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Supplementary Information for: Stratification and Two Glass-Like Thermal Transitions in Aged Polymer Films

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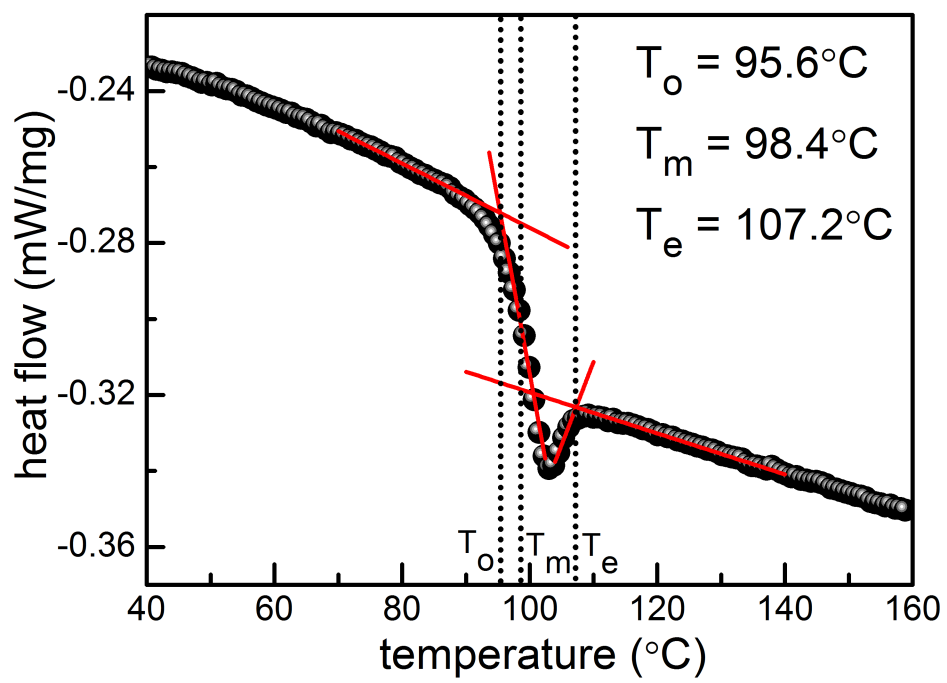


Fig. S1 DSC curve of bulk PS ($M_w = 20$ kD and PDI= 1.02), obtained at a heating rate of 10 °C/min. The positions of the onset temperature (T_o), the mid-point of the heat capacity jump (T_m) and the endset temperature (T_e) are marked by the vertical black dotted lines and their values are given in the figure.

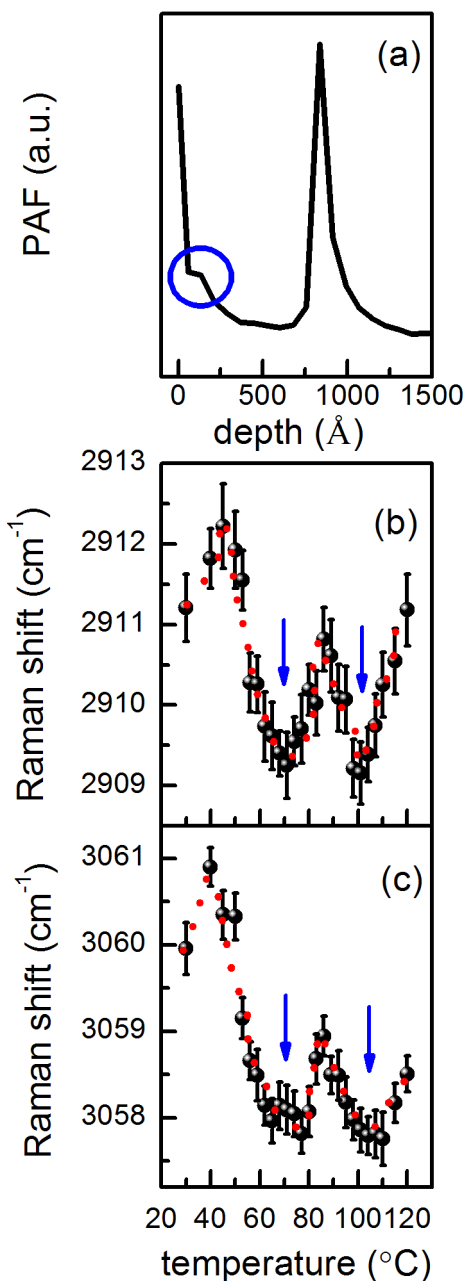


Fig. S2 (a) Pseudoautocorrelation function (PAF) obtained from the measured x-ray reflectivity profile, the blue circle marks a shoulder near the origin observed in the pseudoautocorrelation function. Variation of Raman shift with temperature for (b) the aliphatic ($\sim 2909 \text{ cm}^{-1}$) and (c) the aromatic ($\sim 3057 \text{ cm}^{-1}$) C-H stretching bands. The red dotted curves are guides to the eye and the blue down arrows mark the positions of the two minima. Initial film thickness of the physically aged PS ($M_w = 20 \text{ kD}$) film $\sim 83 \text{ nm}$.

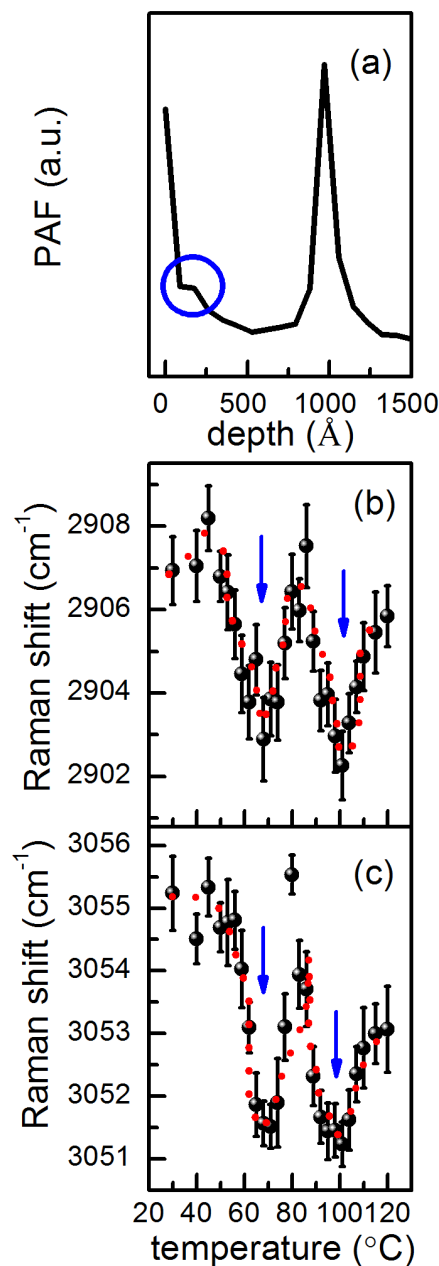


Fig. S3 (a) Pseudoautocorrelation function (PAF) obtained from the measured x-ray reflectivity profile, the blue circle marks a shoulder near the origin observed in the pseudoautocorrelation function. Variation of Raman shift with temperature for (b) the aliphatic ($\sim 2909 \text{ cm}^{-1}$) and (c) the aromatic ($\sim 3057 \text{ cm}^{-1}$) C-H stretching bands. The red dotted curves are guides to the eye and the blue down arrows mark the positions of the two minima. Initial film thickness of the physically aged PS ($M_w = 20 \text{ kD}$) film $\sim 96 \text{ nm}$.

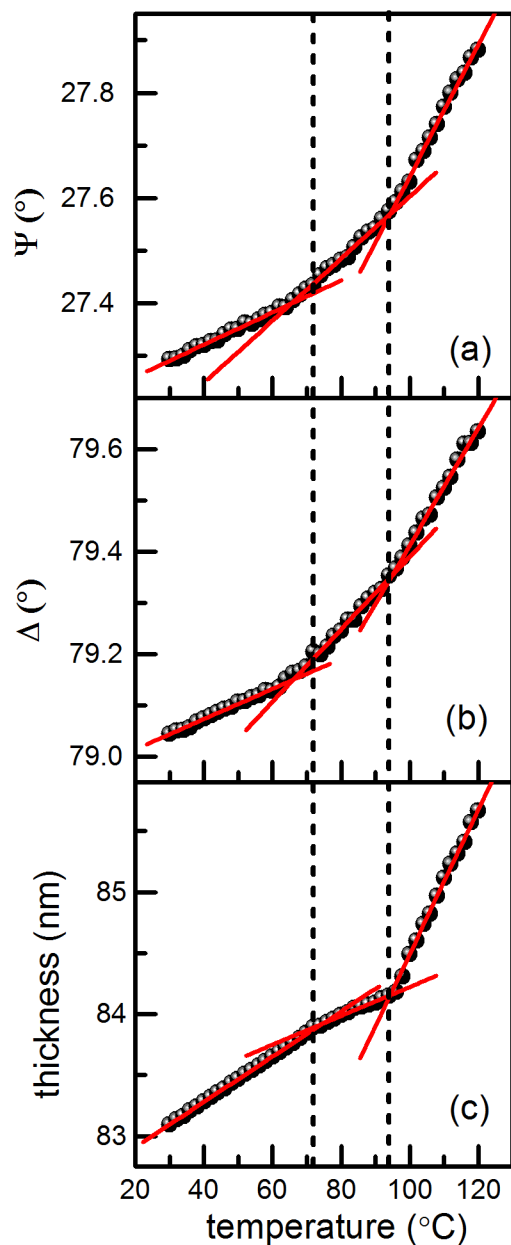


Fig. S4 Variation of the ellipsometric parameters (a) Ψ and (b) Δ with temperature, acquired at the wavelength $\lambda = 842$ nm; (c) Film thickness as a function of temperature for physically aged PS ($M_w = 20$ kD) film of initial thickness ~ 83 nm. The red straight lines are the linear fits to the respective data and the vertical dashed lines portray the positions of the two glass-like thermal transition temperatures. The error bars in the thickness vs. temperature plot are smaller than the symbol size.

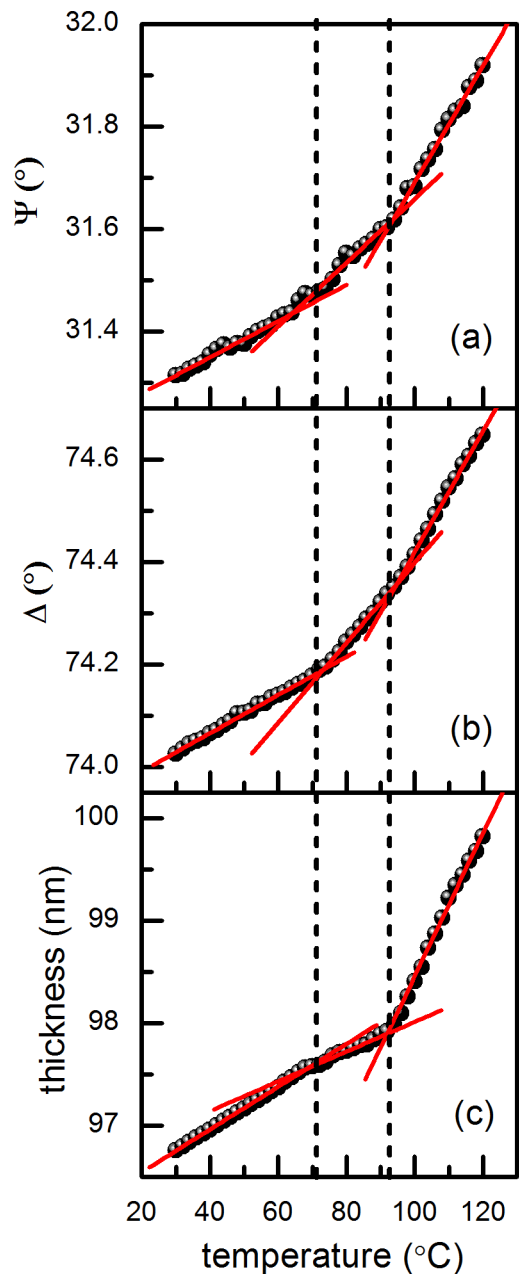


Fig. S5 Variation of the ellipsometric parameters (a) Ψ and (b) Δ with temperature, acquired at the wavelength $\lambda = 842$ nm; (c) Film thickness as a function of temperature for physically aged PS ($M_w = 20$ kD) film of initial thickness ~ 96 nm. The red straight lines are the linear fits to the respective data and the vertical dashed lines portray the positions of the two glass-like thermal transition temperatures. The error bars in the thickness vs. temperature plot are smaller than the symbol size.

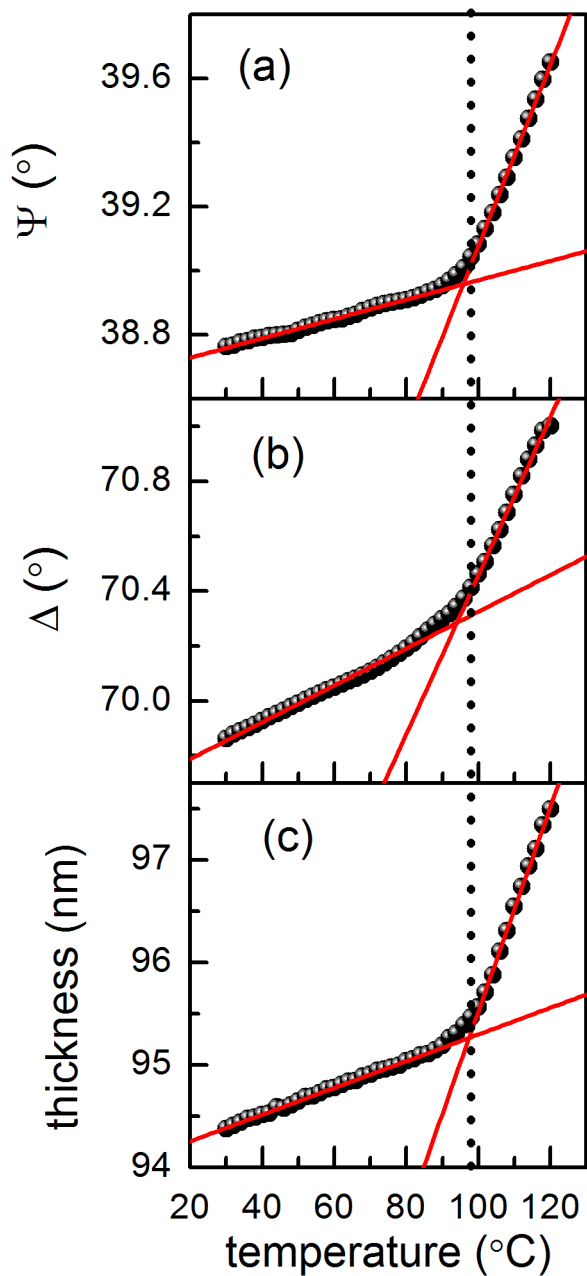


Fig. S6 Variation of the ellipsometric parameters (a) Ψ and (b) Δ with temperature, acquired at the wavelength $\lambda = 842$ nm; (c) Film thickness as a function of temperature for a freshly prepared PS ($M_w = 20$ kD) film of initial thickness ~ 94 nm. The red straight lines are the linear fits to the respective data and the vertical dotted line portrays the position of the single thermal transition temperature. The error bars in the thickness vs. temperature plot are smaller than the symbol size.