

CHAPTER I

INTRODUCTION

1.1 Statement of Problem

Development of methods for surface modification of solid substrate is of crucial importance in many areas of science and technology such as modern electronic and nanotechnology. Formation of polymer brushes is recognized as one of novel routes for surface modification. Conventionally, polymer brushes are prepared by adsorption of block copolymers where one block is strongly adsorbed to the surface with the other block forming the brush layer. The non-covalent nature of this grafting strategy is a weakness, however, since desorption of the brushes can subsequently occur. In addition, the demanding block copolymer synthesis limits the choices of functional groups for the block copolymer structure. The other approach, in principle more versatile, is the “grafting from” or the “surface-initiated polymerization” technique, in which polymerization is initiated from initiators coupled covalently to the surface. One should be able to grow very high-density polymer brushes on a substrate using the latter method, if proper conditions are employed.

There is growing interest in atom transfer radical polymerization (ATRP) since it was discovered in 1995. The living characteristic and the compatibility with a variety of functional monomer render ATRP an attractive method for surface-initiated polymerization in producing well-defined polymer brushes. The process allows a better control of target molecular weight and molecular weight distribution. The success of ATRP in synthesizing hydrophilic polymers provides an additional advantage over the traditional living ionic polymerization.

From both theoretical and practical perspectives, several aspects related to the graft density of polymer brushes and surface properties are very important. In principle, the graft density of polymer brushes depends upon the density of grafted initiator on a substrate surface. In this research, chemically grafted tris(trimethylsiloxy)silyl (tris(TMS)) monolayer on the silicon oxide substrate is used as a nanometer-scaled template for controlling the graft density of polymer brushes. By controlling the kinetic of a reaction between silanol groups on the silicon oxide surface with tris(trimethylsiloxy) chlorosilane (tris(TMScI)), surfaces having a range of tris(TMS) coverage can be generated. The incomplete reaction between the sluggish tris(TMScI) and silicon oxide surface allows a mixed tris(TMS)/silanol surface to be formed. α -bromoester groups can be subsequently attached to the residual silanol groups in nanopores of the substrate. Polymer brushes of 2-methacryloyloxyethyl phosphorylcholine (MPC) and *tert*-butyl methacrylate (*t*-BMA) which are representatives of hydrophilic and hydrophobic monomers, respectively, are then prepared by surface-initiated ATRP from nanoporous surface.

Effects of the chain length between the substrate surface and the α -bromoester groups, solvent and monomer on the efficiency of polymer brush formation are investigated. The correlation between the graft density of polymer brushes and surface topography is explored. We anticipate that chemically grafted mixed monolayer of tris(TMS)/silanol groups can be used as nanometer-scaled template for controlling the graft density of both hydrophobic and hydrophilic polymer brushes, as well as tuning surface topography and surface properties of the material's surface at nanoscopic scale.

1.2 Objectives

1. To synthesize poly(2-methacryloyloxyethyl phosphorylcholine) brushes and poly(*tert*-butyl methacrylate) brushes by surface-initiated atom transfer radical polymerization from nanoporous surface.

2. To study the correlation between graft density and surface topography and surface properties of polymer brushes.

1.3 Scope of investigation

The stepwise investigation was carried out as follows.

1. Literature survey for related research work.
2. To study the kinetic of reaction between tris(trimethylsiloxy) chlorosilane tris(TMScI) and silicon oxide surface.
3. To immobilize α -bromoester-containing initiator on silicon oxide surfaces containing a mixed monolayer of tris(TMS)/silanol groups
4. To synthesize poly(2-methacryloyloxyethyl phosphorylcholine) brushes and poly(*t*-butyl methacrylate) brushes by surface-initiated polymerization from silicon oxide surfaces containing mixed monolayer of tris(TMS)/ α -bromoester groups.
5. To investigate the effects of the graft density of polymer brushes on the surface topography and surface properties.

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