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## Swollen structure and electrostatic interactions of polyelectrolyte brush in aqueous solution

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### ABSTRACT

Surface grafting of polyelectrolytes on materials brings about various significant changes in surface properties such as wettability, adhesion, and friction, because of their excellent hydrophilicity and unique intermolecular interactions that depend on the ionic strength of the solution. This review paper describes the characterization of the swollen structure and electrostatic interaction of polyelectrolyte brushes in aqueous solution by use of optical tweezers and neutron reflectivity, in order to discuss the dissociation of ionic groups and charge distribution in the polyelectrolyte brush. In addition, the spreading and structure of water on the polyelectrolyte brush surface were characterized by high spatial resolution IR spectroscopy.

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### 1. Introduction

Polyelectrolytes constitute many biological macromolecules such as DNA, proteins, and carbohydrates and hence play an important role in living organisms and in nature. Various biological functions of these bio-macromolecules are triggered by changes in the molecular conformation and molecular interaction of the polyelectrolyte segments, induced by pH, ionic strength, and temperature; this is because polyelectrolytes are polymers containing ionic groups that can dissociate into polyvalent macroions and counterions of opposite charge in water [1]. Electrostatic interactions between charges strongly depend on the ionic strength of the solution, and they result in complex intra- and intermolecular interactions that have strong consequences for the dimensions of polyelectrolytes in the solution [2,3]. A polyelectrolyte chain in a

solution of low ionic strength forms an extended chain structure as a result of intramolecular repulsive interactions between the charged groups on the polymer chains. On the other hand, polyelectrolytes behave like electrically neutral polymers upon the addition of salt ions in aqueous solutions, because electrostatic interactions between charged monomers are screened by mobile ions. Therefore, analysis of the molecular conformation of polyelectrolytes is fundamentally important for understanding biological and biophysical processes [4–9].

Recently, surface-grafting of polyelectrolytes on materials has drawn much attention because of its widespread applicability of surface-modifications in wettability control [10], anti-fouling [11–13], adhesion [14–16], tribology [17–20], and fabrication of stimuli-responsive surfaces. Grafting polymerization from surfaces produces additional functional thin layers on the surface. Since 1996–1998, several research groups have applied living/controlled polymerization to surface-initiated polymerization processes [21,22] to produce brush like polymers with predictable molecular weights and narrow molecular weight distributions, which resulted in significant improvement of the graft density. Surface-tethered polymers with a considerably high graft density are called “polymer brushes” [23,24], which exhibit unique surface properties different from those of conventional low-density brushes.

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Because one chain end of the brush polymers is covalently immobilized on the substrate surface, polymers cannot be removed from the surface even in the solution state. When polymer brushes with a significantly high graft density are immersed in a good solvent, the chains are forced to stretch away from the tethering site, forming a concentrated brush layer because of the high osmotic pressure; this environment is markedly different from the random coil state of free polymers in a solution state. Polyelectrolyte brushes, in particular, are expected to show unique dissociation of ionic groups in the swollen brush layer, in water, because of the extremely high concentration of ionic groups.

This review paper describes the characterization of the swollen structure and electrostatic interactions of polyelectrolyte brushes in aqueous solution by means of optical tweezers and neutron reflectivity (NR), and discusses the dissociation of ionic groups and charge distribution in the polyelectrolyte brush. We hereafter focus on the positively charged polymethacrylate, poly[2-(methacryloyloxy)ethyl]trimethylammonium chloride (PMTAC). In addition, water spreading and the structure of water on the polyelectrolyte brush surface were characterized by high spatial resolution IR spectroscopy. Direct nanoscale observations of polyelectrolyte brushes under wet conditions, at atmospheric pressure and room temperature, were recently carried out using atmospheric scanning electron microscopy (ASEM) [25], although these are not discussed in detail herein.

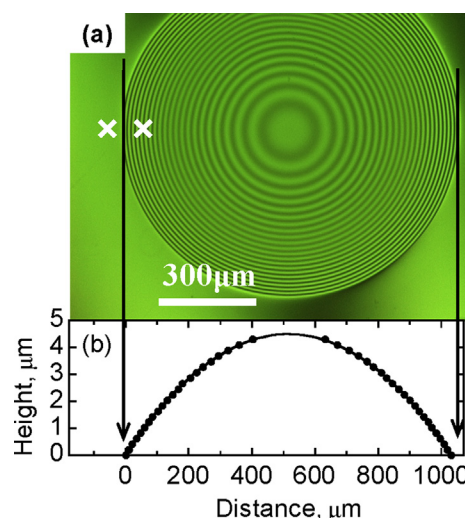
The PMTAC brushes described in this paper are prepared by surface-initiated atom transfer radical polymerization (SI-ATRP) from a silicon substrate or silica particles bearing a (2-bromo-2-methyl)propionyloxyhexyltrimethoxysilane monolayer, as shown in Scheme 1 [26,27]. SI-ATRP of 2-(methacryloyloxy)ethyltrimethylammonium chloride in trifluoroethanol and imidazolium chloride gave well-defined PMTAC having predictable molecular weights and relatively narrow molecular weight distributions.

## 2. Wettability of PMTAC brush surface

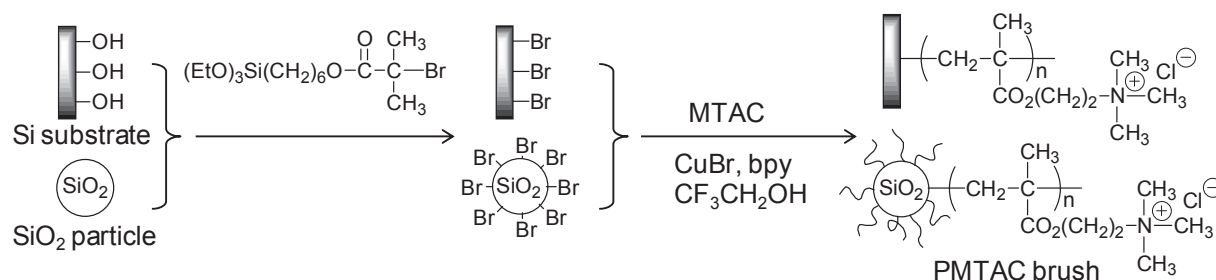
Most polyelectrolyte brushes have a super hydrophilic surface whose water contact angle is smaller than  $10^\circ$  [10]. Therefore, accurate measurement of the contact angle from the side view of the water droplet on a flat surface is difficult. For quantitative measurement of such small contact angles of water on the PMTAC brush, reflection interference contrast microscopy [28] was employed [29]. In this technique, the optical interference at the liquid surface is used to construct an accurate drop shape profile with an experimental error within  $\pm 0.1^\circ$ . Fig. 1(a) and (b) show a representative image of the interference rings obtained in our contact angle measurements and the droplet profile calculated from the interference, respectively. The figure includes the section of fit by a sphere equation. The drop profiles were well reproduced with sections of a circle, indicating that gravitational effects are not significant. The average contact angle of water on the PMTAC brush

was  $0.95 \pm 0.09^\circ$ , demonstrating the outstanding hydrophilicity of the surface.

This result led us to raise a fundamental question: *Why doesn't complete wetting occur, even on super hydrophilic polyelectrolyte brushes?* Water contact angle on hydrophilic polymer brushes cannot be explained simply by surface tension balance of Young's equation. Polyelectrolyte brushes with high graft density become hydrated in water to form an extended conformation due to the osmotic pressure. The work of hydration at the contact line of water droplet should be considered to describe the wetting behavior of hydrophilic brushes. This issue has been discussed sometimes so far. Cohen Stuart et al. argued that the polymer brush formed the bridges between the solvent/substrate and the solvent/vapor interfaces which lead to the partial wetting of the surface [30]. Müller et al. discussed about the enthalpy of hydration of polymer brush required to create the hydrated polymer/air boundary at the three phase contact line [31]. Murakami et al. answered this question from the viewpoint of the water structure in the PMTAC brush [29]. Water structure was examined by high spatial resolution IR spectroscopy at beamline BL43IR of SPring-8 (Japan) [32,33]. The IR spectra were obtained from the beam reflected from the interior and exterior of the water droplet, approximately 10–50  $\mu\text{m}$  away from the boundary (cross indicators in Fig. 1(a)), with a well-focused IR beam ( $10 \times 10 \mu\text{m}^2$ ). Fig. 2 shows the spectra of water on the PMTAC brush. A broad peak centered around  $3450 \text{ cm}^{-1}$ , due to the O–H stretching vibration mode, appeared in the spectrum recorded from the interior of the droplet (solid line). This is a typical



**Fig. 1.** (a) Representative image of interference rings at the surface of a droplet. The crosses (x) indicate the points measured by IR spectroscopy. (b) The drop profile calculated from the interference (●) and the fit by the sphere equation (–). These images were first reported in Ref [27], and was redrawn for this review.



**Scheme 1.** Preparation of PMTAC brush on Si substrate and silica particle by surface-initiated ATRP.

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