosan with $M_w = 50$ kD obtained during the first heating at the heating rate of 10 °C/min. The endothermic peak around 100 °C is attributed to the loss of water, and the exothermic peak around 310 °C corresponds to the degradation and deacetylation of chitosan. The blue dashed line marks the range up to which the temperature dependent XRR and SE measurements were carried out.

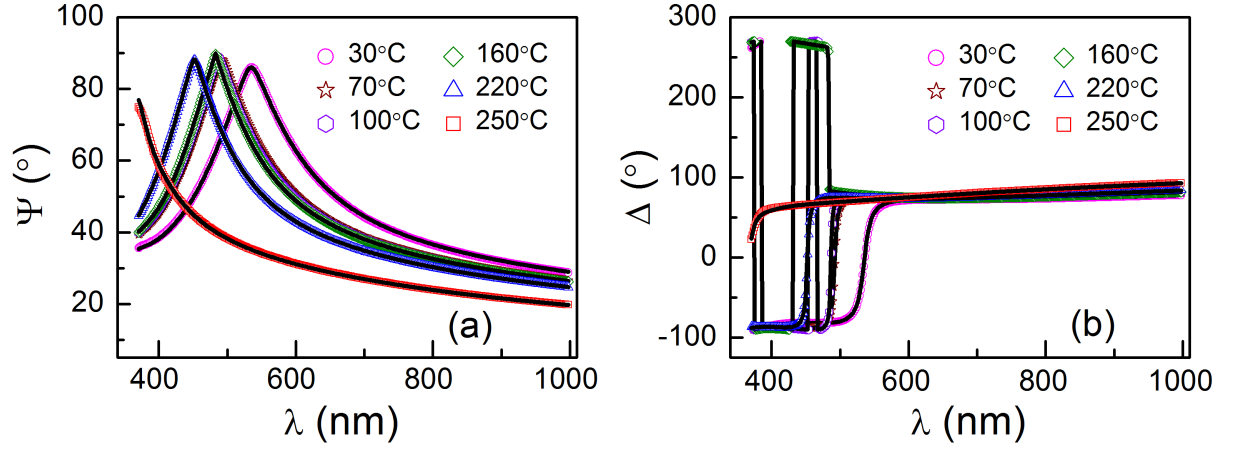


Figure S2: Ellipsometric parameters (a) Ψ and (b) Δ as a function of wavelength of the incident light at different temperatures during heating of a chitosan thin film of initial thickness 110 nm. The symbols are the experimental data and the black solid curves are the simulated data.

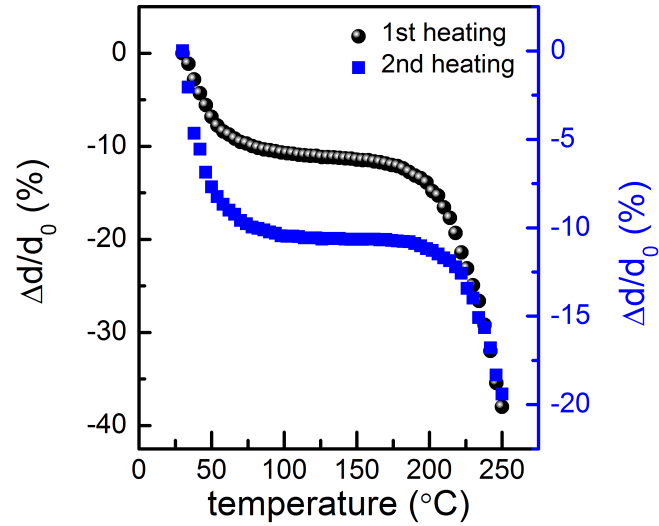


Figure S3: Percentage change in film thickness as a function of temperature during the first heating (black spheres) and second heating (blue squares) for chitosan film of initial thickness about 100 nm exposed to humid environment before the second heating scan (see text).

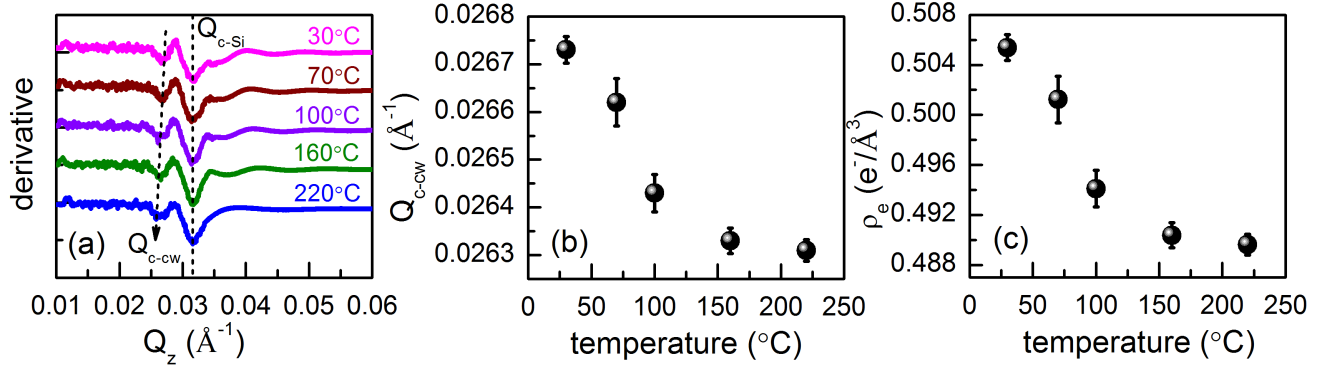


Figure S4: (a) The first derivative of the XRR profiles at different temperatures. The vertical dotted line marks the position of the critical wave vector of silicon (Q_{c-Si}) and the dotted arrow indicates the shifting of the critical wave vector of chitosan-water complex (Q_{c-cw}). Variation of (b) Q_{c-cw} and (c) the calculated electron density (ρ_e) with temperature for a chitosan thin film of initial thickness 61 nm coated on Si/Si-O substrate.

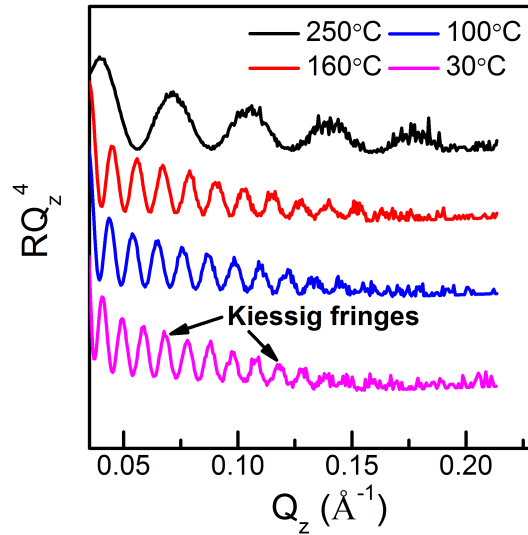


Figure S5: Normalized XRR profiles for chitosan film of thickness 61 nm at 30 $^{\circ}\text{C}$ (magenta), 100 $^{\circ}\text{C}$ (blue), 160 $^{\circ}\text{C}$ (red) and 250 $^{\circ}\text{C}$ (black).

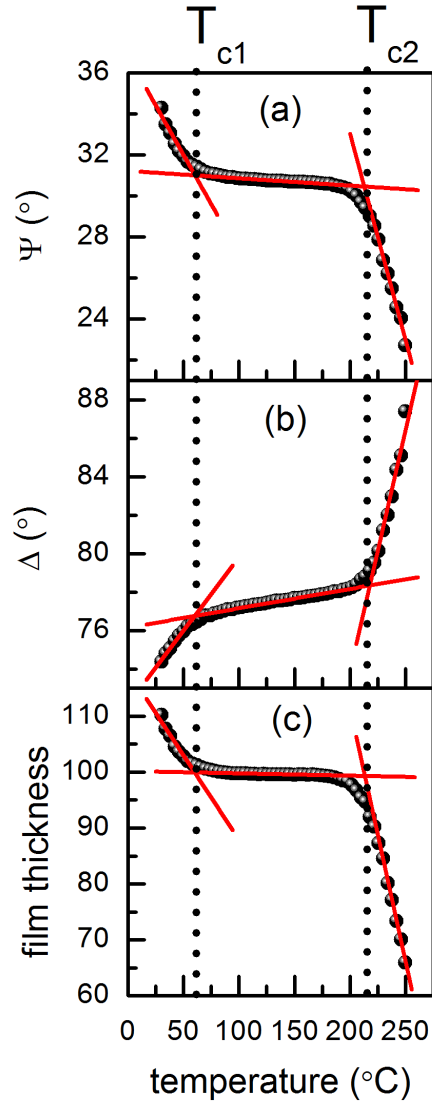


Figure S6: (a) Ψ , (b) Δ and (c) film thickness as a function of temperature for a chitosan film of initial thickness 110 nm. The straight lines are the linear fits to the data and the dotted vertical lines mark the positions of the two characteristic temperatures, T_{c1} and T_{c2} .

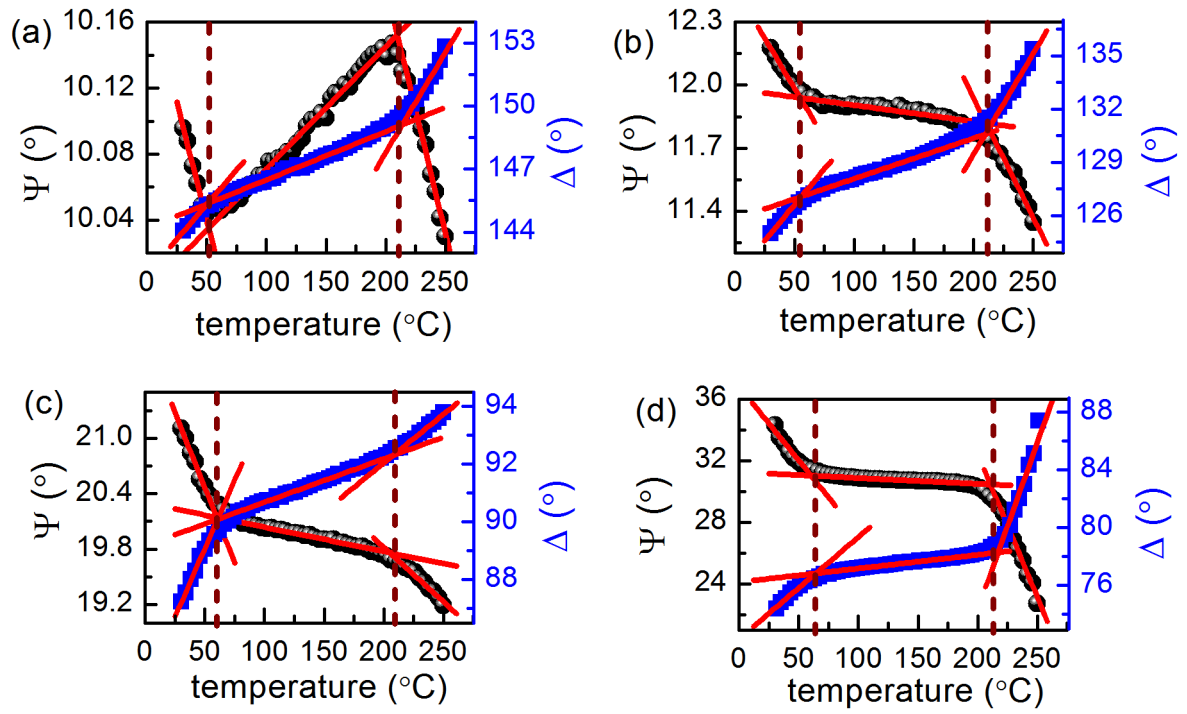


Figure S7: Ψ (black solid spheres) and Δ (blue solid squares) as a function of temperature for chitosan films of initial thickness (a) 11 nm, (b) 22 nm, (c) 52 nm and (d) 110 nm. The red lines are the linear fits to the data and the vertical dashed lines mark the positions of the two characteristic temperatures, T_{c1} and T_{c2} .