Decoupling Charge and Screening: Small-Ion-Controlled Electrostatics in Random Copolymer Polyelectrolytes

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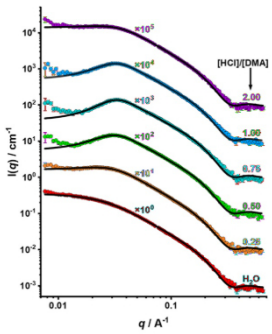
Electrostatic screening fundamentally determines the conformation and interactions of polyelectrolytes, yet the relative contributions of polymer-bound charges and mobile small ions remain unresolved for weakly charged systems. Using synchrotron small-angle X-ray scattering (SAXS) combined with a rigorous modelling framework, we study the electrostatic behaviour of P(DMA-stat-PEGMA) copolymers with tunable charge density (dimethylaminoethyl methacrylate (DMA) and poly(ethylene glycol) methyl ether methacrylate (PEGMA)). The SAXS data are analysed using a Kratky–Porod worm-like chain (WLC) model that explicitly incorporates excluded-volume interactions and mimics electrostatic swelling, providing an accurate form factor for semi-flexible chains. To capture interchain electrostatics, we employ a PRISM-like (PRISM = polymer reference interaction site model) structure-factor expression derived from earlier Monte Carlo simulations, which links direct correlation functions to measurable scattering features and provides the second virial coefficient. By independently varying degree of protonation, ionic strength, and polymer concentration, we uncover a clear principle: electrostatic screening is governed predominatly by mobile small ions (H^+, Cl^-, K^+), not by the polymer macroions. Classical scaling emerges only when ionic strength is defined using small ions alone, both the persistence length and the second virial coefficient collapse onto an OSF-type (OSF = Odijk–Skolnick–Fixman) electrostatic stiffening law under this definition. Added salt softens the chains, protonation stiffens them, and the interchain structure peak shifts consistently with a single, unified scaling variable. Our results resolve a long-standing ambiguity in weak-polyelectrolyte physics and establish WLC-PRISM, grounded in Monte Carlo simulations, as a physically meaningful and experimentally validated framework for analysing electrostatic interactions in random copolymer polyelectrolytes.

Keywords:
Polyelectrolytes,Electrostatic screening,Small ions,SAXS,Worm-like chain (WLC) model,PRISM theory,Persistence length,Virial coefficient,OSF Theory



Synchrotron SAXS data recorded for 1.0% w/w aqueous solutions of PD8020:150 at various [HCl]/[DMA] molar ratios. All scattering data were fitted using the WLC-PRISM model. For clarity, curves are vertically shifted by an arbitrary factor, as indicated.