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Simultaneous rheology and crystallinity measures of the shear-assisted crystallization of polycaprolactones ANTHONY KOTULA, KALMAN MIGLER, National Institute of Standards and Technology (NIST) — Polycaprolactone is employed in a variety of applications including additive manufacturing, tissue engineering, and drug delivery. Often, non-destructive optical techniques are employed to characterize the degree of crystallinity and chain morphology in polymeric biomaterials, which are key parameters that dictate the mechanical response of these systems. In this talk, we utilize a rheo-Raman microscope to simultaneously measure the Raman spectra, rheology, and birefringent structure evolution of polycaprolactones crystallizing isothermally. We first isolate and identify the quantitative crystalline indicators in the Raman spectra from single chain effects to calculate a crystallinity mass fraction, then apply this analysis to our measurements to correlate crystallinity, small amplitude oscillatory modulus, and polarized optical microscopy. The crystallization kinetics are significantly enhanced when more shear (or specific work) is applied at temperatures between the equilibrium melting point and the temperatures where we perform isothermal crystallization measurements. We compare both the quiescent and shear-assisted crystallization measurements with the wide variety of models describing the modulus evolution as a function of crystallinity to find that a relatively simple suspension-based model works surprisingly well.

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