

Supporting Information

Interlink between Tunable Material Properties and Thermo-responsiveness of Cross-linked poly(N-vinylcaprolactam) Thin Films deposited by initiated Chemical Vapor Deposition

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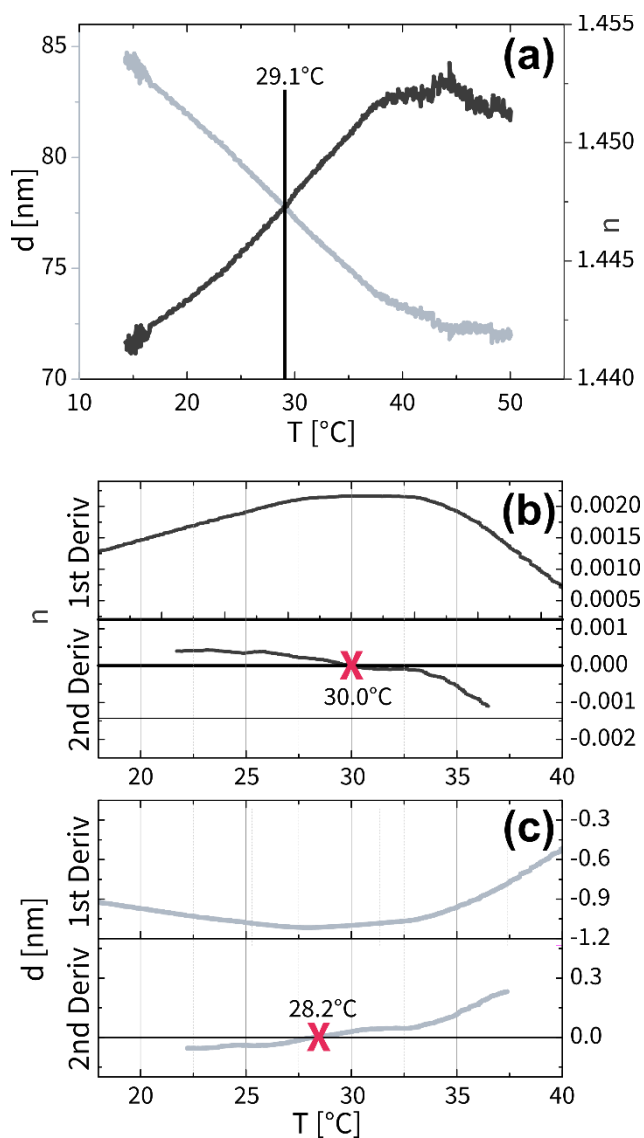


Figure 1: (a) Thickness d as recorded by spectroscopic ellipsometry during swelling in water while applying heating ramps from ~ 15 to 50°C for a nominally 40% cross-linked p(NVCL-co-DEGDVE) thin film sample; (b) and (c) are the corresponding 1st and 2nd derivatives of the

data in (a) for the evaluation of the LCST as the mean values of the respective points of inflection

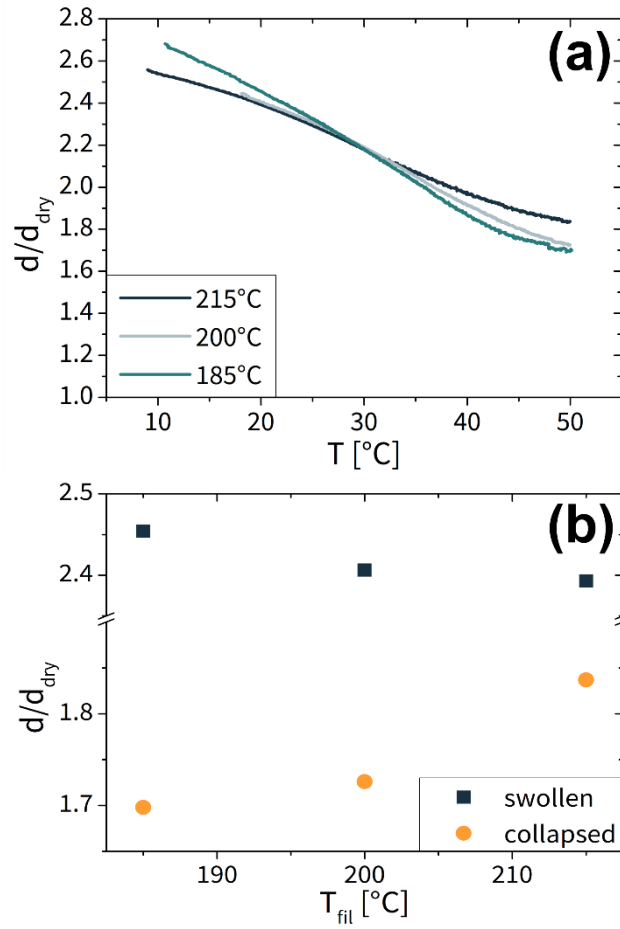


Figure 2: (a) Thickness normalized by the dry thickness d/d_{dry} during swelling in water recorded by spectroscopic ellipsometry while applying heating ramps from ~ 15 to 50°C for various nominally 20% cross-linked p(NVCL-co-DEGDVE) thin film samples deposited at different filament temperatures (T_{fil}) between 185°C and 215°C without N_2 patch flow and (b) d/d_{dry} of the respective samples in the swollen (at 20°C) and collapsed (at 50°C) state plotted as a function of T_{fil}

Figure 2 shows that the swelling degrees remain similar and the transition temperature remains unchanged (in the range of $\sim 33\text{--}35^{\circ}\text{C}$) for 20% cross-linked p(NVCL-co-DEGDVE) thin

film samples deposited at various filament temperatures (T_{fil}) between 185 and 215°C. However, the degree of swelling below (at 20°C) and above (at 50°C) the LCST appear further apart for lower T_{fil} , corresponding to a sharper transition for samples deposited at lower filament temperature. We hypothesize that the mean value of the resulting molecular weight distribution does not change; however, the distribution seems to change slightly, as the transition gets sharper for samples deposited at lower filament temperature.

The reason for the LCST and, thus, the molecular weight remaining similar despite changing T_{fil} could be the fact that the used working conditions (see experimental section) result in a mass transfer limited process during iCVD synthesis of the polymer thin films. There, the filament temperature has been reported to not affect the deposition as it does in the reaction-kinetic regime (i.e., at higher flow rates).¹

- (1) Ozaydin-Ince, G.; Gleason, K. K. Transition between Kinetic and Mass Transfer Regimes in the Initiated Chemical Vapor Deposition from Ethylene Glycol Diacrylate. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **2009**, 27 (5), 1135–1143.