CHAPTER I:

CONTROLLED/"LIVING" FREE RADICAL POLYMERIZATIONS

I.1.0 INTRODUCTION

I.1.1 GENERAL

The field of material science has seen explosive growth since the pioneering work of Staudinger, Carothers, Mark, Flory, and others after the First World War. Initial advances focused on the development of new polymers from novel monomers, enabling unique physical and chemical properties based on individual atomic makeup. The utility of such novel polymers was determined based on their mechanical behavior, which is dependent upon degree of crystallinity, the degree of crosslinking, and the values of T_g and T_m, or the glass and melt transition temperatures, respectively. [1] Accordingly, a polymer was typically classified as a fiber, flexible plastic, rigid plastic, or elastomer [2,3] and this classification was taken as characteristic of the individual polymer.

While the varieties of polymeric materials capable of being produced are limited only to one's imagination, recent advances have shied away from the relatively expensive design of new materials and towards the modification of existent macromolecules. Changing the method of polymer processing can readily alter mechanical properties. For example, perhaps best known for its widespread use as a foam insulator (coffee cups, food service packaging, etc), polystyrene was initially used as a component in synthetic elastomers during the second world war and has since also been used as a rigid plastic (CD jewel cases, plastic utensils, etc.). Simple variations on processing techniques enable polystyrene to take such vastly different forms.

Certain mechanical properties also vary with polymeric preparation methods. Carothers originally classified polymers as being condensation or addition polymers on the basis of preparation methods. [4] In 1956 Szwarc introduced a third classification, that of ionic chain polymerization. [5] The major difference between all three routes is the time required for the growth of individual polymer chains and molecular weight distribution among these chains. Defining the molecular weight distribution, or polydispersity, as M_w / M_n (where M_w is the weight average molar mass and M_n is the number average molar mass), we can return to the polystyrene example from above. Being formed from a vinyl monomer, i.e. a substituted ethylene, polystyrene was first synthesized in an additive free radical chain growth fashion. In this manner, irreversible

chain termination steps produce macromolecules of broad polydispersities and subsequent unpredictable behavior as the degree of polymerization greatly influences material properties. [6] Compare this to Szwarc's preparation of polystyrene via an anionic route which led to a polydispersity approaching unity, thus allowing more predictable macromolecular behavior at any degree of polymerization.

Szwarc defined his anionic route as being a "living" polymerization, characterized by polymer chains that grow linearly with time. Void of such chain breaking steps as chain transfer or termination, anionic chain ends remain alive in the sense that chain growth may be reinitiated by the addition of monomer. It is possible to synthesize block copolymers upon addition of a second type of monomer to a living anionic macromolecular chain. In this way, and unlike random or regular copolymers, the new polymer will retain many of the physical characteristics of the homopolymers that make up the block. In addition, varying monomer composition can lead to a variety of polymeric architectures ranging from linear to highly branched. Ergo, living polymerizations enable architectural and compositional control, thus permitting one to manipulate various properties.

As will be discussed below, and despite the obvious advantages of using living polymerizations over conventional free radical methods, there are two major obstacles one must overcome to utilize living ionic polymerizations. The rest of this chapter will focus on the advantages and disadvantages of free radical versus ionic polymerizations before introducing a recent marriage of the two techniques into a hybrid known as controlled/"living" free radical polymerization.

I.1.2 CONVENTIONAL FREE RADICAL POLYMERIZATIONS

Free radical polymerizations are of significant importance in the industrial sector for a variety of reasons. First, many monomers capable of undergoing chain reactions are available in large quantities from the petrochemical sector. [7a] In addition, free radical mechanisms are well understood and extension of the concepts to new monomers is generally straightforward. A third advantage of free radical routes is that the polymerization proceeds in a relatively facile manner: rigorous removal of moisture is generally unnecessary while polymerization can be carried out in either the bulk phase or in solution.

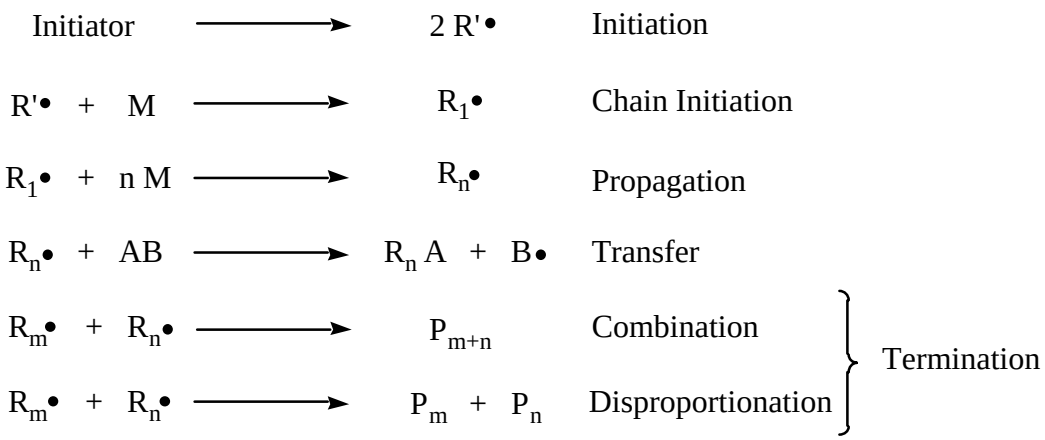
As chain reactions, free radical polymerizations proceed via four distinct processes:

1. *Initiation*. In this first step, a reactive site is formed, thereby "initiating" the polymerization.
2. *Propagation*. Once an initiator activates the polymerization, monomer molecules are added one by one to the active chain end in the propagation step. The reactive site is regenerated after each addition of monomer.
3. *Transfer*: occurs when an active site is transferred to an independent molecule such as monomer, initiator, polymer, or solvent. This process results in both a terminated molecule (see step four) and a new active site that is capable of undergoing propagation.
4. *Termination*. In this final step, eradication of active sites leads to "terminated," or inert, macromolecules. Termination occurs via coupling reactions of two active centers (referred to as combination), or atomic transfer between active chains (termed disproportionation),

The free radical chain process is demonstrated schematically below (Scheme 1): R'• represents a free radical capable of initiating propagation; M denotes a molecule of monomer; R_m• and R_n• refer to propagating radical chains with degrees of polymerization of *m* and *n*, respectively; AB is a chain transfer agent; and $P_n + P_m$ represent terminated macromolecules.

Because chain transfer may occur for every radical at any and all degrees of polymerization, the influence of chain transfer on the average degree of polymerization and on polydispersity carries enormous consequences. Furthermore, propagation is a first order reaction while termination is second order. Thus, the proportion of termination to propagation increases substantially with increasing free radical concentrations. Chain transfer and termination are impossible to control in classical free radical processes, a major downfall when control over polymerization is desired.

Scheme 1. General Free Radical Polymerization Mechanism.



I.1.3 CONVENTIONAL LIVING POLYMERIZATIONS

Living polymerizations are characterized by chain growth that matures linearly with time. Inherent in this definition are two characteristics of ionic polymerizations that both liken and distinguish ionic routes from the aforementioned free radical route. In order to grow linearly with time, ionic polymerizations must proceed by a chain mechanism in which subsequent monomer molecules add to a single active site; furthermore, addition must occur without interruption throughout the life of the active site. Thus, the chain transfer mechanisms described above must be absent. A more exact definition has been established by IUPAC. As defined in *Macromolecular Nomenclature Note No. 12*, living polymerizations may include slow initiation, reversible formation of species with various activities and lifetimes, reversible formation of inactive (dormant) species, and/or reversible transfer. [8] Living polymerizations must not include irreversible deactivation and irreversible transfer.

Classical living polymerizations occur by the formation of active ionic sites prior to any significant degree of polymerization. A well-suited initiator will completely and instantaneously dissociate into the initiating ions. Dependent on the solvent, polymerization may then proceed via solvent pairs or free ions once a maximum number of chain centers are formed. [7b] Solvents of high dielectric constants favor free ions; solvents of low dielectric constants favor ionic pairs. Termination by coupling will not occur in ionic routes due to unfavorable electrostatic interactions between two like charges. Furthermore, chain transfer routes are not available to living polymerizations, provided the system is free of impurities. Polymerization will progress until all of the monomer is consumed or until a terminating agent of some sort is added.

On the flip side, ionic polymerizations are experimentally difficult to perform: a system free of moisture as well as oxygen, and void of impurities is needed. Moreover, there is not a general mechanism of polymerization on which to base one's experiment: initiation may occur in some systems before complete dissociation of initiator. Knowledge of the initiating mechanism must be determined *a priori* to ensure a successful reaction. Despite the advantage of molecular control of living systems, the

experimental rigor involved in ionic polymerization is often too costly for industrial use and free radical routes are preferred.

I.1.4 CONTROLLED/"LIVING" FREE RADICAL POLYMERIZATIONS

Conventional free radical polymerization techniques are inherently limited in their ability to synthesize resins with well-defined architectural and structural parameters. Free radical processes have been recently developed which allow for both control over molar masses and for complex architectures. Such processes combine both radical techniques with living supports, permitting reversible termination of propagating radicals. In particular, three controlled free radical polymerizations have been well investigated. Each of these techniques is briefly presented below and all are based upon early work involving the use of initiator-transfer-agent-terminators to control irreversible chain termination of classical free radical process.

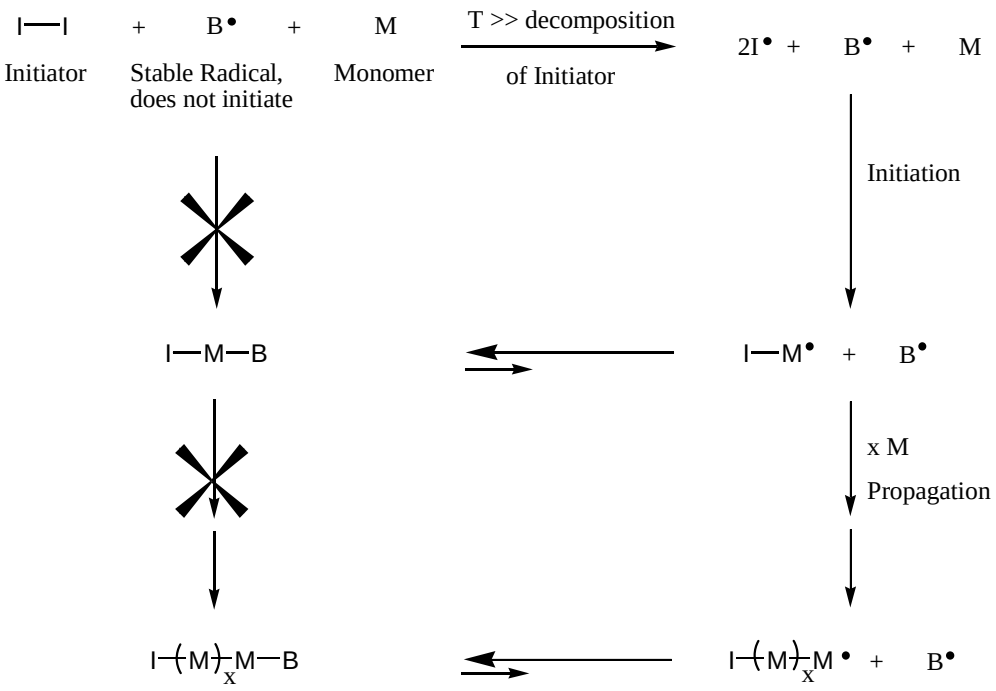
In 1982, Otsu et al. extended the idea of living polymerizations to free radical systems in the use of initiator-transfer-agent-terminators, or iniferters. [9] Such initiators act both as primary radicals to initiate polymerization (R'•, Scheme 1) and as radical chain terminators (R_m• or R_n•, Scheme 1), consequently permitting a near linear increase of molar mass with time and percent conversion. [10] However, the similarities between living anionic systems and Otsu's iniferter reaction end there. The iniferter mechanism yields radicals that can initiate new chains throughout the course of the reaction. [11] The iniferter systems also show significant loss of active end groups from the growing polymers. [11b] Consequently, these systems display relatively large polydispersities with a substantial amount of homopolymer being formed in conjunction with block copolymer. [11a]

In 1986, Solomon, Rizzardo, and Cacioli synthesized methyl acrylate oligomers via reversible capping of the growing radical chain by a stable free radical. [12] Although

they did not realize it at the time, perhaps because the extension of SFRP to polyacrylates has proven to be difficult, [13] the reversible capping of growing chains defined the first mechanism of three general routes to controlled/"living" radical polymerization.

The reversible homolytic cleavage of a dormant chain end to form a stable free radical as well as an active radical site was applied to the polymerization of styrene in 1993, [10] later to the polymerization of acrylates catalyzed by cobalt porphyrin alkyls, [14] and more recently to a wide range of monomers via the preparation of monomer specific initiators. [15] This route was coined "Stable Free Radical Polymerization" (SFRP) by its discoverers. [16] The general SFRP mechanism is shown in Scheme 2.

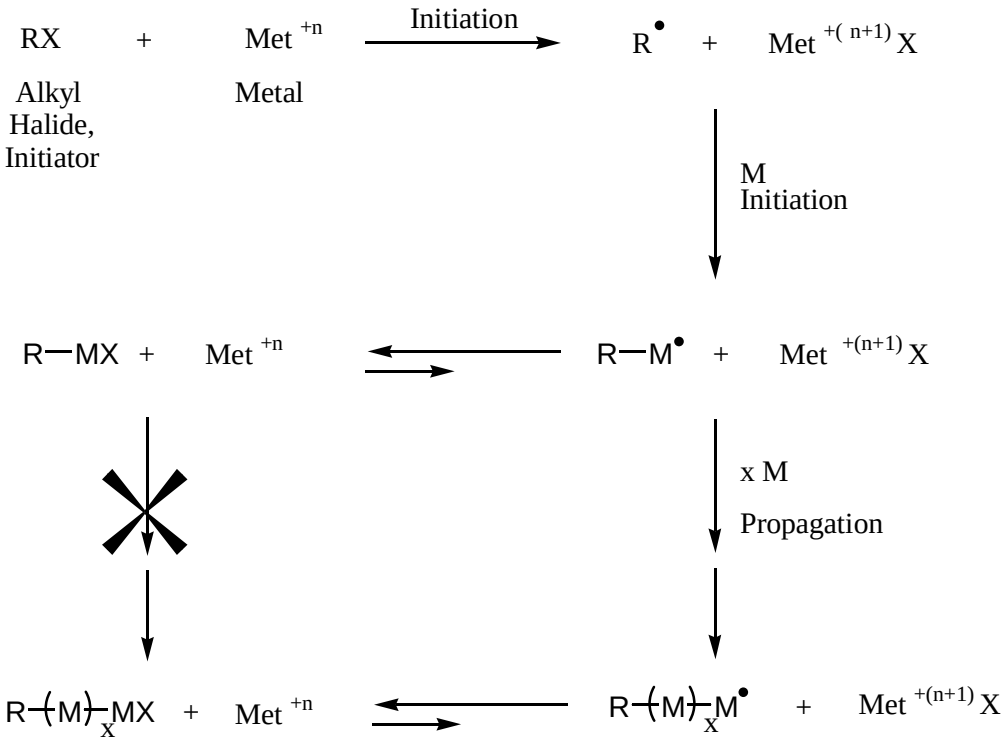
Scheme 2. SFRP Mechanism



Matyjaszewski reported a second route of control over radical polymerization by introducing a catalytic amount of a copper(I) coordination complex which reversibly abstracts a halide from the polymer chain end, thereby affording a switching mechanism between a dormant and an active, propagating state (Scheme 3). [17]

The third and most recent report of a controlled/"living" free radical polymerization has been reported by Haddleton and co-workers as well as Thang et al. [18] Reversible addition-fragmentation chain transfer (RAFT) is achieved by performing a free radical polymerization in the presence of dithio compounds, which act as efficient reversible addition-fragmentation chain transfer agents (Scheme 4). Much like the first two routes, the rapid switching mechanism between dormant and active chain ends affords living polymerization character.

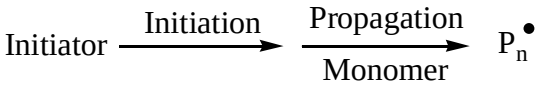
Scheme 3: ATRP mechanism.



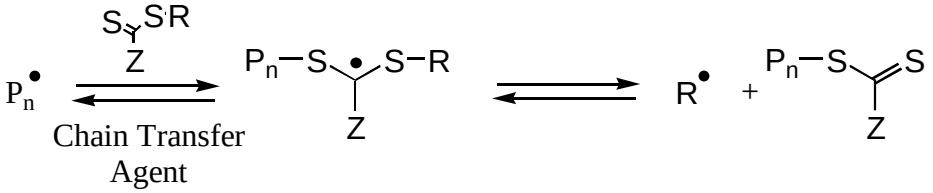
Each of the three new polymerization routes affords the chemist the opportunity to prepare a wide range of polymeric materials. Recent interest in the utilization of SFRP and ATRP towards the development of new materials has seen explosive growth: the homopolymerization of various monomers with well-defined parameters are well documented, [19] block copolymers have been readily prepared by adding additional monomer to the reaction after the complete consumption of the starting material or by isolating and purifying the macromolecule prior its use as a macroinitiator, [20]

Scheme 4. RAFT Mechanism

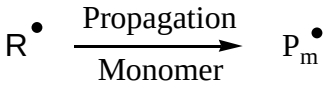
Initiation and Propagation



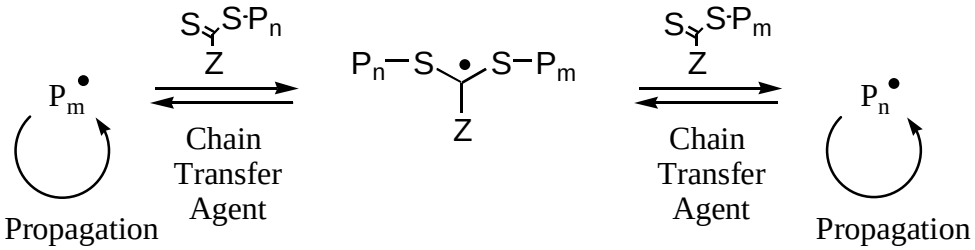
Chain Transfer



Reinitiation



Reversible addition-fragmentation chain transfer Mechanism



hyperbranched polymers with tunable branching density have been synthesized [21], and the grafting of polymers to various materials has been shown. The remainder of the chapter will focus on this latter extension.

I.1.5 SURFACE MODIFICATION VIA CONTOLLED / "LIVING" RADICAL POLYMERIZATIONS

The technology of surface modification has seen rapid expansion over the past two decades. This is due in large part to the growth and development of reliable surface characterization techniques, as well as to advances in the physical and chemical techniques used to modify surfaces. For an assessment of conventional free radical polymerization surface modification, the reader is referred to a review by Waddell et al. [22]

A major chemical modification technique, covalent grafting of macromolecules onto various surfaces allows one to alter the physical behavior of the composite system in efforts to exact desired and/or unique properties. [23] The branching of dendrimers provides an exaggerated example where each branch can be thought of as a newly grafted molecule: many dendritic physical properties differ substantially from their linear counterparts. Early grafting techniques utilized reactive surfaces onto which the macromolecule could attach. For instance, the surface of silicone rubber was commonly modified for biomedical applications, [24] while coatings applied to silica enable its use in the separation of proteins. [25] Other reports describe grafting to less reactive polymer surfaces such as polystyrene and polyacrylonitrile via hydroxylation of the treated surface prior to grafting by the ceric ion technique. [26] Hydroxylation of polymers necessarily brings about some degradation of the treated surface; [26b] their extension to biomedical materials have thus proven difficult. [27]

The majority of early surface modifications were performed utilizing the "grafting to" approach, in which large macromolecules are attached to the appropriate surface (Figure 1A). Thus, a well-understood macromolecule of known molar mass and polydispersity could be attached. The "grafting to" approach, however, is inherently limited in its ability to create densely packed grafts as crowding of chains at the surface prevents further attachment. Moreover, formation of islands or mushrooms on the "grafted to" surface is common. Recent modifications involve the "grafting from"

approach, whereby initiating sites are attached to the surface from which the polymer may grow (figure 1B). Although the "grafting from" approach has been known for decades, it was experimentally difficult to accurately control film thickness using polymerization routes of the day. [25] Layer-by-layer deposition, in which a charged surface is dipped into an aqueous solution of an oppositely charged polyelectrolyte and the process repeated until the desired multi-layered thin film is constructed, has been developed to controllably alter surface properties. [28] The obvious disadvantage of deposition is the need to continuously dip and rinse the substrate to build up the surface in nanoscopic segments. In contrast, grafting of "living" polymers from various surfaces allows one to predictably and reproducibly control the attached polymer while affording the ability to grow macroscopic segments in a one step process. Living polymers also bear the added luxury of being able to produce block copolymers at any chain length.

Figure 1. General Mechanism for "Grafting To" (1A) and "Grafting From" (1B)

Figure 1A

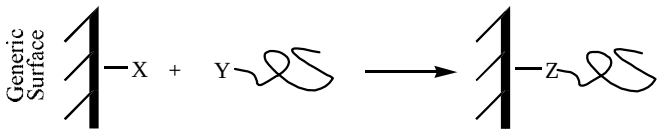
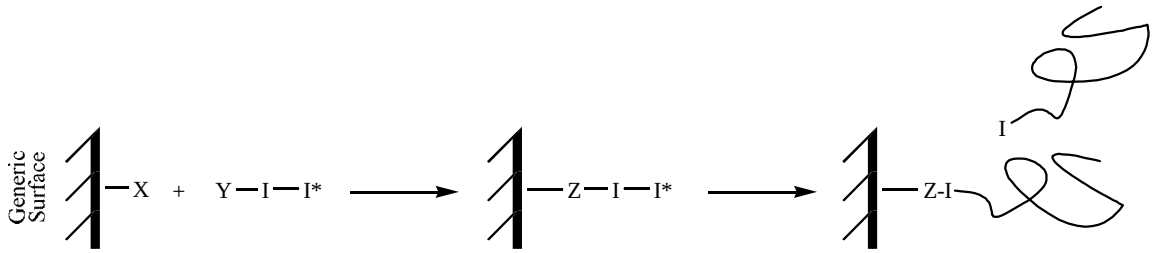


Figure 1B



In 1994, Hawker predicted that the surface grafting polymerization could be expected to favor living free radical polymerization routes for at least two reasons. [29] First, the solid surface onto which initiating groups are placed confers a mobility barrier on termination by coupling. Secondly, a limited number of initiating groups need be attached to the surface to promote property changes, thereby reducing the concentration of free radicals present in the system (recall that controlled free radical polymerization works by maintaining a low concentration of radicals present at any one time during the course of the reaction). Brittain and coworkers experimented with this approach in 1995, when they prepared tethered diblock copolymer brushes in a sequential process by utilizing carbocationic polymerization followed by ATRP. [30]

1996 saw an early report solely utilizing living radical graft polymerizations on polymeric surfaces. Yang and Rånby polymerized methacrylic acid and acrylic acid from the surface of five films utilizing both photo- and thermal activation. [31] Their conclusions were based on measurement of the increases in weight of the substrate upon activation, a valid approximation given the ease of separation of residual polymer grown in the initiation stage from the grafted polymer or substrates.

Hawker and co-workers introduced a novel approach to graft and dendritic graft copolymers when in 1997 they grew a linear backbone incorporating latent ATRP-initiating sites by a nitroxide mediated (SFRP) mechanism (Scheme 5). [32] The backbone ATRP halogen initiating sites could then be activated without degradation of the main chain to introduce grafted copolymers. The grafted macromolecules were again studied according to their weight difference from the main chain.

In 1998, Tsubokawa et al. attached TEMPO terminated polystyrene onto the surface of carbon black. [33] The group had previously attached other well defined polymers onto both carbon black [34] and ultra-fine silica [35] in efforts to prepare high performance nano-composites. Whereas preceding efforts necessitated functionalized surfaces on which to react, the 1998 grafting was unique in that the labile TEMPO end group was used to establish free radical coupling on the virgin carbon black surface, which is a well-known radical scavenger. [36] Grafting efficiency was calculated by the

polystyrene-grafted carbon black's weight loss when subjected to thermal gravimetric analysis.

Shortly after Tsubokawa's report, Tsujii and co-workers announced one of the earliest successful controlled graft polymerizations onto a solid substrate. [37] This technique has since been referred to as surface-confined living radical polymerization (SCLRP). Utilizing the Langmuir-Blodgett technique [38] to homogenously immobilize a well-organized set of ATRP capable initiating sites, the group went on to initiate polymerization of methyl methacrylate (MMA) under ATRP conditions (see Figure 2). Repeated rinsing of the substrate with a theta solvent for the polymer revealed that the polymer chains were indeed grown from the surface and were not simply physically adsorbed. Because the grafted polymer chains were anchored to the surface without a cleavable bond, the group was not able to directly analyze the modified surface.

Scheme 5. Graft Copolymer Preparation by Consecutive Controlled Radical Polymerizations. [32]

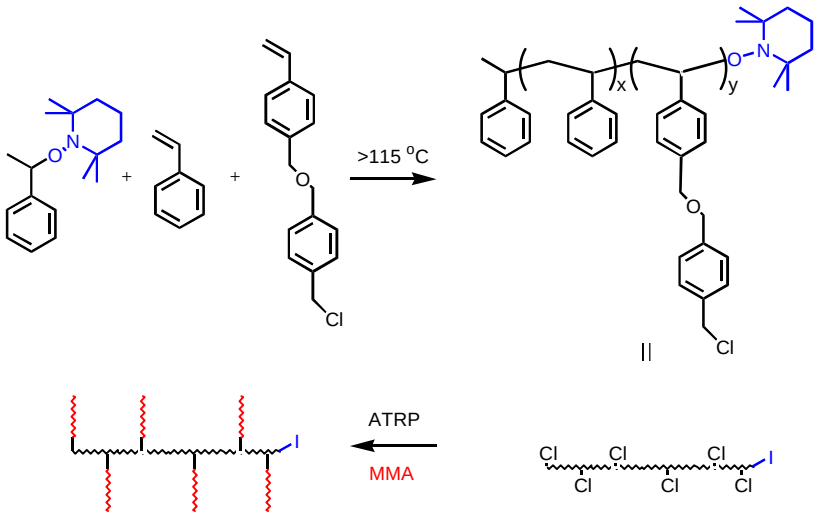
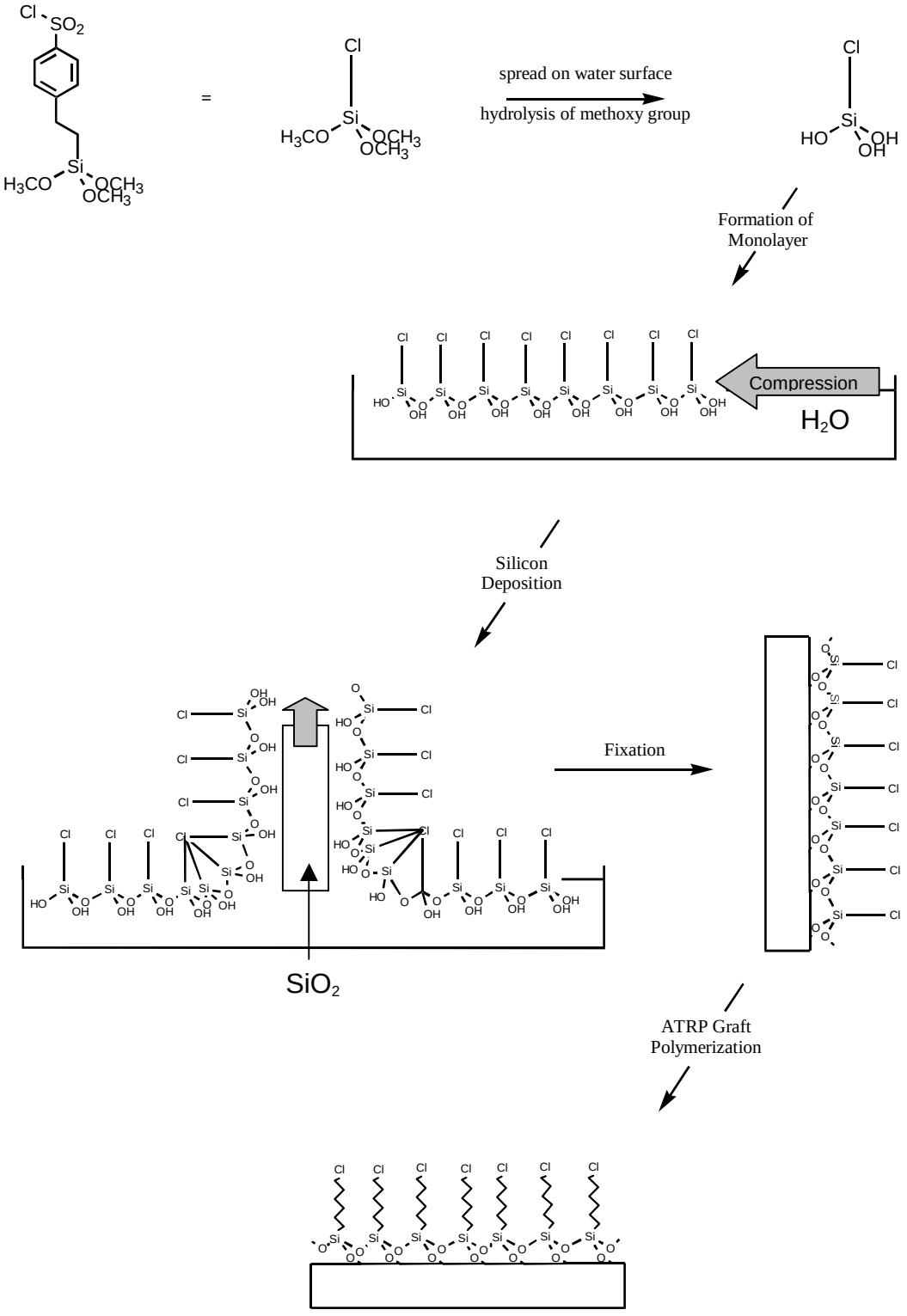


Figure 2. Representation of the Langmuir-Blodgett Immobilization of Initiator and Subsequent Graft Polymerization. [37b]



Asserting that the thickness of the solid substrate increased linearly with the number average molar mass (M_n) of the free PMMA formed during the reaction, the authors suggest that the M_n of the attached polymer is at least proportional to that formed in bulk, if not almost equal in weight.[†] The group has since gone on to successfully grow gylcopolymers from similar silicone surfaces; the bulky side group character of the sugar-carrying monomer used (3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-*D*-glucofuranose, (MAIpGlc)) does not appear to influence grafting capability. [39] This technology has since been used for coatings in capillary electrophoresis. [40]

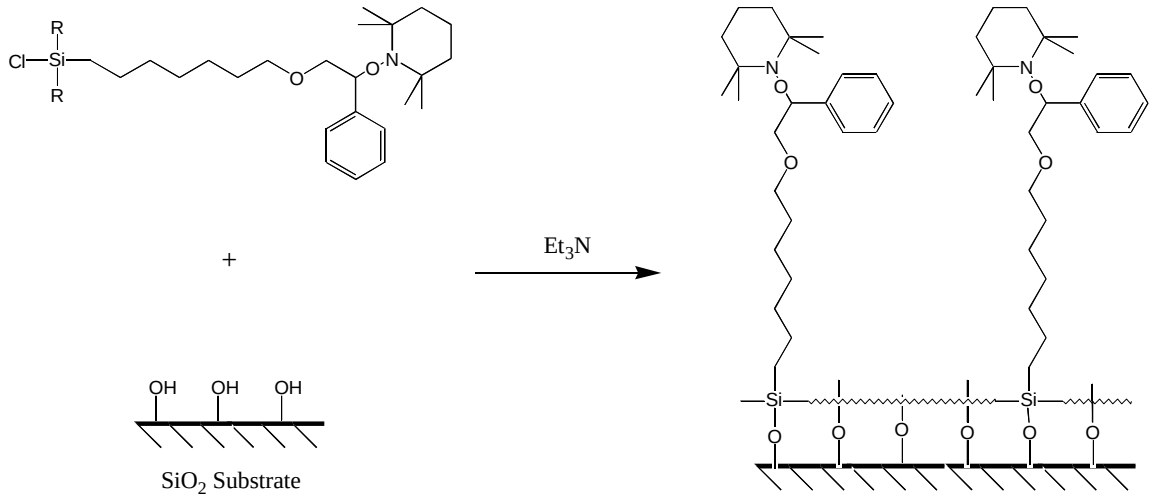
Hawker et al. reported similar SCLRP findings almost simultaneously. [41] This work was based on a study by Prucker and Rühe on the kinetics and mechanism of a radical chain polymerization initiated by silica surface bound azo compounds. [42] In preparing the initiating silica surface, Prucker and Rühe ingeniously included a cleavable ether linkage, enabling the experimenters to detach and investigate any polymer grown from the surface. [42] Hawker modified the azo-initiators to include alkoxyamine (TEMPO) SFRP initiating groups (Figure 3) as well as α-bromoester ATRP initiators. [41] The group found that it was necessary to add "free" initiators into the reaction mixtures to enable polymerization from the surface; polymerizations lacking free initiators were unsuccessful, perhaps a result of the small number of initiating sites relative to amount of monomer added. Addition of free initiators results in unbound macromolecules that can be separated from the polymer brush by repeated washing with an appropriate solvent. Much like Tsujii's results, Hawker noted that the thickness of the dried brush varied linearly with the molar mass of the bulk (unattached) polymer.

[†] Theoretical predictions by Wittmer et al. suggest that strong differences between macromolecules grown at surfaces versus those grown free in solution exist. [43] Prucker and Rühe, however, go on to argue that Wittmer et al.'s prediction is invalid for controlled free radical polymerizations since the model used assumes that many simultaneously growing chains compete for a small influx of monomers available at the surface. [42] In fact, in free radical polymerizations, especially controlled radical polymerizations, the number of active sites is several magnitudes of order lower than the number of monomer molecules present at the surface.

Comparison of cleaved surface bound polymers to those formed in bulk agreed with these results: both molar masses and polydispersities were in harmony. Interestingly, a slightly greater degree of control was observed for the surface bound polymers. This observation may be ascribed to the ability to remove autopolymerized homopolymer formed in the reaction from the silica surface; it is difficult, if not impossible, to selectively remove such polymer from unbound macromolecules.[†]

Hallensleben et al. [44] studied the initiating and re-initiating efficiency of the silica gel bound ATRP initiating groups described by Hawker above. [41] Based on determinations of initiator graft density, bound macromolecule density, and molar mass of surface grown macromolecules, they determined that approximately 17% of the initiating sites were active. They go on to note that the GPC traces of detached block macromolecules (formed upon re-initiation of the surface bound homopolymer) show

Figure 3. Cleavable, Surface Bound Nitroxide Initiating Groups. [41]



[†] A low molar mass GPC tailing effect is characteristic of controlled free radical processes, presumably due to the contamination of the macromolecule by autopolymerized monomer. In fact, it has recently been argued that in bulk controlled processes, autopolymerization is the major limitation, especially at higher molar masses. [45]

tailing in the molar mass range of the starting homopolymer. This result is equated to a termination of around 10 to 15% of active initiating sites. Unfortunately, the authors do not describe the mode of active site termination, which is a curious finding given that Hawker and others [41] have correctly noted that curvature of the silica gel particles would promote easy access to the surface bound macromolecular end groups, thereby alleviating steric issues that would otherwise retard chain growth.

Recently, Hadziioannou et al. have prepared surface-grafted iniferter monolayers on chromium patterned silicon wafers and glass. [46] Patterning allows the researchers a reproducible means of following thickness increases as the surface bound polymers grow. [47] Interestingly, the group allowed the polymer to develop in thickness beyond the patterned surface (resulting in a negative image of the clean surface) and found that the macromolecule did not grow or overflow onto the chromium strips. Their findings hint at the potential uses of polymer functionalized surfaces in the area of microcontact printing. [48]

We below demonstrate continued modification of inorganic materials by formation of surface-grafted monolayers via controlled radical polymerizations.

I.1.6 POLYMER SURFACE MODIFICATION: CONTROLLED RADICAL GRAFT POLYMERIZATIONS FROM THE SURFACE OF SILICA GEL

I.1.6.1 INTRODUCTION

As described above, the grafting of polymeric chains onto a solid surface allows one to permanently alter performance characteristics of the surface without disrupting the overall properties of the bulk phase. [49] A few reports have recently described such grafting to silicon substrates, be they in the form of wafers or glass beads, by utilizing controlled free radical polymerization routes such as ATRP and SFRP [30 ,31, 37, 39-41, 44, 48, 50]. Of these reports, only Hawker [41] and Brittain [50] make use of a tri-functional initiating group to attach to the substrate (for example, the R groups in Figure 3 on page 22 above would both be chlorides in the tri-functional situation). Importantly, the introduction of three identical attachment sites is believed to result in a more stable initiating layer. Indeed, Hawker notes that the degree of control obtained with the tri-functional initiator is greater than that obtained with the monofunctional derivative. [41]

The synthesis and attachment of a tri-functional initiating group to the surface of silica gel is described below. [51] Subsequent polymerization from the surface and characterization of the macromolecule grown is also discussed.

I.1.6.2 RESULTS

*I.1.6.2.1 Synthesis of ω-undecenyl p-chloromethylbenzoate (**1**).* [51]

To a solution of *ω*-undecylenyl alcohol (4.26 g, 250 mmol) and anhydrous pyridine (1.98 g, 25 mmol) in 50 mL THF, a solution of 4-(chloromethyl)benzoyl chloride (4.73 g, 25 mmol) in 25 mL dry THF was added dropwise and the mixture stirred at room temperature under nitrogen for sixteen hours. Precipitated pyridinium salt was removed via vacuum filtration and the solvent evaporated from the filtrate to yield a colorless oil **1** (Scheme 6) in a 93% yield. ^{1}H NMR ($CDCl_3$) δ 8.03, 7.46 (each d, J = 8.0 Hz, 2H, ArH), 5.81 (m, 1H, =CH), 4.95 (m, 2H, $=CH_2$), 4.62 (s, 2H, CH_2), 4.32 (t, J = 6.6 Hz, 2H, CH_2), 4.03 (q, J = 7.2 Hz, 2H, CH_2), and 1.76 (br, 12H, CH_2). ^{13}C NMR ($CDCl_3$) δ 166.17, 142.12, 139.22, 130.51, 129.99, 128.46, 114.15, 77.03, 65.23, 45.42, 29.47, 29.41, 29.26, 29.11, 28.93, 28.71, and 26.03. Mass Spectrum (EI) m/z 323.

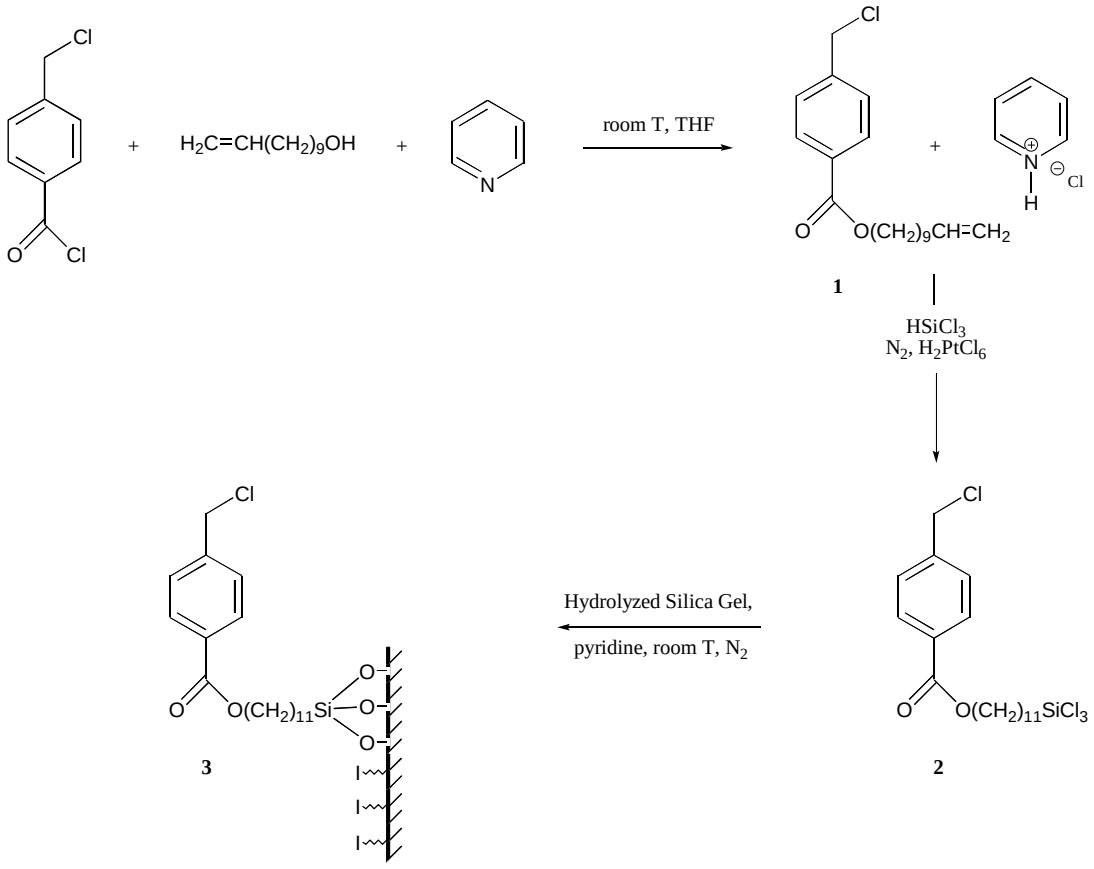
*I.1.6.2.2 Synthesis of ω-trichlorosilylundecyl p-chloromethyl-benzoate (**2**).* [51]

A 1:1 ethanol/ethyl ether solution of chloroplatinic acid, H_2PtCl_6 (30 mg, 1 mL), was added to the alkene **1** (3.00 g, 9 mmol) in trichlorosilane (30 mL , 298 mmol) and the reaction mixture stirred at room temperature under nitrogen for 20 hours. Excess trichlorosilane was then removed under reduced pressure (Scheme 6). ^{1}H NMR ($CDCl_3$) δ 8.04, 7.46 (each d, J = 8.4 Hz, 2H, ArH), 4.61 (s, 2H, CH_2Cl), 4.32 (t, J = 6.8 Hz, 2H, OCH_2), 1.77 (q, J = 6.8 Hz, 2H, CH_2), and 1.56-1.22 (m, 18H, CH_2). ^{13}C NMR ($CDCl_3$) δ 166.19, 142.14, 130.49, 129.99, 128.47, 65.29, 45.41, 31.81, 29.50, 29.48, 29.33, 29.26, 29.00, 28.71, 26.02, 24.32, and 22.26.

I.1.6.2.3 Attachment of Initiating Sites to Silica Gel Surface. [51]

The silica gel used below, purchased from Aldrich, has a mean particle diameter of 58 Å (5.8 nm) and a specific surface area of 155 m^2 / g . To hydrolyze its surface, a suspension of silica gel in concentrated nitric acid was heated at reflux for 12 hours before being washed with copious amounts of water. The gel was then allowed to dry at 102 ^oC for 36 hours. 5 grams of the treated silica was added to unpurified **2** in THF and

Scheme 6. Synthesis of Surface Grafted 1-Phenylethyl Chloride Ester **3** Initiators.

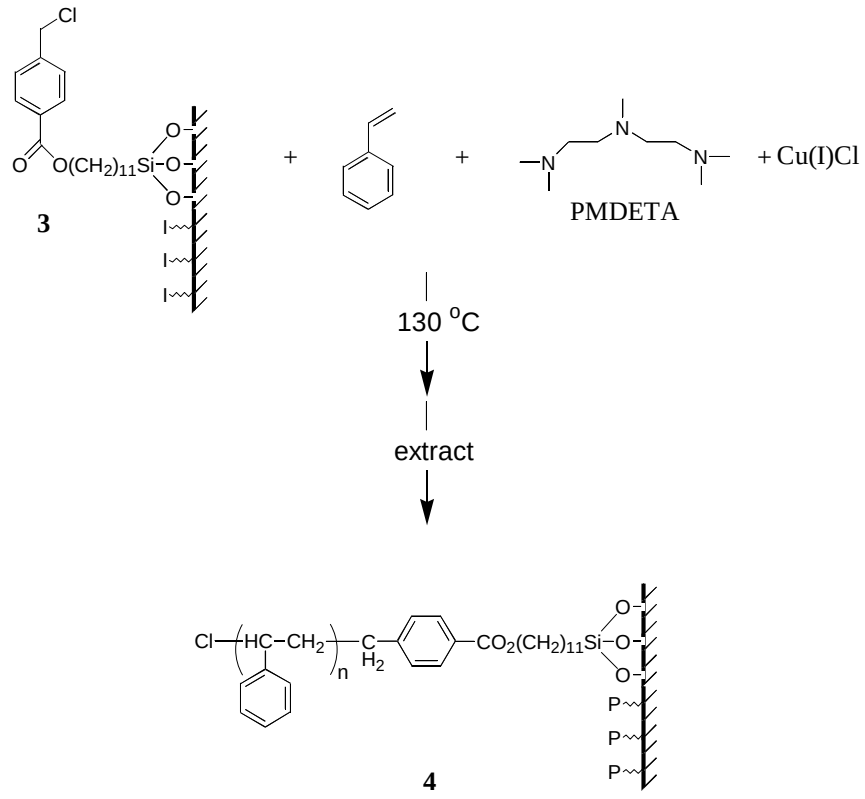


pyridine (3.0 mL, 37 mmol) and stirred at room temperature under nitrogen for 12 hours (Scheme 6). The gel was then filtered, washed successively by THF, H_2O, MeOH, CH_2Cl_2, stirred in THF at room temperature for 24 hours, filtered again and dried at 65 ^oC for 36 hours to yield 7.5 g of **3**.

I.1.6.2.4 Preparation of Polystyrene Grafts on Silica Gel. [51]

3.0 g of **3** was added to a reaction flask equipped with an Ar inlet, mechanical stirrer, and reflux condenser. Benzyl chloride (12.8 mg, 0.1 mmol), styrene (33.50 g, 322 mmol, vacuum distilled over CaH_2), Cu(I)Cl (0.30 g, 3.0 mmol), and *N,N',N"*-pentamethyldiethylenetriamine (PMDETA) (0.50 g, 3.0 mmol) were added to the flask, the system was flushed thoroughly with Ar, and heated at 130 ± 0.5 ^oC for two hours, according to the literature (Scheme 7). [52] The suspension was then extracted with

Scheme 7. Polymerization of Polystyrene from the Surface of Silica Gel.

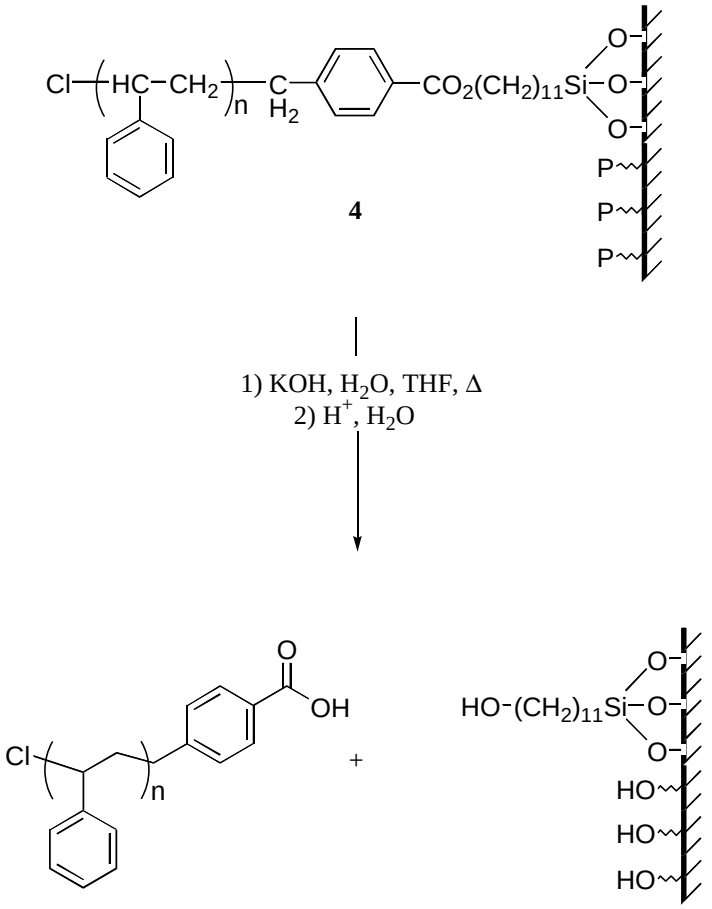


$CHCl_3$ and a portion of the solution removed for workup. The silica grafted polymer **4** was centrifuged and washed multiple times to remove all catalyst residues prior to being placed in a Soxhlet apparatus for five days to afford rigorous extraction via THF of any ungrafted polymer still remaining.

I.1.6.2.5 Cleavage of GraftedPolymer from Silica Surface.

The initiator was designed in such a way that the ester linkage could be readily cleaved under the appropriate conditions to allow characterization of the surface grown polymer. Hence, the grafted polymer was subjected to hydrolysis under basic conditions as shown in Scheme 8: Polystyrene grafted Si gel (277.7 mg) and potassium hydroxide

Scheme 8. Detachment of Surface Constricted Polymer Grafts.



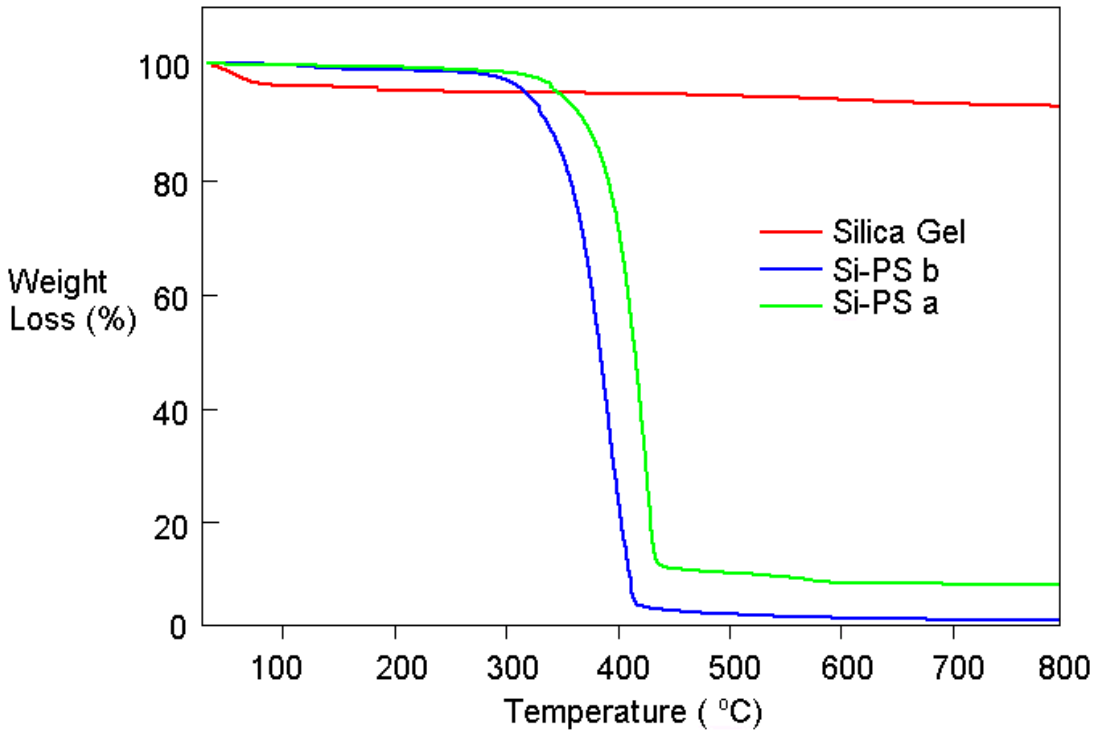
(175.0 mg, 3.12 mmol) were added to approximately 10 mL H_2O in 100 mL tetrahydrofuran and allowed to reflux for 72 hours. Acidic aqueous workup (1 M HCl in H_2O was added to a point where pH = 2, according to pH paper) and extraction of the resultant products with chloroform yielded a high molar mass polymer, which was subsequently precipitated into methanol and analyzed by ^{1}H NMR and GPC.

I.1.6.3 DISCUSSION

According to Scheme 6, **3** was prepared and its labile halide utilized to perform atom transfer radical polymerizations (ATRP) from the surface of silica gel. Analysis of the resultant polymer was afforded by detachment via the hydrolysable ester linkage.

Thermal gravimetric analysis (TGA) of the grafted polystyrene when subjected to a nitrogen atmosphere heat ramp of 10 ^oC per minute between 30 and 800 ^oC shows considerable weight loss beyond 300 ^oC for two specimens, indicating that the samples

Figure 4. TGA of Grafted Polystyrene on Silica.



are 85-90% polystyrene. Following TGA interpretations found in the literature [44], there is a negligible loss of volatile material between the 30 and 200 ^{o}C temperature range in the polystrene graft cases while the virgin silica gel shows ~5 % loss. The absorption of atmospheric water by silica is well documented; [53] adding hydrophobic polystyrene chains to the surface minimizes this event.

Samples of the functionalized silica were hydrolyzed according to Scheme 8. In early trials, low molar mass material was evident on the gel permeation chromatography (GPC) traces; this was attributed to incomplete removal of autopolymerized chains formed in the bulk phase. Subsequent trials used grafted silica gel that had been placed under Soxhlet extraction in THF for a minimum of 48 hours. Purification of the specimens prior to polystyrene cleavage resulted in the identification of a single GPC peak, with polydispersity indices of 1.57 and 1.58 for two different grafted Si samples (see Table 1). Hallensleben and co-workers found PDI's of 1.47 and 1.75 for first and second- generation polystyrene grafts, respectively, polymerized under similar conditions from silica gel, utilizing bipyridine as the solubilizing agent. [44] These results are contrasted with the findings of Hawker et al., in which SFR Polymerized polystyrene grafts show PDIs of 1.14; ATR Polymerized graft PDIs were not reported. [41]

Table 1. GPC Data of Cleaved Polystyrene from Functionalized Silica.

	g St monomer added per g **3**	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI
Si brush A[1]	11.2	89 K	140 K	1.57
Si brush B[2]	52.0	120 K	190 K	1.58

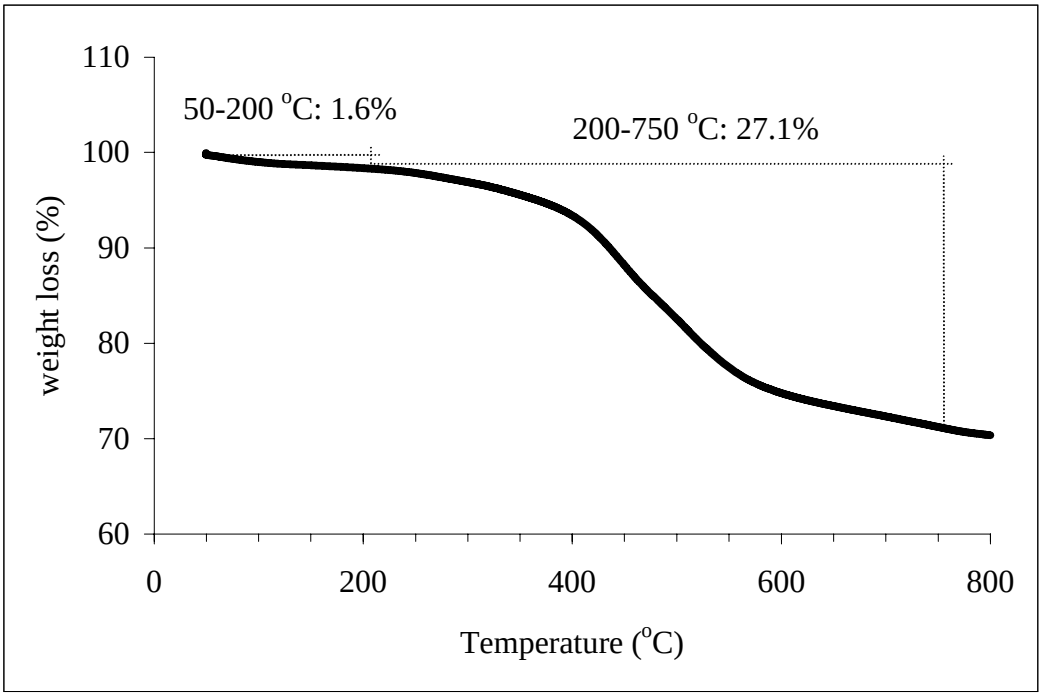
[1] GPC run in $CHCl_3$ using polystyrene standards.

[2] Absolute MW (IR and light scattering) run in THF

The increase in molecular weight distribution of surface bound controlled polymers versus controlled macromolecules grown in the bulk (~1.5 vs. 1.2-1.4) may be indicative of termination by coupling of two surface bound propagating centers. In studying polystyrene grafted Si gel initiated by azo compounds, Prucker and Rühe found that higher propagation temperatures result in a decrease in the average distance between growing chains ends. [42] While the experimenters varied polymerization temperatures between 50 and 90 ^{o}C, [42] the above polymerizations were carried out at 130 ^{o}C. Although the likelihood of coupling in ATRP systems is much less than in the corresponding free radical case, one cannot altogether rule out this possibility.

Also described by Hallensleben et al., TGA analysis of initiator-functionalized silica gel was utilized to determine the density of initiating sites on the surface. Figure 5 describes these results, where 13.2 mg of functionalized silica gel was subjected to the same conditions described for Figure 4. Again according to interpretations found in the

Figure 5. TGA of Initiator-Functionalized Silica Gel **3**.



literature, a small loss of volatile material between 50 and 200 ^{o}C is due to the adsorbed water on the silica gel surface [44, 53]; the remaining loss (27%) may be attributed to the weight of initiator bound to the silica surface[†]. The amount of surface-bound initiator was determined to be 0.84 mmol per gram of Si gel.[‡]

Given a specific surface area of 155 m^2 / g, the initiator density is thus 5.3 μmol / m^2; Hallensleben et al. investigated initiator grafted Si gel with an initiator density of 2.0 umol / m^2. The differences in molecular weight distributions (1.57 vs. Hallensbleben's value of 1.47) between systems may be attributable to initiating density, hinting at termination by two active radical centers.

[†] TGA interpretations are here used specifically to compare published values. Admittedly, the choice of 200 ^{o}C is somewhat arbitrary: H_20 loss may still occur beyond such temperatures.

[‡] Calculated according to the following:

0.271 g initiator per gram SiO_2 / 324 g initiator per mol = 0.837 mmol initiator per gram SiO_2

I.1.6.4 CONCLUSION

Initiator functionalized surfaces allows one to permanently alter performance characteristics of the surface without disrupting the overall properties of the bulk phase. [49] The attachment of ATRP initiators to silica substrates has been demonstrated and subsequent grafting from the surface shown. Molar mass control of such grafted macromolecules differs only slightly from the bulk phase, thus substrate thickness can be reliably predicted and performance characteristics varied accordingly. While it has been stated that it is very difficult to control the grafting density of initiator, [46] only a handful of studies exist which describe the grafting density of tethered polymeric initiating groups. [39, 42, 44] Even then, the available discussions refer to different tethered initiating groups. Typically, TGA, DSC, and elemental analysis are applied to ascertain grafting density. It is important that future workers investigate the role of tri- versus uni-functional tethering and establish theories based on the reproducibility and control of each. Additional work must be done to describe the mode of propagation and termination at the surface, taking note of the influence of temperature on neighboring latent initiating site separation distances.

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[6] Such termination routes include disproportionation and coupling. Typical free radical chain polymerizations show polydispersities in the range 2-5, while theoretical calculations show that the limiting polydispersity is 1.5.

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