CHAPTER V

CONCLUSION AND SUGGESTION

By controlling the kinetics of a reaction between silanol groups on the silicon oxide surface with tris(trimethylsiloxy) chlorosilane (tris(TMSCl), surfaces having a range of tris(TMS) coverage were generated. The incomplete reaction between the sluggish tris(TMSCl) and silicon oxide surface allowed a silicon-supported mixed tris(TMS)/silanol monolayer to be formed. The reaction progress can be monitored by ellipsometry, contact angle measurements and XPS analysis. Nanoscaled holes (nanopores) in tris(TMS) monolayer containing unreacted silanol groups of silicon-supported mixed tris(TMS)/silanol monolayer further reacted with silane compounds having end-functionalized α-bromoisobutyrate and yielded silicon-supported mixed tris(TMS)/α-bromoisobutyrate monolayer. The signal of bromine as detected by XPS analysis warranted the existence of α-bromoisobutyrate groups which should act as surface-immobilized initiators. These substrates were later used as nanoscaled templates for the synthesis of surface-tethered polymer brushes.

It has been demonstrated that hydrophilic polymer brushes of 2-methacryloyloxyethyl phosphorylcholine (MPC) successfully grew from silicon-supported α-bromoisobutyrate monolayer using CuBr/bpy as a catalytic system in the presence of either propyl(2-bromo-2-methyl)propionate as a sacrificial initiator or $CuBr_2$ as a deactivator. The linear dependence of molecular weight and thickness on polymerization time clearly suggested that polymerization is living in character. The graft density of 0.3-0.4 chains/nm^2 was calculated.

Due to the hydrophobicity of tris(TMS) groups surrounding α-bromoester initiators, the growth of PMPC brushes from silicon-supported mixed tris(TMS)/α-bromoisobutyrate monolayer was more favorable in a more surface-wettable solvent,

methanol in this particular case, than water. PMPC brushes grew faster from surface-immobilized α-bromoisobutyrate initiators having hexyl (n_6) and decyl (n_{10}) as alkyl spacers than the one having propyl (n_3) as an alkyl spacer. The better mobility and the longer alkyl spacer of n_6 and n_{10} allowed them to conquer the steric hindrance of the surrounding tris(TMS) and reach monomers more efficiently than n_3.

Surface topographies of polymer brushes were investigated by AFM analysis. Nanoscopic distribution of PMPC brushes which appeared as protrusions having a diameter of less than 100 nm was only visualized when the graft density of PMPC brushes in the nanopores was not too high. Under such circumstance, the size of protrusions depended upon both %tris(TMS) coverage as well as the graft density of PMPC brushes itself in the nanoporous. Certain space in the nanopores was necessary for the polymer chains to adopt more coil-like architecture or aggregated form instead of being in extended forms which are thermodynamically unfavorable. In the case of high graft density of PMPC brushes in the nanopores, the surfaces became quite smooth due to two possible actions of polymer brushes. The first action involves the polymer chains being forced to stretch away from the surface and thus covering the nanopores while the other involves the folding of polymer chains over the tris(TMS) layer. This latter action should be favorable only when the polymer chains are sufficiently long. Unlike PMPC brushes, Pt-BMA brushes are hydrophobic so they should be quite compatible with tris(TMS). The mixed tris(TMS)/Pt-BMA brushes system thereby did not exhibit nanoscopic phase separation although the graft density of Pt-BMA brushes in the nanopores was quite low. These results also implied that self-aggregation of PMPC brushes in the nanopores was truly a consequence of phase incompatibility between hydrophilic PMPC brushes and hydrophobic tris(TMS).