Rheology of Supramolecular Polymers

Supramolecular polymers are a broad class of materials that include all polymers capable of associating via secondary interactions. These materials represent an emerging class of systems with superior versatility compared to classical polymers with applications in food stuff, coatings, cost efficient processes or biomedical areas. Design and development of supramolecular polymers using ionic, hydrogen bonding or transition metal complexes with tailored properties requires deep understanding of dynamics both in linear and non-linear deformations. While linear rheology is important to understand the dynamics under equilibrium conditions, extensional rheology is relevant during the processing or in the usage of polymers utilizing supramolecular associations for example, acrylic based pressure sensitive adhesives are subjected to extensional deformations during the peeling where strain hardening is often desirable. Such data is also needed to develop sophisticated multiscale models that can later be used for predicting the flow behavior and molecular dynamics of supramolecular networks. This thesis focuses on the experimental rheological study of two class of supramolecular polymers namely: (a) hydrogen bonding polymers, and (b) ionic bonding polymers (hereafter termed as ionomers). We study linear and non-linear rheology for a model system of entangled pure poly(n-butyl acrylate), PnBA, homopolymer and four poly(acrylic acid), PnBA-PAA, copolymers with varying AA side groups synthesized via hydrolysis of pure PnBA homopolymer. Second, we investigate the linear viscoelastic response of unentangled 2-ureido-4[1H]-pyrimidones (UPy) based supramolecular networks. Third, we investigate the rheological response of ionomers synthesized via condensation of sulfonated pthalates with poly(tetramethylene glycol)PTMO, both in non-linear shear and extensional flows. Finally, we study brittle fracture of the above ionomers in extensional flow.