ABSTRACT

DHAWAN, ABHISHEK. Synthesis of Block Copolymers from Cellulose Nanoparticles via Atom Transfer Radical Polymerization. (Under the direction of Bruce M. Novak).

Cellulose by far is the most abundant natural polymer that exists on this planet and presents scientists with the advantage to utilize it as an inexhaustible source of raw material in the synthetic development of environmentally friendly and biocompatible products. Due to its availability and low cost, cellulose and its derivatives are extensively used in industries consisting of textiles, plastics, wood and paper products, coatings, and pharmaceuticals among others. Its structural framework consists of extensive intra and intermolecular hydrogen bonding that makes it completely insoluble in normal aqueous solvents and solutions. Cellulose fibrils contain highly crystalline regions that co-exist with amorphous regions, which has a capacity of holding relatively large amounts of water, thus making it a very hygroscopic molecule. These crystalline regions can be conveniently separated from the low order regions to form rod-like cellulose microcrystallites. The rod-like particles can be coupled with various synthetic polymer structures forming hybrid copolymer blocks that display properties of amphiphiles. Atom Transfer Radical polymerization, a controlled radical polymerization process, is used an effective tool to bridge this carbohydrate molecule with a synthetic macromolecule to generate a hybrid amphiphilic copolymer block that can aggregate in aqueous environments to form micelles.

Rod-like nano-crystals were prepared by acid hydrolysis of fibrils in filter paper powder through a heterogeneous acid diffusion process that resulted in breaking of β-glycosidic linkages in cellulose fibrils. By controlling the strength of sulfuric acid, reaction time, and temperature, the crystalline regions were separated from the amorphous regions giving

individual rod-like crystals that contained the non-reducing end on one side and the reducing end on the other.

Cellobiose, a basic repeat unit of cellulose, was used as a model study in polymerization of styrene to create cellobiose end-capped polystyrene polymer. The reducing end aldehyde group was reacted with 4-vinylaniline forming a derivative compound (CB-d-4AS) that was used as a functionalized initiator for ATRP. Among the various solvents tested, owing to solubility reasons, DMF gave considerable yields of CB-d-4AS. The reaction of cellobiose derivative compound with 1-(bromoethyl)benzene in presence of Cu(I)Br, pentamethyldiethylenetriamine (PMDETA) catalyst system produced an efficient initiating system in the ATRP of styrene to give CB end-capped PS polymer.

With the intention of following the model study, hydrolyzed cellulose crystals were also derivatized with 4-vinylaniline creating a compatible derivatized initiator for ATRP of styrene. Amphiphilic diblock copolymer (Cellulose-*block*-Polystyrene) was successfully synthesized by ATRP using C-d-4AS, 1-(bromoethyl)benzene in presence of Cu(I)Br, PMDETA catalyst system. FT-IR, ^{1}H NMR, and TGA measurements compliment the results of model study and confirm the formation of diblock (Cell-PS) copolymer. The appearance of PS protons in the ^{1}H NMR spectra and the absence of cellobiose and cellulose protons indicated the formation of aggregates in $CHCl_3$ solvent, which is good selective solvent for polystyrene and not for cellobiose and cellulose.

SYNTHESIS OF BLOCK COPOLYMERS FROM CELLULOSE NANOPARTICLES VIA ATOM TRANSFER RADICAL POLYMERIZATION

by

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A thesis submitted to the Graduate Faculty of
North Carolina State University
In partial fulfillment of the
Requirements for the degree of
Master of Science

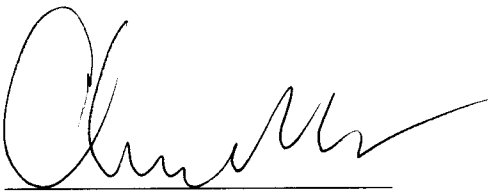
Chemistry

Raleigh, North Carolina

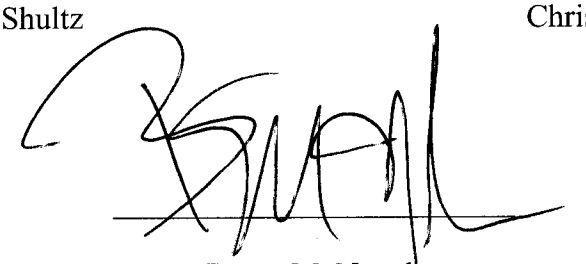
2007

Approved by:

David A. Shultz



Christian Melander



Bruce M. Novak
Chair of Advisory Committee

DEDICATION

This work is dedicated to my parents, Vinod and Renu Dhawan, my wife Ami, and my brother Akshay. Education has always been a key element for growth and success for my parents. They have always maintained its importance and encouraged me to achieve higher standards. Through their many sacrifices and continued support, my parents ensured that I receive the best possible education. I am forever grateful to my parents, brother, and wife for their unrelenting love, encouragement and support.

BIOGRAPHY

The author was born in Mumbai (India) in 1978. As an inquisitive student, Abhishek realized his inclination towards chemistry while he was in secondary school. Upon finishing secondary and higher secondary education in science and mathematics, he began his undergraduate studies in Chemical Engineering at University of Bombay in India. In his second year as an engineering student, Abhishek received a one-year industrial internship opportunity with Sanvy Inks and Coatings Pvt. Ltd. After completing two years of engineering studies, Abhishek transferred to the Chemical Engineering department at North Carolina State University in Fall 2000. Successfully completing his undergraduate studies as a cum laude graduate, Abhishek received his Bachelors of Science Degree in Chemical Engineering and Bachelors of Arts degree in Chemistry. His educational experience involved opportunities and internships as a polymers intern at Honeywell Specialty Chemicals, and a process-engineering intern at Chemicoat. With an attitude of achieving higher education in polymers, Abhishek began his graduate studies at North Carolina State University with Dr. Bruce M. Novak and has worked on Cellulose polymer chemistry.

ACKNOWLEDGMENTS

My graduate education at North Carolina State University would not have been possible without the support and encouragement from my family. I would like to thank my parents for their immense encouragement, my wife for being so supportive and patient, and my brother for being very encouraging.

Research and studies in polymer chemistry, especially one facilitated by Professor Bruce M. Novak had always been the focus of my graduate experience. Professor Novak not only shows immense enthusiasm in research arena, but also in his research group members whom he treats with complete professionalism. Professor Novak has been a great advisor who has helped and guided at both professional and personal levels. He provided a great learning environment, excellent research facility, and the independence to conduct research. I would therefore like to thank Professor Novak for his guidance and support during my journey at NC State University.

Scientific research inherently involves difficulties, road-blocks, obstacles, and sometimes failures. However, all of these can be successfully dealt-with by the support of fellow group members. I would thus like to thank my fellow group members for their help and friendship during my research days. In particular I would like to thank Keitaro Seto and Yoko Aoyama for guiding me in the laboratory and explaining concepts that were not very clear to me. I enjoyed sharing ideas with Hyun Su Lee, who always showed an attitude to never give up. From education to politics to religion, I have had some interesting discussions with J.B Clark. I am grateful to all colleagues and friends for their support.

Finally, a sincere thanks to Professor David Shultz and Professor Christian Melander for being very kind and supportive committee members.

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Chapter 1

Introduction to Cellulose Chemistry and Atom Transfer Radical Polymerization

1.1 Cellulose Chemistry

1.1.1. Origin

Cellulose is the primary structural material of the cell walls of higher plants and is a basic constituent of all plant life. It is the world's most abundant organic biopolymer with an estimated of more than 1 x 10^{11} tons being produced on land and in water each year on our planet.[1] This natural polymer outranks every other natural organic substance in abundance and diversity of sources and is virtually inexhaustible source of renewable bioenergy. The cellulose content varies significantly that are found in many tree and plant tissues. Dry young leaves contain about 10% cellulose and old leaves tend to contain about 20% cellulose. Wood tissues of trees and shrubs contain about 60% cellulose whereas flax fiber holds up to 80% cellulose content. The highest cellulose content of any naturally occurring substance is contained by seed hair of cotton plant that is more than 90%.[2]

In addition to plants and trees, cellulose is also produced by a large variety of living organisms. Cellulose can be found in bacteria and prokaryotes such as acetobacter, rhizobium, and agrobacterium.[3] Nobles et al.[4] have recently shown that cyanobacteria also produces cellulose. It is also found in some fungi, amoeba, green algae and slime molds. Valonia ventricosa[5] found in green algae contains about 20-30% cellulose, forms a highly ordered crystalline structure with a high degree of polymerization. Besides plant sources (Table 1.1) found on land, cellulose is also found in fresh water and marine algae. Tunicates[7], add animals in the list for sources of cellulose on the face of this planet.

Table 1.1. Cellulose content in plant sources. Reprinted from reference 6.

Source	*Cellulose content %*
Wood	40-50
Cotton	90-99
Jute	60-65
Straw	40-50
Bacteria	20-30
Green Algae	20-40
Bamboo	40-55
Hemp	70-75
Bark	20-30
Flax	75-80

The vast and long presence, for more than 3.5 billion years,[8] makes the diversity of its applications range from basic necessities of food to clothing to shelter. In the day and age of synthetic polymers, cellulose continues to be an influential organic species in industry verticals like textiles, paper, fibers, lumber, and pharmaceuticals among others. Many scientists continue to publish papers on structure, solubility, and applications mainly comprising of cellulose derivatives. Based on its capability of being the backbone for synthetic derivatives, organic chemistry continues to examine cellulose as a potentially reactive molecule. Its versatility and diversity in industrial application have made chemists approach cellulose at an organic, physical, and macromolecular level.

1.1.2. Molecular & Supramolecular Structure

The chemistry of cellulose had its beginning in 1838, when a French chemist by the name of Anselme Payne succeeded in separating various plant tissues into their components. He then suggested that the cell walls of plants comprised of the same material.[9] By elemental analysis, Payen determined the molecular formula for cellulose to be $C_6H_{10}O_5$. Cellulose was further characterized by English cellulose chemists Cross and Bevan[10] in the early 1900's. With the discovery of structure of cellobiose, basic repeat unit of cellulose, by Haworth followed the proposal of cellulose structure by Dore at al.[11] In 1930, Haworth et al. proved that cellobiose was the only building block for cellulose.[12]

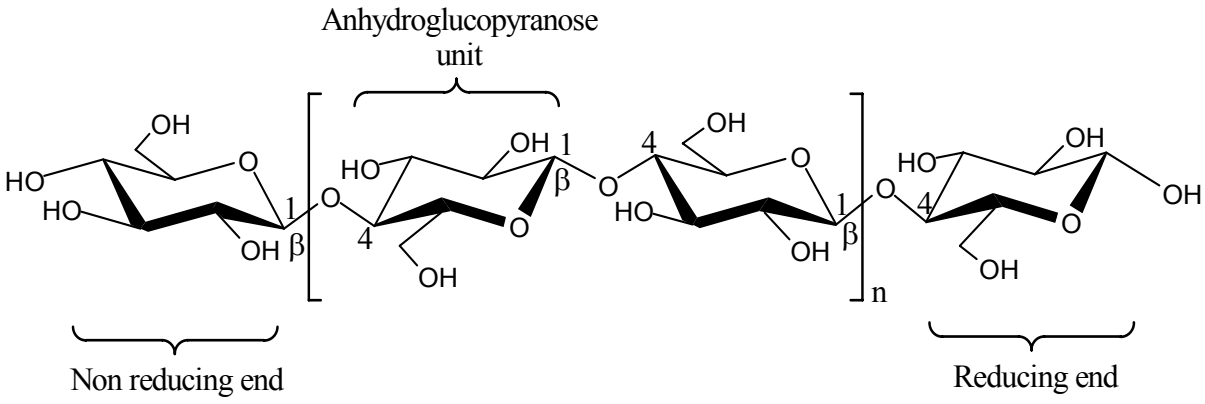


Figure 1.1. Molecular Structure of Cellulose.

From the molecular structure of cellulose in Figure 1.1, it can be seen that cellulose is a homopolymer of D-anhydroglucopyranose monomeric units connected through β (1-4) glycosidic linkages. In general, cellulose can be seen as a long chain polymer with D-glucose, a sugar, as its repeating units. Since the glucose units are in 6 member rings within

cellulose chain, they are known as pyranoses. These pyranose rings are joined by single oxygen atoms, acetal linkages, between the C-1 of one pyranose ring and the C-4 of the next ring. The glucose units in cellulose polymer are referred to as anhydroglucose units when an alcohol and a hemiacetal react to form an acetal.

Every two monomeric units in cellulose are rotated by approximately 180° in the plane about their axial chain as compared to the neighbouring two monomeric units. In this manner two adjacent units identifies the disaccharide cellobiose which is considered to be the basic repeat unit of the natural polymer. Because of the orientation of the glycosidic bonds linking the glucose monomers, the rings of glucose are arranged in a flip-flop manner. This produces a long straight rigid molecule. The stereochemistry of the acetal linkages is very important as the pyranose rings of the cellulose molecule have all of the larger groups in the equatorial positions. In glucose molecule the stereochemistry at carbons 2, 3, 4 and 5 is fixed. When forming a pyranose ring, the hydroxyl at C-4 can approach the carbonyl at C-1 from either side of glucose, resulting in two different stereochemistries at C-1. Thus when the hydroxyl group at C-1 is on the same side of the ring as the C-6 carbon, it is considered to be in the α configuration. In cellulose, the C-1 oxygen is on the opposite side, or β configuration. This β configuration, with all functional groups in equatorial positions makes cellulose a good fiber forming polymer due to straight line extension of the chain. As seen in Figure 1, cellulose molecule has two non-equivalent chain ends. The terminal hemiacetal group can act as a reducing end aldehyde group and hence called as the reducing end, while the opposite end with closed ring structure is termed as the non-reducing end.

It is very important to note the difference between the basic monomer repeat unit glucose and

the polymer cellulose. Glucose is a water-soluble carbohydrate whereas cellulose is insoluble polymer due to its extensive hydrogen bonding between the hydroxyl groups.[13] Cellohexaose, made of six monomers, does not dissolve in water[14] and cellulose along with cellulose oligomers of degree of polymerization (DP) greater than 8 are insoluble in water and most organic solvents.[6] Therefore glucose and cellulose completely differ in their property.

Often in nature, cellulose is associated and mixed with other substances such as lignin, pectins, hemicelluloses, fats, and proteins. Cellulose that is produced by plants is referred to as native cellulose, which is found in two crystalline forms, cellulose I and cellulose II.[15] Cellulose II, generally occurring in marine algae, is a crystalline form that is formed when cellulose I is treated with aqueous sodium hydroxide.[16-18] Among the four different crystalline polymorphs cellulose I, II, III, and IV, cellulose I is thermodynamically less stable while cellulose II is the most stable structure. A liquid ammonia treatment of cellulose I and cellulose II gives crystalline cellulose III form,[19-21] and the heating of cellulose III generates cellulose IV crystalline form.[22] Recently a non crystalline form known as nematic ordered cellulose has been described.[23] From a solution in lithium dimethylacetamide a highly ordered cellulose is produced which is crystalline.

Purification and separation process of cellulose involves various steps such as pulping process, partial hydrolysis, dissolution, re-precipitation, and extraction with organic solvents. Such isolation and treatment procedures almost always degrade cellulose and it also reacts with both acids and bases undergoing oxidation. The source of cellulose and its nature of cell development combined with isolation methods affect the degree of polymerization of

Table 1.2. Average DP of cellulose obtained from different sources. Reprinted from reference 6.

Source	*$*DP_w$ (10^3)*
Wood	8-9
Valonia	25-27
Cotton	8-15
Acetobacter xylinum	2-6
Cotton linters	1-5
Flax	7-8
Pulp	2.1
Kapok	9.5
Ramie	9-11

*DP_w weight average DP determined by viscometric methods[6].

cellulose. Table 1.2 shows the average DP of cellulose obtained from different sources. The β (1-4) glycosidic linkage gives cellulose the linearity that results in a rigid rod-like molecule. The hydroxyl groups on the cellulose chain that are in the equatorial position protrude laterally along the extended molecule. This position makes them readily available for intramolecular and intra-strand hydrogen bonding. The hydrogen bonds cause the chains to group together in highly ordered, crystal-like, structure and hold the network flat. Figure 1.2 shows a representation of cellulose chains that are usually longer than the ordered crystalline regions and are thought to pass through several different crystalline regions which

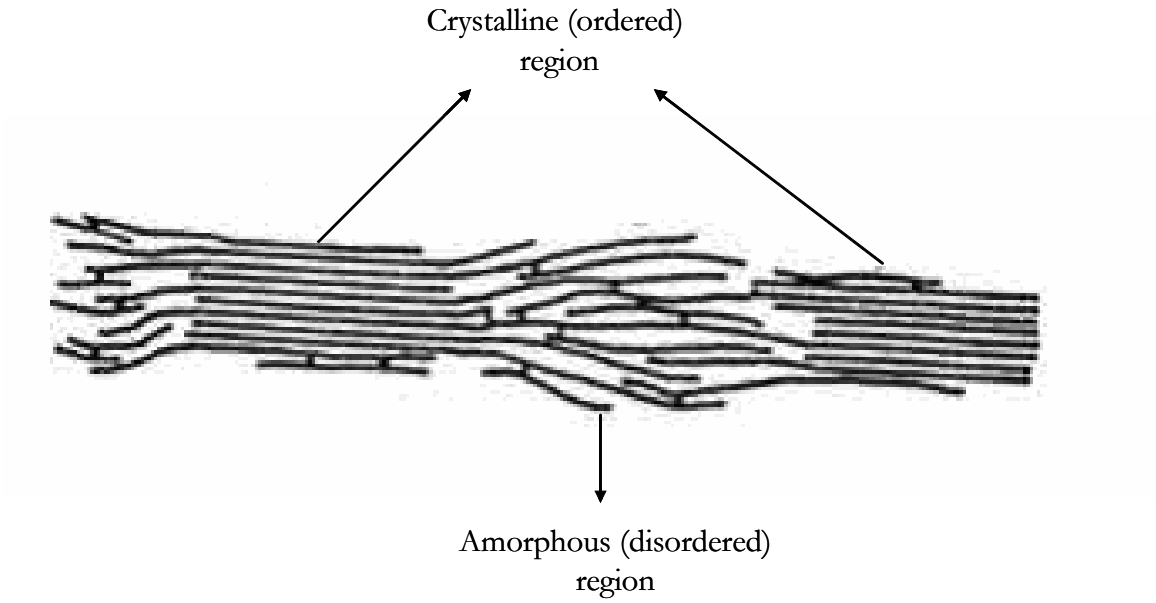


Figure 1.2. Crystalline and amorphous regions in cellulose microfibril. Reprinted from source: http://aic.stanford.edu/jaic/articles/jaic31-01-014_2.html

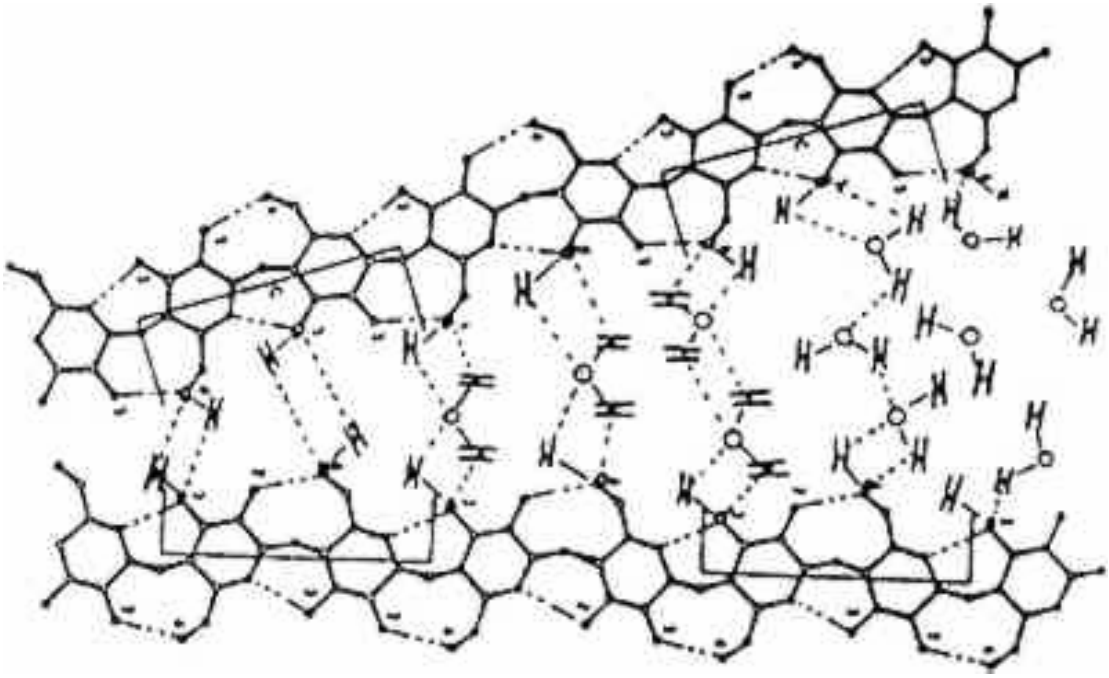


Figure 1.3. Structure of cellulose microfibril, showing hydrogen bonding with water. Reprinted from source: http://aic.stanford.edu/jaic/articles/jaic31-01-014_2.html

also have areas of amorphous regions in between them. Within the crystalline regions, the extensive and strong inter-chain hydrogen bonds give the resultant fibers good strength and insolubility in most solvents. This also prevents cellulose from melting at elevated temperatures. In the less ordered regions, the chains are further apart and more available for hydrogen bonding to other molecules, such as water (Figure 1.3). Most cellulose structures can absorb large quantities of water and is thus very hygroscopic. As a result cellulose swells, but does not dissolve in water.

The structure of cellulose resulting from the strong hydrogen bonding network (Figure 1.4) between the hydroxyl groups has been under investigation ever since its discovery.

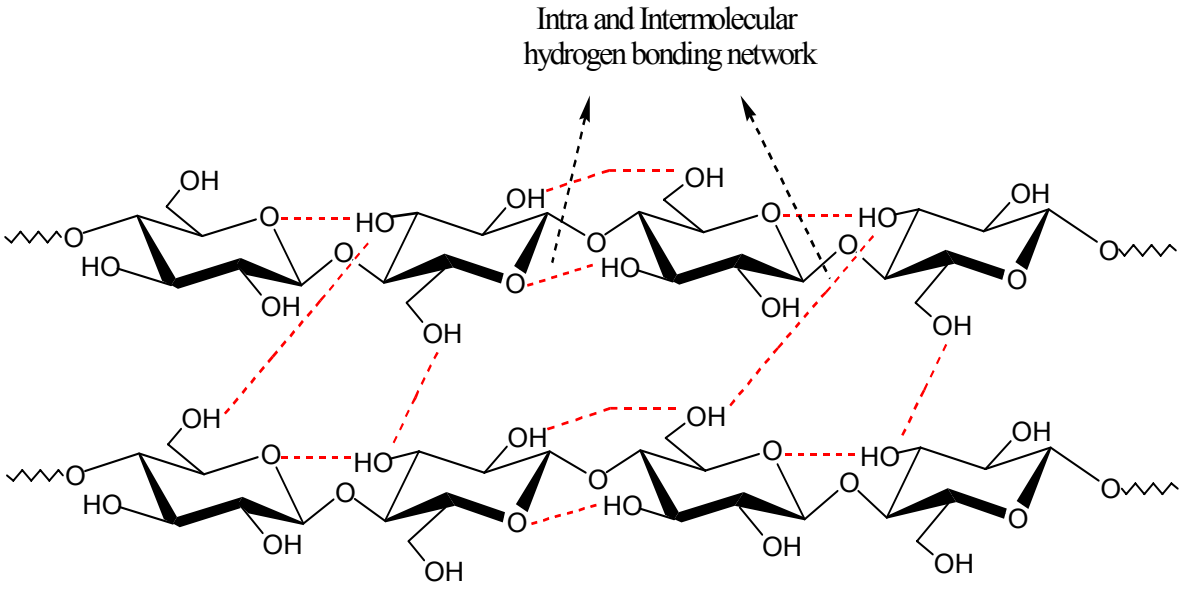


Figure 1.4. Representation of the extensive intra- and intermolecular hydrogen bonding network occurring in cellulose.

Various analytical methods such as electron microscopy, X-ray diffraction, ^{13}C NMR spectroscopy (solid state), and neutron diffraction have been employed to conduct structural analysis.[24-26] Electron microscopy of cellulose shows that the fibrillar structure consists of structural units know as microfibrils. X-ray diffraction and electron microscopy studies have determined the dimensions of these microfibrils[27-28] with length up to several micrometers, and width and thickness around 5-20 nm depending on the source of cellulose. The supramolecular structure of cellulose shows high order crystalline regions with low order amorphous regions throught the length of microfibrils, which have been notably seen in x-ray diffractograms. Many researchers have proposed various models that accommodate the presence of crystalline and paracrystalline regions in native cellulose. Some models and results have been a subject of controversy while others have provided useful information that is being used for further analysis.[24]

1.1.3. Properties

Cellulose, a colloidal substance, is a long chain polymer polysaccharide carbohydrate. It is a main structural component of plants and is an insoluble natural polymer. The strong hydrogen bonding network within the molecules play an important role in displaying the properties of cellulose. The internal surface of cellulose is in a swollen state of about 3×10^6 square centimeters per gram.[29] The study of such internal surface through scientific knowledge determines the properties of swelling, dissociation, absorption, optical properties, and macro structure.

The amount of water vapor in the air reflects the amount of moisture that cellulose and cellulose derivatives adsorbs. With the gradual increase in humidity, there is a decrease in the rate of increase of water adsorption by cellulose to about 80% relative humidity which at the fiber saturation point increases to maximum.[29] However when there is a gradual decrease in relative humidity causing the sample to dry again, a similar sigmoidal curve is formed as before.[2] The two curves formed by gradual increase and decrease in relative water vapor content in the atmosphere usually do not coincide. This causes a phenomenon of hysteresis at equilibrium when desorption has high moisture content values than adsorption.[30] Such effect is seen due to the hydrogen bonding of the hydroxyl group within cellulose. The hydroxyl groups are generally satisfied in a moist condition, but on drying they satisfy each other through adjacent free hydroxyl groups. At this point when the relative vapor content is increased, not many hydroxyl groups are free to adsorb water. However, close to the fiber saturation point more hydroxyl groups are free above 80% relative vapor content which then increases the rate of adsorption.[2] To dry cellulose completely is extremely difficult which is why cotton retains 0.35% water in spite of drying in vacuum with the presence of phosphorous pentoxide. Cellulose is considered to be a much powerful dehydrating agent than phosphorous pentoxide,[30] as it readily adsorbs water vapor even after it has been heated to 100°C for complete removal of moisture. Electrical properties can be seen in dry fibers as they are said to be good electrical insulators. Cellulose fibers readily adsorb water vapor from the atmosphere and depending on the level of humidity, their conductivity increases or decreases with the fluctuation in their moisture level. Due to its conductivity, cellulose has a characteristic zeta potential arising from the electro-kinetic phenomenon.[2] When in contact

with water, cellulose selectively adsorbs ions and assumes an electrical charge with respect to water. To maintain a neutral electric charge, the oppositely charged ions are immobilized in water very close to the adsorbed ions. This sets a negative electro kinetic potential difference for cellulose between water and adsorbed ions known as zeta potential of cellulose.

1.1.4. Cellulose Derivatives and Cellulose Solvents

As we know that the crystalline nature of cellulose and the crystalline packing forces from the hydrogen bonding between the hydroxyl groups of cellulose, shown in Figure 1.5, makes it a difficult molecule for dissolution in normal organic solvents and water. Over the years, many researchers have devoted immense time and effort in trying to dissolve it in different solvent systems. Fundamentally, dissolution can be achieved when the hydrogen bonding in cellulose system is either broken or when cellulose is derivatized. Thus many solutions from protonic acids, such as phosphoric acid, to solutions containing metal complexes were devised that were able to dissolve cellulose.[31-34] The different methods for dissolution of cellulose are categorized in four types namely, cellulose as an acid, cellulose as a base, cellulose derivatives, and cellulose complexes.[31]

The derivatization reactions of cellulose normally involve heterogeneous mixtures in the reaction, making such derivatizations usually very complicated compared to normal organic substances. Generally reagents and solvents have better access to the amorphous regions compared to the high crystalline regions. As can be seen in Figure 1.1, a typical cellulose molecule comprises of three different kinds of anhydroglucopyranose monomers in the interior, the reducing end with a free hemi-acetal or aldehyde group at C-1, the non reducing

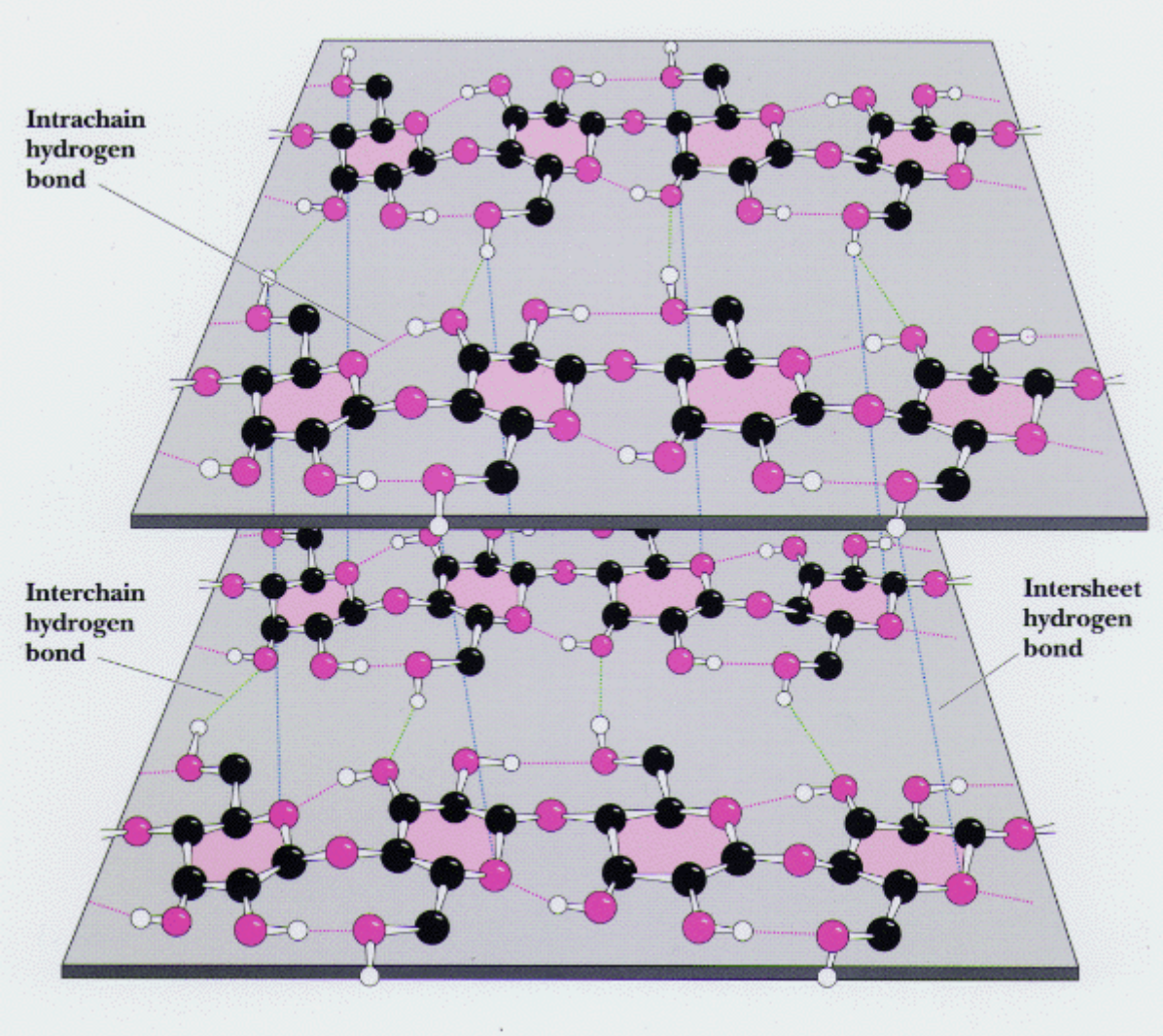


Figure 1.5. Cellulose Structure showing the hydrogen bonding network. Reprinted from source: http://www.nd.edu/~aseriann/cellulose.html.

end with a free hydroxyl at C-4, and the internal rings joined at C-1 and C-4 forming the β (1-4) linkage. The non reducing end with the glucose monomer unit contains four hydroxyl groups, and the reducing end contains three hydroxyl groups besides the terminal aldehyde group. The anhydroglucopyranose repeat units contain two secondary hydroxyl and one

primary hydroxyl group. Due to the presence of several hydroxyl groups in a long chain molecule, the chemistry of alcohol is the main reaction type for cellulose. Steric factors in crystalline molecules tend to dominate cellulose reactions inspite of the presence of different hydroxyl groups within the molecule that are expected to inherently react like a normal alcohol group. With the presence of three hydroxyl groups on the anhydroxyglucopyranose units, the derivatives are characterized in terms of (DS) degree of substation which is considered as an average for the whole chain, ranging from 0 to 3. In many cases when the hydroxyl groups in the crystalline regions do not react but all of the hydroxyls in the amorphous, less ordered, regions are derivatized, a partial reaction occurs of DS < 3 and block copolymers are formed as expected products. Reactions and reaction conditions that disrupt the highly ordered crystalline regions maintaining a high degree of substitution tend to reduce the extensive intramolecular hydrogen bonding network. These kinds of reaction give such cellulose derivatives that are soluble in more common solvents.

Cellulose derivatives can be used as explosives, adhesives, moisture-proof coatings, and thickening agents in food. Historically, some of the first synthetic polymers like cellulose acetate, cellulose nitrate, rayon, and ethyl cellulose were made from cellulose. The general methods for the preparation of ethers and esters with simple alcohols are applicable to cellulose. With the known fact that cellulose is insoluble in reaction mixtures, such derivatization reactions are topochemical where in a surface reaction works into the interior wall of the fiber. As a result, the reaction is heterogeneous since neither all the hydroxyl groups react uniformly nor do they react completely except when a fully substituted derivative is formed. Esterifictaion of cellulose takes place by reacting the hydroxyl groups

with acids or other acylating agents. In 1833, Braconnot developed a method to prepare cellulose nitrate with a mixture of nitric acid and sulphuric acids.[35] In 1845, Schoenbein prepared trinitrate and used it in explosives.[36] Cellulose nitrate was used in the automotive industry when lacquers were developed in the 1920s. Many different products with differing properties can be made by acetylation with acetic acid or acetic anhydride. Cellulose ethers are made by using different kinds of alkylating agents. Depending on the degree of substation, many partially substituted ethers are made that find commercial use. Methyl cellulose is synthesized by the reaction of methyl sulphate or chloride on alkali cellulose. Carboxymethyl celluloses are made by reaction of cellulose with chloroacetic acid. Benzyl cellulose is not attacked by acids and alkali and is very resistant to water.[37] Based on DS and the length of the hydroxyalkyl side chains, reaction of cellulose with ethylene oxide gives hydroxyethyl cellulose. Acetal formation is seen when the hydroxyl groups in cellulose react with aldehydes and hemiacetals. The reaction of cellulose with formaldehyde and its derivatives like urea formaldehyde resin helps in achieving dimensional stability to cellulose textiles such as rayon and cotton.[38] In 1875 Girard[2] investigated the reaction of cellulose with dilute acids which resulted in a noticeable change in its tenacity and strength. Later it was found that cellulose is susceptible to hydrolysis by acids and to a small extent by alkali, even though its poses some resistance towards being dyed, laundered, and finished.[39] When cellulose reacts with an acid, the β (1-4) glycoside bond is attacked and the acetal linkage is broken resulting in the hydrolysis of the chain. Usually, hydrolysis takes place at low pH values, thus the β (1-4) glycosidic linkage is a somewhat stable under alkaline, high pH, conditions. Certain cellulase enzymes are also known to cause chain scission. Oxidizing

agents have an impacting effect on the cellulose chain. The damaging effect of oxidation on cellulose was first observed during bleacing of textiles. The modified product from such a reaction was termed oxycellulose by Witz[40] in 1882. The oxidation reaction of cellulose shortens the average length of the cellulose chain and the hydroxyl groups react to form carbonyl and carboxyl groups. At higher temperatures, direct air oxidation of cellulose produces carbon monoxide, carbon dioxide, and water. Cellulose undergoes thermal degradation reactions at various different temperatures.

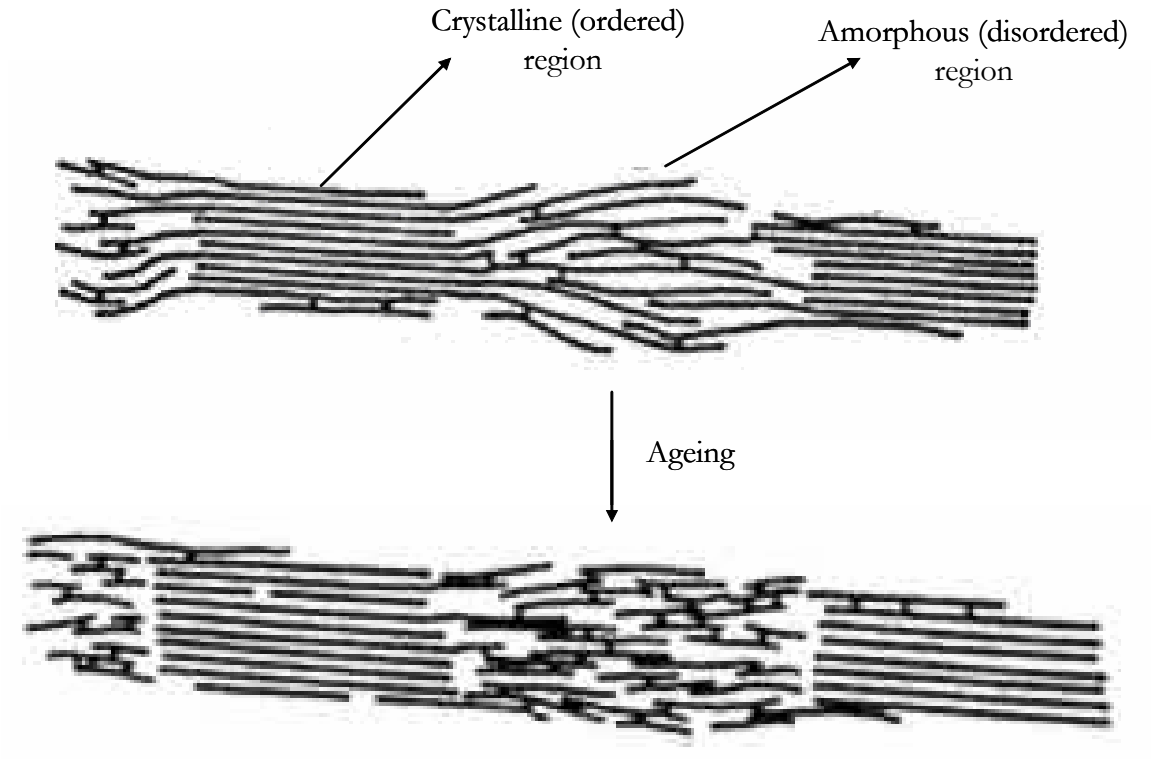


Figure 1.6. Proposed ageing mechanism in cellulose micro-fibrils. Reprinted from source: http://aic.stanford.edu/jaic/articles/jaic31-01-014_2.html

At low temperatures cellulose degradation is thermo oxidative or hydrolytic, a similar effect as seen in aging cellulose materials (Figure 1.6). Thus besides temperature, the aging of cellulose is also affected by light, oxygen, and humidity.

At temperatures above 200°C, the absorbed water by hydroxyl groups in the cellulose matrix is lost followed by loss of water by β elimination of hydroxyl groups. At temperatures that are higher than 250°C, the cellulose chains begin to undergo de-polymerization and anhydroxyglucose derivatives are formed. As the temperature is increased, the β (1-4) glycoside bonds begin to randomly cleave and a number of low molecular weight compounds are formed as decomposition products.

1.1.5. Industrial Applications

The natural polymer, cellulose, and its many derivatives have been applied to various industrial and commercial applications. Since its discovery, cellulose has been applied to plastics, fibers, wood and paper products, and coatings. Based on its structure and source, its applications range from being used as a dispersing agent, thickener, emulsifier, anticake agent, gelling agent, and stabilizer.[41,42] The overall structure of cellulose is of aggregated particles with extensive pores, which gives it the capability of holding relatively large amounts of water by capillarity thereby making this its most important use. Low order amorphous cellulose absorbs water readily becoming soft and gains flexibility, unlike the highly ordered crystalline regions. The structural qualities from the fibrous forms of natural cellulose such as strength, tenacity, specific gravity, and elasticity, enable its use in the manufacturing of paper and textiles. The long rigid microfibrils of cellulose are well resistant

to chemical change, and this resistant nature helps fabrics to withstand rough wear and tear. Neither does the chemical treatment in the laundry nor the contact with water and atmosphere affect cellulosic fibers. Various fibers such as jute, cotton, flax, and hemp have been subject to printing and dying while others were adapted in the brush and rope making industries. The large cellulose industry mainly relies on certain specific chemical properties of cellulose which are either intrinsic or based on their modified structures from derivatization reactions such as esters. Thus cellulose nitrate, or flash paper, which is a highly flammable species, is formed by exposing cellulose with nitric acid. It is also referred as gun cotton when used as a low order explosive. The invention of cellulose nitrate introduced explosives to mankind, and is also routinely used in photographic films, nail polish, and hair coloring among others.[42,43] Diagnostic tests such as pregnancy test utilize nitrocellulose. Celluloid and xylonite industries depend upon the nitric esters of cellulose. They assume a plastic state when treated with liquid solvents like alcohol, amyl acetate, camphor and other auxiliaries which can be readily moulded and fashioned.[42,44] Based on their electrical properties of high insulation and low inductive capacity, cellulose acetates are used in coating fine wires for electrical purposes.[2] Mercerization of cellulose is used in making high lustrous cotton goods that gives it the appearance of silk.

More recent and important developments in the fiber industry involve spinning and drawing of cellulose or derivative solutions to produce artificial fibers of all dimensions. These artificial fibers are produced in several different methods. The first method involves the dissolution of cellulose nitrates in alcohol-ether solution which is then spun through fine glass jets into air or water, where the unit threads are twisted together forming the thread

used for weaving. In a different method, the cupro-ammonium solution of cellulose is employed in a similar way and the resulting solution is spun or drawn in a strong acid bath which instantly regenerated cellulose hydrate.[2] In a more recent process, artificial silk was produced by a viscose solution of cellulose. In the viscose process, the alkaline solution of the cellulose derivative is drawn into a concentrated ammonium salt solution or into an acid bath giving artificial silk as the product. The viscose solution of cellulose is further used in the industry for the production of book cloth and leather cloth, paper-coating, paper sizing, and textile finishing.

Cellulose industry is concerned with discovery and use of functions that are easily reproducible with a constant market value. Table 1.3 highlights some of the reproducible

Table 1.3. Summary of uses and properties of some common cellulose derivatives.[42]

No.	*Derivative Product*	*Main Property*	*Principal Application*
1	Viscose	Film formation, spinnable	Textile fibres, cellophane, sponges, casings, staple filament
2	Acetate	Film formation, spinnable, plasticizer take-up, acetyl value	Fibres, textiles, cigarette tow, plastics, moulding powders, optical membrane sheet
3	Nitrate	Film formation, plasticizer take-up, DP	Smokeless powders, lacquers, propellants, membranes
4	Propionate	Plasticizer take-up	Plastics moulding powders
5	Mixed Esters (Acetate butyrate, Acetate phthalate)	Specific plasticizer take-up	Special coatings, lacquers
6	Mixed Ethers/Esters	Specific solubility	Pharmaceutical, tablet coatings

uses of cellulose derivatives based on their properties.

Like many other derivatives of cellulose, hydroxyethyl cellulose also has many applications.[129] Due to the fact that this molecule cannot undergo crystallization because of the hydroxyethyl functional groups; hydroxyethyl cellulose tends to readily dissolve in water. This property of hydroxyethyl cellulose makes it a good cleansing agent in the soap industry. It is generally used as a thickener in shampoos and soaps. Figure 1.6 shows an illustration where the hydroxyethyl cellulose chains surround the insoluble dirt particle in water. Since the dirt is insoluble and hard to clean, the soluble hydroxylethyl cellulose chains encapsulate the particle which is then easily washed away with water.

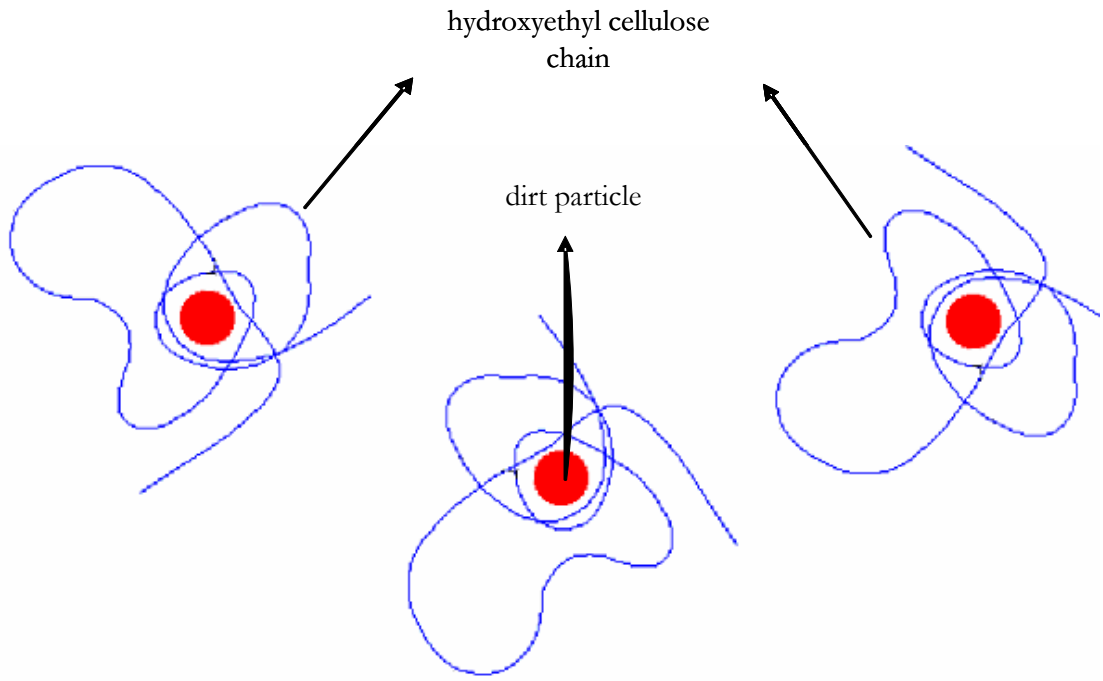


Figure 1.7. Illustration of a hydroxyethyl cellulose chain encapsulating dirt particle. Reprinted from source: http://www.pslc.ws/mactest/cell.htm

1.2 Polymerization Reactions

1.2.1. Introduction

In 1929, W.H. Carothers suggested that polymers were formed either by condensation reactions or by addition reactions.[45] Condensation reactions involved the reaction of monomers which resulted in the loss of some small molecule, while addition reactions did not accompany a loss in molecule with the addition of monomer. It was not until the 1950's when P.J. Flory categorized and proposed mechanisms for polymerization reactions.[45] With the advent of different polymerization methods such as condensation reactions, cationic and anionic polymerization, free radical polymerization, coordination polymerization, and ring opening polymerization, several polymers and polymer architectures were synthesized with new and improved molecular properties. Among all the above mentioned polymerization techniques, free radical polymerization remains a popular synthetic method for preparing high molecular weight polymers. The simplicity of this system has sparked some major developments such as the use of supercritical CO_2 as a solvent.[46] The popularity and usage of this technique is due to the fact that reactants did not require extreme purity and several kinds of monomers could be polymerized involving simple reaction conditions. The polymers obtained by this technique, however, did not have good control over its polydispersity and molecular weights. During polymerization reactions, uncontrolled generation of radicals and subsequent chain transfer and termination processes were responsible for high polydispersity index (PDI) values.[47] Thus for a long period of time, very limited control over molecular weight was possible and most samples obtained were polydisperse. There has been a constant development of ionic living systems in past years, however due to stringent reaction

conditions, such systems could rarely be used in the industry.[48] Thus, in order to develop living systems for immediate industrial scale application, the focus in the area of free radical polymerization has increased in the last decade with the intention of having a better control over the molecular weight and polydispersity of the resulting polymer.

1.2.2. Controlled-Living Polymerization

Traditionally, free radical polymerizations involved processes of initiation, propogation, chain transfer, and chain termination.[49] The occurrence of chain transfer and termination during polymerization process resulted in polydisperse samples with uncontrolled molecular weights. In 1956 Szwarc was able to achieve the much desired control over the resulting polymer with predetermined molecular weight and a narrow molecular weight distribution, and called such polymerization as living polymerization.[50,51] The living or controlled nature of such reactions is characterized by fast rate of initiation compared to rate propagation.[52] With this, all the propagating chains form simultaneously and grow at the same rate until all the monomer is consumed. If the propagating chains do not form simultaneously then the initial chains would be longer than the ones initiated later resulting in a broad molecular weight distribution. Living polymerizations are generally highlighted by low PDI's of resulting polymer (usually less than 1.2). The strength of living polymerization enables propagating species to undergo polymerization until complete monomer conversion, which can further polymerize upon addition of other monomers. The sequential addition of monomer is used to make block copolymers from the active and stable chain ends. Synthetic polymer chemists are now able to develop a wide variety of polymer architectures

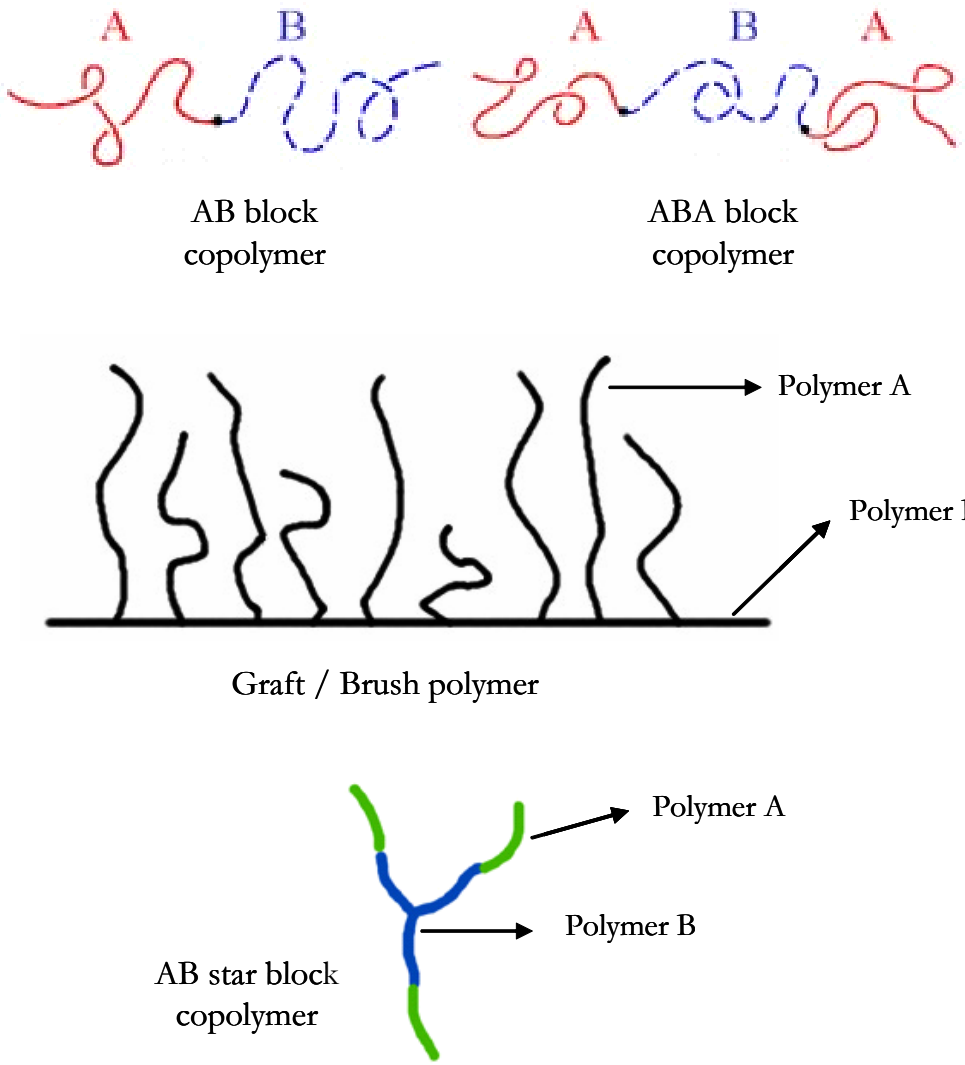
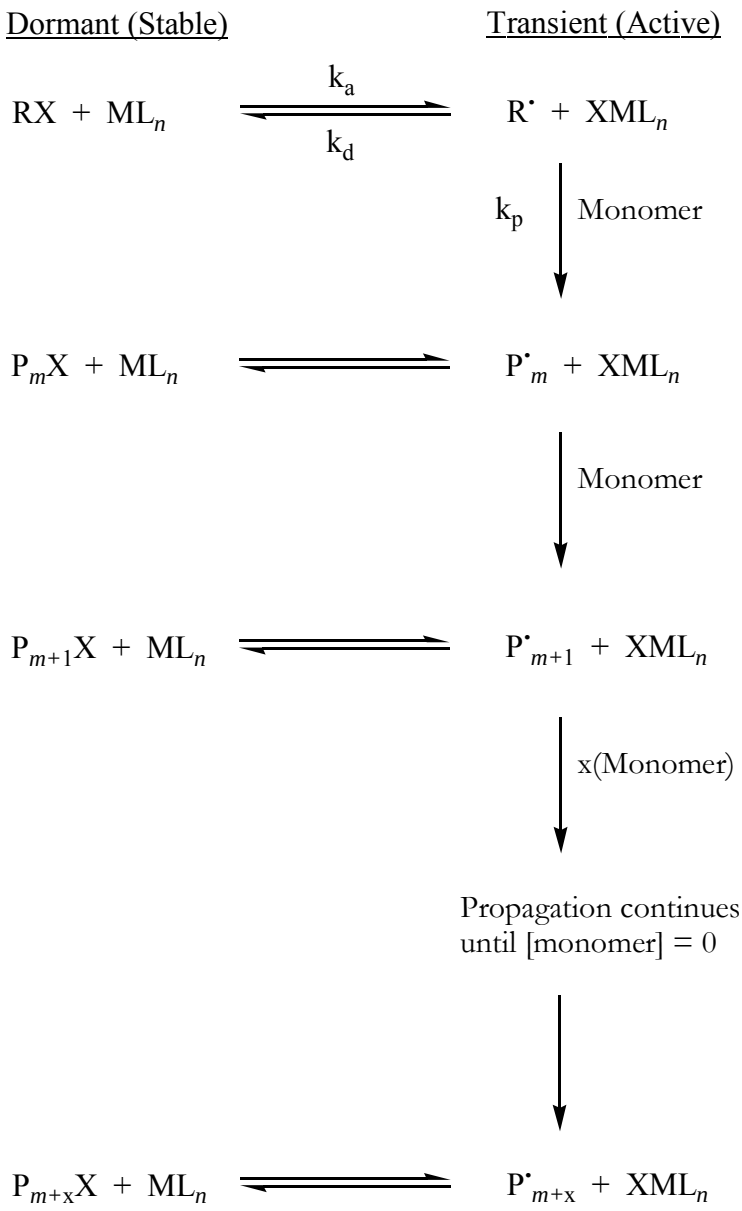


Figure 1.8. Various copolymer structures that can be synthesized by living polymerization techniques. Reprinted from sources: http://www.princeton.edu/~polymer/block.html ; http://www.msri.org/about/sgp/jim/models/copolymers/chemistry/main.html; http://en.wikipedia.org/wiki/Image:PolymerBrush.jpg

(Figure 1.8) such as block copolymers, graft polymers, ladder type polymers, star polymers based on the living polymerization techniques.[53] These architectures were difficult to make with uncontrolled methods such as free radical polymerizations.[54] Group transfer polymerizations, ring opening polymerization, living anionic and cationic polymerization are examples of some living radical systems. Most of these reaction systems require high reactant and solvent purity along with absence of water and oxygen. Such criteria have limited many chemists to manufacture variety of polymer architectures on an industrial scale. Thus, to gain a better control, several methods of controlled radical polymerization have been developed including reversible addition fragmentation chain transfer polymerization (RAFT), nitroxide mediated radical polymerization (NMP), and atom transfer radical polymerization (ATRP).[55-66]

1.2.3. Atom Transfer Radical Polymerization (ATRP)

Many controlled polymerization techniques that have been recently developed, allow the preparation of monodisperse samples from monomers like acrylates, acronitrile, styrene which gain a controlled architecture in a living fashion. These preparation methods are based on a common strategy which involves suppressing the bio molecular termination reactions by converting the growing radicals into dormant species reversibly and temporarily. With this the radical concentration in the reaction media decreases and the rate of termination that is second order in radical concentration slows down significantly.[47] Atom transfer radical polymerization (ATRP), a catalytic step growth technique, is one of these techniques that were first described by two independent researchers, Sawamoto and Matyjaszewski, in



Scheme 1.1. General mechanism for ATRP. (ML_n = metal ligand complex, where M is the metal, L is the ligand). Reprinted from Reference 128.

1995.[59] In the synthesis of many polymers, ATRP has proved to be a powerful tool and has attracted wide research interest.[67-75] With the use of variety of monomers, ATRP is also

efficient with many transition metal complexes such as Cu, Pd, Ru, Fe, and Ni.[76-82] The polymerization process can be conducted in bulk or in common solvents like water, benzene, and others.[81-82] These reactions can be easily carried out at room temperatures to moderate temperatures ranging from 60°C-140°C. The versatility, convenience, low cost, and efficiency makes ATRP an ideal system for synthesizing tailor made, novel materials.[69,87] ATRP is developed from atom transfer radical addition reaction, wherein the transition metal catalyst acts as a carrier of the halogen atom in a reversible redox process. The general mechanism of ATRP is outlined in Scheme 1.1. In a typical ATRP reaction, one electron oxidation of a transition metal takes place with the concomitant abstraction of a halide atom from the stable (dormant) organic halide (RX) leading to the formation of a highly reactive organic radical ($R^{\bullet}$). This organic radical, which is in the transient state, propagates freely in the presence of the monomer. The dormant polymer, $P_{m+x}X$ is formed by the subsequent reductive abstraction of the halide from the metal by the propagating organic radical. Thus to elaborate Scheme 1.1, the initiating system consists of an alkyl halide (RX), and transition metal complex such as Cu(I) that is present with a ligand (usually nitrogen based) such as N,N,N′,N″, N″ pentamethyldiethylenetriamine (PMDETA). ATRP follows a modified version of Kharash reaction wherein the transition metal catalyst system acts as a carrier of the halogen atom in a reversible redox process.[85,86] Based on the reversibility of this process, an exchange equilibrium is present between the dormant (stable) and transient (active) polymer chains. In a process similar to conventional radical polymerization, polymer chains grow by addition of monomer to free radicals in ATRP with k_p as rate constant for propagation. The number of radical species is maintained lower by insuring that the reaction

equilibrium favors the dormant species. Thus when the concentration of growing radical is kept low and the redox reaction is fast compared to biomolecular coupling of the radicals, termination reactions are minimized.[87] Also, narrow molecular weight distributions are seen when k_d is higher than k_p. If k_p is higher than k_d , then the reaction becomes uncontrolled. Thus a successful ATRP can be summarized as a process for synthesizing polymers with predetermined molecular weights ($DP=\Delta[M] / [I]_o$), controlled functionality, and low polydispersity.

Matyjaszewski et al. have shown that initiator efficiency is of prime importance for better control of polymerization process. Tertiary alkyl halide initiators, specifically alkyl bromide initiators when used with copper(I) chloride catalyst are preferred for highly controlled reaction results.[47,48] The initiator which is usually an alkyl halide, should have a structure homologous to the corresponding polymer group. Thus for instance, initiators such as 1-bromo-1-phenyl ethane and 1-chloro-1-phenyl ethane are used in initiating styrene monomer, while initiators such as 2-bromo ethyl isobutryate, 2-bromo ethyl propionate, p-toluene sulphonyl chloride are used in initiating methylmethacrylate monomer. Along with a homologous structure offering better control, the initiating step must be faster or equal to propagating step.

Many transition metals have been employed in the ATRP process. Copper based catalysts continue to dominate as the choice for various reactions due to its low cost and versatility towards various monomers. The important factors in selecting good ATRP catalyst are dynamics of exchange between dormant and transient species, and equilibrium position. Besides copper, other important metal based catalysts used in ATRP are palladium,

ruthenium, iron, and nickel.[76-82] As a basic requirement, the metal participates in the one electron oxidation & reduction process and not in the atom transfer process. The metal should have a high affinity for the halogen and low affinity for hydrogen, which is important to avoid transfer reactions such as β-hydrogen elimination and formation of organometallic derivatives that reduces control of the process.

Studies have shown that solvents tend to influence the solubility of the catalyst and the solvent reactivity directly affects the reaction kinetics in ATRP.[88-94] Matyjaszewski et al. investigated the effects of various solvents in ATRP reaction of n-butyl acrylate[88]. Their investigations indicated a fast homogeneous reaction process when ethylene carbonate was used as a polar solvent. In other studies, hydroxyl containing solvents were found to accelerate the rate of reaction, thereby affecting the rate of ATRP.

In ATRP, a wide variety of ligand systems were also investigated along with transition metals.[95] Ligands are an important part of ATRP process as it plays three very distinct roles. To begin they are used to aid solubility of the metal complex in the organic media. Through their steric and electronic effects they control the selectivity. Most importantly, ligands affect the redox chemistry with their electronic effects.[96] The most effective ligand systems used in ATRP have been derivatives of 2,2-bipyridine. Other ligands applied in ATRP processes are N,N,N′,N″, N″ pentamethyldiethylenetriamine (PMDETA), Tris[2-(dimethylamino)ethyl]amine (Me6-TREN), 1,14,7,10,10-hexamethyltriethylenetetraamine (HMTETA), and tetramethylethylenediamine (TMEDA).[97-99]

Like other common polymerization procedures, ATRP also possesses a drawback in the procedure. ATRP reaction generates a large amount of redox active transition metal which

requires the product to be purified thoroughly. This makes the industrial application of the contaminated polymer, with large quantities of metal in it, more difficult as it affects the production cost of the polymer product. This problem has prompted various researchers to investigate the application of immobilized catalysts in the polymerization process.[101-104] For this the catalyst was bound to an insoluble support such as resin particles. Some of other techniques studied to remove the catalyst system from the formed polymer include the usage of ligands that solubilize with variable temperatures, a hybrid immobilized catalyst system, using ionic liquids as solvents, and using ion exchange resins.[105-111]

1.3 Amphiphilic Block Copolymers

Amphiphilic block copolymers can be categorized as a new class of functional polymers. They are thought as unique building blocks for many practical applications. Their molecular structure is composed of at least two parts (blocks) with differing structural, chemical, and physical properties. Thus the block copolymers are termed amphiphilic, where amphi means of both kinds and philic means having an affinity for. Since both have hydrophobic and hydrophilic blocks, probable parallels can be drawn between amphiphilic copolymers and surfactants. Generally amphiphilic block copolymers are nonionic surfactants that have received continued attention due to its tremendous solution properties offering a wide range of application on an industrial scale. From a scientific research perspective, these materials are very interesting because they exhibit great self assembling properties in the presence of selected solvents.[100] Block copolymers that contain two different moieties such as a hydrophobic moiety like polystyrene, poly(methyl methacrylate) and a hydrophilic moiety

like cellulose, polyethylene oxide are of great interest due to their properties. Such properties include phase separation of the hard component from the soft component, cylindrical and lamellar phase organization, and mechanical properties such as elongation, deformation, elasticity, among many. Due to the various structure property relationships, amphiphilic block copolymers find applications as dispersants, thickeners, compatibilizers, rinse aids, emulsifiers, and foamers. When block copolymers are dissolved in a selective solvent, a liquid which is a good solvent for one copolymer block but a non-solvent for the other block in the copolymer chain, then the copolymer associates reversibly to form micelles in analogy to low molar mass surfactants.

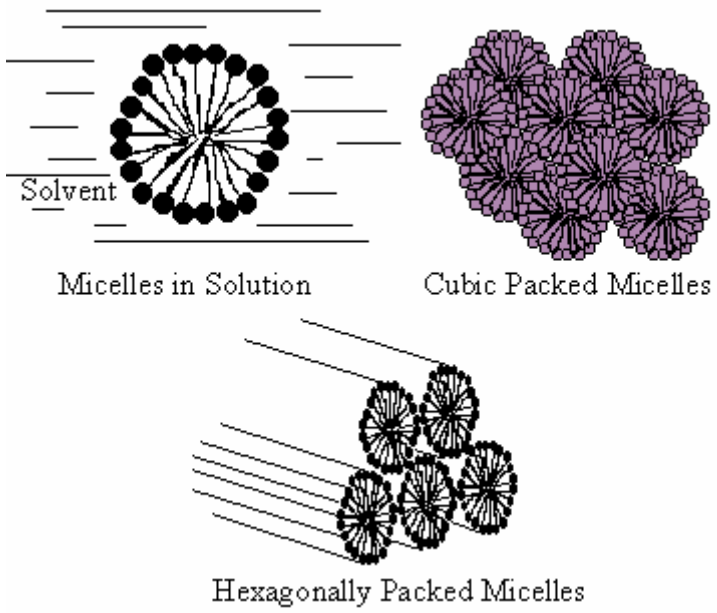


Figure 1.9. Self assembly of block copolymers forming various micelle structures. Reprinted form source: http://www.engr.sjsu.edu/WofMatE/polymers.htm

These micelles consist of a compact core of the non-soluble blocks surrounded by a highly swollen shell (corona) of the soluble copolymer block. Block copolymer systems that contain polyethylene oxide blocks are readily soluble in water. This has attracted many researchers and developers and such an aqueous system has been reviewed on a large scale.[112-121] Amphiphilic copolymers assemble in various various ordered structures such as hexagonal packed, cubic packed micelles, cylinders, and lamellar structures as shown is Figure 1.9. These micellar structures can be controlled by varying the composition of the block copolymer and the segregation in between the blocks by temperature or degree of polymerization.[124] The Flory-Higgins parameter χ, governs the phase segregation between the two blocks. The weight fractions of various blocks have an influence on this parameter.[125] The ordered structures of the different copolymer blocks are characterized by the presence of two glass transition temperatures (T_g). Hard blocks tend to have high glass transition temperatures while soft blocks reflect a low glass transition temperature. This property of block copolymer structures continues to attract industrial attention because of its potential application as thermoplastic elastomers.[122,123]

1.4 Summary

Cellulose is a fascinating, most abundant, inexpensive, and a natural biopolymer that continues to attract constant attention with regards to its application as a renewable polymer resource. Its distinct polyfunctionality differentiates cellulose from all other synthetic polymers. The tendency to form crystals utilizing extensive intra and intermolecular hydrogen bonding makes it completely insoluble in normal aqueous solutions. It has been

used for over 100 years as a chemical raw material to form various esters, ethers, nitrates, and other derivatives. Cellulose derivatives are very commonly used for fibers, optical films, laminates, explosives, pharmaceuticals, food products, coatings, and cosmetics among others. Cellulose and cellulose derivatives are becoming increasingly important in the development various polymer architectures for newer and better applications. With the fusion of carbohydrate chemistry and polymer chemistry in a bio-macromolecule, many diverse architectures, functions, and activities can be obtained. Controlled radical polymerization techniques, such as ATRP can be applied to generate amphiphilic block copolymer structures from cellulose comprising of natural carbohydrate cellulose block linked with a synthetic polymeric block such as polystyrene. Amphiphilic block copolymers essentially act as surfactants in which one block is hydrophilic (water/solvent soluble) while the other block is hydrophobic (water/solvent insoluble). In an aqueous environment, surfactants aggregate in to various structures that are termed as micelles. In such an environment, the hydrophobic blocks are usually surrounded by the soluble hydrophilic blocks. Depending on the composition and condition of surfactant molecules, the aggregates may take the form of spheres, discs, worm-like micelles, rods, and lamellar sheets among other forms. The controlled nature of ATRP enables the synthesis of a wide range of amphiphilic (hydrophilic and hydrophobic) copolymer architectures that were not feasible with conventional polymerization techniques.[126,127] The focus of this work is to utilize a well controlled polymerization system, ATRP, to create synthetic amphiphilic copolymer hybrid structures leading to enhanced physical and chemical property relationship.

1.5 References

1. Brown, R. M.; *J. Pure Appl. Chem.* **1996**, *10*, 1345.
2. Plunguian, M. *Cellulose Chemistry*; Chemical Publishing Co., Inc: New York, 1943.
3. Brown, R. M.; *J. Polym. Sci Part A. Polym. Chem.* **2004**, *42*, 487-495.
4. Nobles, D.; Romanoviez, D.; Brown, R. M. *J. Plant Physiol*. **2001**, *127*, 529.
5. Shibazaki, H.; Kuga, S.; Onabe, F.; Brown, R. M. *J. Polym*. **1995**, *36*, 4971.
6. Conner, A. H. Size Exclusion Chromatography of Cellulose and Cellulose Derivatives. In *Handbook of Size Exclusion Chromatography*; Wu, C., Eds.; Chromatographic Science Series; Marcel Dekker: New York, 1995.
7. Kimura, S.; Itoh, T. *Protoplasma*. **1995**, *186*, 24.
8. Schopf, J. W.; Walter, M. R. In *The Biology of Cyanobacteria*; Carr, N.; Whitton, B., Eds., Black-well: Boston, 1982.
9. Payen, A. *Compt. Rend*. **1838**, *7*, 1052-1125.
10. Cross, C. F.; Bevan, E. J. *Paper Making*, London, E., F.N Spon, Ltd., 1920.
11. Dore, W. H.; Sponsler, O.L. *Colloid Symposium Monogr*. **1926**, *4*, 174.
12. Hirst, E. L.; Thomas, H.A.; Haworth, W. N. *Nature*, **1930**, *126*, 438.
13. David, S. *The Molecular and Supramolecular Chemistry of Carbohydrates*; Oxford University Press: Oxford, 1997.
14. Heinze, U.; Philipp, B.; Heinze, T.; Wagenknecht, W.; Klemm, D. *Comprehensive Cellulose Chemistry*; Wiley-VCH: Weinheim, 1998, Vol.1, pp. 10-11.

15. Kuga, S.; Brown, R. M. *J. Carbohydr. Res*. **1988**, *180*, 345.

16. Andress, K. R. Z. *Phys. Chem. Abt*. B **1929**, *4*, 190.

17. Blackwell, J.; Kolpak, F. J. *Macromolecules*, **1976**, *9*, 851.

18. Chanzy, H.; Nishiyama, Y.; Langan, P. *Am. Chem. Soc*. **1999**, *121*, 9940.

19. Watanabe, S.; Ohkita, J.; Hayashi, J.; Sufoka, A. *Polym. Lett*. **1975**, *13*, 23.

20. Southwick, J.; Hayashi, J.; Sarko, A. *Macromolecules.* **1976**, *9*, 857.

21. Tanner, S. F.; Belton, P.S.; Chanzy, H.; Vincendon, M.; Henrissat, B. *Carbohydrate Res*. **1987**, *160*, 1.

22. Chanzy, H.; Buleon, A. *J. Polym. Sci. Polym. Phys. Ed*. **1980**, *18*, 1209.

23. Togawa, E.; Brown, R. M.; Kondo, T. J. *Biomacromolecules* **2001**, *2*, 1324.

24. Atalla, R.H. *The Structures of Cellulose*; ACS Symposium Series 340; 1987.

25. O'Sullivan, A. C. *Cellulose*. **1997**, *4*, 173-207.

26. Zugenmaier, P. *Prog. Polym. Sci*. **2001**, *26*, 1341-1417.

27. Conrad, C.; Tripp, V.W. In. *Instrumental Analysis of Cotton Cellulose and Modified Cotton Cellulose*; O'Connor, R. T., Ed.; Marcel Dekker: New York, 1972.

28. Cannizzaro, A. M.; Goynes, W. R.; Rollins, M. L. In. *Instrumental Analysis of Cotton Cellulose and Modified Cotton Cellulose;* O'Connor, R. T., Ed.; Marcel Dekker: New York, 1972.

29. Millet, M. A.; Stamm, A. J. *J. Phys. Chem*. **1941**, *45*, 43.

30. Wise, L. E. *Paper Industry*, **1938**, *20*, 413-540.

31. Davies, R. E.; Hergert, H. L.; Turbak, A. F.; Hammer, R. B. *Chemtech*. **1980**, 10, 51

32. Johnson, D. C. In. *Cellulose Chemistry and Its Applications*, Zeronian, S. H., Nevell, T. P., Eds.; Halsted Press: New York, 1985.

33. Jayme, G. In. *Cellulose and Cellulose Derivatives*, Segal, L., Bikales, N. M., Eds.; Interscience: New York, 1971.

34. Schleicher, H.; Wagenknecht, W.; Philipp, B. *Chemtech*. **1997**, *7*, 702.

35. Utracki, L. A. *Polym. Eng. & Sci*. **1995**, *35*, 2.

36. Cameron, S. J. *Nephrol Dial Transplant* **2000**, *15*, 1086.

37. Wood, F. C.; Marsh, J. T. *An Introduction to the Chemistry of Cellulose*; Chapman and Hall Ltd: London, 1938.

38. Colom, X.; Carillo, F. *European Polym. J*. **2002**, *38*, 2225.

39. Aubert, J. P.; Beguin, P. *FEMS Microbiology Reviews* **1994**, *13*, 25.

40. Bancroft, W. D. *J. Phys. Chem*. **1915**, *19*(2), 159.

41. Tonnesen, H. H.; Karlsen, J. *Drug Development & Industrial Pharmacy 2002*, *28*(6), 621.

42. *Cellulose and its derivatives, chemistry, biochemistry and applications*; Kennedy, J. F.; Phillips, G. O.; Wedlock, D. J.; Williams, P. A.; Halsted Press: New York, 1985.

43. Huang, M. R.; Li, X. G. *J. Appl. Polym. Sci*. **1998**, *68*, 293.

44. Stoner, J. O. *Nuclear Instruments and Methods in Physics Research* **1995**, *362*, 167.

45. Stuart, B. H. In: *Analytical Techniques in the Sciences: Polymer Analysis*; Ando, D. J., Eds.; John Wiley & Sons, Ltd: New York, 2002.

46. Cooper, A. I. *J. Mater. Chem*. **2000**, *10*, 207-234.

47. *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series 685; American Chemical Society: Washington, DC, 1998.

48. Matyjaszewski, K.; Grimaud, T.; Shipp, D. A.; Wang, J. L. *Macromolecules* **1998**, *31*, 1527.

49. Odian, G. In *Principals of Polymerization*, 3rd edn., Wiley Interscience: New York, 1991.

50. Milkovich, R. J.; Levy, M.; Szwarc, M. *J. Am. Chem. Soc.* **1956**, *78*, 2656.

51. Szwarc, M. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*.

52. Lee, B.; Quirk, R. P. *Polym. Int*. **1992**, *27*, 359.

53. Webster, O. W. *Science* **1991**, *251*, 887.

54. Campbell, T.W.; Sorenson, W. R. *Preparative Methods of Polymer Chemistry*, Wiley Interscience: New York, 1968.

55. Higashimura, T.; Kamigaito, M.; Kato, M.; Sawamoto, M. *Macromolecules* **1995**, *28*, 1721.

56. Hedrick, J. L.; Hawker, C. J. *Macromolecules* **1995**, *28*, 2993.

57. Hamer, G.; Veregin, R.; Georges, M.; Kazmaier, P. *Macromolecules* **1993**, *26*, 2987.

58. Bosman, A. W.; Harth, E.; Hawker, C. J. *Chem. Rev*. **2001**, *101*, 3661.

59. Wang, J.; Matyjaszewski, K. *J. Am. Chem. Soc*. **1995**, *117*, 5614.

60. Veregin, R. P.; Hamer, G.; Kazmaier, P.; Georges, M.; Saban, M. D. *Macromolecules* **1995**, *28*, 7032.

61. Davis, T. P.; Matyjaszewski, K. *Handbook of Radical Polymerization*, John Wiley & Sons, Inc: New York, 2002.

62. Kee, R. A.; Kazmaier, P.; Georges, M.; Veregin, R. P.; Hamer, G. *J. Phys. Org. Chem*. **1995**, *8*, 301.

63. Matyjaszewski, K.; Wang, J. S. *Macromolecules* **1995**, *28*, 7901.

64. Hawker, C. J. *J. Am. Chem. Soc*. **1994**, *116*, 11185.

65. Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L; Rizzardo, E.; Moad, G.; Thang, S. H.; Le, T. P.; Chiefari, J.; Ercole, F.; Chong, Y. K.; Krstina, J.; Jeffery, J. *Macromolecules* **1998**, *31*, 5559.

66. Mayadunne, R. T. A.; Rizzardo, E.; Moad, G.; Thang, S. H.; Chiefari, J.; Chong, Y. K. *Macromolecules* **1998**, *32*, 6977.

67. Matyjaszewski, K.; Wang, J. S. *Macromolecules* **1997**, *30*, 6398.

68. Hoffman, H.; Vallant, T.; Pakula, T.; Siclovan, T.; Kickelbick, G.; Luokola, B.; Shukla, N.; Gelman, A.; Miller, P.; Immaraporn, B.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 8716.

69. Sawamoto, M.; Ando, T.; Kamigaito, M. *Chem. Rev*. **2001**, *101*, 3689.

70. Weavers, J.; Armes, S.; Save, M. *Macromolecules* **2002**, *35*, 1152.

71. Shooter, A.; Haddleton, D.; Kukulj, D.; Duncalf, D.; Heming, A.; Crossman, M.; Dana, B. *Macromolecules* **1999**, *32*, 2110.

72. Barboiu, B.; Percec, V. *Macromolecules* **1995**, *28*, 7970.

73. Bon, S.; Perrier, S.; Haddleton, D. *Macromolecules* **2000**, *33*, 8246.

74. Senninger, T.; Teyssie, P.; Jerome, R.; Dubois, P.; Moineau, G. *Macromolecules* **1998**, *31*, 545.

75. Granel, C; Teyssie, P.; Jerome, R.; Dubois, P.; Moineau, G. *Macromolecules* **1998**, *31*, 542.

76. Sawamoto, M.; Ando, T.; Kamigaito, M. *Macromolecules* **1997**, *30*, 4507.

77. McDermott, N. E.; Xia, J.; Wei, M.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 8161.

78. O'Reilly, R. K.; Gibson, V.C. *Polymer Preprints* **2004**, *45*, 680.

79. Teyssie, P.; Jerome, R.; Dubois, P.; Granel, C. *Macromolecules* **1996**, *29*, 8576

80. Sawamoto, M.; Ando, T.; Kamigaito, M.; Nishikawa, T. *Macromolecules* **1997**, *30*, 2244.

81. Teyssie, P.; Jerome, R.; Dubois, P.; Lecomte, P.; Drapier, I. *Macromolecules* **1997**, *30*, 7631.

82. Zhang, G.; Li, M.; Zhu, S.; Yan, D. *Macromol. Chem. Phys*. **2000**, *201*, 2666.

83. Wang, X. S.; Armes, S. P.; Robinson, K. L.; De PazBanez, M. V. *Macromolecules* **2001**, *34*, 5799.

84. Wang, X. S.; Armes, S. P.; Jackson, R. A.; Lascelles, S. F. *Chem. Commun*. **1999**, *18*, 1817.

85. Fischer, P.; Skell, P. S.; Karasch, M. S. *J. Am. Chem. Soc*. **1948**, 1055.

86. Urry, W. H.; Jensen, E. V.; Karasch, M.S. *Science* **1945**, *102*, 128.

87. Xia, J.; Matyjaszewski, K. *Chem. Rev*. **2001**, *101*, 2921.

88. Boutevin, B.; Alric, J.; Destarac. M. *Macromol. Rapid Commun*. **2000**, *21*, 1337.

89. Nakagawa, A.; Jasieczek, C.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 1535.

90. Fernandez-Garcia, M.; Madruga, E.; Fernandez-Sanz, M.; Fuense, J. *Macromol. Chem. Phys*. **2001**, *202*, 2565.

91. Ying, S. K.; Wang, X. S.; Luo, N. *J. Polym. Sci. Part A: Polym. Chem*. **1999**, *37*, 1255.

92. German, A.; Chambard, G.; Klumperman, B. *Macromolecules* **2000**, *33*, 4417.

93. Polton, A.; Varion, J.; Coutin, B.; Pascual, S.; Tardi, M. *Macromolecules* **1999**, *32*, 1432.

94. Zhang, X.; Matyjaszewski, K.; Xia, J. *Macromolecules* **1999**, *32*, 3531.

95. Matyjaszewski, K.; Patten, T.E. *Acc. Chem. Soc*. **1995**, *117*, 5614.

96. Matyjaszewski, K. J.M.S. *Pure Appl. Chem*. **1997**, *A34*, 1785.

97. Matyjaszewski, K.; Gaynor, S. G.; Queffelec, J. *Macromolecules* **2000**, *33*, 8629.

98. Hannon, M. J.; Haddelton, D. M.; Shooter, A.; Jasieczek, C. B. *Macromolecules* **1997**, *30*, 2190.

99. Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7697.

100. Riess, G. *Prog. Polym. Sci*. **2003**, *28*, 1107.

101. Kukulj, D.; Radigue, A. P.; Haddleton, D.; Duncalf, D. J. *Macromolecules* **1999**, *32*, 4769.

102. Zhu, S.; Pelton, R.; Shen, Y. *Macromol. Rapid Commun*. **2000**, *21*, 956.

103. Kukulj, D.; Radigue, A. P.; Haddleton, D. *Chem. Comm*. **1999**, *1*, 99.

104. Zhu, S.; Pelton, R.; Shen, Y. *Macromolecules* **2000**, *33*, 5427.

105. Chen, X. F.; Zhou, Q. F.; Wan, X. H.; Ma, H. Y. *Polymer* **2003**, *44*, 5311.

106. Paik, H. J.; Matyjaszewski, K.; Hong, S. C. *Macromolecules* **2001**, *34*, 5099.

107. Chen, C. F.; Xi, F.; Zhao, Y. L. *J. Polym. Sci. Part A: Polym. Chem*. **2003**, *41*, 2156.

108. Pallack, M. E.; Malaba, D.; Brittain, W. J.; Liou. S.; Rademacher, J. T. *Macromolecules*, **2000**, *33*, 4295.

109. Chen, X. F.; Zhou, Q. F.; Wan, X. H.; Ma, H. Y. *J. Polym. Sci. Part A: Polym. Chem*. **2003**, *41*, 143.

110. Gaynor, S. G.; Matyjaszewski, K.; Pintauer, T. *Macromolecules* **2000**, *33*, 1476.

111. Haddleton, D.; Seddon, K. R.; Carmichael, A. J.; Bon, S. A. *Chem. Commun*. **2000**, *14*, 1237.

112. Verrall, R.; Wettig, D.; Li, X. *J. Colloid. Interf. Sci*. **2005**, *282*, 466.

113. Attwood, D.; Booth, C. *Macromol. Rapid Commun*. **2000**, *21*, 501.

114. Penfold, J.; Bloor, D.; WynJones, E.; Sidhu, J.; Azouani, S.; Holzwarth, J. *Langmuir* **2004**, *20*, 9320.

115. Bloor, D.; WynJones, E.; Holzwarth, J.; Li, Y.; Couderc, S.; Xu, R. *Langmuir* **2001**, *17*, 5742.

116. Wei, X.; Liu, H.; Su, Y. *Langmuir* **2003**, *19*, 2995.

117. Taton, D.; Gnanou, Y.; Hou, S.; Chaikof, E. *Macromolecules* **2003**, *36*, 3874.

118. Varade, D.; Bahadur, P.; Joshi, T.; Ghosh, G.; Mata, J. *Colloids Surf A: Physicochem and Eng Aspects* **2004**, *247*, 1.

119. Nakashimapp, K.; Li, Y. *Languir* **2003**, *19*, 548.

120. Gopalakrishnan, I.; Aswal, P.; Yakhmi, J.; Ganguly, R.; Hassan, P. *J. Phys. Chem*. **2005**, *109*, 5653.

121. Loh, W.; Schillen, K.; Olofsson, G.; Silva, R. *J. Phys. Chem*. **2002**, *106*, 1239.

122. Jerome, R.; Tong, J. D.; Bredas, J. L.; Leclere, P.; Lazzaroni, R.; Moineau, G. *Macromolecules* **2000**, *33*, 470.

123. Jerome, R.; Minet, M.; Bredas, J. L.; Leclere, P.; Lazzaroni, R.; Moineau, G. Dubois, P. *Langmuir* **1999**, *51*, 3915.

124. Hamley, I. W. *The Physics of Block Copolymers*; Oxford Science Publications: New York, 1998.

125. Fredrickson, G. H.; Phan, S. *Macromolecules* **1998,** *31*, 59.

126. Hayes, W.; Frechet, J, M.; Leduc, M. R. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 1.

127. Dao, J.; Frechet, J. M.; Grubbs, R. B.; Hawker, C. J. *Agew. Chem., Int. Ed. Engl*. **1997**, *36*, 270.

128. *Polymer Chemistry: A Practical Approach*; Davis, F. J.; Oxford University Press: Oxford, 2004.

129. Reuben, J. *Macromolecules*, **1984**, *17*, 156.

Chapter 2

Cellulose Nanocrystals

2.1 Introduction

A nanocrystal is defined as a material having crystalline structure with dimensions that are measured in nanometers. It can also be seen as a nanoparticle with at least one dimension that is less than 100 nm and a crystalline form. The continued interest in nanocrystals is due to its single domain crystalline structure, which is conveniently studied to provide physical and chemical information of macroscopic samples. Thus, from a scientific stand point, nanoparticles and nanotechnology are of great interest as they effectively bridge the gap between atomic and macro/bulk structures. Normally, the physical property of materials remains steady (constant) at the bulk level, but often differs when approaching the smaller (micro to nano scale) level. This is because the percentage of atoms at the surface level of the bulk material is not comparable to the total number of atoms of the material. The benefits of nanotechnology are potentially revolutionary with a projection to have immense growth in the near future.[1] It encompasses a broad range of applied science and technology and currently continues to be a promising area of technology development. Researchers have categorized the fabrication of nano scale materials in two scientific methods.[2] Among the two, the 'top-down' approach involves in creating nano scaled materials from larger materials, essentially descending the synthetic path from top (large piece) to down (smaller piece). The second method is termed as 'bottom-up', which involves an opposite approach to nano objects. In this case, the desired materials are built from atomic or molecular components that assemble together on the basis of atomic and molecular similarity. A major

driving force in nanotechnology is the presence of high ratio of surface area to volume in nanoparticles, which has enhanced surface chemistry. Some of the obvious changes in physical properties of substances in the top to down approach include gold nanoparticles appearing blackish in solution, platinum functioning as a catalyst at nano level, copper nanoparticles as being transparent, and silicon nanoparticles behaving as a conductor rather than an insulator. While the bottom to up procedure requires atoms to self assemble in the structures that are analogous to the top to bottom approach, it is viewed by some scientific researchers as being a complex task. With nano material technology, various materials and chemicals have been synthesized that have been put to pharmaceutical and industrial applications. This technology has also seen the development of various polymer nanocomposites, which essentially are polymers comprised with high aspect ratio nano scale particles.[3] Generally, an inorganic nano particle is mixed with a polymer nano particle that leads to the formation of a hybrid nanocomposite (Figure 2.1). Such polymer based nanocomposites find a wide variety of commercial importance ranging form advanced aerospace systems to commodity plastics.[4]

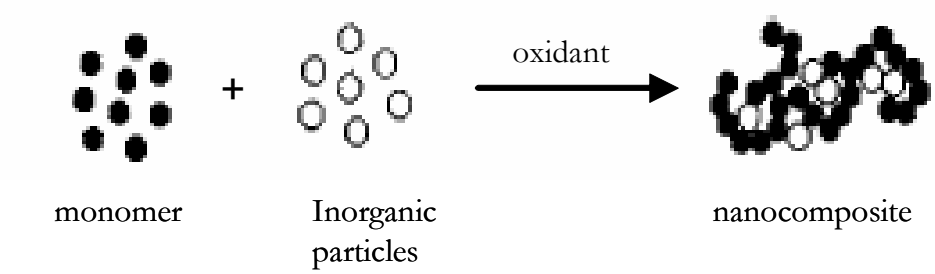


Figure 2.1. Illustration of nanocomposite formation. Reprinted from reference 3.

The technology of nanoparticles is not only limited to organic and inorganic particles in nature, but natural polymers such as cellulose also find immense application owing to its microstructure. Native cellulose is composed of distinct number of glucan chains that are arranged in manner to form nanostructure called microfibrils. These microfibrils are known to have regions of order (crystalline forms) along with regions of disorder (amorphous forms). The crystalline regions within these microfibrils constitute the nanocrystals, which can be effectively derivatized and used in various industrial applications including nanocomposites.

2.2 Crystal Structure

Since its discovery in 1838, cellulose has been one of the most studied natural polymers. It is a high molecular weight liner homopolymer of D-anhydroglucopyranose monomeric units connected through β glycosidic linkages between C1 of one glucose unit with the C4 of the other. The hydrogen bonding network forms the basis of cellulose structure and reactivity. Science has seen over 100 years of dedicated investigation in determination of true structure of cellulose.[21-23] The much studied molecular structure determines cellulose properties such as hydrophilicity, degradability, and its chemical reactivity based on multiple hydroxyl groups. As a naturally available polymer, cellulose, in its raw form occurs as aggregates that form microfibrils. These microfibrils contain regions or order and disorder in them, which are scientifically termed as crystalline and amorphous regions.[8] Several structural analysis techniques including X-ray diffraction, neutron diffraction, and electron microscopy among others have been employed in determining the structure of crystalline cellulose. As

discussed in the previous chapter, cellulose that is produced by plants is referred to as native cellulose which is found in two crystalline forms, cellulose I and cellulose II.[9] Studies suggest that Cellulose I contains large amounts of disordered regions (amorphous form) along with high ordered regions of cellulose.[10,11] Cellulose II, generally occurring in marine algae, is a crystalline form that is formed when cellulose I is treated with aqueous sodium hydroxide.[12-14] Among the four different crystalline polymorphs cellulose I, II, III, and IV, cellulose I is thermodynamically less stable while cellulose II is the most stable structure. A liquid ammonia treatment of cellulose I and cellulose II gives crystalline cellulose III form,[15-17] and the heating of cellulose III generates cellulose IV crystalline form.[18] The type of intra and inter chain hydrogen bonding network is used as a means to distinguish Cellulose I from Cellulose II. The hydrogen bonding between the ring oxygen of one glycoside unit and the hydrogen of C3 hydroxyl unit imparts chain stiffness to cellulose by hindering the free rotation of the pyranose rings to their adjacent glycoside bonds. Both cellulose I and II have intra chain hydrogen bonding between oxygen O3 of one glucan chain and oxygen O5 of the other. Whereas the inter chain bonding differs for cellulose I and II. Inter chain hydrogen bonding in cellulose I is seen between oxygen atom O6 of one glucan chain and oxygen atom O3 of the other. Cellulose II shows inter chain hydrogen bonding between oxygen atom O6 and O2. The X-ray data analysis by Langan et al. suggested that chains in Cellulose II are in antiparallel direction and chains in cellulose I are aligned in parallel direction.[19,20]

The introduction to the general features of native crystalline cellulose was done in 1928 by the work of Meyer et al.[5-7] Through their investigation of native cellulose, they proposed a structure that consisted of a monoclinic unit cell of two polysaccharide chains oriented in anti

parallel direction. Most of these studies assumed that all native cellulose had similar structure and called it cellulose I. In a similar study, Watanabe et al. proposed a similar model by use of electron diffraction to determine cellulose structure.[24] With the continuation of new developments in structural analysis methods, Sarko et al. achieved new results in crystalline structure determination of cellulose.[25] They proposed a model wherein the packing of the chains was parallel. A similar result was observed by Gardner and Blackwell, who also suggested that the cellulose chains within the same crystals were oriented in the same direction. Such results obtained by Gardner and Sarko contradicted the results of Meyer et al., for their model had chains oriented in the anti parallel direction.[5-7]

The idea of all native celluloses having cellulose I as their crystal structure was proven wrong by the outstanding work of Atalla and Vandelhart.[26] Utilizing solid-state ^{13}C NMR analysis to generate spectrums of cellulose samples from varying sources, they concluded

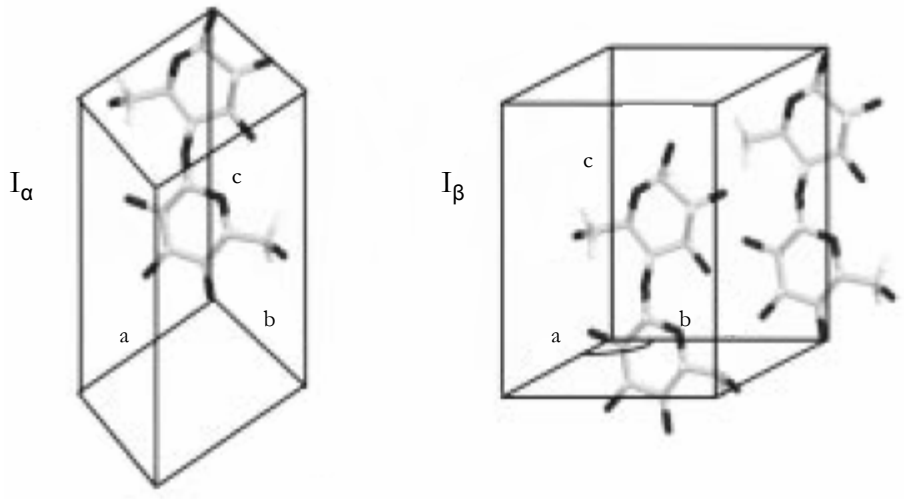


Figure 2.2. Representation of proposed crystalline forms cellulose I_α and I_β, and packing of polysaccharide chains in them.[32]

that each native cellulose contained two different crystalline forms, I_α and I_β. [26,27] Around the same time, X-ray diffraction analysis of varying native cellulose sources including alga Valonia supported the model for existence of two types of crystalline cellulose with monoclinic and triclinic structures.[28] IR spectroscopy was effectively used by Mann et al. in determining the difference in cellulose structures of varying origins, but they were unable to identify the two distinct crystalline sources.[29] With the advancement in structural analysis techniques, crystalline forms cellulose I_α and I_β were successfully identified (Figure 2.2). Electron diffraction analysis of cellulose from green marine algae showed cellulose I_α having a triclinic unit cell structure containing one chain and cellulose I_β having a monoclinic unit cell with two polysaccharide chains arranged in parallel orientation.[30,31]

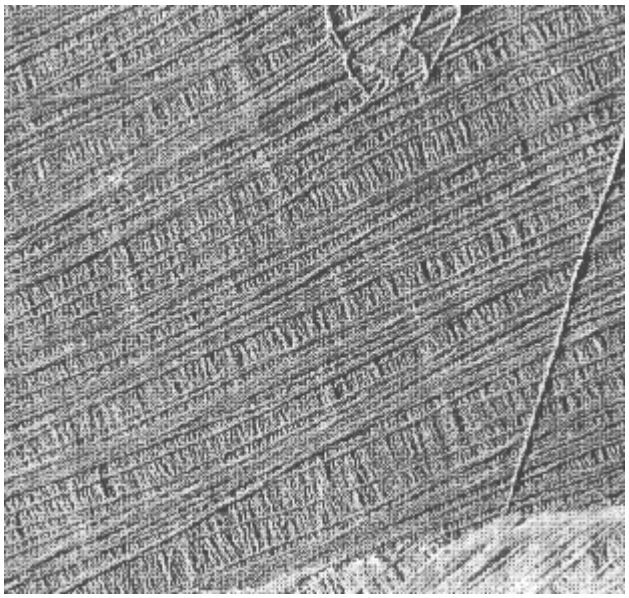


Figure 2.3. Electron micrograph image representing cellulose microfibrils in cell walls of green algae. Reprinted from source:

http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/C/Carbohydrates.html

The work of Kroon, et al. suggest that cellulose I_α and I_β are packed "parallel-up" in the unit cell, which leaves the reducing end in the direction of c axis.[34]

Based on their crystal structures, native cellulose from cotton and ramie are considered rich in cellulose I_β while those originating from algae and bacteria are considered high in cellulose I_α content.[32,33] Figure 2.3 shows an electron micrograph of cellulose fibrils in the cell walls of green algae that highlights the long and rigid fibril like nature of native cellulose molecule. A distinguishing aspect in the two lattices, cellulose I_α and I_β, is that the hydrogen bonding pattern differs while the conformations of the chains remain the same.[35] Cellulose I_α can be converted to more thermodynamically stable form I_β by hydrothermal treatment of the cellulose chains in the solid state.[36,37] A pure form of cellulose I_β is rarely synthesized in nature, but tunicates are an exception as it only contains I_β form that is highly crystalline[38]. The source of native cellulose along with the differing amounts of I_α and I_β are responsible for diverse molecular structures of cellulose I that exist in nature.[38,39]

2.3 Cellulose Nanocrystals

Since its discovery in 1839 by Payen, cellulose has constantly been investigated for its structure, chemical and physical properties, solubility, and reactivity. Numerous studies attempted to propose a viable structure of cellulose, and various solvents were tested for solubility of cellulose. During these investigations, cellulose was tested with a treatment of dilute acids that gave a notable difference in the physical properties, such as strength and tenacity, of the fibers. A chemist by the name of Girard was the first to explain this effect as hydrolysis of cellulose fibers, which was initially recognized in the textile industry.[40]

With structural analysis it was clear that cellulose microfibrils consisted regions of high order in combination with regions of less order. Cellulose nanocrystals originate form the highly ordered crystalline segment of cellulose whereas the amorphous (less ordered) regions constitute a random arrangement of cellulose chains. These randomly arranged chains are easily attacked by an acid where the hydronium ions cause a hydrolytic cleavage of glycosidic bonds by penetrating the low order regions. The breaking of glycosidic linkage results in the separation of highly ordered crystalline regions, which appear like individual rods. These rod-like nanoparticles essentially have the reducing end on side and the non reducing end on the other.

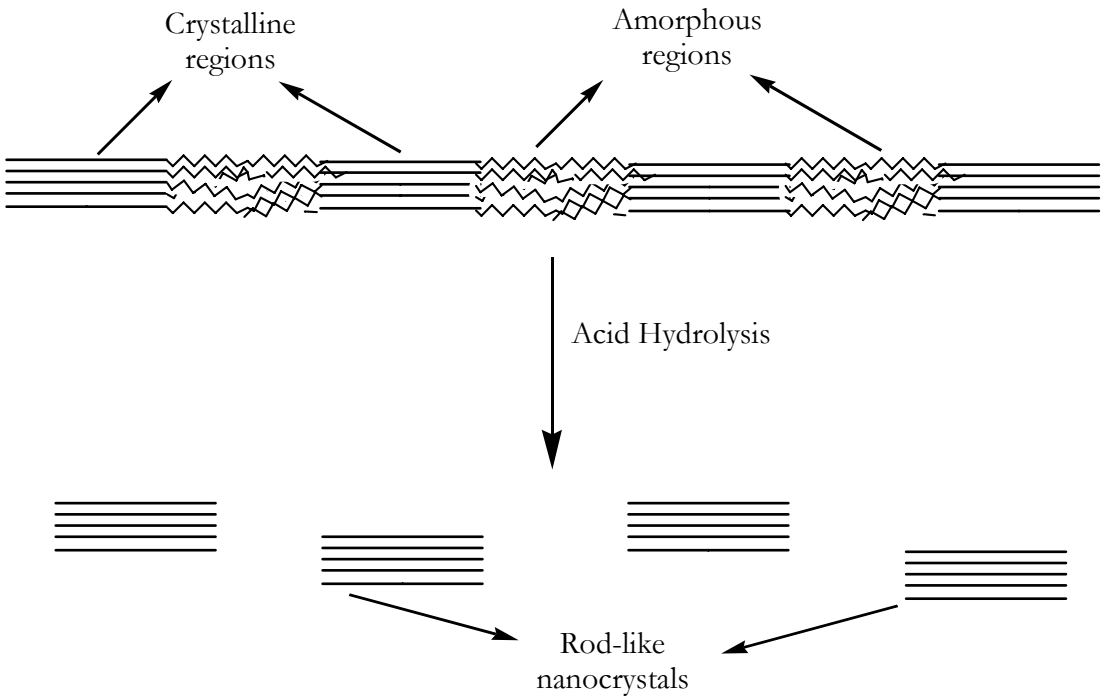
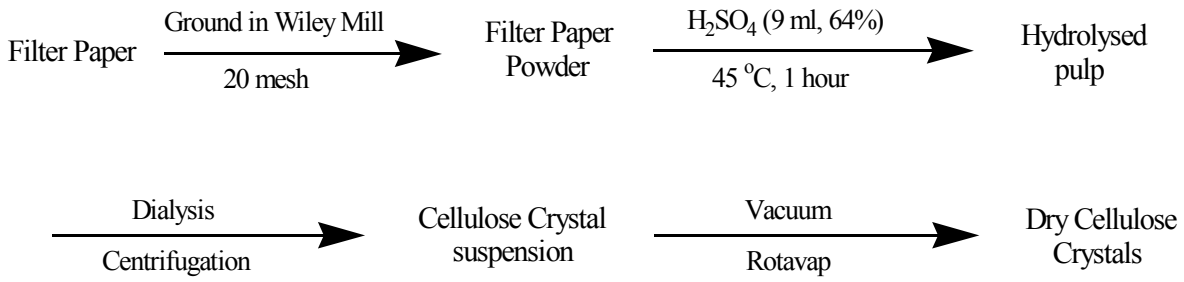


Figure 2.4. Formation of cellulose crystals from acid hydrolysis of cellulose fibers.

This method of producing cellulose nanocrystals in an acidic environment, initially reported in 1951 by Ranby, is called as acid hydrolysis.[41] The breaking of the cellulose chain, which contains high order crystalline regions connected with low order amorphous regions, by acid hydrolysis and the consequential formation of rod like crystals is represented in Figure 2.4. Acid hydrolysis proceeds with a hydronium ion (proton) from acid interacting rapidly with the glycosidic oxygen that links two sugar units in the low order region, forming a conjugate acid. The C-O bond is then cleaved and the conjugate acid breaks down to the cyclic carbonium ion.[43] Highly ordered crystals are then formed with the addition of water.[43] The acid hydrolysis of fibrous regions in cellulose is a heterogeneous acidic cleavage process that depends on type of acid, time duration of hydrolysis, concentration of acid, and the temperature of the reaction.[42] The hydrolysis process that begins by diffusion of acid through the accessible amorphous regions, continues until all of the glycosidic linkages within those low order regions are hydrolyzed. The reaction eventually slows down when the acid reaches the surface of residual crystalline regions. The hydrolysis reaction must be controlled in order to avoid complete hydrolysis of the cellulose chain to its basic monomer, glucose. The reported average dimensions of nanocrystals that are produced from hydrolysis of cotton cellulose chains are 300 nm lengths with a diameter of 4 nm.[50]

2.3.1. Hydrolysis with Sulfuric Acid

Cellulose chains can undergo hydrolysis with acids such as sulfuric and hydrochloric acid. Cellulose microcrystallites are usually solid particles of colloidal dimensions prepared by hydrolysis of cellulose.[47] In this study, we have used sulfuric acid for preparation of cellulose



Scheme 2.1. Preparation of cellulose nanocrystals.

nanoparticles by hydrolysis of cellulose chains in a method similar to Revol et al.[45] (Scheme 2.1). In their study, suspensions of nanocrystals were prepared from filter paper that was ground to smaller than 20 mesh powder. They used Whatman No.1 filter paper as it contains about 98% cotton fiber, which has a very high crystalline structure. Since the acid hydrolytic cleavage is dependant on the acid species, temperature, concentration of the acid, and time of the reaction; cellulose microcrystallites were prepared under controlled conditions. Thus, sulfuric acid concentration of 64% and a reaction time of 60 mins were selected to obtain a colloidal suspension. Ground filter paper powder was mixed with sulfuric acid in a ratio of 1:9 (g/ml). A hydrolysis temperature of 45°C was maintained for the diffusion of acid into the amorphous region of the fibers resulting in a subsequent cleavage of the glycosidic bonds. After hydrolysis and separation of the acid from the particles, the suspension was further dispersed by an ultrasound treatment. The ultrasonification of microcrystallites permits the dispersion of aggregates and produces a colloidal suspension. Due to their strength, thickness, and length, these rod like particles are commonly called as whiskers.[46] The rod-like particles that were produced as a result of ultrasound treatment were about 200nm in length. The work of Revol et al. highlights the formation of a chiral nematic ordred

phase when the stable colloidal microcrystal suspension exceeded a critical concentration. Since, we are interested in preparing cellulose nanoparticles that can be further used to for derivatization and polymerization; we have followed the procedure outlined by Revol et al. to achieve partial hydrolysis of cellulose fibers. The crystals obtained from this procedure not only measure on a nanometer scale (around 200nm) but also give a better access to the reducing end of the chain that can be subject to further reactivity.

2.3.2. Experimental

Reagents and Instruments

All air sensitive and moisture sensitive synthetic procedures were performed using a Schlenk line under an atmosphere of purified nitrogen. The glassware was dried by placing it in the oven overnight. Prior to sample analysis, solvents were removed with a rotary evaporator and under Schlenk line vacuum (approximately 60 mTorr). Fischer Scientific FS30 Ultrasonic instrument was used for dispersion of cellulose nanoparticles. Dialysis as conducted with Spectra/Por® CE, cellulose ester, membrane (MWCO:500) from SPECTRUM®. Centrifugation was conducted on Fischer Scientific Model Marathon 3200R, which is manufactured by International Equipment Company.

Unless otherwise noted all reagents used were obtained from commercial suppliers and were used without further purification. Whatman No.1 filter paper was used as a source of cellulose fibers. Unless otherwise noted, all other solvents were reagent grade and used without further purification.

Cellulose Hydrolysis

In a procedure adapted from Revol et al.[45], Whatman No. 1 filter paper (98% cotton fiber) was ground to smaller than 20 mesh powder in a Wiley mill. For every 1g of powdered filter paper, 9ml of 64% sulfuric acid was used. Thus 10 g of powdered filter paper and 90 ml sulfuric acid were added to a 250 ml round bottom flask equipped with mechanical stirrer, thermometer and gas inlet (N_2). After stirring the reaction mixture for 60 minutes at 45°C under nitrogen atmosphere, the heterogeneous mixture was washed and separated with repeated steps of centrifugation and re-suspension in de-ionized water. The acid was further removed from the mixture by dialysis with de-ionized water for two days. The crystallites were then dispersed by ultrasound treatment, carried out in an ice bath, in 20-minute segments with intermediate cooling intervals. Dry cellulose crystals were obtained by removing water from the crystalline particle suspension in a rotary evaporator under a schlenk line vacuum.

2.4 Conclusion

The last decade has seen a renewed interest in raw materials that can be easily obtained from renewable sources. Due to their natural availability, easy access, low cost, biocompatibility, biodegradability, and non toxicity, cellulose crystals can be used to substitute synthetic polymers in the development of new and improved materials. The shape and size of crystallites from natural cellulose are usually dependant on the source of cellulose.[48] Similar experimental conditions produce microcrystallites that are usually different in shape and size, which is normally attributed to the source of cellulose fibers such as cotton, wood, ramie, and

Pulp.[49] The properties of micro crystals that are obtained from natural fibers such as cotton depend on the hydrolysis conditions. Thus cellulose nanoparticles have been prepared in a procedure adapted from Revol et al. with relatively mild hydrolysis of filter paper powder. By controlling the acid strength, reaction time, and temperature, rod-like cellulose crystals were separated from the low order amorphous regions in a heterogeneous acid diffusion process. Cellulose crystalline particles find many applications on an industrial level within several fields.[44] These rod-like nanoparticles, with reducing end on one side and non reducing end on the other, continue to offer reactivity towards forming modified and derivatized products.

2.5 References

1. Havancsak, L. *Mat. Sci. Forum* **2003**, *414*, 85.
2. Babcock, W.; Lane, R.; Craig, B. *Amptiac* **2002**, *6*, 31.
3. Gangopadhyay, R.; De, A. *Chem. Mater*. **2000**, *12*, 608.
4. Misra, R. D. K. *Mater. Sci. Tech*. **2006**, *22*, 741.
5. Mark, H,; Meyer, K. H. *Phys. Chem*. **1929**, *B2*, 115.
6. Mark, H,; Meyer, K. H. *Chem. Ber*. **1928**, *B61*, 593.
7. Misch, L.; Meyer, K. H. *Helv. Chim. Acta.* **1937**, *20*, 232.
8. Hon, D. *Chemical Modification of Lignocellulosic Material*; Marcel Dekker: New York, 1996.
9. Kuga, S.; Brown, R. M. *J. Carbohydr. Res*. **1988**, *180*, 345.
10. Philipp, B.; Heinze, T.; Klemm, D.; Wagenknecht, W.; Heinze, U. *Comprehensive Cellulose Chemistry*; Wiley VCH: Weinheim, 1998.
11. O'Sullivan, A. C. *Cellulose* **1997**, *4*, 173.
12. Chanzy, H.; Nishiyama, Y.; Langan, P. *Am. Chem. Soc*. **1999**, *121*, 9940.
13. Blackwell, J.; Kolpak, F. J. *Macromolecules*, **1976**, *9*, 851.
14. Andress, K. R. Z. *Phys. Chem. Abt*. B **1929**, *4*, 190.
15. Tanner, S. F.; Belton, P.S.; Chanzy, H.; Vincendon, M.; Henrissat, B. *Carbohydrate Res*. **1987**, *160*, 1.
16. Southwick, J.; Hayashi, J.; Sarko, A. *Macromolecules.* **1976**, *9*, 857.
17. Watanabe, S.; Ohkita, J.; Hayashi, J.; Sufoka, A. *Polym. Lett*. **1975**, *13*, 23.
18. Chanzy, H.; Buleon, A. *J. Polym. Sci. Polym. Phys. Ed*. **1980**, *18*, 1209.

19. Langan, P.; Chanzy, H.; Nishiyama, Y. *Biomacromolecules* **2000**, *2*, 410.

20. Langan, P.; Chanzy, H.; Nishiyama, Y. *J. Am. Chem. Soc*. **2002**, *124*, 9074.

21. Atalla, R.H. *The Structures of Cellulose*; ACS Symposium Series 340; 1987.

22. O'Sullivan, A. C. *Cellulose*. **1997**, *4*, 173.

23. Zugenmaier, P. *Prog. Polym. Sci*. **2001**, *26*, 1341.

24. Watanabe, M.; Hongo, G. *Nature* **1958**, *181*, 326.

25. Sarko, A.; Woodcock, C. *Macromolecules* **1980**, *13*, 1183.

26. Atalla, R. H.; Vandelhart, D. L. *Science* **1984**, *223*, 283.

27. Atalla, R. H.; Vandelhart, D. L. *Macromolecules* **1984**, *17*, 1465.

28. Millane, R. P.; Finkenstadt, V. L. *Macromolecules* **1998**, *31*, 7776.

29. Mann, J.; Marrinan, J. *J. Polym. Sci*. **1956**, *21*, 301.

30. Chanzy, H.; Sugiyama, J.; Vuong, R. *Macromolecules* **1991**, 24, 4168.

31. Okano, T.; Yamamoto, H.; Horii, F.; Sugiyama, J. *Macromolecules* **1990**, *23*, 3196.

32. Imai, T.; Sugiyama, J. *Trends in Glycoscience and Glycotechnology* **1999**, *11*, 23.

33. Persson, J.; Chanzy, H.; Sugiyama, J. *Macromolecules* **1991**, *24*, 2461.

34. Kroon, J.; Kroon, B, L. M. *Glycoconj J*. **1997,** *14*, 677.

35. Brickmann, J.; Reiling, S. *Macromol. Theory Simil*. **1995**, *4*, 725.

36. Tekely, P.; Chanzy, H.; Excoffier, G.; Debzi, E. M.; Sugiyama, J. *Macromolecules* **1991**, *24*, 6816.

37. Odani, H.; Yamanoto, H.; Horii, F. *Macromolecules* **1989**, *22*, 4130.

38. Tanner, S. F.; Chanzy, H.; Belton, P. S.; Cartier, N. *Macromolecules* **1989**, *22*, 1615.

39. Fujiwara, M.; Kawai, M.; Yunoki, S.; Erata , T.; Shikano, T.; Kono, H. *J. Am. Chem. Soc*. **2002**, *124*, 7506.

40. Plunguian, M. *Cellulose Chemistry*; Chemical Publishing Co., Inc: New York, 1943.

41. Ranby, G. The colloidal properties of cellulose micelles. *Discussions Faraday Society* **1951**, *11*, 158.

42. Moore, W.; Millet, M. *Ind. Eng. J*. **1954**, *46*, 1493.

43. Pettersson, P. O.; Torget, R. W.; Xiang, Q.; Lee, Y. Y. *Appl. Biochem. Biotech*. **2003**, *105*, 505.

44. Mattews, S.; Flemming, K.; Gray, D. G. *Chem. Eur. J*. **2001**, *7*, 1831.

45. Kimura, T.; Dong, X. M.; Gray, D. G.; Revol, J. F. *Langmuir* **1996**, *12*, 2076.

46. Lima, M. M.; Borsali, R. *Macromol. Rapid. Commun*. **2004**, *25*, 771.

47. Dong, X. M.; Gray, D. G.; Revol, J. F. *Cellulose* **1998**, *5*, 19.

48. Batista, O. A. *Microcrystalline Polymer Science*; McGraw Hill: New York, 1975.

49. Koch, M. J.; Marchessault, R. H.; Morehead, F. F. *J. Colloid Sci*. **1961**, *16*, 327.

50. Chanzy, H.; Cavaille J.; Favier, V. *Macromolecules* **1995**, *28*, 6365.

Chapter 3

Block-Copolymers via Atom Transfer Radical Polymerization

3.1 Introduction

Well known to the field of science and technology, polymers play a vital role in modern society. The significance of this material is often unnoticed, yet polymers are fundamental to most aspects of daily life such as clothing, packaging, transportation, building, and communication. The desire to produce new materials with new applications has driven polymer industry to successfully manufacture materials like polystyrene, polyethylene, and polypropylene on a huge scale. An important feature of success is the ability to synthetically create and alter macromolecules to generate specific properties in polymers. Kevlar®, a relatively new material, is a great example for the use of rigid molecules in making high strength fibers.[1] A growing demand of highly specialized materials for use in electrical and optical applications among many provides polymers with prime potential in developing new technology.[2,3]

Polymers made by linking only one type of monomer are known as homopolymers, but two different kinds of monomers link together to form a copolymer chain. Block-Copolymer, a special type of copolymer, is made up of blocks of different polymerized monomers (Figure 3.1). Block-copolymers contain long sequence of all type A monomers grouped together with another long sequence of all type B monomers. A block copolymer can be thought of as two homopolymers joined together at the ends.

A-A-A-A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B-B-B-B-B

Figure 3.1. Schematic representation of block copolymer.

Block copolymers are of great commercial importance due to their synthetic properties and applications. Poly(styrene-butadiene-styrene) block copolymer, or SBS, is a hard rubber used for things like the soles of shoes, tire treads, and other places where durability is important. Polystyrene is a tough hard plastic, and this gives SBS its durability. Polybutadiene is rubbery, and this gives SBS its rubber-like properties. In addition, the polystyrene chains tend to clump together.

Cellulose, the single most abundant organic molecule in the biosphere, is a long chain natural polymer polysaccharide carbohydrate. The importance of cellulose, as an essential organic ingredient in textiles, and in the manufacture of rayon, paper, cellophane, explosives, lacquers, and in plastics is very well known to everyone. It forms crystals where intramolecular and intermolecular hydrogen bonds hold the network flat. The tendency to form crystals utilizing extensive intra- and intermolecular hydrogen bonding makes it completely insoluble in normal aqueous solutions. Due to many hydroxyl groups, cellulose is very hydrophilic in nature giving it an overall structure of aggregated particles with extensive pores capable of holding relatively large amounts of water by capillarity. The rigidity and insolubility of cellulose limits its abilities and properties towards possible applications in many systems. This work thus focuses on creating a block copolymer that is amphipathic, containing a cellulose hydrophilic head and polystyrene hydrophobic tail. The polystyrene chain attached to the reducing end of cellulose acts as the hydrophobic block, which enhances the physical properties of cellulose-*block*-polystyrene copolymer. Utilizing Atom Transfer Polymerization (ATRP) as chemical modification of cellulose results in improved adhesion, oil and water repellency, improved elasticity, antibacterial activity, and heat

resistance.[4-6] Block copolymers synthesized from cellulose act as surfactants and can play a vital role in many applications and products such as paints, adhesives, emulsifiers, detergents, laxatives, wetting, sanitizers, and detergents.

Block copolymers have demonstrated various characteristic properties in the recent past.[7] Many authors have reported formation of such block copolymers using cellulose derivatives. Cersa[8] produced benzyl cellulose-styrene copolymers by formation of polymeric free radicals on cellulose backbone. Kim et al.[9-10] reported the reaction of cellulose acetate with diisocyanate developing a biodegradable polymer. Cellulose containing block copolymers were produced by acidolytic cleavage of a monofunctional cellulose derivative.[11-14] Synthesis of polyurethane block copolymers from cellulose triacetate was reported by Eklund et al.[15] Block copolymers containing cellulose propionate were prepared by Glasser et al.[16-17] Furthermore, Carlmark et al.[18] reported the modification of cellulose to create block copolymers by grafting techniques. In their work, they modified cellulose fibers by reacting the hydroxyl groups on the surface utilizing the grafting from process. To our knowledge, most of the work that has been reported till date relates to the use of commercially available cellulose derivatives to create block copolymers and utilizing grafting from process for co polymerization of cellulose fibers. This work reports the synthetic modification of cellulose fibers into a derivatized initiator for Atom Transfer Radical Polymerization (ATRP) of styrene monomer generating cellulose-*block*-polystyrene copolymer. The combination of such a natural biopolymer with a synthetic polymer functions as micelles when dissolved in selective solvent.

3.2 Model Compounds

3.2.1. Cellobiose Molecule as Model Study

In the view of its functionality and applicability, this work focuses on synthesizing cellulose block copolymers thereby enhancing physical and chemical properties to create amphiphilic synthetic macromolecules via Atom Transfer Radical Polymerization (ATRP). This technique is used to ensure control of molecular weight, block size, mono dispersity and is relatively tolerant to many functional groups. Being a relatively inexpensive technique, ATRP allows the use of various monomers to create block copolymers. Block copolymers from these cellulose nano crystals behave like a rod coil system where hydrophobic blocks like polystyrene enhance cellulose adhesion to many natural fibers and synthetic polymers. In cellulose micro fibrils, hydrogen bonding & rigidity makes it insoluble in normal solvent solutions and thereby reducing the derivatizing capability of the reducing end.

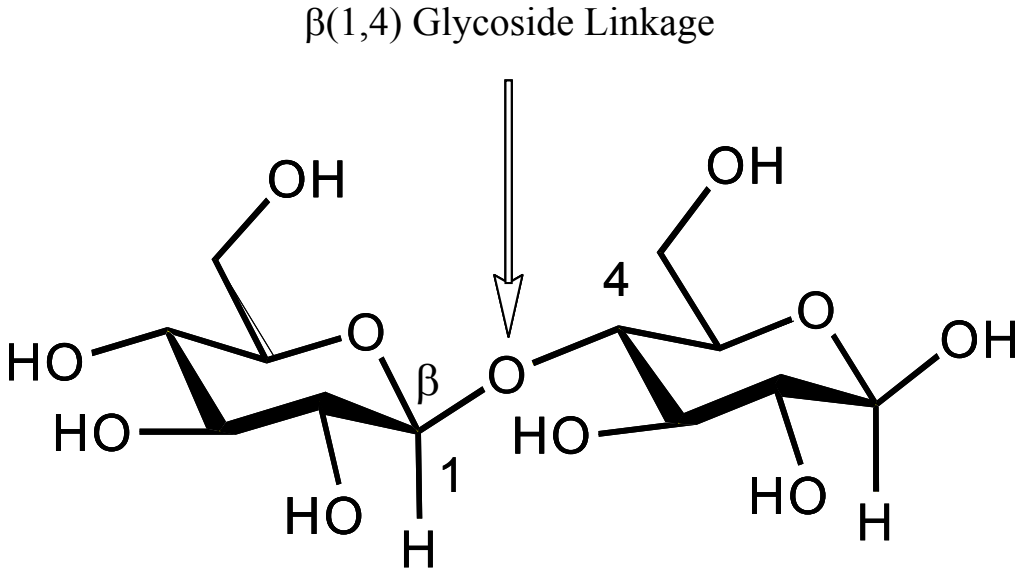


Figure 3.2. Cellobiose Molecule.

Thus cellobiose, a basic repeat unit of cellulose molecule, is used to create derivative model compounds to better understand the reactivity of reducing end aldehyde group.

Cellobiose is composed of two glucose units linked together by a glycosidic bond between C-1 of one glucose and C-4 of another glucose molecule. The stereochemistry at the anomeric carbon of the glycosidic linkage is β and the glycosidic linkage is known as β(1,4).

Cellobiose can be viewed as a repeating collection to form the cellulose chain. Here we investigate a basic synthetic strategy to create cellobiose end-capped polystyrene by well-controlled functionalization at the reducing end of cellobiose molecule. This model was then used in the polymerization of monomers to create synthetic copolymer blocks with cellulose nano particles.

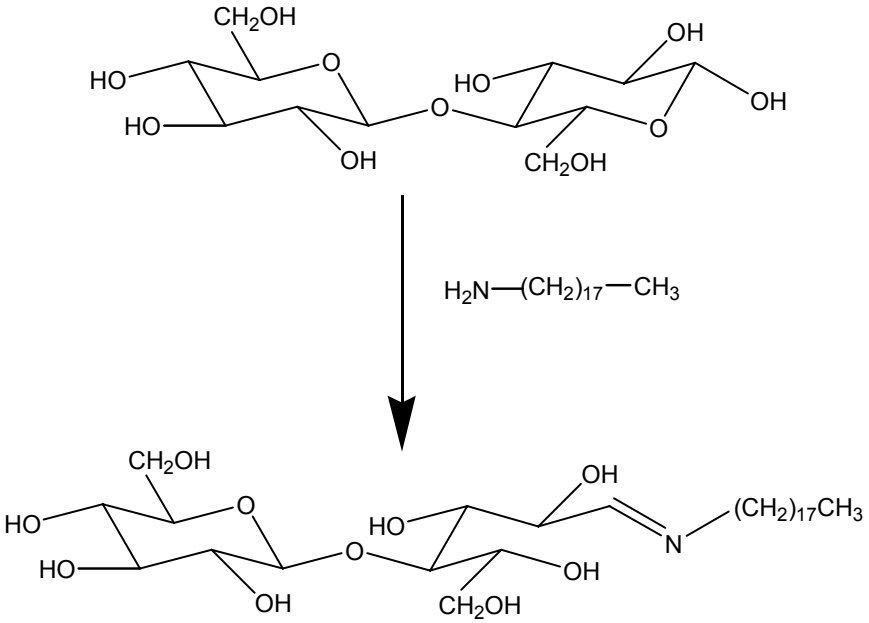
3.2.2. Derivatization of Cellobiose

Cellobiose molecule has only one hemiacetal at the reducing end and one secondary hydroxyl group at the C-4 position of the non-reducing end. This hemiacetal group can be reacted to create derivative compounds, which act as functionalized initiators in the initiation of styrene polymerization by ATRP.

In order to create functionalized initiator, it was important to select a functional group that would connect blocks A with B. Given the limitations of available functionalized initiators that are compatible for ATRP, primary amine group was selected to react with the terminal aldehyde in cellobiose forming a schiff base which facilitated in the formation of a functionalized initiator.

3.2.2.1. Reaction with octadecylamine

As a starting step, it was necessary to verify the reactivity of the reducing end aldehyde group with a primary amine reagent forming an imine functional group. Thus cellobiose was tested for reaction with octadecylamine reagent in a synthetic process as shown in Scheme 3.1. In a reaction span of 3 hours, the terminal aldehyde group reacts with the primary amine group forming the desired imine derivatized product when cellobiose is treated with octadecylamine in chloroform. The formed product was then subject to extensive fractionation to achieve product purity.



Scheme 3.1. Derivatization of cellobiose with octadecylamine.

As can be seen from the FT-IR spectra of the product, Figure 3.3, cellobiose was successfully derivatized with the formation of a schiff base. On comparing the spectrums of unreacted cellobiose with reaction product, the product shows the presence of characteristic

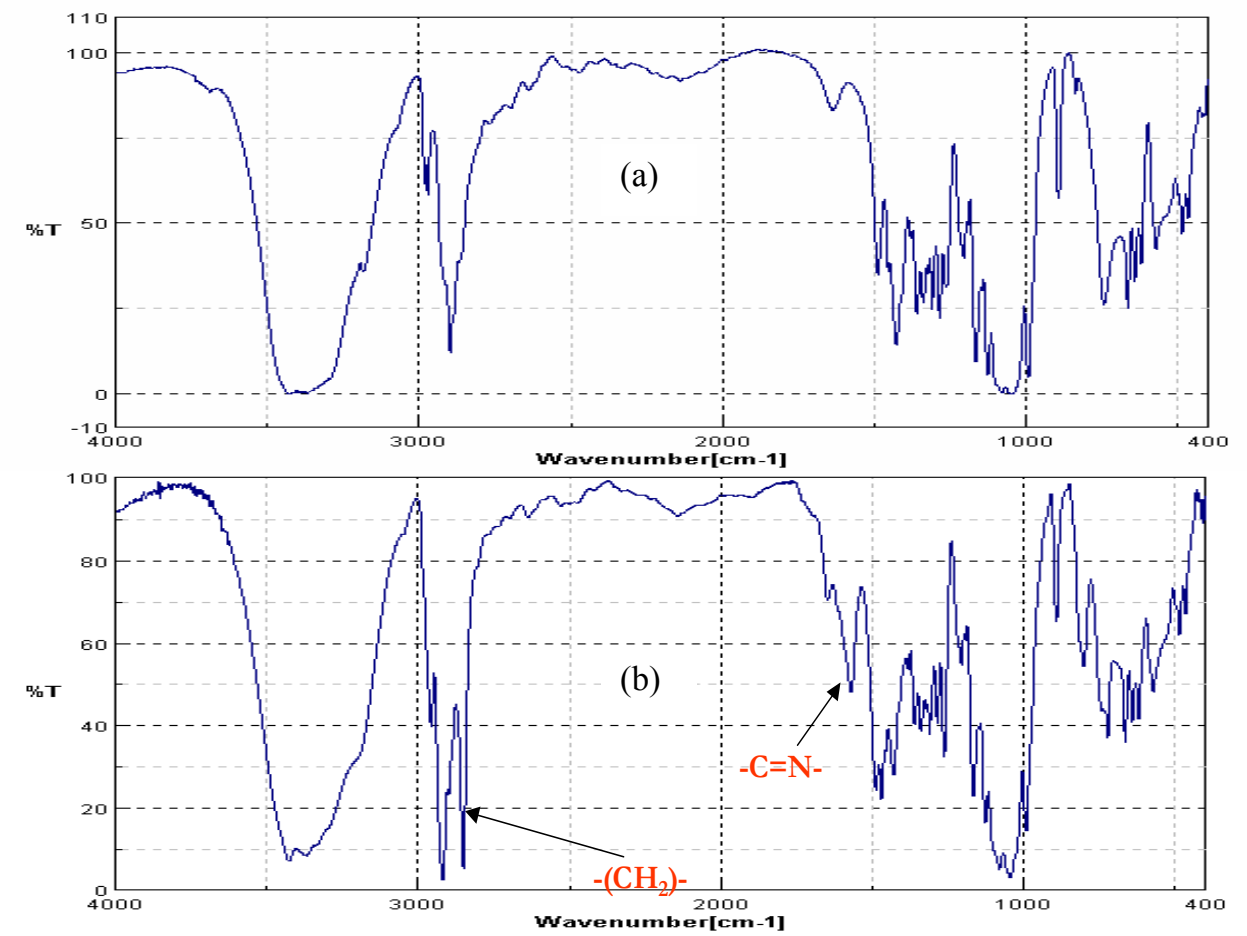


Figure 3.3. (a) FT-IR spectra of cellobiose (b) FT-IR spectrum of cellobiose derivatized with octadecylamine forming a schiffs base.

imine stretch at 1568.81 cm^{-1} and octadecyl hydrocarbon aliphatic $–CH_2$, $–CH_3$ stretch at 2917.77 and 2850.27 cm^{-1}, which arises from octadecylamine reagent.

The data from ^{1}H NMR and ^{13}C NMR spectroscopy further support the result and formation of a product that was successfully derivatized from the reducing end of cellobiose. In figure 3.4, the ^{1}H spectrum of the reaction product shows chemical shifts for cellobiose protons and

additional shifts at δ = 1.234 and 0.825 corresponding to methyl and methylene protons of octadecylamine.

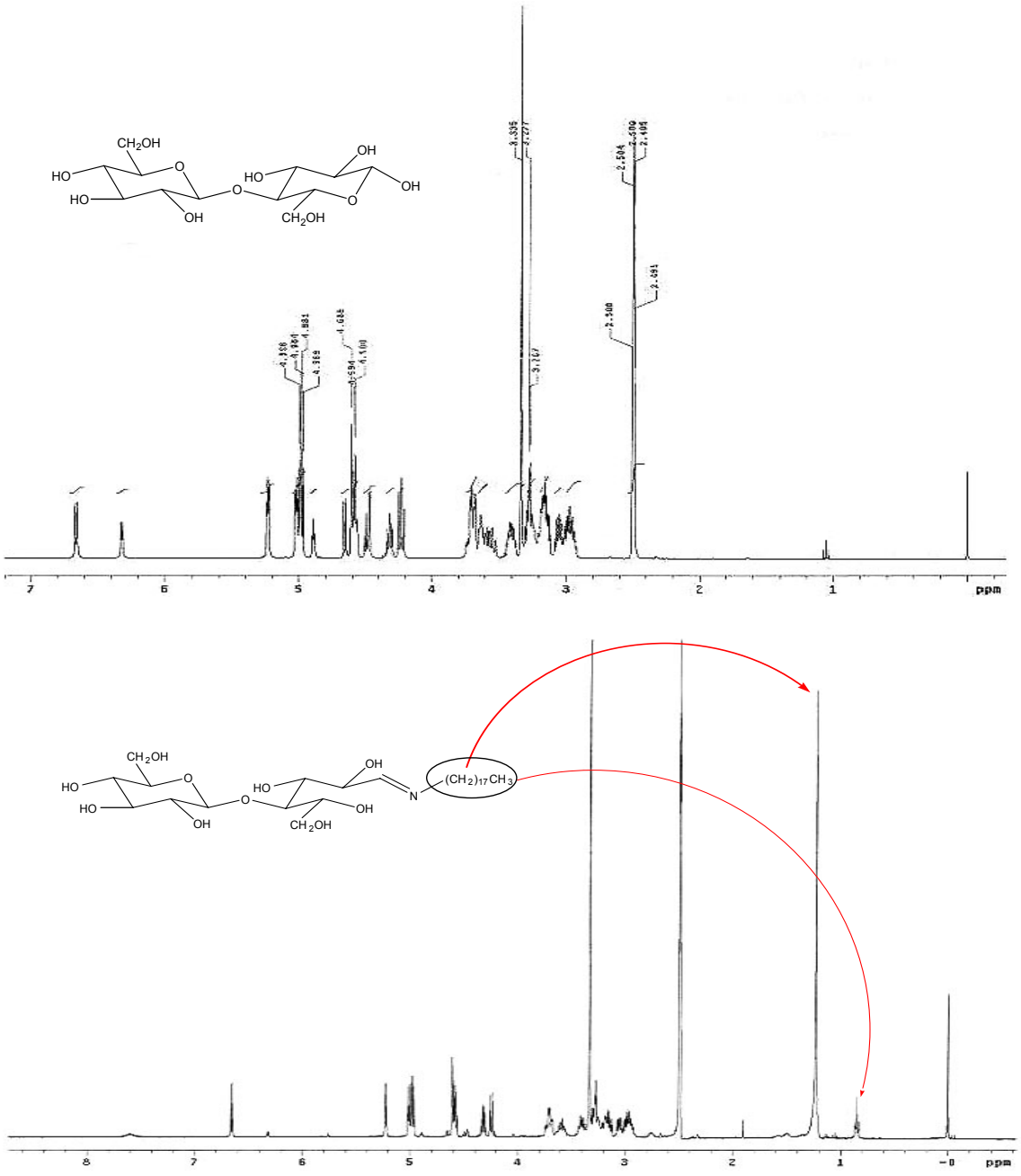
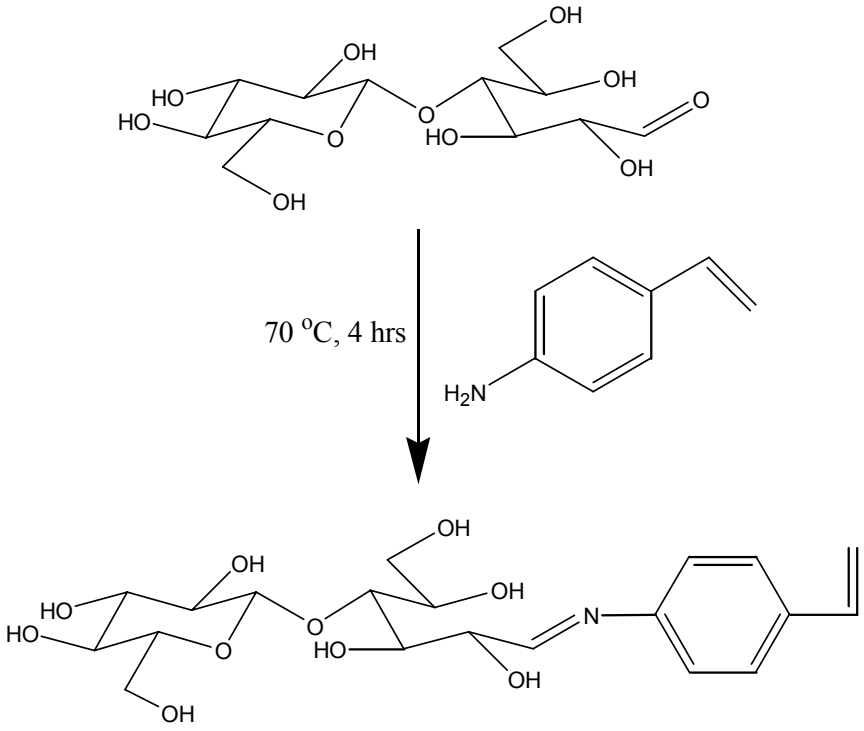


Figure 3.4. (a) ^{1}H NMR spectrum of cellobiose in d-DMSO solvent. (b) ^{1}H NMR spectrum of cellobiose derivatized with octadecylamine in d-DMSO solvent.

3.2.2.2. Reaction with 4-vinylaniline

Working towards derivatizing cellobiose into a compatible initiator for ATRP, it is essential that the structure of initiator be homologous to the corresponding polymer end group. Since styrene was the monomer of choice in the polymerization reaction, 4-vinylaniline was selected as the derivatizing reagent. Kipper et al.[19] have shown that cellobiose can be derivatized in a reaction by using anthralic acid as their primary amine reagent. Thus CB-d-4AS (cellobiose derivatized with 4-vinylaniline) was prepared using a modification of previously published procedures.[20-21] In a typical reaction (Scheme 3.2), 4-vinylaniline was added to the reaction flask containing the solvent. After a nitrogen purge, cellobiose was added to the mixture which was heated to about 70°C for about 4 hours. Following the reaction, the formed product was subjected to fractionation to purify the product.



Scheme 3.2. Derivatization of cellobiose with 4-vinylaniline.

Due to solubility reasons, various solvents were tested as reaction solvents. Table 3.1 summarizes the results and solvent use for derivatization of CB. DMSO, a good solvent for cellobiose and 4-AS was first used to test the reactivity of both compounds. While it was useful in derivatizing cellobiose, the reaction yield was very low and the product was very hard to isolate. Toluene did not prove to be a facilitative reaction solvent, thus reaction run S55 did not yield the desired product. Cellobiose when reacted with 4-vinylaniline in presence of chloroform gave the desired imine derivatized product but with very low yield as well. Among the tested solvents dimethylformamide gave better reaction yields. In reactions S51 and S63 a 1:2 mole ratio of CB to 4AS gave over 50% yields in separate trials.

Table 3.1. Solvents tested for derivatizing CB with 4-AS.

Sample (S)	Solvent	[CB] : [4AS]	Reaction Temperature	Yield (%)*
39	DMSO	1:4	70°C	8%
41	$CHCl_3$	1:4	50°C	21%
51	DMF	1:2	80°C	71%
55	Toluene	1:2	70°C	None
63	DMF	1:2	70°C	60%

* Yields obtained after fractionation.

For sample 63, a mole ratio of 1:2 between cellobiose and 4-vinylaniline was utilized towards a Schiff's base formation and the reaction yielded about 60% product which was then subjected to FT-IR spectroscopy. The spectrum of the product showed characteristic

imine stretch at 1610.27cm^{-1}, as can be seen in Figure 3.5, indicating the formation of CB-d-4AS. In the ^{1}H NMR spectrum of the formed product (S63), the presence of phenyl protons at δ = 7.10, 7.07, 6.99, 6.95 and vinyl protons at δ = 5.43, 5.23, 4.96 of 4-vinylaniline along with cellobiose protons can be clearly identified (Figure 3.6).

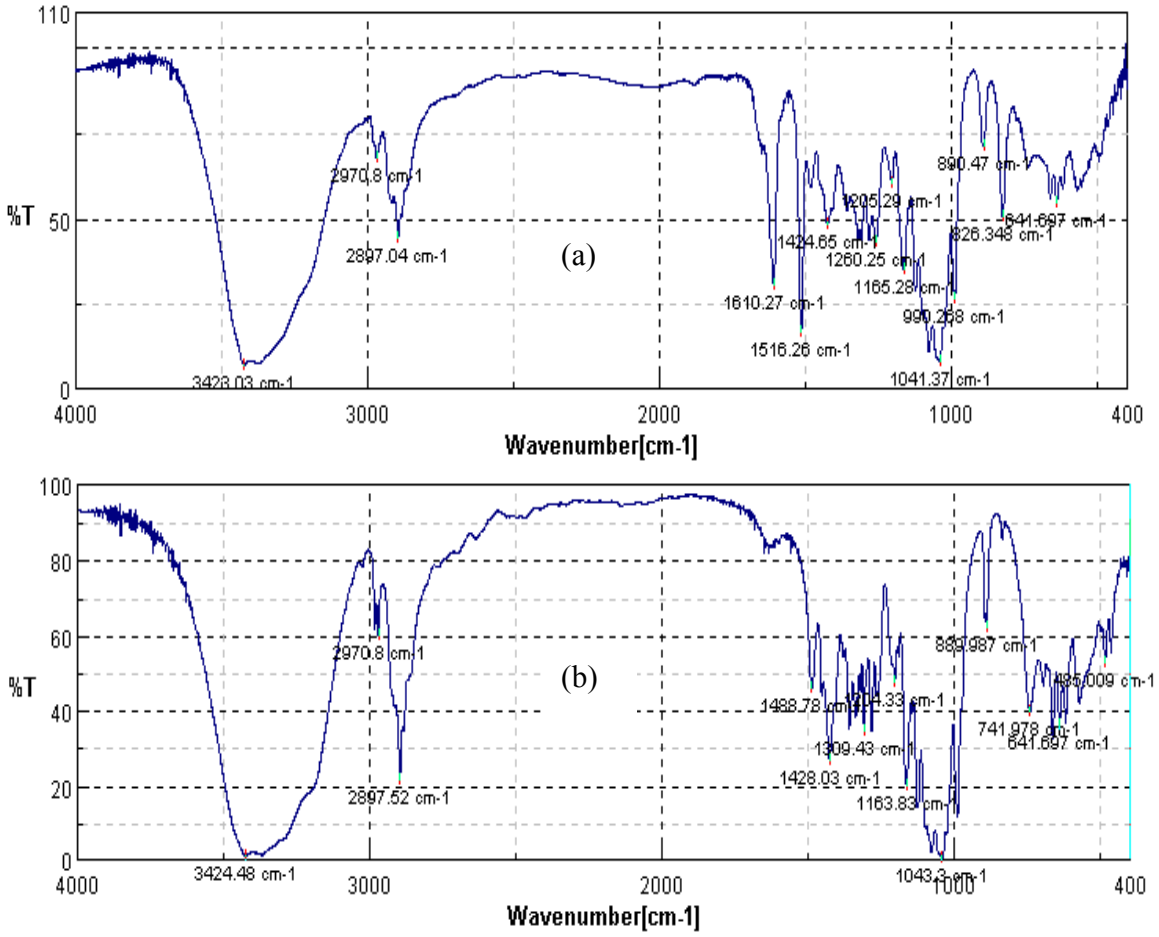


Figure 3.5. (a) FT-IR spectrum of cellobiose derivatized with 4-vinylaniline (b) FT-IR spectrum of cellobiose.

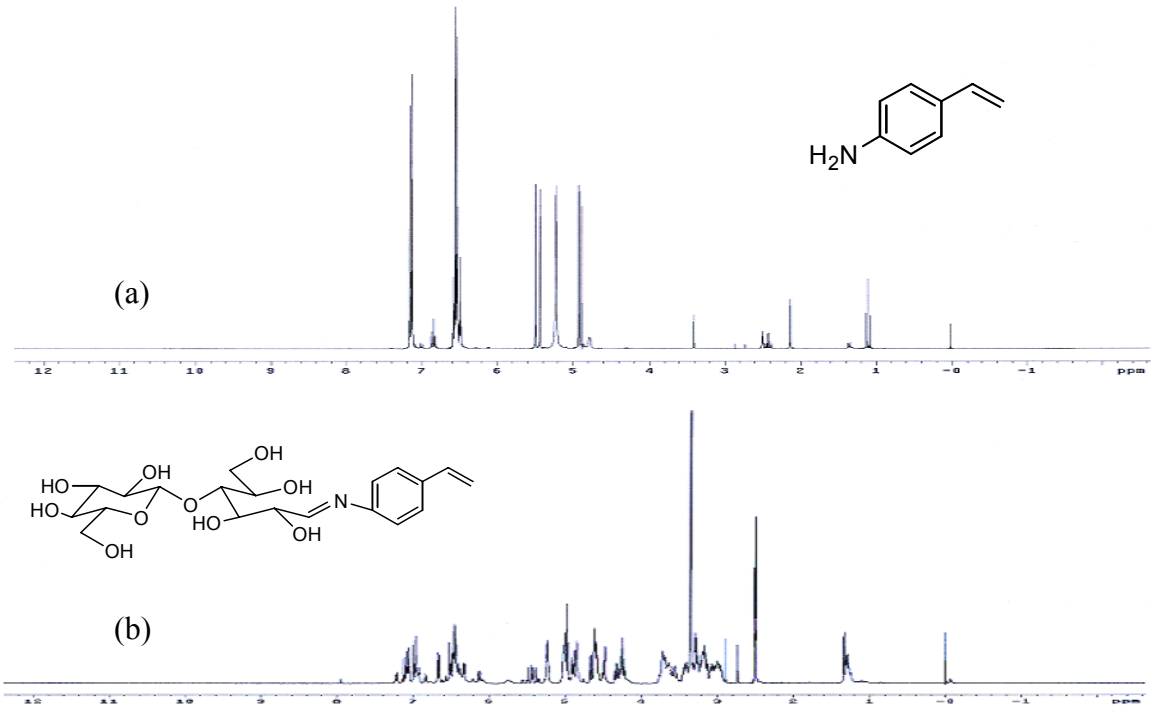
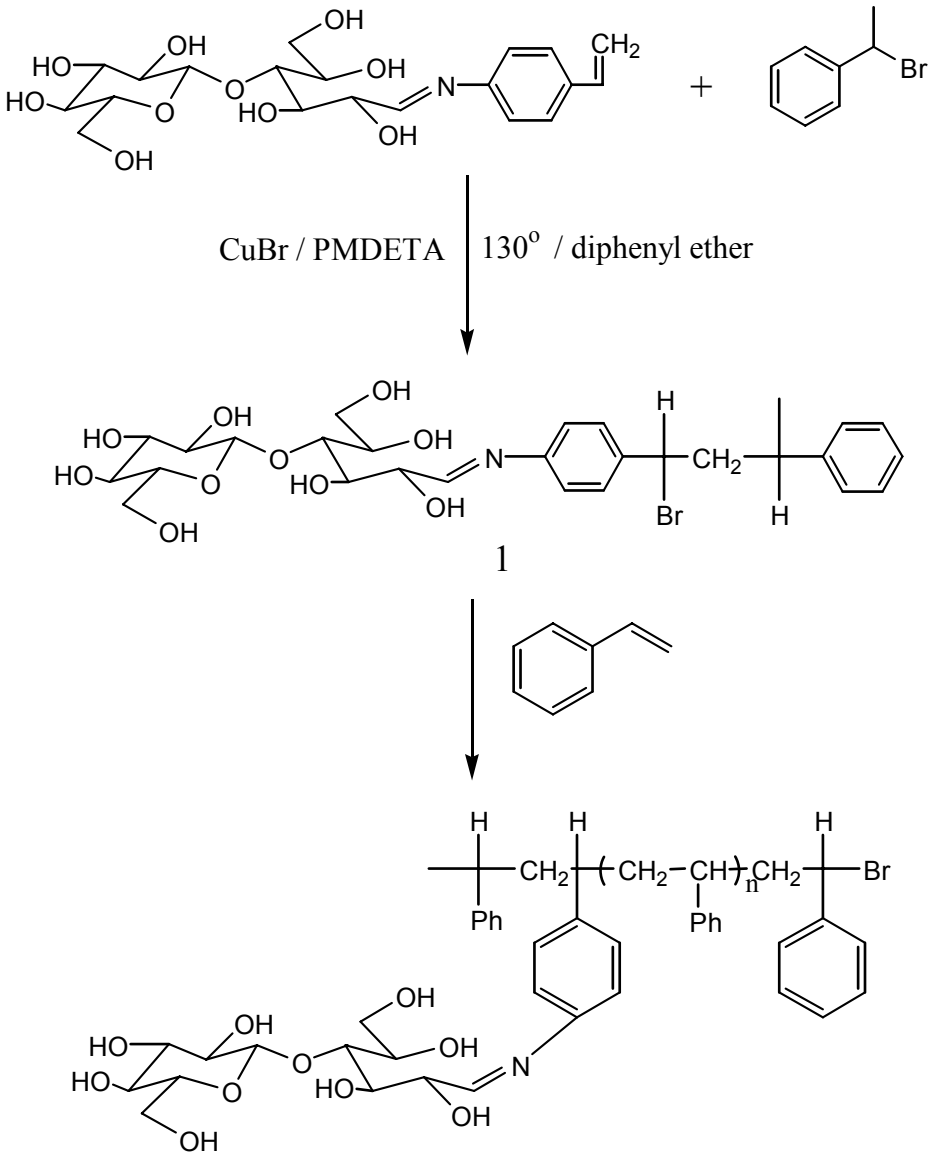


Figure 3.6. (a) ^{1}H NMR spectrum of 4-vinylaniline in d-DMSO. (b) ^{1}H NMR spectrum of sample 63 (CB-d-4AS) in d-DMSO.

3.2.3. ATRP of styrene from derivatized cellobiose

Cellobiose derivatized with 4-vinylaniline was used in the polymerization of styrene to create cellobiose end-capped polystyrene. At a temperature of 130°C, polymerization reaction was performed in the presence of Cu(I)Br and pentamethyldiethylenetriamine (PMDETA). Summers et al. have shown that styrene can be polymerized by ATRP at 130°C when using PMDETA as a ligand in conjunction with Cu(I) as a transition metal.[22] The polymerization process afforded amine functionalized polystyrene with predictable molecular weights and relatively narrow molecular weight distribution. The same reaction conditions were therefore

adapted in polymerization of styrene to create desired end-capped polymers. The general synthetic route for the preparation of cellobiose end-capped polystyrene by ATRP, as illustrated in Scheme 3.3, proceeds via formation of adduct 1 as a functionalized initiator.



Scheme 3.3. Synthetic route for polymerization of styrene creating cellobiose end-capped polystyrene.

In a typical run of polymerization, end-capped polymers were prepared under dry nitrogen in a dried Schlenk flask equipped with a magnetic stir bar. The flask was charged with the required amounts of Cu(I)Br, PMDETA, CB-d-4AS, 1-(bromoethyl)benzene, diphenyl ether and sealed with a rubber septum. The heterogeneous reaction mixture was degassed by freeze pump-thaw cycles and heated to 130°C for an hour. Distilled styrene was added to the resultant green reaction mixture and the reaction was heated to 130°C for 12 hours. After the specified time, the reaction was stopped and mixture was diluted with addition of tetrahydrofuran (THF). The obtained polymer was purified and precipitated in methanol followed by concentration in vacuum. Prior to addition of styrene, adduct 1 was quantitatively prepared by reacting stoichiometric amounts of CB-d-4AS with 1-(bromoethyl)benzene in presence of Cu(I)Br and PMDETA as catalyst system in diphenyl ether. The quantitative formation of adduct 1 was determined by TLC analysis by monitoring the disappearance of CB-d-4AS with $R_f = 0.31$ (in toluene), and concomitant appearance of adduct 1 with $R_f = 0.82$ (in toluene).

Table 3.2. SEC analysis of cellobiose end-capped polymers formed by ATRP.

Run(R)	[M]:[I]	Mn (theo)	Mn (exp)[a]	PDI	Yield
47	29:1	3660	-	-	18%
59	29:1	3660	55231	1.04	20%
79	35:1	4290	12908	2.20	32%

[a]Molecular Weight measured by SEC in THF using standard calibration.

As can be seen in table 3.2, styrene was successfully polymerized from adduct 1. The polymerization yielded end-capped polymers with relatively narrow polydispersities. The end-capped polymers were subject to fractionation to purify the product prior to analysis. The polymers were analyzed with SEC, FT-IR, ^{1}H NMR, DSC, and TGA. Linear polystyrene standards were used for calibration in order to determine molecular weights and polydispersities by SEC analysis. In this study diphenyl ether was used as the polymerization solvent owing to monomer solubility.

In sample run R47, a monomer to initiator ratio of 29:1 was used in polymerization of styrene. FT-IR spectrum (Figure 3.7) of the product (R47) has absorption bands at 3408.57

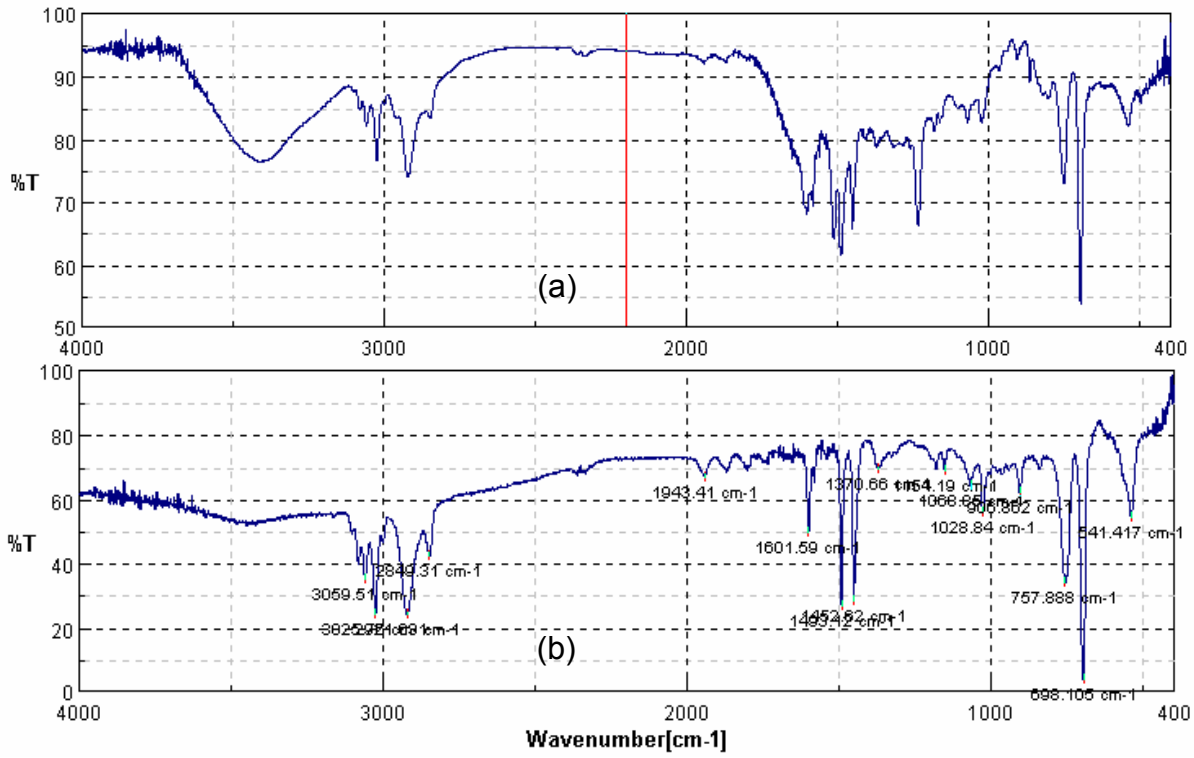


Figure 3.7. (a) FT-IR spectrum of cellobiose end-capped polystyrene (R47). (b) FT-IR spectrum of polystyrene standard.

cm^{-1} characteristic of the –OH stretching vibration arising from cellobiose, at 3024.8 cm^{-1} and 2922.59 cm^{-1} characteristic of $–CH_2$ and –CH polystyrene backbone stretch respectively. The ^1H NMR spectrum of R47 showed characteristic polystyrene chemical shifts but not clear representation for derivatized cellobiose peaks. ^1H NMR was measured in $CDCl_3$ which is good solvent for polystyrene and poor solvent for cellobiose. The amphiphilic behavior of the block copolymer was clearly noticed when the solution in the NMR tube appeared to be a hazy milky dispersion. The results for FT-IR and ^1H NMR analysis clearly reflect the formation of cellobiose end-capped polystyrene polymer however a yield of 18% did not leave us enough sample to perform SEC, TGA and DSC analysis.

In order to obtain similar results as above, the ratio of monomer-to-initiator was maintained. Typical size exclusion chromatogram of sample run R59, where a ratio of 29:1 was used, gave number average molecular weight (M_n) of 55231 g mol^{-1} and polydispersity index (PDI) of 1.04 compared with a theoretical Mn value of 3660 g mol^{-1}. FT-IR analysis showed results analogous to run R47 with clear absorption bands for cellobiose and polystyrene. ^1H NMR spectrum also had characteristic polystyrene chemical shifts with the absence of derivatized cellobiose proton peaks. Differential scanning calorimetry (DSC) analysis of run R59 displayed a glass transition temperature (T_g) at 96.14°C which further supports the presence of polystyrene block connected to cellobiose segment. According to literature data the T_g of free polystyrene is around 100°C.

For run R79, a monomer-to-initiator ratio of 35:1 was used, targeting a number average molecular weight of 4290 g mol^{-1}. The formed end-capped polymer in this run when subjected to SEC analysis, showed a broad chromatogram with polydispersity index (PDI) of 2.2.

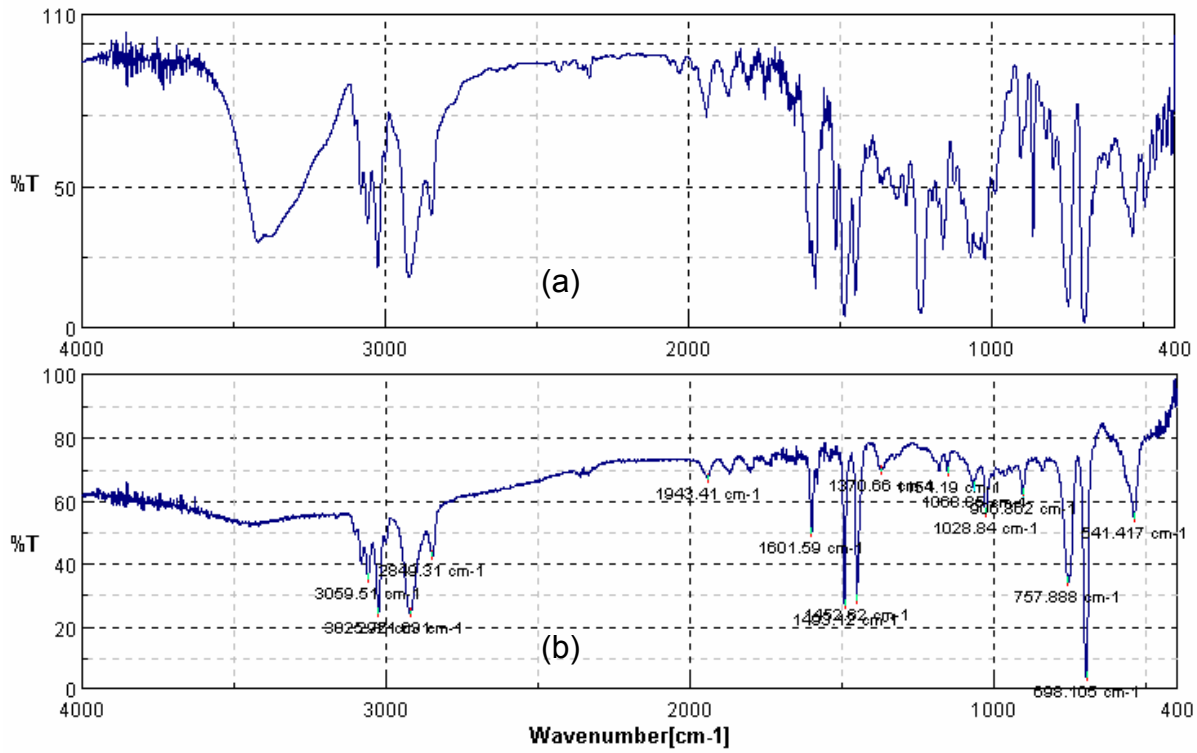


Figure 3.8. (a) FT-IR spectrum of cellobiose end-capped polystyrene (R79). (b) FT-IR spectrum of polystyrene standard.

The FT-IR analysis of R79 shows absorption bands at 3419.17 cm^{-1}, 3024.8 cm^{-1}, and 2922.11 cm^{-1} representing –OH, $–CH_2$, –CH stretching vibrations respectively for cellobiose segment and polystyrene block (Figure 3.8). Our results are analogous to the results obtained by Stadler et al.[23] where in they have demonstrated the synthesis of amylase-*block*-polystyrene copolymers by enzymatic polymerization of amylase.

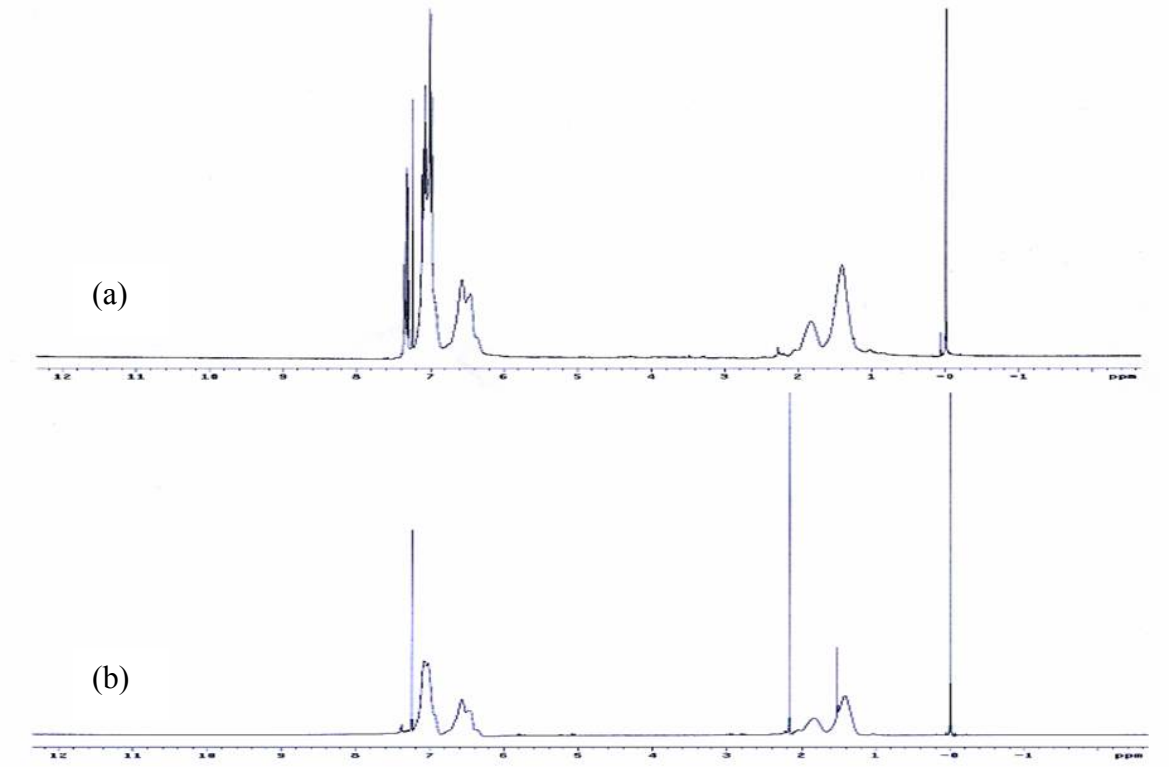


Figure 3.9. (a) ^{1}H NMR spectrum of cellobiose end-capped polystyrene (R79) in $CDCl_3$ solvent. (b) ^{1}H NMR spectrum of polystyrene standard in $CDCl_3$ solvent.

Figure 3.9 shows ^{1}H NMR spectra of CB end-capped PS in $CDCl_3$. As expected, the spectrum of run R79 was not different from the ones measured for R47 and R59. When $CDCl_3$ solvent was used, δ=1.4 and 1.9 appeared for methylene protons and δ=6.5 and 7.1 for the phenyl ring protons of PS block. However, the chemical shifts for cellobiose segment cannot be seen in the spectrum. The absence of peaks for CB protons indicated that aggregates had been formed. Although $CDCl_3$ is a good solvent for PS blocks, it is a poor solvent for CB segment. Thus, as a consequence, the cellobiose end-capped polymers tend to self assemble and associate forming aggregates with inner insoluble CB segments and outer soluble PS blocks.

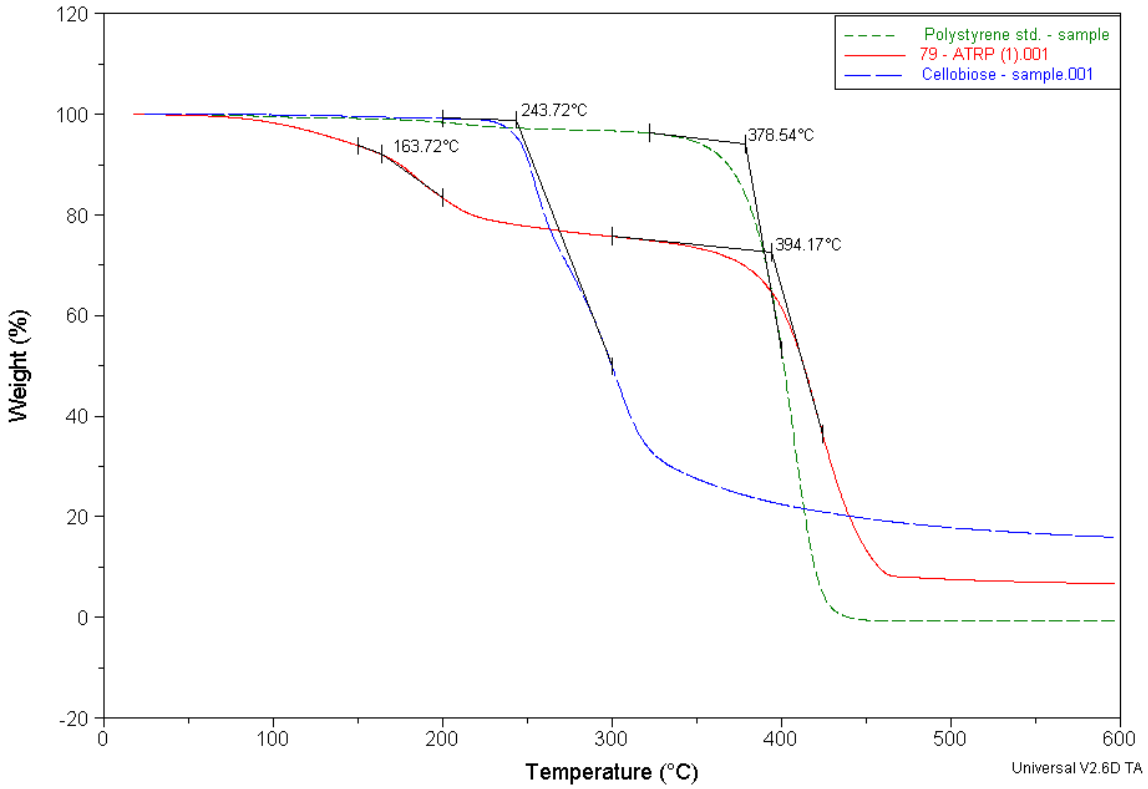


Figure 3.10. Results from TGA analysis of R79, cellobiose, and polystyrene standard.

Thermal analysis of R79 further supports the formation of CB end-capped PS polymer. The data obtained from Thermo gravimetric Analysis (TGA) is shown in Figure 3.10. TGA analysis was performed for linear polystyrene standard along with derivatized cellobiose. The thermal decomposition data of R79 shows two decomposition temperatures. A lower temperature of 163.72°C and higher temperature of 394.17°C correspond to component cellobiose at 243.72°C and polystyrene standard at 378.54°C respectively. DSC analysis of R79 displays a T_g of 93.52°C which further supports the corresponding data pertaining to formation of CB end-capped PS polymer.

3.3 Polymerization with Cellulose

3.3.1. Derivatization of cellulose nano-particles

Cellulose is a homopolymer of D-anhydroglucopyranose monomeric units connected through β(1-4) glycosidic linkages. It is apparent from Figure 3.11 that every other monomer unit is rotated by 180° about the long axis of cellulose chain compared to its two neighboring monomer units. Due to this fact, cellobiose is truly considered the repeat unit of cellulose polymer. After successfully investigating the synthetic strategy to create cellobiose end-capped polystyrene polymer by well controlled functionalization at the reducing end of cellobiose molecule, the model is then used in polymerization of styrene to synthetically create cellulose-*block*-polystyrene amphiphilic copolymers.

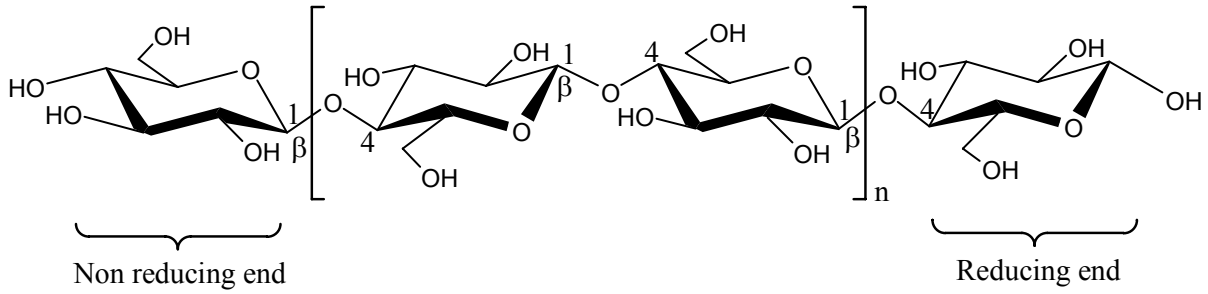


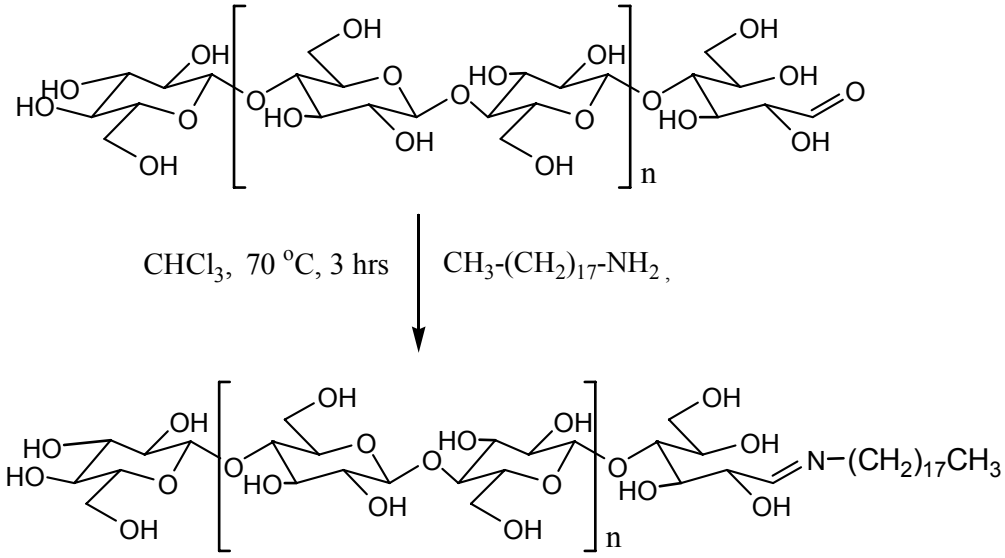
Figure 3.11. Cellulose molecule.

Similar to cellobiose, cellulose has only one hemiacetal at the reducing end and one secondary hydroxyl group at the C-4 position of the non-reducing end. This hemiacetal group can be reacted to create derivative compounds that act as functionalized initiators in the initiation of styrene polymerization by ATRP. However, derivatization reactions are more complicated compared to simpler compounds because such derivatizations usually involve heterogeneous reactions. The heterogeneous nature of reactions exists not only due to

insolubility of cellulose in reaction medium but also because cellulose is heterogeneous itself. It is also generalized that reagents have greater access to amorphous regions than highly crystalline regions. Given the limitations of available functionalized initiators that are compatible for ATRP, primary amine reagent was reacted with the terminal aldehyde in cellulose forming a schiff base which facilitated in the formation of a functionalized initiator.

3.3.1.1. Reaction with octadecylamine

Following the synthetic model for derivatization of cellobiose, cellulose nano-crystals were reacted with octadecylamine reagent as shown in Scheme 3.4. In a reaction span of 3 hours and reaction temperature of 70°C, the terminal aldehyde group in cellulose reacts with the primary amine group forming an imine-derivatized product when treated with octadecylamine reagent in chloroform. The derivatized product was then subject to extensive fractionation to achieve high product purity.



Scheme 3.4. Derivatization of cellulose nano-crystals with octadecylamine.

Figure 3.12 compares the FT-IR spectrum of hydrolyzed cellulose crystals and cellulose derivatized with octadecylamine reagent. The spectrum of the product appropriately has aliphatic $–CH_2$, $–CH_3$ vibrational stretch at 2916.81 cm^{-1} which is different from the hydrolyzed cellulose crystal spectra.

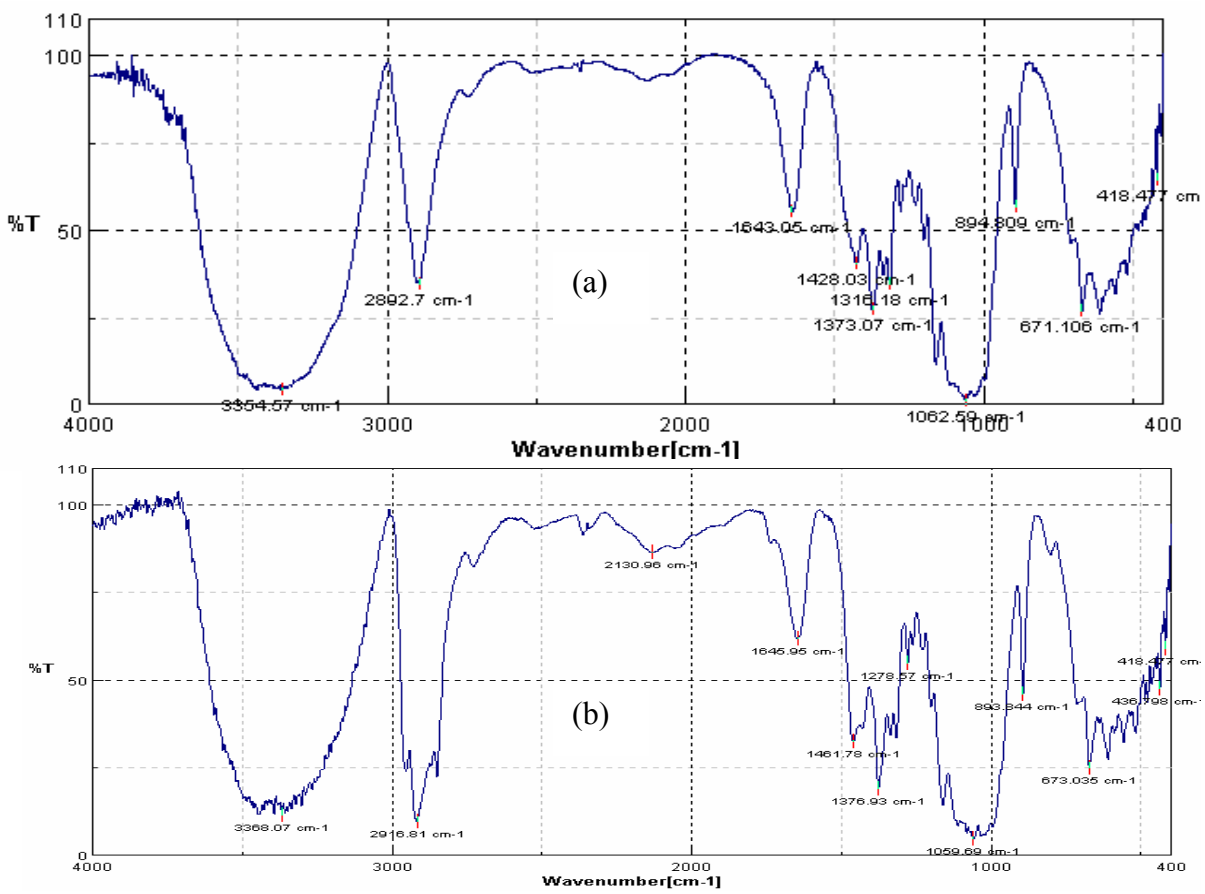
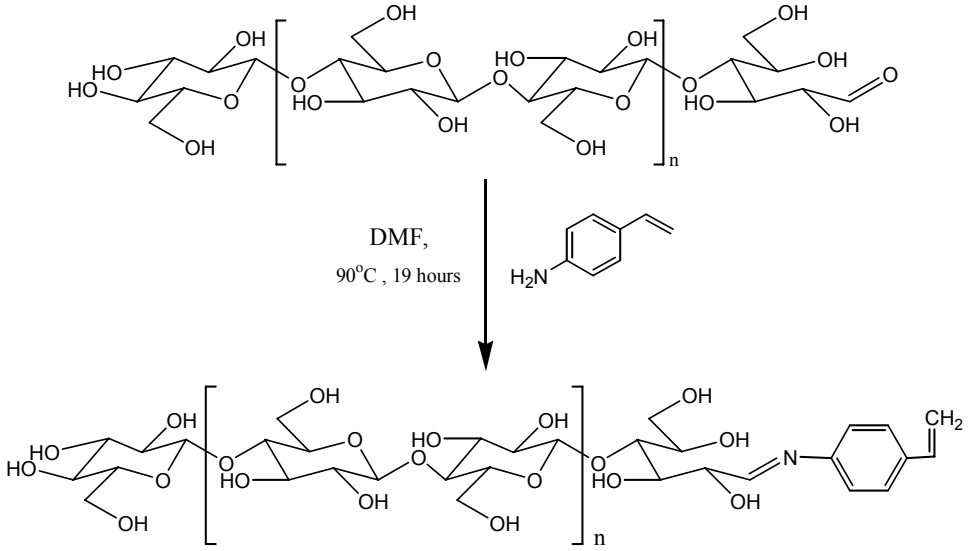


Figure 3.12. (a) FT-IR spectra of cellulose (b) FT-IR spectrum of cellulose derivatized with octadecylamine.

Due to the insolubility of cellulose nano-crystals in normal NMR solvents, ^{1}H and ^{13}C NMR measurements were not performed.

3.3.1.2. Reaction with 4-vinylaniline

Scheme 3.5 shows the synthetic pathway for derivatization of cellulose nano-crystals with 4-vinylaniline. In order to create a compatible derivatized initiator for ATRP, the structure of the initiator was kept homologous to the corresponding polymer end group by reacting 4-vinylaniline with cellulose. In our earlier work we saw successful derivatization of cellobiose with 4-vinylaniline that was then subject to ATRP of styrene. Cellulose, which has much the same reducing end chemical reactivity, was also attempted to react with 4-vinylaniline under similar reaction conditions. Cellulose derivatized with 4-vinylaniline (C-d-4AS) was prepared using a modified procedure for preparing CB-d-4AS. The formed product was fractionated to achieve product purity.



Scheme 3.5. Derivatization of cellulose nano-crystals with 4-vinylaniline.

Due to insolubility of cellulose in almost all organic solvents, the reaction medium for this procedure was based on the solubility of the primary amine reagent. Being soluble in

dimethylformamide (DMF), 0.2 M and 0.5 M of 4-vinylaniline was reacted with 10 mg/mL of cellulose to a temperature of 90°C.

Table 3.3. Reaction conditions and thermal analysis of C-d-4AS.

Sample (S)	Cellulose	4-AS	Decomposition Temperature (TGA)	Yield
73	10 mg/mL	0.2 M	311.63°C	63%
77	10 mg/mL	0.5 M	317.97°C	79%

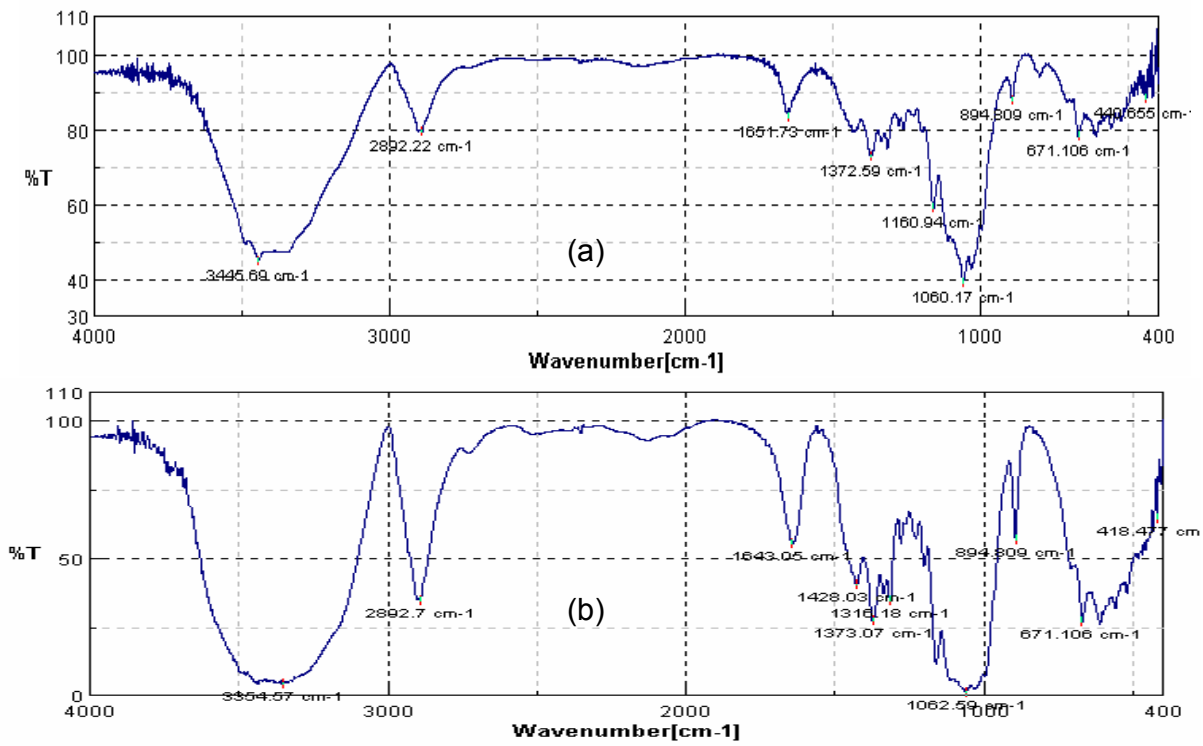


Figure 3.13. (a) FT-IR spectrum of C-d-4AS (cellulose derivatized with 4-vinylaniline). (b) FT-IR spectra of cellulose.

Table 3.3 summarizes the results of derivatization experiments when 0.2 M & 0.5 M of 4-AS was reacted with cellulose nano-crystals. The reaction yield increased from 63% obtained from S73 to 79% in S77 when the amount of 4-AS was increased.

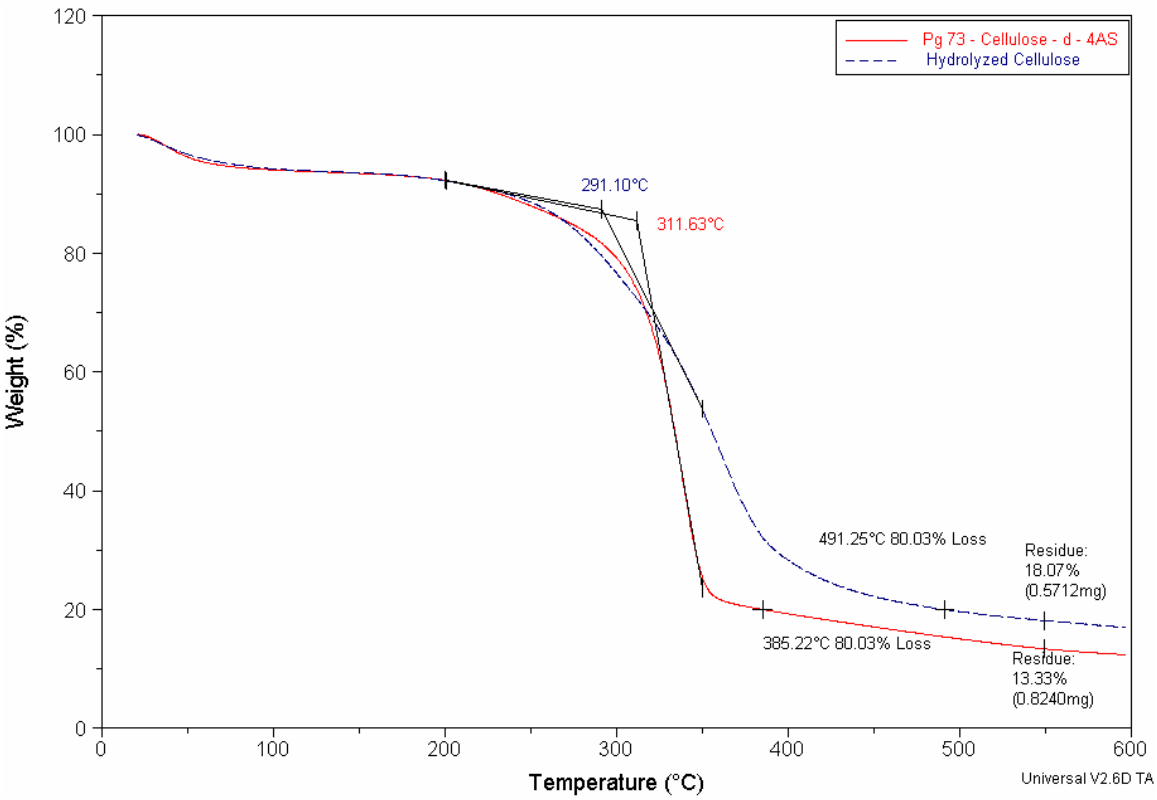


Figure 3.14. TGA thermogram of S73 and hydrolyzed cellulose crystals.

While the FT-IR spectrum of S73 did not show a notable difference between hydrolyzed cellulose crystals and derivatization product of cellulose crystals (Figure 3.13), thermogravimetric analysis did show activity in the decomposition temperatures which can be seen Figure 3.14. It is important to note that the reaction of reducing end group aldehyde with 4-vinylaniline brings about a small change in the overall mass of the natural polymer,

which can easily go undetected in normal characterization techniques. However, thermal analysis of S73 displays an increased decomposition temperature from 291.10°C (of hydrolyzed cellulose crystals) to 311.63°C. This clearly supports the formation of a derivatized product, which has an increased mass.

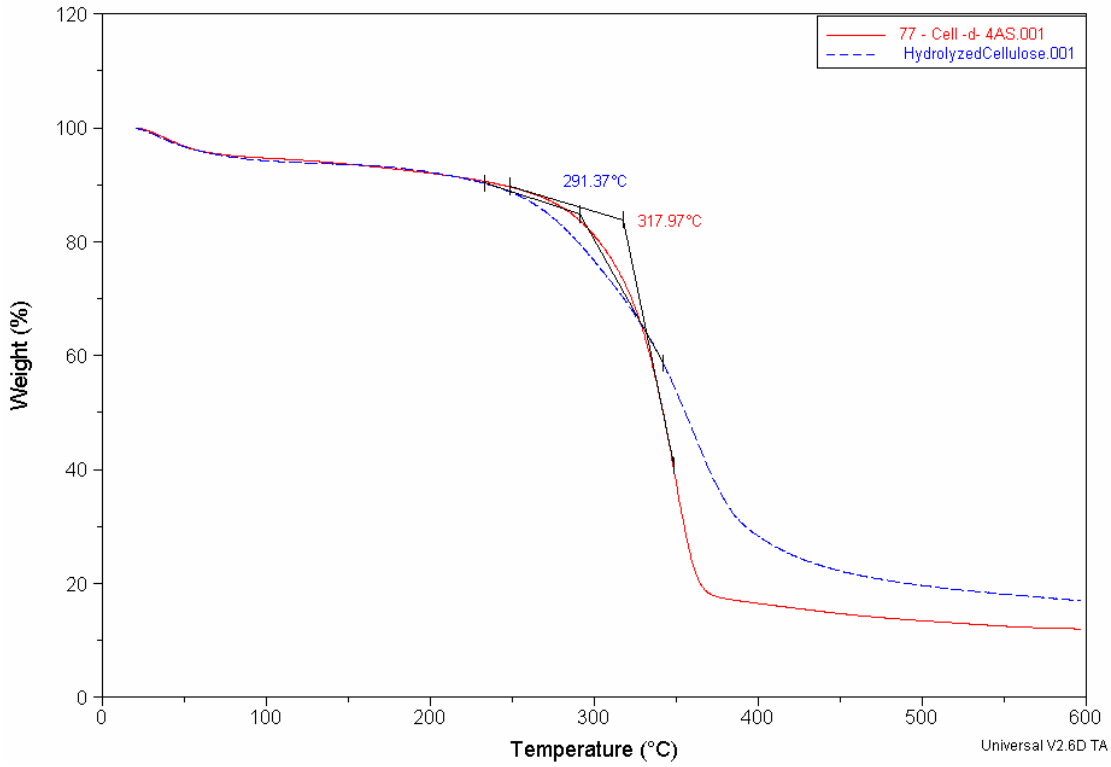
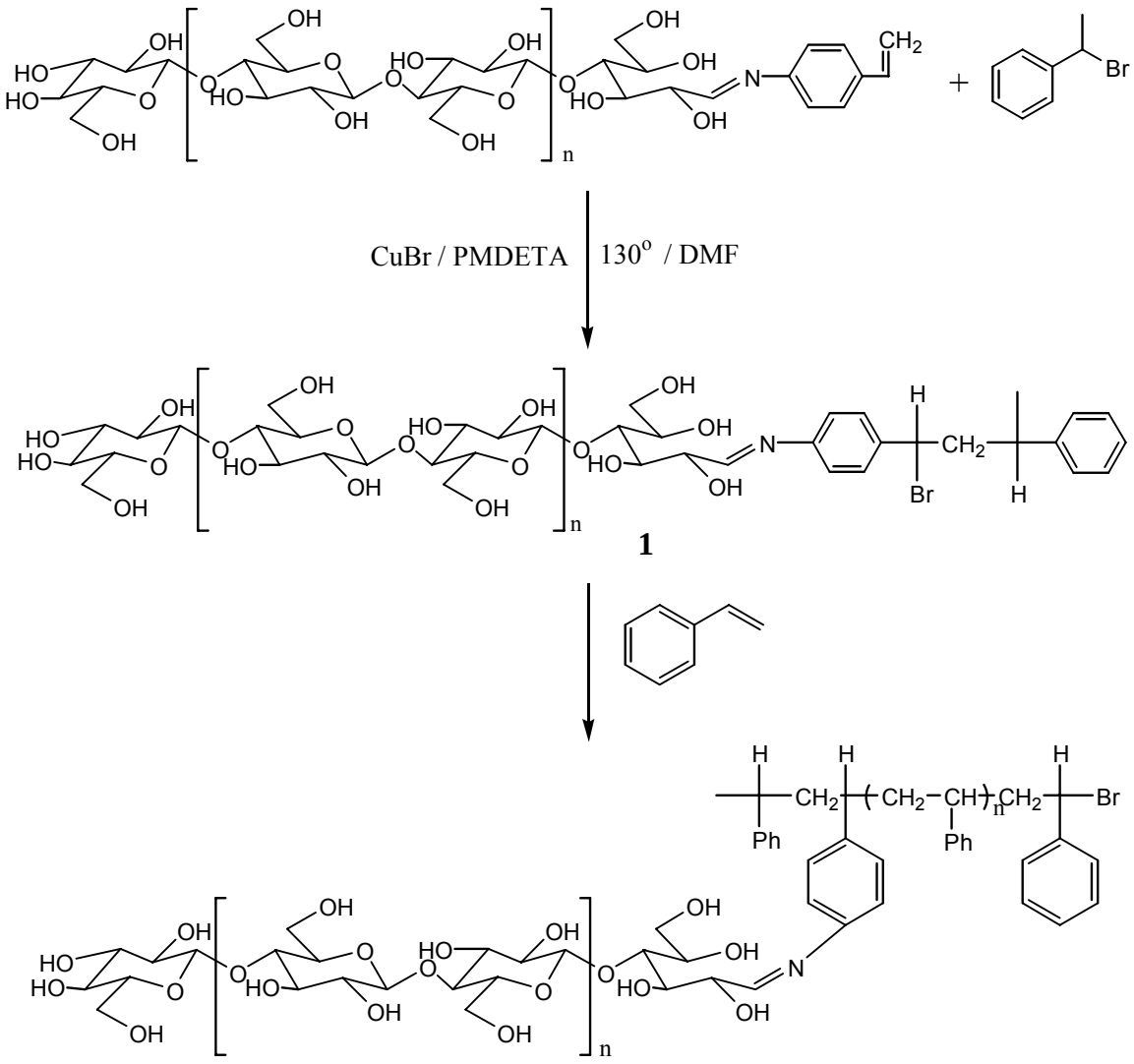


Figure 3.15. TGA thermogram of S77 and hydrolyzed cellulose crystals.

The characterization of S77 gave similar results compared to S73 where the FT-IR spectrum could not detect any changes in the product spectrum and ^{1}H NMR measurements were not possible due to insolubility of cellulose crystals and its derivatized counterpart. Thermogravimetric analysis of S77 displayed a higher decomposition temperature of 317.97°C compared to a lower decomposition temperature of 291.37°C of hydrolyzed cellulose crystals.

3.3.2. ATRP of styrene from derivatized cellulose nano-crystals

Polymerization of styrene was performed under similar conditions used towards formation of cellobiose end-capped polystyrene polymer.



Scheme 3.6. Synthetic route for polymerization of styrene forming Cell-b-PS (cellulose-*block*-polystyrene copolymer).

Based on the similarity of cellobiose chemical reactivity, cellulose-*block*-polystyrene copolymer was synthetically prepared (Scheme 3.6) by the ATRP of styrene using adduct 1 as functionalized initiator. At a temperature of 130°C, adduct 1 was quantitatively prepared by reacting C-d-4AS with 1-(bromoethyl)benzene in presence of Cu(I)Br and PMDETA catalyst system. Distilled styrene was added to the resultant heterogeneous green reaction mixture and the reaction was heated to 130°C for 12 hours. After the specified time, the reaction was stopped and mixture was diluted with addition of tetrahydrofuran (THF). The obtained polymer was purified and precipitated in methanol followed by concentration in vacuum. The resulting block copolymer was analyzed with FT-IR, ^{1}H NMR, DSC, and TGA. Prior to analysis, the copolymer was fractionated in selective solvents to achieve product purity.

In experimental run R83 a 1:1:3 ratio of Cu(I)Br, 1-(bromoethyl)benzene, and PMDETA was used in the polymerization reaction. On characterization by FT-IR spectroscopy, R83 copolymer spectrum corresponded to the superposition of standard polystyrene sample and hydrolyzed cellulose crystals spectra. As can be seen in Figure 3.16, R83 has absorption bands at 3450 cm^{-1} characteristic of the hydrogen bonding of alcohol groups in cellulose, at 3025 cm^{-1} and 2930 cm^{-1} characteristic of $–CH_2$ and –CH polystyrene backbone stretch. Our results have been consistent and analogous to the results obtained by Stadler et al.[23] in their work of synthesizing amylase-*block*-polystyrne copolymer by enzymatic polymerization of amylose. ^{1}H NMR spectroscopy displayed protons and chemical shifts pertaining to polystyrene only. As noted in the formation and characterization of CB end-capped PS, similar results were observed when $CDCl_3$ solvent was used for ^{1}H NMR measurement of

R83. The appearance of polystyrene protons and absence of cellulose protons suggested the formation of micelles, which is based on the dissolution of one block in a selective solvent forming aggregates.

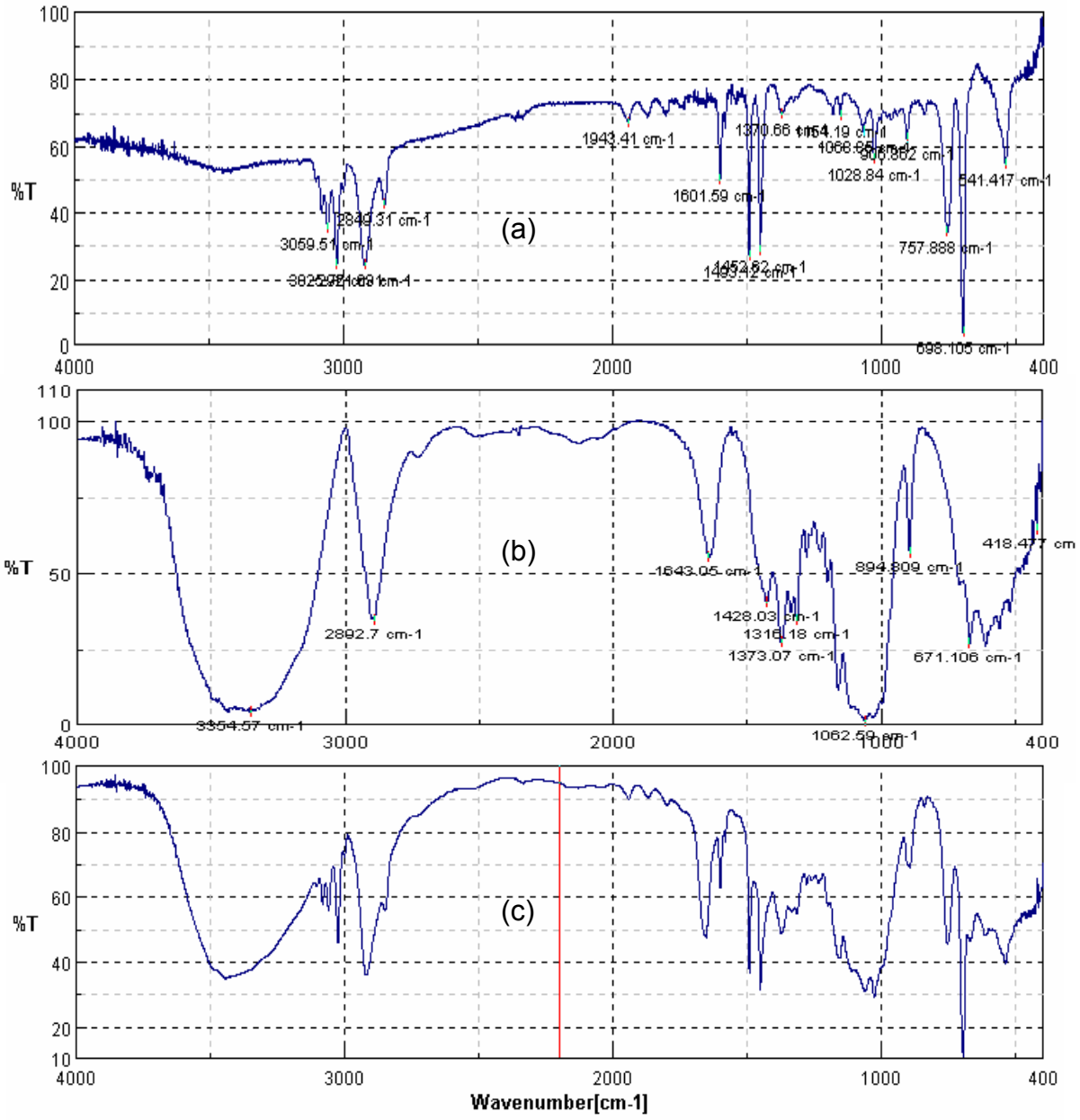


Figure 3.16. (a) FT-IR spectrum of polystyrene standard. (b) FT-IR spectrum of C-d-4AS. (c) FT-IR spectrum of cellulose-*block*-polystyrene copolymer (R83).

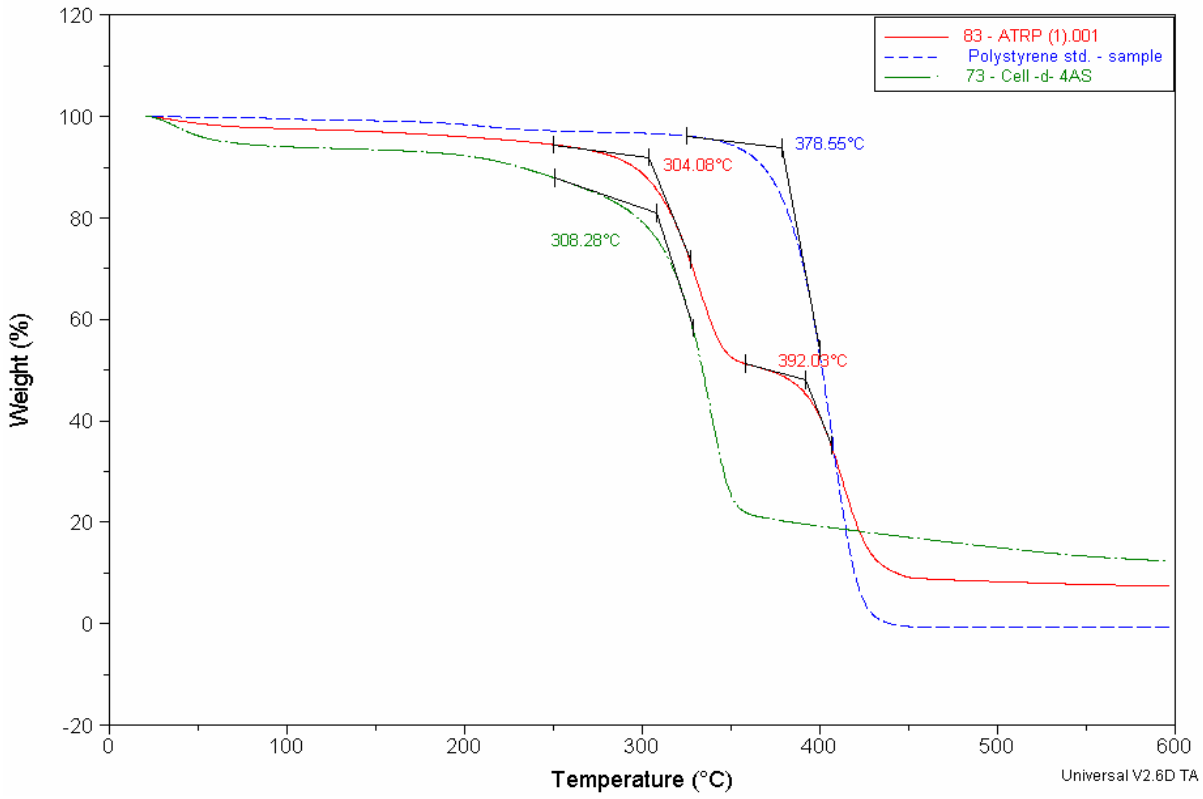


Figure 3.17. TGA thermogram of cellulose-*block*-polystyrene copolymer (R83), S73 (C-d-4AS), and polystyrene standard.

TGA results of R83 (cellulose-b-polystyrene copolymer) are very similar to R79 (cellobiose end-capped polystyrene), wherein the analysis gave two decomposition temperatures suggesting the phase separation in CB end-capped PS. Figure 3.17 shows decomposition temperatures of polystyrene standard, S73 (C-d-4AS), and R83 (Cell-b-PS). In R83, the lower decomposition temperature of 304.08°C and higher decomposition temperature of 392.03°C correspond to component temperatures of S73 (C-d-4AS) and polystyrene standard respectively. DSC thermogram of R83 as shown in Figure 3.18 displays glass transition temperature of 98.31°C for polystyrene block in the copolymer, which supports the presence

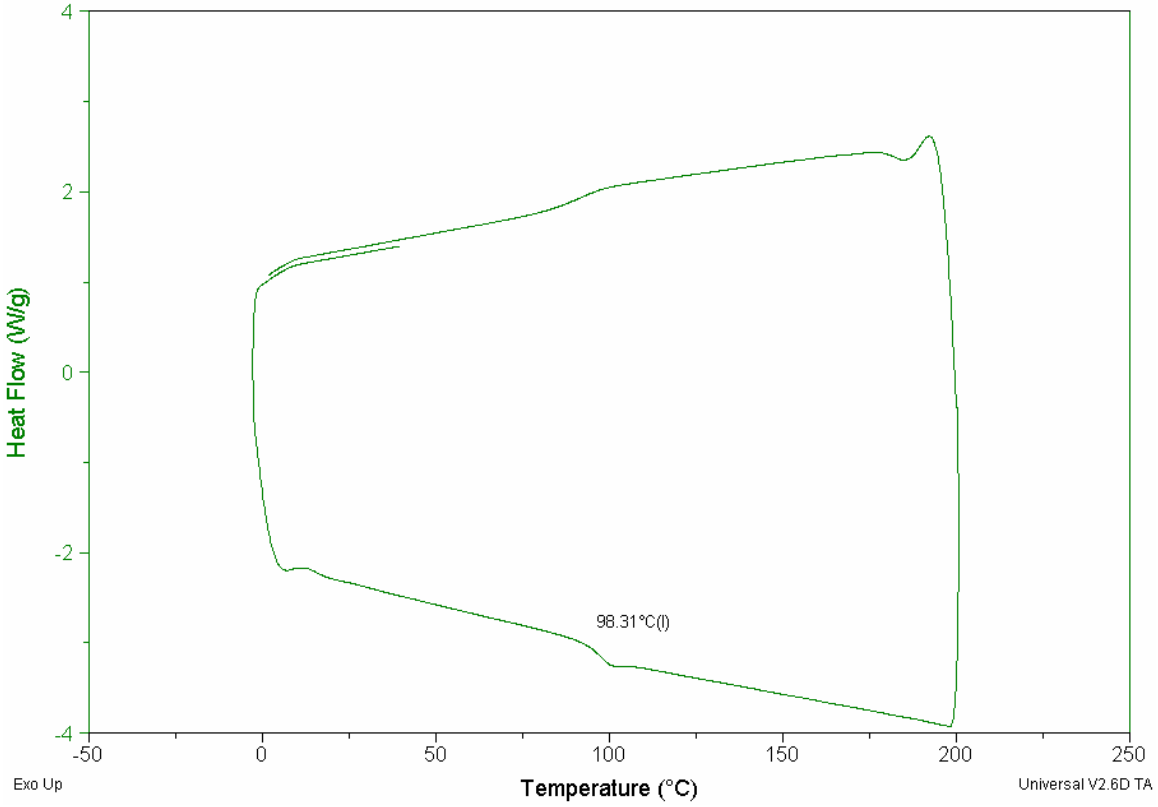


Figure 3.18. DSC thermogram of cellulose-*block*-polystyrene copolymer (R83).

of polystyrene block connected to cellulose block. According to literature, the T_g of linear polystyrene standard is around 100°C.

It is worth noting that by dissolution of one block in a selective solvent makes ^{1}H NMR measurement possible of our diblock copolymer. However, there was no known solvent system that could be used to fully dissolve our product due to unchanged and extensive hydrogen bonding originating from cellulose crystals. Thus, we were unable to perform SEC analysis of our diblock copolymer.

3.4 Conclusion

ATRP, a controlled synthetic process, allows for the preparation of polymer structures with predictable molecular weights and molecular weight distributions based on uniform growth of chains. Such a simple, inexpensive, and versatile technique is very useful in polymerizing and copolymerizing various monomers like styrene, acrylates, and methacrylates. Block copolymer structures obtained by combination of incompatible units via ATRP present us with very interesting properties.

It was demonstrated that cellobiose, which is considered as a basic repeat unit of cellulose, was successfully used as a model study in the polymerization of styrene to create cellobiose end-capped polystyrene polymer. The reducing end aldehyde group was reacted with 4-vinylaniline forming derivative compound that was further used towards the formation of functionalized initiator for ATRP. Due to solubility reasons, various solvents were tested in the formation of CB-d-4AS, wherein DMF gave good yields of 60% to 70%. The addition reaction of CB-d-4AS with 1-(bromoethyl)benzene in presence of Cu(I)Br, PMDETA catalyst system produced an efficient initiating system in the ATRP of styrene to give CB end-capped PS polymer. FT-IR, ^{1}H NMR, DSC, and TGA spectra confirmed the architecture of the cellobiose end-capped polymer.

Despite its structure and insolubility in solvents, hydrolyzed cellulose crystals were successfully derivatized with octadecylamine to test the reactivity of its reducing end. With the intention of following the model study, hydrolyzed cellulose crystals were also derivatized with 4-vinylaniline creating a compatible derivatized initiator in ATRP of styrene. Amphiphilic diblock copolymer (Cellulose-*block*-Polystyrene) was successfully

synthesized by ATRP using C-d-4AS, 1-(bromoethyl)benzene in presence of Cu(I)Br, PMDETA catalyst system. FT-IR, ^{1}H NMR, and TGA measurements compliment the results of model study and confirm the formation of diblock (Cell-PS) copolymer. The appearance of PS protons in the ^{1}H NMR spectra and the absence of CB and Cell protons indicated the formation of aggregates in $CHCl_3$ solvent, which is good selective solvent for PS and not for cellobiose and cellulose. Thus all copolymer chains in the solution aggregated to form micelles.

3.5 Experimental Section

Instruments and Characterizations

All air sensitive and moisture sensitive synthetic procedures were performed using a Schlenk line under an atmosphere of purified nitrogen. The glassware was dried by placing it in the oven overnight.

Infrared spectra were recorded using a Jasco FT/IR-410 spectrometer. NaCl plates were used to acquire the spectrum, where all the data was reported in units of wavenumbers (cm^{-1}) for characteristic functional group peaks.

^{1}H NMR spectra were recorded with Varian-Mercury NMR spectrometer at 300 MHz and 400 MHz. Chemical shifts for ^{1}H NMR spectra are reported in δ (ppm), where positive values indicate shifts downfield of tetramethylsilane (TMS) and are referenced to selected residual proton peaks of the solvent as follows: $CDCl_3$, 7.27, singlet; DMSO-d_6, 2.5, quintet. Significant ^{1}H NMR data are tabulated in order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), number of protons. ^{13}C {^{1}H} NMR spectra

were measured on a Varian-Mercury spectrometer at 100 MHz. Chemical shifts for ^{13}C $\{^{1}H\}$ NMR spectra are reported in δ (ppm), positive values indicating shifts downfield of tetramethylsilane, and are referenced to selected residual peaks of the solvents as followed: CDCl3, 77.23, triplet; DMSO-d_6, 39.51, septet.

Prior to sample analysis, solvents were removed with a rotary evaporator and under Schlenk line vacuum (approximately 60 mTorr).

Molecular weight and molecular weight distributions were determined by Size Exclusion Chromatography (SEC) using a Jasco PU-1580 pump and a Jasco RI-1530 refractive index detector. The stationary consisted of two PL-Gel mixed C columns. THF was used as the mobile phase, 1.0 ml min^{-1}. Linear polystyrene standards (Pressure Chemical, Inc.) were used for calibration.

Thermal analysis was performed using Hi-Res TGA 2950 and DSC 2920 TA instruments using a nitrogen purge and heating and cooling rates of 10°C min^{-1}.

Reagents

Unless otherwise noted all reagents used were obtained from commercial suppliers and were used without further purification. The solvents used for air and water sensitive procedures were purified via chromatography except for the THF, which were distilled from a sodium / benzophenone ketyl under nitrogen. The solvents used for SEC analysis were HPLC grade. Unless otherwise noted, all other solvents were reagent grade and used without further purification.

Experimental procedures and characterizations

Cellobiose derivatized with octadecylamine

2 g (7.4 mmol) of octadecylamine was dissolved in 10 mL of chloroform in a 50 mL round bottom flask equipped with mechanical stirrer, thermometer and gas inlet (N_2). Then 1 g (2.9 mmol) of cellobiose powder was added to the reaction flask. After stirring the reaction mixture for 3 hours at room temperature, the heterogeneous mixture was washed and separated with repeated steps of centrifugation and re-suspension in $CHCl_3$ solvent. Octadecylamine is readily soluble in $CHCl_3$, thus by washing the mixture 5-6 times in $CHCl_3$ removes any unreacted octadecylamine. The residual solvent was removed by drying under vacuum. In a similar way, the solid was then washed 5-6 times with water to achieve removal of unreacted cellobiose. After drying under vacuum, the desired compound was recovered as white milky powder (1.57 g, 91%). IR (KBr): 3426.89, 2917.77, 2850.27(s), 1568.81(C=N). ^{1}H NMR δ: 6.66 (d, 1H), 5.22 (d, 1H), 4.99 (dt, 1H), 4.59 (dd, 1H), 4.26 (dt, 1H), 3.70 (t, 2H), 3.59 (dd, 1H), 3.40 (d, 2H), 3.27 (dd, 1H), 3.15 (dd, 1H), 3.04 (dd, 1H), 2.97 (d, 1H), 1.51 (dt, 2H), 1.23 (s, 32H), 0.85 (t, 3H). ^{13}C {^{1}H} NMR δ: 158.95, 103.18, 96.66, 80.76, 76.78, 76.47, 75.07, 74.73, 74.49, 73.32, 70.03, 61.02, 60.53, 40.13, 39.92, 39.72, 39.30, 39.09, 38.88, 29.06, 28.72, 16.82.

Cellulose derivatized with octadecylamine

Using a similar procedure as above, 2 g (7.4 mmol) of octadecylamine was dissolved in 10 mL of chloroform in a 50 mL round bottom flask equipped with mechanical stirrer, thermometer and gas inlet (N_2). Then 2 g of hydrolyzed cellulose crystal powder was added

to the reaction flask. After stirring the reaction mixture for 3 hours at 70°C, the heterogeneous mixture was washed and separated with repeated steps of centrifugation and re-suspension in $CHCl_3$ solvent. Octadecylamine is readily soluble in $CHCl_3$, thus by washing the mixture 5-6 times in $CHCl_3$ removes any unreacted octadecylamine. The residual solvent was removed by drying under vacuum. After drying under vacuum, the desired compound was recovered as white powder (2.8 g). IR (KBr): 3368.07, 2916.81, 1645.95 (C=N).

Cellobiose derivatized with 4-vinylaniline

S63 (CB-d-4AS)

By a similar procedure reported by Kipper et al.,[19] 6.6×10^{-3} mol (0.78 g) of 4-vinylaniline (4-AS) was added to 50 mL of DMF in a 100 mL round bottom flask equipped with mechanical stirrer, thermometer and gas inlet (N_2). At 30°C the contents of the flask was gently stirred for 20 minutes. Then 3.3×10^{-3} mol (1.1418 g) of cellobiose was added to the reaction flask. Under N_2 gas and at 70°C, the reaction was run for 4 hours. After the given time, the reaction mixture was allowed to cool to room temperature. The heterogeneous mixture was then filtered using a whatman no.1 filter paper to separate the solid from the liquid. The liquid in the flask was then concentrated by using a rotary evaporator, and was precipitated by addition of DMF. This precipitate was washed several times with DMF through centrifugation and re-suspension in solvent and the dried under vacuum. Similarly the precipitate was then washed 5-6 times with water to achieve removal of unreacted cellobiose. Finally, the residual solvent was removed by drying under vacuum giving a pale

white solid (0.92 g, 60%). IR (KBr): 3423.03 (br), 2970.8, 2897.04, 1610.27 (C=N). ^{1}H NMR (DMSO-d_6) δ: 7.22 (d, 1H), 7.07 (d, 1H), 6.99 (d, 1H), 6.52 (d, 1H), 6.47 (d, 1H), 6.12 (d, 1H), 5.44 (t, 1H), 5.23 (d, 1H), 5.01 (dt, 1H), 4.91 (d, 1H), 4.66 (dd, 1H), 4.26 (dt, 1H), 3.70 (t, 2H), 3.62 (dd, 1H), 3.43 (t, 2H), 3.28 (dd, 1H), 3.16 (dd, 1H), 3.03 (dd, 1H), 2.73 (d, 1H).

S39 (CB-d-4AS)

Based on the same procedure as above, 4.4 x 10^{-3} mol (0.52 g) of 4-vinylaniline (4-AS) was added to 22 mL of DMSO in a 100 mL round bottom flask equipped with mechanical stirrer, thermometer and gas inlet (N_2). Then 1.1 x 10^{-3} mol (0.38 g) of cellobiose was added to the reaction flask. Under N_2 gas and at 70°C, the reaction was run for 4 hours. After the given time, the reaction mixture was allowed to cool to room temperature. The heterogeneous mixture was then filtered using a whatman no.1 filter paper to separate the solid from the liquid. The liquid was then concentrated by using a rotary evaporator, and was precipitated in $CHCl_3$. This precipitate was washed several times with $CHCl_3$ through centrifugation and re-suspension in solvent and the dried under vacuum. Similarly the precipitate was then washed 5-6 times with water to achieve removal of unreacted cellobiose. Finally, the residual solvent was removed by drying under vacuum giving a brownish white solid (0.038 g, 8%). IR (KBr): 3396.12, 2974.68, 2879.41, 1623.29 (C=N). ^{1}H NMR (DMSO-d_6) 7.18 (d, 1H), 7.09 (d, 1H), 7.04 (d, 1H), 6.63 (d, 1H), 6.48 (d, 1H), 6.46 (d, 1H), 5.42 (t, 1H), 5.22 (d, 1H), 4.98 (dt, 1H), 4.86 (d, 1H), 4.59 (dd, 1H), 4.42 (dt, 1H), 3.66 (t, 2H), 3.49 (dd, 1H), 3.40 (t, 2H), 3.28 (dd, 1H), 3.17 (dd, 1H), 3.05 (dd, 1H), 2.97 (d, 1H).

S41 (CB-d-4AS)

Based on the same procedure as above, 4.4 x 10^{-3} mol (0.52 g) of 4-vinylaniline (4-AS) was added to 20 mL of $CHCl_3$ in a 100 mL round bottom flask equipped with mechanical stirrer, thermometer and gas inlet (N_2). Then 1.1 x 10^{-3} mol (0.38 g) of cellobiose was added to the reaction flask. Under N_2 gas and at 50°C, the reaction was run for 4 hours. After the given time, the reaction mixture was allowed to cool to room temperature. The heterogeneous mixture was then filtered using a whatman no.1 filter paper to separate the solid from the liquid. This solid was washed several times with water to remove any unreacted cellobiose. The solid was then washed several times with $CHCl_3$ to remove unreacted 4-vinylaniline through repeated steps of centrifugation. Finally, the residual solvent was removed by drying under vacuum giving a yellowish white solid (0.1026 g, 21%). IR (KBr): 3388.91, 2965.74, 2892.22, 1619.61. ^{1}H NMR (DMSO-d_6) δ: 7.13 (d, 1H), 7.11 (d, 1H), 7.01 (d, 1H), 6.67 (d, 1H), 6.52 (d, 1H), 6.50 (d, 1H), 5.47 (t, 1H), 5.23 (d, 1H), 4.99 (dt, 1H), 4.90 (d, 1H), 4.60 (dd, 1H), 4.24 (dt, 1H), 3.71 (t, 2H), 3.61 (dd, 1H), 3.42 (t, 2H), 3.27 (dd, 1H), 3.19 (dd, 1H), 3.09 (dd, 1H), 2.97 (d, 1H).

S51 (CB-d-4AS)

Based on the same procedure as above, 2.2 x 10^{-3} mol (0.26 g) of 4-vinylaniline (4-AS) was added to 25 mL of DMF in a 100 mL round bottom flask equipped with mechanical stirrer, thermometer and gas inlet (N_2). At 30°C the contents of the flask was gently stirred for 20 minutes. Then 1.1 x 10^{-3} mol (0.38 g) of cellobiose was added to the reaction flask. Under N_2 gas and at 80°C, the reaction was run for 4 hours. After the given time, the reaction mixture

was allowed to cool to room temperature. The heterogeneous mixture was then filtered using a whatman no.1 filter paper to separate the solid from the liquid. The liquid in the flask was then concentrated by using a rotary evaporator, and was precipitated by addition of DMF. This precipitate was washed several times with DMF through centrifugation and re-suspension in solvent and the dried under vacuum. Similarly the precipitate was then washed 5-6 times with water to achieve removal of unreacted cellobiose. Finally, the residual solvent was removed by drying under vacuum giving a pale white solid (0.36 g, 71%). IR (KBr): 3422.06, 2970.8, 2896.56, 1611.23 (C=N). ^{1}H NMR (DMSO-d_6) δ: 7.20 (d, 1H), 7.10 (d, 1H), 6.99 (d, 1H), 6.67 (d, 1H), 6.52 (d, 1H), 6.45 (d, 1H), 5.42 (t, 1H), 5.24 (d, 1H), 5.00 (dt, 1H), 4.89 (d, 1H), 4.60 (dd, 1H), 4.31 (dt, 1H), 3.70 (t, 2H), 3.54 (dd, 1H), 3.39 (t, 2H), 3.27 (dd, 1H), 3.16 (dd, 1H), 3.06 (dd, 1H), 2.98 (d, 1H).

Cellulose derivatized with 4-vinylaniline

S73 (C-d-4AS)

Based on a similar procedure in forming CB-d-4AS as above, 0.2 M (0.24 g) of 4-vinylaniline (4-AS) was added to 10 mL of DMF in a 100 mL round bottom flask equipped with mechanical stirrer, thermometer and gas inlet (N_2). At 30°C the contents of the flask was gently stirred for 20 minutes. Then 100 mg (10 mg/mL) of hydrolyzed cellulose crystals was added to the reaction flask. Under N_2 gas and at 90°C, the reaction was run for 19 hours. After the given time, the reaction mixture was allowed to cool to room temperature. The heterogeneous mixture was washed and separated with repeated steps of centrifugation and re-suspension in DMF solvent. 4-vinylaniline is soluble in DMF, thus by washing the

mixture 5-6 times in the solvent removes any unreacted 4-vinylaniline. The residual solvent was removed by drying under vacuum. After drying under vacuum, the desired compound was recovered as white solid (63 mg). IR (KBr): 3445.69, 1651.73. TGA: 311.63°C.

S77 (C-d-4AS)

Using similar procedure as above, 0.2 M (0.48 g) of 4-vinylaniline (4-AS) was added to 20 mL of DMF in a 100 mL round bottom flask equipped with mechanical stirrer, thermometer and gas inlet (N_2). At 30°C the contents of the flask was gently stirred for 20 minutes. Then 200 mg (10 mg/mL) of hydrolyzed cellulose crystals was added to the reaction flask. Under N_2 gas and at 90°C, the reaction was run for 19 hours. After the given time, the reaction mixture was allowed to cool to room temperature. The heterogeneous mixture was washed and separated with repeated steps of centrifugation and re-suspension in DMF solvent. 4-vinylaniline is soluble in DMF, thus by washing the mixture 5-6 times in the solvent removes any unreacted 4-vinylaniline. The residual solvent was removed by drying under vacuum. After drying under vacuum, the desired compound was recovered as white solid (158 mg). IR (KBr): 3446.17, 1653.18. TGA: 317.97°C.

Cellobiose end-capped polystyrene

R79 (CB end-capped PS)

Using a literature procedure,[22] Schlenk flask and nitrogen inert atmosphere was used in the polymerization of styrene by ATRP. In this procedure, 0.0713 g (0.49 mmol) of Cu(I)Br and 0.31 mL (1.49 mmol) of PMDETA were added to a Schlenk flask. Nitrogen gas was

constantly purged during the successive addition of 0.23 g (0.498 mmol) of CB-d-4AS, 0.068 mL (0.498 mmol) of 1-(bromoethyl)benzene, and 2 mL of diphenyl ether. This heterogeneous reaction mixture was allowed to stir for 5 minutes and then degassed up to 3 times by freeze pump thaw cycles. Maintaining a nitrogen inert atmosphere, the reaction mixture was heated to 130°C for an hour with constant stirring. After an hour, the reaction mixture was allowed to cool to room temperature. About 2 mL (17.45 mmol) of freshly distilled styrene was added to the green reaction mixture via steel syringe. The reaction was then heated for 12 hours at 130°C. After cooling the mixture to room temperature, THF was added to the resultant green solution. Methanol was added to the heterogeneous mixture and purified by repeated steps of centrifugation. The centrifugation process was continued till all the catalyst impurities were not removed. The residual methanol in the mixture was removed by drying under vacuum. $CHCl_3$ was used to further wash the product to achieve removal of unreacted styrene. Residual $CHCl_3$ was removed by drying under vacuum. Water was then used to wash the white product, which would remove any unreacted cellobiose. Finally the product was concentrated by drying under vacuum overnight giving a whitish product (0.68 g, 32%). IR (KBr): 3419.17, 3059.51, 3024.8, 2922.11, 2848.35, and 1652.7. ^{1}H NMR ($CDCl_3$) δ: 7.11-6.12 (3H), 6.82-6.41 (2H), 2.10-1.17 (1H), 1.16-1.12 (2H).

R59 (CB end-capped PS)

Using a similar procedure as above, Schlenk flask and nitrogen inert atmosphere was used in this polymerization of styrene by ATRP. In this procedure, 0.0735 g (0.5122 mmol) of Cu(I)Br and 0.266 g (1.537 mmol) of PMDETA were added to a Schlenk flask. Nitrogen gas

was constantly purged during the successive addition of 0.235 g (0.5122 mmol) of S51 (CB-d-4AS), 0.0947 g (0.5122 mmol) of 1-(bromoethyl)benzene, and 1.7 mL of diphenyl ether. This heterogeneous reaction mixture was allowed to stir for 5 minutes and then degassed up to 3 times by freeze pump thaw cycles. Maintaining a nitrogen inert atmosphere, the reaction mixture was heated to 130°C for an hour with constant stirring. After an hour, the reaction mixture was allowed to cool to room temperature. About 1.7 mL (14.83 mmol) of freshly distilled styrene was added to the green reaction mixture via steel syringe. The reaction was then heated for 12 hours at 130°C. After cooling the mixture to room temperature, THF was added to the resultant green solution. Methanol was added to the heterogeneous mixture and purified by repeated steps of centrifugation. The centrifugation process was continued till all the catalyst impurities were not removed. The residual methanol in the mixture was removed by drying under vacuum. $CHCl_3$ was used to further wash the product to achieve removal of unreacted styrene. Residual $CHCl_3$ was removed by drying under vacuum. Water was then used to wash the white product, which would remove any unreacted cellobiose. Finally the product was concentrated by drying under vacuum overnight giving a whitish product (0.36 g, 20%). IR (KBr): 3422.06, 3081.69, 2921.6, and 1652.21. ^{1}H NMR ($CDCl_3$) δ: 7.11-6.90 (3H), 6.63-6.39 (2H), 1.59-1.61 (1H), 1.15-1.13 (2H). DSC: T_g = 96.14

R47 (CB end-capped PS)

Using a similar procedure as above, Schlenk flask and nitrogen inert atmosphere was used in this polymerization of styrene by ATRP. In this procedure, 0.0735 g (0.5122 mmol) of Cu(I)Br and 0.266 g (1.537 mmol) of PMDETA were added to a Schlenk flask. Nitrogen gas

was constantly purged during the successive addition of 0.235 g (0.5122 mmol) of S41 (CB-d-4AS), 0.0947 g (0.5122 mmol) of 1-(bromoethyl)benzene, and 1.7 mL of diphenyl ether. This heterogeneous reaction mixture was allowed to stir for 5 minutes and then degassed up to 3 times by freeze pump thaw cycles. Maintaining a nitrogen inert atmosphere, the reaction mixture was heated to 130°C for an hour with constant stirring. After an hour, the reaction mixture was allowed to cool to room temperature. About 1.7 mL (14.83 mmol) of freshly distilled styrene was added to the green reaction mixture via steel syringe. The reaction was then heated for 12 hours at 130°C. After cooling the mixture to room temperature, THF was added to the resultant green solution. Methanol was added to the heterogeneous mixture and purified by repeated steps of centrifugation. The centrifugation process was continued till all the catalyst impurities were not removed. The residual methanol in the mixture was removed by drying under vacuum. $CHCl_3$ was used to further wash the product to achieve removal of unreacted styrene. Residual $CHCl_3$ was removed by drying under vacuum. Water was then used to wash the white product, which would remove any unreacted cellobiose. Finally the product was concentrated by drying under vacuum overnight giving a whitish product (0.327 g, 18%). IR (KBr): 3408.57, 3024.8, 2922.59, and 1602.07. ^{1}H NMR ($CDCl_3$) δ: 7.10-6.94 (3H), 6.61-6.39 (2H), 2.10-1.62 (1H), 1.60-1.12 (2H).

Cellulose-*block*-polystyrene

Using the above procedure, Schlenk flask and nitrogen inert atmosphere was used in the polymerization of styrene by ATRP. In this procedure, 0.120 g (0.83 mmol) of Cu(I)Br and 0.52 mL (2.50 mmol) of PMDETA were added to a Schlenk flask. Nitrogen gas was

constantly purged during the successive addition of 60 mg of C-d-4AS, 0.11 mL (0.83 mmol) of 1-(bromoethyl)benzene, and 3 mL of diphenyl ether. This heterogeneous reaction mixture was allowed to stir for 5 minutes and then degassed up to 3 times by freeze pump thaw cycles. Maintaining a nitrogen inert atmosphere, the reaction mixture was heated to 130°C for an hour with constant stirring. After an hour, the reaction mixture was allowed to cool to room temperature. About 3 mL (31.68 mmol) of freshly distilled styrene was added to the green reaction mixture via steel syringe. The reaction was then heated for 12 hours at 130°C. After cooling the mixture to room temperature, THF was added to the resultant green solution. Methanol was added to the heterogeneous mixture and purified by repeated steps of centrifugation. The centrifugation process was continued till all the catalyst impurities were not removed. The residual methanol in the mixture was removed by drying under vacuum. $CHCl_3$ was used to further wash the product to ensure removal of free polystyrene and unreacted styrene. Finally the product was concentrated by drying under vacuum overnight giving a whitish product (0.68 g, 32%). IR (KBr): 3444.72 (br), 3025.58(s), 2920.33. TGA: 304.08°C, 392.03°C. DSC: T_g = 98.31°C

3.6 References

1. Higashi, F.; Ogata, S.; Aoki, Y. *J. Polym. Sci., Polym. Chem. Ed*. **1982**, *20*, 2081.
2. Dalton, L.R.; Steier, W.H.; Robinson, B.H.; Zhang, C.; Ren, A.; Garner, S.; Chen, A.T.; Londergan, T.; Irwin, L.; Carlson, B.; Fifield, L., Phelan, G.; Kincaid, C.; Amend, J.; Jen, A. *J. Mater. Chem.* **1999**, *9*, 1905.
3. Gurdag, G.; Guclu, G.; Ozgumus. S. *J. Appl. Polm. Sci.* **2001**, *80*, 2267.
4. Chauchan, G.S.; Lal, H; Sharma, R.; Guleria, L.; Sarwade, B.D. *J. Appl. Polym. Sci.* **2002**, *83*, 2000.
5. Vigo, T.L. *Polym. Adv. Technol.* **1998**, *9*, 539.
6. Kamitakahara, H.; Nakatsubo, F.; Enomoto, Y. *Cellulose.* **2005**, *12*, 527.
7. Ceresa, R.J. *Polymer.* **1961**, *2*, 213.
8. Kim, S.; Stannett, V.T.; Gilbert, R.D. *J. Polym. Sci. Polym. Lett. Edit.* **1973**, *11*, 731.
9. Kim, S.; Stannett, V.T.; Gilbert, R.D. *J. Macromol. Sci. Pt. A, Chem.* **1976**, *10(4)*, 671.
10. Feger, C.; Cantow, H.J. *Polym. Bull.* **1980**, *3*, 407.
11. Mezger, T.; Cantow, H.J. *Angew. Makromol. Chem.* **1983**, *116*, 13.
12. Mezger, T.; Cantow, H.J. *Makromol. Chemie-Rapid Commun.* **1983**, *4(5)*, 313.
13. Mezger, T.; Cantow, H.J. *Polym. Photochem.* **1984**, *5(1-6)*, 49.
14. Pohjola, L.; Eklund, V. *Pap. Puu.* **1977**, *3*, 117.
15. Glasser, W.G.; Olivera, W. *Polymer.* **1994**, *35(9)*, 1977.
16. Glasser, W.G.; Olivera, W. *Cellulose.* **1994**, *1(1)*, 77.

17. Carlmark, A.; Malmstrom, E. E. *Biomacromolecules*. **2003**, *4*, 1740.

18. Kipper, K.; Johansson, G.; Valjamae, P. *Biochem J.* **2005**, *385*, 527.

19. Sato, K.; Sato, K.; Okubo, A.; Yamazaki, S. *Anal. Biochem*. **1998**, *262*, 195.

20. Huang, Z.; Prickett, T.; Potts, M.; Helm, R. *Carbohydr. Res.* **2000**, *328*, 77.

21. Summers, G.; Ndawuni, M.; Summers, C. *Polym Int*, **2003**, *52*, 158.

22. Stadler, R.; Loos, K. *Macromolecules*, **1997**, *30*, 7641.