CAN SOFTER JUNCTIONS LEAD TO STIFFER GELS? UNDERSTANDING THE ROLE OF STEREOCHEMISTRY IN ASSOCIATIVE POLYMER GELS

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The ability to create synthetic materials that mimic the structural and mechanical properties of soft biological tissues remains a significant challenge. In this presentation, we focus on creating stiff hydrogels and novel nanoscale and microscale structure by engineering crystalline domains into associative hydrogels of poly(lactic acid)-poly(ethylene oxide)-poly(lactic acid) (PLA-PEO-PLA) triblock copolymers. In aqueous media, these materials form associative gels of micelles with PLA cores that serve as network junctions. We extend previous studies from our group and others by varying the stereochemistry of the PLA block to create polymers with PLA blocks with ratios of L/D lactide units varying from 100/0 to 50/50. We had previously found that the 100/0 systems (triblocks with poly(L-lactide) blocks) formed gels with nanoscale crystalline domains, and these gels displayed a high value of the elastic modulus which was strongly dependent on PLA block length. Interestingly, our most recent results show that the storage modulus of these gels does not vary monotonically with L/D ratio. Rather, systems at intermediate L/D values are stiffer than the 100/0 systems, displaying higher storage moduli in spite of the fact that the PLA domains are expected to have a lower degree of crystallinity than in the 100/0 systems. Small-angle neutron scattering (SANS) results also indicate that the strongest interactions between micelles occurs for systems with intermediate L/D ratios, and ultra-small angle neutron scattering (USANS) shows evidence of larger structures in these gels, reminiscent of the hierarchical structures observed in biological gels. Collectively, our work shows that stereochemistry can be used in unexpected ways to access novel structures and properties in relatively simple synthetic polymers, giving insight into new routes for creating complex soft materials.