

CHAPTER I

INTRODUCTION

1.1 Statement of Problem

Layer-by-layer (LBL) assembly of oppositely charged polyelectrolytes (PEL) has been recognized as a powerful, yet simple strategy to engineer surfaces with specific properties. This versatile technique offers the benefit of solvent-free processing as well as the ability to coat all available surfaces of virtually any material, irrespective of shape or size, with uniform ultrathin films of precisely controlled thickness. Surface properties of the assembled multilayer film depend on the type of polyelectrolytes, thickness and roughness. However, the stability of the multilayer system is often of concern, especially in the environment that causes the displacement of the first adsorbed layer of polyelectrolyte and the subsequent desorption of the whole multilayer assembly i.e. changing the sign of the surface charge of the substrate or by addition of competing low molecular weight electrolytes.

This research aims to use a surface-tethered polyelectrolyte brushes as a substrate for multilayer assembly. It is believed that the problem of stability can be overcome since the polyelectrolyte chains, generated by surface-initiated polymerization (SIP) or so-called “grafting from” approach, are attached to the substrate by covalent bonds. The “grafting from” method, involves a stepwise growth of polymer chain from the surface by insertion of monomer. This allows a better control over polymer chain length and graft density.

The research begins with the formation of poly(*tert*-butyl acrylate) (Pt-BA) brushes by surface-initiated atom transfer radical polymerization of *tert*-butyl acrylate. Poly(acrylic acid) (PAA) brushes are subsequently obtained after *tert*-butyl groups of Pt-BA brushes are removed by acid hydrolysis. PAA brushes is weak anionic polyelectrolyte when pH of the solution is appropriately adjusted and thus can be used as charged substrate for fabrication of multilayer films by LBL method. Generated by “surface-initiated polymerization”, it is anticipated that the graft density

of the PAA brushes is high enough to induce chain stretching allowing a thicker individual layer to be formed. In principle, the carboxyl group density and graft density of the PAA brushes can be varied as a function of reaction condition (polymerization time, monomer to initiator ratio). In general, the greater carboxyl group density and graft density of the PAA brushes should yield the thicker individual layer. The concept of using surface-tethered polyelectrolyte brushes as a substrate for multilayer assembly not only can help improving the stability of the multilayer film, but also reduce the number of deposition step. This approach offers a great benefit for applications which require fabrication of nanometer-thick film without having to use many cycles of deposition.

In this particular study, two multilayer systems are fabricated. The first system is carboxyl-terminated polydiacetylene vesicles (PPCDA)/PAA. The effect of PAA molecular weight and adsorption time on the growth of PPCDA/PAA multilayer on glass-tethered PAA brushes can be conveniently monitored using UV-Vis spectroscopy. The second system is chitosan (CHI)/PAA. CHI is of particular interest because of its natural origin and favorable physicochemical and biological properties. CHI is a partially deacetylated form of chitin, a natural substance found abundantly in the exoskeletons of insects, shells of crustaceans, and fungal cell walls. Also, it is biocompatible, non-toxic, and antibacterial. CHI is thus considered as an attractive material that can be potentially used in many biomedical-related applications. The growth of CHI/PAA multilayer on silicon-tethered PAA brushes is characterized by water contact angle measurements, ellipsometry, infrared spectroscopy and atomic force microscopy. The deposition of bioactive polyelectrolytes such as heparin sodium salt, *N*-[(2-hydroxyl-3-trimethylammonium)propyl] chitosan chloride as the outermost layer on the CHI/PAA multilayer is studied to generate the biofunctional thin film. Biological responses in terms of protein adsorption and antibacterial activity of some multilayer films are tested. We hypothesize that alternate response can be achieved as long as each layer is thick enough and overall biological response depends on the outermost layer. The consequence of this study should provide fundamental information that can lead to the development of thin-film fabrication for applications in nanotechnology and biotechnology.

1.2 Objectives

1. To synthesize surface-tethered PAA brushes having controlled thickness by surface-initiated atom transfer radical polymerization.
2. To fabricate multilayer films on surface-tethered PAA brushes by layer-by-layer technique.
3. To determine bioactivities of the multilayer film on the surface-tethered PAA brushes.

1.3 Scope of the Investigation

The stepwise investigation was carried out as follows.

1. Literature survey for related research work.
2. To immobilize α -bromoester-containing initiator on silicon oxide surfaces.
3. To synthesize *Pt*-BA brushes by surface-initiated polymerization from silicon oxide surfaces containing a monolayer of α -bromoester groups.
4. To prepare PAA brushes by hydrolysis of *Pt*-BA brushes.
5. To fabricate and characterize the multilayer film on surface-tethered PAA brushes.
6. To test bioactivities of the fabricated multilayer film.