40c Using Crystallinity to Control Structure and Rheology of Pla-Peo-Pla Hydrogels

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We report on the structure and viscoelasticity of solutions and gels of poly(lactide)-poly(ethylene oxide)-poly(lactide)(PLA-PEO-PLA) triblock copolymers. In aqueous environments, these copolymers self-assemble into associative networks, with hydrophobic PLA domains serving as junction points in the network. By controlling the stereochemistry of the PLA block, we can create gels that have either crystalline or amorphous PLA domains. The addition of crystalline domains significantly increases the elastic modulus of the hydrogels, allowing for the first time physical gels of PLA-based copolymers with moduli in the range of ~ 10 kPa. The crystallinity of the PLA domains can also be used to tune the release of hydrophobic pharmaceuticals from PLA-PEO-PLA solutions and gels. We have used small-angle neutron scattering (SANS), ultra-small-angle x-ray scattering (USAXS), and fluorescence microscopy to probe the structure and assembly of these copolymers over a wide range of length scales. All systems show micellar assemblies that are roughly 20-30 nm in size with PLA cores; however, in the case of amorphous cores, the assemblies are well-defined spherical micelles, while for crystalline PLA cores, the assemblies are highly polydisperse and nonspherical. Gels with crystalline PLA domains also appear to have structure on larger scales, as evidenced by USAXS and microscopy. The assemblies form micron-sized aggregates with narrow water channels between them. We believe the rich multiscale structure of these polymers, along with their tunable mechanical properties and release properties, make them excellent candidates for soft tissue engineering.