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Development of a Tunable Platform for the Study of Geomacromolecular Matrices Using Controlled Radical Polymerization

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DEVELOPMENT OF A TUNABLE PLATFORM FOR THE STUDY OF GEOMACROMOLECULAR MATRICES USING CONTROLLED RADICAL POLYMERIZATION

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
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in partial fulfillment of the
requirements for the degree of
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in

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by
Arjun Pandey
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December 2019

To my family
Father Lalmani Pandey
Mother Subhadra Pandey
Uncle Chetnarayan Pandey
Sisters Amrita and Asha Pandey

Acknowledgements

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List of Abbreviations

ACs	Agricultural Chemicals
ARGET	Activators regenerated by electron transfer
ATRP	Atom transfer radical polymerization
CP	Cross-polarization
CRP	Controlled radical polymerization
Cs	Concentration of sorbate present in the sorbent (mg/kg)
RP	Controlled radical Polymerization
DP	Degree of polymerization
DTRP	Degenerative transfer radical polymerization
ESS	Engineered Soil Surrogates
GHG	Greenhouse gases
HOCs	Hydrophobic organic compounds
Gt	Gigaton
ICAR	Initiators for continuous activator regeneration
K_{ATRP}	ATRP equilibrium constant
K_d	Distribution coefficient (L/kg)
K_F	Freundlich affinity coefficient $(kg/L)^{-N}$
K_{OC}	Organic content normalized distribution coefficient (L/kg)
k_p	Propagation rate constant
k_t	Rate of termination
ITRP	Iodine transfer radical polymerization
MALDI-TOF	Matrix Assisted Laser Desorption/Ionization Time of Flight
MAA	Methacrylic acid
MAS	Magic Angle Spinning
MMA	Methylmethacrylate
MW	Molecular weight
[M]/[I]	Concentration of (monomer to initiator) ratio

MONT	Montmorillonite
N	Sorption linearity
NMR	Nuclear Magnetic Resonance
NOR	Norflurazon
OECD	Organization for economic cooperation and development
Olig	Oligomer
PAS	Poly (4-acetoxystyrene)
PASH	Poly (4-acetoxystyrene) hydrolyzed
PAMS	Poly (4-acetoxy-3-methoxy styrene)
PAMSH	Poly (4-acetoxy-3-methoxy styrene) hydrolyzed
PDI	Polydispersity Index
PMAA	Poly(methylacrylic acid)
PMDETA	N,N,N′,N″,N″-pentamethyldiethylenetriamine
PMMA	Poly(methylmethacrylate)
PS	Polystyrene
RAFT	Reversible addition−fragmentation chain-transfer polymerization
RDRP	Reversible deactivation radical polymerization
SI	Surface initiated
SMRP	Stable radical mediated polymerization
SOC	Soil Organic Carbon
SOM	Soil Organic Matter
SOR	Sorption
TGA	Thermogravimetric analysis
TOF	Total organic fraction
XPS	X-ray photoelectron spectroscopy

Abstract

Soil is an important environmental component, and the study of soil processes have many practical implications such as improvement in agriculture, mitigation of climate change etc. The widespread use of Agricultural Chemicals (ACs) in modern agriculture has resulted in adverse effects in environment and human health mostly through contamination into food and water sources. Study of fate, bioavailability, and transport of ACs involves molecular level understanding of their interactions with soil. This can be challenging due to complex and heterogeneous nature of soil. One common approach used is the correlation of macroscopic properties of soil, (e.g. sorption) with empirical parameters such as carbon content, elemental ratios etc. While these metrics provide insight into important soil characteristics, the results are not sufficient to elucidate in-depth molecular level interactions of soil with ACs. Several attempts to synthesize artificial test soil substrates have been proposed to overcome this limitation. However, the exact composition of these "artificial soils" are also ill-defined as they use organic components from plant derived materials. This work demonstrates the design and synthesis of Engineered Soil Surrogates (ESSs) using controlled radical polymerization for use in study of geomacromolecular processes including sorption of ACs into the soil. The initial design of ESSs consisted of SiO_2 as an inorganic matrix tethered with multi-block oligomers containing alky (tier-1), O-aryl (tier-2) and polar (tier-3) blocks carefully selected to *echo* hydrophobic, aromatic and hydrophilic components of the Soil Organic Matter (SOM) respectively. A series ESSs of increasing complexity were used in concert with sorption isotherm data obtained by batch mode experiments using Norflurazon (NOR) as a model AC. As the polarity of the second tier increased, the ability of the ESS to sorb NOR decreased, as was the case when a polar third tier was added, pointing to a largely hydrophobic driving force for NOR adsorption to the ESSs. Hydrogen bonding, pi-stacking, confirmation and hydration were also shown to influence binding of NOR to ESS.

Additionally, the results from isotherm based sorption studies of ESS are compared with that of chemically modified real soil in a quest to develop realistic soil model.

Chapter 1. Introduction to Soil and Its Sorption properties

1.1 Soil

Soil is an abundant natural resource with enormous economic and environmental significance. FAO food balance sheets show that more than 99.7% of human food calories come from terrestrial environment.[1] The world population is increasing at an alarming rate; doubling to 7.3 billion between 1960 and 2010.[2] By 2050, the population in projected to be about 9-10 billion and the food demand is expected to rise from 50-90%.[3] The increasing population puts an additional stress on the available land affecting the amount and quality of available soil. The amount of available land decreased from 7.91 to 5.15 and then to 2.02 hectares per capita from year 1900 to 1950 and 2005 respectively.[2] The conversion of natural lands to croplands, pastures, urban areas, reservoirs, and other anthropogenic landscapes represents the most visible and pervasive form of human impact on the environment.[4] In 2002, roughly 40% of Earth's land surface was under agriculture, and 85% had some level of anthropogenic influence.[5] Almost 50% of all potentially vegetated land surface globally has been converted to croplands, pastures and rangelands.[6-9]

Soil is complex mixture of minerals, water, air, organic matter, and countless organisms that live on decaying remains of once-living things.[10] The typical soil consists of approximately 45% minerals, 5% organic matter, 20-30% water, and 20-30% air.[11] The mineral portion of the soil is formed by the weathering of rocks while Soil organic matter (SOM) comes from decomposition of living entities that are recycled by numerous micro-organisms. Plants intake the nutrients formed by degradation of organic compounds which subsequently gets passed to animals and then released back to the soil through decomposition. Globally, SOM is estimated to contain two-thirds of the global terrestrial carbon storage and is critical for maintaining soil fertility and

long-term agricultural sustainability.[12] As a ubiquitous natural resource and an important ecological component, there is an enormous interest in soil for a) sustainable agriculture and b) combating climate change.

1.1.1. Sustainable agriculture

Human use and management of soil and water resources have shaped the development, persistence, decline, and regeneration of human civilizations that are sustained by agriculture.[13-15] The evolution of human societies is closely intertwined with the evolution of agricultural practices since the adoption of agrarian lifestyle sometime between 10000 and 12000 years ago.[16-18] The optimum utilization of soil for sustainable and environmental friendly agriculture requires knowledge of the composition and transformation of the components that make up the soil.

In the natural forest ecosystem where the nutrients on the soil are absorbed by plants and recycled upon decomposition, the soil composition remains relatively unaltered for years. However, in the agriculture ecosystem, the nutrients, especially the macronutrients (N, P and K) need to be replenished as the biomass produced are removed from soil for harvest. This leads to continuous change in the composition of soil over time which can lead to decreased productivity if proper soil amendment techniques are not applied. The nutrients in the soil are recycled through a complex nutrient cycle that involves a range of physical, chemical and biological processes; and the maintenance of healthy soil needs optimization of the relative amounts of essential ingredients to the soil. Ideal soils for agriculture are balanced in contributions from mineral components, soil organic matter (SOM), air, and water. The balanced contributions of these components allow for water retention and drainage, oxygen in the root zone, nutrients to facilitate crop growth; and they provide physical support for plants. The distribution of these soil components in a particular soil is influenced by the five factors of soil formation: parent material, time, climate, organisms, and

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topography.[19] With molecular level understanding of soil, the efficacy of the traditional soil amendment techniques can be increased. Also, use novel humic acid based carbon materials have prepared by pyrolysis techniques such as biochar and black carbon etc. have proven useful in not only for increased productivity of soil but also in prevention of leaching of herbicides into groundwater and reduction of anthropogenic emission of CO_2 into the atmosphere.[20-22]

1.1.2. Combating climate change

The Earth's climate is directly dependent on the composition of the atmosphere, especially the amount of greenhouse gases (GHG) in the atmosphere. Because GHG absorb infrared radiation, an increased concentration of GHG in the Earth's atmosphere is linked to a global increase in temperature. This is turn, affects global climate such as rainfall, air pressure etc. with potential for catastrophic damage through floods, storms, hurricane, wildfire etc.[23-24] Greenhouse gases such as CO_2, CH_4, N_2O, O_3 and H_2O are produced by both natural processes and human activities, whereas chlorofluorocarbons are produced by human activity for use as cleaning agents, refrigerants and electric insulators. Carbon dioxide and methane are the primary contributors to global warming caused by human activity; methane being roughly 25 times more potent GHG per mass than carbon dioxide.[24-25]Annual GHG emissions are estimated to be 10 billion tons (10 GT), 15% of which comes from land-use changes, while the majority is attributed to fossil fuel use and production.[26-27]

Until the beginning of the industrial revolution in 18th century, the reported concentrations of CO_2 and CH_4 had never exceeded approximately 280 ppm and 790 ppb respectively. Current concentrations of CO_2 are about 390 ppm and CH_4 levels exceed 1,770 ppb. Both numbers are much higher than at any time during the last 650,000 years. This increase in CO_2 content in the atmosphere has led to about 0.3 - 0.6 °C increase in global temperature in recent years. [23]At present,

GHG are estimated to be at the level of 430 ppm carbon dioxide equivalent .[24, 28] It is predicted that in the year 2050, the global temperature rise may be as high as to 7.5 °C, if current trends and practices are continued.[23] In addition, the increased temperature leads to more production of greenhouse gas through a feedback loop exacerbating the already existing climate change. A 26-year-long soil warming study in a hardwood forest found that warming temperatures could spur recurring pulses of carbon dioxide emissions from soils. In order to limit a global increase in temperature to a conservative 2 - 2.4 °C, in order to keep the planet from the most detrimental effects of climate change, the GHG in the atmosphere should not exceed 490 ppm CO_2. [24, 27]

The global soil carbon pool of 2500 gigatons (Gt) includes about 1550 Gt of soil organic carbon and 950 Gt of soil inorganic carbon(SOC). The soil C pool is 3.3 times the size of the atmospheric pool (760 Gt) and 4.5 times the size of the biotic pool (560 Gt). The SOC pool to 1-m depth ranges from 30 tons/ha in arid climates to 800 tons/ha in organic soils in cold regions, and a predominant range of 50 to 150 tons/ha.[29] This creates an enormous potential for use of soil in mitigating climate change by storing atmospheric CO_2 and other greenhouse gases in soil, and preventing the escape of carbon as potent greenhouse gases. Even a small shift in the carbon pool from atmosphere to soil per specific area can have a profound effect because soil is an abundant resource. With proper management of global croplands, there is a potential to store an additional 1.85 Gt of carbon each year; which equals to the amount of carbon emission from global transportation sector.[9] With a proper understanding of the carbon sequesterion process in soil, SOM could play an important role in mitigating the increased levels of GHG in atmosphere and their adverse effects because SOM serves both as a carbon source and carbon sink.

1.1.3. Inorganic matrix in soil

The mineral component of the soil is produced from weathering of rocks over several years. This can be roughly classified as sand (0.05–2 mm), silt (0.002–0.05 mm) and clay (< 0.002 mm) based on the particle size; the relative amounts of each component determines the overall soil texture. Chemically, the mineral portion of soil is predominantly composed of silicates while oxides, carbonates and sulfates etc. are also found in smaller amounts.[30] Because of the small particle size and complex porous structure with high specific surface area that allows strong physical and chemical interactions among themselves and with dissolved species, clay particles play a major role in the sorption of nutrients and agricultural chemicals (AC) in soil. The nature of interactions includes electrostatic attractive and repulsive forces, hydrophilic and hydrophobic interactions and specific cation exchange reactions.[31] Layer charge, type of exchangeable cation and the sizes of the clay mineral particles are the most important clay mineral parameters that determine the surface chemistry. For the sorbate molecules on clay, the size, shape, charge and hydrophobic/hydrophilic character are the dominant factors.[32]

Clay minerals are organized into sheets of silicates and aluminates that form a three dimensional structures with repeating pattern. Silicates and aluminate sheets stacks upon each other to form layers. The nature of stacking of sheets determine the rigidity, wettability and types of molecules present in between the layers. For example, stacking of silicate and aluminate ratio 1:1 layer does not contain water molecules, and hence only slightly swell upon wetting. Clays with silicates to aluminates ratio 2:1 accommodate water and metal cations sandwiched between layered units. Layer silicate clays are primarily negatively charged because their stacks of aluminum-oxygen and silicon-oxygen sheets are often chemically substituted by ions of lower valance. In many soils, they represent the largest source of negative charge. Metal-(oxyhydr)oxides

are variably charged because their surfaces become hydroxylated when exposed to water[33] and assume anionic, neutral, or cationic forms based on the degree of protonation, which varies as a function of solution pH. Thus, these variably charged minerals adopt a net positive surface charge at low pH and a net negative surface charge at high pH.[34-35] Inner spheres of clay contain layers of sheets of Al-O or Si-O bonds as repeating backbone structures which are negatively charged and often complexes with metal cations. Through cation exchange, the physical properties of clay can be altered, especially the surface charge. Outer sphere contains hydroxy groups as the water molecules first physically adsorb to surface and then react to convert Si-O-Si or Al-O-Al bonds to Si-OH or Al-OH.[31, 36-37] Figure 1.1 shows a diagrammatic sketch of sodium enriched montmorillonite clay with stacked layers to form sheets and sodium cations in between two sheets.
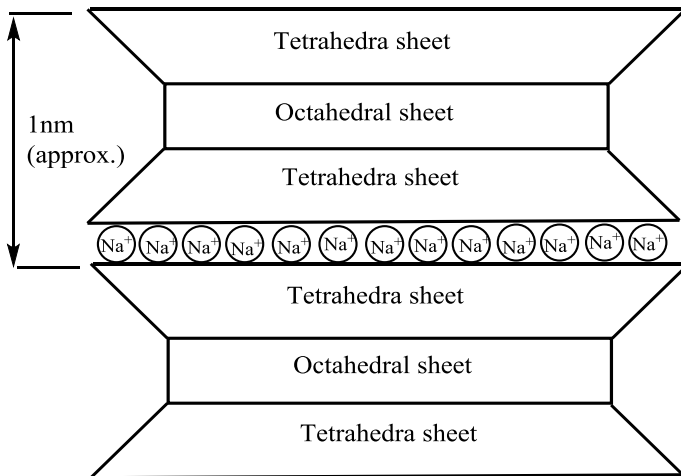
Figure 1.1. Illustrative structure of sodium enriched montmorillonite with closely packed tetrahedral and octahedral sheets with exchangeable Na^+ ions in between the stacked sheets.

1.1.4. Soil Organic Matter (SOM)

SOM is composed plant and animal residues at various stage of decomposition; vegetal source being the primary contributor. Residues of plant polysaccharides, fats, lignin etc. are rich in soil and their relative abundance gives characteristic properties to the soil. Sugars represent the majority of organic compounds in the biosphere because they are the basic components of all polysaccharides: cellulose, hemicellulose (polyoses), starch, pectin, fructanes, and glucanes as well as chitin.[38] Since polysaccharides make up about 50-70% of dry mass of the plants, they are the most important source of organic carbon in soil.[39] Cuticle, a water- impervious protective layer found in the epidermis of higher plants is composed of cutin is the most abundant lipid polyester in vascular plants, and is composed of glycerol and C_{16}-C_{18} inter-esterified fatty acid derivatives, such as hydroxy and hydroxy-epoxy substituted fatty acids.[40] Lignin forms important structural materials in the support tissues of vascular tissues such as cell wall of wood and bark and their structure consists of aromatic rings with -OH and -OCH_3 substitutions, linked by various strong covalent bonds (alkyl-aryl ether and C-C). Lignin is the biggest contributor of aromatic moieties as a plant component in terrestrial ecosystems and represents approximately 20% dry mass of plant litter input into soils.[38, 41] In higher plants, lignins are chemically connected to cellulose and hemicellulose in the cellulosic fiber walls, providing strength and rigidity to the plant structures as well as resistance to the biodegradation of carbohydrates and to environmental stresses.[42-44]

Organic compounds derived from plants, animals, and microorganisms undergo a continuous state of chemical transformation via many possible routes such as catalysis by light, enzymes, and mineral surfaces etc. known as humification. All living things have a mechanism (for eg. cell membrane in animals, cell wall in plants, cuticle layers in leaves of plants) that serve to compartmentalize their body structures to prevent water from dissolving away the structural

features and essential chemicals. The flow of water in and out of living systems is regulated through features such as semipermeable membrane. Once the body of living systems make its way into the soil after death, the hydrophilic barriers are gradually decomposed by microorganisms. Decomposers in aerobic soils utilize oxygen, a strong electron acceptor to introduce functional groups such as -OH or -COOH into hydrocarbons through oxidation, thereby increasing the polarity of SOM. As the polarity increases, hydrophobic organic compounds gradually transform to amphiphilic compounds; the magnitude of which depends on the extent of oxidation. Although it is practically impossible to determine exact chemical structures and their amounts in the soil, the functional groups and their relative abundance can be determined by wet-lab and spectroscopic methods.[45] These analyses suggest that SOM contains a multitude of reactive sites such as ionizable alcohols and phenols (-OH), carboxylic acids (-COOH), thiols (-SH) and amino groups (R-NH$_2$), as well as aromatic (-Ar-) and aliphatic [(-CH$_2$-)$_n$] moieties that are the principally un-charged regions of the soil solid phase as illustrated in Figure 1.2.
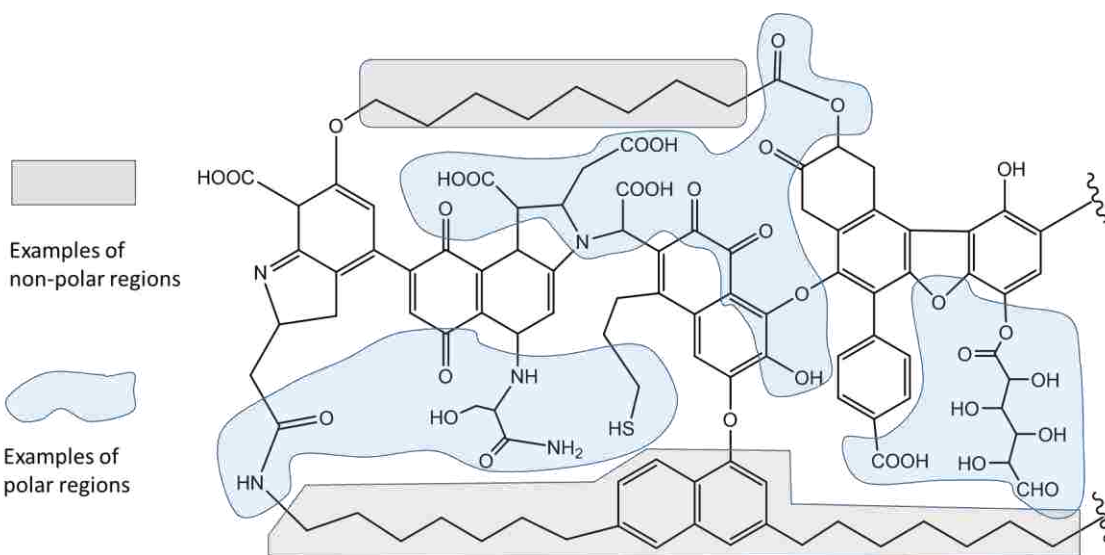
Figure 1.2. Illustrative sketch of chemical structure of humic acid containing aliphatic, aromatic and polar groups.

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Early studies to elucidate the structure of SOM involved base extractions of soil that yields a dark colored material relatively resistant to further chemical treatments. This "recalcitrant" known as humic substances was hypothesized to possess characteristics of the structure of humus, the dark colored decomposed organic matter in soil. Humic substances have been used as a proxy for SOM, and additives for soil amendment. However, there is a debate among scientific community on whether the extraction of soil through alkaline treatment renders soil extract with structure and properties of humus. Various studies have been done to address this hypothesis by subjecting plant-based compounds to reaction conditions that imitate the humification process such as enzymatic/biotic syntheses by polypheoloxidase or tyrosinase treatment of "lignin-like" compounds in a phosphate buffer at neutral pH.[46-47] Similarly, Abiotic/mineral-catalyzed syntheses such as autoxidative reactions of trihydroxyphenols and benzoic acids at pH $\geq$ 6 are shown to form quinones, which link with other phenols, phenol polymers, amino acids or peptides to form macromolecular substances.[48] Recent publications have demonstrated mechanistically the formation of cross-linked polyphenolic materials from simple phenolic monomers such as caffeic acid, coumaric acid and fumaric acid.[49]

Based on evidence thus far, alkaline extractions of soil to some extent imitate the formation of humus from degraded fragments of larger polymers, and small molecules at different stages of humification process. A lot of earlier theories on structure of SOM and its characteristics are influenced by studies performed with humic materials obtained from such extraction process. At alkaline pH >13, all the phenolic OH and carboxyl moieties of the SOM exist in deprotonated anionic state and hence are soluble in aqueous solution. At this pH, lignin moieties are also shown to break down into smaller fragments which can undergo base catalyzed condensation reactions, autoxidative reactions etc. to cross-linked polymer with the constituent building blocks rearranged

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differently than that in the original animal or plant source. This eclectic pool of cross-linked organic compounds obtained from the extraction process cannot be specifically classified into any class of biopolymers or characterized through isolation. However, as an effective solubilization of organic fraction of the soil in aqueous medium, alkaline extraction of soil certainly is a useful approach to separate most organic components from the inorganic matrix and allows more effective characterization of humic materials and SOM.

1.2. Agricultural Chemicals (ACs)

Farmers have been aware of the fact that the nutrients in soil need to be replenished since ancient times and they used manures, decayed plant leaves and animals to increase yields. There are also records of use of sulphur compounds to kill insects by Sumerians as about 4500 years ago.. Pyrethrum, which is derived from dried flowers of Chrysanthemum cinerariaefolium, also known as "Pyrethrum daisies" has been used as an insecticide for over 2000 years. Many inorganic chemicals such as have also been used as pesticides. For example, Bordeaux mixture based on copper sulfate and lime is still used as a fungicide.[51] The rise of ACs has significantly increased in recent years with about 28 billion dollars spent on fertilizers and 15 billion dollars on other agricultural chemicals in US alone in 2013.[52] Although various types of chemicals make their way into soil and subsequently into food and water, the majority of them are ACs as they are widely used around the globe to support global food demand.

Fertilizers provide plants with essential nutrients to growth and replenish the soil with the nutrients once the crops are harvested. Since the end of World War II, there was a significant spike in use of chemical fertilizers in soil, especially the N based fertilizers. This was followed by widespread use of synthetic chemicals supplements as macronutrients (N, P, K fertilizers), secondary nutrients (Ca, Mg, S) and micronutrients (B, Cl, Cu, Fe, MN and Zn). Mineral forms of

N and P fertilizer were widely used to replenish and supplement the essential nutrients in soil which resulted in a significant increase in agricultural production. Howeveron the downside,this form of mineral easily finds its way to surface water which led to eutrophication or algal blooms that kill the aquatic animals by depriving them of dissolved oxygen in water.[53] These days, fertilizers are available in markets as a single nutrient as well as mixture of more than one nutrient.

Pesticides (herbicides, insecticides, fungicides etc.) are chemicals that prevent or mitigate the harm done to crops by weeds and insects. The use of synthetic pesticides accelerated in the 1940s after the discovery of the effects of   chlorinated pesticides such as DDT, BHC, aldrin, dieldrin, endrin, chlordane, 2,4-D etc., with DDT the most widely used pesticide because of its efficacy with broad range of pests. However, in 1947, house flies were found to have developed a resistance to DDT and its adverse effects were seen in the plants and animals.[54] In the 1950s, there was an increased use of these pesticides along with new formulations that lead to increased production and availability of food. In 1962, Rachel Carson highlighted the adverse effects caused by the indiscriminate use of pesticides in her book "Silent Spring" which raised concern over widespread use pesticides and also incited research on environmentally benign pesticides for agricultural use.[55] Subsequent decades saw development of new pesticides and herbicides such as imidazolinone, dinitroanilines, aryloxyphenoxypropionate, cyclohexanediones families including glyphosphate, the world's highest selling herbicide. These new pesticides have been proven to be more environmentally benign and lesser chance of resistance by pests and weeds but there exist several potential risks that could arise because of the improper use of these ACs by farmers and their accumulation in soil and surface water and eventually in ground water through leaching.

Contamination of pesticide chemicals into our food and water as well as the pollution of groundwater causes many short and long term problems. A major risk posed by the use of pesticide

chemicals is that they not only eliminate the target species but also kill or adversely affect the health of other species including plants, animals and human beings. Introduction of harmful pesticides in the aquatic food chain has been shown to adversely affect aquatic organisms manifested by the decreased motility and fertility and increased mortality of those organisms.[56-57] The contamination also adversely affects wildlife through consumption of pollutant directly present on their food and water or through consumption of fish and other aquatic animals.[55, 58-59] The consumption of pesticides contaminated food and water have also been proven to adversely affect human health. For example, halogenated pesticides such as dichlorodiphenyl trichloroethane, atrazine, 2.4-D, trifluralin have been shown to act as endocrine disruptors.[60] Furthermore, the health risk associated with the contamination of human body by pesticides include developmental toxicity, teratogenicity, pregnancy loss, neurologic effects, and disorders on cognitive abilities.[61-65] Most of these health effects are irreversible may be seen for long time in the future, even after these chemicals are no longer in use because of the accumulated pesticide in soil and ground water.

1.3. Sorption of ACs in soil

Sorption is a dynamic relationship between numerous chemicals (eg. ACs), soil and water. Sorption plays a major role in determining the bioavailability, transport and fate of ACs in environment. The functional groups in soil form stable complexes with ions in solution. The outer sphere of soil has water around them and therefore, the complex formed by outer spheres of soils are formed by relatively weak electrostatic interactions and H-bonding and hydrophobic interactions. These types of interactions are rapid, reversible and strongly affected by ionic strength of solution. The inner-sphere complexes sphere is composed of strong ionic or covalent bonds. These interactions take longer to form or break because of the slower nature of interactions as well

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as lower availability of functional groups than outer sphere. The sorbents in soil are comprised mainly of layers of silicate clay, metal ions as oxides and hydroxides and SOM. Variations in the abundance, surface area and chemical composition of these three sorbents significantly influence the sorption characteristics of a given soil.[35]

Water acts as a dynamic media for transport of nutrients in soil and plays a critical role in distribution of hydrophobic, hydrophilic and amphiphilic domains within SOM. Water as a polar solvent surrounds amphiphilic structures where polar domains are situated in the interface and non-polar domains orient themselves in a cluster through hydrophobic interaction to minimize contact with water. The driving force for this process is the increase in entropy of the system through decrease in surface area of SOM and hence the decrease in entrapment of water in a solvation shell around SOM.[50] Other forces such as electrostatic interactions, hydrogen bonding and π-π interactions also determine the confirmation of SOM within soil. Hydration can allow certain polar group in SOM to be available for sorption opening a new binding site. Sorption can also occur through physical entrapment of ACs which is directly dependent on the confirmation of SOM and hence, the extent of hydration. Therefore, the interface of soil and water allows sorption through complex interactions among amphiphilic SOM and polar inorganic surfaces and ACs. Surface functional groups available for sorption determine the characteristics of the interaction such as affinity, equilibrium binding constants etc.

1.4. Methods of sorption studies

Sorption studies are conducted by equilibrating sorbate with sorbent under isothermal conditions and controlled ionic strength and pH. Sorption parameters such as partioning coefficient, binding constant, etc. can be determined through batch mode or flow-through experiments. Batch equilibration method is commonly used by soil scientists because it is

relatively easy and quick process although it is an unrealistic compared to flow or column experiments. The sorbate (soil) is stirred/shaken with sorbent (chemical of interest) until an equilibrium is reached between the sorbent sorbed to soil and that remaining in the solution. The concentration of sorbate in solution is measured using chromatographic/spectroscopic methods such as (HPLC, UV-Vis, NMR) and through mass balance, concentration of sorbed material can be determined. Prior to these measurements, the optimum soil to solution ratio and the required time for sorbate and sorbent to equilibrate are determined. Various protocols are proposed to create uniformity in sorption experiments and the one prescribed by OECD is most commonly used by soil scientists worldwide.[66] For one soil type, the sorption studies are done at a range of sorbent concentrations the sorption process is highly dependent on concentration of sorbent.

The data obtained from sorption experiments can be fitted to sorption models such as Langmuir, Freundlich etc. Although the Freundlich model is purely empirical and does not accurately account for the sorption process in soil, it is widely used among soil scientists to study sorption in soil.[67-71]. Freundlich isotherms give two parameters: K_F and N which provide a mechanistic view of the sorption process. The K_F value also known Freundlich binding parameter describes the sorption capacity. The higher K_F value represents the larger intensity of binding interaction or affinity towards sorbate and sorbent. The N value represents the sorption linearity or the heterogeneity of sorption sites. N values ranges from 0 to 1 and the lesser it deviates from 1, the more linear the sorption is. Linear sorption means the sorption of molecules without any specificity in binding site such the case with octanol-water partitioning of a chemical where the sorbent distributes between the two phases based on the hydrophobicity (or hydrophilicity) of the chemical. In soils, linear sorption is only seen at lower concentration of sorbate or if there is only pure partitioning. Most soils show a non-linear sorption behavior with N values lesser than 1

implicating the role of site-specific binding site filling in addition to linear partitioning between two phases; and hence the presence of heterogenous binding sites.

In this study, isotherms for the binding of ACs to soil are determined using the concentration of sorbate present on the sorbent (C_s) at sorption equilibrium plotted against the concentration of sorbate remaining in the aqueous phase (C_{aq}). The isotherm data was analyzed using two approaches: the distribution coefficient (eq. 1) and the Freundlich isotherm (eq. 3):

$$K_d = \frac{C_s}{C_{aq}} \hspace{5cm} Eq. 1$$

$$K_{oc}^{sor} = K_d^{sor} \cdot \frac{100}{fraction\ of\ organic} \hspace{3cm} Eq. 2$$

The term K_d is known as distribution coefficient and is the ratio of concentration of sorbent on sorbate to the concentration of sorbate in solution and is highly dependent on the nature of sorbent. The higher value of K_d at a sorbate concentration means that sorbent has a greater amount of sorbent adsorbed on sorbent. In most soils, as the hydrophobicity of AC increase, they show increased K_d value as these molecules preferentially interact with and adsorb on SOM than the surrounding aqueous solution. On the contrary, hydrophilic molecules show relatively lower K_d values as they are solvated by water and repelled by the hydrophobic moieties in SOM. K_d can be normalized with respect to the organic carbon fraction (Eq. 2) to give K_{oc}^{sor} representing the dependence of sorbate binding to the amount of organic fraction found in SOM.[72-73]

$$logC_s = logK_F + NlogC_{aq} \hspace{3.5cm} Eq. 3$$

1.5. Engineered natural organic sorbents for environmental applications

The complex and heterogeneous nature of soil makes an objective study of the composition and their interaction with other chemicals challenging. This puts a detailed molecular level understanding of the structure/property relationships that apply to soil studies interfacing state of

the art biochemical and macromolecular fields outside of current capabilities. The currently available studies are based on the characterization of the bulk properties of natural soils and correlation of bulk parameters to the observed behavior through empirical evidence in order to gain insight into the fate and transport (e.g. bioavailability) of organic pollutants in soil such as hydrophobic organic compounds(HOCs) that includes agricultural chemicals (ACs). Initial studies in this area showed that there is a direct correlation between the amount of SOM and the sorption capacity for ACs.[74] Followed by this finding are the studies based on correlation of other parameters such as oxygen content[75] or polarity indices of SOM based on elemental ratios[76-77] on sorption capacity. There are several studies that link the relationship between aromatic content and sorption capacity of HOC[78-80] supported by isotherm based analyses of non-linear and competitive sorption.[81-83] However, similar isotherms have been reported in studies with soil containing highly aliphatic NOM demonstrating the role of aliphatic moieties as well.[84-86] While these studies are very useful in broad categorization of soil and to some extent in the prediction of properties of soil based on bulk characterization, a detailed mechanistic understanding of the molecular level interactions of soil with HOCs is lacking.

In an attempt to create uniformity in soil composition for scientific studies, various artificial soil test substrates have been proposed with simple to complex compositions depending on the nature of the study. One of the most commonly known artificial soil test substrates was proposed by Organization of Economic Cooperation and Development (OECD) in 1984 which specifies soil composition as a mix of 70% industrial sand (fines in the range 50-200 microns), 20% kaolin clay (>30% kaolinite), and 10% organic content which was recommended to be sphagnum peat with pH close to 5.5-6.0.[87] However, there are several reports of artificial soils prepared by the OECD prescribed recipe producing variable results.[88-92] In addition, sphagnum

peat is scarce and completely unavailable in many regions, including the tropics. Several other recipes have been proposed that contain only the most essential components of soil with reduced heterogeneity and biological complexity and have been utilized in several studies such as microbial growth, ecotoxicity etc.[93-94] Most of the proposed artificial soil test substrates lack any control of soil structure or mineral nutrient content, although these two factors are critical for soil functioning.[95] The inorganic matrix can be somewhat accurately replicated but artificial examples of the organic component of soil suffers a large inconsistency in composition and properties due to variation in source of the peat/ humic acid component utilized and hence are not reliable test substrates for critical studies.[96-99]

In this work, a novel platform for the study of environmental processes, with focus on the sorption of hydrophobic pollutants is demonstrated. This platform known as Engineered Soil Surrogates (ESS) are prepared by tethering multi-block oligomers with carefully selected chemical composition onto mesoporous silica. The multi block oligomers are designed to *echo* the structure of SOM and consist of an aliphatic (tier-1), O-aryl (tier-2) and polar (tier-3) blocks as surrogates for hydrophobic, aromatic and polar domains of SOM. A series ESSs of increasing complexity were used in concert with sorption isotherm data obtained by batch mode experiments using Norflurazon (NOR) as a model AC.

1.6. Notes

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Chapter 2. Design and Synthesis of Engineered Soil Surrogates by SI-ATRP and Their Sorption with Agricultural Chemicals

2.1. Design and synthesis of Engineered Soil Surrogates

The primary objective of Engineered Soil Surrogate (ESS) synthesis is to echo the molecular level composition of soil organic matter with simple and well-defined chemical structure in a controlled and scalable manner. For this purpose, the chemical components of building blocks were chosen based on established models of SOM with some generalizations.[27-31] Based on these models, three major classes of chemical moieties, namely alkyl, O-aryl and polar domains were considered as building blocks of SOM. The alkyl components represent hydrophobic domain and the polar groups represent hydrophilic domains. The aryl groups represent both hydrophilic and hydrophobic (amphiphilic) components as their polarities depend on the nature of substituent(s) present on aromatic rings. Another factor to consider is the organization of these domains or components within the ESS based on hydrophilic, hydrophobic and other interactions in aqueous environment that determines the overall ESS architecture. When SOM consisting of hydrophilic, amphiphilic and polar domains is associated with a central mineral particle, the SOM is assumed to rearrange itself forming condensed/glassy inner layer close to the mineral surface and loose/rubbery outer layer away from mineral surface according to polymer based models of SOM.[5-6, 27, 32] The non-polar moieties situate themselves in the interface of mineral/SOM as condensed inner layer in order to minimize contact with water. On the contrary, the polar domains situate themselves on the outside where they can solvate in the outside water shell resulting in a thermodynamically stable confirmation. The stepwise incorporation of the above mentioned components or "tiers" onto a silica particle (illustrated in Figure 2.1) allowed for a systematic study of the role of each component on soil morphology and sorption properties.

The exact chemical structures that serve as a surrogate for each component of SOM were carefully selected to echo the actual structure of soil components. The alkyl groups composed of linear aliphatic chains served as a surrogate for plant lipids such as cuticular materials, one of the major constituents of the non-polar groups in SOM. [33-34] The linear hydrocarbon chain consisting of 6, 12 and 18 carbons were immobilized on silica to give Tier-I ESS (Figure 2.2). On the terminal end of Tier-I ESS was appended a series of oligo(O-aryl) groups of 5-10 units to form Tier-II ESS. The O-aryl groups constituted hydroxy, methoxy and acetyl substituted aromatic rings that were chosen to i)echo the building block of lignin, as this is the major source of aryl moieties in SOM[35-36] ii) vary polarity and iii) examine a range of potential molecular level interactions, including π-π interactions and H-bonding. Finally, an oligomethylmethacrylate and an oligo(methacrylic acid) was appended to the terminal end of Tier-II ESS to give tier-III ESS. The tier-III oligomer chains serve as a surrogate for polar groups such as plant sugars within SOM that represents the majority of dry weight in plant biomass.[37] A series of ESSs with increasing complexity (Figure 2.2) was synthesized for systematic study of the effects of each domains within SOM for sorption of ACs.
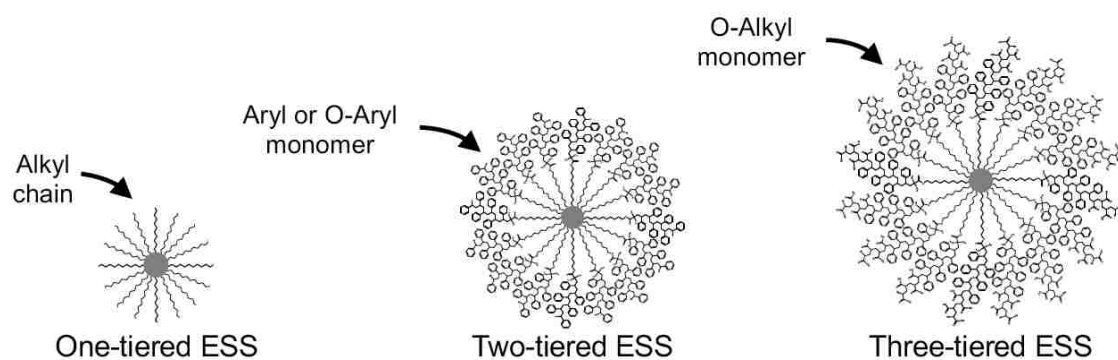
Figure 2.1. An illustrative representative of one, two, and three tired ESSs, starting with a central silica particle.
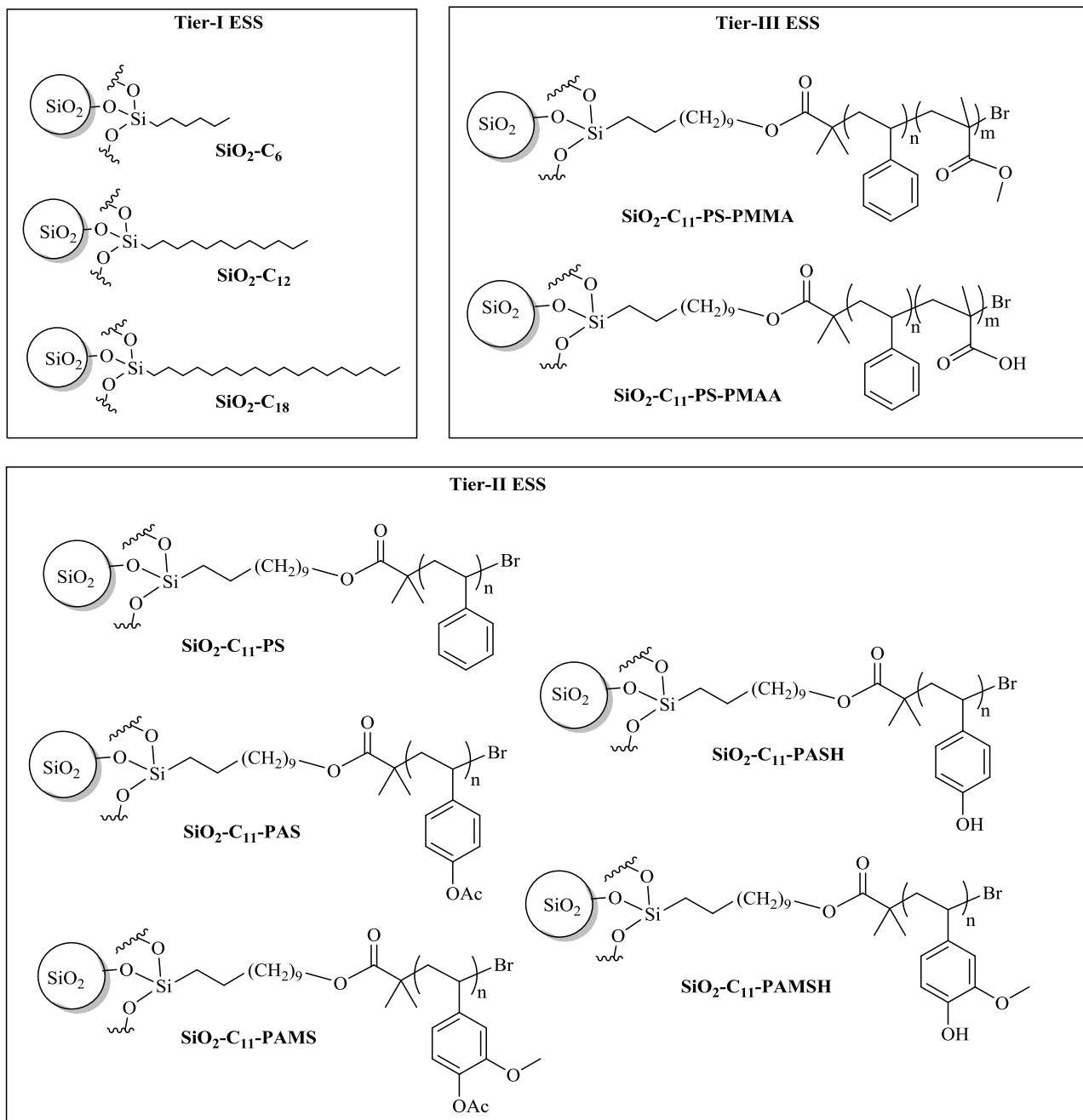
Figure 2.2. Molecular structures of the specific tiers incorporated into the range of ESSs.

2.1.1. Synthesis of Tier-I ESS.

Aliphatic hydrocarbons C_6, C_{12} and C_{18} were immobilized onto silica by a reaction of corresponding hydrocarbons having a trichlorosilyl end group with silica in toluene (as shown in Scheme 2.1) at 90 ℃ for 24 hours followed by a washing step. The resulting ESSs were characterized using thermogravimetric analysis (TGA) and ^{13}C CP-MAS (solid state) NMR.
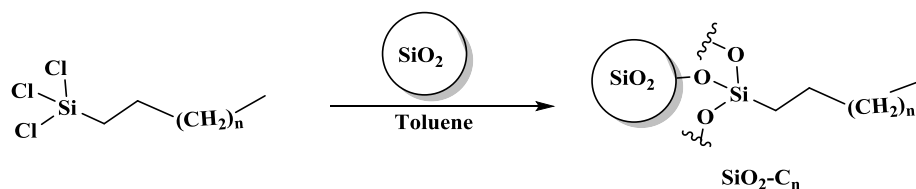
Scheme 2.1. Synthetic route to Tier-I ESS.

2.1.2. Synthesis of Tier-II ESS through polymerization of (O-) aryl monomers.

To extend the Tier-I aliphatic hydrocarbon chain with an oligo aryl and O-aryl chain of 5-10 units, an atom-transfer radical polymerization (SI-ATRP) initiator (2-bromoisobutyryl bromide **2**) was condensed with 10-undecen-1-ol **1** to synthesize 10-undecen-1-yl 2-bromoisobutyrate **3** following a procedure reported previously with slight modification (as shown in scheme 2).[38] The compound 10-undecen-1-ol **1** was chosen because it was the largest commercially available aliphatic compound with alcohol and olefin end groups. The alkene terminus of **3** was converted into a trichlorosilyl end group by Pt catalyzed hydrosilation reaction with trichlorosilane. Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution, also known as Karstedt's catalyst (1 mole %) was used in this reaction leading to quantitative conversion into 11-(2-Bromo-2-methyl)propionyloxy undecyltrichloriosilane **4** verified by disappearance of vinyl proton signals in ^1H NMR (Appendix). Subsequently, **4** was immobilized onto silica by refluxing in toluene. Surface coverage was verified by TGA and XPS (which is sensitive to the surface composition of the particles) and verifies the presence of the C_{11}-Br compound on the surface (Figure 2.3). The

XPS results confirm the attachment of ATRP initiator on the silica particles showing a C1s peak and the C1s/Si2p ratio of 6.54 for a sample with 12.0% TOF, versus the unmodified silica showing only Si2p, Si2s and O1s peaks as expected.
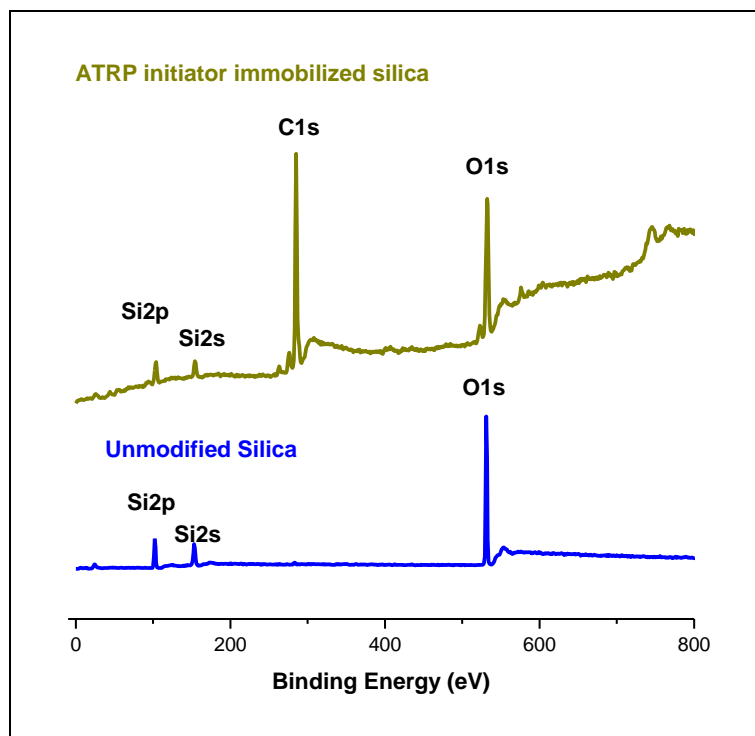
Figure 2.3. XPS of unmodified silica compared to initiator immobilized on silica (**SiO$_2$-C$_{11}$-Br**) (Note: This work was contributed by Balamurugan Subramanian)

In **SiO$_2$-C$_{11}$-Br**, the terminal bromine acts as a site of ATRP polymerization upon extraction by transitional metal catalyst such as Cu(I)Br.[39] The loading of initiator attached to the aliphatic chain on SiO$_2$ can be controlled by adjusting the ratio of 11-(2-Bromo-2-methyl) propionyloxy undecyltrichlorosilane **4** to SiO$_2$ during the grafting process as shown in Scheme 2.2. Figure 2.4 shows the relation between **4**: SiO$_2$ ratio and the amount of loading on silica reported as percentage of total organic fraction (%TOF) measured by TGA. For the systematic study of effects of adding a tier-II of poly(o-aryl) oligomers and subsequent addition of tier-III

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polar oligomer, **SiO₂-C₁₁-Br** with %TOF of 3-5% was targeted to keep the overall % TOF in the

range of 5-25% as in typical soil models.
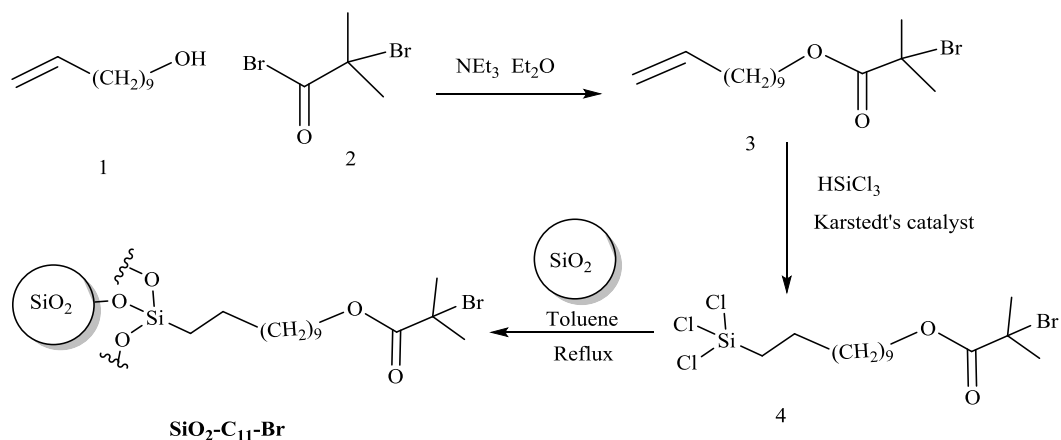
Scheme 2.2. Synthesis of 11-(2-Bromo-2-methyl)propionyloxy undecyltrichloriosilane and subsequent immobilization onto silica particles to synthesize **SiO₂-C₁₁-Br**.
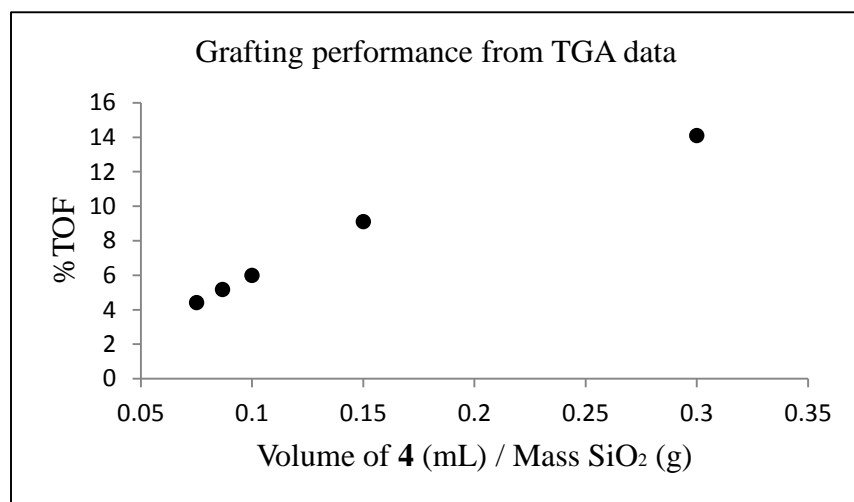
Figure 2.4. Percent loading of the total organic fraction (% TOF) onto SiO₂ as a function of the quantity of reagent 11-(2-Bromo-2-methyl) propionyloxy undecyltrichlorosilane **4**.

Starting with **SiO₂-C₁₁-Br**, SI-ATRP (Scheme 2.3) was employed to polymerize aryl and

O-aryl monomers using Cu(I)Br catalyst and PMDETA ligand to append oligomers of 5-10 units

on Br terminus. ATRP was the method of choice as it is a well-established method of controlled

polymerization, especially with styrene derivatives, and many options were available for surface initiated polymerization in literature to obtain targeted DP and low polydispersity values.[40-43] Styrene polymerized readily in toluene at 90 ºC and the average degree of polymerization (DP_{avg}) was controlled by adjusting the monomer to initiator ratio as shown in figure 2.5. In order to introduce O-aryl groups as second tier, commercially available acetyl protected 4-vinyl phenol monomer was chosen because the phenolic monomers are challenging for ATRP.[44-46] The polymerization of 4-acetoxystyrene required roughly 4 times the monomer concentration and an elevated temperature of 140 ºC which was accomplished using xylene as a solvent. The introduction of O-aryl groups on the aromatic portion was intended to model the structure of lignin which contains cross-linked polyaryl rings with abundant hydroxyl substitutions on aromatic ring. The introduction of polar groups into polyaromatic second tier domain in a sense mimics the humification process in soil that transforms non-polar structural moieties into relatively more polar groups through oxidation processes. To take this even further, acetyl protected 2-methoxy 4-vinyl phenol was used as the monomer of choice for the introduction of methoxy substitution on the aromatic ring next to phenolic –OH groups which provides intermolecular H-bonding and potential polar changes in electron density of the ring. The commercially available monomer 2-methoxy 4-vinylphenol **5** required protection of the phenolic group, using acetic anhydride to form the ATRP compatible monomer 3-methoxy 4-acetoxystyrene **6** (Scheme 2.4).[47] The polymerization of 4-acetoxty 3-methoxystyrene also required roughly 5 times the concentration than styrene and elevated temperature of 140 ºC in xylenes resulting in successful synthesis of O-aryl tier-II ESSs with required DP_{avg}.

Followed by the polymerization of the tier-II block, the acetyl protecting groups were hydrolyzed to expose the phenolic –OH in aromatic rings. The selective hydrolysis of acetyl ester

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was accomplished by stirring Tier-II ESS in hydrazine hydrate ($NH_2.NH_2$) and THF for 12 hrs (Scheme 2.5). The hydrolysis of the acetyl group was confirmed with solid state ^{13}C NMR and TGA. The expected mass loss from hydrolysis matched closely with the observed mass loss with TGA indicating selective and quantitative removal of the acetyl protecting group.
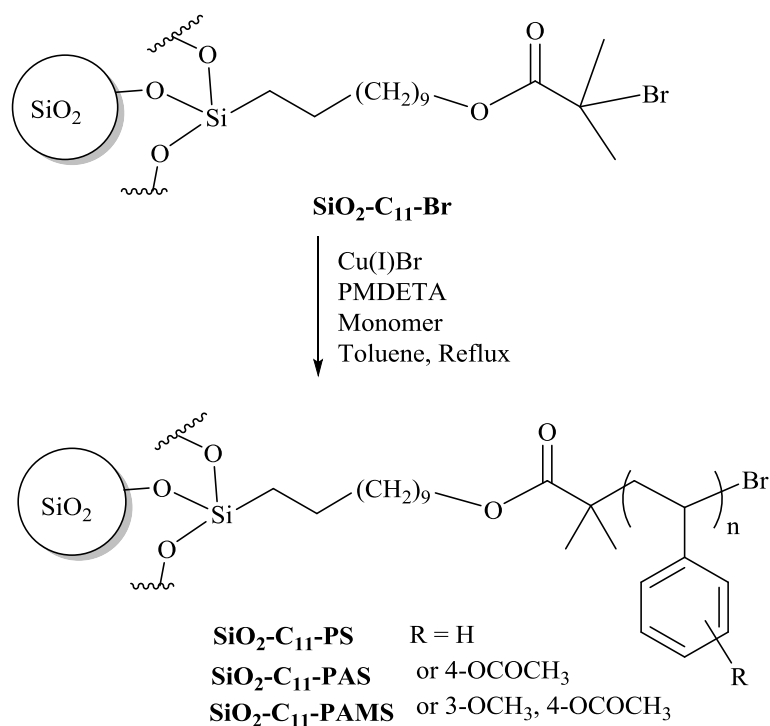
Scheme 2.3. ATRP approach to fabricating Tier-II lignin model structure of natural soil.
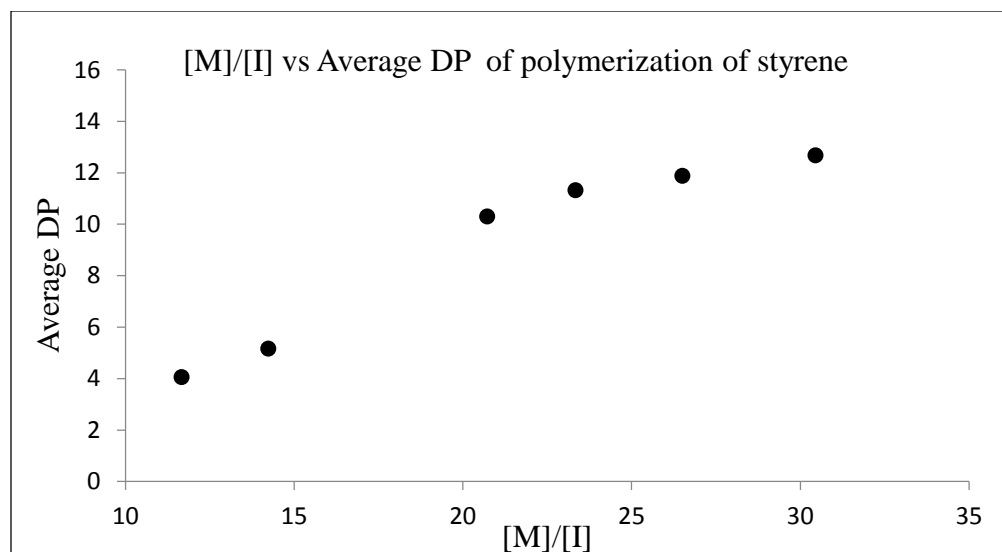
Figure 2.5. Average degree of polymerization (DP$_{avg.}$) of the tier-two oligomeric styrene (in toluene at 90°C for 2 hr) as a function of the ratio of monomer to initiator [M]/[I].
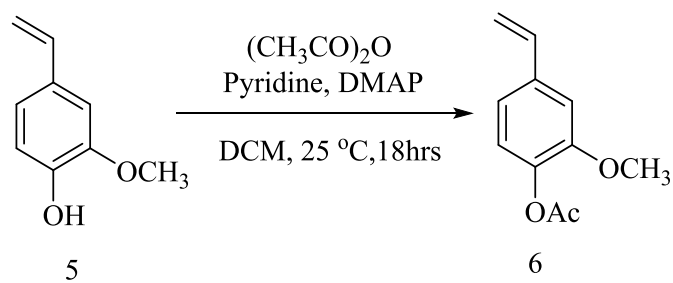
Scheme 2.4. Protection of phenolic group of 2-methoxy 4-vinylphenol **5**.
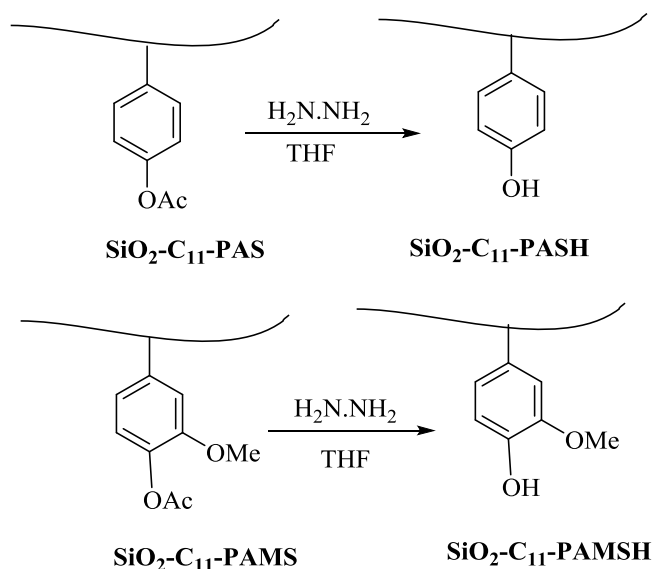
Scheme 2.5. Deprotection of phenolic groups on **ESS6** and **ESS8**.

2.1.3. Synthesis of Tier-III ESS through polymerization of polar monomer.

The third tier of the ESS was envisioned to be a monomer with carboxyl groups to model polar groups in SOM. Although methacrylic acid seemed to be an ideal repeating unit, ATRP of acidic monomers is challenging and therefore, methyl methacrylate was chosen.[44-46] Methyl methacrylate (MMA) was readily available and there are numerous reports of MMA polymerization through SI-ATRP in literature.[40, 48-49] The terminal Br caps the propagating radical at the end of polymerization (as shown in Scheme 2.3) allowing a subsequent polymerization of a second monomer giving the reaction characteristics of a "living polymerization".[39, 50] MMA was polymerized using Toluene at 90 ℃ to yield ESS with a polar third tier as shown in Scheme 2.6. Upon polymerization of MMA, attempts of the hydrolysis of the methyl ester by stirring in NaOH solution and then LiOH solution yielded the desired conversion indicated by solid state ^{13}C NMR but also resulted in the hydrolysis of silica particles apparent from the change of texture from particles to clumped solid. Following a report of selective cleavage of the methyl ester using NaCN/HMPA to convert the carboxylate esters to carboxylic acids, the desired chemical

transformation was achieved indicated by loss of methyl groups by solid state ^{13}C NMR (Figure 2.6) .[51] However, TGA showed more mass loss than expected indicating potential loss of oligomer chains through cleavage of ester located in between 1st and 2nd tier of the oligomer.
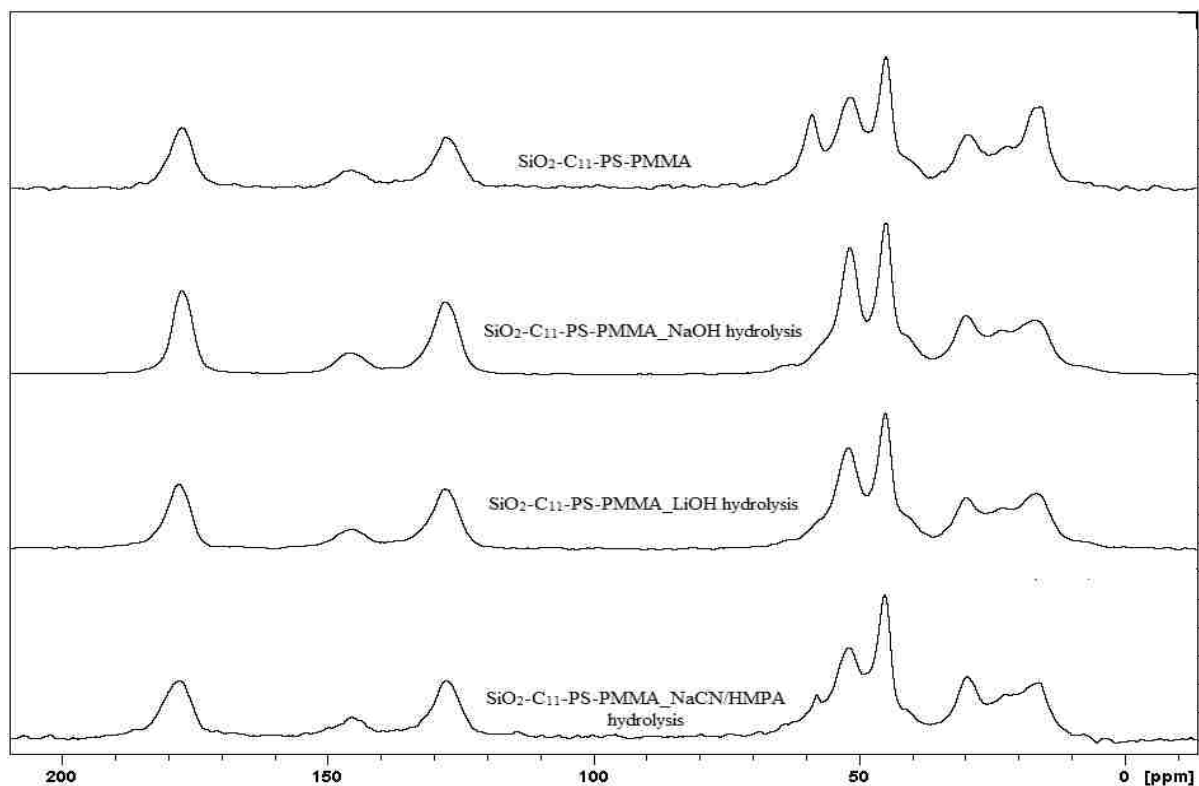
Figure 2.6. ^{13}C solid state NMR of hydrolysis of SiO$_2$-C$_{11}$-PS-PMMA using various approaches.
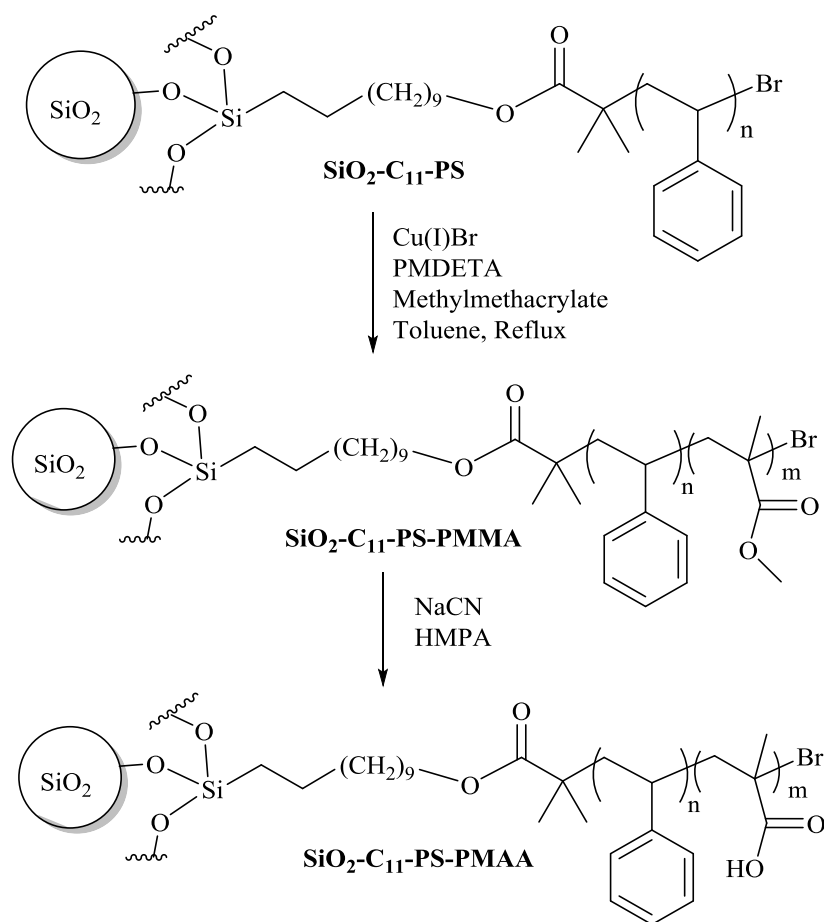
Scheme 2.6. ATRP approach to Tier-III ESS through polymerization of methylmethacrylate followed by conversion to methacrylic acid.

2.1.4. Replacing PMMA with P(t-Butyl)MA as an alternative route to SiO₂-C₁₁-PS-PMAA

As an alternate route to tier-III ESS synthesis with poly(methacrylic acid) as the polar third tier, an oligomeric (t-butyl) methacrylate was appended to tier-II SiO₂-C₁₁-PS using similar ATRP conditions as in PMMA polymerization (Scheme 2.7). Selective hydrolysis of t-butyl ester is shown to proceed under mild conditions with butylene gas as only side product and is therefore popularly used as a protecting group for carboxylic acids.[52-54] Following a report from literature[55], small scale (0.2g ESS material) hydrolysis attempt of SiO₂-C₁₁-PS-(t-But) MA using conc. H₃PO₄ (5eq) in toluene gave the required selective cleavage of t-butyl ester (without hydrolysis of the ester between first and second tier). This was confirmed by ¹³C solid state

NMR (Figure 2.7), and TGA (Appendix N); with the observed %mass loss matching the theoretical % mass loss upon selective hydrolysis. However, with an upscale reaction (2g ESS material), the TGA data on hydrolyzed product showed more % mass loss than expected most likely due to cleavage of the ester between first and second tiers leading to loss of oligomer. Milder conditions such as organic acids or diluted inorganic acid solution is recommended for the selective hydrolysis in larger scale reactions.[56-58]
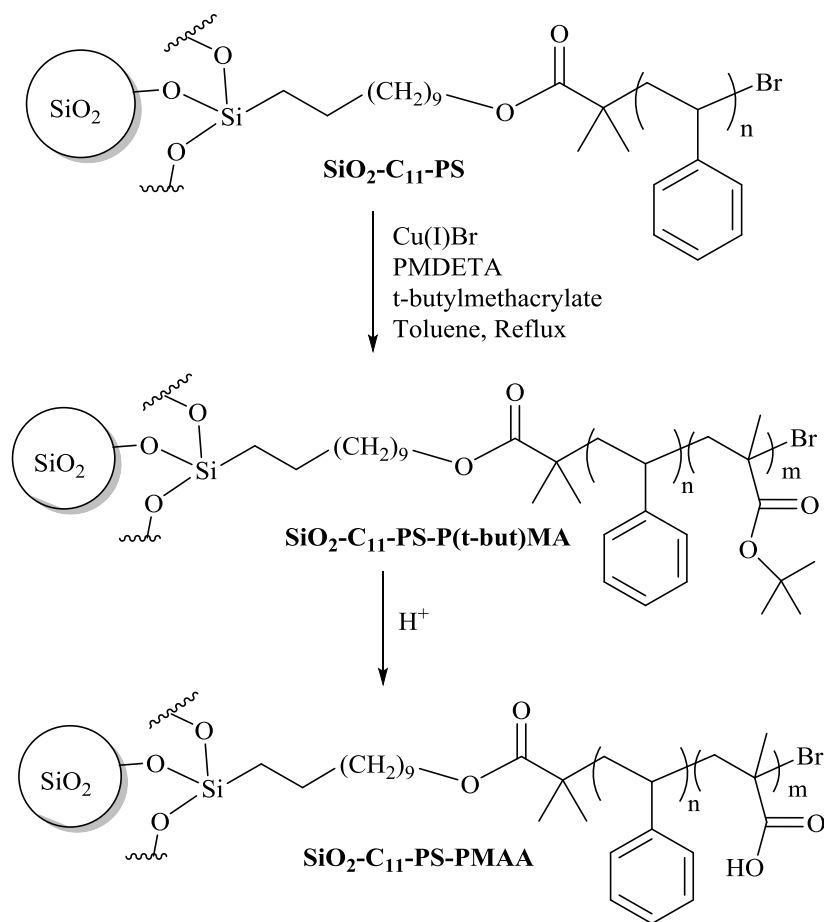
Scheme 2.7. ATRP approach to Tier-III ESS through polymerization of (t-butyl)methacrylate followed by conversion to methacrylic acid.
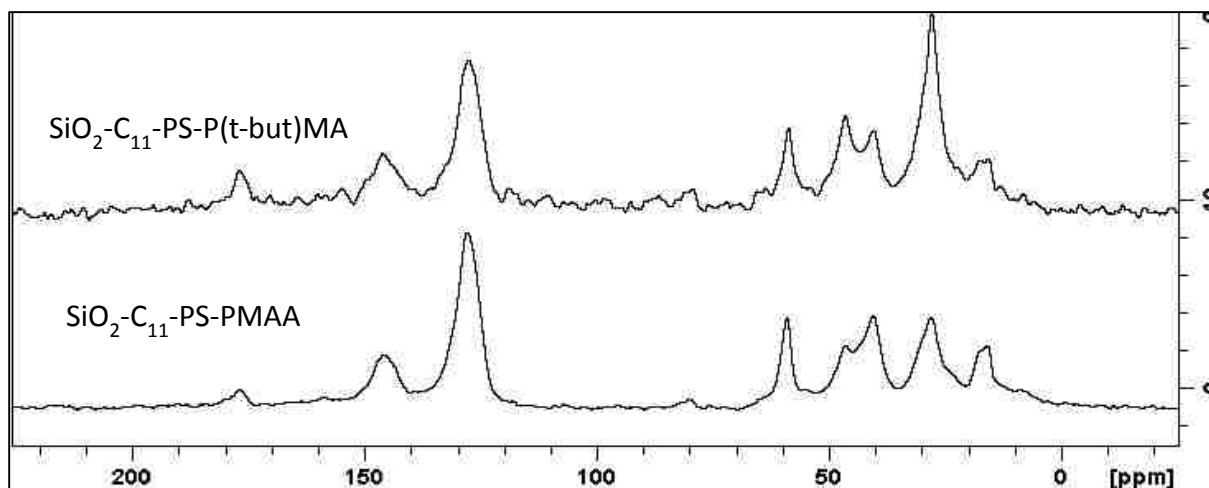
Figure 2.7. ^{13}C solid state NMR of hydrolysis of SiO_2-C_{11}-PS-(t-butyl)MA to give SiO_2-C_{11}-PS-PMAA indicated by the loss of intense peak at around 30 ppm (Note these samples contain EtOH with peaks at 18 and 58 ppm as it was the last solvent in washing step.)

2.2. Physical Characterization of ESSs

The analysis of the synthesized small molecule precursors was done using a Bruker 400MHz ^1H NMR. The analysis of the ESS materials posed a challenge as they were immobilized on solid silica surface. 13C CP-MAS (solid state) NMR proved to be useful in the characterization of ESS materials as it is not only qualitative toward functional group elucidation but also semi-quantitative. The percentage of total organic fraction (%TOF) and average degree of polymerization (DPavg) were calculated using data obtained by thermogravimetric analysis (TGA).

2.2.1. ^{13}C CP-MAS (solid state) NMR

The solid-state NMR analysis employed ^1H-^{13}C cross polarization magic angle spinning (CP-MAS) technique and was performed on an AV 400 MHz Bruker solid-state instrument with sample packed into a 4 or 2.5 mm ZrO_2 rotor. Spectra were acquired using the following parameters: 2048 scans, ramp cross-polarization, contact time of 2 ms, 2.0 s delay between scans; spinning speed of 12-15 kHz, a 120 Hz line broadening function was applied, and referenced to y-glycine -CH_2- signal at 43.5 ppm. XPS data were acquired with a Kratos AXIS 165 system with a

monochromatic AlKα source and a hemispherical electron energy analyzer. The pressure in the analyzing chamber was less than 3×10^{-9} torr. Survey spectra were recorded with 80 eV pass energy and high-resolution elemental spectra were recorded with 40 eV pass energy 150 W X-ray beam power. High-resolution elemental spectra were recorded with 40 eV pass energy. The X-ray beam power used in all spectra collection is 150 W. The reported binding energies were based on the analyzer energy calibration (Au 4f measured at 84.0 eV for all samples). The peaks in the high-resolution elemental spectra were fit using the software supplied with the instrument. A linear background was used for the data processing. Figure 2.8 shows stacked ^{13}C CP-MAS NMR spectra of all three tier examples. The NMR spectra of all ESSs along with small molecule precursors with labelled peaks are included in Appendix 2.
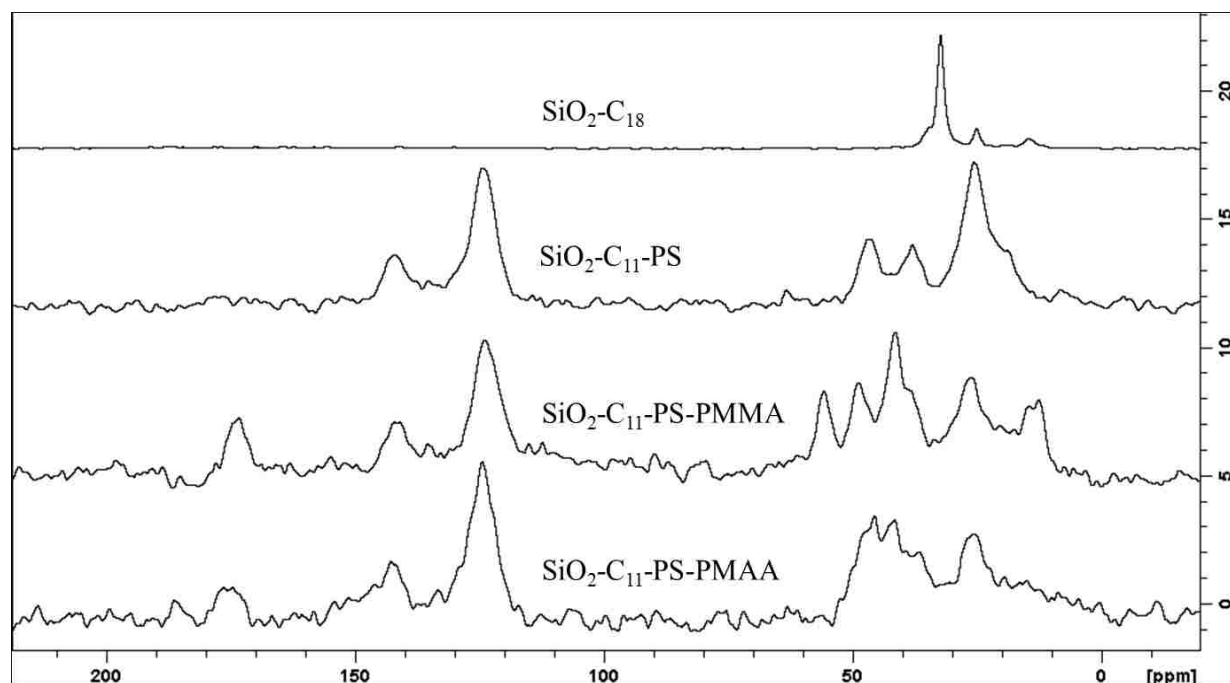
Figure 2.8. Solid State ^{13}C NMR of ESS materials with increasing complexity.

2.2.2. TGA

The TGA analysis was performed on 4 to 8 mg of sample using a TA System TGA 2950 with a ramp temperature of 25°C to 600 °C at 10 °C /minute under nitrogen atmosphere and % mass loss of surface grafted silica was plotted against the temperature. TGAs of **SiO$_2$-C$_{11}$-Br** precursor (Figure 2.9) and ESS materials (Appendix) showed a steep mass loss from around 100 °C to 180 °C followed by little mass loss up to 180 °C and then another steep mass loss up to 600 °C. The initial mass loss from 25 °C to 180 °C was attributed to loss of water and volatile compounds introduced in sample from washing steps and the mass loss above 180 °C to the loss of actual organic matter introduced onto silica through grafting process. The % mass loss of organic content was adjusted by subtracting the %TOF of low boiling point impurities (B.P < 180 °C) followed by subtraction of % organic loss on blank silica as shown in equation 2. Equation 1 demonstrates the %TOF calculation for blank silica before modification heated overnight at 100 °C (**ESS1**) which gives the value 2.13%.
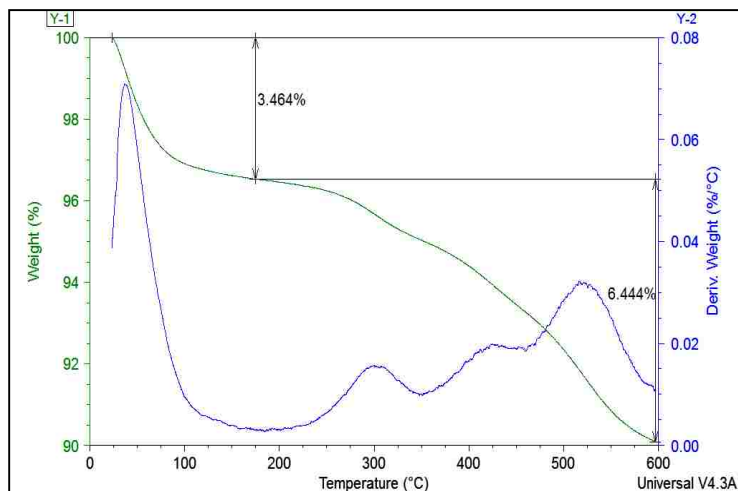
Figure 2.9. TGA thermogram of SiO$_2$-C$_{11}$-Br. The derivative of weight loss (%/°C) plot shows steep mass loss up to 120 °C, no mass loss at 120-220 °C and further mass loss above 220 °C

$$W_{180-600}^{corr}{}^{Silica} = \left(\frac{W_{180-600}{}^{Silica}}{100-W_{25-180}{}^{silica}}\right) = \left(\frac{2.055}{100-3.867}\right) = 0.0213 \qquad Eq.\,1$$

Where,

$W_{180-600}^{corr}{}^{Silica} = W_{180-600}$ corrected by the W_{RT-180} for blank silica (**ESS1**)

$W_{180-600}$ = weight loss (%) from 180-600 °C for **ESS1**

W_{25-180} = weight loss (%) from room temp to 180 °C for **ESS1**

$$W_{180-600}^{corr} = \left(\left(\frac{W_{180-600}}{100-W_{25-180}}\right) - \left(\frac{W_{180-600}{}^{Silica}}{100-W_{25-180}{}^{silica}}\right)\right) \times 100 \qquad Eq.\,2$$

Where,

$W_{180-600}^{corr} = W_{180-600}$ corrected by the W_{RT-180} (ESS organic fraction)

$W_{180-600}$ = weight loss (%) from 180-600 °C for ESS

W_{25-180} = weight loss (%) from room temp to 180 °C for ESS

The % TOF values of **SiO$_2$-C$_{11}$-Br** precursor along with ESS materials after each polymerization were used to quantitatively determine the average degree of polymerization (DP$_{avg}$). The calculation of DP$_{avg}$ for the two and three-tiered ESS is shown below along with a generic equation for nth tier. For DP$_{avg}$. calculations, imagine a solid substrate like SiO$_2$ of mass **S** grafted with initiator functionalized block of mass **I** which initiates a polymerization to add a block of polymer of mass **P**. After grafting of initiator on SiO$_2$ and after each polymerization, TGA data is collected. If S is the mass of an inorganic surface from TGA; and I, P are the masses of organic oligomers on the inorganic surface determined from TGA (e.g. I=aliphatic,

P=Aromatic), we can calculate the dimensionless fraction of organic matter (%TOF) of I, P and Q using equations 3-5 respectively.
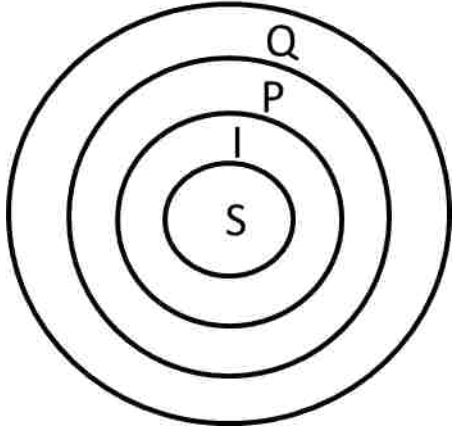
$$A = \frac{I}{I + S}$$

Eq 3

where A is the mass fraction of organic matter after initial grafting onto inorganic matter

$$B = \frac{I + P}{I + P + S}$$

Eq 4

where B is the organic fraction after first polymerization step

$$C = \frac{I + P + Q}{I + P + Q + S}$$

Eq 5

where C is the organic fraction after second polymerization step

A, B and C can be easily determined from TGA data.

Equation 3 can be rewritten as follows.

$$I + S = \frac{I}{A}$$

Eq 6

Equation 4 can be written as follows:

$$I + P + S = \frac{I + P}{B}$$

Eq 7

Substituting equation 6 in equation 4,

$$B = \frac{I + P}{\left(\frac{I}{A}\right) + P}$$

Eq 8

Dividing both numerator and denominator of equation 8 by I, we get

$$B = \frac{\left(1 + \frac{P}{I}\right)}{\frac{1}{A} + \frac{P}{I}}$$

Eq 9

Rearrangement of equation 9 leads to equations 10, 11 and 12.

$$\frac{B}{A} + B\frac{P}{I} = 1 + \frac{P}{I}$$

Eq 10

$$\left(\frac{P}{I}\right)(B - 1) = \frac{A - B}{A}$$

Eq 11

$$\frac{P}{I} = \frac{A - B}{A(B - 1)}$$

Eq 12

The mass I can be written as

$$I = number\ of\ moles\ of\ I * MW\ of\ I$$

Eq 13

Equations 12 and 13 combined give equation 14.

$$\frac{P}{\#moles\ of\ I} = \frac{(A - B)}{A * (B - 1)} * MW\ of\ I$$

Eq 14

The quantity $\frac{P}{\#moles\ of\ I}$ is the average mass of added block P per initiator and dividing it by the

molecular weight of repeating unit gives the degree of polymerization (DP).

Substituting equation 7 in equation 5,

$$C = \frac{I + P + Q}{\frac{I + P}{B} + Q}$$

Eq 15

Dividing both numerator and denominator in equation 15 by I gives equation 16

$$C = \frac{1 + \frac{P}{I} + \frac{Q}{I}}{\frac{(I + P)}{BI} + \frac{Q}{I}}$$

Eq 16

Rearrangement of equation 16 gives equations 17-23.

$$\frac{C(I + P)}{BI} + \frac{CQ}{I} = 1 + \frac{P}{I} + \frac{Q}{I}$$

Eq 17

$$\left(\frac{Q}{I}\right)(C - 1) = 1 + \frac{P}{I} - \frac{CI}{BI} - \frac{CP}{BI}$$

Eq 18

$$\left(\frac{Q}{I}\right)(C - 1) = 1 - \frac{C}{B} + \left(\frac{P}{I}\right)\left(1 - \frac{C}{B}\right)$$

Eq 19

$$\left(\frac{Q}{I}\right)(C - 1) = \left(\frac{(B - C)}{B}\right)\left(1 + \frac{P}{I}\right)$$

Eq 20

$$\frac{Q}{I} = \left(\frac{B - C}{B(C - 1)}\right)\left(1 + \frac{A - B}{A(B - 1)}\right)$$

Eq 21

$$\frac{Q}{I} = \left(\frac{B - C}{B(C - 1)}\right)\left(\frac{AB - A + A - B}{A(B - 1)}\right)$$

Eq 22

$$\frac{Q}{I} = \frac{(B - C)B(A - 1)}{AB(C - 1)(B - 1)}$$

Eq 23

Equations 23 and 13 combined give equation 24.

$$\frac{Q}{\#moles\ of I * MW\ of\ I} = \frac{(B - C)(A - 1)}{A(C - 1)(B - 1)}$$

Eq 24

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$$\frac{Q}{\#moles\ of\ I} = \frac{(B-C)(A-1)}{A(C-1)(B-1)} * MW\ of\ I \qquad\qquad Eq\ 25$$

The quantity $\frac{Q}{\#moles\ of\ I}$ is the mass of polymerized block Q per initiator chain and dividing it by

the molecular weight of repeating unit gives the degree of polymerization (DP). The above

calculation can be done for further tiers to obtain a generic equation for $DP_{avg.}$ calculation for nth

block as follows.

$Avg\ DP\ of\ nth\ tier =$

$$\frac{(W^{corr}_{180-600(n-1)} - W^{corr}_{180-600(n)})(W^{corr}_{180-600(1st\ tier)} - 1)}{W^{corr}_{180-600(1st\ tier)}(W^{corr}_{180-600(n)} - 1)(W^{corr}_{180-600(n-1)} - 1)} * \frac{MW\ of\ the\ first\ tier}{MW\ of\ repeating\ unit\ of\ nth\ block}$$

$$Eq\ 26$$

Where, $W^{corr}_{180-600(n)}$ = corrected weight loss (%) from 180-600 °C after nth tier polymerization

Using the above generic equation 26, the DP_{avg} of the nth tier can be calculated assuming

each initiator leads to a polymer growth without termination. Table 2.1 shows the DP_{avg} of tier-2

and tier-3 ESS along with %TOF and grafting density of all ESS.

Table 2.1. Calculated values of total organic fraction, grafting density and degree of polymerization from TGA analysis of ESS materials.

	Entry	ESS Identifier	%TOF	Graft density* #mmol/g	$DP_{avg.}$ (tier-II)	$DP_{avg.}$ (tier-III)
	ESS1	SiO_2	2.241			
Tier-I	**ESS2**	SiO_2-C6	2.589	0.3040		
	ESS3	SiO_2-C12	4.319	0.2550		
	ESS4	SiO_2-C18	4.972	0.1961		
Tier-II	**ESS5**	SiO_2-C_{11}-PS	15.30	0.1379	8.935	
	ESS6	SiO_2-C_{11}-PAS	18.36	0.1407	7.427	
	ESS7	SiO_2-C_{11}-PAMS	18.50	0.1377	6.524	
	ESS8	SiO_2-C_{11}-PASH	13.94	0.1479	6.001	
	ESS9	SiO_2-C_{11}-PAMSH	17.65	0.1479	7.062	
Tier-III	**ESS10**	SiO_2-C_{11}-PS-PMMA	15.54	0.0892	10.69	5.674
	ESS11	SiO_2-C_{11}-PS-PMAA	9.501	0.0892	(10.69)[‡]	(5.674)[‡]

*Values for the Tier-II and Tier III materials are based on the mmol/g of the C_{11}-Br initiator.
[#] DP: Degree of polymerization
[‡] Based on DP of **ESS10**
(Note: Synthesis of **ESS2-ESS5** was contributed by Benjamin Haywood and **ESS7** by Ghada Abdalla)

2.3. Sorption study of ESS with Norflurazon (NOR)

Following the synthesis and characterization of the ESSs, they were used in sorption studies with a model AC. Norflurazon (Figure 2.10) was employed as a model AC because it is widely applied as a preemergence herbicide to control many annual broadleaf and grass weeds as

brand names Zorial or Evital with 500,000 Kg of Norflurazon applied in United States alone.[59-60]

In addition, there are several reports of absorption and desorption studies of Norflurazon with various soil types in literature[61-64] as their pervasive presence in environment[60, 65] is of concern to scientific community. Norflurazon is expected and proven to form various kinds of interactions with soil such as Van der Waals[61, 66], π-π interactions[62, 67], and hydrogen bonding[62]. Norflurazon also contains –CF$_3$ group which can be used as an analytical handle in ^{19}F NMR as well as ^{19}F-^{13}C heteronuclear correlation NMR spectroscopy.[68]
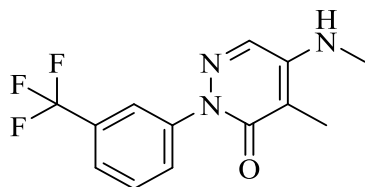
Figure 2.10. Chemical structure of Norflurazon

The sorption study of ESSs with ACs was performed based on OECD guideline for testing of chemicals: Adsorption-Desorption using bath equilibrium method with some modifications outlined in Appendix N.[69] A typical sorption experiment for each ESS involves determination of soil to solution ratio and equilibration time prior to the determination of actual sorption parameters through batch mode experiments. Once these two factors are measured, the ESSs are stirred with NOR solutions of various concentrations for the number of days determined by equilibration time experiment. The liquid portion from sorption mixture (ESS + background solution + NOR) is then centrifuged and supernatant is injected into HPLC to determine the equilibrium sorbent concentration in solution. For each NOR concentration, the sorption experiment was done in three repetitions along with a control and a blank. By mass balance, the equilibrium sorbent concentration in ESS is calculated. The measured values of NOR present on the sorbent (C_s) at sorption equilibrium and the concentration of sorbate remaining in the aqueous phase (C_{aq}) can be

used to characterize sorption behavior of soil using two approaches that are popularly used among soil scientists for characterization of sorption behavior : i) the Distribution coefficient and ii) the Freundlich Isotherm.[62, 70] The distribution coefficient K_d is calculated using equation 27 which is normalized with the organic content (%TOF) in equation 28. The Freundlich equation 29 which gives useful parameters such as Freundlich binding parameter (K_F) and exponent of linearity (N) can also be written in log form as shown in equation 30.

$$K_d = \frac{C_s}{C_{aq}} \hspace{5cm} Eq.\,27$$

$$K_{oc}^{sor} = K_d^{sor} \cdot \frac{100}{W_{180-600}^{corr}} \hspace{3cm} Eq.\,28$$

$$C_s = K_F C_{aq}{}^N \hspace{4.5cm} Eq.\,29$$

$$logC_s = logK_F + NlogC_{aq} \hspace{3cm} Eq.\,30$$

Where C_s is the equilibrium concentration of NOR present on the sorbent and C_{aq} is the equilibrium concentration of sorbate remaining in the aqueous phase.

2.4. Sorption Analysis of NOR by ESSs

The obtained data on sorption of NOR by ESSs can be analyzed through various approaches such as the nature and the amount of organic carbon, physical availability of the binding sites, partitioning of sorbent in aqueous and solid phase, and specific physical and chemical interactions. Extent of hydration of each ESS was expected to be a major factor in sorption as it influences the morphology of the oligomeric chains in aqueous conditions. In addition, the experimental pH condition is critical as it determines the state of protonation and hence the nature of interactions with NOR.

Table 2.2. Freundlich adsorption isotherm binding parameter (K_F), linear regression constant (N), and goodness of fit (R^2) for NOR with each of the ESSs; and calculated organic fraction normalized distribution coefficient (K_{oc}^{sor}) at selected sorption aqueous equilibrium concentration (C_{aq}) of 1, 8, and 20 ppm.

		Sorption			log K_{oc}^{sor}		
	Entry	log K_F^{sor}	N^{sor}	R^2	$C_{aq} = 1$ ppm	$C_{aq} = 8$ ppm	$C_{aq} = 20$ ppm
Tier-I	**ESS1**	1.185 (0.103)[c]	0.746 (0.134)	0.838	2.855 (2.151)	2.626 (1.922)	2.525 (1.821)
	ESS2	2.051 (0.075)	0.992 (0.095)	0.948	3.633 (2.617)	3.626 (2.609)	3.622 (2.606)
	ESS3	2.824 (0.011)	0.910 (0.018)	0.998	4.179 (2.482)	4.098 (2.401)	4.062 (2.365)
	ESS4	3.199 (0.008)	0.797 (0.015)	0.998	4.493 (2.773)	4.310 (2.590)	4.229 (2.51)
Tier-II	**ESS5**	3.033 (0.010)	0.853 (0.020)	0.997	3.846 (2.209)	3.714 (2.077)	3.655 (2.018)
	ESS6	2.837 (0.022)	0.974 (0.041)	0.99	3.571 (2.190)	3.548 (2.167)	3.537 (2.157)
	ESS7	2.246 (0.052)	0.993 (0.08)	0.963	2.972 (1.879)	2.966 (1.872)	2.963 (1.869)
	ESS8	2.699 (0.010)	0.909 (0.016)	0.998	3.551 (1.789)	3.469 (1.706)	3.433 (1.67)
	ESS9	2.543 (0.018)	0.785 (0.029)	0.992	3.269 (1.841)	3.075 (1.646)	2.989 (1.56)
Tier-III	**ESS10**	2.524 (0.009)	0.907 (0.014)	0.999	3.329 (1.525)	3.245 (1.440)	3.208 (1.403)
	ESS11	2.540 (0.029)	0.861 (0.043)	0.985	3.556 (2.255)	3.431 (2.130)	3.376 (2.075)

[a]Units of $K_F = (\mu g/g)/(\mu g/l)^n$ [b]Units of $K_{oc}^{sor} = (\mu g\ kg/C)$ [c]() = Standard deviation
(Note: The work in this table was contributed by Benjamin Haywood and Ghada Abdalla)

ESS1 acts as a baseline sorbent and its sorption parameters are used as a reference to compare that of other ESSs. **ESS2** through **ESS4** are one-tiered ESSs with aliphatic chains of C_6, C_{12} and C_{18} respectively which model lipids in SOM. With increase in the length of aliphatic tiers, there was direct increase in log K_F^{sor} and log K_{oc}^{sor} values showing increased sorption onto ESS. This is expected because the increased length of carbon chain and %TOF creates additional binding sites for hydrophobic NOR. The N^{sor} values show a decreasing trend with increasing aliphatic chain length indicating that the sorption behavior deviates from linear partitioning between sorbent and solution phases possibly due to creation of new binding sites. These can occur as shown in Figure 2.11 for the one-tiered system; the longer chains fold over in the aqueous environment to minimize contact with water giving rise to heterogeneous binding sites. Such conformational changes can be envisioned to introduce internal and external binding sites, with the internal sites being strong but more sterically hindered, and hence, demonstrating less linear NOR sorption behavior as seen by the decreasing N^{sor} values in Table 2.2. From this finding one can infer that the extent of hydration in ESSs plays a critical role in sorption of NOR as it influences the confirmation of oligomers in solution.

In **ESS 5**, an oligostyrene block of about 9 units is appended to the aliphatic end of C_{11} aliphatic block to give the first model of tier-II ESS (Table 2.1). With an additional block, the %TOF increases about thee fold compared to **ESS3** and **ESS4** but the log K_F^{sor} and log K_{oc}^{sor} values show a slight decrease. This important observation indicates that the sorption capacity is not only a function of the amount of organic matter in surrogate soil but also the nature of the organic matter. One reason for this decrease in sorption could be hydrophobic interaction of oligomer chains among themselves thereby decreasing the number of sorption sites available for NOR. Another explanation could be the hydration of oligostyrene block which forms a polar hydration

shell around the oligomer preventing NOR from sorption onto the oligomer. This effect is more pronounced with introduction of polar groups as substituents on aromatic rings in **ESS6**-**ESS9**.

ESS6 differs from **ESS5** by the presence of polar acetyl group on para position of aromatic rings and a slightly larger %TOF. As mentioned earlier, the log K_F^{sor} and log K_{oc}^{sor} values decreases due to hydration of the polar block. This is also accompanied by increase in N^{sor} value toward 1 indicating the decrease in heterogeneity of binding sites. This trend continues with the introduction of a methoxy group on adjacent carbon to the acetyl group in aromatic ring in **ESS 7** which shows further decrease in log K_F^{sor} and log K_{oc}^{sor} values and increase in N value to 0.993 compared to 0.853 (**ESS5**) and 0.974 (**ESS6**). This shift in sorption behavior towards linear partitioning must be due to loss of binding sites as the hydrated second block stretches the aliphatic first-tier (as shown in Fig 11) that is primarily responsible for NOR binding as observed so far.

The acetyl groups in **ESS6** are hydrolyzed to give -OH substitution on aromatic rings of **ESS8** which is expected to increase the polarity and hence the extent of hydration. As expected, the log K_F^{sor} value decreased (from 2.837 to 2.699) upon hydrolysis as did log K_{oc}^{sor}. It is also possible that the acetoxy addition of **ESS6** sterically blocks access of the hydrophobic NOR binding to the hydrophobic portion of the surrogate soil. Hydrolysis of the acetyl group leaves a phenolic group to give **ESS8** which is capable of hydrogen bonding, however the phenol at the buffer pH of 5.75 is still protonated and may only provide a small increase in polarity of the aromatic region (Figure 2.12). The N^{sor} value goes to 0.998 further corroborating the loss of binding sites by stretching of the first aliphatic tier.
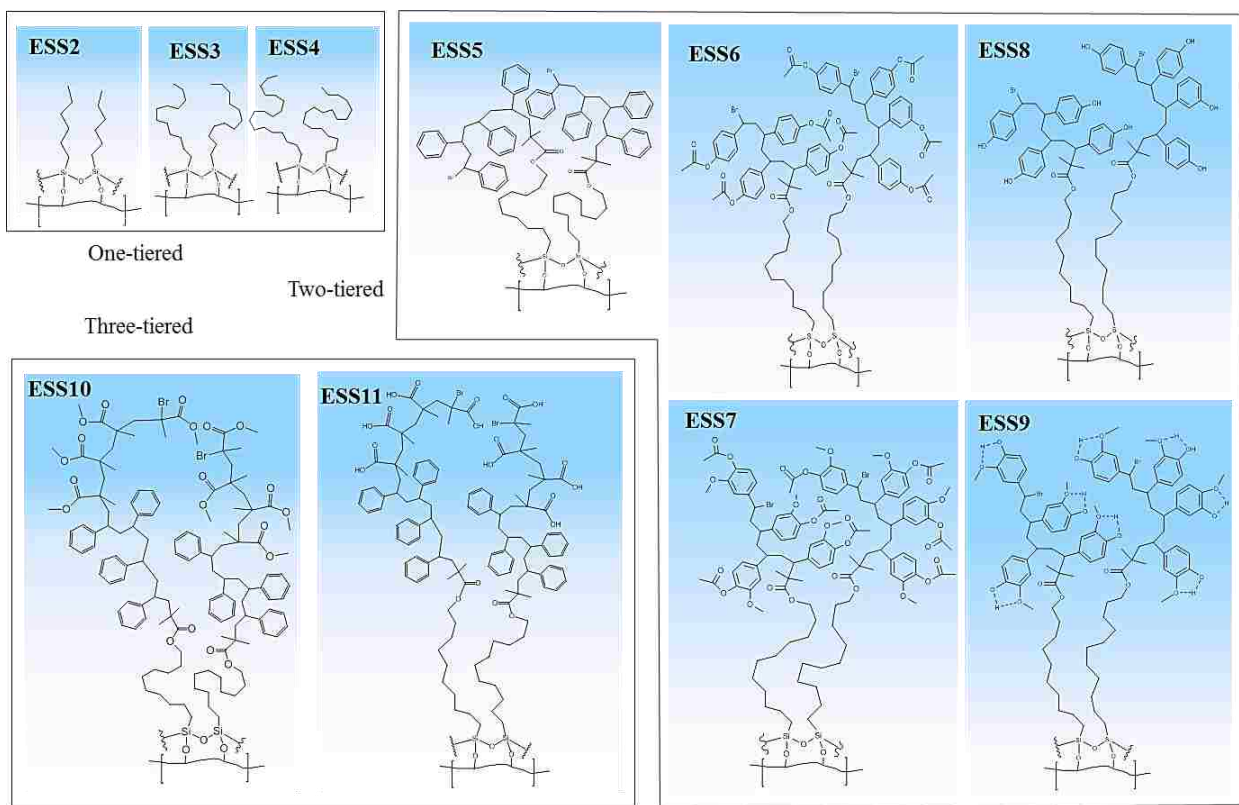
Figure 2.11. Illustration of surface oligomer morphology of ESSs accounting for extent of hydration, oligomer functionality and intramolecular interactions.

The hydrolysis of **ESS7** to **ESS9** however showed slight increase in $\log K_F^{sor}$ and $\log K_{oc}^{sor}$ values which was surprising at first but can be explained by the presence of a nearby -OCH$_3$ group next to phenolic -OH in **ESS9** which is capable of intramolecular H-bonding. (Fig 12) This chemical structuring increases the negative ionic character of the oxygen of the phenolic group and consequently the entire aromatic group. This affords electron donation into the **ESS9** aromatic ring which promotes pi-pi interactions with the electron deficient aromatic ring of NOR. The partially ionized aromatic ring of **ESS9** is also capable of electrostatic interactions with NOR, since NOR has several amine groups that are at different stages of protonation under the buffer pH of 5.75. The greater polarity of the **ESS9** would also be anticipated to increase hydration which has a repelling effect on NOR, however, this appears to be overcome by the molecular level

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binding interactions between NOR and **ESS9** described above. Thus, sorption non-linearity is seen to be influenced by specific binding sites within the polar part of the oligomer chains arising from a range of non-covalent interactions with NOR, such as π-π interactions and hydrogen bonding.

a.   OH   b.
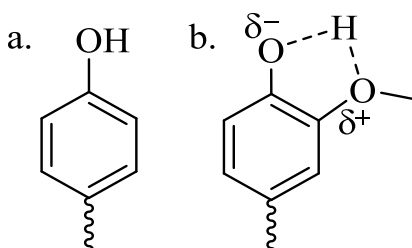
Figure 2.12. Illustration of intramolecular H-bonding between phenolic –OH and nearby methoxy oxygen in **ESS 9** a. Phenolic group of **ESS8** remains neutral at pH = 5.75 b. An additional methoxy group of **ESS9** affords hydrogen bonding that creates a dipole capable of hydration.

The addition of methylmethacrylate to the polystyrene based **ESS5** as the third tier gave **ESS10**, which was converted to methacrylic acid as a polar third tier in **ESS11**. Compared to the oligostyrene functionalized **ESS5**, both **ESS10** and **ESS11** exhibit significant reduction in log K_F^{sor} and log K_{oc}^{sor} values for NOR, which follows suit with the earlier hypothesis that polar groups create a hydration shell that inhibits the affinity and binding of NOR. This important observation supports the idea that interactions of NOR are directed toward the hydrophobic oligostyrene and aliphatic tiers. Hydrolysis of **ESS10** to give carboxylic acids in the third tier (**ESS11**) does not show a significant change in log K_F^{sor} and only a small increase in log K_{oc}^{sor}, indicating that the third tier chain only provides a hydration shell and is not participating directly in the binding of NOR. Overall for the **ESS5** through **ESS11** series, the lower log K_F^{sor} and log K_{oc}^{sor} can be explained by the hydration process blocking non-linear sorption sites; with these sites eliminated, one will obtain both a lower log K_F^{sor} and log K_{oc}^{sor} value and a higher initial N value as the polarity of the block oligomer chain increases, until specific chemical interactions in the hydrated layer cause the N^{sor} value to decrease.

2.5. Notes

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Chapter 3. Expansion of Synthetic Approach and Scope of Surface Modified with Multi-Block Oligomers in Study of Geomacromolecular matrices

3.1. Background

3.1.1. Controlled Radical Polymerization (CRP)

Although traditional radical polymerization methods are widely used for majority of the everyday products, they give poor control in molecular weight and high polydispersity of polymer chains which is a disadvantage for synthesis controlled architecture for important applications. The poor control is the result of high concentration of active radicals and rapidly growing polymer chains leading to frequent termination events, chain transfer to another polymer molecule or solvent, cross-linking and autoacceleration. Controlled radical polymerization (CRP) is also known as reversible deactivation radical polymerization (RDRP) and is widely used to synthesize polymers with controlled structure and architecture. CRP or RDRP utilize a dynamic equilibrium between the propagating radicals and the dormant species, with the equilibrium highly favorable towards dormant species to keep the concentration of the propagating radical to a small fraction in order to reduce the termination events and facilitate controlled addition of monomers to each growing chain uniformly. For example, atom-transfer radical polymerization (ATRP) approach employs reversible deactivation of propagating radicals to form dormant species that can be intermittently reactivated in a catalytic manner [1-3]. Another type of CRP, stable radical mediated polymerization (SMRP) uses a similar approach but the reversible deactivation of propagating radicals occurs spontaneously with aminoxyl (e.g. nixtroxide mediated) radicals[4] or organometallic species.[5] Another approach to CRP such known as degenerative transfer radical polymerization (DTRP) employs degenerate transfer between propagating radicals and a dormant species such as in reversible addition−fragmentation chain-transfer polymerization (RAFT),[6-7] or iodine transfer radical polymerization (ITRP).[8-9]

3.1.2 Atom-transfer radical polymerization (ATRP)

ATRP is a widely used Controlled Radical Polymerization CRP which employs an alkyl halide initiator and transition metal complex catalyst. It is attractive because of the simple experimental setup, with readily available initiators and catalysts that can be used in a range of solvents under a broad spectrum of reaction conditions, allowing precise control over final polymer MW and architecture.[2-3, 10-11] Unlike conventional radical polymerization with slow continuous initiation, fast propagation, and inevitable radical termination; CRP creates and exploits a dynamic equilibrium between growing radicals and dormant species. Because of this equilibrium and faster initiation, only 1-10% of the growing chains are terminated while the remaining chains are dormant species, capable of reactivation, functionalization, and chain extension to form block copolymers; thus CRP behaves as a 'living' system.[10, 12-13] Additionally, relatively fast initiation gives control over molecular weight with a narrow distribution. The average degree of polymerization (DPavg) is given Eq. 1 where p is the extent of reaction. For total conversion of monomer, $p = 1$ and hence, DPavg = [M]/[I]. In a relatively efficient polymerization such as ATRP, the desired DPavg can be obtained by adjusting the [M]/[I] ratio equal to the desired DPavg.

$$P_n\text{-}X + Mt^m/L \quad \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} \quad P_n{}^* + X\text{-}Mt^{m+1}/L$$

$$M \quad k_p \qquad k_t \rightarrow P_n\text{-}P_n$$
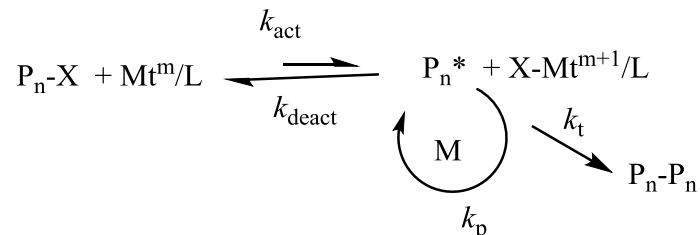
Scheme 3.1. General scheme of an ATRP[10]

$$DPavg = p * \frac{[M]}{[I]} \qquad\qquad Eq.\,1$$

The general scheme of an ATRP is shown in Scheme 3.1. Pn-X is the dormant species which can be either an alkyl halide initiator or the growing polymer chain with halide end cap. The activation takes place with reversible abstraction of halogen by metal catalyst (Mt^m) through oxidation to one higher oxidation state (Mt^{m+1}). The abstraction of halogen by metal is an equilibrium phenomenon with the equilibrium constant (K_{ATRP}) relatively much higher towards the dormant species Pn-X; converting only a small fraction to active species. P_n^* acts as an active species and can repetitively add monomer (M) to it in a small time window before it is converted back to the dormant phase. Typical ATRP equilibrium constants (K_{ATRP}) are in the order of 10^{-9} which means that about one in a billion polymer molecules are in activated to Pn^* at a moment.[14] This results in very small radical concentration and hence the reduced termination events keeping the rate of termination (k_t) minimal. This allows the monomers to add to all the propagating radicals in a relatively even fashion leading to narrow polydispersity of the resulting polymer.

The rate of polymerization of ATRP (R_p) depends on the propagation rate constant (k_p) and on the concentrations of monomer and growing radical. The concentration of the growing radical depends on the ATRP equilibrium constant (K_{ATRP}), as well as on the concentrations of the dormant species, activators, and deactivators. The equilibrium constant K_{ATRP} is equal to the ratio of rate of activation to the rate of deactivation (as shown in Eq. 2) and depends on the strength of both the P^n–X and the Mt^{m+1}–X bonds. For a ATRP system catalyzed by Cu(I)X, the equilibrium constant increases with the strength of the CuII–X bonds, or the halogenophilicity of the CuI complex, and decreases with the strength of the C–X bonds.[16]

$$K_{ATRP} = \frac{k_{act}}{k_{deact}} \qquad\qquad \text{Eq. 2}$$

Several studies on ATRP of vinyl monomers such as styrenes[15] and methacrylates[16] are largely available in the literature. Many of these studies have been conducted by utilizing transition metal catalyst such as copper,[17-18] iron,[19] ruthenium,[20] and rhenium[21] systems. For the polymerization of styrenes, heterogeneous mixtures of a copper(I) halide and a neutral chelating amine, imine or pyridine ligand are most commonly used.[17] One major limitation of traditional ATRP is that it requires extremely strict oxygen-free condition and relatively large amounts of Cu catalyst compared to recently developed variations of ATRP. Techniques that require low amount of Cu such as initiators for continuous activator regeneration (ICAR) ATRP and activators regenerated by electron transfer (ARGET) ATRP have gained attention. ICAR ATRP utilizes a source of organic free radicals to continuously regenerated the Cu(I) activator, which is otherwise depleted through termination when used in small quantity.[27] In ARGET ATRP, an excess reducing agent such as tin(II) 2-ethylhexanoate, or vitamin C etc. are used to convert Cu(II) to Cu(I) and to improve oxygen tolerance.[8] Another limitation of ATRP is that it is challenging and often incompatible for polymerization of monomers containing acidic and phenolic groups such as methacrylic acid and 4-vinylphenol etc. The possible reasons include ligand protonation at low pH, coordination of the catalyst to the carboxyl group of monomers and and displacement of the halide anion from the oxidise Cu(II) dormant phase. [22-23] For polymerization acidic and phenol monomers, they can be converted to ATRP compatible polymers before polymerization and deprotected post-polymerization. For this work, ATRP was chosen as a method of polymerization for the synthesis of multi-block oligomers in because of it's robustness and ease of synthesis of polymers with controlled molecular weights and narrow polydispersity using various monomers under mild conditions.

3.1.3 Surface modification of solid substrates with polymers

Surface functionalized polymers have been shown to be useful to improve mechanical, physical, chemical, mechanical and functional properties of surface for biocompatibility[24], adhesion[25], lubrication[26], corrosion resistance and anti-fouling[27], removal of metals[28], separation[29], immobilization of catalyst[30], etc. The diverse nature of possible solid surfaces such as gold[31], carbon nanotube[32], graphene (oxide)[33-34], mesoporous carbon[35] and mesoporous silica [36-37] etc. The development of controlled polymerization techniques and effective surface chemistry has allowed for synthesis of surface grafted polymers with controlled architecture and design an array of composite materials containing inorganic and organic components. These materials possess diverse structural and functional features that have proven useful in novel applications such as drug delivery [38], stimuli responsive surfaces[39], electrochemical capacitors[40], molecular recognition [41], CO_2 adsorption[42] etc.

There are various approaches to modification of solid surface with polymeric materials. The first method is to physically adsorb polymer onto the surface followed by cross-linking to entrap the surface in polymer matrix. This method has found useful application in chromatography[43-44]; however, degradation and loss of polymer under harsh conditions was observed.[45] There are also reports of non-covalent modification of nanoparticles through emulsion polymerization in the presence of nanoparticles. The second method is to immobilize polymers on surface through formation of covalent linkage with the surface, known as grafting. Methods to form covalent bond formation with a solid surface in literature include thiol end-functionalization of polymer for grafting to gold [46-47], amidation of peptides[48] and dendritic polymers[49], silane functionalization of polymer for grafting to silica surface[50] etc. In general, assembly of surface grafted polymers is accomplished using two approaches: a) "grafting from" and b) "grafting onto"

3.1.3.1. "Grafting from" approach

Grafting from approach involves in situ growth of the polymer on solid surface. The first step of grafting from approach usually requires introduction of initiator for polymerization onto the solid surface. For conventional radical polymerization[44] the radical initiators are attached to the solid substrate. Similarly, for CRP, the initiating species can be covalently functionalized on solid surface followed by the polymerization reaction. The "grafting from" approach is good for achieving higher grafting densities of polymers on a surface because there are relatively smaller steric interactions among small initiating species as opposed to immobilization of large polymeric molecules in "grafting onto" approach. However, the presence of a solid surface in the polymerization reaction adds an additional variable to otherwise well understood solution phase polymerization. The characterization of such materials also may pose a challenge, often requiring additional and less elucidative techniques depending on the nature of the surface/polymer composition.
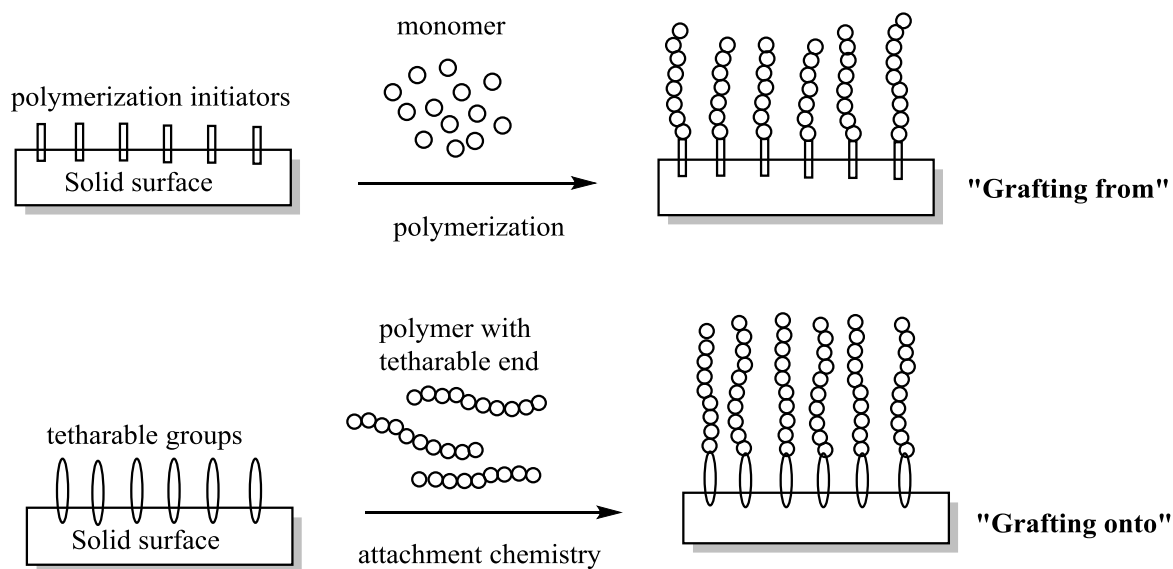
Figure 3.1. Illustrative scheme of "grafting from" and "grafting onto" approach to modification of solid surface with polymers.

3.1.3.2. "Grafting onto" approach

The "grafting onto" approach involves chemical reactions of end-functional group of pre-formed polymer chains with the solid substrate to form a covalent linkage. The reactions of the already prepared polymer end group can be performed in solution of the polymer or from the polymer melt, and may require chemically modified surface chemistry for attachment. While this approach is not ideal for densely distributed polymers on a surface because of steric hindrance, the structural features of the polymers such as degree of polymerization (DP) and polydispersity index (PDI) can be precisely controlled because of more homogeneous reaction conditions and compatibility with most state-of-art characterization techniques.

In chapter 2, the "grafting from" approach was utilized to grow polymers from a silica surface for ESS synthesis. Based on popular soil models, the targeted grafting density were low with % TOF in the range of 5-25% which can also be easily achieved through "grafting onto" approach. This approach has been shown to yield higher grafting density and %TOF and therefore expected to show great potential for improved scalability while also improving the control in the structure. During the synthesis of a multi-block oligomer platform, the polymer chains can be characterized in-situ and after polymerization of each block using popular techniques such as (solution state) NMR and mass spectroscopy. Several controlled radical polymerization techniques are commonly used to synthesize multi block oligomers with controlled DPavg and PDI. In this Chapter, synthesis of multi-block oligomers through solution-phase ATRP followed by grafting onto approach is utilized for ESS is synthesis in a quest to improve control and scalability of the ESS structures.

3.1.4. Grafting of polymers on mesoporous SiO$_2$ substrate

Use of silica-based materials is common in fields of bioengineering[51], catalysis[52], separation[29, 53], composite materials[54] etc. Because of their porous structure, silicates and silica nanoparticles have useful surface related applications[55] such as removal of metals[56], large surface for catalysis[52], CO$_2$ capture[57], controlled drug release[58], template for nanowire synthesis[59], aerogels[60] etc. Si-O and Si-C bonds are longer and more polarized than the analogous C-C bond, with lower steric hindrance barrier for rotation for the siloxane backbone.[61] Because of the diverse use of silica, several approaches to modify silica surface with polymers have been explored. Mesoporous organic-silica composite materials are either prepared directly by co-condensation of organosilanes during the synthesis of mesoporous silica[62] or by grafting of organosilanes onto pre-prepared mesoporous silica surfaces.[63-64] Polymer modification of SiO$_2$ surface is achieved through traditional radical polymerization approaches such as i) physical adsorption of monomer followed by polymerization[65] ii) emulsion polymerization in the presence of nanoparticles[66] iii) "grafting from" surface initiated polymerization[37, 63] and iv) "grafting onto" [67-68] approaches. Conventional polymerization techniques as well as CRP techniques such as ATRP[37, 63, 69], RAFT [70-71], nitroxide-mediated polymerization (NMP)[72-73] using monomers such as methyl methacrylate[63, 69, 74-75], styrene [63, 72, 75], N-isopropylacrylamide [76-77] acrylonitrile etc. Although these techniques have proven useful in design and synthesis of polymer modified silica, precise control of brush thickness, composition and architectures still remains a major challenge.

3.2. Solution phase polymerization of block oligomers for ESS development by "grafting onto" approach

As demonstrated in Chapter 2, engineered soil surrogates (ESSs) prepared by grafting multi-block oligomers on SiO$_2$ served as a useful platform in study of molecular-level interaction of soils with model Agricultural Chemicals (ACs) and their effects in bulk property of the materials

such as sorption. The ability to precisely control the platform architecture and scale them as per the subject of study provides a prospect for design of simple to complex architectures to gain insight into the geomacromolecular processes that are elusive because of their complexity and heterogeneity of the chemical structures involved. Although SI-ATRP synthesis of ESS as shown in Chapter 2 proved to be successful in synthesis of one, two and three- tiered oligomers on SiO_2 surface, the process showed some limitations related to solid-phase synthesis. For the solid phase synthesis, problems encountered included the following: a) the polymerization was monomer inefficient; requiring approximately 5, 20, 25 times the amount of monomer than theoretically required for styrene, 4-acetoxystyrene and 4-acetoxy 3-methoxystyrene respectively and b) the characterization of the ESS materials was difficult because of their insolubility in solvents for solution-state Nuclear Magnetic Resonance (NMR) spectroscopy and mass spectrometric analyses.

Scheme 3.2 shows the synthesis ATRP initiator coupled C_{11} aliphatic chain (**3**) followed by synthesis of multi-block oligomer chains consisting of aliphatic, O-aryl and polar blocks in solution using ATRP, and subsequently grafting onto SiO_2. For the synthesis of a C_{11} aliphatic chain with an ATRP initiator (C_{11}-initiator, **3**), 10-undecen-1-ol **1** was coupled with 2-bromoisobutyryl bromide **2**. ATRP was employed to polymerize vinyl monomers such as styrene and substituted styrenes, and methyl methacrylate as the first polymerized block appended to C_{11}-initiator to give tier-2 oligomer. ATRP was carried out in refluxing toluene for 24 hours using initiator (**3**) to Cu(I)Br catalyst ratio of 4:1 (25 mol% cat. based on initiator) and [M]/[I] ratio equal to the desired average degree of polymerization (DPavg).
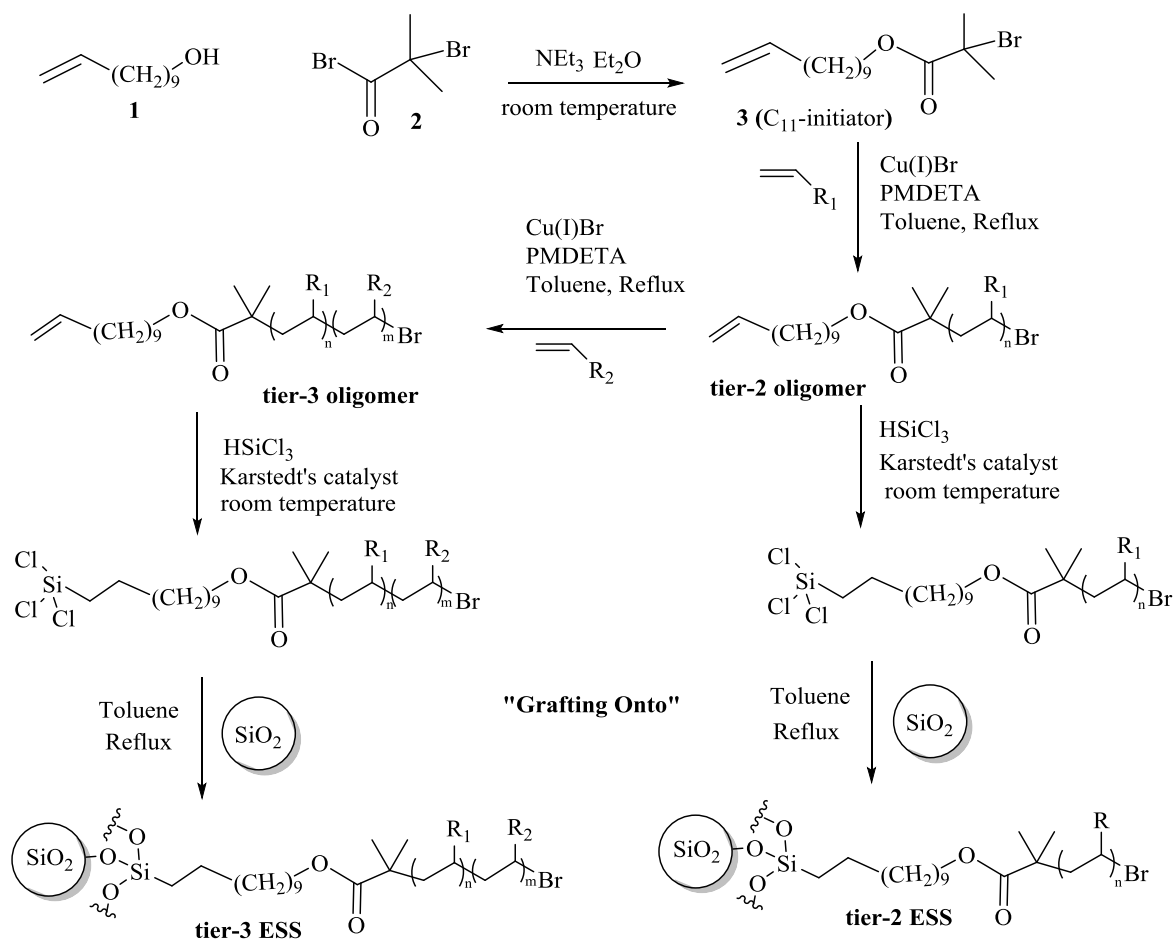
Scheme 3.2. Grafting onto approach to ESS synthesis

To synthesize tier-3 oligomers with alkyl (tier-1), O-aryl (tier-2) and polar(tier-3) blocks, a tier-2 oligomer was used as a macroinitiator for subsequent polymerization after workup procedure exploiting the "living" characteristic of the ATRP. Also, multi-block oligomers were synthesized with the composition of tier-2 and tier-3 reversed (i.e. polar block as tier -2 and O-aryl block as tier-3). Similar to the polymerization of tier-2 oligomers, the polymerization was achieved using (macro)initiator to Cu(Br) ratio of 4:1 (25 mol% cat. based on initiator), [M]/[I] ratio equal to the desired average degree of polymerization (DPavg), with PMDETA ligand (catalyst: ligand =1:1.1) by refluxing in toluene (110 °C) for 24 hours. Finally, tier-2 and tier-3 oligomers were hydrosilated using 5.5 mol. equivalent trichlorosilane and Karstedt's catalyst (vinyl groups: Pt

=100:1). The resulting trichlorisilyl end-group containing tier-2 and tier-3 oligomers were covalently attached to silica by refluxing in toluene for 24 hours as shown in Scheme 3.2.

3.2.1 Physical Characterization of multi-block oligomers

Prior to the grafting process, the structures tier-2 oligomers and the polymerization of the blocks was verified by using Bruker 400 MHz ^{1}H NMR. Figure 3.2 shows the ^{1}H NMR of C_{11}-initiator (**3**) (top), tier-2 (middle) and tier-3 (bottom) oligomers with oligostyrene as second block and oligo (methyl methacrylate) as third block. The DPavg of the oligomers were calculated by using integration of vinyl chain end of the C_{11}-initiator and the aromatic protons for oligostyrene, and O-CH$_3$ peak for methyl methacrylate as shown in subsequent sections (Figures 3.4, 3.7).
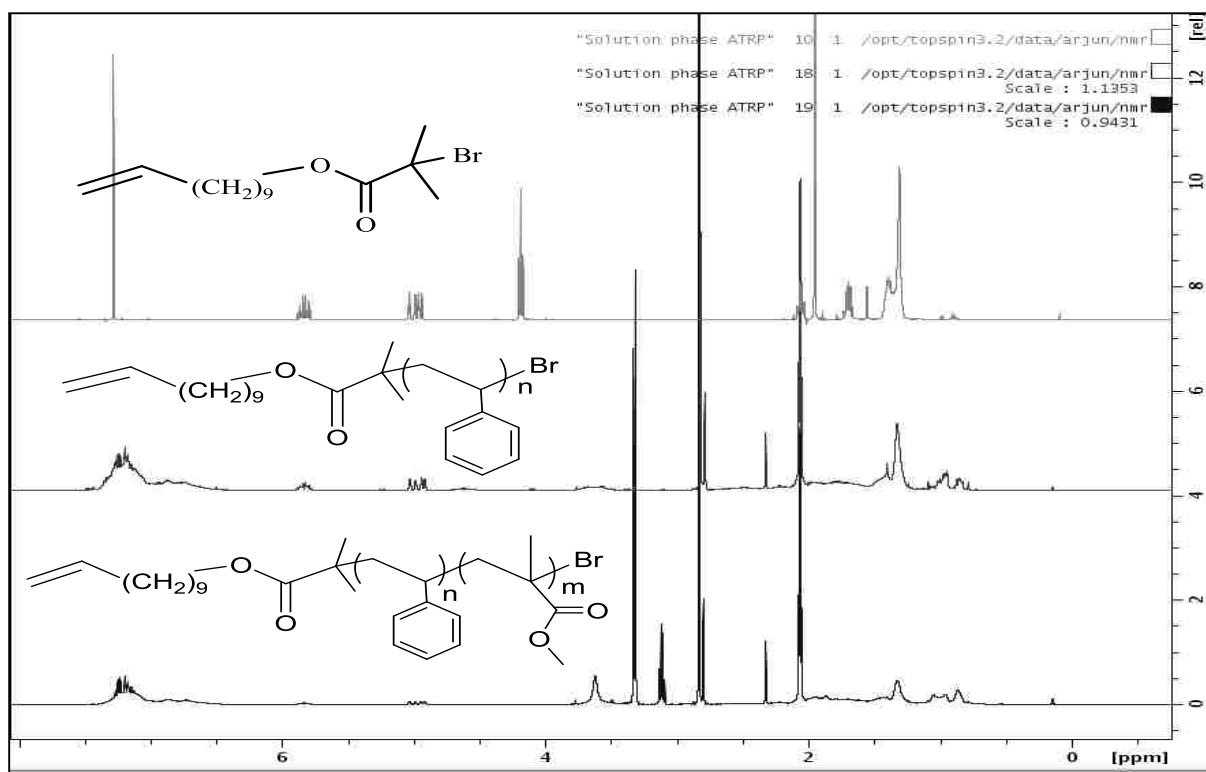
Figure 3.2. ^{1}H NMR of C_{11}-initiator (**3**) in CDCl$_3$ (top) and subsequent addition of tier-2 oligostyrene in acetone-D$_6$ (middle) and tier-3 oligo (methylmethacrylate) in acetone-D$_6$ (bottom).

The tier-2 and tier-3 oligomers were also characterized by matrix assisted laser desorption ionization (MALDI). The MALDI results were used to verify the structures and determine the

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degree of polymerization (DP) and polydispersity index (PDI). A MALDI-TOF spectrum of tier-2 oligomer containing oligo (4-acetoxy-3-methoxystyrene) as second block is shown in Figure 3.5 along with interpretation of the molecular weights observed in Table 3.2. For tier-3 oligomers, the identification of exact MW peaks was challenging; however, the molecular weights were in the range corresponding to the DPavg values obtained from NMR data. The MALDI of tier-2 and tier-3 oligomers are also shown in Appendix 3.

3.2.2 Initial results for solution phase synthesis of oligostyrene on C$_{11}$-initiator (3)

Initially, polymerization of styrene was investigated with C$_{11}$-initiator (3) using 10:1 initiator: Cu(I)Br ratio (10 mol% based on initiator) with an aim to polymerize an oligostyrene block (tier-2) with approximate DPavg of 5. The polymerization reaction used [M]/[I] ratio of 5.5 and the polymerization was carried out in toluene at 110 °C for 24 hours with aliquots collected after 12, 18 and 24 hours. Following the removal of unreacted monomer with high vacuum, the samples were analyzed by ^{1}H NMR. The DPavg were calculated for each aliquot by using the relative integration of vinyl peaks of C$_{11}$-initiator and the aromatic peaks of oligostyrene. NMR results indicated polymerization with DPavg of 2.1 in 12 hr., a slight increase to 2.3 in 18 hr., and no further polymerization indicated by the same DPavg of 2.3 for 24 hr. aliquot (Figure 3.3). This was suspected to be caused by insufficient amount of catalyst. Increasing the catalyst to 16 mol % (based on initiator) showed 41% conversion in 6 hours proving our initial suspicion. For subsequent studies, catalyst loading of 25 mol% based on initiator was adopted which is relatively low amount of catalyst compared to literature. For comparison, 25 mol% catalyst based on initiator for [M]/[I] of 10 translates to 2.5mol % based on monomer.
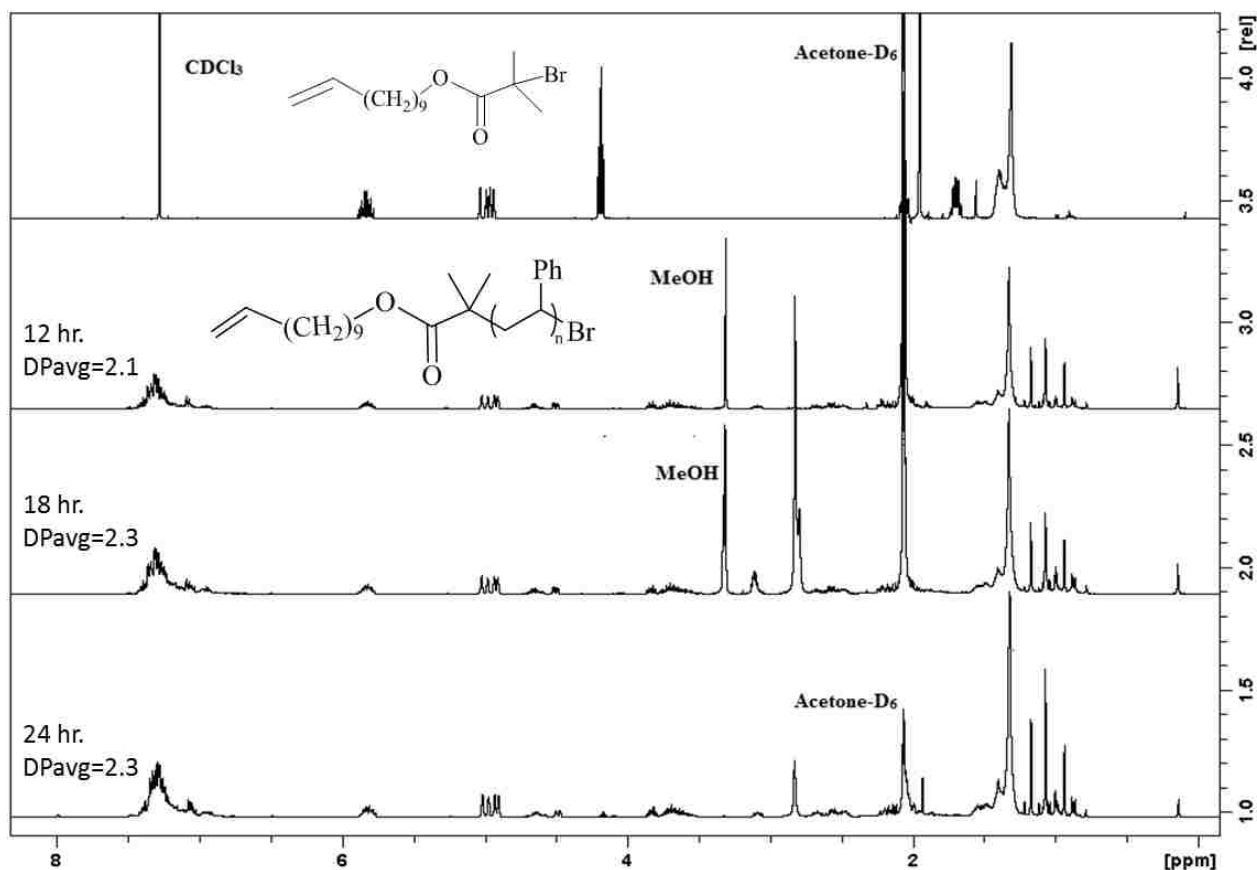
Figure 3.3. ^{1}H NMR of initiator (top) followed by the polymerization of styrene for 12, 18, 24 hr and the 25 mol% catalyst (based on initiator).

3.2.3 Polymerization of (tier-2) styrene and styrene derivatives on C₁₁-initiator (3)

The polymerization of styrene, 4-acetoxystyrene and 4-acetoxy3-methoxystytene with desired DPavg was obtained by using 25mol% Cu(I)Br and refluxing toluene for 24 hr. to obtain oligomers with DP approximately equal to [M]/[I]. The polymerization of styrene with [M]/[I] ratio of 5.4 gave a DPavg of approximately 5 which upon purification yielded pure oligomer with DPavg of 6.3. The increased DPavg upon trituration with methanol is possibly due to loss of small molecular weight oligomers because of their higher solubility. Fig 3.4 shows the ^{1}H NMR of tier-2 oligostyrene with labeled peaks and illustration of DPavg calculation by using vinyl protons of the aliphatic chain as reference integral.
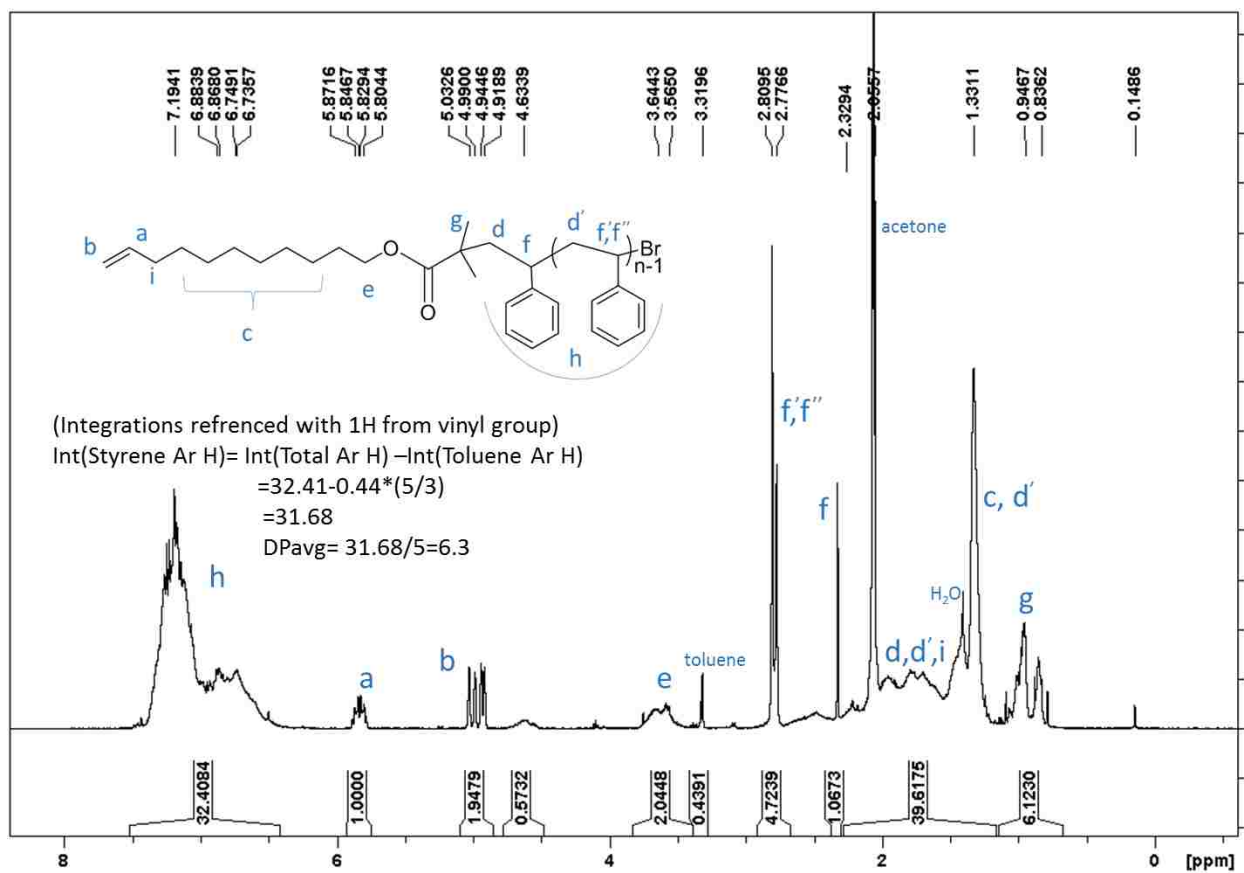
Figure 3.4. 1H NMR of C_{11}-$PS_{6.3}$ oligomer chain with labeled peaks and illustration of DPavg calculation using integration of peaks.

The polymerization of 4-acetoxystyrene and 4-acetoxy 3-methoxystyrene gave similar results to styrene. Table 3.1 shows the reaction conditions and the DPavg of the polymerization of the aforementioned monomers obtained from NMR analysis of crude and purified products. Figure 3.5 shows the MALDI-TOF spectrum of oligo (4-acetoxy 3-methoxystyrene). The molecular weights of MALDI spectrum are interpreted in Table 3.2. Because the sample was dissolved in acetone for MALDI analysis, the observed MW are a sum of MW of expected oligomer and one or more two molecules. The bolded MWs in Table 3.2 are the MWs that match with the spectrum in Fig 3.5.

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Table 3.1. Reaction conditions and results of polymerization of PAS and PAMS monomers.

Entry	Monomer	Rxn temp./ Solvent/Time	Cu(I)Br (based on Ini)	[M]/[I]	DPavg by NMR/MALDI
1	4-acetoxystyrene	Refluxing toluene, 24hr	25 mol%	5.52	(5.6/ NA) (crude)
2	4-actoxy 3-methoxystyrene	Refluxing toluene, 24 hr.	25 mol%	5.93	(8.0/7.0) (purified)
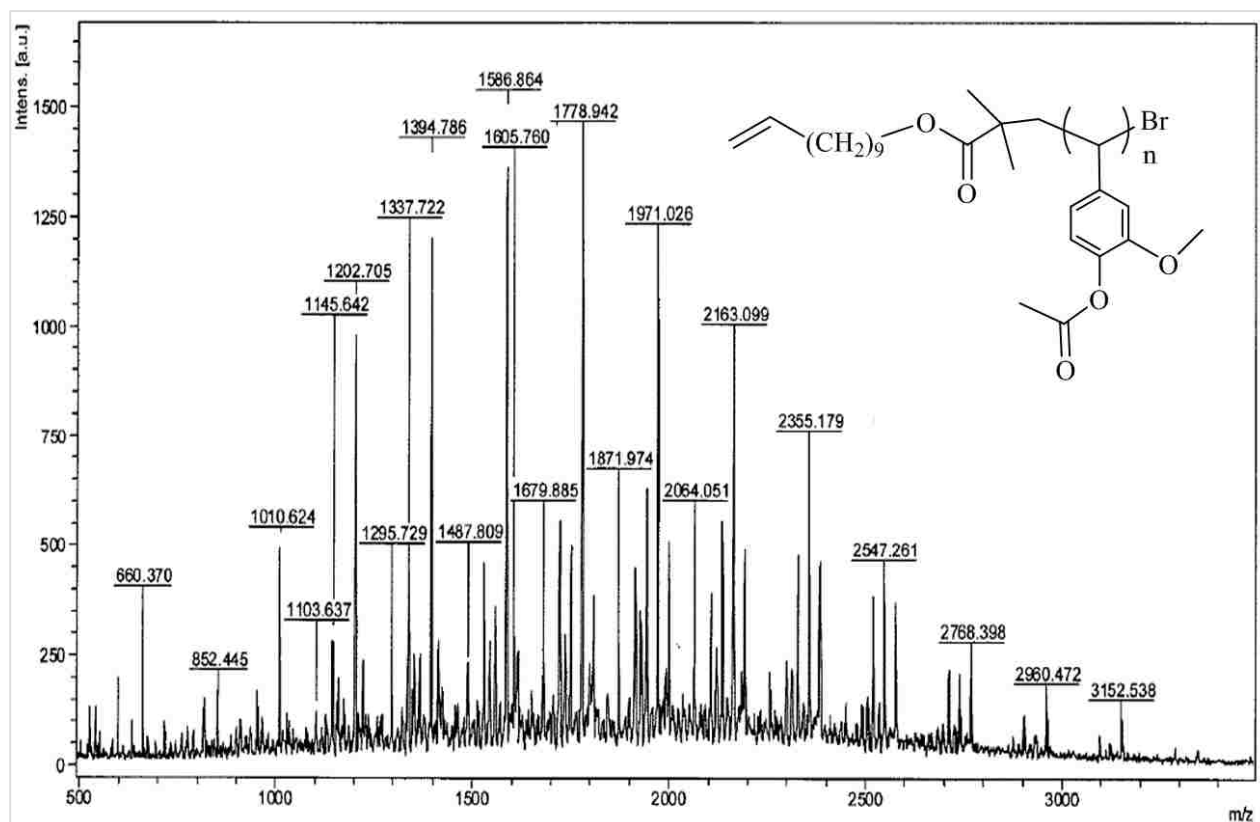
Figure 3.5. MALDI spectrum of oligo (4-acetoxy 3-methoxystyrene) on C_{11}-initiator (**3**). PDI was calculated to be 1.05

Table 3.2. Interpretation of MALDI spectra of C_{11}-oligo(PAMS) in Figure 3.5 by calculation of MW of each oligomer chain and possible changes to MW in MALDI. Bolded numbers represent matching MW from spectrum.

DP	MW of oligomer	MW of (oligomer + acetone)	MW of (oligomer +acetone)-1	MW of (oligomer + 2X acetone)-1
2	703.7	761.78	760.78	818.86
3	895.91	953.99	952.99	**1011.07**
4	1088.12	**1146.2**	1145.2	**1203.28**
5	1280.33	**1338.41**	**1337.41**	**1395.49**
6	1472.54	1530.62	1529.62	**1587.7**
7	1664.75	1722.83	1721.83	**1779.91**
8	1856.96	1915.04	1914.04	1972.12
9	2049.17	2107.25	2106.25	2164.33
10	2241.38	2299.46	2298.46	**2356.54**
11	2433.59	2491.67	2490.67	**2548.75**
12	2625.8	2683.88	2682.88	2740.96
13	2818.01	2876.09	2875.09	2933.17
14	3010.22	3068.3	3067.3	3125.38

3.2.4 Polymerization of (tier-2) methylmethacrylate with on C₁₁-initiator (3)

Although initial design of ESS in Chapter 2 consisted of oligo (methyl methacrylate) and oligo (methacrylic acid) as a polar third tier, incorporation of oligo (methyl methacrylate) as a second tier was explored in solution phase synthesis. The reversal in position of polar third tier and O-aryl second tier may be one of the systematic changes in ESS required to test the role of polar moieties in SOM. With an aim to polymerize a PMMA oligomer block with C₁₁-initiator with approximate DPavg of 5 and 10, similar ATRP conditions as in styrene polymerization were employed. Polymerization were carried out in refluxing toluene using 25mol% Cu(I)Br catalyst based on the initiator, and PMDETA as a ligand for 24 hours. The polymerization was also seen to go to completion in 24 hours using reduced amount of copper, 16 mol% based on initiator. The washing of the crude products with hexane for purification led to increased DPavg, as seen for styrene derivatives possibly due to higher solubility of lower MW oligomers in the solvent.
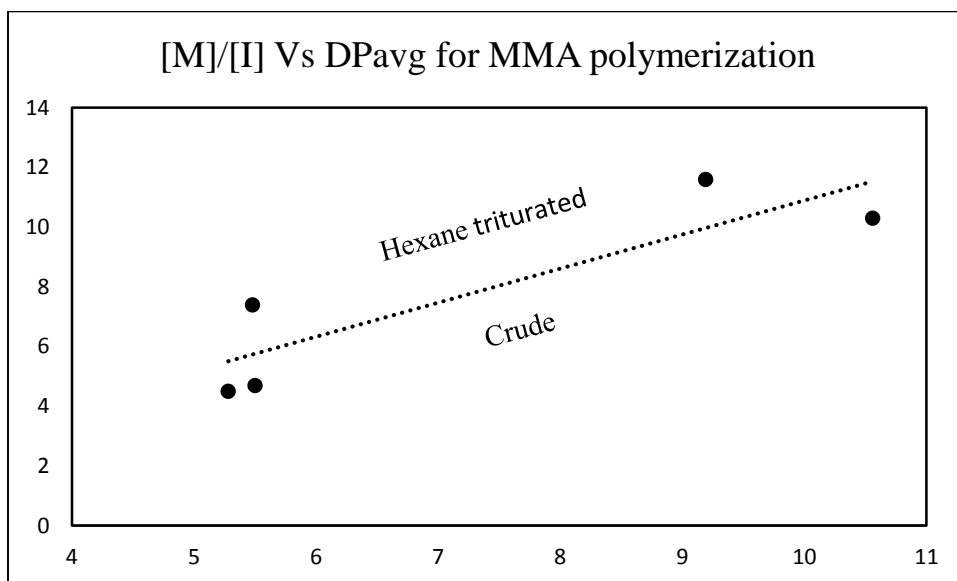
Figure 3.6. Polymerization of methylmethacrylate to synthesize oligomers of approximately 5 and 10 units with obtained DPavg for crude and washed samples as a function of [M]/[I].

3.2.5 Polymerization of a subsequent (tier-3) oligomer block from (tier-2) macroinitiators

Using Similar ATRP conditions utilized in previous sections (Table 3.1), subsequent block of styrene and PMMA were added to tier-2 oligomers using C_{11}-oligostyrene and C_{11}-oligo (methyl methacrylate) as macroinitiators. The tier-2 oligomers were used as macroinitiators because the ATRP with Cu(I)Br leads to capping of chain ends with −Br groups, known as chain end functionality (CEF). The preservation chain end functionality can be a challenge as some propagating chains can terminate by recombination, disproportionation and chain transfer processes. Large initiator concentration is known to lead to low CEF as a result of increased bimolecular termination.[78] Diluting the polymerization reaction was expected to mitigate termination events by decreasing the concentration of initiator and propagating radical, and hence the increase CEF. However, the increased amount may lead to higher chain transfer to the solvent leading to decreased CEF. In synthesis of tier-2 oilgomers, all polymerization reactions were conducted in relatively dilute conditions. The diluted reactions in toluene, which is popularly used in many radical polymerizations, including ATRP was expected to give preserved CEF and hence the extendibility of tier-2 oligomers with subsequent polymerization of another block to synthesize tier-3 oligomers. Figure 3.2 shows ^{1}H NMRs of sequential polymerization of oligostyrene and oligo (methyl methacrylate) with C11-initiator (**3**, Scheme 3.2) The ^{1}H NMR of of tier -3 oligomer C_{11}-$PS_{4.7}$-$PMMA_{4.2}$ with labelled peaks and DPavg calculation is shown in Figure 3.7.

Based on these results the solution phase approach to oligomer synthesis is superior to solid-phase synthesis. The solution phase polymerization required smaller amount of catalyst (25 mol% based on initiator as opposed to 50 mol%) than SI-ATRP. The solution phase polymerization demonstrated 5, 20 and 25 times greater monomer efficiency for polymerization of styrene,
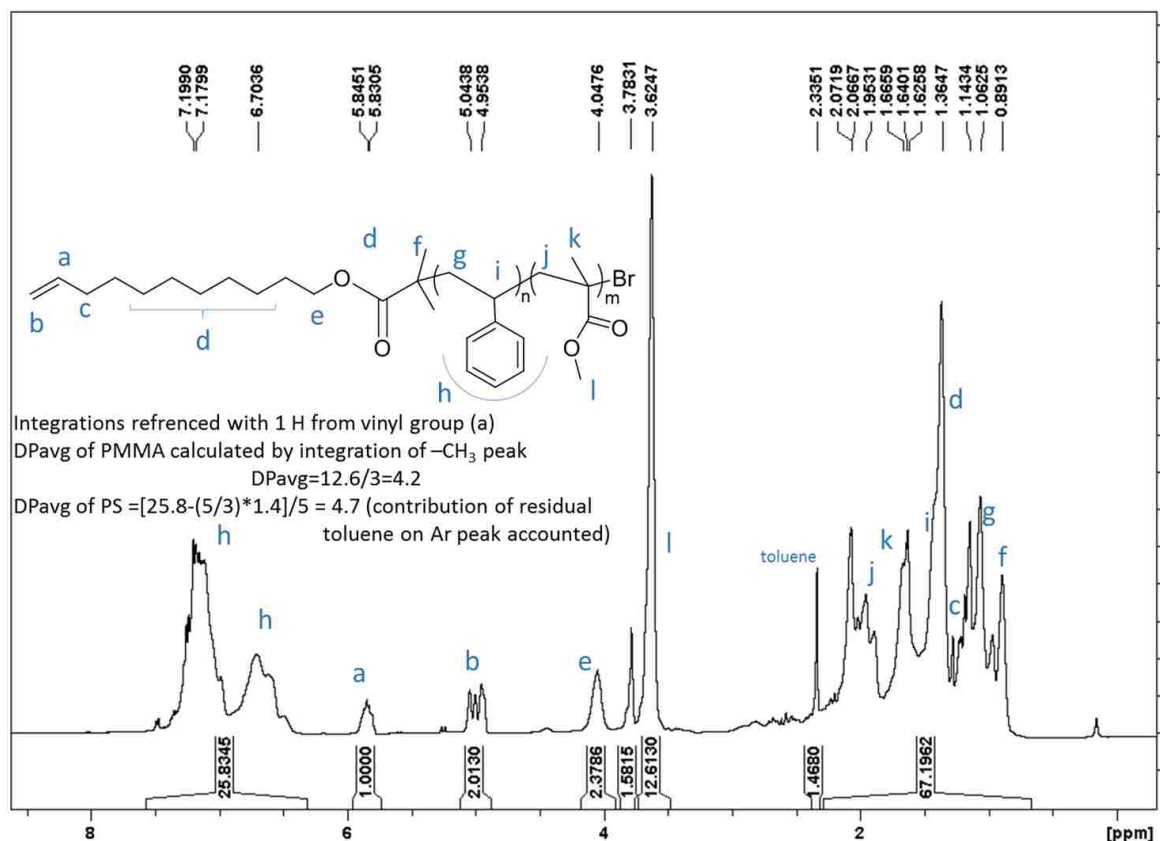
Figure 3.7. ^{1}H NMR of C_{11}-PS$_{4.2}$-PMMA$_{4.7}$ tier-3 oligomer chain with labeled peaks and illustration of DPavg calculation.

4-acetoxystyrene and 4-acetoxy-3-methoxystyrene respectively, giving almost quantitative conversions in all polymerization including methylmethacrylate. While the SI-ATRP required refluxing in xylenes at temperature of 145°C for 24 hours for polymerization of 4-acetoxystyrene and 4-acetoxy 3-methoxystyrene, solution phase ATRP was conducted by refluxing toluene at 110°C to obtain desired oligomer. This relatively milder condition was also effective for solution phase ATRP of styrene and methyl methacrylate.

3.3. Grafting of block oligomers onto silica

Following the synthesis of tier-2 and tier-3 oligomers by solution phase ATRP, the vinyl end group of the oligomer was converted into a trichlorosilyl group for tethering the oligomer chains onto silica. For hydrosilation, the oligomer was dissolved in toluene and 5 mol equivalents

of trichlorosilane 1% Karstedt's catalyst (platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene). The resulting –$SiCl_3$ chain ends of oligomers were used for attachment on SiO_2 surface by refluxing toluene for 24 hours (Scheme 3.2).

The efficiency of grafting step was analyzed by using a tier-2 oligomer containing PMMA with DP_{avg} of 10, attached to a C_{11}-initiator with trichlorosilyl end group. On three separate reactions with 5.0g SiO_2 on each, 0.7g, 1.4g and 2.1g Cl_3Si-C_{11}-$PMMA_{10}$ were added and refluxed in 50ml toluene for 24 hours. After a three step washing process with toluene, acetonitrile and ethanol followed by drying, the oligomer grafted silica were analyzed by TGA to calculate %TOF of each grafting reactions. The obtained %TOF from TGA were plotted against theoretical %TOF as shown in Figure 3. Theoretical %TOF is the percentage of total organic fraction that would be seen for the perfect grafting efficiency, as shown in equation 3. The calculation of %TOF using TGA data is demonstrated in Chapter 2.

$$Theoretical\ \%TOF = \frac{mass\ of\ oligomer}{mass\ of\ oligomer + mass\ of\ SiO2} * 100 \qquad Eq.3$$
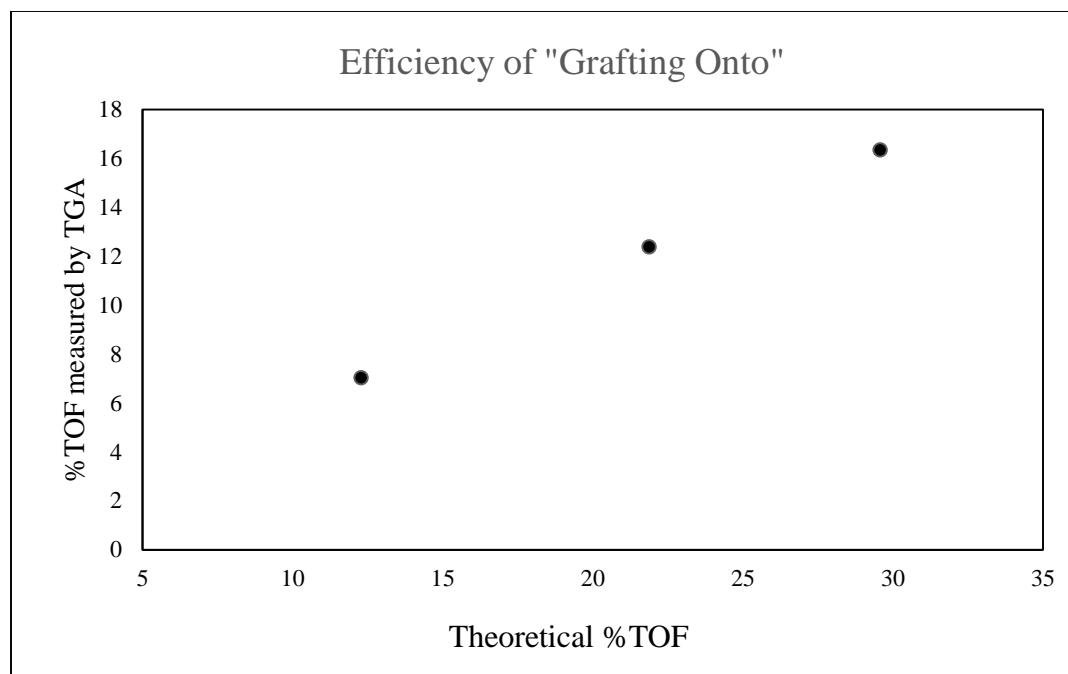
Figure 3.8. Grafting performance of $Cl_3Si-C_{11}-PMMA_{10}$ tier-2 oligomer on SiO_2 plotted as a function of %TOF measured by TGA and theoretical %TOF.

Grafting of tier-3 oligomer $Cl_3Si-C_{11}-PS_5-PMMA_5$ showed resulted in 15% TOF (Entry 1, Table 3.3). However, switching the order of blocks to $Cl_3Si-C_{11}-PMMA_4-PS_5$ (Entry 2, Table 3.3) showed significantly lower TOF of 3% although the theoretical % TOF is higher than the former oligomer. Increase in DPavg of tier-2 PMMA block to 10 (Entry 2, Table 3.3) resulted in low %TOF as well. This indicated the effect of relative positon of PS and PMMA segments on the availability of SiO_2 surface for trichlorosilyl end groups. This is probably due to the confirmation of oligomer in a non-polar solvent such as toluene where the polar trichlorosilyl end groups folds into nearby polar PMMA block making them inaccessible to the surface. Table 3.3 shows the grafting conditions of tier 3 oligomers along with theoretical %TOF and the values observed by TGA.

Table 3.3. Grafting performance of tier-3 oligomers and reaction conditions

Entry	Oligomer (Olig)	Mass of Olig (g)	SiO_2 (g)	Toluene (ml)	%TOF (theory)	%TOF (by TGA)
1	$Cl_3Si-C_{11}-PS_5-PMMA_5$	1.5 g	5.0 g	50 ml	23%	15%
2	$Cl_3Si-C_{11}-PMMA_4-PS_5$	2.2 g	5.0 g	50 ml	31%	3.0%
3	$Cl_3Si-C_{11}-PMMA_{10}-PS_5$	0.9 g	3.3 g	35 ml	21%	3.4%

3.3.1 Physical Characterization of multi-block oligomers post surface grafting

Once the oligomer chains were grafted onto solid surface, they were analyzed by two approaches: i) thermogravimetric analysis ii) ^{13}C CP-MAS (solid state) NMR. The TGA data was used to determine the percentage of the organic fraction (%TOF) of the surface grafted materials. The detailed methods to determine %TOF by accounting the mass of volatiles (in 25-180 °C range) and subtraction of %TOF from blank silica are outlined in Chapter 2. Figure 4 shows ^{13}C CP-MAS (solid state) NMR of tier-2 and tier-3 oligomers after "grafting onto" silica.
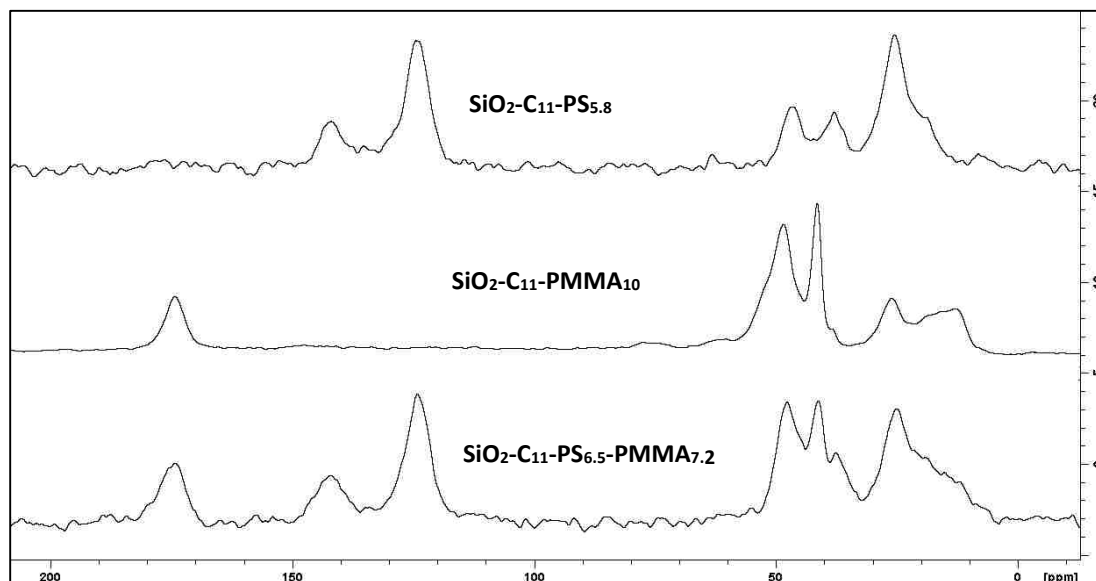
Figure 3.9. ^{13}C CP-MAS (solid-state) NMR of tier-2 tier-3 oligomers post grafting.

3.4. Clay based ESSs by "grafting onto"

In addition to silica, clay is another major mineral component of soils, and it is of interest to study the binding effects of ACs on clay-supported ESSs in addition to silica supported ESSs. Clay is an important inorganic component of soil consisting of layers of tetrahedral silicates and octahedral aluminates in a nanometric ordered structure. As discussed in Chapter 1, most of the clay materials are negatively charged. Therefore, natural and chemically modified clays have been studied for the adsorption and removal of toxic metal ions from water solution. The excellent adsorption towards metals is also aided by large potential for ion exchange, high specific surface area and pore volume. Clays uptake heavy metal ions through a series of complex adsorption mechanisms such as bonding to the edges, surface complexation and ion exchange. Often, the chemical modification of clays involves pre-treatment with organic compounds either by mixing or by covalent bond formation to convert them to hydrophobic and organophilic materials for adsorption of HOCs. A study on effect of surface modification showed that the sorption of cypermethrin to particulate organic matter increased with the increasing coating of the clay mineral montmorillonite by humic material. Similarly, Ahangar et al. reported that the removal of clay minerals increased sorption capacity of soils for diuron and phenanthrene[79-80]. the lower sorption associated with increased amount of clay may be a result of blockade of sorption sites of SOM by mineral SOM interactions. Also the polar edges of the clay structure form a hydration layer in aqueous solution which prevents sorption of non-polar organic pollutants onto the surface of the mineral. This is also supported by the increased sorption of organic pollutants by inorganic rich soil in non-aqueous solutions where the high sorption intensity by minerals often interferes with the study on effect of SOM interactions with organic pollutants.[81-82]

Aforementioned properties of clay minerals indicate that incorporation of clay component in an artificial soil such as engineered soil surrogates (discussed in Chapter 2) will further help in understanding in depth the molecular level interactions involving clay-based soils and ACs. Following a systematic study of the effects of organic matter's chemical structure on AC sorption through functionalization of multi-block oligomer chains on mesoporous SiO_2, one obvious question arises- will replacement of SiO_2 by clays in ESS show similar trends in sorption of norflurazon as in Chapter 2? Based on the previous arguments and findings in Chapter 2, the sorption of norflurazon in aqueous solution is not expected to change significantly as the organic phase is mainly responsible for sorption, inorganic phase acting as a solid support surrounded non-polar first tier and possibly water in exposed mineral surface. However, this cannot be said for other pollutants of different size, polarity or ability to create specific chemical interactions with clay minerals. Another topic of interest is the structural features of pollutant that causes differences in sorption between mesoporous silica and clay minerals. To answer these questions and verify the predictions, a novel design of ESS with clay as inorganic matrix was envisioned. Similar to SiO_2 based ESS, the preparation of clay based ESS involves modification of clay with multi-block oligomer chains with each block as a model for components of SOM such as lipids, lignin and polar groups.

Initial attempts to modify sodium (ion-exchanged) montmorillonite (Na-MONT) (source: SWY-2) was done by refluxing trichlorosilyl end-functionalized multi-block oligomer Cl_3Si-C_{11}-$PMMA_5-PS_5$ (DPavg are approximate) refluxing in toluene for 24 hr. yielded low TOF of 2% on clay surface (Entry 1, Table 3.4) measured by TGA (Appendix). Increasing the concentration of oligomer by i) reducing the amount of solvent and ii) increasing the relative amount of oligomer was expected to improve grafting performance. However, doing so led to even lower %TOF (Entry

2, Table 3.4). The relatively low %TOF in clays is consistent with the findings from grafting on

SiO_2 (Table 3.3, Entry 2 and 3) where oligomers with PMMA as a second block gave poor grafting

efficiency possibly due oligomer confirmation with trichlorisilyl groups unavailable for surface

chemistry. The poor grafting efficiency may have been caused by lower availability of SiOH

functional groups on montmorillonite because of the ordered structure of the clay mineral with

closely stacked tetrahedral and octahedral sheets with no significant Si-OH groups available for

grafting. However, more work is needed, especially grafting of oligomers with Cl_3Si-PS-PMMA

which gave significantly better grafting performance for grafting onto Silica (Table 3.3, Entry 1)

^{13}C CP-MAS NMR of the modified clay minerals showed no carbon signals, most likely due very

low organic content.

Table 3.4. Grafting of tier-3 Cl_3Si-C_{11}-$PMMA_5$-PS_5 oligomer on sodium montmorillonite with theoretical and observed %TOF

Entry	Mass of Na MONT	Mass of Oligomer	Volume of Toluene	%TOF (Theoretical)	%TOF (by TGA)
1	5.0g	1.7g	50ml	25	2.0
2	1.6g	1.58g	15ml	50	1.2

Another approach to modification of clay surface is the immobilization of cation containing

polymerization initiators (for grafting from) and cation end terminated polymers (for grafting

onto). In the literature, most of the modification of clay with hydrophobic organic compounds is

achieved by replacing the clay's natural inorganic exchange cations with organic cations through

ion exchange process. This is because organic cations form the organic-clay complex by inserting

into the interlayer galleries. Most commonly used organic cations are quaternary ammonium salts

with a general structure $[(CH_3)_3NR]+$ or $[(CH_3)_2NR_2]+$, where R is an aromatic or aliphatic

hydrocarbon.[83-84] Pure clays are modified with initiators or monomers containing a such organic cations followed by a polymerization reaction.

3.5. Comparison between ESS and real soil: Acetylation of Pahokee peat

Humic substances are described as heterogeneous polyelectrolytes that are predominantly negatively charged at natural soil pH values. The major sources of negative charge in humic substances are oxygen containing groups such as carboxylic and phenolics, although other less abundant N and S containing functional groups also contribute to the anionic character.[85] These polyelectrolytic anions act as binding sites for protons and metal ions. Various attempts to determine the nature of oxygen containing functional groups are done using methods such as direct and indirect potentiometric titrations, radiometric determination, infrared spectroscopy, ^{13}C-NMR or ^{29}Si-NMR.[86] Humic substances are chemically derivatized to enhance and separate the NMR signals of the hydroxyl groups.[87-89] There are several reports on the contribution of specific functional groups on the total humic acidity by selective derivatization of hydroxyls and carboxylic acids using "protecting groups".[85-86, 90-91]

To compare the sorption data of a series of Engineered Soil Surrogates (ESSs) from Chapter 2 with real soils, Elliott soil and Pahokee peat were acetylated and characterized. Scheme 3.3 outlines the reaction conditions for acetylation of the soils. Approximately 2g of soils were immersed in 30 ml neat acetic anhydride and six drops of concentrated H_2SO_4 were added followed by stirring at 70°C for 5 hours. For a control reaction, exact same process was done using DMSO instead of acetic anhydride. ^{13}C NMR analysis of the dried Eliott soil did not show any significant extent of acetylation due to lower percentage of total organic fraction (%TOF). However, acetylation of Pahokee peat was successful indicated by the 5% increased TOF in the TGA and the enhanced carbonyl C peak (around 180ppm) in ^{13}C CP-MAS NMR (Figure 3.10) The

acetylated Pahokee peat was used to test the sorption of norflurazon and compared with previously reported [92] sorption parameters of unmodified Pahokee peat along with acetylated and non-acetylated ESS with results outlined in Table 3.5.
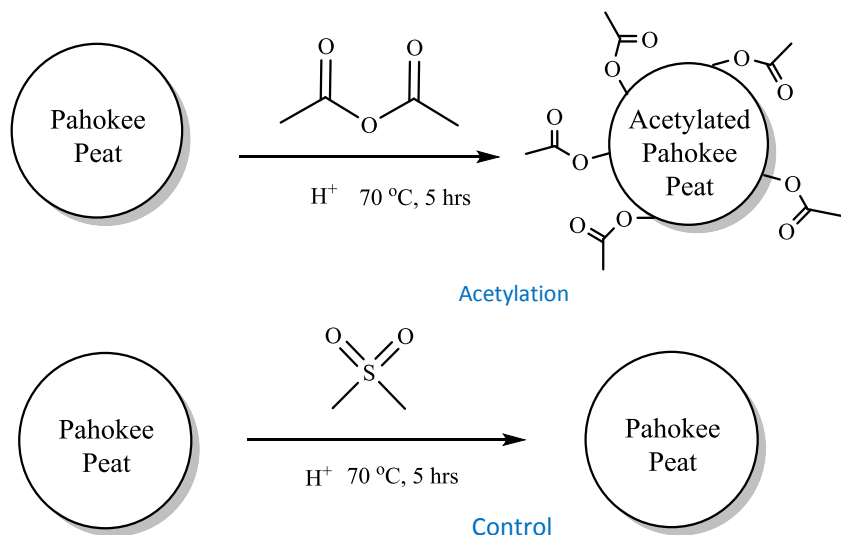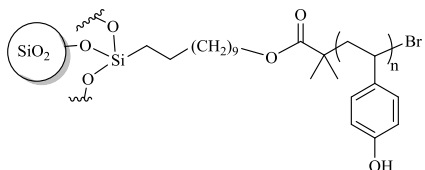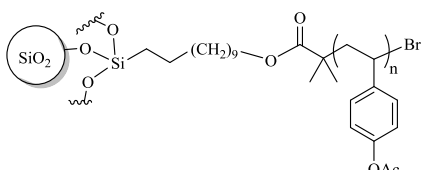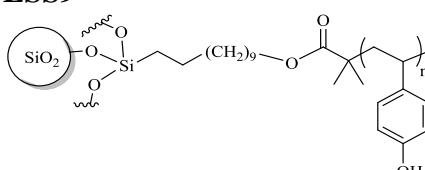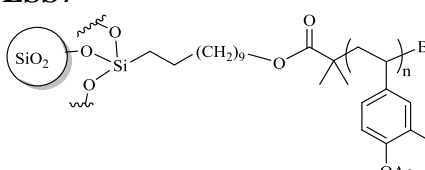
Scheme 3.3. Acetylation of Pahokee peat and the control reaction
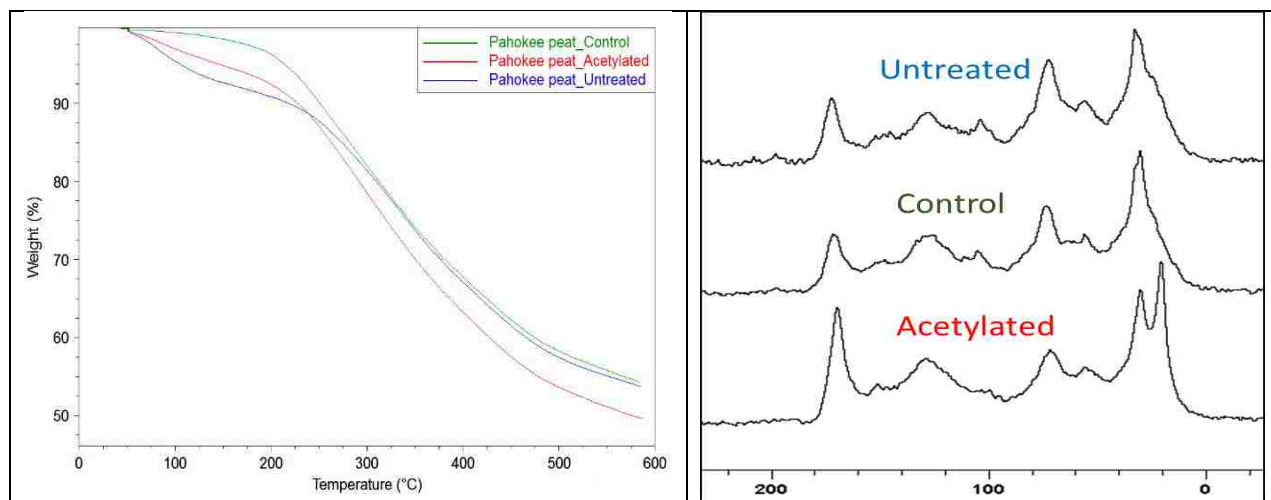
Figure. 3.10. **a)** TGA thermogram of Pahokee peat (left) **b)** ^{13}C CP-MAS (solid-state) NMR of Pahokee peat (right)

Table 3.5. Comparison of log K_F^{sor} values of non-acetylated and acetylated ESS/Pahokee peat obtained from batch mode sorption experiment.

Non-acetylated Soil/ ESS	log K_F^{sor}	log K_F^{sor}	Acetylated Soil/ESS
ESS8 (SiO₂—O—Si—(CH₂)₉—O—C(=O)—...—Br, OH)	2.669	2.837	**ESS6** (SiO₂—O—Si—(CH₂)₉—O—C(=O)—...—Br, OAc)
ESS9 (SiO₂—O—Si—(CH₂)₉—O—C(=O)—...—Br, OH, OCH₃)	2.543	2.246	**ESS7** (SiO₂—O—Si—(CH₂)₉—O—C(=O)—...—Br, OAc, OCH₃)
Pahokee peat	2.334	2.515	Acetylated Pahokee peat

(Note: Determination K_F^{sor} value of acetylated Pahokee peat was contributed by Ragib Hasan)

The sorption capacity for norflurazon was found to be greater in the acetylated Pahokee peat compared to the natural Pahokee peat as shown in Table 1. For interpretation of this result, the chemical change brought about by acetylation should be considered. Andjelkovic et al. reported acid catalyzed acetylation of humic substances with acetic anhydride for blocking of hydroxyl groups in alcohols and phenols.[85] The same study reported that the acetylation lead to modification of some of the carboxyl groups along with alcohols and phenols determined by direct and indirect titrations. Therefore, the acetylation process leads to conversion of polar –OH and –COOH groups to relatively less polar groups. In unmodified Pahokee peat at pH of 5.7 of the sorption experiment, the majority of the phenol and almost all of the alcohol are in the protonated –OH form while the carboxylic acids may be in both protonated and deprotonated forms in comparable numbers.

Based on the state of protonation at sorption condition, unmodified Pahokee peat contains highly polar groups and has high affinity towards water. Acetylation of the Pahokee peat significantly reduces the polarity and hence decreased affinity towards water. This is supported by early reports that esterification greatly decreases the water-sorbing capacity of the hydroxyl groups in cellulose.[93-95] During the sorption of norflurazon from aqueous solution, the hydration of unmodified Pahokee peat is expected to form hydration layers around abundant polar groups that hinders adsorption of hydrophobic norflurazon on the organic matter. However, once the polarity of these sites is decreased through acetylation, the inhibiting effect of hydration layer on adsorption is decreased leading to increased sorption of norflurazon. This can be viewed as a competitive sorption where Pahokee peat is a sorbate whereas water and norflurazon are sorbents. The decrease in polarity of SOM and soil overall gives the hydrophobic norflurazon an increased competitive advantage for sorption onto the soil.[82]

After systematic investigation on role of the chemical structures of each *tiers* in sorption of organic compound, as shown in Chapter 2, one question arises- what makes a surrogate soil more "soil-like" so that better models of soils can be synthesized? One pragmatic approach to design of ESS for modeling soils is to incorporate chemical structures that creates comparable bulk properties and eliminate the ones that show contrary bulk properties to the real soils. Comparison of sorption trends between ESS and Pahokee peat shows that **ESS8** exhibited a trend in sorption affinity similar to Pahokee peat with K_F^{sor} value greater for acetylated phenolic group which can be explained from hydration perspective as discussed earlier. On the contrary, **ESS9** showed the sorption trend in contrary to that of **ESS8** and Pahokee peat. This is attributed to the ability of ESS9 to create specific binding interactions with norflurazon as a result of intermolecular H-bonding between phenolic –OH and the nearby O-methyl oxygen (as illustrated in Figure 2.12,

Chapter 2). Although comparison of acetylation between tier-2 ESSs and Pahokee peat (specifically ESS8, ESS9 versus Pahokee peat) may seem difficult because of the much complex and heterogeneous nature of Pahokee peat and the lack of selectivity of the acetylation reaction for phenolic moieties, this could be a guide to design for more realistic soil models. The presence of neighboring phenolic and methoxy groups in ortho position to each other as in **ESS9** has been shown to be a recurring structure in native lignin.[96-98] However the particular arrangement of native structure may not remain intact. This is also supported by various studies that show the role of phenolic –OH in lignin to participate in condensation reactions resulting in inter-connected macromolecular structure of humic acid as they degrade in natual environments.[99-100] This may lead to low abundance of lignin derived chemical functionalities in Pahokee peat that possess structural features such as the one incorporated in O-aryl block of **ESS9**.

3.6. Future work: Cross-linking of ESSs

In synthetic polymers, cross-linking leads to increased molecular weight, mechanical strength as well as physical and chemical stability. The formation of interconnected polymer network also leads to decreased solubility and biodegradability.[101] There are growing evidence of cross-linking processes in geomacromolecular matrices such as the presence of matrix bound dicarboxylic acids in peat, humin and humic acid, [102-104] and kerogens[105-106] as confirmed through chemolysis studies. There are indications on roles of cross-linking in humification, the process by which smaller molecules undergo secondary synthesis through mineral/biotic catalyzed condensation reactions to give oxidized, amphiphilic, high molecular weight, condensed materials. A study on a non-hydrolysable organic fraction of a deep tropical soil ^{14}C dated about 8300 years revealed the presence of highly condensed cross-linked structure.[107] Therefore, cross-linking reaction is responsible for stabilization and protection of soil by physical, chemical and mechanical

reinforcement, and by decreasing the bioavailability of the chemicals and microbes that are responsible for soil's degradation. Cross-linking is also shown to play an important role in diagenesis of organic polymers. Brown coal, a soft combustible sedimentary rock formed by naturally compressed peat is shown to possess densely cross-linked, supramolecular structure.[108] Through cross-linking reactions, polysulfides, ammonia and amino acids are shown to introduce S and N containing functional groups into the structure of marine sediments.[109-111] This phenomenon has been observed observed in early diagenesis of kerogen[112], protokerogen and humics in marine environments.[109]

Cross-linking of macromolecules in soil has a significant effect on the sorption of HOC. In soil, the cross-linking can occur by two ways: a) covalent cross-links by organic compounds and b) complexation cross-links by polyvalent metal ions. Covalent cross-links are relatively irreversible under ambient conditions and are part of permanent structure of soil.[113] However, cross-links formed through complexation of SOM polyelectrolyte with polyvalent metal are dynamic and reversible.[114] The effect of cross-linkers on the overall morphology of soil depends on the nature and the extent of cross-links present in it. Cross- can create new binding sites within SOM and hence increase the affinity of the sorbent towards sorbate molecules. For example, For example, Cross-linking of leonardite potassium humate with N,N -methylene bisacrylamide greatly increased its water absorbing capacity.[115].The creation of new binding sites due to cross-links can increase the heterogeneity of binding sites leading to non-linear sorption. For example, Lu and Pignatello demonstrated that complexation of a soil humic acid with Al^{3+} reduced sorption linearity of hydrophobic compounds because of increase in the glassy character of humic acid through cross-linking.[116] Large extent of cross-linking in soil may cause decrease in sorption of

HOC by soil as a result of formation of condensed structure with minimal free volume limiting the access of sorbate molecules to the binding sites.

As discussed earlier, the cross-linking has significant effects on structure, confirmation and degradability of soil as well as its sorption properties. Therefore, incorporation of cross-links in the design of ESS is important for improving their prospects in study of geomacromolecular matrices including soil. The polar third tier consisting of poly (acrylic acid) or poly (methyl methacrylate) could be a site where cross-links can be easily formed using typically used bifunctional molecules such as dicarboxylic acids, diamines etc. Figure 3.11 shows cross-linking of polar third-tier of existing ESS structures with hexamethylenediamine, one of many possible ways of cross-linking the oligomers on ESS surface to design more complex soil models.
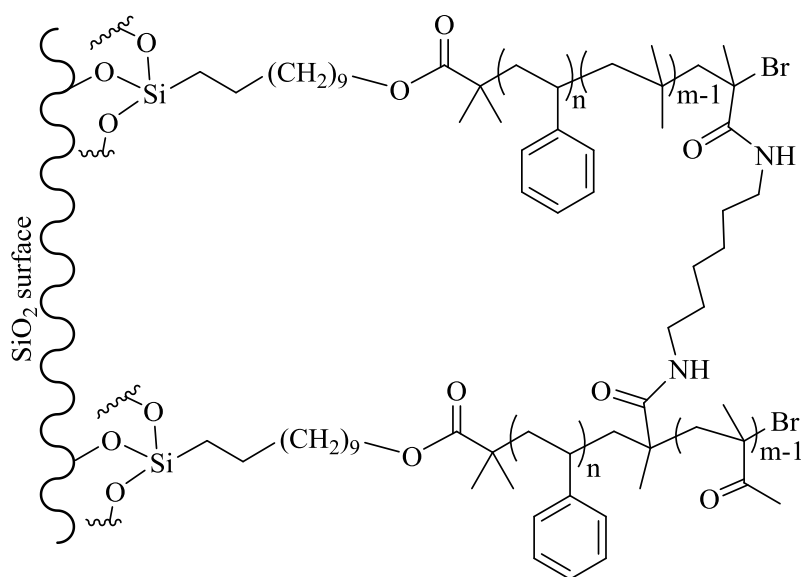
Figure 3.11. Illustration of the possible cross-link formation in between outermost polar blocks of tier-3 ESS.

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3.7. Notes

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Appendix 1. Experimentals for Chapter 2

Materials and Methods. *Chemicals:* The monomers styrene, 4-vinylphenyl acetate, 4-vinyl-2-methoxy phenol, methyl methacrylate were obtained from Aldrich and used after passing through alumina column to remove the inhibitor except 4-vinyl-2-methoxy phenol. Trichlorohexylsilane, trichlorododecylsilane and trichlorooctadecylsilane were obtained from Gelest. Silica gel (Merck grade 9385, pore size 60 Å, 230-400 mesh) 10-unden-1-ol, 2-bromoisobutyryl bromide, triethyl amine, trichlorosilane, Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst), copper bromide (CuBr), N,N,N',N",N"-pentamethyldiethyltriamine (PMDETA), acetic anhydride, pyridine, dimethylaminopyridine (DMAP) and hydrazine hydrate were obtained from Aldrich. Solvents (toluene, diethylether, hexane, acetonitrile, ethanol, ethyl acetate) were obtained from VWR.

Synthesis of 10-undecen-1-yl 2-bromoisobutyrate 3. The synthesis of 10-undecen-1-yl-2-bromoisobutyrate was accomplished following a procedure reported previously with slight modification.[43] To a solution of 10-undecen-1-ol **1** (4.08mL, 20.36mmol) in 100 mL diethyl ether in a 500mL round bottom flask (RBF) was added triethylamine (3.13 mL, 22.40 mmol). The flask was cooled to 0°C and a solution of 2-bromoisobutyryl bromide **2** (2.8mL, 22.4 mmol) in dry diethyl ether (50mL) was added dropwise through a dropping funnel with stirring over 10 minutes. The reaction mixture was allowed to come to room temperature and stirred for 15 hours. During the reaction, triethylammonium bromide ($Et_3N^+Br^-$) precipitated out from the reaction mixture. After the completion of reaction, 50 mL of hexanes was added and the precipitate was removed by gravity filtration. The solvent was removed under reduced pressure to give a colorless liquid which was purified by column chromatography using a 25:1 mixture of hexane and ethyl acetate. ^{1}H NMR was used to confirm the formation of the product. ^{1}H NMR (400 MHz, CDCl3) δ: 5.81

(ddt, J = 17.2, 10.1, 6.7 Hz, 1H), 5.02-4.92 (m,2H), 4.93 (t, J = 6.6 Hz, 2H), 4.17 (t, J = 6.6 Hz, 2H),2.90-1.98(m, 2H) 1.94 (s, 6H), 1.78-1.61(m, 2H), 1.56(s,6H), 1.44-1.23(m, 13H) ppm.

Synthesis of 11-(2-Bromo-2-methyl)propionyloxy undecyltrichloriosilane 4. To a 100 mL RBF at 0°C was added 10-undecen-1-yl 2-bromoisobutyrate **3** (7.11g , 22.27 mmol) and trichlorosilane (11.33mL, 112mmol) under nitrogen atmosphere followed by platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt ~2 % (Karstedt's catalyst) from Sigma(140 µL, 12µmol) and the reaction mixture was allowed to stir at room temperature for 24 hrs. The excess reagent ($HSiCl_3$) was removed under reduced pressure and the remaining product was dissolved in 50 mL hexanes and quickly filtered through a plug of silica to remove the catalyst. The product was obtained as a colorless liquid and the purity of the product was confirmed with disappearance of vinyl signals in ^{1}H NMR. 1 H NMR (400 MHz, CDCl3) 4.17 (t, J = 6.6 Hz, 2H), 1.94 (s, 6H), 1.70-1.60 (m, 4H), 1.55-0.89 (m, 16H) ppm

Synthesis of 2-methoxy-4-vinylphenyl acetate 6. Acetic anhydride (63mL, 666 mmol), pyridine (65 mL, 806 mmol) and DMAP (0.4 g, 3.27 mmol) were dissolved in DCM (50 mL) at 0 °C in a clean 500 mL RBF. Using a dropping funnel, 2-methoxy-4-vinyl phenol (10 g, 66.6 mmol) in DCM (50 mL) was added under nitrogen over 20 minutes, then allowed to come to room temperature and the reaction mixture stirred for 24 hr at room temperature. The reaction mixture was washed with 3 x 100 mL 10% $CuSO_4$ solution, 3 x 100 mL of saturated $NaHCO_3$ solution and 3 x 100 mL NaCl solution then dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the resulting yellow oil product was purified by column chromatography using 1:9 ethyl acetate: hexane mixture yielding a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.02-6.99 (m, 3H), 6.69 (dd, 1H), 5.70 (dd, 1H), 5.26 (dd, 1H), 3.87 (s, 3H), 2.32 (s, 3H) ppm.

Surface grafting of Tier-I ESSs on silica. In preparation, the SiO_2 gel was activated by heating overnight in an oven at 120 °C. The functionalization of silica with C_6, C_{12} and C_{18} aliphatic hydrocarbon chains was accomplished by heating corresponding trichlorosilyl-end group containing hydrocarbons with 3.0 g SiO_2 in Toluene at 80 °C. In a standard reaction, the toluene is added to a RBF charged with SiO_2, then the trichlorosilyl-end functionalized hydrocarbon (0.216mL C_6, 0.350mL C_{12} and 0.245mL C_{18}) was added via a syringe dropwise and the reaction mixture heated at 80 °C for 15 hours. Afterwards, the reaction mixture was allowed to cool to room temperature and the toluene was decanted after allowing the product to fully settle. The product was washed (2 x 25mL each) using toluene, acetonitrile, then methanol. The resulting material was dried in an oven overnight at 80 °C. TGA and ^{13}C CP MAS NMR were used to confirm the product.

Surface grafting of Tier-I ESS with terminal ATRP initiator (SiO_2-C_{11}-Br). In a 100 mL RBF, 6g of silica gel and 50mL Toluene were added together under nitrogen atmosphere and placed in oil bath at 80 °C. After 5 minutes, 11-(2-Bromo-2-methyl)propionyloxy undecyltrichloriosilane **4** (0.45mL) was added dropwise over 10 minutes and refluxed for 18 hr. The reaction mixture was then cooled and the silica particles were washed with toluene, then with acetonitrile and finally with ethanol (2 x 50mL solvent each wash). The particles were then dried under nitrogen in an oven at 50 °C for 48 hr. TGA and ^{13}C CP MAS NMR were used to confirm the product.

Surface graft extension for Tier-II oligo-(styrene)$_n$ block ESS (SiO_2-C_{11}-PS). In a 500 mL RBF charged with 50 mL of toluene, 5.0g SiO_2-C_{11}-Br with 4.37% TOF (w/w) coverage (0.218 g C_{11}-Br, 0.68 mmol) was added. The mixture was purged with N_2 gas for 5 minutes followed by addition of CuBr (212 mg, 1.48 mmol) catalyst and N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) ligand (0.32 mL, 1.53 mmol). While purging, styrene monomer (3.0 g, 28.8 mmol)

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was added via pipette, and the RBF fitted with a condenser. The reaction mixture was purged with N_2 gas for another 5 minutes then placed in an oil bath at 90 °C with stirring for 1 hr. The resultant product mixture was cooled down to room temperature and washed with 2 x 50 mL toluene, 2 x 50mL acetonitrile, 2 x 50mL ethanol, 2 x 50mL half-saturated EDTA solution, 2 x 50mL water and 2 x 50mL ethanol and then placed in oven at 50º C for 48 hours. The resulting faintly blue colored powder was analyzed by TGA and solid-state NMR.

Surface graft extension for Tier-II oligo-(4-acetoxystyrene)$_n$ block ESS (SiO$_2$-C$_{11}$-PAS). In a 250 mL RBF charged with 17 mL of xylene, 2.28g of SiO$_2$-C$_{11}$-Br with 4.52% TOF (w/w) coverage (0.10g, 0.32 mmol C$_{11}$-Br) was added. The mixture was purged with N_2 gas for 5 minutes followed by addition of CuBr (182mg ,1.27 x 10^{-3} mol) catalyst and N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) ligand (0.32mL, 1.53 m mol) . While purging, the monomer 4-acetoxystyrene (7.8 g, 48 mmol) was added via pipette, and the RBF fitted with a condenser. The reaction mixture was purged with N_2 gas for another 5 minutes and placed in an oil bath at 145 °C with stirring for 24 hrs. The resultant mixture was cooled down to room temperature and washed with 2 x 50mL toluene, 2 x 50mL acetonitrile, 2 x 50mL ethanol, 2 x 50mL half-saturated EDTA solution, 2 x 50mL water and 2 x 50mL ethanol and then placed in oven at 50 °C with stirring under positive N_2 pressure for 48 hours. The resulting tan colored powder was analyzed by TGA and solid-state NMR.

Surface graft extension for Tier-II oligo-(4-acetoxy-3-methoxystyrene)$_n$ block ESS (SiO$_2$-C$_{11}$-PAMS). In a 250 mL RBF charged with 17 mL of xylene, 2.26g of SiO$_2$-C$_{11}$-Br with 4.42 %TOF(w/w) coverage (0.099g, 0.31mmol C$_{11}$-Br) was added. The mixture was purged with N_2 gas for 5 minutes followed by addition of CuBr (184mg,1.28 mmol) catalyst and N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) ligand (0.32mL, 1.53 mmol). While purging with N_2,

the monomer 2-methoxy-4-vinylphenyl acetate **6** (10.0g, 52 mmol) was added via pipette, and the RBF fitted with a condenser. The reaction mixture was purged with N_2 gas for another 5 minutes and placed in an oil bath at 145 °C with stirring for 24 hours. The resultant mixture was cooled down to room temperature and washed with 2 x 50mL toluene, 2 x 50mL acetonitrile, 2 x 50mL ethanol, 2 x 50mL half-saturated EDTA solution, 2 x 50mL water and 2 x 50mL ethanol and then placed in oven at 50 °C for 24 hours. The resulting tan colored powder was analyzed by TGA and solid-state NMR.

Hydrolysis of acetoxy group of SiO_2-C_{11}-PAS and SiO_2-C_{11}-PAMS. Polymer functionalized silica SiO_2-C_{11}-PAS/ SiO_2-C_{11}-PAMS (Approximately 2.0 g) was added to a 250mL RBF and 40mL THF per gram of the polymer functionalized silica gel was added and stirred. Hydrazine hydrate (1.165mL/g polymer functionalized silica) was added drop wise and the RBF was flushed with N_2 gas and sealed with stopper. The mixture was stirred at room temperature for 10 hrs. Afterward, the resulting mixture was washed with 2x50mL THF, 50mL ethyl acetate and 50 mL ethanol and then oven dried under N_2 at 50 °C for 48 hrs. The resulting solid was analyzed by TGA and solid-state NMR.

Surface graft extension for Tier-III oligo-(styrene)$_n$-(methylmethacrylate)$_M$ block ESS (SiO_2-C_{11}-PS-PMMA). In a 500 mL RBF, 50 mL of toluene was added. 5.0 g of initiator functionalized silica gel with 2.87% (w/w) coverage (0.14 g, 0.45 mmol C_{11}-Br) was added. The mixture was purged with N_2 gas for 5 minutes followed by addition of CuBr (212 mg ,1.48 mmol) catalyst and N,N,N′,N″,N″- pentamethyldiethylenetriamine (PMDETA) ligand (0.32 mL, 1.53 mmol) were added respectively. Styrene monomer (2.0 g, 19.2 mmol) was added and a condenser was attached to the RBF. The reaction mixture was purged with N_2 gas for another 5 minutes and placed in an oil bath at 90 °C with stirring for 1 hour. The reaction was cooled down to room

temperature and the solvent along with dissolved unreacted monomer was decanted off under nitrogen atmosphere. 50 mL of toluene was added to the flask and bubbled with N_2 for 5 minutes. Again, CuBr (212 mg ,1.48 mmol) catalyst and N,N,N′,N″,N″- pentamethyldiethylenetriamine (PMDETA) ligand (0.32mL, 1.53mmol) were added to the flask followed by the addition of methyl methacrylate monomer (4.0g, 40mmol) under nitrogen atmosphere and the reaction mixture was refluxed with stirring at 90°C for 18 hrs. The reaction mixture was cooled down to room temperature, and washed with toluene, (2x50mL) acetonitrile,(2x50)mL ethanol,(2x50mL) half-saturated EDTA solution, (2x50mL) water and (2x50mL) ethanol and then placed in oven at 50° C under positive N_2 pressure for 24 hours. The resulting product SiO_2-C_{11}-PS-PMMA(**ESS10**) was analyzed by TGA and solid-state NMR.

Synthesis of SiO₂-C₁₁-PS-PMAA. In a 100 mL RBF, added 0.5g NaCN and 10 mL hexamethylphosphoramide (HMPA) and the mixture was placed in sonicator for 10 minutes. NaCN partially dissolved in HMPA leaving few chunks of NaCN suspended in the mixture. Added 2.0g of SiO_2-C_{11}-PS-PMMA to the RBF and capped with a septa. The mixture was placed in oil bath at 70°C with stirring for 24 hours. The reaction mixture was cooled and washed with toluene, (2x20mL) acetonitrile , 0.01M HCl solution (2X20mL) and finally with ethanol,(2x20mL). The resulting product SiO_2-C_{11}-PS-PMAA (**ESS11**) was placed in oven at 50° C for 24 hours and was analyzed by TGA and solid-state NMR.

Washing. After the grafting of each tier in SiO_2 gel, there are several washing steps involved with solvents of wide-range of polarities in order to make sure the ESS is free from the reagents from the reaction. The initiator-functionalized SiO_2 is washed with 2 x 50mL each of toluene, acetonitrile and ethanol. The post-polymerization washing step is more rigorous as it requires the removal of Cu catalyst residues. This washing involves 2 x 50mL each of toluene, acetonitrile,

ethanol, half-saturated ethylenediaminetetraceticacid (EDTA) solution, water and ethanol again. The washed ESS sample is then dried in an oven under N_2 flow at 50 °C for 24 hrs.

Thermo-Gravimetric Analysis (TGA), Solid State Nuclear Magnetic Resonance (NMR) Analysis, and X-ray Photoelectron Spectroscopy (XPS). All ESSs were characterized by a combination of TGA, solid-state NMR, and XPS. The TGA analysis was performed on 4 to 8 mg of sample using a TA System TGA 2950, with a temperature ramp of room temperature (RT) to 600 ºC at a rate of 10 ºC per minute. The percent mass loss versus temperature was plotted. The solid-state NMR analysis employed ^{1}H-^{13}C cross polarization magic angle spinning (CP-MAS) technique and was performed on an AV 400 MHz Bruker solid-state instrument with sample packed into a 4 or 2.5 mm ZrO_2 rotor. Spectra were acquired using the following parameters: 2048 scans, ramp cross-polarization, contact time of 2 ms, 2.0 s delay between scans; spinning speed of 12-15 kHz, a 120 Hz line broadening function was applied, and referenced to y-glycine -CH_2-signal at 43.5 ppm. XPS data were acquired with a Kratos AXIS 165 system with a monochromatic AlKα source and a hemispherical electron energy analyzer. The pressure in the analyzing chamber was less than 3×10^{-9} torr. Survey spectra were recorded with 80 eV pass energy and high-resolution elemental spectra were recorded with 40 eV pass energy 150 W X-ray beam power. High-resolution elemental spectra were recorded with 40 eV pass energy. The X-ray beam power used in all spectra collection is 150 W. The reported binding energies were based on the analyzer energy calibration (Au 4f measured at 84.0 eV for all samples). The peaks in the high- resolution elemental spectra were fit using the software supplied with the instrument. A linear background was used for the data processing.

NOR Sorption and Desorption Isotherms. The background solution used for all experiments consisted of 18 Ωm water containing 0.01 M $CaCl_2$ (96.0 %, Sigma-Aldrich St. Louis, MO), 100

ppm NaN$_3$ (99 %, Acros), and 0.05 M MES (high purity, VWR Radnor, PA) at a pH of 5.75 to maintain a constant ionic strength, suppress biological activity,[17] and maintain pH, respectively. Additionally, 0.1% v/v methanol (reagent grade, VWR Radnor, PA) was used to help dissolve NOR into the background solution to create a stock solution of NOR.

The batch sorption and desorption isotherm experiments were carried out in accordance with the OECD method 106 (OECD (2000), *Test No. 106: Adsorption -- Desorption Using a Batch Equilibrium Method*, OECD Guidelines for the Testing of Chemicals, Section 1, OECD Publishing, Paris).[44] Each experiment was performed with sets consisting of four replicates for each data point, a background solution with ESS blank, and a NOR solution control (NOR concentration control). Two "sizes" (i.e., normal- and small-scale) of sorption-desorption experiments were performed due to a limitation in available ESS quantity for some of the ESSs. For **ESS 1** through **ESS 9**, 8 mL of sorbate solution in an 8 mL clear glass scintillation screw-cap vial with Teflon-lined septa (VWR Radnor, PA) was used. For **ESS 10** and **11** (because of small quantity available), 2 mL of sorbate solution in a 2 mL plastic micro conical vial (VWR Radnor, PA) was used. No NOR sorption was found for either type of vessel (vial and cap) used.

The required amount of ESS was added to each sample and blank vessel and recorded with a deviation of ± 0.1 mg or less. The appropriate solution was then added to the to the appropriate samples and controls (NOR solution) as well as blanks (background solution) vessels and the weights were appropriately recorded. Specifically, the isotherms were performed with eight NOR concentrations of 1, 2, 4, 6, 8, 12, 16, and 20 ppm. The mixtures were then horizontally shaking (i.e., agitated) in the dark at 150 rpm with a temperature of 25 ± 1 ºC (Refrigerated Incubator Shaker, New Brunswick Scientific Edison, NJ). After the samples were centrifuged at 3400 rpm

for 10 minutes (Sorvall Biofuge Stratos). Then 7 mL (normal-scale) and 1.8 mL (small-scale) of the supernatant was removed for analysis and the remaining mixtures were weighed.

Prior to isotherm experiments of NOR with the ESSs, the soil-to-solution ratio and mass balance, as well as sorption kinetics equilibrium experiments, were performed to determine the appropriate solution-to-soil ratio and equilibrium time for each ESS studied, again in accordance with the OECD method 106.

Soil to solution ratio and sorption kinetics of ESSs

Table A.1. Soil-to-solution (S_2S) ratio, sorption kinetics, and desorption kinetics with 20 ppm Norflurazon (NOR) of each ESS; weight (S_2S), time (kinetics) and the percent sorption-desorption of NOR (standard deviation) included.

Entry	S_2S ratio	Sorption kinetics	Desorption kinetics
ESS1	300 mg - 22.27 (1.02)	5 days - 26.97 (0.88)	5 days - 76.60 (0.02)
ESS2	20 mg - 47.31 (0.17)	5 days - 48.28 (0.22)	5 days - 11.80 (0.02)
ESS3	20 mg - 65.46 (0.10)	5 days - 58.55 (0.14)	5 days - 36.40 (0.01)
ESS4	20 mg - 73.13 (0.11)	5 days - 69.85 (0.13)	5 days - 25.00 (0.01)
ESS5	20 mg - 65.12 (0.62)	5 days - 67.23 (0.34)	5 days - 24.45 (0.02)
ESS6	20 mg - 74.88 (0.91)	5 days - 74.03 (0.12)	5 days - 14.58 (0.02)
ESS7	40 mg - 51.95 (0.16)	6 days - 45.09 (0.21)	6 days - 26.47 (0.03)
ESS8	20 mg - 53.01 (0.21)	5 days - 52.89 (0.16)	5 days - 24.67 (0.03)
ESS9	40 mg - 51.95 (0.15)	6 days - 53.82 (0.21)	6 days - 20.70 (0.02)
ESS10	5 mg - 44.17 (1.10)	5 days - 35.73 (0.22)	5 days - 37.68 (0.07)
ESS11	5 mg - 38.56 (0.48)	2 days - 39.34 (0.32)	4 days - 41.67 (0.09)
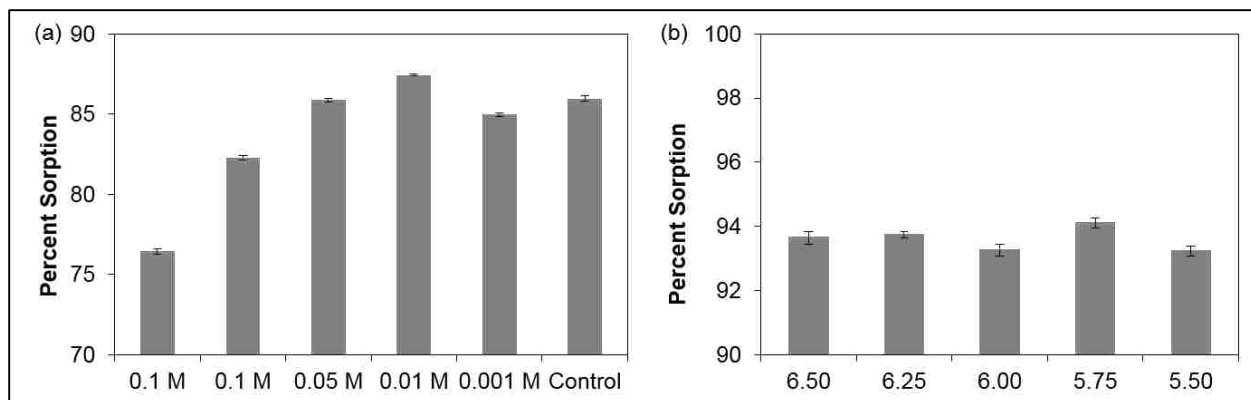
Figure A.1. Percent sorption of 20 ppm Norflurazon on 10 mg of **ESS3** at (a) pH 6.00 and a concentration of 0.1 - 0.001 M of MES buffer as well as a non-buffered set as control and (b) various pH in buffer of 0.05 M MES. With concentration of 0.01 M Mes buffer and pH 5.75 chosen for all experiments.
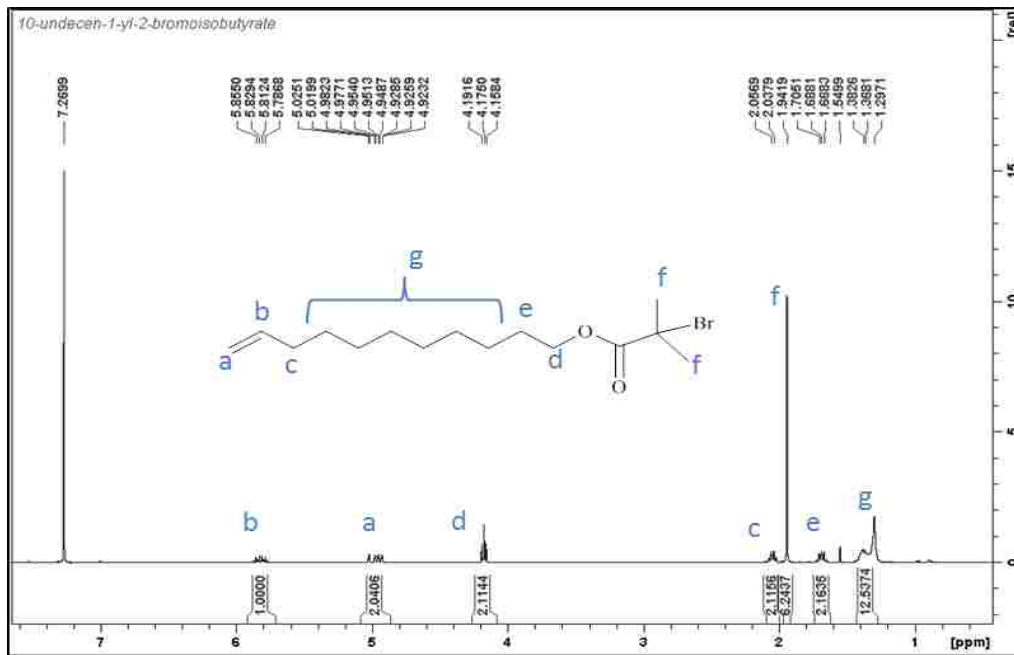
Appendix 2. Spectra for Chapter 2

NMR spectra

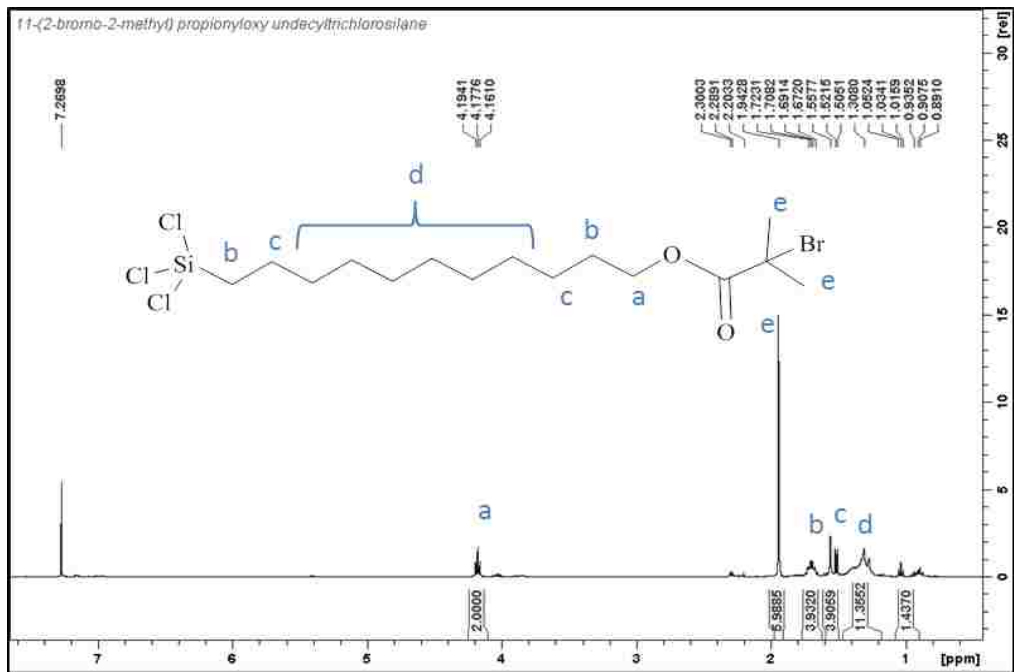**Figure A.2.** ^{1}H NMR spectra of 10-undecen-1-yl-2-bromoisobutyrate (**3**)

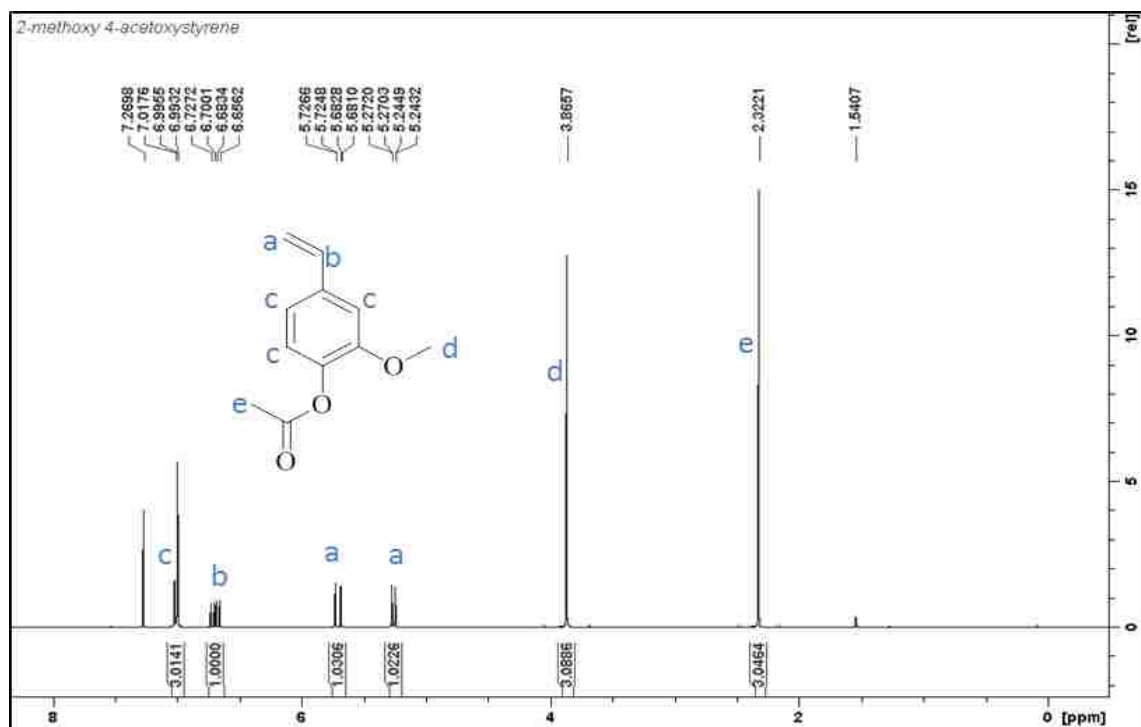**Figure A.3.** ^{1}H NMR spectra of 11-(2-Bromo-2-methyl) propionyloxy undecyltrichloriosilane (**4**)

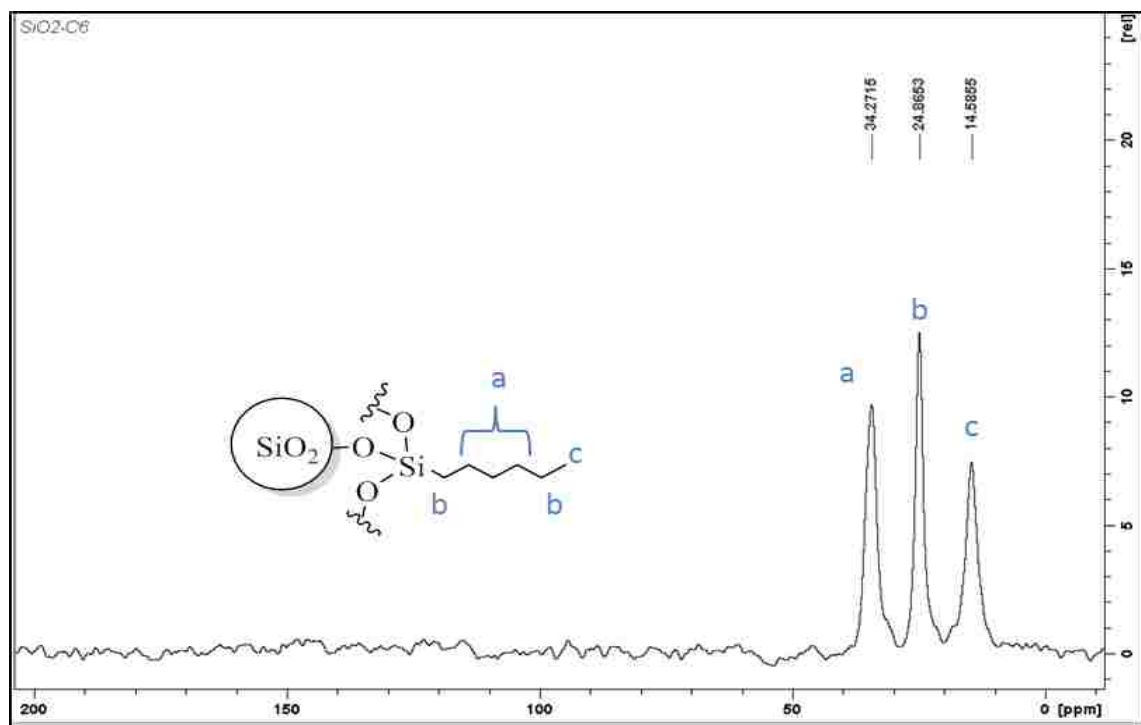**Figure A.4.** ^{1}H NMR spectra of 2-methoxy-4-vinylphenyl acetate (**6**)

Figure A.5. CP-MAS ^{13}C NMR of SiO$_2$-C$_6$ (**ESS 2**)
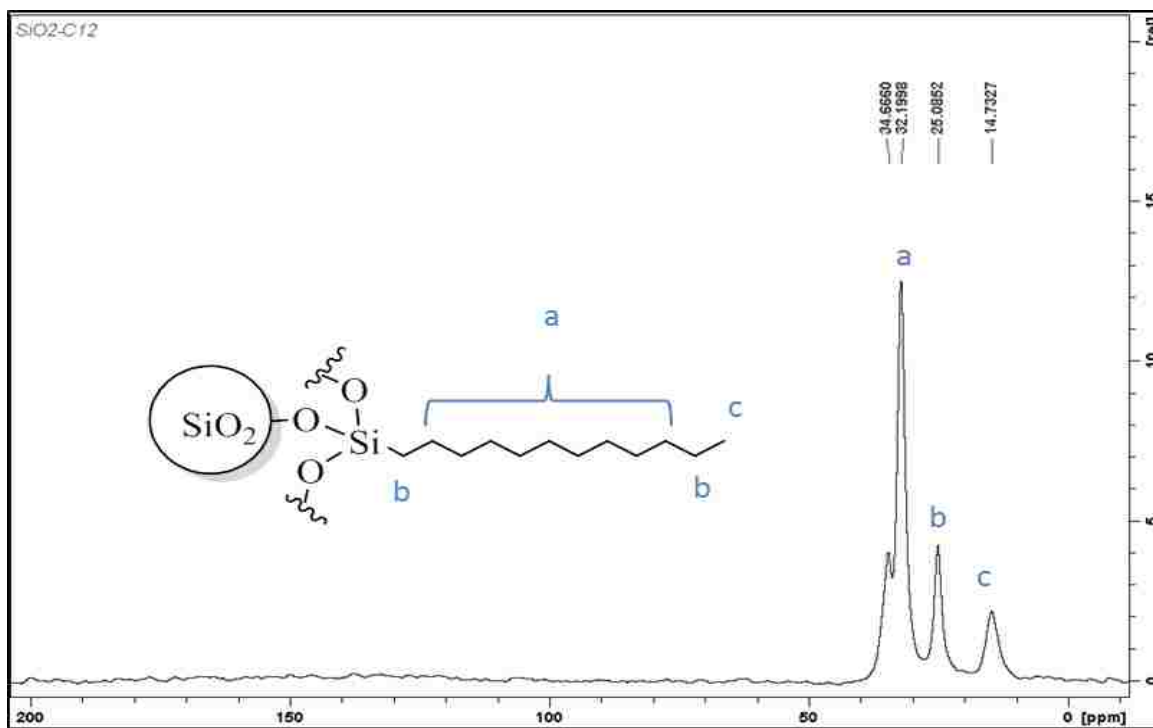
Figure A.6. CP-MAS ^{13}C NMR of SiO$_2$-C$_{12}$ (**ESS 3**)
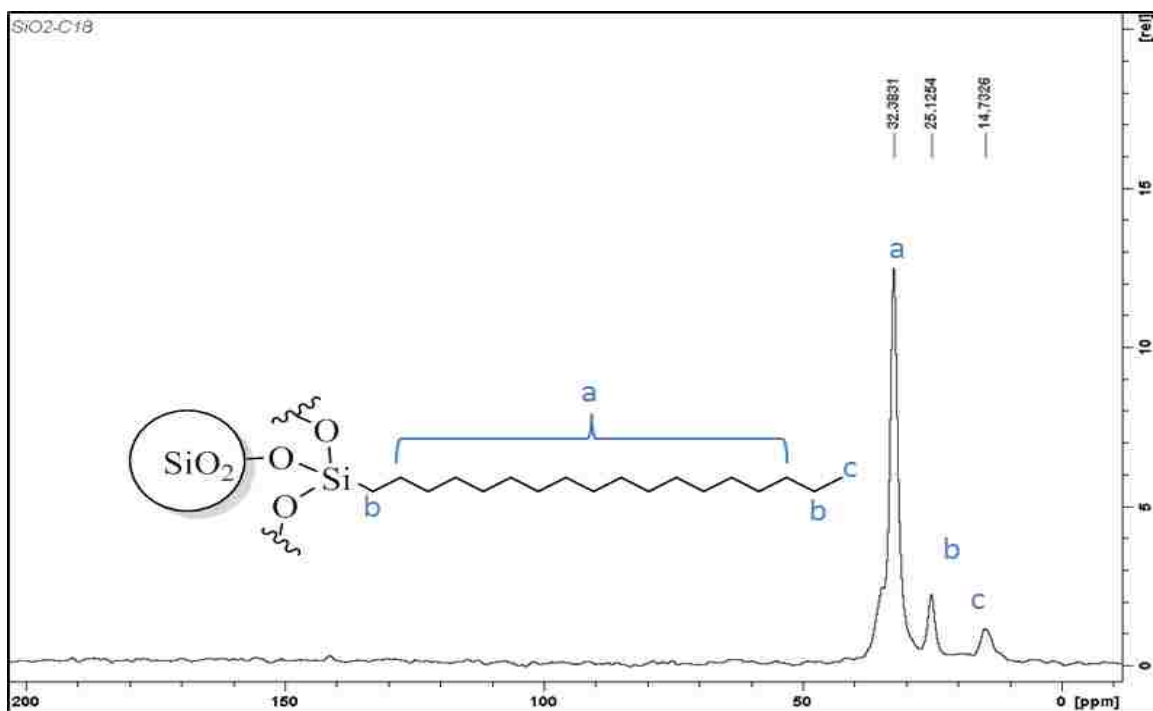
Figure A.7. CP-MAS ^{13}C NMR of SiO$_2$-C$_{18}$ (**ESS 4**)
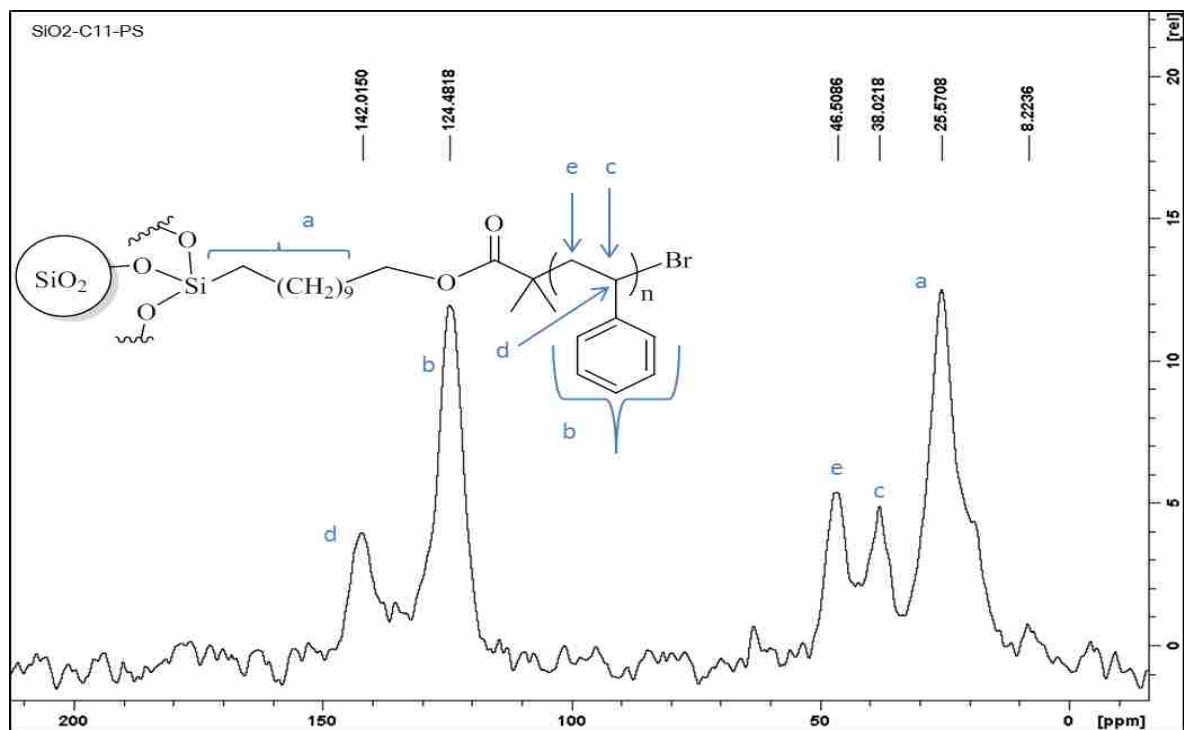
Figure A.8. CP-MAS ^{13}C NMR of SiO$_2$-C$_{11}$-PS (**ESS 5**)
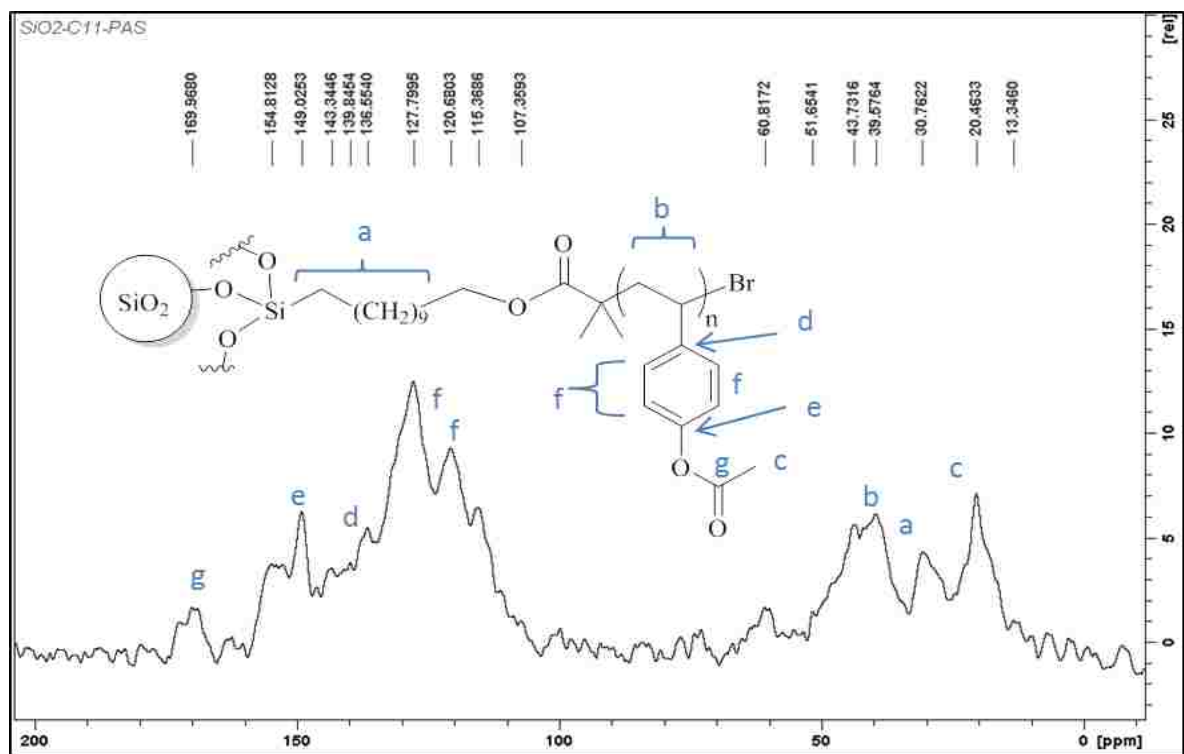
Figure A.9. CP-MAS ^{13}C NMR of SiO$_2$-C$_{11}$-PAS (**ESS 6**)
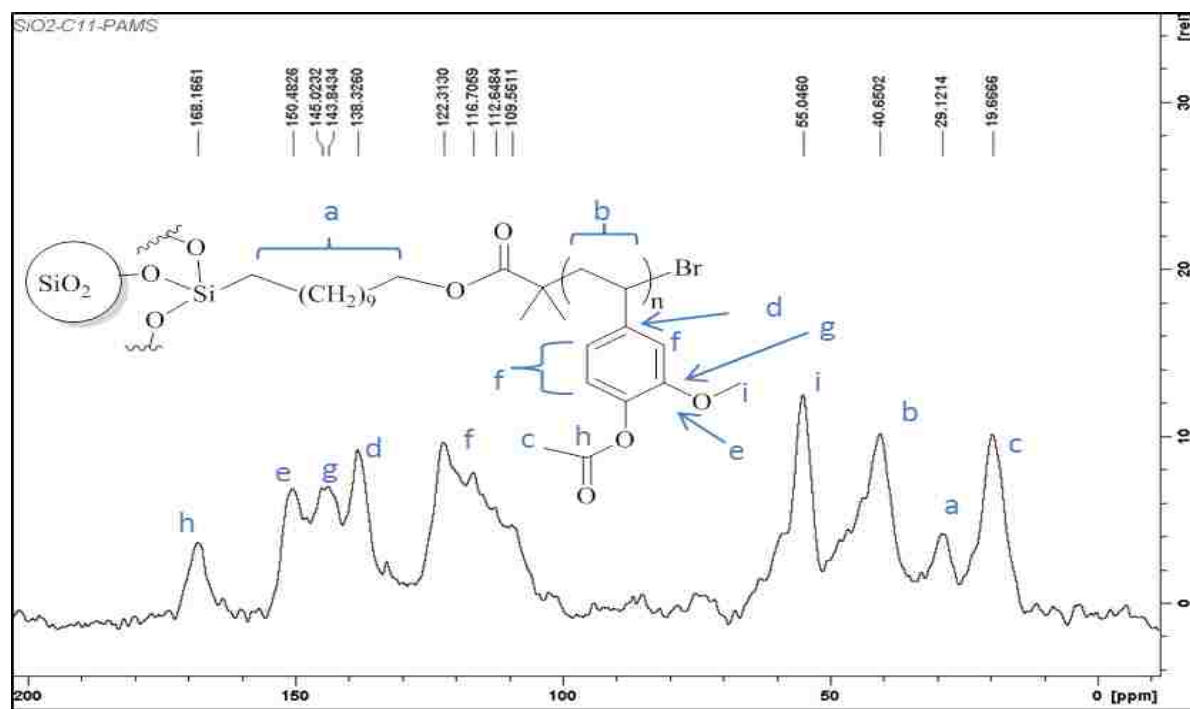
Figure A.10. CP-MAS ^{13}C NMR of SiO$_2$-C$_{11}$-PAMS (**ESS 7**)
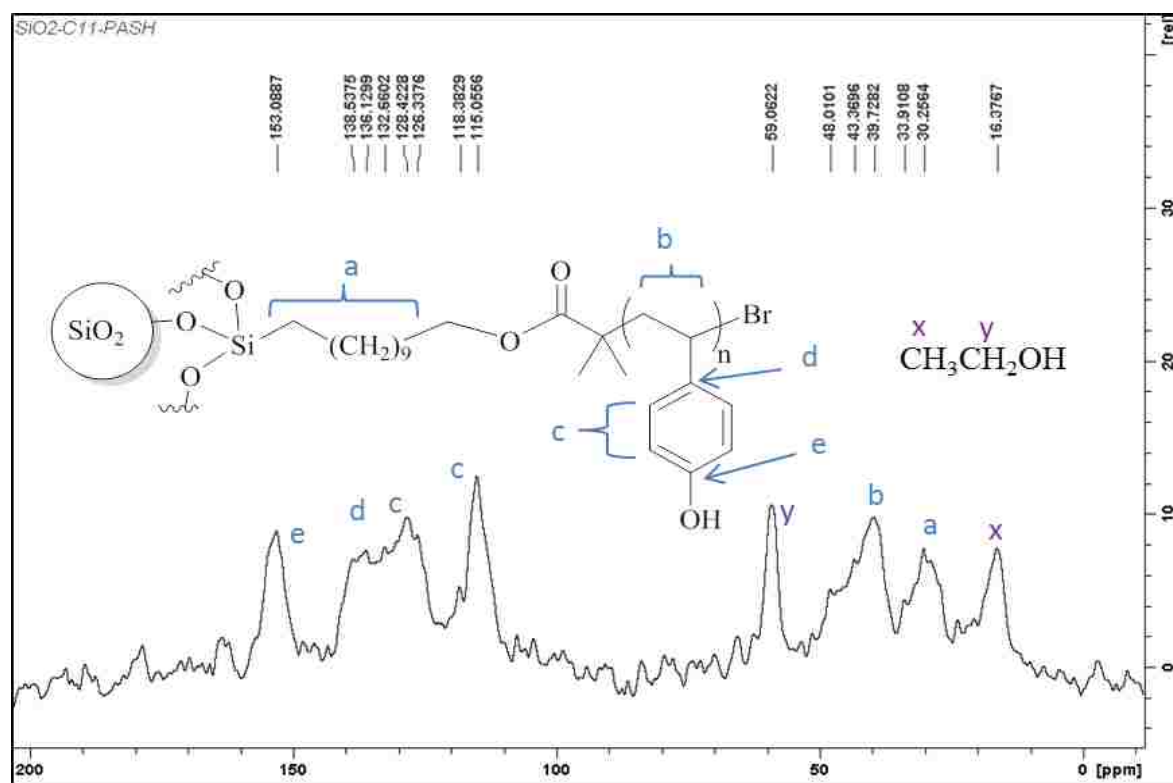
Figure A.11. CP-MAS ^{13}C NMR of SiO$_2$-C$_{11}$-PASH (**ESS8**). The NMR also shows some residual solvent from final washing step (peaks x and y).
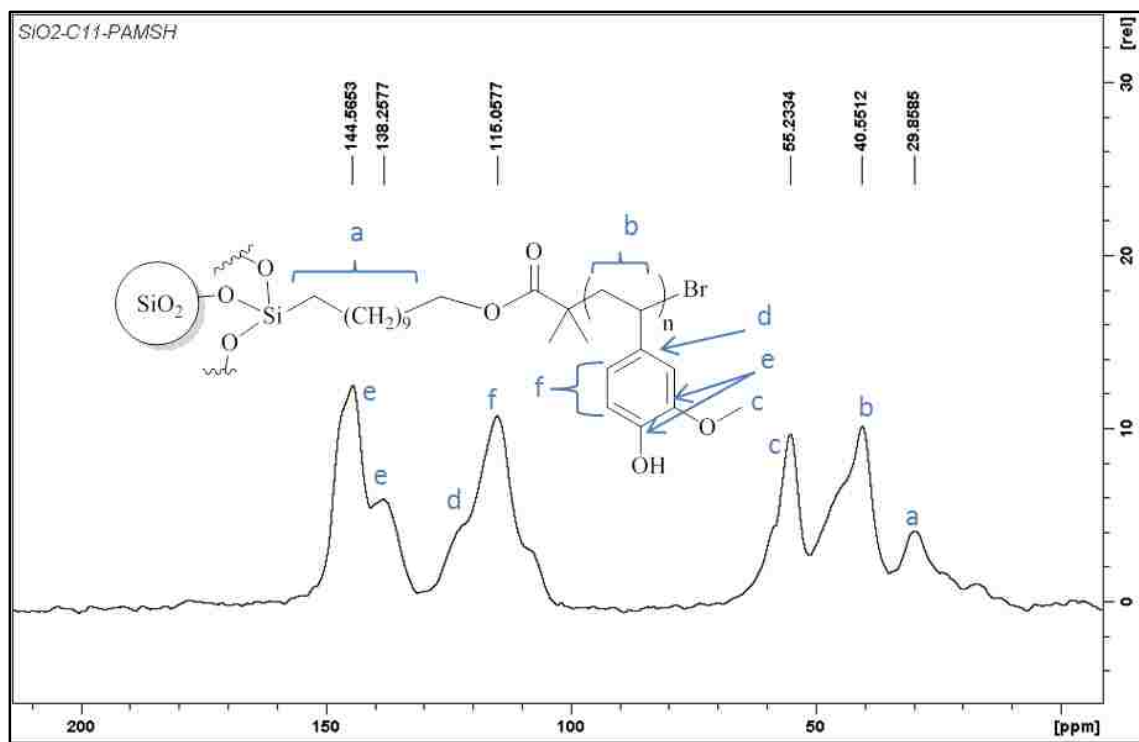
Figure A.12. CP-MAS ^{13}C NMR of SiO$_2$-C$_{11}$-PAMSH (**ESS9**)
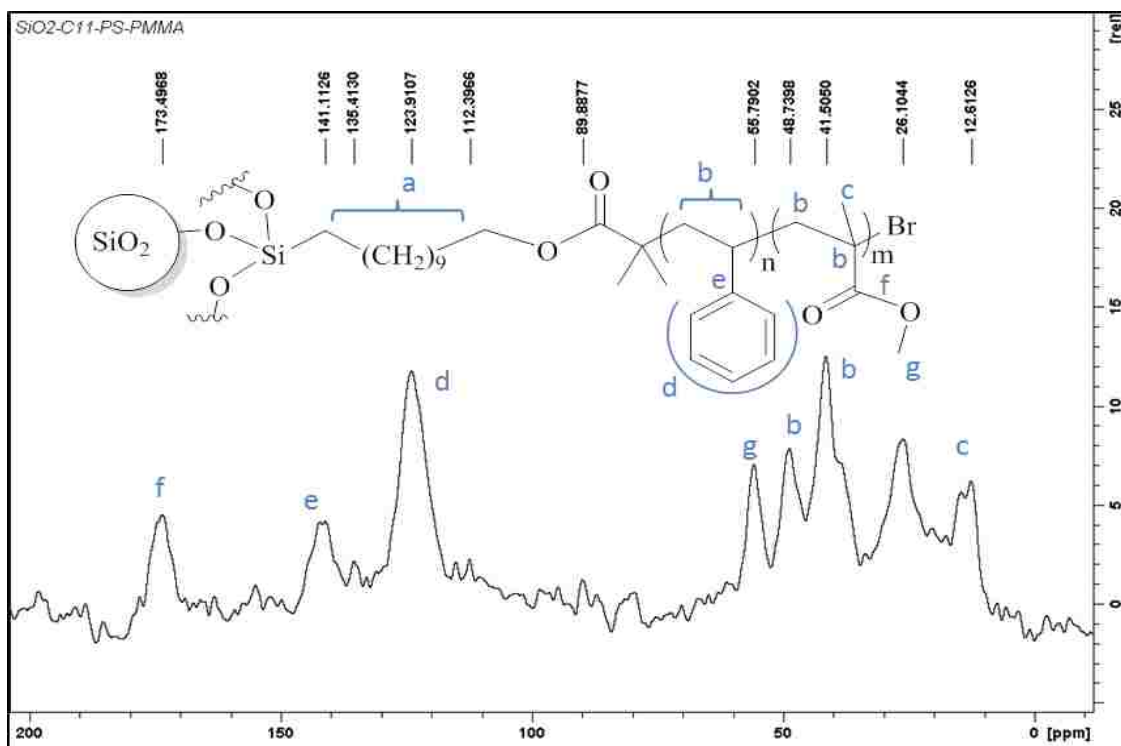
Figure A.13. CP-MAS ^{13}C NMR of SiO$_2$-C$_{11}$-PS-PMMA (**ESS10**)
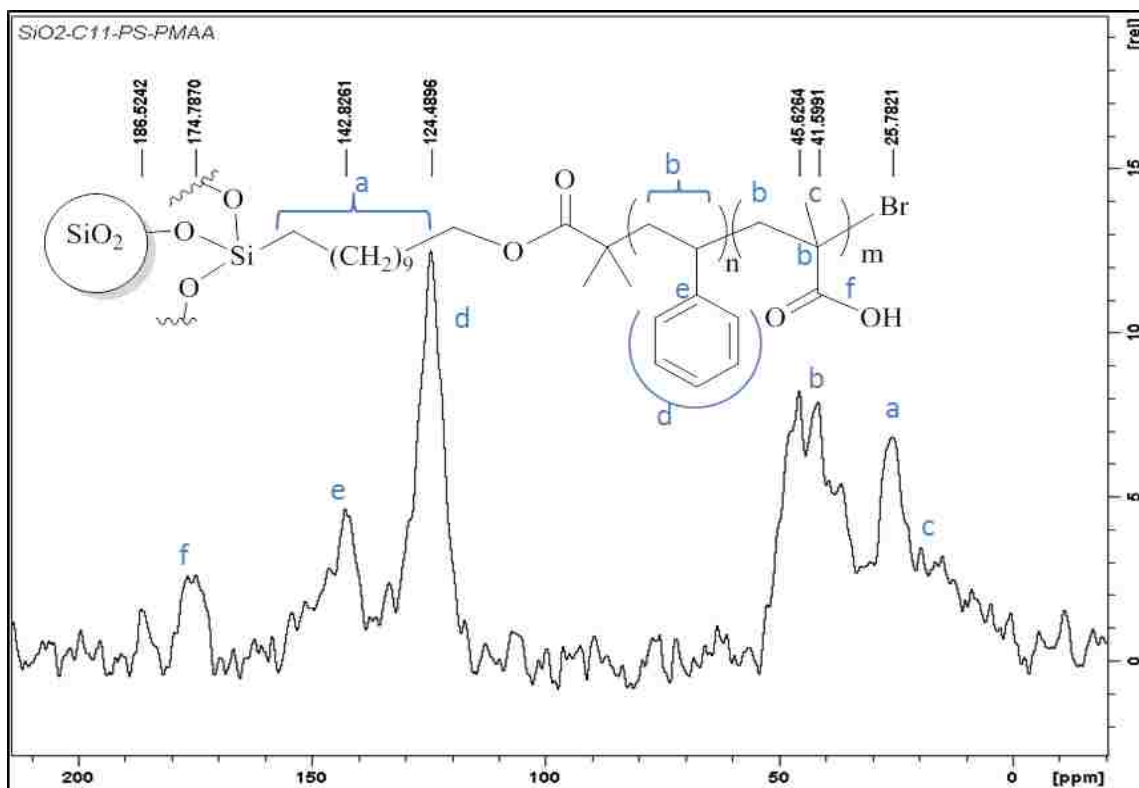
Figure A.14. CP-MAS ^{13}C NMR of SiO$_2$-C$_{11}$-PS-PMAA (**ESS11**)

TGA Thermograms
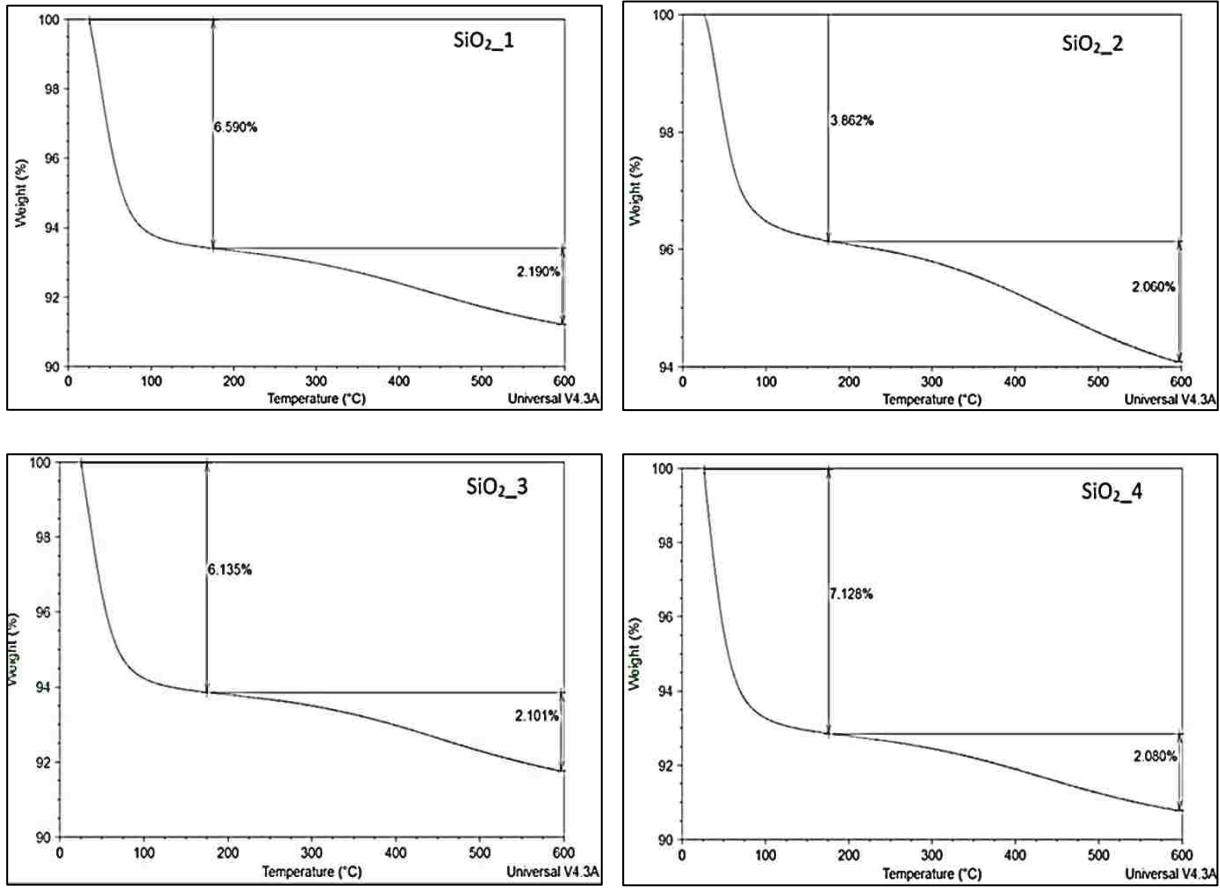
Figure A.15. TGA thermograms of blank silica
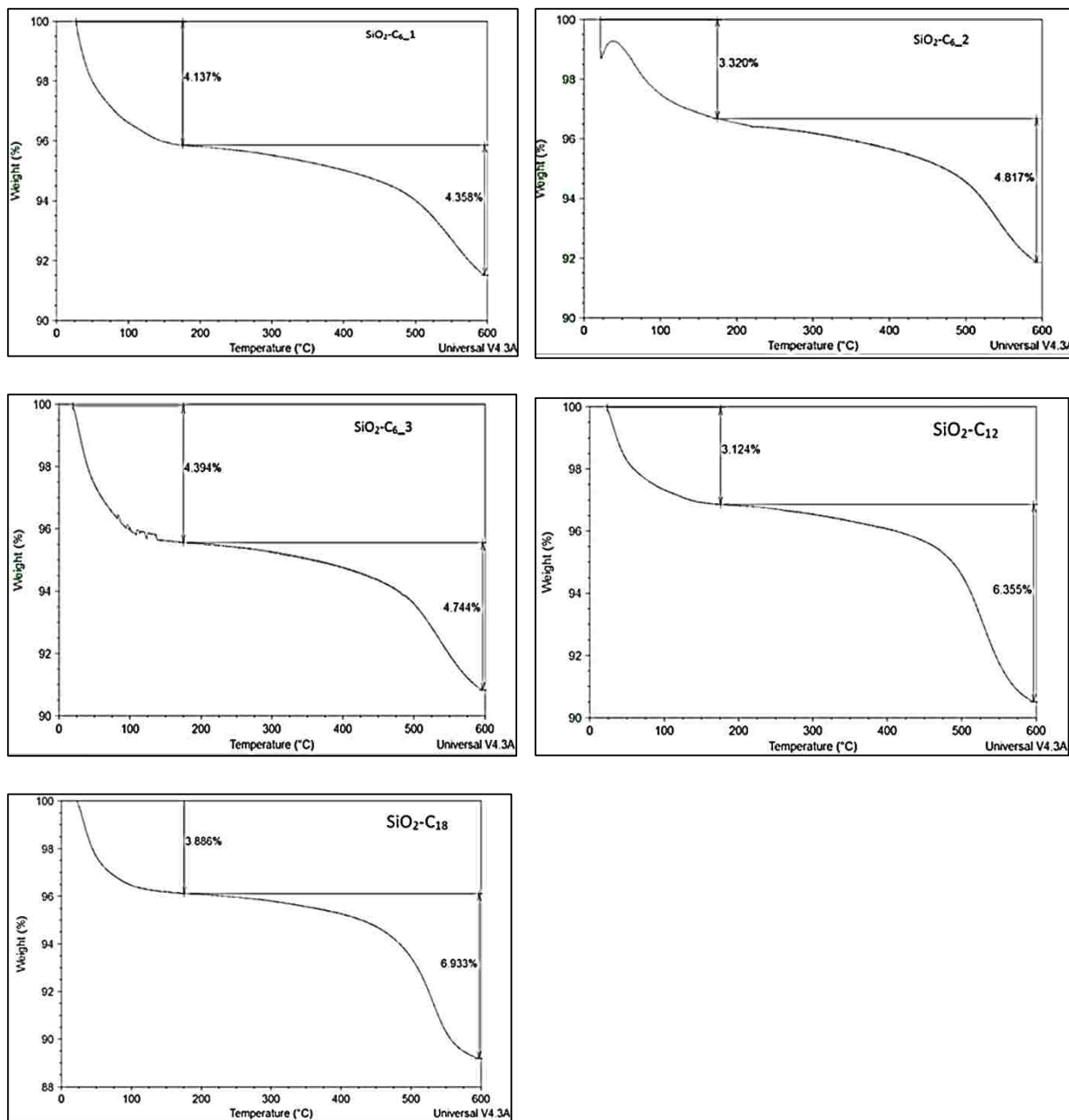
Figure A.16. TGA thermograms of Tier-I ESSs. SiO_2-C_6 was synthesized in 3 batches and the mixture in equal amounts was used for sorption studies.
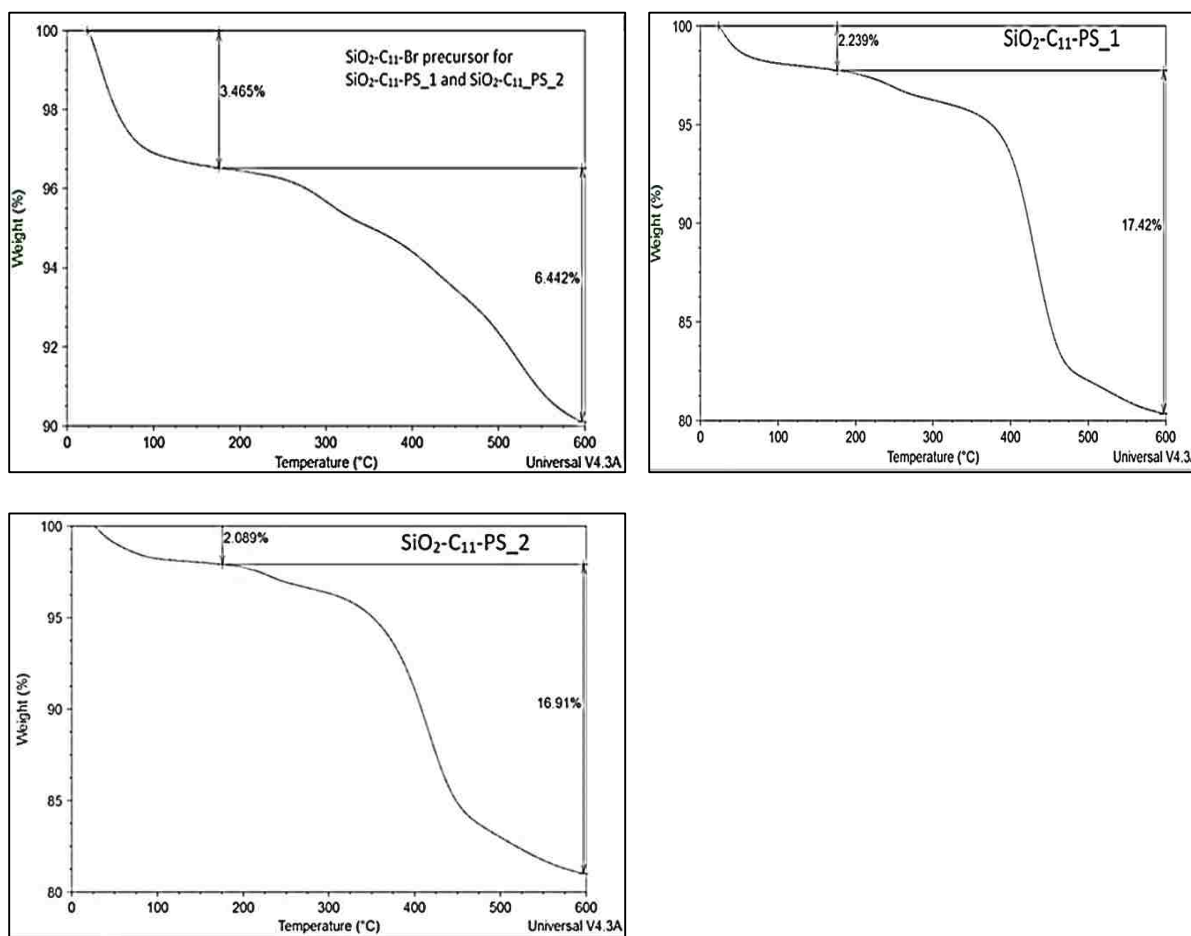
Figure A.17. TGA thermograms of SiO$_2$-C$_{11}$-PS Tier-II ESSs and their SiO$_2$-C$_{11}$-Br precursor. SiO$_2$-C$_{11}$-PS was synthesized in two batches and mixed in equal amounts for use in sorption studies.
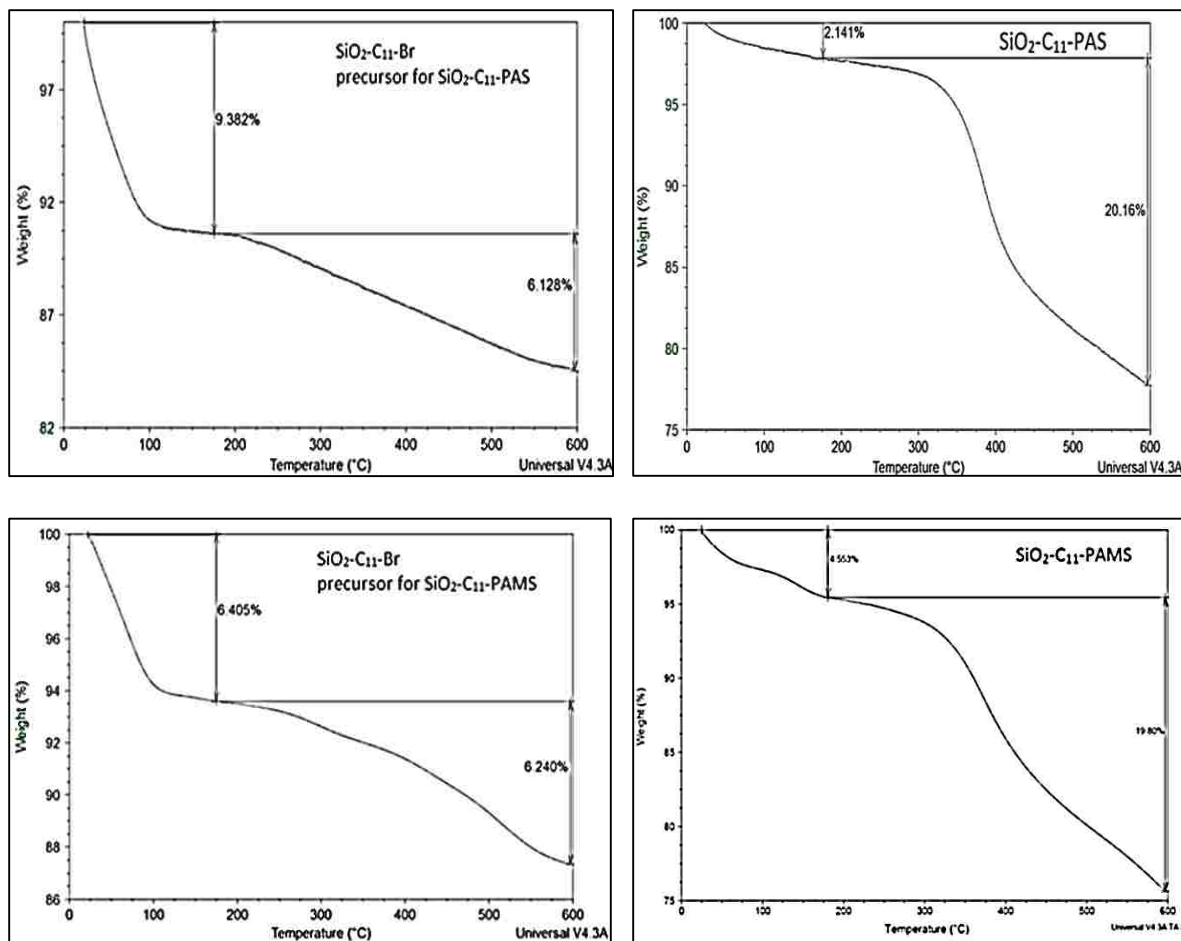
Figure A.18. TGA thermograms of SiO_2-C_{11}-PAS and SiO_2-C_{11}-PAMS Tier-II ESSs and their SiO_2-C_{11}-Br precursor
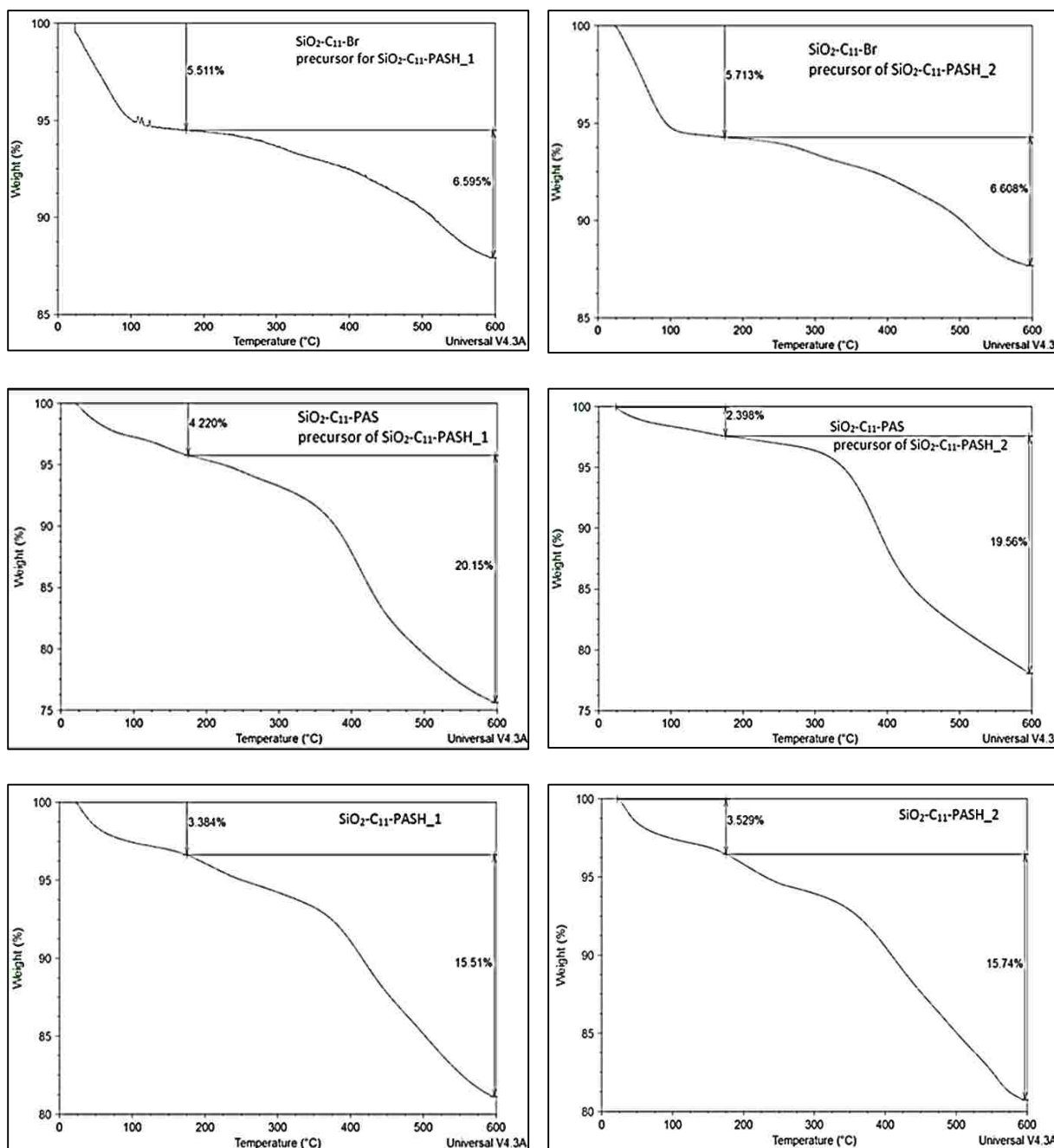
Figure A.19. TGA thermograms of SiO_2-C_{11}-PASH Tier-II ESSs and their SiO_2-C_{11}-Br and SiO_2-C_{11}-PS precursors. SiO_2-C_{11}-PASH was synthesized in two batches and mixed in equal amounts for use in sorption studies.

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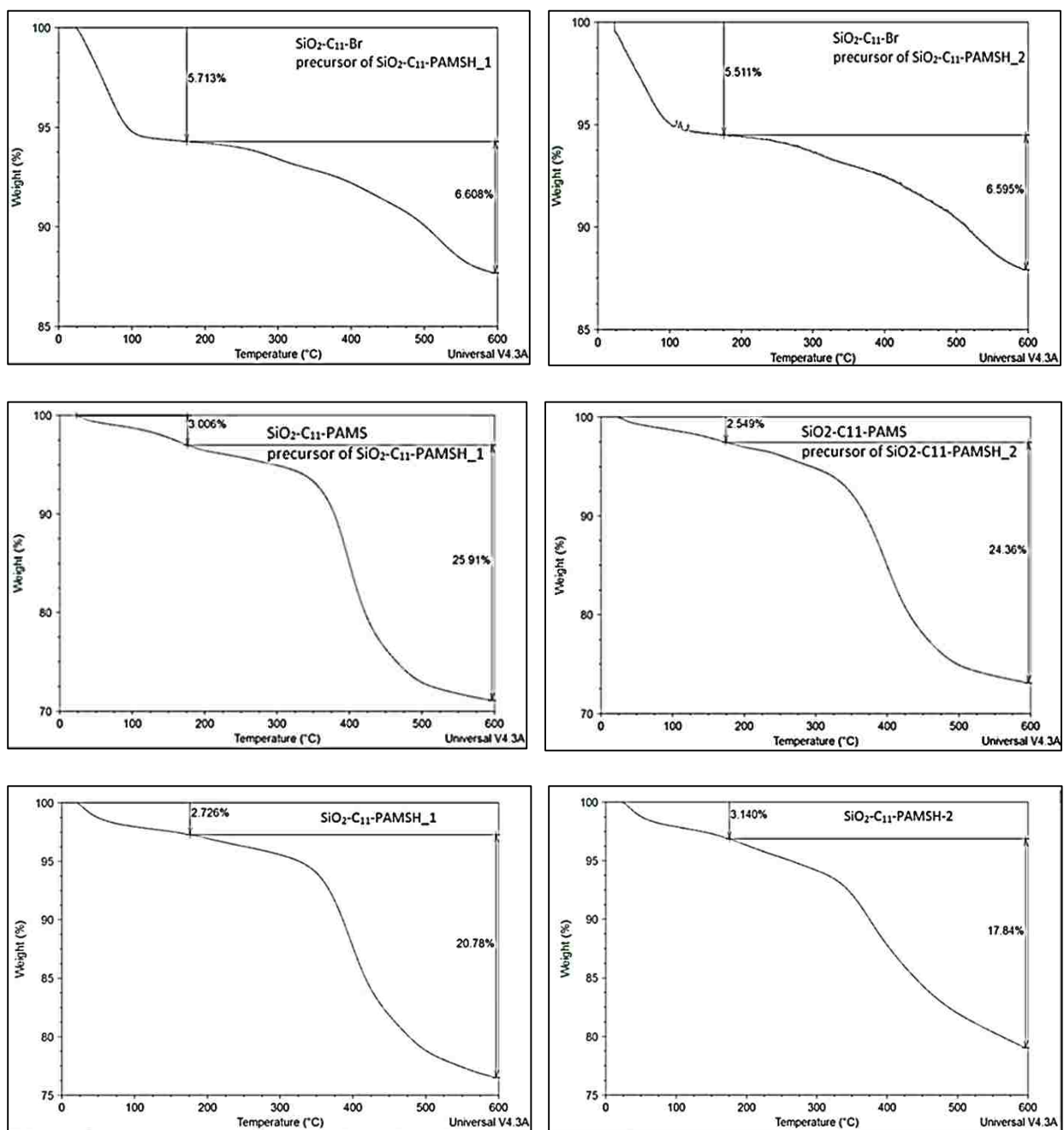
Figure A.20. TGA thermograms of SiO_2-C_{11}-PAMSH Tier-II ESSs and their SiO_2-C_{11}-Br and SiO_2-C_{11}-PS precursors. SiO_2-C_{11}-PAMSH was synthesized in two batches and mixed in equal amounts for use in sorption studies.
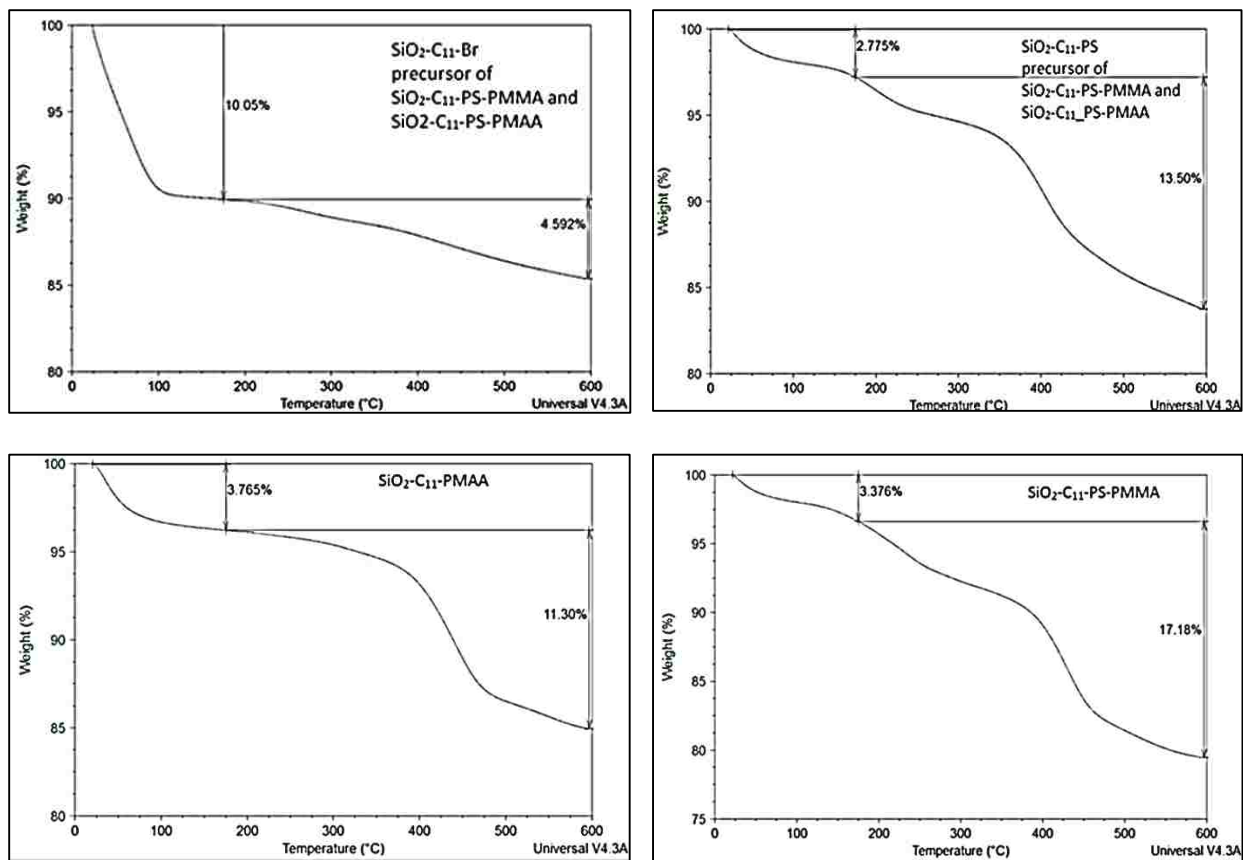
Figure A.21. TGA thermograms of SiO_2-C_{11}-PS-PMMA and SiO2-C_{11}-PS-PMAA tier-III ESSs and their SiO_2-C_{11}-Br and SiO_2-C_{11}-PS precursors.

Appendix 3. Experimental and Spectra for Chapter 3

Screening reaction with (0.1 equivalent 10mol% Cu(I)Br based on moles of initiator)

In a 100ml RBF charged with 25 ml of toluene, 2.0g initiator (6.3 mmol) was added and the RBF was purged with N2 for 5 minutes. Cu(I)Br (89 mg, 62mmol) and PMDETA (0.13ml, 62 mmol) were added followed by purging with N2 for another 5 minutes. Styrene (3.58g, 36 mmol) was added and the reaction was refluxed in toluene. Aliquots were taken in 12, 18 and 24 hr and analyzed by NMR.

ATRP for tier-II oligomer to obtain approx. 5 units of styrene

In a 250 ml RBF charged with 50 ml Toluene, 2.0g initiator (6.3 mmol) was added and the RBF was purged with N2 for 5 minutes. Cu(I)Br (224 mg, 156mmol) and PMDETA (0.32 ml, 156ml) were added followed by purging with N2 for another 5 minutes. Styrene (3.58g, 36 mmol) was added and the reaction was refluxed in toluene for 24 hours. The crude product was washed with 5x20 ml methanol and put under high vacuum for 5 hours. Resulting product was characterized with NMR and MALDI.

To obtain DP of N, [M]/[I] ratio adjusted to slightly more than N.

ATRP f for tier-II oligomer to obtain approx. 5 units of PMMA

In a 250 ml RBF charged with 50 ml Toluene, 2.0g initiator (6.3 mmol) was added and the RBF was purged with N2 for 5 minutes. Cu(I)Br (224 mg, 157mmol) and PMDETA (0.32 ml, 156 mmol) were added followed by purging with N2 for another 5 minutes. Methyl methacrylate (3.45g, 35 mmol) was added and the reaction was refluxed in toluene for 24 hours. The crude product was washed with 5x20 ml hexane and put under high vacuum for 5 hours. Resulting product was characterized with NMR and MALDI.

To obtain DP of N, [M]/[I] ratio adjusted slightly more than N.

Generic reaction to obtain tier-III oligomer form tier-2 macroinitiator to obtain DP N

In a 250 ml RBF charged with 50 ml Toluene, approximately 4g tier-2 macroinitiator was added and the RBF was purged with N2 for 5 minutes. Cu(I)Br (25 mol % or 0.25 mol equivalent) and PMDETA (25 mol% or 0.25 mol equivalent) were added followed by purging with N2 for another 5 minutes. Momomer (Slightly excess than N* moles of initiator) was added and the reaction was refluxed in toluene for 24 hours. The crude product was washed with 5x20 ml methanol and put under high vacuum for 5 hours. Resulting product was characterized with NMR and MALDI

Experimental for MALDI

A sample solution of about 0.1 mg/mL was prepared by adding acetone into a sample. A saturated solution of 2,5-Dihydroxybenzoic acid (DHB; Sigma-Aldrich, St. Louis, MO, USA) dissolved in methanol was used as the matrix. A sample solution of 0.5 uL was first deposited to the MALDI target plate followed by 0.5 uL matrix deposition above it and mixing before the drying of the components. MALDI-TOF MS measurements were performed on a commercial instrument (Ultraflextreme, Bruker Daltonics, Billerica, MA, USA). Mass spectra were recorded in positive ion reflectron mode with an accelerating voltage of 25 kV and analyzed in the mass range of 500–4500 Da. The spectra were acquired after calibration of the instrument with a peptide standard (Peptide Calibration Standard II, Bruker Daltonics, MA, USA). A minimum of 500 laser shots per sample was used to generate each mass spectrum.

Experimental for solid-state TGA and ^{13}C-NMR

All ESSs were characterized by a combination of TGA, solid-state NMR, and XPS. The TGA analysis was performed on 4 to 8 mg of sample using a TA System TGA 2950, with a temperature ramp of room temperature (RT) to 600 ºC at a rate of 10 ºC per minute. The percent mass loss versus temperature was plotted. The solid-state NMR analysis employed ^{1}H-^{13}C cross

polarization magic angle spinning (CP-MAS) technique and was performed on an AV 400 MHz Bruker solid-state instrument with sample packed into a 4 or 2.5 mm ZrO_2 rotor. Spectra were acquired using the following parameters: 2048 scans, ramp cross-polarization, contact time of 2 ms, 2.0 s delay between scans; spinning speed of 12-15 kHz, a 120 Hz line broadening function was applied, and referenced to y-glycine $-CH_2-$ signal at 43.5 ppm.

S3. Grafting performance of SiCl$_3$-C$_{11}$-PMMA$_{10}$
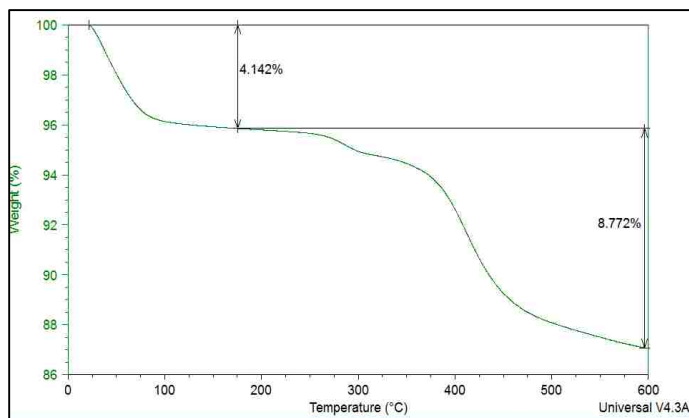
Figure A.22. TGA of 7.0% TOF grafted SiO$_2$-C$_{11}$-PMMA$_{10}$
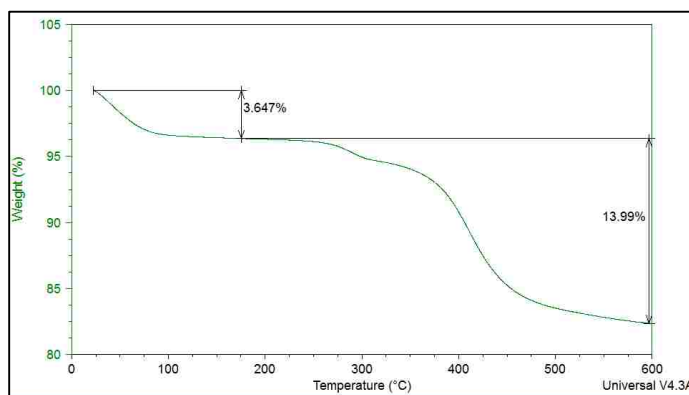
Figure A.23. TGA of 12.4% TOF grafted SiO$_2$-C$_{11}$-PMMA$_{10}$
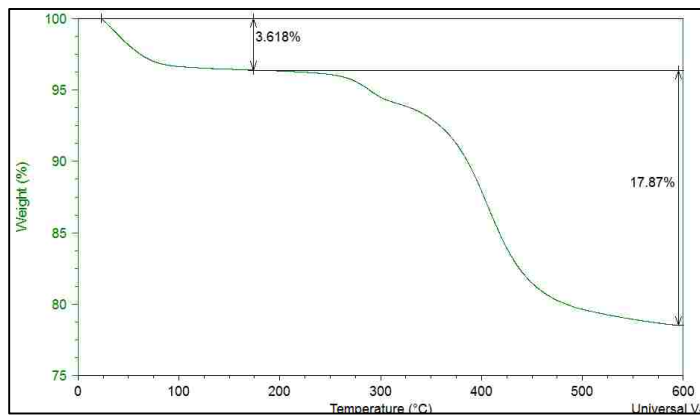
Figure A.24. TGA of 16.4% TOF grafted SiO$_2$-C$_{11}$-PMMA$_{10}$

S4. MALDI-TOF spectra of oligomers
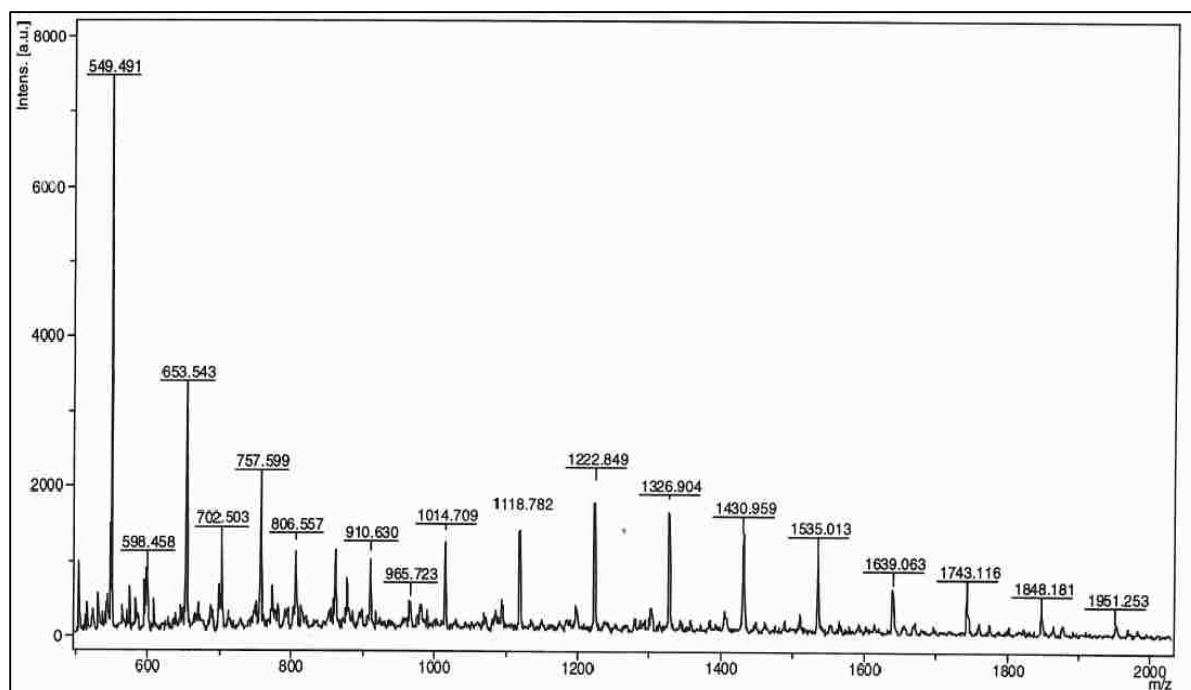
Figure A.25. MALDI TOF of C$_{11}$-PS oligomer showing peaks with MW difference of 104. (styrene repeating unit). Although the exact peak MW was not seen, the MW ranges shows DPavg 10.
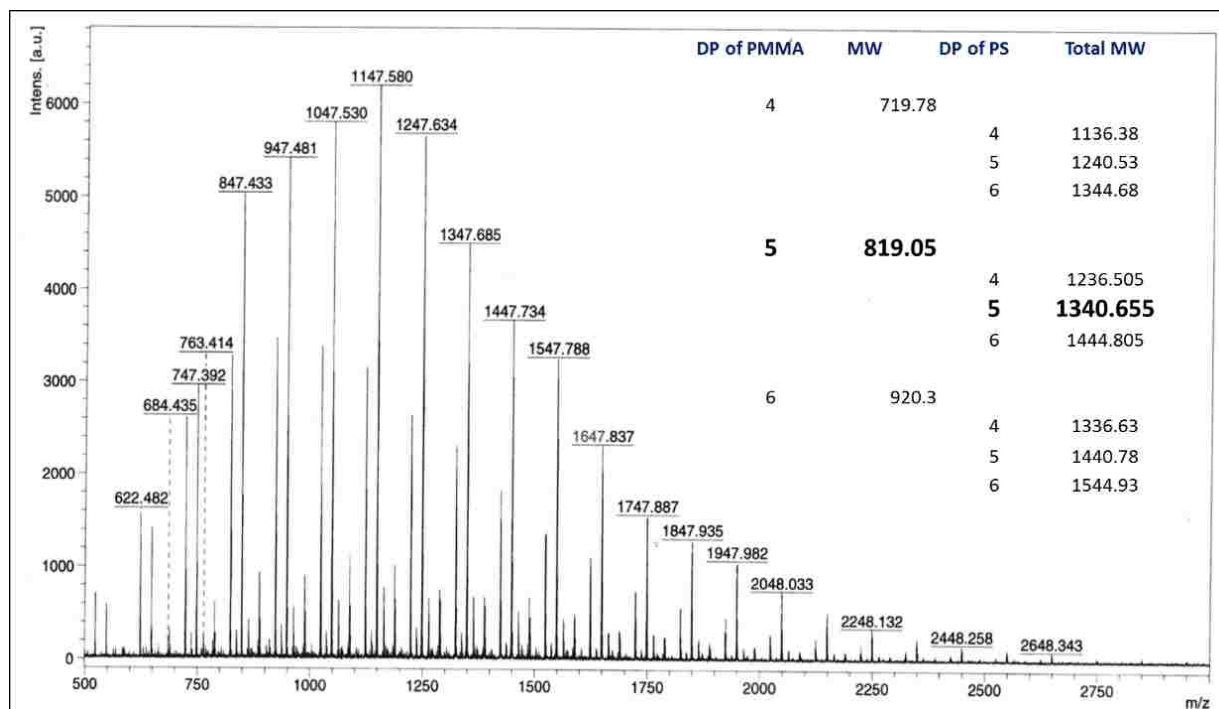
Figure A.26. MALDI TOF of C_{11}-PMMA-PS oligomer showing peaks with MW difference of 100 (MMA repeating unit). Although the MWs did not match exactly with the peaks, MW range suggests DPavg of both PS and PMMA to be 5 from MW calculations shown in the figure.

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Vita

Arjun Pandey was born in Western Nepal and he completed high school education from Kathmandu Model College. He moved to United States to pursue undergraduate study in chemistry where he attended Southeastern Louisiana University. While at Southeastern, Arjun worked on synthesis and characterization of small molecules and polymers under supervision of Dr. Debra Dolliver and Dr. David Norwood, and worked as a part of an interdisciplinary research and outreach program. With an aim to expand his knowledge and skills in chemistry, Arjun joined graduate chemistry program at Louisiana State University where he worked on various projects under supervision of Dr. David Spivak with a focus on polymer chemistry. During his time at LSU, Arjun taught several semesters of general and organic chemistry labs as a teaching assistant, and served as executive committee member in student organizations. Arjun has presented several talks and posters at national and regional conferences, and volunteered in various outreach activities to promote science education among school and college students.