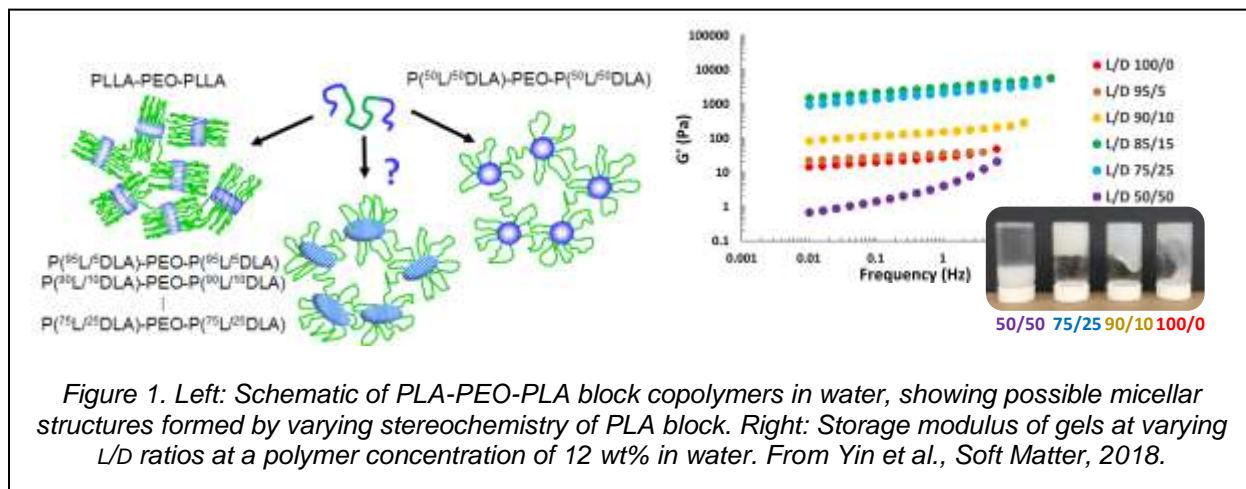


**SOFTER JUNCTIONS CAN RESULT IN STIFFER GELS:  
ASSOCIATIVE POLYMER GELS WITH CRYSTALLINE AND SEMICRYSTALLINE DOMAINS**

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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 discuss rheology and structural studies of poly(lactide)-poly(ethylene oxide)-poly(lactide) (PLA-PEO-PLA) triblock copolymer gels with various ratios of L-lactide and D-lactide in the PLA blocks (Figure 1). These materials form associative micellar gels in water, and previous work has shown that stereoregular triblocks with a L/D ratio of 100/0 form much stiffer gels than triblocks with a 50/50 L/D ratio. Our systems display an unexpected maximum in the storage modulus,  $G'$ , of the hydrogels at intermediate L/D ratio. The impact of stereochemistry on the rheology is very striking; gels with an L/D ratio of 85/15 have storage moduli that are ~1-2 orders of magnitude higher than hydrogels with L/D ratios of 100/0. No stereocomplexation is observed in the gels, although PLLA crystals are found for gels with L/D ratios of 95/5 and 90/10, and SANS results show a decrease in the intermicellar spacing for intermediate L/D ratios. We expect the dominant contribution to the elasticity of the gels to be intermicellar bridging chains and attribute the rheology to a competition between an increase in the time for PLA endblocks to pull out of micelles as the L/D ratio is increased and PLLA crystallization occurs, and a decrease in the number of bridging chains for micelles with crystalline PLA domains, as formation of bridges may be hindered by crowded crystalline PLA domains. Ultra-small angle neutron scattering (USANS) and confocal microscopy shows evidence of larger structures in these gels, reminiscent of the hierarchical structures observed in biological gels. These results provide a new strategy for controlling the rheology of PLA-based hydrogels for potential applications in biomaterials, as well as fundamental insights into how intermicellar interactions can be tuned via stereochemistry. 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.



*Figure 1. Left: Schematic of PLA-PEO-PLA block copolymers in water, showing possible micellar structures formed by varying stereochemistry of PLA block. Right: Storage modulus of gels at varying L/D ratios at a polymer concentration of 12 wt% in water. From Yin et al., Soft Matter, 2018.*