

Abstract Submitted
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Electrophoretically Assessing Polyelectrolyte Effective Charge

ALEXEY POPOV, DAVID HOAGLAND, Polymer Science & Engineering, University of Massachusetts, Amherst, MA — Capillary electrophoresis revealed how polyelectrolyte effective charge density varies with backbone charge spacing and solvent dielectric constant. The study focused on ionenes, polyelectrolytes that possess regularly spaced quaternary ammonium groups in the backbone. Complete ionization of functional units and good solvency in water and mixtures of water with methanol or acetonitrile enabled measurements of ionene effective charge density as solvent dielectric constant continuously varied. Ionenes with aliphatic and oxyethylene spacers in the backbone were examined. As expected, effective charge density rose linearly with fixed charge density to a critical value, above which effective charge was nearly constant. Deviating from expectation, the onset of condensation did not occur at a critical fixed charge density predicted by Manning theory. Instead, condensation initiated at the constant critical Bjerrum length. The same onset condition was found for quaternized poly(vinyl pyridine). These results suggest a new type of condensation, one driven by ion-pairing. In support of the ion-pairing hypothesis, the onset of condensation correlates with counterion size.

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