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Neutron reflectivity as a tool to understand polyelectrolyte brushes

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ABSTRACT

Because polyelectrolytes are perhaps the least understood form of soft synthetic matter, polyelectrolyte brushes are important model systems for learning how chain stretching is controlled by conditions that set the charge state of the system, as well as interactions with biological and bio-inspired molecules. Motivated by this fact, we describe situations where the application of neutron reflectivity to the study of polyelectrolyte brushes is poised to deepen understanding of the complex connections between charge and nanostructure. This theme is especially pertinent because the nanoscale structure dictates interactions across interfaces.

1. Introduction

Polymer chains end-tethered at solid-fluid interfaces – so-called polymer brushes – are widely viewed as archetypical systems. They are conceptually attractive because tethering allows a variety of surface-sensitive techniques to be brought to bear to tease apart the intertwined connections between brush organization, structure, and properties. Brushes are practically useful for their ability to confer desirable properties to the underlying surface and to mediate interactions across the solid–fluid boundary through control of the extent and areal density of the chains as well as the nature of the monomer type. In his seminal publication, de Gennes envisioned [1] that polymer brushes would find application as coatings appropriate for tailoring wetting and adhesion of surfaces, promoting biocompatibility and stabilizing colloidal dispersions, and enhancing the efficacy of chromatographic separations.

Polyelectrolytes (PEs) in particular are of great interest because of their relevance to biology and medicine; however, their ionizable nature, the solvophobicity of their backbones and the "Coulombic soup" through which interaction forces are transmitted [2••] and in which PEs function, present exceptional complexities that make PEs perhaps the least understood form of soft matter. For these reasons and also because brushes are model systems, PE brushes (Fig. 1) offer considerable opportunities for understanding how chain conformation is influenced by charge and intermolecular interactions with oppositely charged chains or other complex species in solution, such as surfactants, oligopeptides, and proteins.

Our intention here is neither to review neutron reflectometry as a method for studying soft interfaces, nor to summarize preparations and physical behaviors of PE brushes. A number review articles comprehensively treat both of these subjects [3•,4•, 5,6]. Rather, in this *Article* we address particular areas where the application of neutron reflectivity measurements to PE brush systems is poised to contribute new knowledge and insights into the behavior of these complex systems, with a focus on brush structure. For this purpose, in certain situations we draw from research outside the bounds of PE brushes and reflectometry studies thereof.

In what follows, we first describe the advantages of neutron reflectivity for the study of soft matter and how studies of these systems may benefit from a relatively new class of polymerization methods suitable for making polymer brushes. We then use recent studies, to the extent possible, to provide a view of how the field has advanced, and also to motivate areas of need and opportunity. Much of our discussion centers on the structure and behavior of "weak" polyacid brushes, which are of additional interest because the degree of dissociation varies with pH and salt concentration, whereas the extent of dissociation of "strong" PE brushes is fixed. Regardless of the nature of the polyelectrolyte, our basic stance here is that the themes identified would benefit from the type of insights and observations that can be provided by neutron reflectivity studies, though certainly not to the exclusion of other complementary methods.

2. Enabling features and capabilities

Neutron reflectivity offers compelling and unique capabilities for studying soft matter thin films organized on flat substrates or at air-liquid interfaces. Specular reflectivity measured as a function of the

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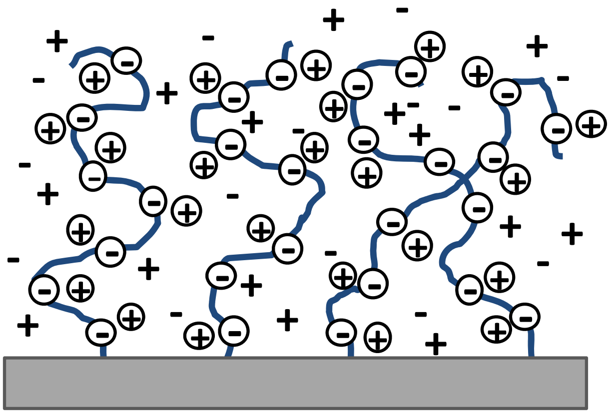

Fig. 1. Schematic of a tethered polyelectrolyte brush. Circled charges represent polymer ions and paired counterions. Un-circled charges represent added salt ions. Brushes may be made by covalently tethering chains to surfaces through reactive end groups, growing chains from surface-anchored initiators, or by preferential adsorption of amphiphilic copolymers.

wavevector transfer normal to the surface contains information related to the laterally-averaged segment density profile of a polymer film normal to the substrate, which is related to both the film's material composition and its density. Because neutrons are deeply penetrating, they are able to "see" buried interfaces as well as to probe materials encased in a variety of sample environments, including liquid and humidity cells. The variation in the neutron refractive index normal to surface governs the reflection of neutrons from that surface [7]. The neutron refractive index depends on the scattering length density, the density of nuclei in space weighted by the neutron-nuclear scattering length, which can be manipulated through the use of isotopic substitution. Compounds can be synthesized with deuterium, the hydrogen isotope consisting of a proton and a neutron ($^2H \equiv D$), instead of natural hydrogen, which overwhelmingly consists of protons ($^1H \equiv H$). Since the neutron interacts with the nucleus, such substitutions dramatically alter the scattering length densities of materials without appreciably altering their chemistry [3•,4,7]. Furthermore, the reflectivity depends on scattering length density differences between different layers, which allows one, for example, to use deuteration to highlight selected regions or phases.

Beyond simply highlighting phases or stratified layers by judicious use of isotopic substitution, synthetic chemistry enables a number of strategies that impart significant contrast to neutron scattering density. An elegant example of this is embodied in the recent work of Pispas et al. [8], who created polystyrene brushes having two blocks: the first consisted of a statistical random copolymer of styrene and styrene-d8 (d8 indicates isotopic substitution of 8 D for 8 H) at a composition matched to toluene-d8, which was used as the solvent. The second block that formed the free, outer edge of the brush chains was made by chain extension with protonated styrene. Careful neutron reflectivity measurements in toluene-d8 enabled the location of the free chain ends, distinguished by the isotopic contrast between polystyrene and toluene-d8, to be deduced. Analysis of the measured reflectivity revealed that the chain ends were distributed throughout the brush, with a preference for the outer periphery; however in contrast to predictions from self-consistent field theory, an appreciable concentration of free ends was observed at the confining surface (substrate). While the size of the end blocks (16 mol%) is, of course, larger than the last monomer unit at the chain end, which can be tracked using computation, these studies inspire ideas of how isotopic substitution and scattering length contrast may be used to dissect structural information on distinct portions of brushes.

Translating a measured reflectivity curve to a physical representation of a system can often be a challenge or, rather, determining which is the correct physical representation of the many possible for a given curve. Neutron reflectivity, in common with all scattering techniques that measure intensity (e.g. powder diffraction or small-angle scattering), does not yield a unique structure from direct inversion of the data [9,10••]. The reflectivity curve is instead fitted by a model scattering length density profile consisting of the layer compositions, thicknesses, and densities, along with the shapes of the interfacial mixing profiles between layers in the film. In practice, therefore, one must utilize as many ancillary measurements as possible to constrain the models used to fit a neutron reflectivity curve. It will always be possible to fit a data set simply by adding more model parameters. The key to robust structural characterization is construction of a scattering-density profile consistent with other measurements of the same sample containing the minimum number of adjustable parameters needed for a good fit.

In order both to control and to quantify polymer properties and thereby optimize structural information, another important, enabling capability is the suite of techniques available in modern polymerization methods. Early efforts to examine "strong" PE brushes based on sodium poly(styrene sulfonate) by neutron reflectivity relied on chemical conversion of pre-made, well-defined polystyrenes synthesized using "living" anionic polymerization. In the case of Mir et al. [11], PS chains were end-grafted through terminal chlorosilane groups and then sulfonated in situ. Sulfonation levels of ~80% were attained, but scission of chains was also evident. The polyolefin-*block*-polystyrene and poly(*tert*-butyl styrene)-*b*-polystyrene diblock copolymers studied by Guenoun et al. were sulfonated to (near) completion (90–95%) before anchoring them to either a solid surface [12] or confining them at the air-water interface [13] using the uncharged blocks. While these studies were among the first experimental investigations of the influential role of added salt on the stretching of strong polyelectrolyte brushes, incomplete conversion leaves hydrophobic repeat units that may complicate experimental interpretation due to their tendency to drive phase segregation in water. The development of controlled (free) radical polymerization techniques, which are tolerant of a variety of monomer types, and their adaptation for surface initiated polymerizations, has considerably broadened the type of PE brushes that can be created, either by direct polymerization of electrolyte monomers or by polymerization of protected forms that are subsequently transformed (to electrolytic form) after polymerization [14••]. Among the different polymerization techniques, surface-initiated atom transfer radical polymerization (SI-ATRP) is the most widely practiced method for making polymer brushes. Until recently, the synthesis of PEs in aqueous media was very challenging. As shown by Sankhe et al. through experiments and kinetic modeling, complexation of charge-negative monomers and basic catalyst/ligand complexes, disproportionation, and dissociation led to the rapid loss of control [15], though this could be overcome by using added salt [16].

Even a tacit mention of so-called "grafting to" and "grafting from" strategies for making brushes brings to mind a persistent conundrum bedeviling studies of brushes made on flat, low area substrates: tethering premade chains to an interface to form a brush allows grafting density, σ, to be easily determined from measured dry-layer thicknesses, T: $\sigma = \rho T N_{Av}/M$. However, due to entropic effects the resultant brushes are marked by lower areal densities than those made by growing chains from surface anchored initiators. However, when surface-initiated polymerizations are used, it is nearly impossible to accurately determine characteristics such as molecular weight and polydispersity index because it is difficult to cleave and recover a sufficient quantity of chains. This limitation prevents the grafting density, which governs inter-chain interactions, from being known. In most cases, brush chain molecular weights are taken to be equal to those of free chains recovered from sacrificial initiator added in the solution to provide control. Only a few cases exist where neutral brush chains have been recovered and characterized, and differences of up to 20% between free and tethered chain molecular weights have been found in systems where the brushes were made by free radical