Influence of charge density and backbone rigidity on the structure and properties of polyelectrolyte solutions

S.I. YUN, Y.B. MELNICHENKO, G.D. WIGNALL, K. HONG, J. MAYS, ORNL, R.M. BRIBER, University of Maryland — The influence of chain stiffness on the structure and thermodynamic properties of neutral polymer solutions is significant in both the good and poor solvent domains. The conformational properties of a dissolved polymer can undergo large dimensional changes depending on the value of the stiffness parameter ($\eta$), polymer concentration and temperature. At the same time, the collective behavior can develop long-ranged correlations as the phase boundary is approached. Recent theoretical considerations have suggested that the chain stiffness should also play a key role in determining the structure and thermodynamic properties of polyelectrolyte solutions, where a complex crossover from the second order critical phenomena ($\eta \to 0$) to the first order isotropic – nematic transition ($\eta \to 1$) may be observed. The key experimental variable of our research is backbone stiffness and the charge density of polyelectrolyte. For an ionizable group (sulfonate), the effect of chain stiffness can be elucidated through studies of poly(styrene sulfonate) (PSS) as a flexible molecule and poly(cyclohexadiene sulfonate) (PCHDS), with a “semiflexible” backbone. We also varied the degree of sulfonation to couple the effect of hydrophobic interactions with backbone stiffness. Small angle neutron scattering (SANS) and zero averaged contrast methods were used to characterize the PCHD backbone and PCHDS polyelectrolyte in solutions.

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