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Polyelectrolyte brushes studied by surface forces measurement

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A R T I C L E I N F O

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A B S T R A C T

Brush layers of polyelectrolytes, ionized chains of poly(glutamic acid) (PLGA) and poly(lysine) (PLL), prepared by the Langmuir–Blodgett method, were characterized using the surface forces measurements at various pHs, salt concentrations and chain densities. This paper reviews the major results: (1) the effective charge density of the brush layer calculated from the force profiles was much lesser than the density of the ionized groups of the polyelectrolyte brushes, indicating that nearly all the ionized groups were neutralized by the counterions in the brush layer; (2) the thickness of the brush layers agreed with the length of the extended polyelectrolytes and was practically independent of the salt concentrations studied (0.43–10 mM). The thickness was proportional to the polymerization degree of polyelectrolytes; (3) the initial elastic compressibility modulus of the brush layer of PLGA or PLL increased with increasing ionization degree, while it decreased with increasing salt concentration because of a decrease in the osmotic pressure of the counterions; (4) stress profiles between the brush layers were scaled for polyelectrolytes of various polymerization degrees according to the contour length of the polyelectrolyte. Similar scaling was also found for stress profiles obtained at various salt concentrations (0.43–10 mM) and pHs; (5) the "osmotic pressure of counterion" model reproduced well the steric components of the stress profiles, thus supporting that the steric repulsion was mainly due to the osmotic pressure of the counterions; and (6) a density-dependent jump in the properties of polyelectrolyte brushes such as transfer ratio, compressibility and surface potential has been found, indicating the existence of the density (interchain distance)-dependent transition of polyelectrolytes in solutions. We have proposed a counterion model to account for this transition.

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1. Introduction

Polyelectrolytes form an essential class of substances because of their importance in multiple disciplines such as materials science and chemistry, where they are widely used as smart gels, viscous agents, and agents of improved colloidal stability; the physics of soft matters, where the polymer is one of the main subjects; and biology as many biological molecules are polyelectrolytes including DNA, proteins and polysaccharides [1–3]. Being polymers with charges and counterions, they exhibit interesting, albeit complicated properties, which precludes us from fully understanding their properties. It is possible to simplify the complexities of (three-dimensional) polyelectrolyte solutions using two-dimensionally organized brush layers of polyelectorolytes, where polymer chains are anchored by one end on the solid (or liquid) surface. This approach has been adopted to study polyelectrolytes both theoretically [4–10] and experimentally [4,11–

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19]. The significance of polyelectrolyte brushes is not limited in these fundamental aspects but extends to many technological applications as a stabilizing agent for colloidal particles, for fine control of surface properties such as adsorption, wetting and adhesion, for designing molecular systems (molecular architectures), and for their extensive biological relevance [4]. Because of this obvious importance, research studies on polyelectrolyte brushes have been increased in the last decade especially in experimental studies due to the recent rapid development of surface characterization and surface modification [4].

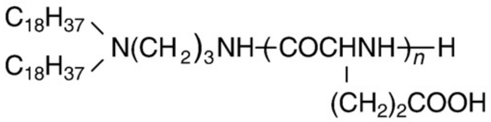
Direct measurement of surface forces has been proven useful in obtaining information about the concrete structures of polypeptide and polyelectrolyte brush layers. Taking advantage of the LB method, we prepared well-defined brush layers of chain–end-anchored polypeptides and polyelectrolytes [11–14,17]. We then investigated them based on the force profiles together with FTIR spectra and surface pressure-area isotherms by systematically varying the polymer chain length, chemical structure, brush density, and solution conditions (pH, salt concentrations, etc). When the surfaces of the opposed polymer layers approach a separation distance of molecular dimensions, the steric repulsion becomes predominant and hence measurable. By analyzing this, it is possible to obtain key parameters such as thickness (length) and compressibility of polyelectrolyte layers, which are difficult to obtain by other methods, and to correlate them with polymer structures. The obtained information should form a basis for elucidating their properties and developing physical models. Moreover, it is more probable to explore new phenomena by a novel approach: we have found the density-dependent transition of polyelectrolyte brushes, which we have accounted for in terms of the change in the binding modes of counterions to polyelectrolytes [19]. In this review, we intend to describe the characteristics of polyelectrolytes obtained by these approaches and their advantages.

2. Brush layers of poly(glutamic acid) and poly(lysine)

Polypeptides form various secondary structures (α-helix, β-sheet, etc.) depending on solution pHs. We have investigated end-anchored poly(L-glutamic acid) and poly(L-lysine) in various secondary structures [12,13], using an analytical method for the steric force, in order to examine, more quantitatively, the structures and structural changes in polyelectrolyte layers. The elastic compressibility modulus of polypeptide brushes was obtained, to our knowledge, as the first quantitative determination of the mechanical modulus of an oriented, monomolecular polymer layer in a solvent.

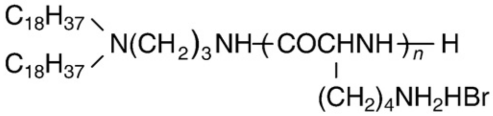
Poly(L-glutamic acid) and poly(L-lysine) brush layers were prepared using amphiphiles **1** and **2**, respectively, carrying the poly (L-glutamic acid) (2C18PLGA(*n*), degree of polymerization, *n* = 21, 44, and 48) and the poly(L-lysine) segment (2C18PLL(*n*), *n* = 41) (Fig. 1). They formed a stable monolayer at the air–water interface in which different secondary structures, such as α-helix and β-structures, were formed through intra- and intermolecular hydrogen bonding depending on surface pressure and subphase pH. They were deposited onto hydrophobic mica surfaces and subjected to the surface forces measurements. We used FTIR spectroscopy to study the formation and orientation of their secondary structures [14].

Fig. 2A shows a force–distance profile measured for poly(L-glutamic acid) brushes (2C18PLGA(44)) in water (pH = 3.0, 10^{-3} M HNO_3) deposited at 40 mN/m from the water subphase at pH = 3.0. The majority of peptides are in the forms of an α-helix (38% determined from the amide I band) and a random-coil. Two major regions are clearly seen in the force–distance profiles. At surface separations longer than 35 nm, the interaction is a typical double layer electrostatic force with a decay length of 10 ± 1 nm, which agrees well with the Debye length (9.6 nm) for 10^{-3} M HNO_3, due to



$$(C_{18}H_{37})_2N(CH_2)_3NH\left(CO\underset{(CH_2)_2COOH}{\underset{|}{C}}HNH\right)_n H$$

1:2C18PLGA(*n*), *n*=21, 44, 48



$$(C_{18}H_{37})_2N(CH_2)_3NH\left(CO\underset{(CH_2)_4NH_2HBr}{\underset{|}{C}}HNH\right)_n H$$

2: 2C18PLL(*n*), *n* = 41, 52

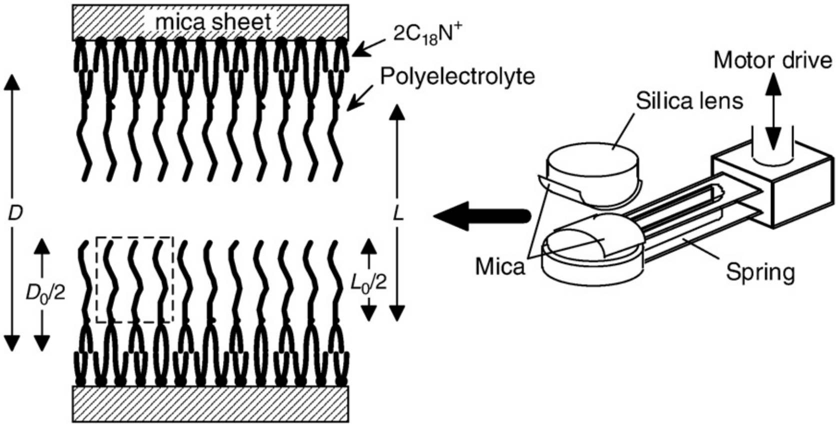


Fig. 1. Schematic drawing of surface forces measurements on charged polypeptide brushes prepared by LB deposition of amphiphiles **1**and **2**.