**Origins of polysaccharide conformation and viscoelasticity in miscible heterogeneous solvent**

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Polysaccharide polymers constitute the fundamental building blocks of life and display a diverse set of conformations; the origins of which need further understanding. Utilising a model high molecular weight, high Trouton ratio bottlebrush-like 'pectin' polysaccharide extracted from okra (*Abelmoschus esculentus*) mucilage, we combine theoretical (molecular dynamics simulation) and experimental (extensional rheology, dielectric relaxation spectroscopy, calorimetry, and neutron scattering) investigations, to unveil the underlying microscopic hydrodynamic origins of polysaccharide conformation. In miscible heterogenous solvents of water and glycerol (cosolvent), we observe that the polysaccharide chain undergoes a non-monotonic conformational transition from flexible-to-extended-to-collapsed configurations, resulting in pronounced viscoelastic responses. Molecularly structured water molecules within ca. 0.40 nm of the chain surface are observed with an increase of glycerol in the solvent composition. We postulate that this increased water elicits an entropically unfavourable dynamic solvent heterogeneity, which is ameliorated by swelling and collapse of polysaccharide chains. Together with elastic fixed window scans on the thermal backscattering spectrometer IN13 (Institute Laue-Langevin, France), we demonstrate water’s confinement near pectin chains. Our results offer new insights applicable to fundamental biopolymer science and biomaterial engineering, previously inaccessible through mean-field assumptions.