

# Stability, interactions, and architectures of colloids with adsorbed zwitterionic and ethylene-oxide polymer coatings

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## ABSTRACT

Zwitterionic polymer coatings have recently gained attention as stabilizing materials in drug delivery, diagnostic, and other biomedical applications. However, claims of improved stabilization and antifouling properties over traditional polymer chemistries are somewhat inconsistent, and with an unclear mechanistic link between studies at the molecular (e.g. atomic) and macromolecular (e.g. polymer surface) levels.

This thesis uses single-particle,  $kT$ -scale measurements of colloidal interactions to probe the mechanics and colloidal stabilization of zwitterionic polymer coatings. Novel amphiphilic block copolymers form dense zwitterionic polymer layers through adsorption onto colloids. Adsorbed copolymers of sufficient repeat units stabilize colloids against deposition and aggregation in high-salt (0-3M NaCl) and physiological media (serum, cell media). Approximately 2-3 fold reduced repeat units are needed to stabilize  $\mu\text{m}$ -sized colloids when using a common zwitterionic phosphorylcholine polymer (PMPC) than more conventional poly(ethylene oxide) (PEO).

Colloidal interaction measurements show that, relative to PEO coatings of similar contour lengths, zwitterionic PMPC coatings exert repulsion over a 2-3-fold longer range. This increased repulsion length is a result of increased zwitterionic layer thickness, caused by complete chain extension of the PMPC polymer away from the colloid surface. Layer thickness is shown to be the primary property that determines colloidal stability, as colloids with PEO and PMPC layers of

equivalent thicknesses possess equivalent interactions and stability against a variety of model biomaterial surface chemistries.

The molecular mechanisms for the highly extended zwitterionic brush architectures were studied by using dissolved salt to perturb layer properties. Measurements of two contrasting zwitterionic chemistries showed salt-dependent brush extension that is intricately linked to poly-zwitterion solution behavior. Layer architectures result from a balance between attractive dipole-dipole and repulsive solvation and excluded volume molecular interactions. However the relative importance of these attractive and repulsive contributions is dependent on both solution properties (e.g. ion composition) and specific molecular affects (e.g. monomer structure and solvation).

Ultimately, this thesis provides guidance regarding the design of effective polymer coatings for the stabilization of colloids. Polymer layers primarily impart stability through nonspecific macromolecular interactions, and must be of sufficient thickness and density to both screen attractive colloidal interactions and mitigate surface non-uniformities. Zwitterionic monomer chemistries only indirectly impact layer stability by influencing polymer layer extension. However zwitterionic chemistries may be useful for the engineering of additional layer properties, such as salt or pH - responsive thickness and stabilization.

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