SURFACE MODIFICATION OF METALS THROUGH ATRP

GRAFTING OF ACRYLICS

Surface Modification of Metals through Atom Transfer Radical

Polymerization Grafting of Acrylics

By

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ABSTRACT

In this thesis, acrylic polymers (methyl methacrylate, MMA; N,N'-dimethylamino ethyl methacrylate, DMAEMA; oligo-ethylene glycol methacrylate, OEGMA; trifluoroethyl methacrylate, TFEMA) were grafted from various metal surfaces such as cold rolled steel (CRS), stainless steel (SS), aluminum (Al) and nickel (Ni) through surface-initiated atom transfer radical polymerization (s-ATRP). The purpose is to improve corrosion resistance and to introduce multi-functionality to metal surface.

The metal substrates were precisely polished and were facile for characterization by ellipsometry. 3-(α -Bromo-2-methyl) propylamide propyltriethoxysilane was synthesized and immobilized on the metal surfaces under a simple and workplacefriendly condition. Grafting density was estimated to be 0.58 chains/nm² for CRS-g-PMMA, 0.55 chains/nm² for Ni-g-PMMA and 0.18 chains/nm² for SS-g-DMAEMA and 0.66 chains/nm² for SS-g-PDMAEMA. Two strategies, i.e., "adding free initiator" and "adding deactivator", were adopted for the control over polymer molecular weight and grafting density in the CRS-g-PMMA system. The polymer thicknesses up to 80 nm were obtained within 80 min using the "adding deactivator" strategy.

Copper and iron catalyst systems were compared on different metal substrates. A severe deactivation of copper catalyst was observed on the metal substrates. Controlled polymerization with relatively low polydispersity was obtained using the iron catalyst.

The metal surfaces at various stages of modification were characterized by X-ray photoelectron spectroscopy, ellipsometry, goniometry, and atomic force microscopy (AFM). Electrochemical experiments were also carried out to measure the polarization resistance and corrosion potential of CRS-g-PMMA substrates. This thesis work demonstrated that the surface-initiated ATRP is a versatile means for the surface modification of metals with well-defined and functionalized polymer brushes.

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Chapter 1

Introduction

1.1 Polymer coating on Metal surface

1.1.1 Metals

Metals are abundant in our planet, especially aluminium, iron and nickel. Nowadays metals are important and widely used materials in manufacturing, construction and transportation, because of their superior electronic and thermal conductivities, magnetic, mechanical and other physical properties.

Cold rolled steel (iron) is a most commonly used material in automobile manufacturing, gas tank, floor pans, firewall and construction. During manufacturing, the steel is rolled while it is relatively cold (under crystallized temperature) in single-stand and multiple-stand mill. After rolling, CRS undergoes several steps of annealing process to eliminate interior stress. Cold rolled process produces a much stronger steel with tighter dimensional tolerances than the hot rolled steels, but more vulnerable to corrosion.[1,2]

Stainless steels are ferrous alloys. They contain at least 10% chromium (weight percentage). When the ingredient of chromium is over 13%, it shows high oxidation resistance at ambient temperature in atmosphere and 26% chromium makes SS applicable in harsh environments. Certain amount of chromium in SS facilitates to build a passivation film on SS surface. The passivation film can recover when experiences

mechanical damage. Adding molybdenum (Mo) enables SS even better in preventing corrosion, especially higher resistant property against pitting and crevice corrosion at the presence of chlorine.[3-6]

Nickel is in the transition metal category belonging to the iron group with ferromagnetic property. It has a silvery and highly polished appearance. It is ductile, malleable and hard. Because of its magnetic nature, its mechanical performance in atmosphere and its endurance to oxidation, it is used in many industrial and consumer products. In laboratory, nickel is frequently used as a catalyst for hydrogenation, CVD and fuel cell.[7]

Both iron and nickel are in the category of transition metals, having relatively high melting, boiling points and tensile strength. Their nanoparticles have unique physical, optical and magnetic properties that can be utilized as nano-catalyst, biosensor, drug-carrier and microscopic-sized devices. But the compatibility and stability of metal nanoparticles with their surroundings are often challenging.

Aluminium ranks second in metal market, just after iron. It is light, malleable, ductile, and easy to machine and cast. It has superior anti-corrosion performance due to the buildup of tightly compact passivation layer on its surface as well as its light weight over volume, only one-third of the steel or copper density. Consequently, aluminium and its alloys are used in many manufacturing and construction to reduce the weight of machine or building with improved performance. The replacement of structural pieces made from aluminium and its alloys in the aerospace industry greatly improves the overall fuel efficiency.

In this thesis, cold rolled steel samples (provided by Dofasco) were investigated for the development of a new surface technique that prevents the materials from corrosion.[14] Stainless steel 316L (Cr/Ni/Mo-18-10-3), nickel (99.98% purity) and aluminum (99.99%) were also studied for the surface modification with novel functionalities.

1.1.2 Polymer coating

Most metals are chemically unstable, for instance, iron forms dense oxide layer on surface if exposed to air and experiences pitting corrosion while immersed in water for only several minutes. Aluminum decreases its conductivity while exposed to air.[8] The current technologies in the polymer coating rely on non-specific interactions to insulate the metal oxide layer from environment. The adhesion is based on van der Waals forces or other weak interactions. The interface therefore lacks stability and has a relatively short life. The breakdown of organic materials results directly from irreversible damage at the interface, contributing to structural or functional failures. Corrosion results in a huge economic loss to industrialized countries. It is estimated that the annual loss due to metal and alloy corrosion is in the range of \$200-300 billion US dollars in North Currently the common coating technologies, including metallic coating, America. painting, and laminating, are highly productive and cost competitive, but toxic towards environment. Typically, polymer coatings are physically attached to metal surface in highly entangled states. Therefore, the functionality of surface and nano/micro-scale precision become uncertain. In general, the existing polymer coating approach is limited

by the challenge in establishing a stable interface between coating and metal interface, and by the requirement of polymer processability.

Hexa-chromium treatment was adopted to improve the adhesion and anticorrosion performance of metals before polymer coatings. The process is straightforward and inexpensive, but the anti-corrosion performance is not satisfactory. Worse than the poor performance is the toxicity of the process for operators and environment. This process has been prohibited in many countries. Industries are looking for new technologies to replace hexa-chromium treatment.

Silane coupling agent has attracted considerable attention in recent years to replace hexa-chromium treatment. The treatment is fast, simple, and safe, forming chemical bonds between interfaces. Metals such as CRS, hot-dip steel, galvanized steel, electrogalvanized steel, zinc, nickel, aluminum, and their alloys are good candidates for the process.[9, 10] However, the brittleness, porosity and weakness of silane films and the lack of functionality limit their high-tech applications.[11,12]

The development of high value-added metal materials and applications has been demonstrated by the modification of bulk chemistry and mechanical properties. This strategy is approaching the natural limitation of the material and thus continued development of higher value materials has shifted to modification of surface properties. It allows the construction of multifunctional materials with a myriad of possible surface attributes, providing new and often unusual functionality for automotive, space, energy, military, biomedicine, construction, microelectronics industry.[13]

1.2 Surface Grafting

1.2.1 "Grafting from" versus "grafting to"

Polymer grafting technique is originally used to stabilize colloidal particles in order to improve their compatibility with surroundings by changing particle surface chemistry or morphology.[15] The technique is applicable for uses in a variety of applications, for example, stabilizer of colloid, nonfouling coatings, responsive materials, and drug carrier.[16]

Surface grafting means that polymer chains are chemically bonded to surface. There are two important parameters for surface grafting, namely grafting density and polymer chain length. Grafting Density (GD) means the number of polymer chains per unit area surface (often per square nanometer). Polymer grafting density (GP) can be calculated by following equation.[17]

$$\sigma = \frac{d \times Na \times \rho}{Mn} \tag{1}$$

where d is the thickness of polymer film, ρ is the density of bulk polymer, Na is the Avogadro constant, Mn is the number-average molecular weight of polymer chain on surface.

There are two strategies for grafting polymers on surfaces, namely, "graftingfrom" and "grafting to" techniques. The topology of various surfaces is differed dramatically using different grafting methods. The topology can be mushroom structure, semi-dilute brush, and high density brush. See Figure 1.1 [18] Therefore, the thickness of a polymer film and the number of functional groups on surface deviate significantly from different surface topologies. **Grafting to** --Polymer is prepared with functional group at chain end and/or side chain covalently bonded to reactive moieties on substrate. The strategy is straightforward and has well-defined polymer chains, both molecular weight and architecture. However, the early grafted polymer chains spread out on the surface, which is not in favor of the diffusion of later chains to the surface, resulting in low grafting densities. Grafted chains form random coils or "mushrooms" on the surface. The polymer chains often have low molecular weight at a level of thousands, because of the diffusion limitations. See Figure 1.1.

Grafting from (through conventional chain growth polymerization) – It is a two-step process. First, small molecules with anchor groups and initiator moieties are immobilized on surface via covalent bonding. An in-situ polymerization then carries out from the initiator moieties of the attached molecules. Monomer molecules are much smaller in size than polymer chains and therefore the diffusion of monomer to surface is easy compared to the "grafting to" strategy. However, the fast growing polymer chains impose a barrier for monomer to diffuse to the surface initiator sites, preventing effective surface initiation. Also, during the polymerization, the radical concentration on surface is much higher than that in solution, giving rise to significant radical termination and thus resulting in low molecular weight and less uniform chains. This strategy partly overcomes diffusion problem, but has relatively low surface initiation, resulting in medium grafting densities. With such a process, it is difficult to obtain a high-quality surface with designed functionality. In addition, the characterization of polymer chains

on the surface, both molecular weight and architecture, becomes a new problem. See Figure 1.1.

Grafting from (through controlled/living polymerization) — In this approach, small molecules with anchor groups and initiator moieties are immobilized on surface via covalent bonding. An in-situ living polymerization then carries out from the initiator moieties of the attached molecules. During the polymerization, the concentration of propagating radicals is low because radicals are temporarily-deactivated. Surface radical termination is greatly limited. Surface radicals have fast and efficient initiation. They experience frequent activation and deactivation, propagating monomers in a controlled manner. High grafting density can be obtained. Controlled molecular weight with uniform chain length, capability to producing copolymer and designed architecture are also achievable using this approach. See Figure 1.1.

"Polymer brush" means polymer chains tethered to a surface or interface with high grafting density. In a good solvent, polymer chains are fully stretched and oriented away from the surface. Polymer chains do not entangle with each other because of osmotic pressure between close neighbouring chains. When grafting density is as high as 0.7 chains/nm², polymer chains can stretch as much as 80-90% of its full chain length in a good solvent,. An individual chain on dry state can stand out over 40% of its full chain length that is much higher than random coil and semi-diluted brush.[19]



Figure 1.1: Schematic of polymer chains on surface with changeable grafting density

1.2.2 Strategies of Immobilization of Anchor Group

Self-assembly -- Molecular self-assembly is defined as that molecules are spontaneously organized into pattern and structure without guidance and management from an outer source. It is common in nature, for example, DNA, lipid and peptide. Driving forces involved are electrostatic, H-bond, van der Waals, and other weak interactions between molecules that result in reduction of free energy in the system. The process is reversible. Self-assembly occurs in both static and dynamic systems.[20]

Zisman was the first who reported the preparation of monolayer of surfactant on a clean metal surface using self-assembly in 1946.[21] In 1980, Sagiv reported the preparation of a thiol self-assembly monolayer on an Au surface.[22] Other well-known

examples of self-assembly are Langmuir-Blodgett film, alkyl acid on metal oxide, silane coupling agent (alkoxysilanes or halogenosilanes) on silicon/metal/metal oxide, organo sulfur on metal/semiconductor, thiols/disulfides on noble metals, organophosphonates multilayers and supermolecules.[23] Self-assembly is considered as practical technology applications. Little energy is involved. However the process is not always reproducible because it is reversible.

Chemical vapor deposition (CVD) or physical vapor deposition (PVD) -- In a CVD process, the precursor molecules are first vaporized and then react or decompose in a thin layer on surface. More often, volatile by-products (exhaust gas) are produced and carried out by inert gas flow (nitrogen for example) from the reaction chamber. The reaction temperature in chamber ranges from several hundred to several thousand Kelvins.[24,25]

Electrografting method: Electrografting is a powerful strategy to form molecule-to-metal covalent bond. It can be applied to conductive substrates, metals and semiconductors, using electro-active monomers to form covalent bonds between different materials at an interface. It is a high through-put process. Electrografting technology is very different from electrodeposition. The electrical current involves only to initiate grafting step whereas electrodeposition rely on electrical current throughout the process.[81,82] However the requirement of rigorous experiment conditions limits its popularity.

Other surface modification technologies include plasma treatment, ion-beam, sputtering, alloying and electron beam coating. In general, the approach for

immobilizing initiator is crucial for achieving high initiator density and consequently high grafting density.

1.2.3 Challenges of surface grafting from metals

Relatively low grafting density: Free radical polymerization has been industrialized for many years because of its high throughput process, mild reaction condition, wide range of monomers, and high tolerance to impurities. It produces polymers with low costs and satisfactory performance. O.Prucker et. al. reported an insitu polymerization of styrene from silicon gels with SAM of azo anchor group using conventional free radical polymerization.[26] Nevertheless, the slow initiation and rapid chain growth of early chains in conventional free radical polymerization prevent late chains to grow because of diffusion limitations experienced by monomers penetrating the formed polymer layer. It is therefore difficult to achieve a high grafting density resulting in semi-dilute type of brush. Another problem with conventional free radical polymerization is the random molecular weight distribution inherited from radical termination mechanisms resulting in a wide range of molecular weight that is not advantageous for high-tech applications.

Too active substrates: Most metals are chemically unstable and corrodible even exposed to atmosphere. Very thick and porous oxide layer immediately forms as the top layer of reactive metal surface, trapping hydrocarbon, water droplet, oxygen, grease and other contaminants in the atmosphere. They are difficult to clean. Corrodible, rough and

dirty metal surfaces are not in favor for immobilization of anchor group and polymer grafting.

Selection of anchor group and catalyst: Initiator, with bromine-terminated end group, is designed to be densely immobilized onto metal surface. Most commonly used candidate is bromide-terminated halogenosilane, forming SAM on various surfaces such as silicon and glass.[27] There are two obvious shortcomings for halogenosilane in this work. Firstly, halogenosilane molecules immediately crosslink and release hydrochloric acids at the presence of tiny amount of water. Crosslinked alkyltrichlorosilanes form bumps on metal surface that influence the uniformity of initiator layer on surface.[28] Secondly, hydrochloric acid is extremely corrosive for metal. It is difficult for metals to re-build passivation film on surface. In the worst case, it causes pitting corrosion inside and outside of metals.

Another candidate is bromine-terminated alkyloxysilane. Muhammad Ejaz et. al. reported on the immobilization of trimethoxysilane (2-(4-chlorosulfonylphenyl) ethyl trimethoxysilane, CTS) monolayer on silicon wafer using the Langmuir-Blodgett (LB) technique (in water bath).[29, 30] Alkyltrimethoxysilanes are mild towards most metals. The crosslinking of alkyloxysilane in the presence of water is far less severe than halogenosilane. However, the strategy carried out in water for a long period is not applicable for metal substrates causing thick oxide layer and pitting corrosion on surface. Third concerns is the catalyst complex. Claes et al. reported styrene grafting from steel-electrografted-polyCPEA (2-chloro-propionate ethyl acrylate) surfaces via s-ATRP.[81] The authors observed copper catalyst deactivation caused by reactive steel substrates.

The non-sensitive catalysts such as Grubbs catalyst ($RuCl_2(=CHPh)(PCy_3)_2$) and Nickel catalyst NiBr₂(PPh₃)₂ were tried, but high polydispersities, e.g., 1.55-3.3 for Grubbs catalyst and 2.75 for NiBr₂(PPh₃)₂ of polystyrene, were obtained, indicating the lack of control throughout polymerization. The catalyst candidate should be inert to surface and controllable for polymerization.

Surface roughness: Metal surface is very rough. Therefore it is difficult to character the nanometer thickness of polymer films by ellipsometer. To my knowledge, there is no kinetic study of steel s-ATRP up to now. Therefore there is neither evidence nor proof to support the control of s-ATRP on steel. Surface roughness also complicates the amount of initiator per area attached to surface and consequently the reproducibility at a nanoscale is difficult to achieve. Metals within nanometer surface roughness are not commercially available.

In our experiment design, we expect to overcome the aforementioned problems to achieve ultra-clean metal surfaces with several nanometer's roughness, high initiator density using a non-corrosive initiator, controlled polymerization with suitable catalyst.

1.3 Controlled/living radical polymerization

The first solution to the aforementioned problems encountered with convention free radical polymerization is the use of controlled/living (radical) polymerization techniques. Living polymerization is designed for growth of polymer chains without or with limited chain termination and chain transfer. Therefore the polymer chains are propagated in a controlled manner with narrow polydispersity index (PDI) of the final

product. Due to no or limited radical termination during polymerization, the end group of each individual chain is still living, while polymerization ceases. Adding another monomer, polymerization continues and consequently a uniform block copolymer is obtained. The control of polymerization with specific structure, designed molecular weight, and low polydispersity index (PDI) has attracted much attention recently years. See Figure 1.2.[31]

Living polymerization was firstly described by Szwarc in anionic polymerization of styrene with alkali metal/naphthalene system in THF.[32] Nowadays, the main living polymerization techniques include living anionic, cationic polymerization, group transfer polymerization, living Ziegler-Natta polymerization and living radical polymerization. Living radical polymerization becomes a hot area very recently, including nitroxidemediated polymerization (NMP),[44] atom transfer radical polymerization (ATRP),[34] and reversible addition fragmentation chain transfer polymerization (RAFT).[50]

Living anionic and cationic polymerization are able to produce nearly monodispersed polymers (i.e. at very low temperatures). The main limitations of living anionic/cationic polymerization are the strict polymerization condition, sensitivity to moisture and impurities, and confined monomer types.[33] Living radical polymerizations such as ATRP, NMP and RAFT are more attractive to industries because of mild reactive condition, tolerance to impurity, and versatile monomers. Among them, ATRP has arguably the highest possibility to be industrialized. ATRP can be run under both homogenous and heterogenous conditions. Reaction temperatures range from room temperature to over 100 °C. ATRP can be conducted in versatile solvents, such as

organic solvents, water, supercritical carbon dioxide, and ionic liquids or in bulk. The process could be emulsion, microemulsion and miniemulsion polymerization, etc.[31]



Figure 1.2 Examples of the architectures produced by controlled/living polymerization [31]

1.3.1 Nitroxide-Mediated Polymerization (NMP)

Nitroxide-mediated polymerization started in 1993 in the synthesis of narrow dispersed polystyrene.[44 a] The research of the stable mediated radical for LRP emerged over ten years ago. [44 b,c]Since then, the NMP techniques has developed to synthesize a variety of monomers, for example, MMA, 1,3-butadiene, 4-sodium styrenesulfonate, 2-methyl-1,3-butadiene, etc.[45]

The mechanism of NMP is shown in Scheme 1.1. The mechanism involves reversible thermal cleavage of alkoxyamine 1 and nitroxide capped chain into a carboncentered radical 2, which undergoes propagation in the presence of monomer and a very stable mediating radical 3 (no reaction with monomer). The equilibrium is greatly in favor of the formation of the dormant alkoxyamine and thus results in a low concentration of the propagating radicals 2. As a result, side reaction and irreversible termination 5, both combination and disproportionation, are under control during polymerization, giving rise to controlled molecular weight and narrow polydispersity. The chain transfer agent alkoxyamine always appears as an end group in the polymer chain.[45] The most commonly used nitroxides are 2,2,6,6-tetramethylpiperidinoxy (TEMPO) and its derivatives, phosphonate derivatives, and arenes. The structures are shown in Figure 1.3.[45]



Scheme 1.1 Equilibrium equation of NMP

The nitroxide-mediated polymerization can be carried out in solution, bulk and emulsion polymerization. New materials with designed architecture, for example, telechelic polymers, block copolymer, and random copolymer can be synthesized by NMP with controlled molecular weight.[46,47] Moreover, polymer architectures of star, graft, hyperbranched and dendritic structures can be obtained by NMP.[48]

Several difficulties are encountered in the prevalence of NMP. Firstly, most chain transfer agents of NMP, alkoxyamines, are not commercially available. It is luxurious to synthesize and purify them. Secondly, the temperature of polymerization is confined over 100 °C for the thermal cleavage of alkoxyamines. Thus the boiling point of solvent should be very high. Thirdly, the selection of monomer is confined to quite a few monomers such as styrene, MMA, 1-3 butadiene, 4-sodium styrenesulfate, 2-methyl-1,3-butadiene.



Figure 1.3 Molecular structures of mediated radicals in nitroxide-mediated polymerization.[45]

1.3.2 Reversible Addition-Fragmentation Chain Transfer Polymerization

Scientific literature of reversible addition-fragmentation chain transfer polymerization (RAFT) emerged in 1998.[49] The mechanism of RAFT is illustrated in Scheme 1.2. RAFT polymerization proceeds via a degenerative chain transfer mechanism in which an equilibrium is superimposed. Propagating chain P* is generated by an azo compound initiator. Chain transfer agent 2 (dithiolester) reacts with either primary radical or a propagating chain P* to form a new CTA 4 and to eliminate the radical. The equilibrium reaches a steady state with slow initiation and fast termination, resulting in a retardant polymerization, which suggests the existence of preequilibrium.[50,52] See Figure 1.4. The exchange between radical and dormant chains is much fast than propagation. The process is similar to termination except the terminated chain acts as a new transfer agent. Electron spin resonance (ESR) verifies the existence of radical 3 and P^* .[51] The parameter k_{ad} is the addition rate coefficient and $k_{\rm B}$ is the fragmentation rate coefficient. Theoretically, the existence of main equilibrium enables the controlled polymerization and narrow PDI. It is believed that a preequilibrium exists while in pre-equilibrium k_{ad} and k_B are asymmetric until the main equilibrium is reached.[52]



Scheme 1.2 Scheme of pre-equilibrium and main equilibrium of RAFT (2-Chain transfer agent).[50,53]



Figure 1.4 First order kinetic plot of MMA in bulk polymerization using CDB as RAFT agent at various concentrations.[58]

The first order kinetic plot of MMA polymerization in Figure 1.4 revealed an obvious retardance at the beginning of polymerization, indicating the existence of preequilibrium.[58] A successful RAFT polymerization relies much on RAFT agent (CTA). Generally, RAFT polymerization applies to a wide range of monomers. Scheme 1.2 shows a typical structure of RAFT agent (dithiolester). CTA breaks into four categories according to their Z group, which are dithioesters, xanthates, trithiocarbonates and dithiocarbamates. Most CTA are not commercially available. Although a wider range of monomers can be polymerized by RAFT method than ATRP and NMP, there is no CTA versatile for every monomer. A specific CTA only applies for a few monomer types.[52]

The Z group of CTA is designed to stabilize the intermediate radical, to enhance the reactivity of the radical and furthermore to be in favor of the fragmentation of CTA. The candidates for Z group can be phenyl group, benzyl group, alkyl group, O or N and sulphur. Phenyl group is very stable, but the retardance of polymerization is obvious. On the contrary, benzyl group and sulphur are less stable than phenyl group but the retardant is greatly overcome. O and N lower the reactivity of CTA and offer very poor control of molecular weight, but are good for fast propagating monomers, for example, vinyl acetate. In addition, the Z group can be designed to a variety of architectures and were verified for good control of styrene, acrylic acid and methacrylate.[54-57] The R group of CTA 2 (see Scheme 1.2) also contributes to the stability of the intermediate radical, nevertheless less effective than the Z group. The R group can be designed to facilitate efficient fragmentation and re-initiation in the pre-equilibrium or designed to mimic the structure of monomer in polymerization. For the first consideration, $-C(alkyl)_2CN$ OR $-C(Me)_2Ar$ is selected.[57] For the latter, less active monomers are applied. Figure 1.5 shows the polymerization of MMA using CTA with different R groups and having different retardant rates. The R group has the same structure of MMA giving the best result and PEDB (phenylethyl dithiobenzoate) yielding the most severe retardance during polymerization.[52]



Figure 1.5 Pseudo-first-order rate plot of MMA in bulk polymerization using RAFT agent bearing various R groups: [•] 1-methoxycarbonyl ethyl dithiobenzoate; [•]
cyanoisopropyl dithiobenzoate; $[\mathbf{V}]$ PEDB; $[\mathbf{A}]$ poly(methyl acrylate) dithiobenzoate (initial concentrate 7.7x10⁻³ mol/l).[52]

In general, RAFT polymerization applies to a wider range of monomer types than other living radical polymerization. Specific RAFT agent applies exclusively well to a few monomer types. Radical termination is difficult to avoid during polymerization, causing higher ratio of dead chains than other living radical polymerization.

1.3.3 Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) mechanism was discovered in 1995. Wang et al. first reported MMA/styrene polymerization using Cu(Cl or Br)/2,2'bipyridine as catalyst resulting in low polydispersities 1.1~1.5 in the final products.[34] ATRP is implemented by establishing a rapid dynamic equilibrium between propagating free radicals P* and a large amount of dormant chains P-X. See Scheme 1.3. The initiation of ATRP is fast, occurring between initiator P-X (X, may be chlorine or bromine) and transition metal catalyst complex (M_t^n /ligand), undergoing a electron redox reaction. The transition metal catalyst (may be copper, iron, or nickel) oxidizes from lower oxidation state to high valency M_t^{n+1} /ligand and produces radical P*, propagating with monomer. The deactivation of ATRP occurs between propagating P* with M_t^{n+1} /ligand to form the M_t^n /ligand and dormant chain, P-X. The equilibrium is greatly in favor of deactivation (k_{deact} >> k_{act}) resulting in a high concentration of dormant chains and a low concentration of propagating radical. Termination is greatly limited. Each radical has equal chance to activate and deactivate, growing at a similar rate. When the monomer is consumed, polymer chains grow with designed molecular weights and low polydispersities.[31]



Kact<<Kdeact

Scheme 1.3 Equilibrium equation of ATRP

The control of ATRP relies on appropriate kinetic rates and equilibrium constant. $(K_{eq} = k_{act}/k_{deact)}$ The equilibrium between activation and deactivation determines the concentration of propagating radicals and dormant chains.[33] Usually K_{eq} is very small in order to keep low concentration of free radical to minimize termination and chain transfer. If K_{eq} is too high, termination will be significant that results in high PDI's. If K_{eq} is too low, polymerization will not occur or be in a very low rate.[31]

Figure 1.6 shows a typical linear relationship of $Ln(M_0/M_t)$ as a function of time suggesting negligible termination, a constant concentration of propagating radicals and an efficient initiation. $Ln(M_0/M_t)$ as a function of time levels off suggests termination

during polymerization. A upwards trend of $Ln(M_0/M_t)$ as a function of time indicates a slow initiation.[31]



time

Figure 1.6 Scheme of the dependence of conversion on time and $Ln(M_0/M_t)$ as a function of time for ATRP.[33]

Since atom transfer radical polymerization (ATRP) emerged in 1995, it attracted considerable attention due to its obvious merits over other living radical polymerization.[34-37] Figure 1.7 shows the versatility of ATRP process. It can be run under homogenous or heterogenous condition. Reaction temperature ranges from room temperature to over 100 °C, comparable to NMP. Besides, a wide range of solvents, such as organic solvents, water, supercritical carbon dioxide, and ionic liquids, apply very well in ATRP. ATRP method also works in emulsion, microemulsion and miniemulsion polymerization.[38-42] Table 1.1 compares monomer, initiator, temperature and chain transfer agent of ATRP, NMP and RAFT. Catalysts of ATRP are inexpensive and commercially available compared with alkoxyamine for NMP and CTA for RAFT.

Although RAFT polymerization applied to a wider range of monomer types than other living radical polymerization, specific RAFT agent applies well only to one or several monomer types. RAFT agent is difficult to synthesize and not environment-friendly. Furthermore, radical termination in RAFT process is difficult to avoid during polymerization, resulting in a higher amount of dead chains than other living radical polymerization. In surface modification, diffusion in RAFT can be a problem because propagating polymer chains instead of monomer molecules must move to the surface. In general, ATRP has great potentials in surface modification. Its applications include lubricants, wetting agents, coatings, colloid stabilizers, adhesives, paints, plasticizer, grafting polymers, surfactants, compatilizers, thermoplastic elastomers.[43]



Figure 1.7 Versatility for ATRP processes [33]

Table 1.1 Comparison of controlled radical polymerization/living radical polymerization

	NMP	RAFT	ATRP
Monomer	Limited (Styrene)	Broad monomer type	Medium

Initiator	Thermal cleavage	Azo compounds	R-X (Halogen)
СТА	Alkoxyamines	Dithioesters	CuX/ligand
Temperature	Over 100°C	Wide range	Wide range

1.3.4 Surface-initiated Atom Transfer Radical Polymerization (s-ATRP)

Polymer grafting technology can date back to 1950's for the stabilization of colloids. Nowadays polymer chains grafted from surface can be classified as homopolymer brush, block copolymer brush, random copolymer, mixed homopolymer brush, ionic homopolymer brush. zwitterionic homopolymer brush, crystalline polymer and semiflexible homopolymer brush.[64]

Polymer grafting via living polymerization attracts much interest today. The grafting mechanisms include cationic polymerization,[58] anionic polymerization,[59] nitroxide-mediated polymerization,[60] reversible addition fragmentation chain transfer polymerization,[61] and atom transfer radical polymerization.[30,62] They are used in a variety of applications, for example, colloid stabilizers, nonfouling coatings, and responsive materials.[63,71]

Surface modification via atom transfer radical polymerization on different substrates, regardless of their nature (silicon, metal and metal oxide, carbon, PDMS and latex) or their shape (plate, nanoparticle, tube, fiber and film) has been reported to grow dense and well-defined polymer chains from surfaces or interfaces with tailored properties.[65-70] Figure 1.8 illustrates the examples of surface-initiated ATRP (s-

ATRP) process.[33] The living nature of ATRP enables grafting of block copolymer from surfaces and thus introducing multifunctionalities for further applications.



Figure 1.8 Schemes of polymer or copolymer grafted from sphere, flat and oligomer surfaces using s-ATRP.[33]

Ejaz et al. first proposed s-ATRP using flat silicon substrates. A commercially available 2-(4-chlorosulfonylphenyl) ethyl trimethoxysilane (CTS) was deposited as a monolayer on silicon wafer using Langmuir-Blodgett (LB) technique, followed by in-situ atom transfer radical polymerization (ATRP) of methyl methacrylate from the surface. The characterization of surface morphology using AFM confirmed the uniformity of polymer chains on the surface. A grafting density of 0.35 chain/nm² was obtained. TsCl (p-toluenesulfonyl chloride) as a free initiator was explored and verified. The good control of polymerization was achieved.[30,31]

The establishment of equilibrium on surface is similar to that in solution ATRP. However, the number of chains on surface is small and inadequate in maintaining the equilibrium of ATRP. This causes either deviation of living polymerization or slow polymerization. Moreover the characterization of polymer chains becomes a problem.[30,31] In most cases, a sacrifice initiator is added to the system to generate Cu(II) for maintaining the equilibrium of ATRP.[65] In a few cases, the polymerization reactions are carried out with an added amount of deactivator, for example, Cu(II).[66,92,103-105]. Fisher et al. first proposed "adding free initiator" strategy.[65] Both demerits are overcome using "adding free initiator" method. The initiator concentration is then adequately high to produce enough Cu(II) to maintain the ATRP equilibrium. The polymer chains produced in solution are assumed to be similar to those of the surfaces. This assumption was verified in some systems by cleaving and characterizing the graft polymer chains from silicon particles.[72] The method of "adding free initiator" was soon adopted by many researchers. It can speed up the polymerization. Whereas the technique is applicable and gives good control in surfaceinitiated ATRP, complicated clean procedures are necessary to remove residual polymer chains absorbed on surface. Sometimes, researchers need to use soxhlet extractor to wash the surface for several hours.

Matjyaszewski proposed an "adding deactivator" strategy, that is, an excess amount of Cu(II) is introduced to maintain the effective equilibrium, no polymer chains are generated in solution and cleaning steps are simplified.[66] Using the method, thicker polymer films are expected. Huang et al. reported on grafting 1 μ m poly(2hydroxyethyl methacrylate) on an Au-covered silicon wafer surface. [73] Using the "adding deactivator" method, the equilibrium is well maintained, giving rise to a fast

reaction rate. Jeyaprakash et al. observed the first order kinetics in the plot of thickness as a function of time, indicating the living nature with a constant grafting density.[74] A high ratio of monomer over anchor group on surface leads to relatively thicker polymer layer on the surface. However the method has another problem. It is difficult to estimate grafting density because of uncertainty of polymer molecular weight.

Interestingly, the kinetic plots of all the polymerization processes i.e., "adding free initiator", "adding deactivator", without initiator, and without deactivator, are very different from each other. The strategy that raised most questions is "adding free initiator". Some researchers believed that the radical termination occurred and slowed down the polymerization.[77] Prucker and Ruhe investigated the kinetics of conventional free radical polymerization from azo compound functionalized surface. They concluded that the termination on the surface and in the solution were different.[78] The situation is quite different in the s-ATRP system, lowering the surface radical concentration as well as that in solution limits radical termination. Other researchers believed that in a controlled system the decrease of reaction rate should be ascribed to the depletion of monomers, not termination. The system should be still living. [79,80] Yoshinobu et al. summarized the work of his group in grafting PMMA from silicon wafers and particles using two types of initiators (n=6, R'=CH3), two types of catalyst halides (CuBr/CuCl) and two types of ligands ((4,4'-diheptyl-2,2'-dipyridyl) (dHbipy)/(4,4'-dinonyl-2,2'dipyridyl) (dNbipy)). In all the cases, the grafting density remained constant throughout polymerization, suggesting the nature of liveness during the s-ATRP, as shown in Figure 1.9.[19] Grafting densities from 0.1 to 0.7 chains/nm² and thicknesses from 15-80nm for

PMMA prepared by s-ATRP from various surfaces – silicon wafer, gold plates and silicon particles, were reported having the similar results.[28,30,31,70,]

Feng et al. reported the grafting of poly(2-methacryloxyethyl phosphorylcholine) (PMPC) at DP = 50 and 200 from silicon wafer surfaces using "adding free initiator" in the s-ATRP. Figure 1.10 gives the kinetic plots of the thickness of PMPC as a function of time and the thickness as a function of conversion.[79] Although the increase of thickness is not linear with time, the first order kinetic curve of thickness Vs conversion reveals a constant radical concentration during polymerization. The thickness of DP=200 is around 3 times larger than that of DP=50. All these evidences verify the constant radical concentration during polymerization.[80]



Figure 1.9 Relationship between the amount of graft polymers and Mn of free polymers. The graft polymerization was carried out under various conditions, on silicon wafer/silicon particles; two types of initiators (n=6, R"=CH3); two types of copper

halides, CuBr/CuCl and two types of ligands, (4,4'-diheptyl-2,2'-dipyridyl) (dHbipy)/(4,4'-dinonyl-2,2'-dipyridyl) (dNbipy) [18]



Figure 1.10 Thickness of poly(MPC) layer versus [A] reaction time [B] monomer conversion. [OEGBr]/[CuBr]/[bpy]=1:1:2; [MPC]/[OEGBr]=50 and 200.[79]

Feng et al. reported the grafting of poly(2-methacryloxyethyl phosphorylcholine) (PMPC) from silicon wafer surface using "adding excess deactivator" and "without initiator and deactivator" via the s-ATRP.[79] Figure 1.11 gives the kinetic curves of "adding deactivator" and "without initiator and deactivator" strategies. Curve [a] was drawn for the system "without free initiator and deactivator". As assumed, poly(MPC) grew thicker layer using this strategy because of higher molar ratio of monomer over surface initiator. However, the concentration of surface initiator is too low to maintain the ATRP equilibrium. The kinetic plot leveled off with time.[30] Curve [b,c,d] was drawn for the system with different amounts of deactivator (Cu I/Cu II=10/1, 5/1 and 2/1, molar ratio). Curve [b] gave almost a linear relationship of thickness as function of time, indicating livingness of polymerization. In these cases, no polymer is produced in

solution and the concentration of monomer remains constant, especially in a bulk polymerization. The strategy gives thicker polymer layer. Curve [c,d] gave a linear relationship of thickness as function of time. However, the polymerization rate is too low. The deactivation dominates the polymerization and greatly decreases the concentration of propagating radical and consequently reaction rate.

In general, all the evidences support the concept of constant surface radical concentration in the surface-initiated ATRP in most cases. The control of surface-initiated living radical polymerization is practical. Using different strategies, "adding free initiator", "adding deactivator" and "without initiator", the kinetics of the various polymerization systems differ one from the other.



Figure 1.11 Kinetic plot of thickness of PMPC Vs time using "adding deactivator" method with changed Cu I over Cu II molar ratio [a] Cu I/ Cu II=1:0 [b] Cu I/ Cu II=1:0.1 [c] Cu I/ Cu II=1:0.2 [d] Cu I/ Cu II=1:0.5.[79]

1.3.5 Surface-initiated ATRP on metals

The s-ATRP on the noble metal Au or Au-covered silicon wafer/glass surfaces was achieved from halide-terminated thiol or disulfide anchor group, followed by in-situ ATRP from the substrates.[75,76] The thermal stability of halide-terminated thiol is limited to below 60°C. In this case, the monomers are limited to those polymerizable at low temperatures.

Surface modification via ATRP on active metals, CRS, hot-dip galvanized steel, electrogalvanized steel, zinc, nickel and aluminum alloy, was not extensively investigated. Claes et. al. reported styrene grafting from polyCPEA (2-chloro-propionate ethyl acrylate) electrografted steel surfaces via s-ATRP.[81] The authors observed copper catalyst deactivation caused by reactive steel substrates. Non-sensitive catalyst, Grubbs catalyst (RuCl₂(=CHPh)(PCy₃)₂) and Nickel catalyst NiBr₂(PPh₃)₂ were used, but high polydispersities, 1.55 - 3.3 for Grubbs catalyst and 2.75 for NiBr₂(PPh₃)₂ of polystyrene, were obtained. Figure 1.12 [A] shows the schemes of electrografting of polyCPEA (2-chloro-propionate ethyl acrylate) and in-situ polymerization of polystyrene via s-ATRP. Figure 1.12 [B] gives the scanning electron microscopic image of the topology of steel-g-PS surface with a scale bar of 20 microns. The surface is very rough because of the rough substrate and poor control of ATRP. Thus it is difficult to characterize the thickness of polymer layer. Figure 1.12 [C] presents X-ray photoelectron spectroscopy that gives the composition of surface elements. There is no iron peak indicating the good coverage of PcPEA. Later on, the group tried other surface

modification combining living polymerization (nitroxide-mediated polymerization and ring open polymerization) with electrografting techniques on conductive surfaces, steel and stainless steel.[82,83, 84] The difficulty of obtaining thick polymer layer, lack of evidence of living polymerization, and strict reaction condition of electrografting limit further exploration on active metals.



Fe	0	С	Cl	Si
	25.8	65.8	5.9	2.5
0.5	25.1	65.8	3.8	4.9
< 0.1	25.6	67.3	2.0	5.0
0.7	28.9	64.9	5.5	
< 0.1	28.4	68.1	3.5	
	Fe 0.5 < 0.1 0.7 < 0.1	Fe O 25.8 0.5 25.1 < 0.1	Fe O C 25.8 65.8 0.5 25.1 65.8 < 0.1	Fe O C C1 25.8 65.8 5.9 0.5 25.1 65.8 3.8 < 0.1

С

Figure 1.12 [A] Schemes of electrografting of polyCPEA (2-chloro-propionate ethyl acrylate) and in-situ polymerization of polystyrene via SI-ATRP; [B] SEM image of Steel-g-PS; [C] XPS data of SS-Initiator surface [81]

Fan et al. reported on the immobilization of a catecholic initiator on TiO₂ and 316L stainless steel, followed by PolyOEGMA (poly(oligomer)ethylglycol methacrylate) grafted from the surface using s-ATRP.[85] See Figure 1.13 [A]. In this paper, the authors utilized polished TiO₂ substrates to measure the thickness of grafted polymer by ellipsometer. Figure 1.13 [B] gives the kinetic plot of thickness of TiO₂-g-POEGMA Vs time. The fast formation of thick polymer layer at the first 5 min reveals the poor control of ATRP system, indicating the high rate of surface radical termination at the first stage of polymerization. No further experiment results in terms of conversion, molecular weight and polydispersity were reported. In the paper, the author also tried the s-ATRP on stainless steel. They observed the similar results as TiO₂, but no detailed data was revealed. The major advantage with stainless steel is the inhibition of electron transfer reactions at the surface and hence catalyst deactivation should be less of an issue. Stainless steel, however, consists of chromium/iron mixed oxides, and therefore reacts somewhat differently than carbon steel. TiO_2 is inert itself and thus the result is also not transferable to active metal substrate.



Figure 1.13 [A] Schemes of immobilization of initiator and polymerization of POEGMA [B] Kinetic plot of thickness as function of time [85]

Surface-modification via ATRP has great potentials in application of metal materials. The development of high value-added materials is getting smaller and smaller in dimension, in the order of nano or atomic scale. However, processing such materials confronts the challenges of precision, reproducibility and stability. Using the s-ATRP

method we expect to obtain uniform surfaces with a nano-scale precision whereas other techniques cannot offer. Secondly, we can synthesize well-defined block copolymer, facile to introducing multifunction to the surfaces. Thirdly, we can obtain high grafting density and thus the functional groups of polymer chains stand outwards instead of being entangled in a good solvent, greatly increasing the surface performance. Fourth, the less entangled nature of surface will greatly decreases the friction of metal surfaces and viscosity of the solution of metal particles.[71,87]

1.4 Objective and outline of this thesis

The objectives of this thesis are to investigate fundamentals of the s-ATRP of acrylics from reactive metals. The metal substrate cold rolled steel (CRS) was kindly provided by Dofasco and studied in the thesis. The other active metals, nickel, stainless steel, and aluminum, are also explored for understanding of s-ATRP. First of all, a noncorrosive initiator is synthesized and immobilized to the metal surfaces using an efficient and environment-friendly method. Secondly, the s-ATRP of acrylics from the initiator functionalized metal substrates is carried out. High grafting density is expected to assure superior performance, for example, corrosion resistance performance and other designed functionality, hydrophilicity, hydrophobicity, adhesion, anti-protein absorption, etc. Thirdly, the characterization of metal-g-polymer and polymer in solution was carried out to investigate the polymerization kinetics (ellipsometry/NMR), surface chemistry (goniometry), surface morphology (AFM), surface atomic composition (XPS), electrochemical measurement, and molecular weight (SEC). Fourth, a detailed discussion on the experiment results emphasizes the surface chemistry, surface atomic composition, surface morphology, kinetic study, molecular weight and polydispersity, and electrochemical experiment.

Chapter 1 reports on a paper review for polymer coating on metals, for the comparison of "grafting to" with "grafting from", as well as the living radical polymerization, surface grafting via in-situ polymerization, and s-ATRP from various substrates.

In Chapter 2, the synthesis and immobilization of initiator was discussed, including the pretreatment of metal surfaces. A mild initiator, 3-(2-bromo-2-methyl) amino propyl triethoxysilane was designed and synthesized to introduce anchor group to the metal surfaces, targeting for a high initiator density. The substrates were thoroughly cleaned and precisely polished, facile for initiator immobilization and ellipsometric measurement. An efficient and environmental-friendly method for the immobilization of initiator was explored and verified to be effective. The method was confirmed transferable for the other active metals, Ni, SS and Al, and their alloys by partially optimizing the condition.

In Chapter 2, the surface grafting of acrylics from metals was discussed. A variety of acrylics that includes MMA, DMAEMA, OEGMA and TFEMA, were grafted from cold rolled steel (CRS), stainless steel, nickel and aluminum via the s-ATRP. MMA is a typical monomer for fundamental study. It has been intensively studied using the s-ATRP. DMAEMA/OEGMA and their polymers are biocompatible and water-soluble, having extensive applications in biomaterials, paper-making, waster water

treatment and paint manufacturing industries. TFEMA is a fluorinated monomer. Its polymer is one of the excellent candidates for biomaterials because of its high thermal, chemical stability, high surface hydrophobicity. Iron catalyst and copper catalyst complexes were utilized and compared. Catalyst deactivation was observed in some cases and was not favored for the control of the s-ATRP. The kinetic study of CRS-g-PMMA was investigated using both "adding free initiator" and "adding deactivator" methods and all the results support the good control of s-ATRP from the active metal surfaces. The grafting and initiator functionalization of the metal substrates were studied according to their surface chemistry (goniometry), surface morphology (AFM), surface atomic composition (XPS). The first order kinetic study was carried out using ellipsometry and ¹H NMR. The molecular weight of polymer was determined by size exclusion chromatography. The corrosion performance is determined by electrochemical experiment.

Chapter 3 discusses the experimental result from the characterization of grafting surface, initiator functionalize surface and polymer solution. In general, we expect high initiator density, consequently high grafting density and controlled molecular weight from the various metals. Consequently, the perspectives of high corrosion resistance performance and other functionality are offered. The recommendation for the future work is three aspects, i.e., introducing acrylics with specific functionality, s-ATRP of metal nanoparticles, and building block copolymer on metals.

Chapter 2

Experiment

2.1 Metal Surface Preparation

Cold rolled steel (CRS): Cold rolled steel plates were supplied by Dofasco. The specification of CRS is listed as followed: C, Mn, P, S, Si, Cu, Ni, Cr, Sn, Al, N, Mo, V, Nb, Ti, Ca, B (0.55, 0.27, 0, 0, 0, 0, 0, 0, 0.035, 0, 0, 0, 0, 0, 0, 0). Nickel: Aldrich, foil; thickness of 0.5 mm; 99.98% purity, resistivity: 6.97 M Ω -cm, 20 °C; BP: 2732 °C (lit); MP: 1453 °C (lit). Stainless steel 316L: Fe/Cr-18/Ni-10/Mo-3, Goodfellow, foil 0.5 mm, temper: annealed. Aluminum: Aldrich, foil 0.5mm; 99.999% purity, resistivity: 2.6548 $\mu\Omega$ -cm, 20 °C; Autoignition temp: 1400 °F; BP: 2460 °C (lit); MP: 660.39 °C (lit); density: 2.7 g/ml.

Cold rolled steel: CRS plates were cutted into 5x5 mm in size and flatten under high pressure. The plates were fixed to stainless steel holders by glue. One side of these plates was polished by silicon carbide paper using Struers RotoPol-31/RotoForce-4/Multidoser automatic machine. The meshes of the silicon carbide papers are 800, 1200 and 4000, respectively. The machine is programed at 180 N force, 300 rmp, 1.5 min for each step. The polished plates were cleaned by soap and ethanol, dried by compressed air. The next fine polishing was carried out using 1 µm diamond-paste under 120N/120rmp for 3.75 min on a special template. The polished plates were carefully cleaned using soap and enthanol, dried thoroughly via compressed air. The finally fine polishing was carried out under 120N/120RMP for 3.75 min using 50 nm alumina paste. The plates were then carefully cleaned using soap and enthanol, dried thoroughly via compressed air. The polished surfaces had a mirror-like, highly reflective appearance. They were immediately stored immersed in distilled acetone in a container with drier. The stainless steel substrates were treated using the same procedures.

The nickel plates were cutted into 5x5 mm in size and flatten under high pressure. The plates were fixed to stainless steel holders by glue. One side of the plates was polished by silicon carbide paper using Struers RotoPol-31/RotoForce-4/Multidoser automatic machine. The meshes of silicon carbide papers are 320, 500 and 1200, respectively. The machine is programed at 180 N force, 300 rmp, 1.5 min for each step. The polished plates were cleaned by soap and ethanol, dried by compressed air. The next polishing step was carried out using 9 μ m, 3 μ m and 1 μ m diamond-paste under 120 N/120 rmp for 3.75 min on special templates. The polished plates were carefully cleaned using soap and enthanol, dried thoroughly via compressed air. The finally fine polishing was carried out under 120N/120RMP for 3.75 min using 50nm silicon gel. The plates were then carefully cleaned using soap and enthanol, dried thoroughly via compressed air. The precisely polished surfaces had a mirror-like, highly reflective appearance. They were immediately stored in a container with distilled acetone and drier.

The aluminum plates were cutted into 5x5 mm in size and flatten under medium pressure. The plates were fixed to stainless steel holders by glue. One side of the plates was polished by silicon carbide paper using Struers RotoPol-31/RotoForce-4/Multidoser automatic machine. The meshes of silicon carbide papers are 1200 and 4000,

respectively. The machine is programed at 120 N force, 300 rmp, 1.5 min for each step. The polished plates were cleaned by soap and ethanol, dried by compressed air and then followed by fine polish under 120 N/ rmp for 3.75 min under special template using 1 μ m diamond-paste. The plates were then carefully cleaned using soap and enthanol, dried thoroughly via compressed air. The finally fine polishing was carried out under 120N/120RMP for 3.75 min using 50nm alumina powder. The plates were carefully cleaned using soap and enthanol, dried thoroughly via compressed air and enthanol, dried thoroughly via compressed air. The finally fine polishing was carried out under 120N/120RMP for 3.75 min using 50nm alumina powder. The plates were carefully cleaned using soap and enthanol, dried thoroughly via compressed air. The precisely polished surfaces had a medium reflective appearance. They were immediately stored in a container having distilled acetone with drier.

2.2 Initiator Immobilization

2.2.1 Synthesis of initiator

3-(α -Bromo-2-methyl) propylamide propyltriethoxysilane (1) was synthesized under argon atmosphere. See Scheme 2.1 [A]. In a typical run, α -bromoisobutyl bromide (BIB, 9.06 ml, 74 mmol with 60 ml THF) was added dropwise to a solution of THF (290 ml), 3(α -aminopropyl) triethoxysilane (16.36 ml, 70 mmol) and TEA (10.22 ml, 74 mmol) with a magnetic bar. The mixture was kept at 0 °C for at least 3 hr and then it was stirred for overnight at room temperature. After the reaction was completed, the triethylamine hydrobromide by-product was filtered under a reduced pressure. The solvent was evaporated using BÜCHI Rotavapor R-200 under a reduced pressure and finally an orange-like oil was obtained. The oil was purified by passing through a column of silica gel (300 mesh) with hexane/ethyl acetate (6/4, volume ratio) as an eluent to yield 3-(α -bromo-2-methyl) propylamide propyltriethoxysilane. The pure initiator was degassed by argon and kept in container with drier in fridge. ¹H NMR (CDCl₃): δ =0.58-0.67 (2H, -CH₂-), 1.17-1,27 (9H, -CH₃, -CH₃, -CH₃), 1.60-1.68 (2H, -CH₂-), 1.93-2.02 (6H, -CH₃, -CH₃), 3.2-3.3 (2H, -CH₂-), 3.75-3.86 (6H, -CH₂-, -CH₂-), 7.25 (1H, -NH-).

(α-Bromo-N-butyl) propionamide triethoxysilane (**2**) was synthesized under argon atmosphere using the same procedure aforementioned. See Scheme 2.1 [B]. The recipe is that α-bromoisopropyl bromide (11.746 ml, 111 mmol with 125 ml THF) was added drop wise to a solution of THF (400 ml), 3(α-aminopropyl) triethoxysilane (24.54ml, 105.2mmol) and TEA (15.33ml, 111mmol). The pure initiator synthesized was degassed by argon and kept in container with drier in fridge. ¹H NMR (CDCl₃): δ =0.55-0.67 (2H, -CH₂-), 1.17-1,27 (9H, -CH₃, -CH₃, -CH₃), 1.60-1.68 (2H, -CH₂-), 1.93-2.02 (6H, -CH₃, -CH₃), 3.7-3.9 (2H, -CH₂-), 4.2-4.3 (6H, -CH₂-, -CH₂-, -CH₂-), 6.5-6.6(1H, -NH-)



Scheme 2.1 Synthetic scheme of the formation of initiator [A] $3-(\alpha$ -bromo-2-methyl) propylamide propyltriethoxysilane (1); [B] (α -bromo-N-butyl) propionamide triethoxysilane (2)

2.2.2 Immobilization of initiator on metals

The immobilization of initiator was carried out in an aqueous solution. A simple and workplace-friendly strategy was utilized to immobilize triethoxysilane onto the metal substrates. The condensation reaction of silanol groups on the metals was very fast and complete in 2 min. It was believed to form hydrogen bonding between Metal-OH and Si-OH initially. Covalent bonds form after curing. [10, 12, 88] CRS, SS, Ni and Al were all treated with Initiator **1**, and SS was also treated with Initiator **2**.

Prior to the initiator immobilization, the polished metal plates (CRS, SS, Ni and Al) were carefully cleaned under ultrasonic bath in n-heptane, acetone (distilled class), ethanol (anhydrous) and methanol (HPLC), respectively, until a water-break-free surface was obtained.

 $3-(\alpha$ -Bromo-2-methyl) propylamide propyltriethoxysilane (1) of 1 vol % was dissolved in 10 vol % methanol (HPLC) with stirring for 2 min, followed by 89 vol % deionised water addition. The solution turned out to be cloudy. The hydrolysis of 1 was carried out in a thermostated oil bath at 40°C, 1 hr until the cloudy solution became transparent. The immobilization of hydrolyzed initiator was achieved by immersing metal substrates in silane solution for 80 seconds at ambient temperature (adsorption was simultaneous). The water contact angle was tested right after the reaction. The surface

was still wettable. The substrates were rinsed by plenty of fresh methanol and followed 75°C curing treatment for 10 min in a vacuum oven.

After curing, metal plates, CRS, Nickel, SS and Al, were carefully cleaned under ultrasonic bath in methanol (HPLC) for three repeats. Each run took 10 min. The water contact angle was measured and the surface became more hydrophobic, suggesting the immobilization of initiator **1**.

(α -Bromo-N-butyl) propionamide triethoxysilane **2** of 1 vol % was dissolved in 10 vol % methanol (HPLC) with stirring for 2 min, followed by 89 vol % deionised water addition. The solution turned out to be cloudy. The hydrolysis of **2** was carried out in a thermostated oil bath at 40°C, 1hr until the cloudy solution became transparent. The immobilization of hydrolyzed initiator was achieved by immersing SS substrates in silane solution for 80 seconds at ambient temperature (adsorption was simultaneous). The water contact angle was measured right after the reaction. The surface was still wettable. The substrates were rinsed by plenty of fresh methanol and followed 75°C curing treatment for 10 min in a vacuum oven.

The SS plates were carefully cleaned under ultrasonic bath in methanol (HPLC) for three runs. Each run took 10 min. The water contact angle was tested and the surface became hydrophobic, 44/22 ($\theta_{adv}/\theta_{rec}$), suggesting the immobilization of initiator **2**.

2.3 Polymer Grafting

2.3.1 SI-ATRP of MMA by "adding free initiator" method from CRS, Ni, Al and SS 316L

Materials: Methyl methacrylate: Methyl methacrylate (MMA, 99%, Aldrich) See scheme 3.1 [A]. Mw: 100.12 g/mol, vapor density: 3.5 (Vs air), vapor pressure: 29 mmHg (20 °C), autoignition temp: 815 °F, refractive index: n20/D 1.414 (lit), Bp: 100 °C, mp: -48 °C (lit), fp: 50 °F, density: 0.936g/ml at 25 °C (lit). Methyl methacrylate (MMA, 99%, Aldrich) was dried over calcium hydride for overnight with continuous agitation and distilled under vacuum to remove inhibitor (monomethyl ether hydroquinone). The first portion of 10% was redistilled and the final 5% were discarded. The distilled MMA was kept under -18°C.



Scheme 2.2 Molecular structure of MMA [A] and 2-dimethylamino ethylmethacrylate (DMAEMA) [B]

2-Dimethylamino ethylmethacrylate: (DMAEMA, 98%, Aldrich). See scheme 3.1 [B]. Mw: 157.21 g/mol, vapor density: 5.4 (Vs air), vapor pressure: <1 mmHg (25 °C), refractive index: n20/D 1.439 (lit), Bp: 182-192 °C, fp: 159 °F, Density: 0.933g/ml at 25 °C (lit). 2-Dimethylamino ethylmethacrylate was purified by going through a column with inhibitor remover (replacement packing for removing hydroquinone and monomethyl ether hydroquinone (Aldrich)) twice and then passed through basic alumina (Aldrich) column once to remove inhibitor (monomethyl ether hydroquinone). The purified DMAEMA was kept under -18° C.

2,2,2-Trifluoroethyl methacrylate (TFEMA, 99%, Aldrich). See scheme 3.2 [A]. Mw: 168.11 g/mol. refractive index: n20/D 1.361 (lit), Bp: 59 °C 100mmHg (lit), fp: 62 °F, density: 1.181g/ml at 25 °C (lit). 2,2,2-Trifluoroethyl methacrylate was purified by going through a column with inhibitor remover (replacement packing for removing hydroquinone and monomethyl ether hydroquinone (Aldrich)) twice and then passed through basic alumina (Aldrich) column once to remove inhibitor (monomethyl ether hydroquinone). The purified TFEMA was kept under –18°C.

Oligo-ethylene glycol methyl methacrylate (Aldrich): See Scheme 2.3 [B]. average m.w.: 300 g/mol, refractive index: n20/D 1.452 (lit), Bp: 141 °C 15 mmHg (lit), fp: >230 °F, density: 1.05g/ml at 25 °C (lit), 100 ppm MEHQ and 300 ppm BHT as inhibitors. The oligomeric ethylene glycol methyl ether methacrylate was treated by going through a basic alumina column for removing hydroquinone and monomethyl ether hydroquinone twice. The purified poly(ethylene glycol) methyl ether methacrylate was kept under -18° C.



Scheme 2.3 Molecular structure of 2,2,2-trifluoroethyl methacrylate (A) and Poly(ethylene glycol) methyl ether methacrylate (B).

Iron(II) bromide 98%). (Aldrich, iron(III) bromide (Aldrich, 98%). triphenylphosphine (ReagentPlus, 99%), α-bromo-2-methylpropionyl bromide (BIB, Aldrich, 98%), α -bromopropionyl bromide (Aldrich, 97%), ethyl α -bromoisobutyrate (EBIB, Aldrich, 98%), ethyl α-bromopropionate(EBP, Aldrich, 99%) (3-aminopropyl) triethoxysilane (Aldrich, 99%), triethylamine (Aldrich, >99%) were purchased and used without further purification. Methanol (HPLC), n-heptane (Reagent), dichloromethane (Reagent), hexane (ACS, Reagent), acetone (Distilled Class) and ethyl acetate (Reagent) from Caledon, as well as anhydrous enthanol (Commercial Alcohols) were used as received.

Recipes of ATRP of Methacrylates

Bulk polymerization of MMA at 60 °C: Adding free initiator, DP300 = $MMA/FeBr_2(PPh_3)_3/EBIB = 300/1/1$ (molar ratio); DP600 = $MMA/FeBr_2(PPh_3)_3/EBIB = 600/1/1$. Adding deactivator: $MMA/FeBr_2/FeBr_3/PPh_3 = 300/1/0.1/3.3$.

Solution polymerization of DMAEMA at 40 °C in solvent THF: DP50 = DMAEMA/CuBr/HMTETA/EBIB = 50/1/1/1 (molar ratio), DMAEMA/THF = 1.07/1 (v/v).

Solution polymerization of OEGMA at room temperature in solvent methanol: DP100 = OEGMA/CuBr/bpy/EBIB = 100/1/1/1 (molar ratio), OEGMA/Methanol = 0.6/1 (v/v).

Solution polymerization of TFEMA at 90 °C in solvent trifluorotoluene): DP50 = TFEMA/CuBr/dNbpy/EBIB=50/1/1/1 (molar ratio), TFEMA/Trifluorotoluene=1/1 (v/v).

Table 2.1 Summary of the grafting experiments for various combinations of metals and polymers using iron and copper catalyst complexes

Methacrylates Substrates	MMA Fe catalyst	DMAEMA Cu catalyst	OEGMA Cu catalyst	TFEMA Cu catalyst
CRS	X	X	Х	Х
SS	X	X		
Ni	X	X		
Al	X			

Table 2.1 lists the aforementioned recipes for various metal substrates. CRS was studied using all the recipes with iron or copper catalyst complexes.

In a typical ATRP grafting polymerization with "adding free initiator" strategy, methyl methacrylate (MMA, 8 g, 0.08 mol) was added to a 10-ml pear-shaped flask and was degassed under argon for half an hour. Iron II bromide (0.0576 g, 0.267 mmol) and

triphenylphosphine (0.2338 g, 0.8 mmol) were added to a 25-ml pear-shaped flask containing a magnetic stirring bar. The flask was fitted with a septum-inlet adapter (with stopcock) and underwent a vacuum/backfilling cycle using argon three times, followed by degassed MMA monomer transferred to the flask via canula. The mixture was stirred under argon for another half an hour before 39.1 µl degassed EBIB addition to the mixture. Two minutes later the mixture was transferred to a degassed and argon-filled culture media tube containing an initiator-functionalized metal substrate (cold rolled steel, stainless steel, nickel and aluminum) via a cannula. Each tube was putted in a thermostated oil bath at 60°C (4hr for completion) and then the tubes were taken out from oil bath at designed interval. The tube was opened to atmosphere and stored in dry ice to stop polymerization, followed by dichloromethane addition to dissolve the solidified PMMA. Metal substrates (CRS, SS and Ni) were taken out from dissolved solution, rinsed with dichloromethane, cleaned under ultrasonic bath and extracted in dichloromethane for 24 hours to remove physically adsorbed PMMA from surfaces. After extraction, each piece was rinsed by dichloromethane and methanol before characterization. See Scheme 3.3.

2.3.2 SI-ATRP of MMA by "adding deactivator" method from CRS

In a typical ATRP grafting polymerization run using "adding excess deactivator" strategy, methyl methacrylate (MMA, 8 g, 0.08 mol) was added to a 10-ml pear-shaped flask and degassed under argon for half an hour. Iron II bromide 0.267mmol, iron (III) bromide 0.0267mmol and triphenylphosphine 0.8811 mmol were added to a 25-ml pear-

shaped flask containing a magnetic stirring bar. The flask was equipped with septuminlet adapter (with stopcock) and underwent vacuum/backfilling cycles using argon three times, followed by degassed MMA monomer transferred to the flask via a cannula. The mixture was stirred under argon for another half an hour before transferred to a degassed and argon-filled culture media tube containing an initiator-functionalized CRS substrate via a cannula. Each tube was immersed to a thermostated oil bath at 60°C for designed interval (80 min at most). The CRS substrates were taken out from culture tube after reaction and cleaned by the same previously mentioned procedures.

2.3.3 SI-ATRP of (2-Dimethylamino) ethyl Methacrylate (DMAEMA) by "adding free initiator" from CRS, Nickel and SS Surfaces

In a typical ATRP grafting polymerization with the "adding free initiator" strategy, (2-dimethylamino) ethyl methacrylate (DMAEMA, 10 g, 63.61 mmol) and HMTETA (0.847 g, 1.27 mmol) were added to a 10-ml pear-shaped flask and degassed under argon for at least half an hour. Copper I bromide (0.1822 g, 1.27 mmol) was added to a 25-ml pear-shaped flask containing a magnetic stirring bar. The flask was fitted with a septum-inlet adapter (with stopcock) and underwent an vacuum/backfilling cycle using argon three times, followed by degassed MMA monomer transferred to the flask via a canula and degassed THF (10ml) addition to the flask. The mixture was stirred under argon for another half an hour before 186 µl degassed EBIB addition to the mixture. Two minutes later the mixture was transferred to a degassed and argon-filled culture media tube containing an initiator-functionalized metal substrate (cold rolled steel, stainless

steel and nickel) via a cannula. Each tube was putted in a thermostated oil bath at 40 °C (6 hr for completion) and then the tubes were taken out from oil bath at designed interval. The tube was opened to atmosphere and stored in dry ice to stop polymerization. The metal substrates (CRS, SS and Ni) were taken out from solution, rinsed with THF, cleaned under ultrasonic bath and extracted in dichloromethane for 6 hours to remove physically adsorbed PDMAEMA from surfaces. After extraction, each piece was rinsed by methanol before characterization. See Scheme 3.3.

2.3.4 SI-ATRP of OEGMA and TFEMA from CRS

In a typical ATRP grafting polymerization with the "adding free initiator" strategy, (2,2,2-trifluoroethyl methacrylate (TFEMA, 1 ml, 7.03 mmol) and 1.64 ml trifluorotoluene were added to a 10-ml pear-shaped flask and degassed under argon for at least half an hour. Copper I chloride (4.35 mg) and 4,4'-Dinonyl-2,2'-dipyridyl (20.9 mg) were added to a 25-ml pear-shaped flask containing a magnetic stirring bar. The flask was fitted with a septum-inlet adapter (with stopcock) and underwent a vacuum/backfilling cycle using argon three times and then degassed TFEMA monomer was transfer to the flask via a cannula. The mixture was stirred under argon for another half an hour before 6.35μ l degassed EBIB addition to the mixture. Two minutes later the mixture was transferred to a degassed and argon-filled culture media tube containing an initiator-functionalized CRS substrate via a cannula. Each tube was opened to atmosphere and stored in dry ice to stop polymerization. The CRS substrates were taken out from solution, rinsed with trifluorotoluene, cleaned under ultrasonic bath and extracted in

dichloromethane for 6 hours to remove physically adsorbed PTFEMA from surfaces. After extraction, each piece was rinsed by methanol before characterization. See Scheme 3.3.

In a typical ATRP grafting polymerization with the "adding free initiator" strategy, (OEGMA, 4 g, 13.33 mmol) and 6.67 ml methanol were added to a 10-ml pearshaped flask and degassed under argon for at least half an hour. Copper I bromide (38.24 mg) and 2,2'-dipyridyl (83.28 mg) were added to a 25-ml pear-shaped flask containing a magnetic stirring bar. The flask was fitted with a septum-inlet adapter (with stopcock) and underwent an evacuation/backfilling cycle with argon three times and then degassed OEGMA monomer was transfer to the flask via a cannula. The mixture was stirred under argon for another half an hour before 39.1µl degassed EBIB addition to the mixture. Two minutes later the mixture was transferred to a degassed and argon-filled culture media tube containing an initiator-functionalized CRS substrate cannula. Each tube was putted in a thermostat water bath at 35 °C (12 hr for completion). The tube was opened to atmosphere and stored in dry ice to stop polymerization. The CRS substrates were taken out from solution, rinsed with methanol, cleaned under ultrasonic bath and extracted in dichloromethane for 6 hours to remove physically adsorbed POEGMA from surfaces. After extraction, each piece was rinsed by methanol before characterization. See Scheme 3.3.



Scheme 2.4 Reaction scheme for grafting of PMMA, PDMAEMA, POEGMA and PTFEMA from metal substrates

2.3.5 Characterization

Ellipsometry: The ultrathin polymer layer was measured using an Exacta 2000 ellipsometer (Waterloo Digital Electronics, Waterloo, ON, Canada) equipped with a He-Ne laser (wavelength 6328 Angstrom, ambient index: 1.00) at a 70-degree incident angle. The thickness was calculated using the instrument Exacta software. The optical parameters of CRS/SS (refractive index n=2.5-3.35, extinction coefficient k=3.43-3.86), oxide layer (refractive index n=2.1-2.35, extinction coefficient k=0.1), nickel (refractive index n=2.0-2.5, extinction coefficient k=1.5-2), oxide layer (refractive index n=1.9, extinction coefficient k=0.5), aluminum (refractive index n=1.6, extinction coefficient k=7.43) and polymer layer (refractive index n=1.49, extinction coefficient k=0) were used to model the thicknesses of the oxide and polymer layers.[94-97,88] The data were calculated and averaged from three spots on each piece.

Nuclear Magnetic Resonance: The conversion of methyl methacrylate (MMA) and (2-dimethylamino)ethyl methacrylate (DMAEMA) via the s-ATRP using the "adding free initiator" strategy was quantified by a Bruker AC-P200 NMR spectrometer (200 MHz for ¹H) in chloroform-D. The polymer solutions for ¹H NMR were sampled from reactors bearing metal substrates at designed time interval.

Goniometry: The water contact angle was measured by a Ramé-Hart Model 200 contact angle goniometer with Dropimage standard software (Mountain Lakes, NJ). The advancing and receding contact angles were measured using the sessile drop method.

X-ray Photoelectron Spectroscopy (XPS): The surface atomic compositions of the metal, metal-initiator and metal-g-PMMA surfaces were measured using a Leybold

Max 200 XPS with an aluminum anode non-monochromatic source. Survey scans (0-1000 eV) were utilized to distinguish constitutive elements. The high-resolution scans of the peaks relating to these elements determine their atomic existence for CRS-g-PMMA. The takeoff angles of 20 and 90 were utilized for each specimen measurement.

Size Exclusion Chromatography: The relative molecular weight of PMMA/PDMAEMA was measured using Size Exclusion Chromatography (SEC) with three linear columns in series. THF is used as the mobile phase. Narrow polystyrene samples with molecular weights from 550 to 400, 000 g/mol were utilized as standard to generate the calibration curve. All data were recorded and treated using windows based Millenium software package. The polymer solutions for SEC were sampled from reactors bearing metal substrates at designed time interval.

Atomic Force Microscopy (AFM): The topology of CRS, CRS-I and CRS-g-PMMA surfaces was studied by atomic force microscopy (AFM), a NanoScope IIIa Multimode atomic force microscope (Digital Instruments, Inc.). In each case, an area of $5x5 \ \mu m^2$ was scanned. A tapping mode at a scan rate of 0.5 Hz was adopted. The root mean square of the surface roughness (Rrms) was obtained from the roughness profile determined by AFM. The measurement was carried out under dry air at ambient temperature.

Polarization: The electrochemical experiment was conducted to measure the corrosion potential and the polarization resistance for CRS, CRS-I and CRS-g-PMMA in 0.1mol/l potassium sulfate electrolyte. A typical three electrodes system was adopted in the electrochemical study. The sample was the working electrode in this system. A

saturated calomel electrode (SCE) and a platinum counter electrode were used as the reference and counter electrode, separately. Every sample was immersed in 0.1 mol/l potassium sulfate in a cell for 1 h for stabilization prior to the polarization measurement. All the measurements were conducted by Gamry Instruments PC4 Potentiostat/ Galvanostat and Framework software V1.0. The potentiodynamic polarizations were conducted at a scanning rate of 0.1mv/s. The polarization potential was between 0.35V below the open circuit potential and 0.35V above the open circuit potential.
Chapter 3 Results and Discussion

3.1 Water Contact Angles of Functionalized Metal Surfaces

In this thesis, one alkoxysilane was synthesized and immobilized onto metal surfaces. Bromine-terminated halogenosilanes are normally avoided because of their corrosive nature for metals and of the difficulty in achieving a uniform layer with low roughness.[29] Alkoxysilanes are less sensitive to water than halogenosilanes giving rise to more uniform layers. [70] 3-(α -Bromo-2-methyl) propylamide propyltriethoxysilane 1 (1%, volume ratio) was dissolved in a methanol/deionized water mixture (89%/10%, volume ratio). $3-(\alpha$ -Bromo-2-methyl) propylamide propyltriethoxysilane 1 was then hydrolyzed for 1 hr at 40° C in advance, followed by a condensation reaction of silanol group on the precisely polished metal surfaces. The process was very fast and completed in 2 min. Hydrogen bonding between Metal-OH and Si-OH was believed to be the first step.[11-13,88] The ingredient works effectively on CRS, transferable to nickel, SS and After the initiator immobilization, the metal substrates were rinsed with fresh Al. methanol thoroughly, cured at 75 °C for 10 min in a vacuum circumstance. Metal-O-Si covalent bonds were formed. The metal surface was hydrophilic prior to curing and became hydrophobic after. The final water contact angles were be $66\pm3.1/46\pm2.1(\theta_{adv}/\theta_{rec})$ for CRS, agreeing with the literature data, 63 for Θ_{adv} with the same initiator via a chemical vapor deposition method on silicon wafer.[98,99]

Figure 3.1 shows the water contact angles of original and initiator-functionalized metal surfaces, indicating successful attachment of the initiator with sufficient grafting density. All the metal surfaces were very clean and had a water contact angle as low as $15/10 \ (\theta_{adv}/\theta_{rec})$. With a sufficient initiator density, the water contact angles of various metal surfaces were very close.



Figure 3.1 Goniometric data of original and functionalized CRS, SS, Ni and Al

Figure 3.2 shows the water contact angles of the CRS surfaces grafted with various acrylics (MMA, OEGMA and TFEMA), indicating the successful acrylic polymers grafting on CRS. All the specimens were extracted using dichloromethane for over twenty hours before the goniometric measurement, excluding physically absorbed polymers from the surfaces. The obvious changes of surface chemistry revealed substantial grafting of various acrylics. The result of grafting also verified surface initiation and high initiator density. In addition, the closer values of θ_{adv} and θ_{rec} indicate

an improved uniformity of the CRS-g-PMMA substrates, suggesting uniform chain length on CRS, that is, one of the merits of living polymerization. The CRS-g-POEGMA became hydrophilic with water contact angles of 44/14 ($\Theta_{adv}/\Theta_{rec}$). CRS-g-PTFEMA became hydrophobic with water contact angles of 96/63 ($\Theta_{adv}/\Theta_{rec}$), suggesting great potential and versatility for the s-ATRP in the modification of metal surfaces. All the experiment data agreed with those reported by other researchers. [28, 79, 80, 98, 99]



Figure 3.2 Goniometric data of original CRS-I and CRS-g-PMMA, POEGMA and PTFEMA

Figure 3.3 gives the water contact angles of PMMA- and PDMAEMA-grafted metal substrates (CRS, Ni and SS). Despite of varying metal types, all the data of metalg-PMMA were very similar, indicating sufficient grafting density and repeatable s-ATRP from various substrates. Compared to Figure 3.1, the $\Theta_{adv}/\Theta_{rec}$ values of CRS-, Ni- and SS-g-PMMA surfaces after grafting were closer than their initiator counterparts. The metal-g-PMMA surfaces were thus more uniform and smoother after grafting, verifying the improvement of uniformity of grafting polymer layers and the overall coverage on surface. SS had a polymer layer of only 7.8 nm with a grafting density of 0.18 chains/nm², but this grafting density appeared to be sufficient to change the surface chemistry. On the contrary, Al had only 3 or 5 nm PMMA grafted from the surface with a grafting density lower than 0.1 chains/nm². The water contact angle of Al-g-PMMA changed a little compared to Al-I. The observation agreed with other's work in literature.[59] At low grafting density, the water contact angle changed gradually with an increase in polymer film thickness. The gradual changes did not occur for those substrates with high grafting densities.

Table 3.1 summarizes the water contact angles of all the metal, metal-I and metalg-Polymer surfaces with standard deviations. As mentioned before, all the substrates were extracted for several hours in dichloromethane before the goniometric measurement. The grafted metal surfaces had obviously different water contact angles from metals with physically absorbed polymer. Before extraction, the water contact angles of CRS-PMMA substrates ranged from 78/70 to 67/63 ($\Theta_{adv}/\Theta_{rec}$). After extraction, all the substrates showed repeatable data with minor differences.



Figure 3.3 Goniometric data of PMMA and PDMAEMA grafted CRS, SS and Ni surface

	θ_{adv}	θrec
Polished CRS, SS, Al and Ni	<15	<10
CRS-Initiator	66 <u>+</u> 3.1	46 <u>+</u> 2.1
CRS-g-PMMA	66 <u>+</u> 3	59.8 <u>+</u> 5.8
SS-I	73 <u>+</u> 2	46 <u>+</u> 2
SS-g-PMMA	68 <u>+</u> 3.0	55 <u>+</u> 1
Ni-I	68 <u>+</u> 0.2	33 <u>+</u> 3
Ni-g-PMMA	68 <u>+</u> 1.8	52 <u>+</u> 4.5
SS ^a -g-PDMAEMA	55 <u>+</u> 1.2	33+1.1
Al-I/Al-g-PMMA	69	33
CRS-g-POEGMA	44 <u>+</u> 3	14 <u>+</u> 2.2
CRS-g-PTFEMA	96 <u>+</u> 3.4	63 <u>+</u> 2.2

Table 3.1 Goniometric data of various functionalized metal substrates

a: DMAEMA_{DP50} = DMAEMA:CuBr:HMTETA:EBIB = 50:1:1:1 (molar ratio) monomer:THF = 1.07:1 (volume ratio)

3.2 Kinetics of ATRP grafting from metals

As far as we know, the kinetic studies of s-ATRP from active metals are lacking. Figure 3.4 shows the results of grafting PMMA from the CRS substrates. All the specimens were washed with dichloromethane for over twenty hours using soxhlet extractor before the ellipsometer measurement that cleaned physically absorbed polymer chains from the surfaces. The thickness of the PMMA films was controlled by the [Monomer]/[Initiator] molar ratio in solution (DP = 300 represents [Monomer]/[Initiator] = 300 molar ratio). The figure gives the kinetic curves of MMA grafted from CRS using "adding free initiator" and "adding deactivator" strategies. Figure 3.4(A) demonstrates the linear relationship of $\ln([M]_0/[M])$ vs. time throughout polymerization, indicating the livingness of s-ATRP. "Trommsdorf effect" that often appears in a conventional free radical polymerization did not occur in this system. After 4 hr, for DP=300, the thickness grew up to around 21.2+1.4 nm (conversion=90%) on the CRS substrates. The molecular weight measured by SEC was 24,076 g/mol (conversion 90%) with a polydispersity of 1.22. The grafting density was estimated to be 0.58 chains/nm² for PMMA brush using Equation 1.[17]

Figure 3.4(B) gives the plot of thickness vs. conversion. The ellipsometric thickness of grafted PMMA increased linearly against conversion, further verifying the

good control of ATRP, the presence of persistent surface radical and sufficient grafting density.

Figure 3.4(C) gives the first order kinetic plot of the thickness of grafted PMMA vs. time using "adding deactivator" strategy ([MMA]/[FeBr₂]/[FeBr₃]/[PPh₃] = 300/1/0.1/3.3), suggesting the persistence of surface radical concentration and the sufficient grafting density. The polymerization only occurred at the surface. No polymers were originated in solution. The monomer concentration in the bulk polymerization remained almost constant, giving a linear increase of thickness vs. time. A polymer film of over 80nm was obtained at only 80min. Above 100 min, the oscillation of ellipsometry was drastic and it was difficult to give precise data by ellipsometer. The oscillation was also observed by Franquet et al. on an aluminum substrate treated with silane.[88] If the ratio of monomer over catalyst/deactivator complex is reduced, the reaction rate would increase. For example, MMA/FeBr₂/(PPh₃)₃/FeBr₃ (200/1/3.3/0.1) system, polymer layers of over 50 nm were formed within 40 minutes.

In the presence of an excess amount of deactivator, thicker polymer films were expected. The strategy was first proposed by Matyjaszewski et al. in solution ATRP and was extended to s-ATRP by other researchers.[34-38] Feng et al. reported a thickness over 80 nm of poly(2-methacryloloxyethyl phosphorylcholine) (polyMPC) graft from a trichlorosilane functionalized silicon surface via ATRP.[79] Chen et al. reported a thickness over 100 nm of poly(2,2,2-trifluoroethyl methacrylate) using difunctional initiator 1,1-(2,2-bis(2-bromo-2-methyl propionyloxy methyl)propionyloxy) undecyl

trichlorosilane via ATRP.[80] We obtained over 80 nm of PMMA layer from CRS substrates within 80 min. Because of the limitation of ellipsometer, thicker layers could not be measured.

Both strategies, i.e. "adding free initiator" and "adding deactivator", provided evidences for the livingness of s-ATRP using $\text{FeBr}_2(\text{PPh}_3)_3/\text{FeBr}_s/\text{EBIB}$ system. The deactivation of iron catalyst complex did not occur. After 4 hr, for DP=300, the thickness went up to around 21.2 ± 1.4 nm (conversion=90%) on the CRS substrates. The molecular weight measured by SEC was 24,076 g/mol (conversion 90%) with a polydispersity of 1.22. The grafting density was estimated 0.58 chains/nm² for PMMA brush using Equation (1).[17]



Α

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Figure 3.4 (A) First-order kinetic plot, DP300 = [MMA]/[FeBr₂(PPh₃)₃/[EBIB] = 300/1/1 (B) Thickness of PMMA layer versus monomer conversion, DP300 = [MMA]/[FeBr₂(PPh₃)₃/[EBIB] = 300/1/1 (C) Thickness of PMMA layer versus time with adding deactivator, DP300 = [MMA]/[FeBr₂]/[FeBr₃]/[PPh₃] = 300/1/0.1/3.3

The "adding initiator" strategy was also investigated on other metal substrates (SS, Ni and Al) with acrylics (MMA and DMAEMA) via s-ATRP. See Table 3.1. Scheme 2.4 illustrates various acrylics grafting from metal substrates by the "adding free initiator" strategy.

Poly(dimethylamino) ethyl methacrylate (DMAEMA) grafted from SS was studied. It grew as thick as 7.8 nm on SS-I (1 and 2) substrates using DP50 recipe (DMAEMA:CuBr:HMTETA:EBIB=50:1:1:1) with a grafting density as high as 0.66 chain/nm² using Equation (1) The molecular weight measured by SEC was 7843 with a polydispersity of 1.24. However, PDMAEMA did not graft successfully from CRS and nickel substrates. The possible reasons for the deviation on surface ascribes to the deactivation of catalyst with active substrates.

$$\sigma = \frac{d \times Na \times \rho}{Mn} \tag{1}$$

where d is the thickness of polymer brush, ρ is the density of PDMAEMA (1.1g/cm³), Na is the Avogadro constant and Mn is the number average molecular weight.[17]

Table 3.2 gives the ellipsometric thickness and grafting density of polymethacrylate on the metal substrates. Nickel substrates yielded very close but slightly lower thickness of PMMA than CRS, a grafting density of 0.55 chains/nm². SS only grafted 6.4 nm PMMA with a grafting density of 0.18 chains/nm². Aluminum had a grafting density lower than 0.1 chains/nm² with an ellipsometic thickness of 3 nm. The molecular weights of PMMA with SS, Ni and Al were measured by SEC. The data was around 24,076 g/mol (conversion 90%) with a polydispersity of 1.22 indicating the control of ATRP in solution. The possible reason for the deviation on surface could be ascribed to a lower initiator density on Al. Aluminum is too soft to polish with polishing powders embedded into the top layer of Al surface. SS might have lower density of hydroxyl group on its surface. On the other hand, catalyst deactivation could also be responsible for the low grafting density. If it is the case, an inert catalyst such as Grubb catalyst can be a good alternative s-ATRP from Al. In addition, the recipe and the method of initiator immobilization should be optimized for SS and Al.

Table 3.2 Ellipsometric thickness of polymethacrylates on various metals by "adding free initiator" strategy (CRS, SS and nickel substrates)

	Thickness	Mn,sec/PDI	Grafting density
	nm	g/mol	Chain/nm ²
CRS-g-PMMA _{DP300}	21.4 <u>+</u> 1.4	24076/1.22	0.58
CRS-g-PMMA _{DP600}	41.2 <u>+</u> 3.1	41676/1.35	0.65
Ni-g- PMMA _{DP300}	20	23987/1.30	0.55
SS-g- PMMA _{DP300}	6.4	23978/1.21	0.18
Al-g- PMMA _{DP300}	3	27012/1.18	0.09
SS-g-PMDAEMA _{DP50}	7.8	7843/1.24	0.66

- 1) DP represents different monomer ratios, e.g., DP=300 means [MMA]/EBIB=300/1
- 2) Grafting density was calculated from σ =dpNa/Mn (Equation (1))

3.3 Surface Atomic Compositions

The successful immobilization of the initiator and acrylic polymer grafting on various metals (CRS, Ni, SS) were verified by X-ray photoelectron spectroscopy. See Table 3.3, Figure 3.5, 3.6 and 3.7. Table 3.3 lists the atomic compositions of CRS/CRS-I/CRS-g-PMMA, SS/SS-I/SS-g-PMMA and Ni/Ni-I/Ni-g-PMMA. Figure 3.5, 3.6 and 3.7 give the surface surveys of CRS, Ni and SS (polished, initiator-functionalized and grafted PMMA) at a takeoff angle of 90.

Due to the porous structure of the oxide layer, the polished CRS, SS and nickel substrates had large amount of hydrocarbon trapped in the pores and influenced the surface atomic composition. All the XPS results had surprisingly high carbon and oxygen peaks on the bare surfaces.

With the CRS substrates, from Table 3.3, we concluded that the immobilization of anchor group and PMMA grafting were successful. Figure 3.3(B) shows 1.8% atomic composition of bromide, 3.8% of nitrogen and 0.4% of iron confirming a full coverage of initiator. After PMMA grafting, iron and nitrogen signals decreased to 0%, indicating good coverage of polymer. See Figure 3.5(C). The carbon and oxygen contents were close to the theoretical values. See Table 3.3. Figure 3.5(D) gives the high resolution of X-ray spectroscopy of Cls at a takeoff angel of 90°. The existence of carbon structure of grafted PMMA was close to theoretical value, an area of 65.3% for BE 284.56 ev/285.61

ev, 17.9% for BE 287.06 ev and 16.8% for BE 289.10 ev. Their theoretical values are: 63% for 285/285,72ev, 21% for 289.79 and 17% for 289.03.

For the stainless steel, Figure 3.6 gives the detailed information of surface atomic composition. The element content of the bulk is Iron-Chromium-Ni-Mo/74-13-10-3. Figure 3.6 [A] shows the surface survey of the bare SS, a large amount of hydrocarbon and weak signal of iron and chromium elements, 1.3% respectively, a phenomenon similar to the bare CRS. See Table 3.3. After the immobilization of initiator, the iron and chromium levels were reduced to 0.2%. The lack of Br signal suggested a short life time of bromine in vacuumed chamber during XPS measurement. The SS-g-PMMA surface with a polymer layer thickness of 5 nm had the surface composition of iron about 0.1% and that of chromium about 0.1%.

For the Ni surfaces, Figure 3.7 gives the detailed information of the surface atomic compositions. The surface of the bare Ni with a purity of 99.98% in bulk also had a high amount of hydrocarbons on the surface. See Figure 3.7(A) and Table 3.3. After the immobilization of initiator molecules, the overlap of the Ni and Br peaks did not allow us to estimate the exact data of the Ni and Br elements. Compared all the metal-initiator surfaces, the carbon and oxygen contents were very close. The CRS-I surface had 67.5% of carbon and 18.4% of oxygen. The SS-I surface had 76.1% of carbon and 18.5% of oxygen. The Ni-I surface had 72.1% of carbon and 18.4% of oxygen. The Ni-g-PMMA surface with a polymer layer thickness of 24 nm had the surface atomic compositions of carbon 66% and oxygen 29% that were closest to the theoretical values

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of 71% carbon and 29% oxygen. A peculiar peak of silicon appeared and indicated possible contamination of glue during the operation of XPS.

Table 3.3 Atomic concentrations (%) of polished bare, initiator-anchored and Polymer-grafted CRS, SS and Ni substrates measured by XPS at takeoff angle of 90°

	C	N	0	Si	Br	Fe	Cr	Ni/Br
Polished CRS	53.9	0	40.7	0.7	0	4.7		
CRS-Initiator	67.5	3.8	18.4	8.2	1.8	0.4		
CRS-g-PMMA	74.7	0	24.1	1.1	0	0		
Polished SS	70.7	0	26.1	0.6	0	1.3	1.3	
SS-Initiator	76.1	0.9	18.5	4.0	0	0.2	0.2	
SS-g-PMMA	76.2	0.5	21.5	1.5	0	0.1	0.1	
Polished Ni	66.2	0	24.7	1.4				7.7
Ni-Initiator	72.1	0.1	18.4	1.3				8.0
Ni-g-PMMA	65.7	0	28.5	4.5				1.2
РММА	71		29					





Figure 3.5 XPS survey scans at a takeoff angle of 90° on CRS substrates: (A) CRS surface (B) CRS-I surface (C) CRS-g-PMMA surface (D) Cls of CRS-g-PMMA surface at a takeoff angle of 90°



Figure 3.6 XPS survey scans at a takeoff angle of 90° on SS substrates: (A) SS surface (B) SS-I surface (C) SS-g-PMMA surface



Figure 3.7: XPS survey scans at a takeoff angle of 90° on Ni substrates: (A) Ni surface(B) Ni-I surface (C) Ni-g-PMMA surface

3.4 Surface topologies

The topology of polished CRS, CRS-Initiator and CRS-g-PMMA substrates at dry state was studied using AFM, tapping mode, at a scan rate of 0.5 Hz in an image size of $5x5 \text{ }\mu\text{m}^2$ with the height scale ranged from 0 to 25nm. Figure 3.8 gives 2-D and 3-D images of each substrate in an area of 25 μ m². The polished CRS surface was smooth with a Rrms of 2.59nm (Rrms: roughness in root means square). See Figure 3.8(A) and (B). The result confirmed that the polished CRS substrates could be measured by an ellipsometer. Although the substrates were strictly cleaned in an ultrasonic bath with solvent, some polishing residues were readily observed in AFM images. The size of the bumps on surface is around 50 nm and larger, which are probably individual alumina powders. The other researchers reported similar phenomena on the CRS substrates polished by Emery paper of 800 mesh. Powders of >1 micron were observed by SEMQ and Mössbauer spectroscopy after an ultrasonic bath clean.[94,100] Besides, nano-scale pinholes and scratches were also observed on the original CRS substrates. Such a structure drawback was inevitable with these materials. The CRS-I surface gave a Rrms of 2.37 nm. The image confirmed the attachment and the uniformity of the initiator layer. See Figure 3.8(C) and (D). The CRS-g-PMMA substrate with 20 nm polymer layer gave the smoothest surface of Rrms 2.17nm, although an obvious scratch was observed on the surface. The increased smoothness suggests the uniformity of the polymer brushes on the CRS surface. The observation of the Ni surface was similar. The evenly grown polymer chains covered the bumps of residues and smoothened the CRS surface. See Figure 3.8(E) and (F).

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The grafted polymers improved the surface smoothness of the CRS and CRS-I surfaces. The technology shows a great potential in high-tech applications. The other researchers studied the surface topology of steel via electrografting ATRP, ring-open polymerization (ROP) and NMP.[81-84] Figure 1.12 gives the SEM images with a scale bar of 20 µm of steel-g-Polystyrene using electrografting-ATRP. The surface was very rough partly because of the poor control of ATRP. Figure 3.9 shows the morphology of the steel-g-P(ϵ -caprolactone) surface using an electrografting-ring open polymerization method. The AFM images are with a scan size of $1 \times 1 \mu m^2$. The authors did not report the exact data of the bare and initiator-anchored steel surfaces. Figure 3.9(A) and (B) shows that the electrografting PTEA and PEA substrates were very smooth. The roughness of substrates after grafting was measured by AFM. A polymer layer with a roughness of 2.5 nm was achieved using a "grafting to" method, as seen in Figure 3.9(C), and a roughness of 3-5 nm using a "grafting from" method was achieved as seen in Figure 3.9(D). The polymer layers in those studies were very thin. The S-ROP strategy might produce thicker layers but not uniform. No kinetic study revealed in the paper. Therefore there was no strong evidence supporting the livingness of surface grafting.

Figure 3.10 reveals the morphology of the SS-g-copolymer surface using an electrografting-NMP method. The AFM images were presented in 3-D with a scale from 0-60nm. The roughness of substrates was measured by AFM from 1.8 nm to 4.1 nm in a scan size of $1x1\mu m$. The authors did not report the exact data of bare and initiator-anchored steel surfaces and the thickness of the polymer layer. Again, no kinetic data

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supported the livingness of the surface grafting process. It is difficult for us to learn more information from these AFM images.



Figure 3.8: Morphology of CRS, CRS-I and CRS-g-PMMA surfaces: (A) and (b) polished CRS; (C) and (D) CRS-I; (E) and (F) CRS-g-PMMA (20nm). The scale is at 0-25nm



Figure 3.9 AFM images of steel-g-poly(ε-caprolactone) (A) electrografting PTEA, (B) electrografting PEA, (C) steel-g-poly(ε-caprolactone) using "grafting to" method, (D) steel-g-poly(ε-caprolactone) using "grafting" from method.[92]



Figure 3.10 AFM images of SS-g-PS-b-PDAEA: (A) and (B) poly(BuA-b-DAEA), (C) and (D) poly(styrene-b-DAEA), (E) electrografting poly(PTEA) surface. The height scale ranges from 0-60nm.[84]

3.5 Catalyst deactivation

The catalyst deactivation occurred in this work. The redox reactions between catalyst and active substrate (Fe, Ni and Al) led to poor control of ATRP. Claes and co-worker observed severe copper contamination in employing the CuCl/CuCl₂/HMTETA system for the s-ATRP of styrene from polyCPEA (2-chloro-propionate ethyl acrylate)

electrografted steel surfaces. However, their XPS data revealed no iron signal of polyCPEA-covered surface. To overcome the problem, Grubbs catalyst $(RuCl_2(=CHPh)(PCy_3)_2)$ was selected for the s-ATRP of styrene due to its inertness towards steel. Unfortunately, high polydispersities at 1.55 to 3.3 were observed using Grubb catalyst, probably due to metathesis side reactions in styrene polymerization. An alternative NiBr₂(PPh₃)₂ catalyst was adopted, but again a board polydispersity of 2.75 was obtained.[82]

Cold rolled steel has a porous oxide layer on its surface, resulting in higher possibility than any other steel for catalyst deactivation. To avoid the catalyst deactivation in the present study, the Fe(II)Br₂/(PPh₃)₃ catalyst complex and bulk polymerization were adopted. Equation (2) lists the electrochemical potentials of Fe element. The possible reaction is to reduce Fe^{3+} to Fe^{2+} with a positive reduction potential. But this reaction is not able to influence the ATRP equilibrium. On the other hand, the bulk polymerization greatly decreases the possibility of producing a current between cations and iron substrates. As reference, the previous work on iron catalyst for ATRP included Shah and co-worker's that reported the use of the same catalyst in the s-ATRP of MMA grafting from a thiol-functionalized Au surface.[39] Matyjaszewski and co-worker reported the use of FeBr₂/(PPh₃)₃/1-PEBr catalyst complex in a solution ATRP of styrene.[40]. Another advantage of iron catalysts is its low reaction temperature and faster reaction rate. In this work, low polydispersities of 1.18-1.3 in the bulk polymerization of MMA from various substrates were obtained, indicating a good control

of the s-ATRP with iron catalysts. The catalyst deactivation occurred but did not dominate the polymerization.

$$Fe^{2+} + 2e \rightarrow Fe \qquad E = -0.447 \text{ V}$$

$$Fe^{3+} + 3e \rightarrow Fe \qquad E = -0.037 \text{ V}$$

$$Fe^{3+} + e \rightarrow Fe^{2+} \qquad E = +0.771 \text{ V}$$
(2)

Copper catalyst deactivation was observed in aqueous ATRP systems and those with methanol as solvent. See Figure 3.11. But it did not occur in organic solvents such as THF. The electrochemical potentials of Cu element are listed in Equation (3) with the polymerization recipes followed. The positive reduction potentials in Equation (3) suggest the occurring of catalyst deactivation, but the effects would be greatly minimized in organic systems because of difficulty in forming current between cations and substrates.

$$Cu^{+} + e \rightarrow Cu \qquad E = +0.521 \text{ V}$$

$$Cu^{2+} + e \rightarrow Cu^{+} \qquad E = +0.153 \text{ V}$$

$$Cu^{2+} + 2e \rightarrow Cu \qquad E = +0.3419 \text{ V}$$
(3)

DMAEMA: Solution polymerization in THF

DP50=DMAEMA/CuBr/HMTETA/EBIB=50/1/1/1 (molar ratio)

DMAEMA/THF=1.07/1 (v/v)

OEGMA: Solution polymerization with methanol

DP100=OEGMA/CuBr/bpy/EBIB=100/1/1/1 (molar ratio)

OEGMA/Methanol=0.6/1 (v/v)



Figure 3.11 Catalyst deactivation in ATRP using methanol as solvent

3.6 Electrochemical experiment

CRS is the most widely used metal materials in automobile applications. CRS is rolled when it is cold. The process makes it stronger than hot rolled steel counterpart, but more likely to rust than any other steels such as hot rolled steel, hot-dipped steel, galvanized steel. The anti-corrosion performance of the CRS-g-PMMA was assessed in this work.

The electrochemical experiment was carried out to assess the corrosion potential for two CRS-g-PMMA surfaces (with 10 nm and 20 nm thickness respectively), CRS-Initiator surface and CRS bare surface in 0.1 mol/l neutral potassium sulfate electrolyte. All the substrates immersed in 0.1 mol/l neutral potassium sulfate electrolyte for at least 1 hr for stabilization. The cathodic and anodic polarization curves are shown in Figure 3.12. The passivity states for the CRS-g-PMMA surfaces compared to those of the CRS and CRS-Initiator surfaces indicated the anti-corrosion performance of the dense polymer brushes, similar to the passivation states of SS in the electrochemical experiment, figure 3.12 (B).[101] The passivation curves could not be observed in silane-treated metals,

such as hot rolled steel, and their alloys, no matter how thick the silane films were formed.[10,12,13,88,102] The silane-treated CRS-I surface showed very poor resistance to corrosion, agreeing with the literature work.[102] PMMA brushes of 10 nm greatly improved the corrosion resistance of CRS. At the same Ecorr values, the Icorr values of the CRS-g-PMMA surfaces significantly decreased compared to those of the original CRS and CRS-Initiator surfaces from 10^{-9} A to 10^{-3} A. It was several orders of magnitude lower. The low corrosion current indicated a high capacitive nature giving rise to a high degree of anti-corrosion performance. The CRS-g-PMMA surface with 20 nm polymer layer gave a better corrosion resistance performance than that of 10 nm. The initial Icorr value of the 20 nm CRS-g-PMMA surface was lower than 10^{-10} A, close to 10^{-11} A. At an Ecorr between the ranges of -0.4 to -0.2 V, the lcorr remained constant with a sharp increase in ΔE compared to the other three pieces. PMMA itself lacks of functional group for corrosion resistance. It becomes evident that a densely grafted PMMA layer of only 10 nm or 20 nm (0.58 chain/nm²) results in an excellent protection for CRS from rust.

From the electrochemical experiment results, we can see that the surface grafting via living radical polymerization provides a powerful tool to modify metal surfaces under nanoscale precision with superior performance and functionality.



Fig. 1. Anodic polarization curves in a deacrated Hanks' solution at 37°C of the NiTi, Ti6Al4V and AISI 316 LVM samples.

Figure 3:12 (A) Polarization potential of CRS, CRS-I and CRS-g-PMMA (10nm) in 0.1 mol/l neutral potassium sulfate electrolyte; (B) Anodic curve of SS, Ti and Ti/Ni

Chapter 4

Conclusions and Recommendations

4.1 Conclusions

Four acrylics polymers (MMA, DMAEMA, OEGMA and TFEMA) were successfully grafted from the metal substrates of steel and nickel via s-ATRP. $3-(\alpha-$ Bromo-2-methyl) propylamide propyltriethoxysilane was synthesized and immobilized on steel, nickel and aluminum surfaces with good surface initiator densities. The immobilization process was efficient and environmental-friendly. It is also transferable to other active metals and their alloys. The polymerization of methacrylates were carried out in bulk or in solution mediated with iron (II) bromide/triphenylphosphine and copper catalyst complexes (CuBr/BPY, HMTETA and dNnbpy). Catalyst deactivation occurred in aqueous solution, but very minor in organic solution. Using "adding free initiator" method, the monomer/initiator ratio was varied for targeting polymer film thickness. Iron (III) bromide was used as deactivator and obtained the highest thickness of the grafted PMMA layer. The grafting densities were 0.58 chains/nm² for CRS-g-PMMA, 0.55 chains/nm² for Ni-g-PMMA and 0.66 chains/nm² for SS-g-PDMAEMA, 0.18 chains/nm² for SS-g-PMMA. Optimizing the conditions for initiator immobilization yielded the thickness of 30nm PMMA (DP=300) on the nickel surface with a grafting density over 0.8 chains/nm². AFM images proved that the PMMA brushes made the surfaces more uniform with lower roughness. Finally, the electrochemical experiments were carried out and the results supported that well-defined PMMA brushes on CRS substrates provided good protection for CRS from electrolyte corrosion.

The successful grafting of acrylics from the steel and nickel surfaces with high grafting densities enables further exploration of grafting multi-functional polymers or block copolymers for nanopatterning on metal surfaces and of surface grafting from metal nanoparticles.

4.2 Future work

4.2.1 Synthesis of new initiator

Figure 4.1 illustrates the synthesis of a new bromine-terminated alkoxysilane initiator that has potential in increasing initiator density on metal surface. First, the moiety 1 is hydrogen instead of methyl group. There are several merits for this new initiator. Compared to 3-(α -bromo-2-methyl) propylamide propyltriethoxysilane, the new initiator should have less steric effect, leading to a relatively high initiator density. Second, the bromide end group is more stable during the process of synthesis. A very pure grade of initiator can thus be obtained. Third, surfaces functionalized with the new initiator is hydrophilic with the water contact angles around 46/26, which facilitates some applications that require an aqueous environment.



Scheme 4.1 Schematic representation of synthesis of (α-Bromo-N-butyl) propionamide triethoxysilane

Maud et al. compared the initiator grafting density G_I , overall initiator efficiency f_T and grafting initiator efficiency f_G of the initiator with 1 as hydrogen or methyl group. See Table 4.1 and 4.2. The initiator grafting density of the initiator with 1 as hydrogen was 1.16 chains/nm² and that with methyl group was 0.78 chains/nm². The initiator with 1 as hydrogen had a higher grafting efficiency 23% over that of methyl group 16%. From Table 4.2 we can find that the grafted initiator efficiency was much lower than the overall initiator efficiency, for example, from 0.83 to 0.18. The initiator with 1 as hydrogen was more efficient than that with methyl group, but had a relatively higher polydispersity.[87]

Table 4.1 Comparison of initiator density and grafting efficiency of BP and BIB [87]

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Experiment	Grafted initiator	Initiator-	non	W%	Gı	Graft efficiency ^{b)} %	
		grafted silica		TGA	Initiator \cdot nm ²		
1	(CH ₃) ₂ SiCl(CH ₂) ₆ OCOCH(CH ₃)Br	Si-BP-1a	1.08	30	1.16	23	
2	(CH ₃) ₂ SiCl(CH ₂) ₆ OCOCH(CH ₃)Br	Si-BP-1b	0.54	30	1.16	23	
3	(CH ₃) ₂ SiCl(CH ₂) ₆ OCOC (CH ₃) ₂ Br	Si-BiB-2	0.21	-24	0.78	16	

Table 1. Characteristics of the initiator-grafted mesoporous silica particles.

^{a)} The ratio between the number of moles of the initiator introduced and the number of moles of hydroxyl functions is calculated assuming 5 OH \cdot nm⁻² for both the inner and the outer surfaces.

^{b)} Graft efficiency = $(n_{\text{grafted initiator}}/n_{\text{OH}}) \times 100 = (G_1/5) \times 100$.

The initiator with 1 as hydrogen would be a good candidate for high grafting density and initiator efficiency. It worked on SS for PDMAEMA grafting. Future research work should focus on the applications in other metals and their nanoparticles, cold rolled steel, aluminum and nickel with multifunctional chain moieties such as teflon, silicone and amine. The first two are hydrophobic and the last is corrosion inhibitor. The side chain length can be varied for optimal corrosion-resistant properties.

Table 4.2 Comparison of overall initiator efficiency and grafted initiator efficiency of BP

and BIB [87]

Experiment	Initiator- grafted	Time	Conversion	M _{Diteo.} a)	$(\overline{M}_{n_{SBC,d}})^{(b)}$	fr°'	$(\overline{M}_{n_{\text{NEC}}}/M_{n})^{b})$	W% _{polymer + silica} (TGA)	$G_{ m P}$	$f_{g}^{(d)}$
	silica	ica <u>h</u>		$g \cdot mol^{-1}$	$g \cdot mol^{1}$	-	g·mol ⁻¹	%	$Chain \cdot nm^{-2}$	
1	Si-BP-1a	24	0.85	12 100	14130 (1.23)	0.83	17250(1.18)	81	0.215	0.18
2	Si-BP-1b	24	0.31	14 200	30 440 (1.24)	0.46	***	93	0.336	0.29
3	Si-BiB-2	16	0.42	9 300	16390 (1.13)	0.53	16620 (1.08)	53	0.039	0.05
4	Si-BiB-2	6	0.13	10 600	63 440 (2.59)	0.16		49	0.008	0.01
5		.2	0.22	17 750		0.70	24990 (1.08)			

Table 3. Results of styrene and MMA surface-initiated ATRP.

^{a)} Theoretical average molar mass: $\overline{M}_{\text{R}_{\text{fonc.}}} = M_{\text{initiator}} + \frac{[M]_0}{[I_{R_0} + [I]_{R_0}} \times \text{conv.} \times M_{\text{monomer}}$ ^{b)} $\overline{M}_{\text{R}_{\text{SEC},g}}$ and $\overline{M}_{\text{R}_{\text{SEC},f}}$ are the experimental molar mass (SEC) of the grafted polymer chains and the free polymer chains, respectively. ^{c)} Overall initiator efficiency, $f_{\text{T}} = \frac{M_{\text{initiator}}}{M_{\text{sSEC},g}} = \frac{[I]_{\text{cop}}}{[I_{R_0} + [I]_{R_0}}$.

4.2.2 Metal/metal oxide nanoparticles

Metal nanoparticles have electronic, magnetic, catalytic, optical, physical, and mechanical properties from their bulk materials, giving rise to versatile high-tech applications. The uniqueness is determined by their size, surface structure and surface chemistry. There are intensive research on the diffusivity, stability and compatibility of metal particles with their surrounding.

The present research provided basic understanding of surface-initiated atom transfer radical polymerization from metals such as steel and nickel. The technique is believed to be transferable to metal nanoparticles. Thus we can explore and design experiments to surface structure and surface chemistry of tailor metal nanoparticles.

An exciting area is to graft pH-, UV- or temperature-sensitive monomers from metal nanoparticle surfaces. The modified metal nanoparticles can then be spin-coated to other materials. Thus the materials surfaces become environmentally responsive,

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providing a wide range of applications as biomaterials, chemical sensors, drug carriers and more.

Another area worth of pursuing is to graft ultrahydrophobic/ultrahydrophilic monomers from metal nanoparticle surfaces. The modified nanoparticles can also spin-coated to other materials and thus make the materials water-repellent or oil repellent. The surfaces have a function as self-cleaning, known as Lotus effect.

4.2.3 Nickel, Aluminum and Stainless Steel 316L

Nickel: In this thesis, the immobilization of initiator on the Ni surface used the same condition as on CRS. A series of screening experiments should be carried out to identify the optimal operation window. A thick layer of PMMA on the Ni surface with a grafting density over 0.80 chains/nm² was obtained. In addition, the AFM images in this study showed that the morphology of the nickel surface differed from CRS. Further work in this area should focus on the study of morphology of the nickel surfaces and the method to improve polymer grafting density.

Aluminum: Aluminum is a soft and light-weight metal. According to its commercial value and volume, it is ranked second in the metal market, just after iron and its alloys. In the present work, polymer layers with only a few nanometers thick were grafted on aluminum. Aluminum was also too soft for polishing that resulted in the polishing powders heavily embedded to the surface. Silicon gel power should be considered to replace 50 nm alumina paste for polishing aluminum. On the other hand,

an inert catalyst such as Grubb catalyst can be used for controlling surface ATRP from catalyst deactivation.

Stainless 316L has broad applications as biomaterials. The nanoscale precision is driven by the demand of minimizing device planted in body. The protein-repellency and anti-corrosion properties are important for the specific applications. Up to now, none research has been carried out in the area of s-ATRP grafting from SS. The present work on the SS surface can be extended to copolymerization for surface functionality. For example, SS-PS-b-PMPC or SS-PTFEMA-b-PDMAEMA can be prepared via s-ATRP. Both protein absorption and electrochemical experiments, using amine acid (close to body fluid) as electrolyte, can be studied and compared with the coated block copolymers.

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