

Linear Viscoelasticity of Ionic Polymers: Ionomers and Polyelectrolytes

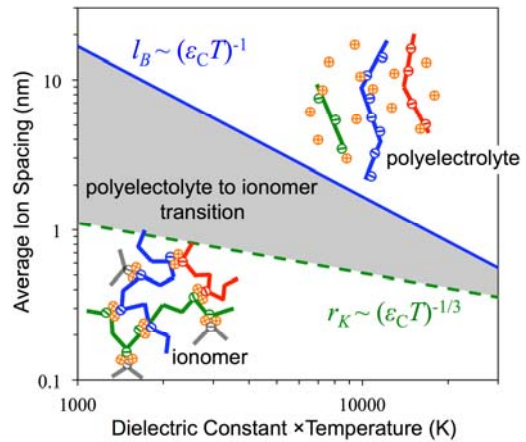
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Polymers with covalently bonded ionic groups exhibit interesting viscoelasticity. In polar media, significant fractions of the unattached counterions dissociate, leaving the polyelectrolyte chain with a net charge that has both conformation and dynamics dominated by charge repulsion. In less polar surroundings, the same polymer is termed an ionomer, with nearly all ions paired and the neutral pairs attract each other and associate to create temporary crosslinks. Solutions of flexible polyelectrolytes with no added salt have a wide range of concentration that is semidilute but not entangled, with dynamics described by the Rouse model [1,2]. In contrast, ionomers have strong dipolar attractions between ion pairs on neighboring chains and are instead described by either sticky-Rouse [3] or sticky-reptation [4,5] models. By diluting an ionomer with a high-polarity, low- T_g , non-volatile solvent, the transition from ionomer to polyelectrolyte is studied. This is understood in terms of the Bjerrum length l_B , the scale at which the pairwise ion interactions equal the thermal energy kT , and the Keesom length r_K , at which the interaction between two ion pairs equals the thermal energy [6-8].



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