2007

The application of controlled radical polymerization processes on the graft copolymerization of hydrophobic substituents onto guar gum and guar gum derivatives

Veronica Holmes
Louisiana State University and Agricultural and Mechanical College, vkholmes@yahoo.com

Recommended Citation

Holmes, Veronica, "The application of controlled radical polymerization processes on the graft copolymerization of hydrophobic substituents onto guar gum and guar gum derivatives" (2007). *LSU Doctoral Dissertations*. 3220.
https://digitalcommons.lsu.edu/gradschool_dissertations/3220

THE APPLICATION OF CONTROLLED RADICAL POLYMERIZATION PROCESSES ON THE GRAFT COPOLYMERIZATION OF HYDROPHOBIC SUBSTITUENTS ONTO GUAR GUM AND GUAR GUM DERIVATIVES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
In partial fulfillment of the
Requirements for the degree of
Doctor of Philosophy

In

The Department of Chemistry

By
Veronica Holmes
B.S., Southern University A&M, Baton Rouge, LA, 1999
May, 2007

Acknowledgements

My matriculation through graduate school would not have been possible without the support and guidance of Dr. William H. Daly. His kindness and patience during my graduate endeavors has been unprecedented. Along with the support of past and present graduate students in our research lab, I have had an excellent support system for the duration of time I have spent with this research.

I would like to thank Dr. Paul Russo for assistance with financial opportunities for research and career development, as well as his advice regarding research, career possibilities, and life in general. I would like to thank Dr. William Crowe for his advice about projects and his encouragement through the years.

I am thankful for the support, patience, and understanding of my entire family. Without their love and prayers, I would have been unable to pursue a graduate degree.

Table of Contents

List of Tables

List of Figures

Abstract

Guar gum is a naturally occurring polysaccharide; guar gum and its derivatives, such as carboxymethyl guar gum (CMG) are widely used in the oil and gas industry. A hydraulic fracturing fluid for rock formations to enhance oil recovery (EOR) is comprised of viscosifier, gelled CMG, and sand particles (proppants). The gel is mixed with proppant (sand) and pumped at high rate and high pressure into an oil/gas well to the hydrocarbon-producing zone. The applied pressure will force the rock formation to fracture allowing entry of the guar gel/sand mixture. The mixture then fills the resultant fracture. The viscosity of the mixture must be sufficient at this point in the process to prevent the settling of the sand particles. The pressure is then released, allowing closure of the fracture onto the guar/sand mixture. Leaving the guar gel in the fracture zone will block the pores, causing formation damage and a resultant decrease in oil or gas production. Thus, to complete the process, guar gum must be degraded chemically and/or thermally, then flushed from the formation back to the surface. If the degradation of the guar gum yielded a surfactant, removal of the guar gum fragments would be facilitated by emulsification. This optimization is achieved by introducing hydrophobic attachment, such as polystyrene and poly-n-butyl acrylate, to the polymer backbone of CMG. The increased hydrophobicity should dramatically improve the fluid loss control and increase viscosities of the fluid.

The free radical graft copolymerization of the hydrophobic monomers onto guar gum in the presence of ceric ammonium nitrate may be moderated using controlled radical polymerization techniques. The synthesis of a hydrophobic modified carboxymethyl guar gum graft through two living free radical techniques: nitroxide mediated living polymerization and photo induced RAFT polymerization is presented in this paper. CMG grafted materials with an average weight gain of 71.87% and short oligomeric side chains (with a low degree of polymerization) were synthesized. Hydrophobic modified graft copolymers with higher gel viscosities than CMG gels were produced by the described living free radical polymerizations techniques. Keywords: Guar Gum, enhanced oil recovery, hydrophobic modification, living polymerization, controlled radical polymerization.

Chapter 1 Introduction

1.1 Hydraulic Fracturing

The petroleum industry may provide a public service by producing valuable oil and gas for massive consumption, but the industry is also driven by the need to reduce operating expenses and increase revenues. After a well is drilled into a rock formation that contains oil, natural gas, and water, every effort is made to maximize the production of oil and gas. One way to improve or maximize the flow of fluids to the well bore is to connect many pre-existing fractures, pockets, and flow pathways in the reservoir rock with a larger created fracture. This larger, created hydraulic fracture starts at the well and extends out into the reservoir rock for as much as several hundred feet.[1] To enhance the production of oil from low yielding formations, which would otherwise be uneconomical to produce, a technique known as hydraulic fracturing is employed. As one of the oil and gas industry's most complex operations, hydraulic fracturing (HF) has been widely used to increase oil and gas productivity since the late 1940's. When a highly viscous fluid is pumped down the well at high pressures for short periods of time, a hydraulic fracture is formed in the rock bed. A proppant, usually sand, is carried by the viscous fluid and deposited into the fractures to support and maintain the opening. After the pressure is released, the fluid's viscosity is decreased and it is recovered from the well. The proppant remains as a permeable pack to hold open the fracture.[2] The first fracturing fluid utilized was war surplus napalm. Napalm is an aluminum gel used to thicken gasoline, diesel fuel, kerosene, and other such fluids. The first treatment was thickened gasoline carried in open top tanks along with a few sacks of sand. Fortunately, there were no major fires reported.[3]

Wells producing from low-permeability underground formations are stimulated by Hydraulic fracturing, a process whereby a suspension of sand (proppant) in a fluid is pumped into a formation (soil or rock) at a rate and pressure high enough to overcome the in-situ confining stress and the material strength of a formation resulting in the creation of a fracture or parting. The process is repeated at increasing depths to create a network of sand-filled fractures in the desired zone. When a hydraulically fractured well is produced, the induced fractures provide a conduit so that fluids can flow to the well at a greater rate than would otherwise be possible. Today, about 70% of all oil wells drilled worldwide are hydraulically fractured to stimulate and enhance oil production.[4] Specialized piston pumps deliver fluids down into a well at pressures and flow rates high enough to split the rock and create two opposing cracks. The induced fracture pathways are filled with permeable sand or “proppant” which keep the fractures propped open once pumping stops and pressure declines.[5] The fracture pathways function as permeable conduits to expedite the removal of petroleum product.

In practice, a slurry mixture containing a proppant and a viscous fluid (guar gum and water mixture) is formulated in the mixing tank. Diesel is frequently used in lieu of water to dissolve the guar powder because its carrying capacity per unit volume is much higher. Diesel does not enhance the efficiency of the fracturing fluid in enhanced oil recovery (EOR); it is merely a component of the delivery system. The sand or grain size proppant is designed to meet geotechnical filter requirements for the native soils being fractured and to provide good permeability. In order for the viscous fluid to hold the proppant in a uniform suspension during the fracturing process, a crosslinker is added to further increase the viscosity of the slurry. An enzyme or chemical “breaker” is then incorporated into the fracture slurry to break down fluid viscosity after the fracturing process. A site specific surfactant is typically incorporated in the slurry to minimize formation damage and expedite the drainage of the fracture network during development of the well.[6]

For many years, gelled oils or refined oils were the only fracturing fluids in use for EOR operations. It was also discovered that tall-oil fatty acids combined with caustic created a soap material that could be used as a fracturing fluid. This fracturing fluid, which was utilized until the mid1980's, was a cheap fluid with controllable viscosity. It was an efficient medium, although the friction properties were not very good. It was marketed commercially as Haliburton's Vis-OFrac or Dowell's PetroGel. Later developed systems were aluminum gels composed of aluminum octate in combination with tall-oil fatty acids, which has limited application today. An aluminum phosphate ester reacted with sodium aluminate is still the most successful and the most utilized oil-gelling agent.[3]

The oil based aluminum esters demonstrated enhanced temperature stability (up to 300ºF) compared to previously developed fluids for EOR. But these gels did not approach the temperature stability and handling ease of water based systems. In the beginning, it was believed that wells were water sensitive. Those oil wells were not water sensitive, but they were plugged with gelling agents. Actually, the problem was a lack of good breakers to degrade the fracturing fluid back to water viscosity and the lack of high proppant concentrations to have enough relative conductivity to give production increases. The first viscosifier examined for a water based system was starch. It was plagued with problems such as shear stability, temperature stability, and salt sensitivity, which lead to an early ending for its tenure as a fracturing fluid. The guar gum bean was selected as a viscosifier, because combined with water it yields a high-viscosity fluid. Water thickened with guar gum served as an ideal fracturing fluid because of low cost and its ability to transport proppant down hole. The ability to obtain an appropriate fracturing fluids was an essential part to developing and implementing the hydraulic fracturing technology needed for today's oil and gas well production.[3]

Breakdown of the gel viscosity, after the fracturing process, restores formation permeability and allows increased production flow of petroleum products. The viscosity of the fracture slurry is designed to break down after a period of time, usually two to eight hours. After this period of time has elapsed, the enzyme or chemical "breaker" activates and breaks down the viscosity of the fracture slurry to that of water. Enzyme breakers slowly break the bonds in the long polymer chains of the gelled material.[5] After the gel breaks down, the sand is deposited and prevents the fracture from caving in. During the development of the fractured recovery well, the broken fracture fluid is removed, leaving high permeability sheets of sand which are prepared for the extraction of oil and gas.[7]

1.1.1 The Composition of Fracturing Fluids

Initially, the development of fracturing fluids was centered on creating systems that would result in successful placement of the planned proppant volume. As the hydraulic fracturing technology matured, the demands on the industry became more advanced. Other important aspects of HF came into play, such as, improvement of post fracturing production and field operation and the development of new fracturing fluids with enhanced rheological properties. More recently the focus of HF has been placed upon developing gel breakers in hope to minimize the damage caused by residues of fracturing fluids in the formation and achieve better fracture permeability.[8,9]

Delivery of sand mixed with water would not be possible without partially gelled carriers. Early fracturing fluid technology used compounds such as benzene, naphthalene, toluene, and xylene as dispersing agents. Their low viscosities diminished their ability to transport proppant, and the health hazards associated with the use of large quantities of toxic material made them undesirable.[10] However, aqueous solutions of polysaccharides provide a higher viscosity fracturing fluid, and the natural, biodegradable compounds offer an environmentally safe alternative.

Fracturing fluids normally consist of many additives that serve two main purposes: to enhance fracture creation and proppant carrying capability and to minimize formation damage.[1] Viscosifiers, such as polymers and crosslinking agents, temperature stabilizers, pH control agents, and fluid loss control materials are among the additives that assist fracture creation. Formation damage is minimized by incorporating breakers, biocides, and surfactants. More appropriate gelling agents are linear polysaccharides, such as guar gum, cellulose, and their derivatives[9].

Guar gums are preferred as thickeners for EOR; guar gum and its derivatives account for most of the gelled fracturing fluids. Guar is more water soluble than other gums, and it is also a better emulsifier, because it has more galactose branch points. Guar gum shows high low-shear viscosity, but it is strongly shear-thinning. Being non-ionic, it is not affected by ionic strength or pH but will degrade at low pH at moderate temperature (pH 3 at 50°C).[11] Guar use allows for achieving exceptionally high viscosities, which improves the ability of the fracturing liquid to transport proppant.[12]

Guar hydrates fairly rapidly in cold water to give highly viscous pseudoplastic solutions of, generally, greater low-shear viscosity than other hydrocolloids.[13] The colloidal solids present in guar make fluids more efficient by creating less filter cake. Proppant pack conductivity is maintained by utilizing a fluid that has excellent fluid loss control, such as the colloidal solids present in guar gum.

1.2 Guar Gum

Guar, a naturally occurring polysaccharide extracted from the guar gum bean plant (*Cyamopsis* tetragonoloba), as shown in **Figure 1.1** is widely used in industrial applications. It consists of a linear backbone with **β**-1,4 mannose units and randomly attached α-1,6 galactose units as side chains (**Figure 1.2**). The average ratio of mannose to galactose units is 1.6:1. The exact ratio of galactose to mannose varies with the growing season. Guar gum is highly dispersible into cold and hot water and brines of various types and salinity.[5]

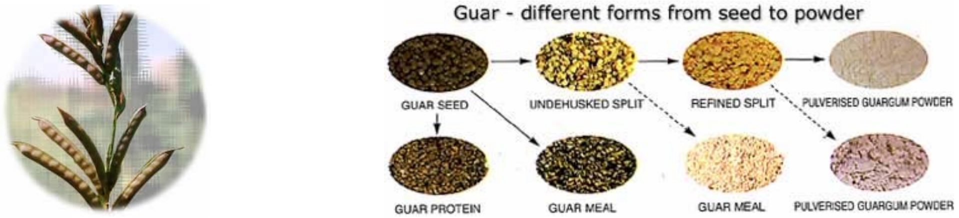


Figure 1.1 Photo of *Cyamopsis tetragonoloba* pods and seeds[14]

Only a small amount of guar is needed to drastically increase the viscosity of aqueous solutions. The high viscosity of guar solutions is a result of the high molecular weight of guar (up to 6 million) and the presence of extensive intermolecular association through hydrogen bonding. [5] Guar gum is made up of non-ionic, polydispersed, rod-shaped polymers consisting of molecules made up of about 10,000 residues. Higher galactose substitution along the anhydrous backbone also increases the stiffness and decreases the flexibility of isolated chains, but reduces the overall extensibility and radius of gyration for the isolated chains.[5] The galactose residues prevent strong chain interactions, as few unsubstituted clear areas have the minimum number of anhydrous mannose units (approx. 6) required for the formation of junction zones.[15]

Guar gum is the most extensively used gum in both food and industrial applications due to its low cost and the above mentioned properties. It is used as a flocculant or flotation agent, foam stabilizer, filtration aid, and water treating agent. In the textile industry, it is used as a sizing agent and thickener for dyes. It facilitates wet end processing and improves the properties of paper. In the food industry, guar gum is used as a stabilizer in ice cream and frozen desserts. Guar has up to eight times the thickening power of starch. Derivatization of guar gum leads to subtle changes in properties, such as, decreased hydrogen bonding, increased solubility in water-alcohol mixture, and improved electrolyte compatibility. These changes in properties result in increased use in different fields, like textile printing, explosives, and oil-water fracturing applications.[16]

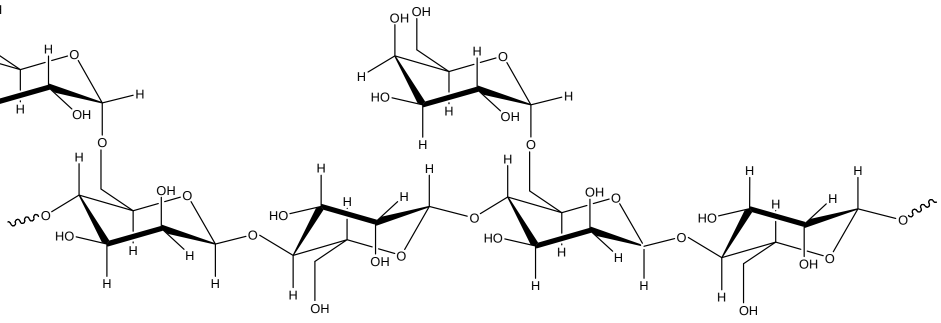


Figure 1.2 Basic chemical structure of guar gum

1.2.1 Guar Gum Derivatives

Guar gum molecules have a tendency to aggregate during the hydraulic fracturing process, mainly due to intermolecular hydrogen bonding. These aggregates are detrimental to oil recovery because they clog the fractures, restricting the flow of oil. Therefore, low residue derivatives of guar gum have been developed in attempts to eliminate this problem. Treatment of guar with propylene oxide or chloroacetic acid in an alkaline medium results in the formation of hydroxypropyl guar (HPG) and carboxymethyl guar, respectively. Substituted guars are more soluble in water than native guar, with less insoluble residues.[5] The derivatization of guar gum occurs on the hydroxyl groups of the D-mannose or D-galactose sugar units. A derivatized guar gum molecule may have a maximum theoretical degree of substitution (DS) of three. The molar substitution (MS) of derivatized guar gum is defined as the average number of hydroxyl bearing substituents per sugar unit and can exceed three due to the additional availability of hydroxyl groups.[17] The most widely known derivatives of guar gum (**Table 1.1**) include: carboxymethyl guar (CMG), hydroxypropyl guar (HPG), carboxymethylhydroxypropyl guar (CMHPG).

Table 1.1 Guar gum substituents

Type of Derivative	**Structure of Substituent**	**Ionic Charge**
Hydroxypropyl Guar (HPG)	$-CH_2-CH(OH)CH_3$	**Nonionic**
Carboxymethyl Guar (CMG)	$-CH_2-COO^-Na^+$	**Anionic**
Carboxymethylhydroxypropy Guar (CMHP)	$-CH_2-COO^-Na^+$ $-CH_2-CH(OH)CH_3$	**Anionic**

1.2.2 Cross-linking Guar Gum

Guar molecules have a tendency to aggregate during the hydraulic fracturing process, mainly due to intermolecular hydrogen bonding. These aggregates are detrimental to oil recovery because they clog the fractures, restricting the flow of oil.[5] Cross-linking guar polymer chains prevents aggregation by forming metal – hydroxyl complexes.[18] The first crosslinked guar gels were developed in the late '60's. Several metal additives have been used for crosslinking, among them are chromium, aluminum, antimony, zirconium, and the more commonly used, boron. Boron, in the form of $B(OH)_4$, reacts with the hydroxyl groups on the polymer in a two step process to link two polymer strands together to form bis-diol complexes (**Equation 1.1**).[19] A thorough study by BJ Services provided NMR data suggesting that the borate ion may be formed in two ways, a 1:1 1,2 diol complex and a 1:1 1,3 diol complex. These complexes place the negatively charged borate ion onto the polymer chain as a pendant group. Boric acid itself does not apparently complex to the polymer so that all bound boron is negatively charged. The primary form of crosslinking may be due to ionic association between the anionic borate complex and adsorbed cations on the second polymer chain.[20]

Equation 1.1: Boric acid equilibrium shift toward borate ions

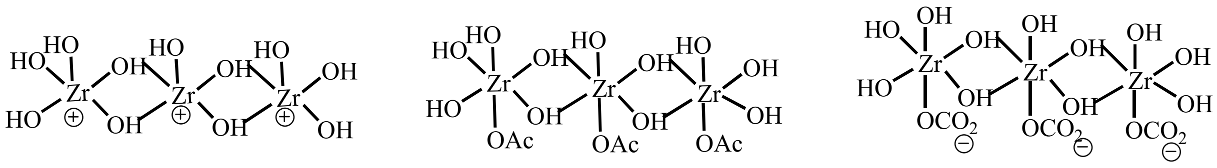
$$H_3BO_3 + OH^- \Longleftrightarrow B(OH)^-_4$$

The development of cross-linked gels was a major advance in fracturing fluid technology. Viscosity is enhanced by tying together the low molecular weight strands, effectively yielding higher molecular weight strands and a rigid structure. Cross-linking agents are added to linear polysaccharide slurries to provide higher proppant transport performance, relative to linear gels.[4] Lower concentrations of guar gelling agents are needed when linear guar chains are cross-linked. It has been determined that reduced guar concentrations provide better and more complete breaks in a fracture. The breakdown of cross-linked guar gel after the fracturing process restores formation permeability and allows increased production flow of petroleum products.[21]

Borate cross-linked guar gum gels are both shear-thinning and thermally thinning; but on cooling, gel restoration is rapid and complete. These fluids are considered reversible gels since the crosslink junctions are not permanent covalent bonds; they are short-lived, temporary junctions. The cross-linking agents do not undergo any permanent chemical change during junction dissociation at higher temperatures or shear. The properties of the gel to be improved include the control of the cross-linking rates, sand suspending properties, and extended thermal stability.[8] During a hydraulic fracturing treatment the fluid is transported down the tubing into the formation. The subsequent temperature rise will alter the chemical equilibrium and the number of cross-linked bonds; therefore, changing the fluid's viscosity. If the fluid's viscosity becomes too low, the setting rate of the proppant may increase, which would give an undesirable proppant distribution over the fracture.[22]

Along with borate, zirconate crosslinkers have been used extensively in fracturing fluids. While the borates lack thermal stability (above 200ºF), zirconium crosslinkers provide reliable performance up to fluid temperatures of ~350ºF in fresh and salt water. However, the borate-guar bond is readily reversible providing for a more predictable fluid viscosity, and the zirconium crosslinking bonds are not reversible. Therefore, the fluid performance of the borate based fluids is much less shear sensitive, than the performance of the fluids formed from the transition metal-polymer bond. Other disadvantages for the borates include the need for high pH (9 – 10) and high friction pressures because of the lack of adequate crosslinking delay mechanisms (for crosslinking to occur down hole and not in the tanker or during mixing of materials).[9,21,23]

Zirconium compounds exist in aqueous and solvent solution as polymeric species, and the properties exhibited by these polymeric species depends on chemical composition and mode of preparation. The polymeric species of zirconium can interact with functional groups on organic polymers. It is suspected that the zirconium reacts strongly with carboxyl groups (such as those of CMG) forming strong bonds. Hydrogen bonds are also formed with hydroxyl groups, which can range from quite weak to fairly strong interactions. Polymeric zirconium species may be cationic (zirconium oxychloride), anionic (ammonium zirconium carbonate, AZC), or neutral (zirconium acetate), as in **Figure 1.3**.[24]



Cationic - Zirconium Oxychloride

Neutral - Zirconium Acetate

Anionic - Ammonium Zirconium Carbonate

Figure 1.3 Structures of polymeric zirconium species

Soluble zirconium compounds (normally carboxylates) have a similar polymeric structure, containing bridging hydroxyl groups. The carboxylated species may behave as bidentate bridging agents. The carboxylates determine solvent solubility; different carboxylates exhibit solubilities in organic solvents.[25] AZC may easily crosslink hydroxylic polymers or carboxylated polymers (**Figure 1.4** and **Figure 1.5** respectively).

The hydroxylic side groups of guar gum could react with AZC to form a guar gum gelation compound, and the carboxyl side groups of CMG are readily available for reacting with AZC to form CMG crosslinks to produce gelled material.

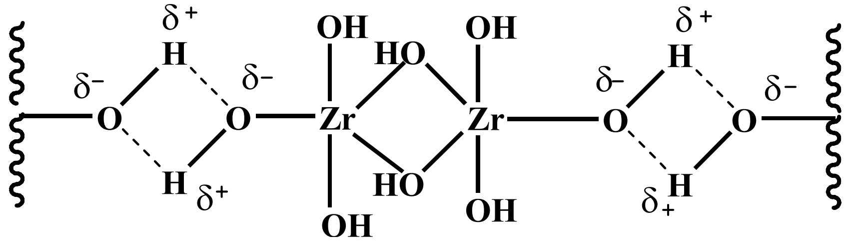


Figure 1.4 Interaction of ammonium zirconium carbonate (AZC) with hydroxylic polymer solutions

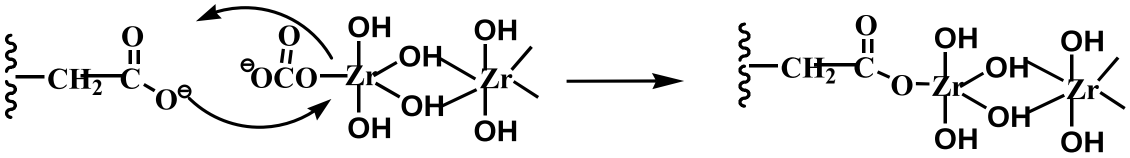
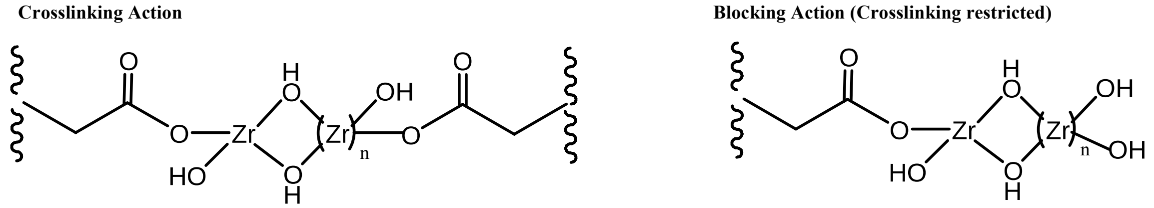


Figure 1.5 Interaction of ammonium zirconium carbonate (AZC) with carboxylated polymers

Varying the aggregation of the zirconium species is possible by adjusting temperature, pH, and chelating agents and the crosslinking reaction may also be affected significantly by the changes to the reaction conditions. At higher levels of zirconium, bridging is reduced by zirconium polymers which are not linked to other carboxyl groups (carboxyl blocking rather than crosslinking), as illustrated in **Figure 1.6**. The more polymeric zirconium species would give a more open structure and can lead to differences in properties. The levels of zirconium present in these systems determine the pot life stability.[25]



Crosslinking Action

Blocking Action (Crosslinking restricted)

Figure 1.6 Modes of crosslinking

Cross-linked gels can be made over a wide pH range. Carboxylated polymers perform best from pH 3 to 4. However, derivatized guars, such as CMG and HPG, may be cross-linked up to a pH of 9 to 10. A change in pH may occur through use of the preferred operational technique for massive hydraulic fracturing treatment offshore, which is to use a liquid gel concentrate mixed with filtered seawater. A major incompatibility arises with use of seawater, because it contains multivalent metal ions. These ions may precipitate as hydroxides, lowering the pH of the fluid with a drastic effect on the fluid properties.[15] The metal ions may also poison enzymatic breakers (which breakdown cross-linked guar) and clog the fracture, preventing the release of oil or gas.

1.3 Hydrophobically Modified Co-Polymers

Employing graft copolymers with a natural polymeric backbone and synthetic side chains provide a safer, cheaper material (as opposed to use of a synthetic polymer backbone), while controlling the properties of the copolymer through selection of side chain groups.[20] Such grafted materials are ideal for use as thickening agents in the field of hydraulic drilling. The literature cites several papers related to grafting a variety of compounds onto guar gum. There is no indication of a current system that would be able to decrease the hydrophilicity associated with using guar as a gelling agent and offer a means of facilitating polymer clean up in a fractured well. Neither is there a described method for controlling chain lengths and molecular weights.[26-28]

Bock and co-workers have examined the effect of hydrophobe content and structure on the viscosity of hydrophilic polymers (associating polymers).[29] They reported that the hydrophobic modification of polysaccharides, such as guar gum, resulted in higher viscosity for the modified polymer. It was concluded that introducing a phenyl group in the hydrophobe monomer significantly enhanced the viscosity of the modified compound. The hydrophobic association changes the apparent viscosity as a function of shear rate. Klucker and colleagues observed the rare phenomenon of shear thickening occurring for the hydrophobically modified polymers.[30] Shear thickening is a reversible increase in viscosity with increasing shear rate.[31] One possible explanation for the shear thickening behavior is that the polymer chains are stretched at high shear rates. This enhances intermolecular association and, as a result, the viscosity increases.[30]

The first hydrophobically modified water soluble polymers were produced by partial esterification of maleic anhydride/styrene copolymers with nonionic ethoxylated alcohol surfactants. However, susceptibility to thermal degradation and alkaline hydrolysis limited their use.[32,33] Associating polymers have been prepared by incorporating hydrophobic groups into the polymer after the polymerization process. The advantage of this approach is that commercially available polymers can be used as starting material. Unfortunately, reactions involving viscous polymer solutions are not easily carried out because of problems associated with mixing and reaction homogeneity.

Guar gum - acrylic acid polymeric grafts have been synthesized. In addition to being a hydrophilic graft, the monovalent Ag^+, in the metal system (peroxydiphosphate - silver(I)) employed to prepare the grafts, complexes with at least two carboxylic groups of the grafted chains to introduce crosslinks. As cross-linking increases, monomers can diffuse easily into the crosslinked matrix.[34] A similar situation is encountered for guar-graft-acrylamide[35].

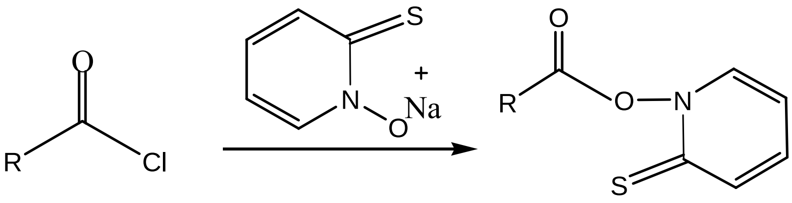
Kevlar® has been modified by adding hydrophobic groups and sulfonate functionality to make it hydrophobically associating, for use in EOR, in up to 10 % (mass) NaCl solution. The product is thermally stable, but the synthesis is relatively expensive.[36] Hydrophobically associating polymers have also been prepared using hydrophobic monomers that are surfactants. These hydrophobic monomers are known as surfomers.[37-39]

There have been research efforts to focus on the efficiency of incorporation of the hydrophobic monomer into the polymer. The effect of surfactant concentration on hydrophobic monomer incorporation into an acrylamide copolymer has been studied by Biggs and colleagues. It was discovered that the reaction rate for acrylamide polymerization in aqueous solution was very similar to its reaction rate in a micellar solution.[40] Solubilization of hydrophobic monomer within the micelles causes a positive increase in their rate of incorporation into the copolymer. The higher the number of hydrophobic monomers per micelle, the greater is the increase in the rate of incorporation of the hydrophobic monomer (conversions greater than 90% were achieved). This means that at values of hydrophobic monomer to micelle of much greater than unity, the hydrophobic monomer can be depleted before the end of the polymerization. This results in a highly polydispersed product, and homopolymer is also produced during the reaction.[41-44]

Chapter 2 The Graft Copolymerization of Guar Gum Utilizing Barton Ester Intermediates

2.1 Introduction

Derek Barton first used thiohydroxamic esters (Barton Esters) as free radical precursors [5]. They behave as initiators of free radical polymerizations by adding across the double bond of vinyl compounds. The decomposition of Barton esters by heat or visible light yields alkyl radicals via the mechanism proposed by Barton for decarboxylation.[15] The driving force for the reaction is the formation of the stable S-Sn bond. Polymers functionalized with Barton esters may graft vinyl monomers onto its backbone. The pyridine thiol radical liberated should not initiate homopolymerization of the vinyl monomer. Resulting reactive radicals may be trapped by TEMPO (2, 2, 6, 6-tetramethyl-piperidine-1-oxyl) to form adducts for controlled radical polymerization.[45] Through the use of different carboxylic acid substrates and thiohydroximes, a wide variety of Barton esters can be synthesized, **Figure 2.1**.



Alternate possible structures

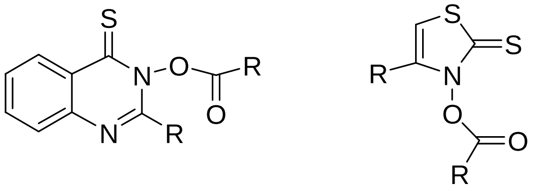


Figure 2.1 Types of Barton esters

Chain reactions involving Barton esters proceed through radical attack at the sulfur of the Barton ester molecule. This attack induces cleavage of the Barton ester's N-O bond. The result is a new liberated radical and the formation of the thiopyridine end group on the attacking species (**Figure 2.2**).

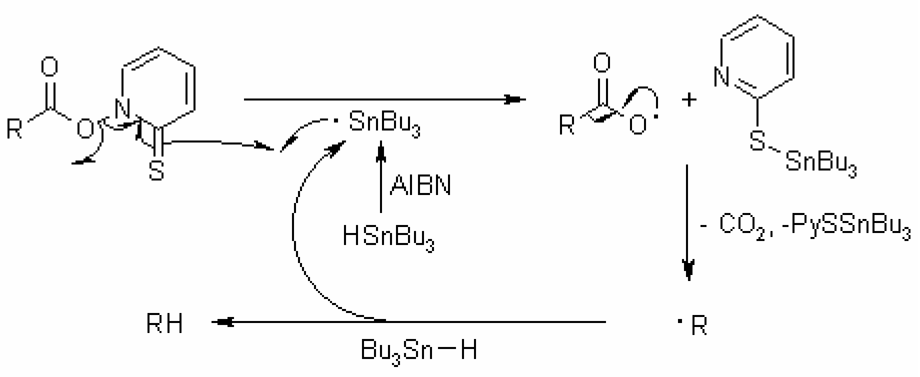


Figure 2.2 The decarboxylation of a Barton ester to produce a carbon-centered radical

Thiohydroxamic carbonate intermediates are employed to promote free radical grafting to guar gum. The molecular architecture and molecular weight of thegrafts may be controlled by varying the concentration of carbonate in the synthesis. The mentioned concept has been applied to grafting of polystyrene to guar. These carbonates behave as both an initiator and a chain transfer agent in the radical polymerization of guar-styrene copolymers. Binding hydrophobic styrene to the hydroxyl group of guar may prevent guar from adhering to the moist walls of the fracture. The bulky polystyrene side chains would be on the outside of cross-linked guar chains. This will allow the walls of the fracture to be coated with oil instead of wet proppant.

The graft copolymers were synthesized from guar gum through radical polymerization, as shown in **Figure 2.3**.

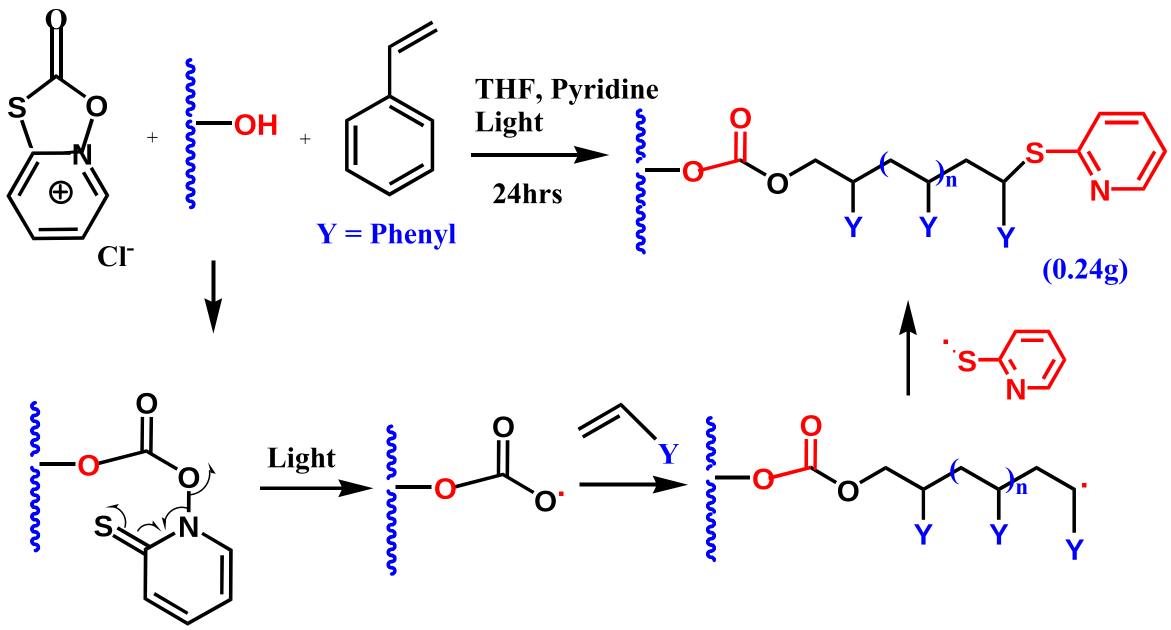


Figure 2.3 Synthesis of a guar – styrene copolymer

The Daly research group has projects which target improving the cleanup and efficiency of guar gum in hydraulic fractures. By modifying guar gum with hydrophobic substituents, it may improve the physical and chemical properties of guar for use as a hydraulic drilling fluid in the oil industry. It is anticipated that hydrophobic interaction will occur among the linear guar chains. The hydrophobic groups, such as styrene, should migrate toward one another in aqueous medium; it may be possible for this aggregation to eliminate the need for cross-linking agent. As oil is pumped through the fracture, the hydrophobic interactions are broken apart and the polymer is washed away with the oil. If the guar gum derivative is not cross-linked, then enzymatic breakers, which break down backbone chains, are not necessary.

2.2 Experimental

2.2.1 Materials

All reagents were obtained from Aldrich chemical company unless otherwise noted. Styrene was passed through a short, inhibitor remover column (to remove catechol), then vacuum distilled. It was then purged with argon before polymerization. Unmodified guar galactomannan was obtained from Dowell Schlumberger and purified by first dissolving in distilled water, centrifuging to remove insoluble matter, precipitating with isopropyl alcohol, and drying under vacuum. All other solid reagents were dried under vacuum. Dichloromethane (DCM) and tetrahydrofuran (THF) were distilled over CaH_2 and stored under argon. Pyridine and dimethyl formamide (DMF) were anhydrous quality.

2.2.2 Characterization

Molecular weights were estimated with gel permeation chromatography (GPC) equipped with a Waters differential refractometer and a Dawn multiangle laser light scattering detector. The dried polymers were dissolved in THF (HPLC grade) and eluted at a flow rate of 0.9mL/min through Phenogel columns (10micron) from Phenomenex.

Proton nuclear magnetic resonance (NMR) was performed on a Bruker 300MHz instrument. Fourier transform FTIR was performed on a Nicolet 320 FTIR spectrometer, utilizing KBr pellets of polymer samples or films cast on KBr plates. Ultraviolet-visible spectroscopy (UV) was performed on a Spectra max plus spectrophotometer.

2.2.3 Synthesis of Carbonic Acid Phenethyl 2-thioxo-2H-pyridin-1-yl Ester

1-oxo-2-oxa-3-thiaindolizinium chloride (0.45g) and pyridine (0.5mL) were added to a solution of 2-phenyl ethanol (6mL) in dried and degassed DCM (25mL). The mixture was stirred at ambient temperature for 2 hours under inert atmosphere. Under vacuum in the absence of heat, solvent was evaporated from the filtered solution. Compounds are light sensitive; all reaction vessels were covered with foil.[11] The reaction produced a viscous, yellow oil (**Figure 2.4**) with a 76%yield (0.43g, d=1.07g/mL). The extinction coefficient was measured to be ϵ=4200 at 320nm. ^{1}H NMR spectrum – 300 MHz ($CDCl_3$) ppm: 2.83 (2H, t), 3.6 (2H, t), 6.8 – 7.2 (4H, m), 7.08 – 7.21 (5H, m).

2.2.4 Control Experiment Using 1-oxa-2-oxo-thiaindolizinium Chloride

In a one pot synthesis, styrene (10mL), 1-oxa-2-oxo-thiaindolizinium chloride (0.32g), DMF (2mL), and pyridine (0.5mL) were added to THF (20mL). Solution stirred exposed to visible light in an argon atmosphere twelve hours. After evaporating 10mL of solvent from solution, the polymer was precipitated into methanol. A 25% conversion to a fine white powder (2.42g) with a molecular weight of 32,000 was obtained. IR (KBr): 3059, 3025, 2923, 2849 cm^{-1} (C-H), 1738cm^{-1} (C=O), 1600, 1492, 1452cm^{-1} (aromatic), 1250cm^{-1} (C-O), 1180cm^{-1} (guar-S), 1028cm^{-1} (C-N).

2.2.5 Guar – graft – styrene (with Phenyl Ethyl Carbonate)

2-phenyl ethanol (6mL), 1-oxo-2-oxa-3-thiaindolizinium chloride (0.45g), and pyridine (0.5mL) were added to a solution of guar gum (0.60g) in THF (60mL). The reaction was stirred in the dark at 60ºC for 12 hours under argon atmosphere.[18,19] After the conversion to Barton carbonate was confirmed by UV spectroscopy (0.2mg/mL polymer in THF, 320nm, ϵ=4200, A=1.32), the solvent was removed by rotary evaporation. ^{1}H NMR spectrum: ($CDCl_3$) ppm: 1.40 (4H, m), 2.5 (2H, d), 3.3 – 3.5 (3H, m), 3.6 (2H, d), 3.88 (2H, s), 5.4 (2H, d), 5.6 (2H, d), 7.9 - 8.6 (4H, m). The resultant polymer residue was dissolved in 42g stock solution of 75 mole % styrene in DMF. The solution was purged with argon, then exposed to visible light at room temperature for 24 hrs. The solution was concentrated to approximately 10mL and poured into 200mLof methanol to precipitate the polymer. The polymer was filtered and dried under vacuum at room temperature (8.98g). The polymer (a soft white powder) was analyzed by FT-IR, NMR, and GPC. IR (KBr): 3400cm^{-1} (O-H), 3025, 2922cm^{-1} (C-H), 1743cm^{-1} (C=O), 1600, 1491, 1450, 757, 698cm^{-1} (aromatic), 1250cm^{-1} (C-O), 1180cm^{-1} (guar-S), 1028cm^{-1} (C-N). NMR 300 MHz ($CDCl_3$) ppm: 1.4 (1H, s), 3.3 (3H, m), 5.3 (2H, t), 5.7 (1H,d), 7.8 – 8.2 (5H, m).

2.2.6 Guar – graft – styrene (One Pot Synthesis)

Guar gum (1g), styrene (1mL), 1-oxa-2-oxo-thiaindolizinium chloride (0.35g), pyridine (0.5mL), and DMF (0.5mL) were dissolved/slurried in THF (25mL). The mixture was purged with argon and exposed to light for 24 hrs. The solution was filtered to recover a light yellow solid product (1.16g). IR (KBr): 3400cm^{-1} (O-H), 3025, 2922cm^{-1} (C-H), 1280cm^{-1} (C-O). A second product was retrieved by precipitating the polymer dissolved in the filtrate with methanol. The beige powder (0.24g) was dried and characterized. FT-IR (KBr): 3400cm^{-1} (O-H), 3025, 2922cm^{-1} (C-H), 1743cm^{-1} (C=O), 1600, 1491, 1450, 757, 698cm^{-1} (aromatic), 1280cm^{-1} (C-O), 1028cm^{-1} (C-N). NMR 300 MHz (dTHF) ppm: 1.4 (1H, s), 3.3 (3H, m), 5.3 (2H, t), 5.7 (1H, d), 7.8 – 8.2 (5H, m), 10.9(1H, s).

2.3 Results and Discussion

The Daly group has been successful with grafting styrene and other monomers to cellulose derivatives. The use of Barton ester compounds, as initiator and chain transfer agents[7], was instrumental in producing the grafts. The Barton esters were used to initiate polymerizations thermally and photolytically. They terminated each chain with a pyridinesulfide functional group.[10] The research on the cellulose grafts serves as an important reference for research involving grafting onto guar gum. Structurally, guar and cellulose are similar, both are water soluble, but it has been more difficult performing reactions on modified guar gum in organic solvents.

A novel thiohydroxamic compound has been synthesized in the Daly lab, modeled after Barton esters. A hydroxyl group of a guar polymer chain attacks the carbonyl center of cyclic thiocarbonate. This carbonate intermediate was used as initiator and chain transfer agent in the grafting of polystyrene to guar gum (**Figure 2.4**).[9] Upon exposure to visible light, the carbonate decomposes forming two radicals, a carbonyl radical and a pyridine sulfide radical. In the presence of styrene, the carbonate initiated radical polymerization begins, resulting in styrene grafted guar. The polystyrene chains are terminated by the pyridine sulfide radical.

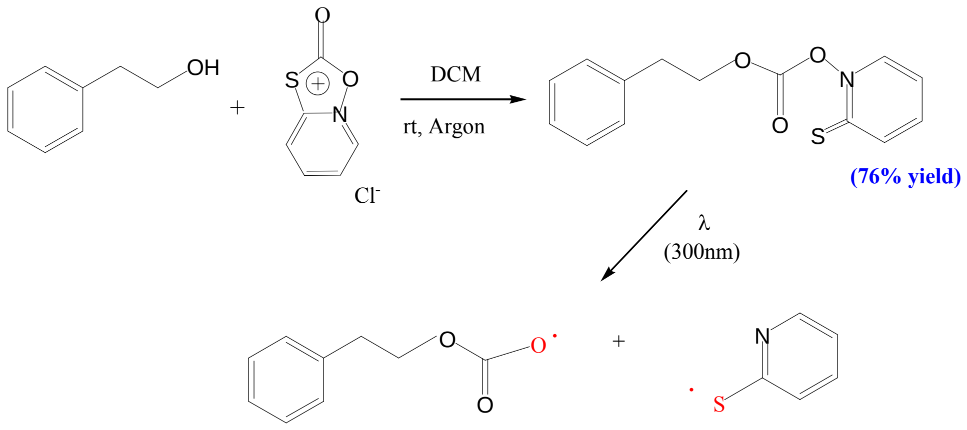


Figure 2.4 Reaction of carbonic acid phenethyl 2-thioxo-2H-pyridin-1-yl ester

- **Reaction of model compound with styrene**

The thiohydroxamic carbonate initiated polystyrene had an average molecular weight of 32,000; while, a polystyrene standard prepared under comparable conditions using AIBN as an initiator had an average molecular weight of 90,000. The dramatic difference in molecular weights may be attributed to chain transfer by the thiohydroxamic compound. The ability of the compound to perform as a chain transfer agent was demonstrated in this exercise.

- **Reaction of model compound with styrene in the presence of guar**

Little or no grafting occurred. The intended reaction was overshadowed by a large amount of homopolymerization of styrene. A large amount of styrene was used in the reaction, relative to the amount of guar. Increased amounts of guar could lead to aggregation of linear guar chains. Some degree of thermally initiated polymerization is possible, but the reaction time frame did not allow so much styrene to homopolymerize without being initiated.

- **Ability of the cyclic carbonate to initiate polymerization**

Analyzing the polystyrene revealed that it was initiated by the carbonate radical. It was confirmed by the presence of a carbonyl group at 1738cm^{-1} in the FT-IR spectrum (**Figure 2.5**). To investigate the phenomena, an alternate procedure was designed to produce polystyrene initiated by ester radicals of the decomposed thiohydroxamic ester.

- **One-pot reaction with guar and styrene**

A one-pot method was used in an attempt to produce guar-graft-styrene. Binding styrene to chains of guar would allow guar to become semi-soluble in the THF solvent used in the reaction. The guar remained on top of the styrene solution for the majority of

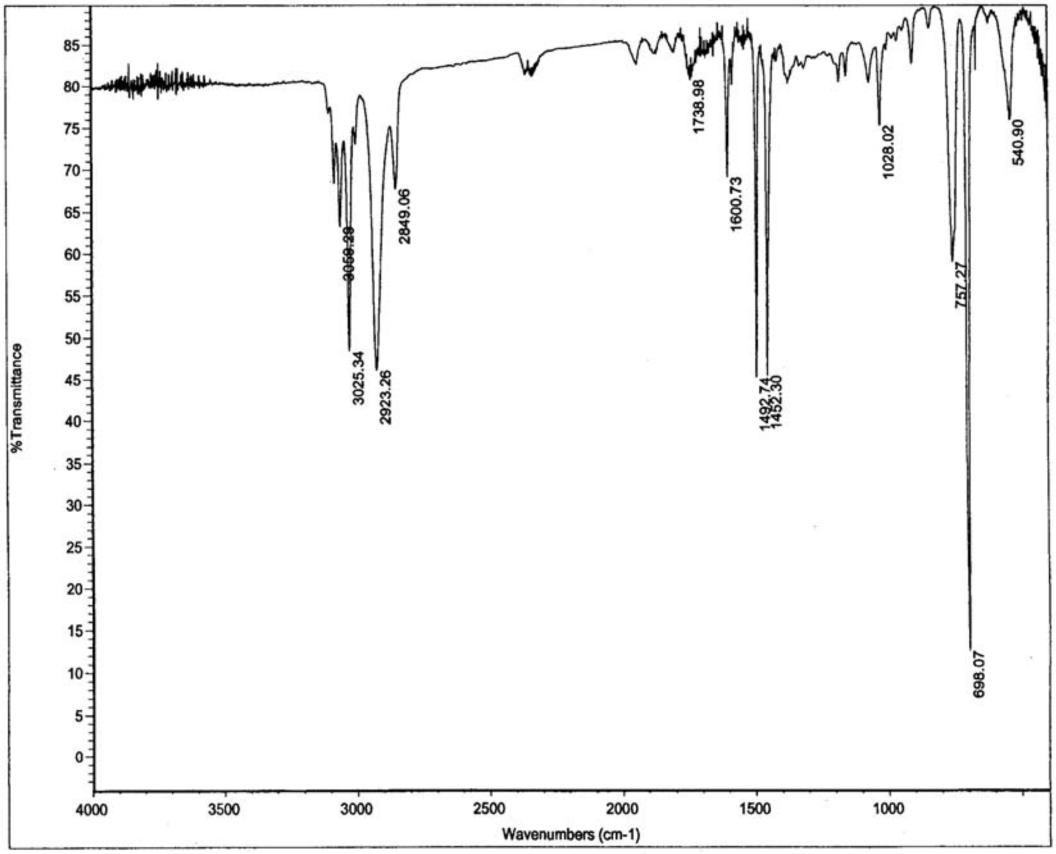


Figure 2.5 FT-IR of polystyrene initiated by the benzoyloxy radical

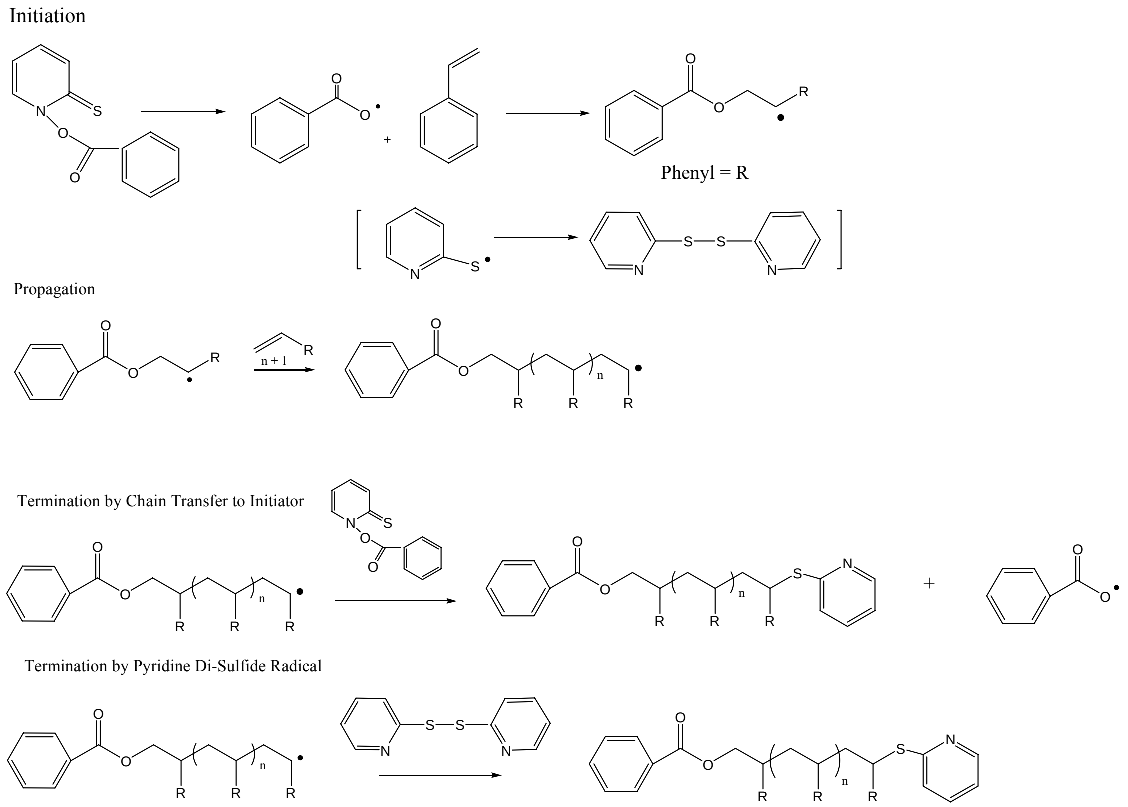


Figure 2.6 Homopolymerization mechanism

the reaction time. A physical change was noticed for both the solid (color changed from white to yellow) and the liquid (color change of light orange to dark orange and liquid appeared heavier) components of the reaction.

Two distinctively different products were obtained. The solid (58% yield), which was filtered from the THF solution, was proven to be guar gum by FT-IR spectrum. It is virtually identical to the FT-IR spectrum of the reagent grade guar gum (**Figure 2.7**), but there was a definite color change and change in texture. The guar gum retrieved from solution was a fine yellow powder, which differs in appearance from the white, short, thin fibers of the reagent guar gum. In order to discern the presence of initiator on the guar gum chains, molecular weights of both samples must be obtained. An increase in molecular weight of the guar from the reaction would confirm the presence of grafting. The majority of recovered material was guar.

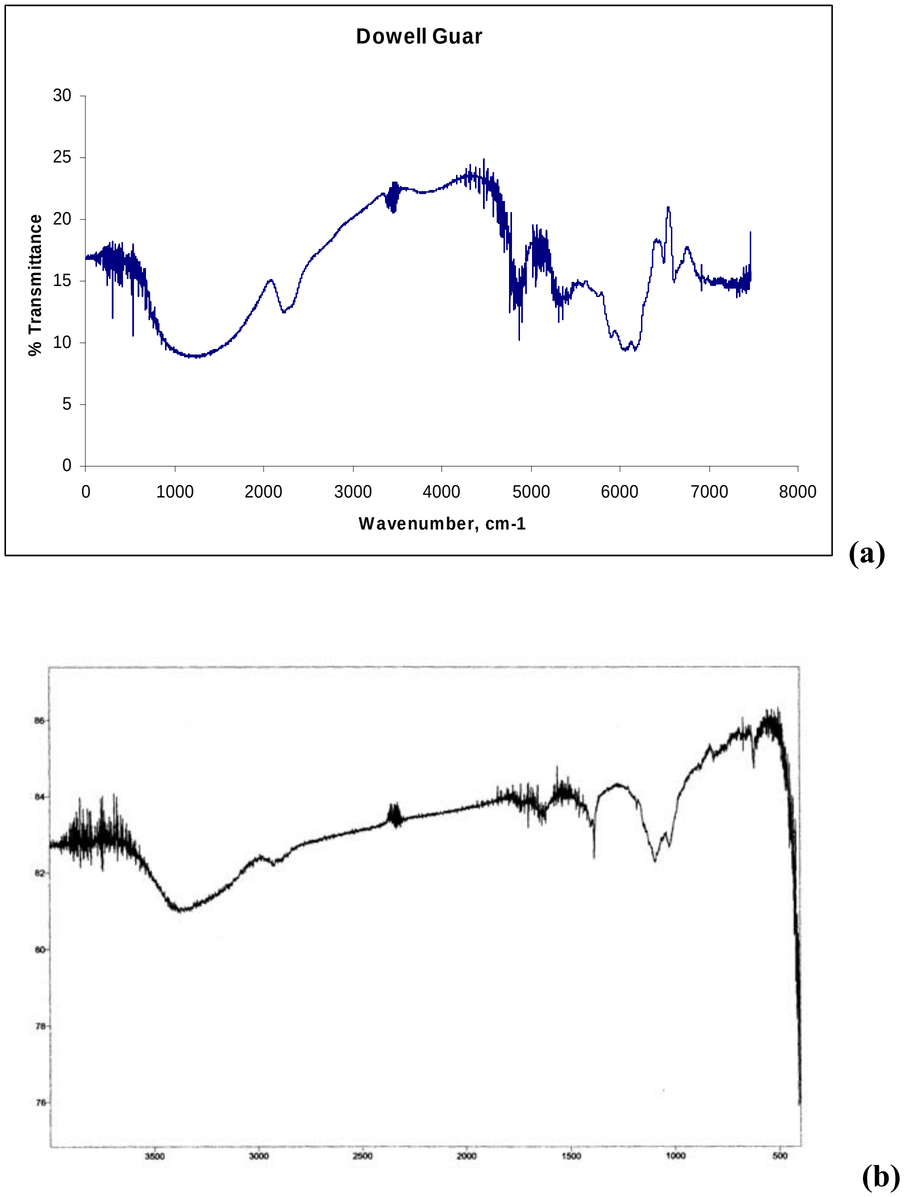


Figure 2.7 FT-IR spectrum of (a) reagent grade guar gum (b) guar gum product

The second material was precipitated from methanol. FT-IR analysis provided a spectrum with both guar and styrene peaks (**Figure 2.8**). Initiation of the styrene grafted to the guar gum produced only a small amount of grafted material (12% yield). The procedure must be revised to provide a better solvent system for guar and conditions must be optimized to provide a better environment for grafting. In situ initiated synthesis of guar did avoid homopolymerization of styrene.

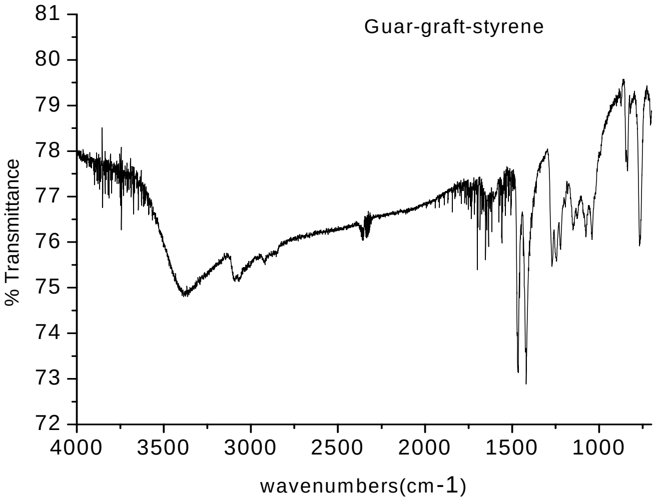


Figure 2.8 FT-IR of guar copolymer

Characterization of the compounds relied heavily on FT-IR analysis. This provided confirmation of the presence of certain functional groups in a material. It was difficult to get well resolved peaks of the carbohydrate backbone from NMR analysis, because the spectra were dominated by the polystyrene resonances. We are searching for a suitable solvent system for the modified guar gum samples, so that molecular weights may be obtained by GPC. An attempt to verify the structures of the end groups by MALDI has not been successful because the molecular weight of the sample was too high. Low molecular weight samples can be provided using higher concentrations of initiator.

2.4 Future Research

It has been established that modifying guar gum may improve hydraulic drilling fluids and polymer recovery from fractured wells. Addition of the appropriate hydrophobic substituents to guar gum may lead to an alternate mode of cross-linking, resulting from hydrophobic interactions. Other hydrophobic monomers, such as methyl methacrylate and butyl acrylate, may be used as an alternative to styrene. The ideal ratio of monomer concentration to polymer concentration has to be established, in order to obtain the most efficient grafting system.

Basic applications and limitations of Barton esters as initiators of polymerizations have been explored, but several factors remain. Other hydroximes may be used in place of the oxypyridinethione unit. Changes there will affect absorbance wavelength and initiation rate. Kinetics of polymerization was determined to be independent of initiator concentration, but may be dependent upon monomer concentration. Further research is needed to determine the extent Barton cyclic carbonate initiate homopolymerizations.

The graft copolymers formed have had limited analysis of their properties. The impact of hydrophobic substituents on the rheology and shear sensitivity of guar must be determined, so that the performance of the materials as dispersing fluids in a fractured well may be evaluated through modeling. Chain lengths must be compared to determine which type of grafted material would be more effective, multiple short chains or few long chains.

Chapter 3 Nitroxide-Mediated Grafting onto Guar Gum and Guar Gum Derivatives in Aqueous Media

3.1 Introduction

The goal of this project is to design hydrophobically modified polysaccharides (HMP) to be used as a hydraulic fracturing fluid in oil and gas applications. A hydraulic fracturing fluid for rock formations to enhance oil recovery (EOR) is comprised of viscosifier, gelled derivatized guar gum, and sand particles (proppants). The gel is mixed with proppant (sand) and pumped at high rate and high pressure into an oil/gas well to the hydrocarbon-producing zone. The applied pressure will force the rock formation to fracture allowing entry of the guar gel/sand mixture. The mixture then fills the resultant fracture.[46] The viscosity of the mixture must be sufficient at this point in the process to prevent the settling of the sand particles. The pressure is then released, allowing closure of the fracture onto the guar/sand mixture.[47] Leaving the guar gel in the fracture zone will block the pores, causing formation damage and a resultant decrease in oil or gas production. Thus, to complete the process, guar gum must be degraded chemically and/or thermally, and then flushed from the formation back to the surface. If the degradation of the guar gum yielded a surfactant, removal of the guar gum fragments would be facilitated by emulsification. This objective is achieved by introducing hydrophobic substituents, such as polystyrene and poly-n-butyl acrylate, to the polymer backbone of CMG. The increased hydrophobicity may improve the fluid loss control as well as provide the potential for surfactancy.

Many literary citations exist for the synthesis of guar gum grafted with both hydrophilic and hydrophobic monomers, such as methacrylate, methyl methacrylate, acrylic acid, and polyacrylonitrile. Guar gum copolymerizations have been initiated by hydrogen peroxide, peroxydiphosphate (PDP)-silver(I) system, and ceric ammonium nitrate (Ce (IV)). The silver ion of the PDP system may lead to a decrease in the degree of polymerization (DP) of the copolymer, by complexing with carboxylic groups of the grafted chains and blocking access to free radical sites. The previously mentioned initiators can not accurately control the molecular weight or DP of a polymeric product without being apart of a bimolecular system, such as the redox system consisting of an initiator and a mediating species, dextrose monohydrate (DM). Those initiators, when used alone, also lead to the production of large quantities homopolymer. Homopolymer is still produced with the redox system, although a smaller amount. Chowdhury and co-workers have reported grafting efficiency of 65% for copolymers produced from the radical reactions initiated by the Ce(IV)/DM redox pair.[26,48-50]

3.1.1 Nitroxide Mediators in Controlled Radical Polymerizations

Synthesizing well defined polymers with architectural control is made possible through controlled radical polymerization (CRP), also referred to as living free radical polymerizations. The term “living polymerization” refers to the free radical polymerization proceeding until all of the monomer has been consumed. Further addition of the monomer results in continued polymerization, because the kinetic steps of termination or chain transfer are absent in controlled radical polymerizations.[51-53] End group control on a polymer may be established through controlled radical polymerizations, which enable the synthesis of macromolecules, such as block copolymers, by sequential monomer addition (monomer is added to the polymeric chain one monomeric unit at a time). In addition to controlling terminal functionality, CRP offer opportunities for topological design (such as linear, star shaped, comb shaped, dendrite, cyclic, etc.), arrangement of co-monomers (as block, graft, gradient), molecular weight determination, and narrow polydispersity.[54-59]

Interactions between radical chains are very fast and one chain easily reacts with another growing chain. Those interactions result in unwanted chain termination and prevent conventional free radical polymerization from being able to control the molecular weight and the polydispersity of the polymer.[53,60,61]

Scheme 3.1 General reaction for controlled radical polymerizations

Initiation $\quad R - S \text{ (unimolecular initiator)} \xrightarrow{H\nu\ /\Delta} R^{\cdot} \text{(unstable radical)} + S^{\cdot} \text{ (stable radical)}$

$\quad R^{\cdot} + \text{Monomer (M)} \xrightarrow{K_i} R - M^{\cdot}$

Propagation $\quad R - (M)_{n-1} - M^{\cdot} + M \xrightarrow{K_p} R - (M)_n - M^{\cdot}$

Reversible Deactivation

$$R - (M)_n - M^{\cdot} + S^{\cdot} \overset{K_t}{\rightleftharpoons} R - (M)_{n+1} - S$$

The ability of stable ditertiary alkyl nitroxides (most notably TEMPO) to scavenge radicals to give stable alkoxyamine procucts was first reported by Neiman and Rozantsev.[31,53,61] The use of the TEMPO radical as a reversible trapping agent in radical polymerizations for a variety of monomers was reported by Rizzardo and Solomon.[56,62] The key features of nitroxide-mediated free radical polymerizations are thermal stability, non-reactivity towards carbon-centered free radicals, and resistance to free radical attack. The nitroxide free radical does not initiate the growth of any extra polymer chains, which ensure production of material with narrow polydispersities from CRP.[31,53,61]

The nitroxide-mediated free radical polymerization of styrene has been studied extensively by many research groups, such as those led by Georges, Sawamoto, and Matyjaszewski. TEMPO-mediated polymerization of styrene proceeds by the initiation of a chain by a primary radical derived from an initiator, such as benzoyl peroxide. The primary radical reacts with styrene to form a carbon-centered radical adduct, **3**, and this is then trapped by a nitroxide molecule to form a unimer. It is possible for more than one monomer unit to be added before the nitroxide reacts, forming an oligomer. The labile bond between the monomer unit and the nitroxide fragment freely dissociates upon continued heating at 125ºC. More monomer is added to the growing chain before it is capped by the nitroxide. The cycle is repeated until all of the monomer is consumed or the reaction mixture is cooled (below 125ºC).[56,61,63]

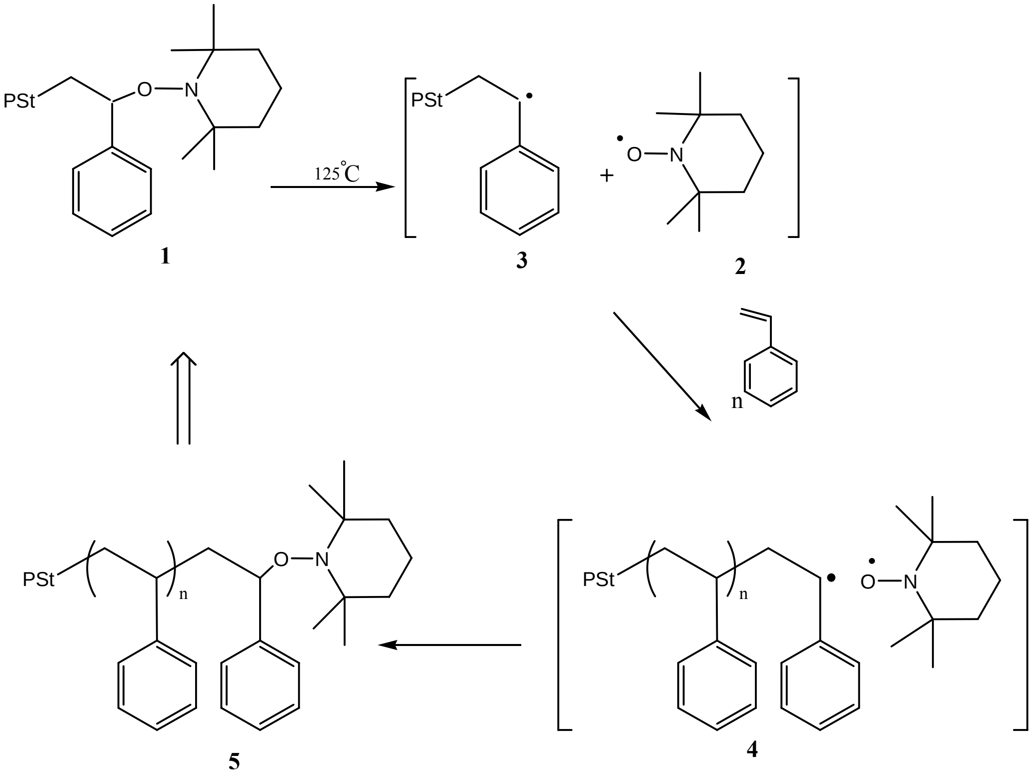
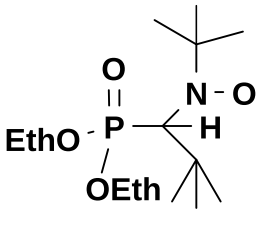
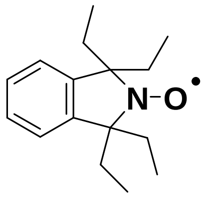


Figure 3.1 TEMPO-mediated living radical polymerization of styrene

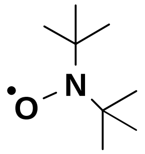
More efficient nitroxides have been discovered, which are suitable for more monomers and can meet specific thermal demands of a radical polymerization. A severe limitation of TEMPO-mediated radical polymerizations is that it only functions appropriately with styrene and dienes. Another limitation of the TEMPO system is the high strength of the C–ON bond. If the bond is too stable to homolytic cleavage, then initiation is slow compared to propagation and samples with broad polydispersities are obtained.[57,64] High temperatures are required for TEMPO-mediated radical polymerizations, 120 - 140ºC. At such high temperatures, some compounds, especially natural products, employed in the controlled radical polymerization may degrade and thermal initiation may also be a possibility.[65] Other nitroxide possibilities for CRP include N-tert-butyl-N-(1-diethylphosphono-2,2-dimethyl propyl) nitroxide (DEPN)[66-69], **6**, 1,1,3,3-tetramethyl isoindolinyl-2-oxy radical, **7** , and ditertiary butyl nitroxide (DTBN), **8**. The optimum temperature range for CRP mediated by DTBN and DEPN is 90 – 100 ºC, which is significantly lower than TEMPO-mediated CRP. DEPN has efficiently controlled the free radical polymerization of n-butyl acrylate through the method of reversible chain termination. Grimaldi and associates have prepared block copolymers of n-butyl acrylate and have reported that DEPN is more efficient than TEMPO in the CRP of styrene.[57,58,61,70,71]



6



7



8

The nitroxide mediators used for the purpose of controlling the grafting of hydrophobic groups onto the guar gum and/or CMG backbone do not initiate radical formation on the polysaccharide. An external initiating system is required to begin the radical polymerization process needed to produce a hydrophobically modified guar gum material. Ce(IV) may be used to initiate the free radical polymerization by forming a coordination complex with guar gum. The Ce(IV) would be reduced to Ce(III), creating a free radical on the guar gum backbone (**Figure 3.2**).[72]

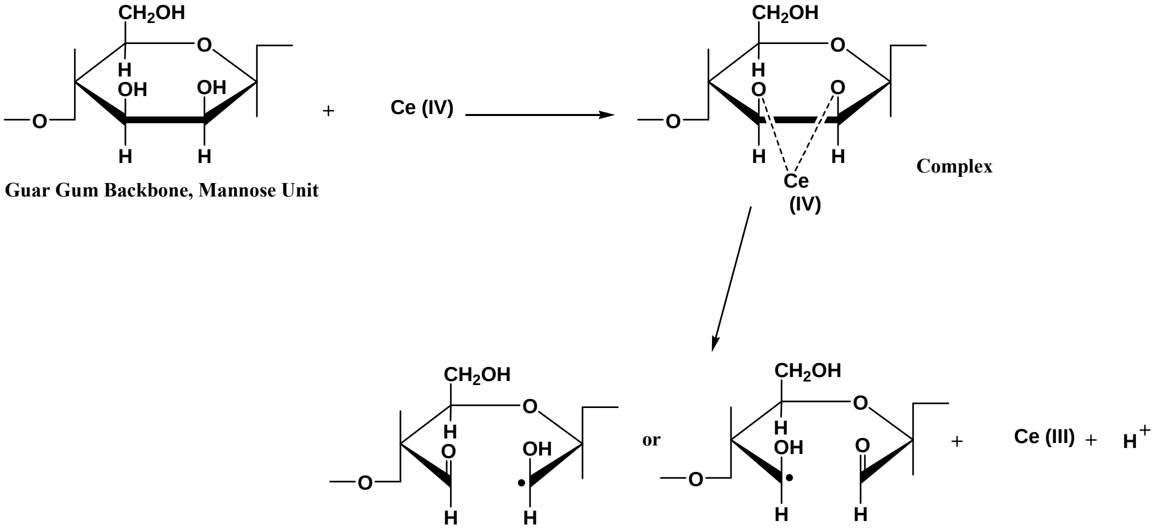


Figure 3.2 Ce(IV) ion initiated graft copolymerization

3.2 Experimental

Materials. All reagents were purchased from Aldrich or Acros. Inhibitor was removed from the monomer using Aldrich inhibitor remover packing resin (for HQ and HEQ removal). CMG, degree of substitution (D.S.) 0.293 (lot #3514) was obtained from Hercules. All other reagents were used without further purification. All solvents were dried using standard laboratory procedures.

Instrumentation. ^{1}H NMR (250MHz) spectra were obtained on a Bruker DPX 250. FT-IR results were obtained from a Bruker Tensor 27. A Bruker Proflex was used to obtain

MALDI data. A Waring industrial blender was used to mix reaction mixtures at high shear rate for the radical polymerization reactions. Elemental analysis samples were submitted to Huffman Laboratories, Golden, CO 80403. Viscosities were measured on the Brookfield PVS003 rheometer.

3.2.1 Graft Polymerization of Styrene onto Guar Gum via Ceric Ammonium Nitrate Initiation (A)

Guar gum (0.524g), styrene (5mL), and water (250mL) were mixed for 20 minutes on high speed using an industrial blender. The guar gum mixture was placed in a three-neck round bottom flask equipped with a condenser, stir bar, and thermocouple in an inert environment (N_2) and heated to 40ºC for 10 minutes. To initiate the grafting process, a 7% molar solution of ceric ammonium nitrate (CeIV) (0.113g) in 1M nitric acid (HNO_3) was added to the flask; the reaction mixture was heated for 5 hours at 40ºC. The reaction mixture was cooled, concentrated by rotary evaporation (rotavaped) to remove excess water, and the product mixture was dialyzed in water for 48 hours. Homopolymer was removed from the grafted product by Soxhlet extraction with 200mL of dichloromethane (DCM) at 45ºC for 24 hours.

Purified grafted product (1.541g) was recovered for a weight gain of 194% (the difference of the amount of backbone material and polysaccharide divided by the weight of polysaccharide) and a grafting efficiency of 89.7%. FT-IR (KBr, cm^{-2}): 3447(w, OH), 3082(C-H), 2894(aromatic(ar), CH), 1610(ar, CH), 1492(CH), and 1069(CO).

3.2.2 TEMPO Controlled Graft Polymerization of Styrene onto Guar Gum via Ceric Ammonium Nitrate Initiation (B)

Guar gum (0.459g), styrene (5mL), and water (250mL) were combined in an industrial blender and mixed on high for 20 minutes. One molar equivalent of tetramethyl piperdinyl oxide (TEMPO) was added to the reaction mixture and blended an additional five minutes. The reaction mixture was poured into a 3-neck round bottom flask equipped with a stir bar, condenser, and thermocouple and heated to 42ºC under a nitrogen atmosphere. At 45ºC a 7% molar solution of ceric ammonium nitrate (CeIV) (0.113g) in 1M nitric acid (HNO_3) was added to the flask; the reaction mixture was heated for 24 hours at 45ºC. Excess solvent was rotavaped from the reaction mixture and the product was precipitated in methanol, filtered, and vacuum dried at room temperature for 24 hours. The dried polymer was placed in a 3-neck round bottom flask equipped with a stir bar, condenser, and thermocouple, 125mL of n-xylene was added, and reaction mixture was heated to 125ºC under a nitrogen atmosphere. The modified guar gum material adhered to the sides of the flask, and a homogeneous reaction mixture was not established. NMR (CDCl3)δ(ppm): polystyrene(6.8, 1.84, 1.67, 1.26), sugar backbone(3.75 – 3.65).

3.2.3 TEMPO Controlled Graft Polymerization of n-Butyl Acrylate onto Guar Gum via Ceric Ammonium Nitrate Initiation (C)

Guar gum (0.521g), butyl acrylate (5mL), and water (250mL) were combined in an industrial blender and mixed on high for 20 minutes. One molar equivalent of TEMPO was added to the reaction mixture and blended an additional five minutes. The reaction mixture was poured into a 3-neck round bottom flask equipped with a stir bar, condenser, and thermocouple and heated to 45ºC under a nitrogen atmosphere. At 45ºC a 7% molar solution of ceric ammonium nitrate (CeIV) 0.113g in 1M nitric acid (HNO_3) was added to the flask; the reaction mixture was heated for 2 hours. Excess water was rotovaped from the reaction mixture and the product was precipitated out in methanol, filtered, and vacuum dried at room temperature for 24 hours. The dried polymer was placed in a 3-neck round bottom flask equipped with a stir bar, condenser, and thermocouple, 125mL of n-xylene was added, and reaction mixture was heated to 125ºC under a nitrogen atmosphere. The modified guar gum material adhered to the sides of the flask, and a homogeneous reaction mixture was not established. NMR (CDCl3)δ(ppm): poly-n-butyl acrylate (2.2, 1.54, 1.25, 0.98) and sugar backbone (3.8 – 3.6).

3.2.4 Synthesis of N-tert-butyl-N-(1-diethylphosphono-2,2-dimethyl propyl) Nitroxide (DEPN) (D)

The procedure used for synthesizing DEPN was developed from the works of Benoit and Guerret as written both in the patent for the compound and literary references.[66,67,69] Pivaldehyde (4mL) was placed in a 3-neck round bottom flask, equipped with a dropping funnel, condenser, stir bar, reflux condenser, and thermocouple, purged with nitrogen. Tert-butylamine (3.8mL) was added dropwise at ambient temperatures. The mixture was heated to 35ºC for 2 hours and the aqueous phase that formed was removed.

The intermediate and diethyl phosphate (5.47g) were heated to 75ºC for 4 hours. The absence of imine was confirmed by ^{1}H NMR to ensure that the reaction went to completion. The product solution was diluted with 10mL of diethyl ether and washed twice with saturated sodium bicarbonate solution (3mL). The solution was dried over magnesium sulfate ($MgSO_4$) and the solvents were rotary evaporated to yield the amine intermediate as an oil.

The amine was dissolved in 4.0mL of DCM and cooled to 0ºC. A solution of m-chloroperoxybenzoicacid (5.74g) in 20mL of DCM was slowly canulated into the reaction flask; upon addition, the reaction mixture became yellow. The reaction was allowed to warm to room temperature and stirred 1.5 hours with enough DCM to dissolve any precipitate. Anhydrous sodium carbonate (3.519g) was added to the solution and the bright orange mixture was shaken with 10mL saturated sodium bicarbonate solution until all solids were dissolved. The organic layer was dried over MgSO4, and the solvent was removed for yield DEPN as an orange oil (44% yield).

DEPN was purified by flash chromatography; the compound was eluted with 2:1 hexane/ethyl acetate solution, and a molybdenum stain was used to detect the compound. The NMR data collected on DEPN is consistent with the literature[57,66,70,71]. NMR (CDCl3)δ(ppm)4.2(2H, CH_2), 2.7(1H, CH), 1.4(4H, CH_2), 1.2(6H, CH_3), 1.4(9H, CH_3), 1.2(9H, CH_3).

3.2.5 DEPN Controlled Polymerization of Acrylamide onto Carboxymethyl Guar Gum via Ceric Ammonium Nitrate Initiation (E)

CMG (degree of substitution, DS, 0.293), (1.125g), acrylamide (5g), and water (450mL) were mixed for 20 minutes on high speed using an industrial blender. One molar equivalent of DEPN (0.6mL) was added to the reaction mixture and blended an additional five minutes. The CMG mixture was placed in a three-neck round bottom flask equipped with a condenser, stir bar, and thermocouple in an inert environment (N_2) and heated to 95ºC for 10 minutes. To initiate the grafting process, a 7% molar solution of ceric ammonium nitrate (CeIV) (0.113g) in 1M nitric acid (HNO_3) was added to the flask; the reaction mixture was heated for 24 hours at 95ºC. The reaction mixture was cooled, rotavaped, and the concentrated product mixture was freeze dried for 24 hours to remove remaining water. The amount of homopolymer recovered from the product was negligible; therefore, Soxhlet extraction of the product was not necessary. A white powder weighing 2.195g was produced (107% weight gain). ^1H NMR (D_2O), δ: 1.7(2H, CH_2), 2.19(2H, CH_2), 3.8(H_2C-O), 2.8 – 3.0(NCHP).

3.2.6 Synthesis of DEPN Controlled Polymerization of n-Butyl Acrylate onto Carboxymethyl Guar Gum via Ceric Ammonium Nitrate Initiation (F)

CMG, (DS 0.293), (1.067g), n-butyl acrylate (5mL), and water (450mL) were mixed in the blender for 20 minutes (maximum speed). One molar equivalent of DEPN (0.06mL) was added to the reaction mixture and blended an additional five minutes. The CMG mixture was placed in a three-neck round bottom flask equipped with a condenser, stir bar, and thermocouple under nitrogen and heated to 95ºC for 10 minutes. To initiate the grafting process, a 7% molar solution of ceric ammonium nitrate (CeIV) (0.113g) in 1M nitric acid (HNO_3) was added to the flask; the reaction mixture was heated for 24 hours at 95ºC. The reaction mixture was cooled, rotary evaporated, and the concentrated product mixture was freeze dried for 24 hours to remove remaining water. The amount of homopolymer recovered from the product was negligible; therefore, Soxhlet extraction of the product was not necessary.

The CMG-g-butyl acrylate product (1.361g) had a weight gain of 27.6%. The amount of phosphorous present on the graft was 0.14%, which is from the DEPN terminating polystyrene chains grafted to the CMG backbone of the polymer. The graft was cleaved with the enzyme mixture pyrolase$^{\text{TM } 200}$. Pyrolase was added to a 1% copolymer aqueous solution between pH 5 – 8, then the solution was heated 2 hrs at 70ºC. The side chains were then extracted with toluene. It was determined through MALDI that the butyl acrylate side chains had an average molecular weight of 600, which includes the sugar moiety attached to the side chain, and a degree of polymerization (DP) of 3. ^{1}H NMR ($CDCl_3$), δ: 0.8(m, 3H), 1.26(6H), 1.6(1H), 3.7(t, 2H). FT-IR (KBr, cm^{-1}): 3384(w, OH), 2913(CH), 1636(carbonyl).

3.2.7 Controlled Polymerization of Lauryl Acrylate onto Carboxymethyl Guar Gum (G)

CMG (3.0g), D.S. 0.293, lauryl acrylate (3mL), and water (1L) were mixed for 20 minutes on high speed using an industrial blender. One molar equivalent of DEPN (0.6mL) was added to the reaction mixture and blended an additional five minutes. The CMG mixture was placed in a three-neck round bottom flask equipped with a condenser, stir bar, and thermocouple in an inert environment (N_2) and heated at 95ºC for 10 minutes. To initiate the grafting process, a 7% molar solution of ceric ammonium nitrate (CeIV) (0.115g) in 1M nitric acid (HNO_3) was added to the flask; the reaction mixture was heated for 24 hours at 95ºC. The reaction mixture was cooled, concentrated to remove excess solvent, and the concentrated product mixture was freeze dried for 24 hours. The resulting polymer product weighed 3.937g, with a weight gain of 44.78%.

3.3 Results and Discussion

Guar gum is not completely water soluble; the polysaccharide swells in water. When introduced to water the guar chains tend to aggregate, preventing complete solvation by water molecules. Grafting hydrophobic monomers onto guar gum with a low DP produced copolymers with better water solubility than guar gum alone. CMG was evaluated for hydrophobic modification through controlled radical polymerization and compared to the performance of hydrophobically modified guar gum. CMG is more water soluble than guar gum, which enabled copolymers with higher viscosities than the hydrophobically modified guar gum copolymers to be produced by controlled radical polymerizations (CRP).

Grafting a hydrophobic monomer onto the backbone of a polysaccharide by CRP presents several obstacles. The most obvious challenge was selecting an appropriate solvent. Hydrophilic guar gum does not swell well enough in organic solvents (THF, DMF, and DMSO) to allow the hydrophobic monomer (n-butyl acrylate or styrene) to properly grow onto the guar backbone. Performing the CRP of styrene onto guar gum in aqueous media eliminated using Barton Esters as chain transfer agents, to control the molecular weight of the product[73]. Ceric ammonium nitrate is a water soluble initiator, and it was cited to have initiated guar gum copolymerizations in water.[48,50]

3.3.1 Ceric Ammonium Nitrate Initiation of Free Radical Polymerizations

The grafting of polystyrene onto guar gum via ceric ammonium nitrate (Ce(IV)) initiation **(A)** in a free radical polymerization was successful. The radical polymerization proceeded rapidly without any control mechanism. The resulting polystyrene side chains are of varying lengths, **Figure 3.3**. The reaction also produced polystyrene homopolymer, which was removed by Soxhlet extraction as described in **3.2.1**. A comparison of the FT-IR of guar gum, **Figure 3.4**, to the FT-IR of the guar gum, polystyrene copolymer, **Figure 3.5,** confirms the presence of polystyrene side chains grafted onto the guar gum backbone. The hydroxyl groups of the guar gum backbone shows up at 3450 (OH)cm^{-1} and the aromatic groups of polystyrene display peaks at 2894 and 1610 (CH)cm^{-1}.

To select the optimum initiator concentration for conducting free radical polymerizations of styrene onto guar gum, grafting efficiency, extent of solubility, amount of homopolymer produced, and amount weight gained after polymerization were

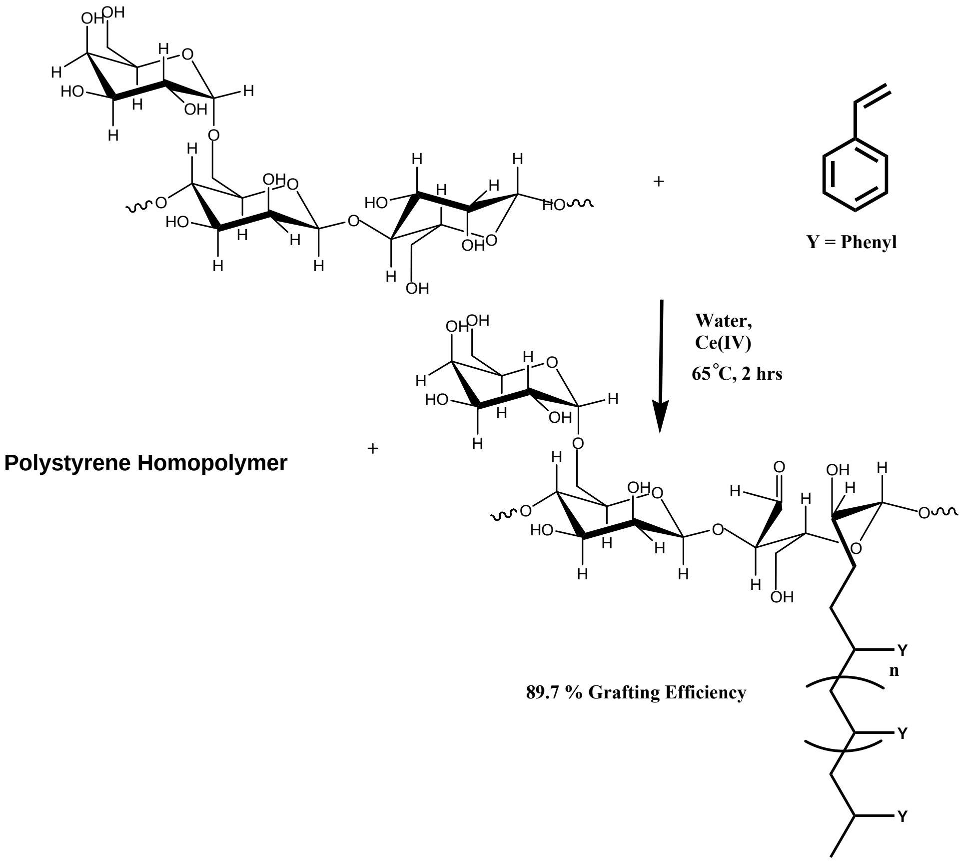


Figure 3.3 Free radical polymerization of polystyrene onto guar gum

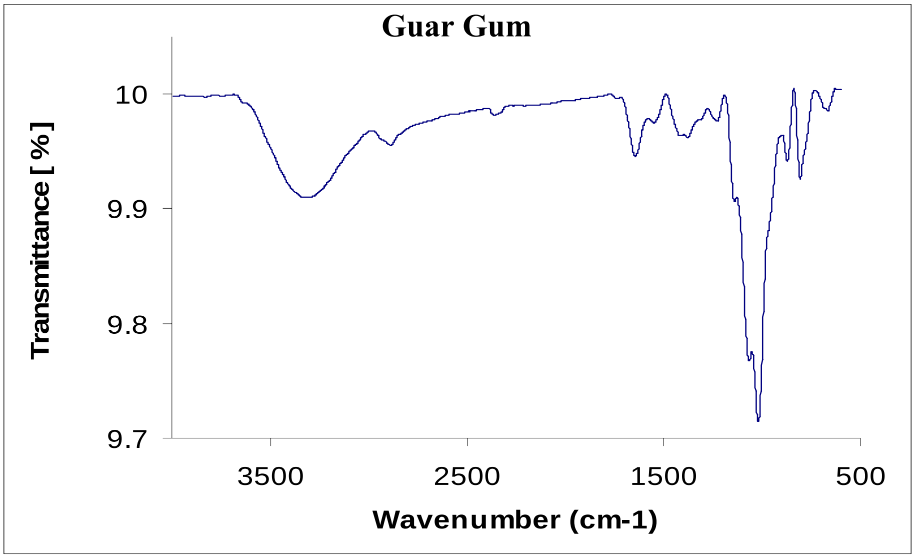


Figure 3.4 FT-IR of guar gum

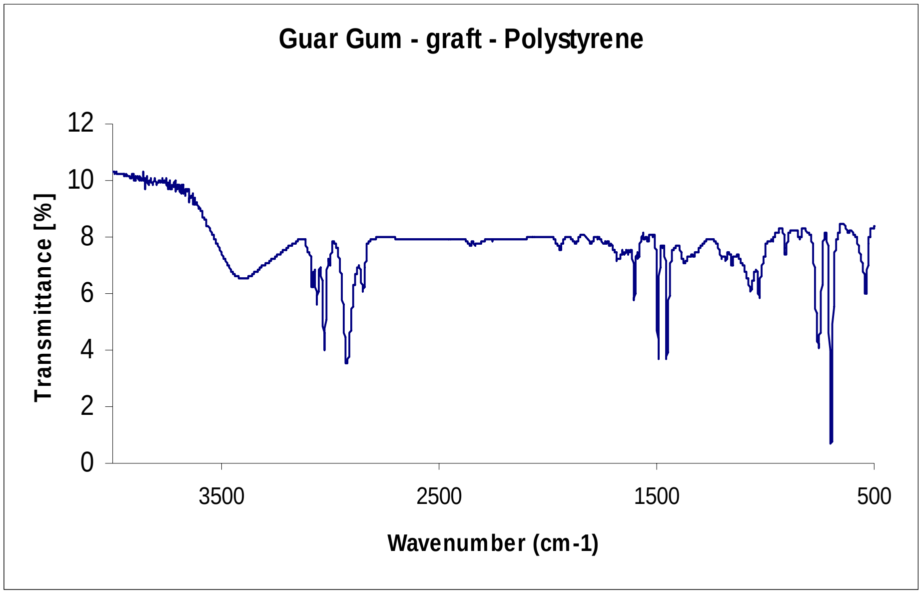


Figure 3.5 FT-IR of polystyrene, guar gum copolymer (A)

considered. The lower the initiator concentration, the fewer initiation sites placed on the guar gum backbone; therefore, the fewer polystyrene side chains grafted onto guar gum. That explains the trends observed in **Table 3.1** The water solubility of the polystyrene, guar gum copolymers improve at lower Ce(IV) concentrations, because enough polystyrene chains are grafted to the guar backbone to disrupt the natural aggregation of the guar gum chains (that occurs in water) allowing water molecules to better solvate the modified polysaccharide. Increasing the initiator concentrations adds more polystyrene side chains to the guar graft, which allows the hydrophobic side chains to form micelle like structures preventing the polystyrene guar gum copolymer from being dissolved.

Decreasing Ce(IV) ion concentration also decreases the availability of free radicals in the free radical polymerization of the polystyrene, guar gum copolymer, which explain the trend of the percent of homopolymer decreasing as the initiator concentration decreases in **Table 3.2.** Both **Tables 3.1 and 3.2** indicate improved grafting efficiency of the copolymer at lower initiator concentrations. The grafting efficiency (**Equation 3.1**)[72] is the amount of grafted product produced in comparison to the amount of homopolymer produced. After comparing the polystyrene, guar gum copolymers at various Ce(IV) concentrations, the best balance of grafting efficiency, water solubility, and weight gain were obtained at the Ce(IV) concentration of 0.221mmol in the free radical polymerizations.

Equation 3.1

$$\text{\% Grafting Efficiency} = \frac{(\text{weight of copolymer})}{(\text{weight of copolymer} + \text{weight of homopolymer})} \times 100$$

Table 3. 1 Water solubility trend of polystyrene, guar gum copolymers

Ce(IV) (mmol)	% Grafting Efficiency	% Swelling* in water (Volume)
0	0 (Guar Gum)	47.83
1.58	42.55	16.67
0.370	63.91	14.29
0.221	89.7	28.57
0.051	88.89	76.19
0.038	70.16	82.76

***The percent swelling of the hydrophobically modified guar gum copolymers was determined quantitatively. Ground samples were packed into a 1mL syringe (syringe tip was filled with silica grease and capped with a needle). Water (0.5mL) was added to each sample. After 72hrs, the amount of swelling was determined from the final volume occupied by the copolymer (Equation 3.2).**

Equation 3.2

$$\text{\% Swelling} = \frac{(\text{final copolymer volume}) - (\text{initial copolymer volume})}{(\text{initial copolymer volume})} \times 100$$

Table 3.2 Effect of initiator concentration on the free radical polymerization of styrene onto guar gum

Ce(IV) (mmol)	% Weight Gain	% Grafting Efficiency	% Homopolymer (wt)
1.58	279.43	55.68	20.09
0.370	170.86	63.91	17.67
0.221	194.08	89.7	3.89
0.051	3.67	88.89	1.32

3.3.2 Nitroxide-Mediated Controlled Radical Polymerizations

Initially TEMPO was selected as the nitroxide mediator for the CRP of guar gum and a hydrophobic monomer, butyl acrylate (**B**) and styrene (**C**). The TEMPO-mediated polymerizations were compromised because of the high temperature (125ºC) requirements to dissociate the labile bond between TEMPO and the monomer, to begin the radical propagation of monomer units onto the guar gum backbone. The polymerizations (**B**) and (**C**) were initiated by Ce(IV) and the monomer added to the guar gum backbone capped by TEMPO were in aqueous solution, but the modified guar (**B**) and (**C**) were isolated and transferred to a solution of additional monomer and n-xylene. The modified guar gum would not remain in solution, and the TEMPO-mediated radical polymerizations of (**B**) and (**C**) could not be completed.

As an alternative to TEMPO, DEPN (**D**) was chosen to mediate the radical polymerization to hydrophobically modify guar gum, because it is a water soluble nitroxide and DEPN can mediate radical propagation at lower temperatures (95ºC). The CRP mediated by DEPN performed well for incorporating the water soluble monomer acrylamide onto the CMG backbone (**E**); this polymerization was used as a model for producing poly-n-butyl acrylate, CMG copolymers. The introduction of DEPN to the CRP of n-butyl acrylate (**F**) and lauryl acrylate (**G**) onto CMG produced water soluble material, **Figure 3.6**. Although Ce(IV) is used to initiate the radicals on the CMG backbone, DEPN is added to control the growth of the side chains onto CMG. This binary system used in the CRP's has accurately produced copolymers of various degrees of polymerization and low molecular weights, with only a negligible amount of homopolymer produced.

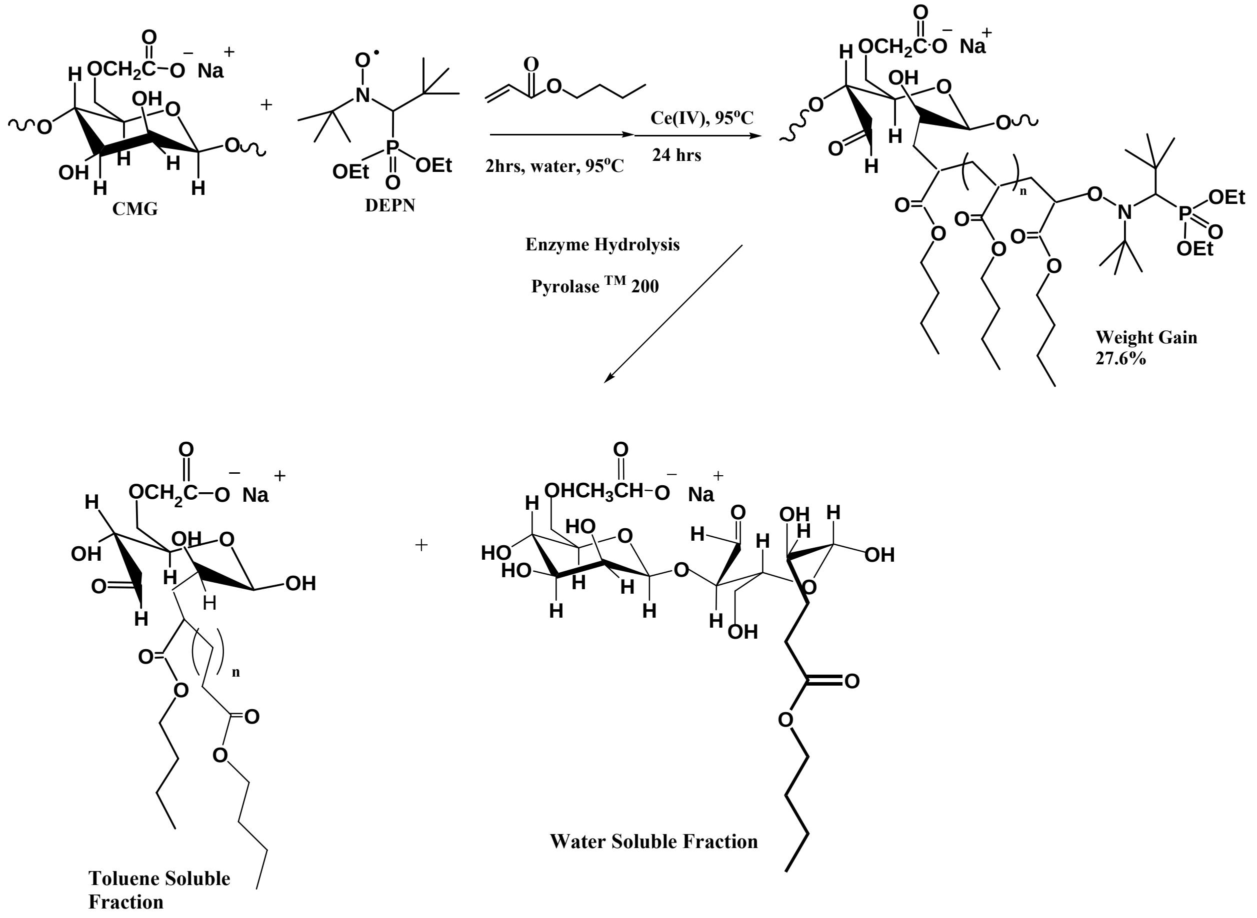


Figure 3.6 Reaction scheme for the CRP of the CMG, poly-n-butyl acrylate copolymer (F)

The extent of poly-n-butyl acrylate grafting onto the CMG backbone can only be determined by cleaving (enzymatically) CMG at the **β**-1, 4 mannose bonds, resulting in poly-n-butyl acrylate chains bonded to CMG monosaccharide units or small oligomers (**3.2.6**). **Figure 3.7** is the ^{1}H NMR in D_2O of the grafted polymer (**F**). The C-H on the anhydrous glucose of the CMG backbone are more defined (3.6 and 4.0 ppm) than the protons associated with n-butyl acrylate, which have secondary protons visible at 1.22pm. The hydrophobic nature of the copolymer prevents it from being properly dissolved in D_2O; the CMG protons are better detected by NMR in an aqueous system (**Figure 3.7**). After the copolymer backbone is enzymatically cleaved, the hydrophobic side chains are extracted from solution with toluene, so that the extent of grafting may be better analyzed. The poly-n-butyl acrylate side chains have well defined peaks in the alkyl region (0.9 – 1.8) of the ^{1}H NMR of **Figure 3.8**. The monosaccharide units attached to the poly-n-butyl acrylate side chains of the copolymer fragments are visible in the NMR spectrum at 3.6 ppm, although the proton NMR sample is dissolved in an organic solvent, deuterated toluene (tol-d8). Guar gum oligomers or monosaccharide with very few (1 or 2) or without any n-butyl acrylate monomers attached would not have been extracted by the toluene with the poly-n-butyl acrylate side chains. The guar gum fragments would have remained in the aqueous layer. The isolated sugar units are clearly seen around 3.5 ppm and the peak at 1.212 ppm represents a butyl acrylate monomer in the ^{1}H NMR spectrum, **Figure 3.9**.

Measuring the viscosity of the hydrophobically modified copolymers provides important rheological information about the material. The effect and extent of grafting may be evaluated from the viscosity data and a comparison of the viscosities of the copolymers could determine the performance of the material in industrial applications for fracturing fluids. At increased shear rates or rotations per minute (10 – 100 RPM), the viscosities of the poly-n-butyl acrylate copolymers (at initiator concentration of 0.2mmol and 0.4mmol) exhibited thixotropic properties, by reducing to the viscosity of water (**Figures 3.10 and 3.11)**. After decreasing the RPM below 10, the viscosities of the copolymers were restored to their previous levels.

The viscosity trends for the copolymers in **Figure 3.10** do not behave in a predictable pattern. The copolymer which reacted for 120 hours has the highest DP, 7, (**Table 3.3**) of the other reacted copolymers, and it has the highest viscosity. Because in CRP the monomer units are added to the backbone of a polymer one monomer at a time, as the reaction times increase more monomers should add forming longer polymer side chains. The poly-n-butyl acrylate, CMG copolymers of **Figure 3.11**, 0.4mmol [Ce(IV)], have a more predictable pattern of viscosity of a copolymer increasing with decreasing reaction times.

Low molecular weight copolymers were produced from the DEPN mediated radical polymerization of poly-n-butyl acrylate and CMG. Initiator concentration determines the number of free radical sites on the polymer backbone, which determines the number of side chains formed on the polymer backbone. Maintaining low initiator concentrations and low reaction times allow for producing water soluble poly-n-butyl acrylate copolymers accurately from CRP, **Table 3.3**. A more consistent trend in molecular weight and DP is observed at the lower initiator concentration, 0.212mmol; molecular weight and DP increase with reaction time. While at 0.418mmol [I], a predictable pattern of molecular weight and DP in respect to reaction time is not established. The number of possible sites available for grafting may have doubled, decreasing the availability of monomer for consistent chain growth.

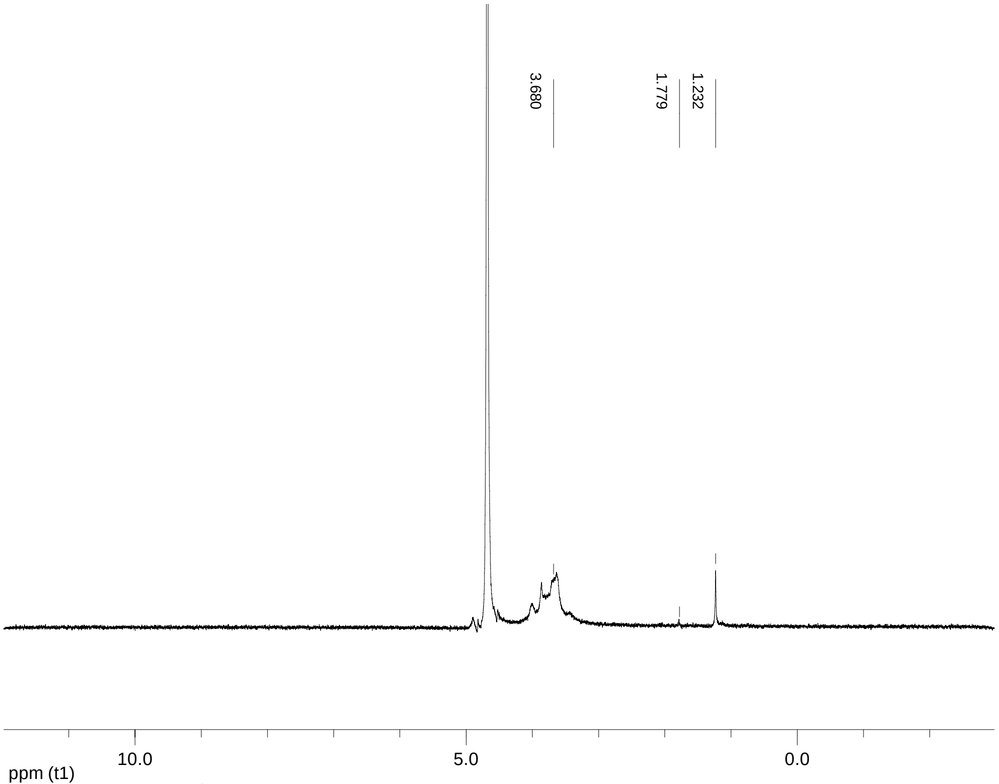
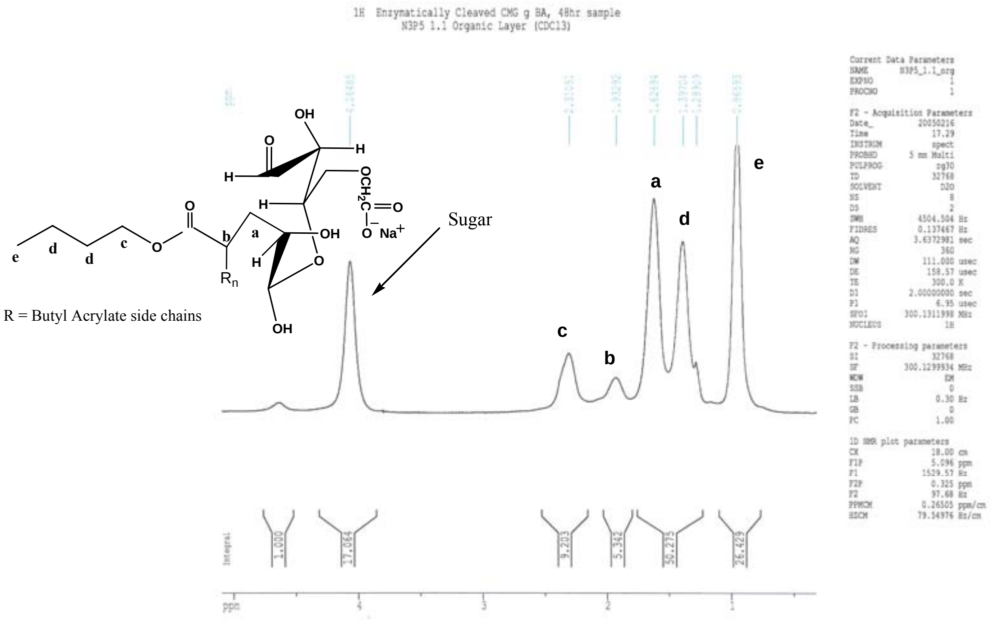


Figure 3.7 ^1H NMR (250MHz, D_2O) of DEPN mediated CMG-poly-n-butyl acrylate copolymer (F)



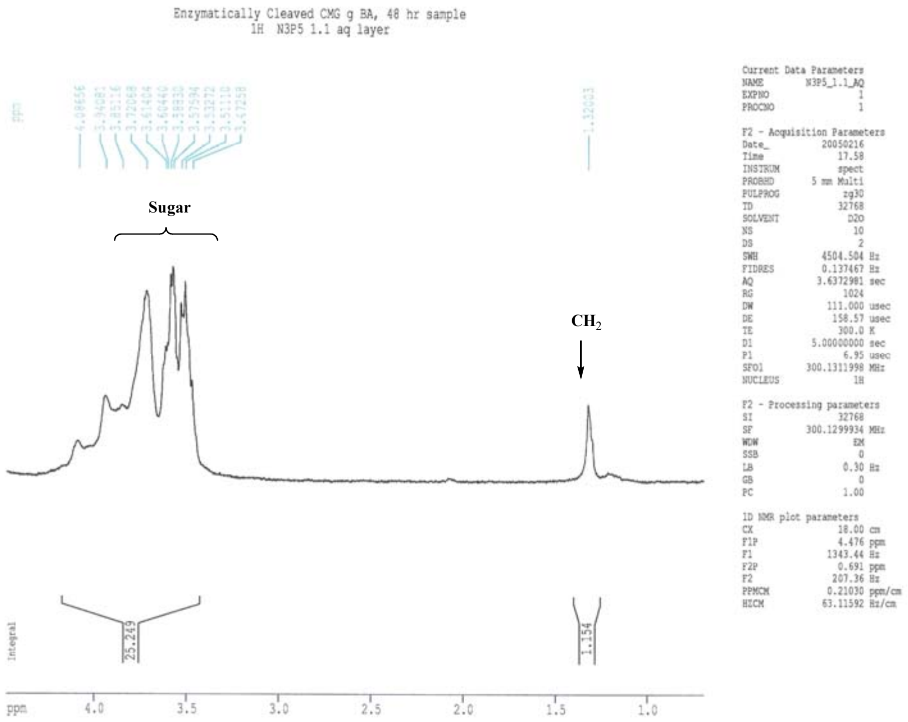
```
Current Data Parameters
NAME       N3P5_1.1_org
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20050216
Time              17.29
INSTRUM           spect
PROBHD       5 mm Multi
PULPROG            zg30
TD                32768
SOLVENT             D2O
NS                    8
DS                    2
SWH            4504.504 Hz
FIDRES         0.137467 Hz
AQ            3.6372981 sec
RG                  360
DW              111.000 usec
DE               158.57 usec
TE                300.0 K
D1           2.00000000 sec
P1                 6.95 usec
SFO1        300.1311998 MHz
NUCLEUS              1H

F2 - Processing parameters
SI                32768
SF          300.1299934 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                18.00 cm
F1P               5.096 ppm
F1              1529.57 Hz
F2P               0.325 ppm
F2                97.68 Hz
PPMCM           0.26505 ppm/cm
HZCM           79.54976 Hz/cm
```

Figure 3.8 ^1H NMR (250MHz, $CDCl_3$) of poly-n-butyl acrylate side chains enzymatically cleaved from the DEPN mediated CMG-poly-n-butyl acrylate copolymer (F)



Current Data Parameters	
NAME	N3P5_1.1_AQ
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20050216
Time	17.58
INSTRUM	spect
PROBHD	5 mm Multi
PULPROG	zg30
TD	32768
SOLVENT	D2O
NS	10
DS	2
SWH	4504.504 Hz
FIDRES	0.137467 Hz
AQ	3.6372981 sec
RG	1024
DW	111.000 usec
DE	158.57 usec
TE	300.0 K
D1	5.00000000 sec
P1	6.95 usec
SFO1	300.1311998 MHz
NUCLEUS	1H
F2 - Processing parameters	
SI	32768
SF	300.1299934 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00
1D NMR plot parameters	
CX	18.00 cm
F1P	4.476 ppm
F1	1343.44 Hz
F2P	0.691 ppm
F2	207.36 Hz
PPMCM	0.21030 ppm/cm
HZCM	63.11592 Hz/cm

Figure 3.9 ^1H NMR (250MHz, D_2O) of the CMG backbone enzymatically cleaved from the DEPN mediated CMG-poly-n-butyl acrylate copolymer (F)

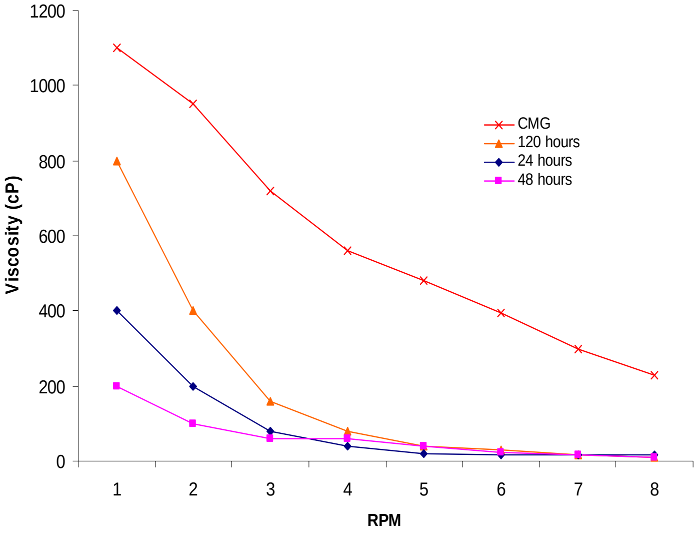


Figure 3. 10 Comparison of viscosities for the copolymer CMG-poly-n-butyl acrylate (0.5% (wt) solution concentration) produced from DEPN mediated CRP, [I] 0.2mmol *

***CMG-poly-n-butyl acrylate solutions were measured at pH 4; CMG solution was measured at pH 6.**

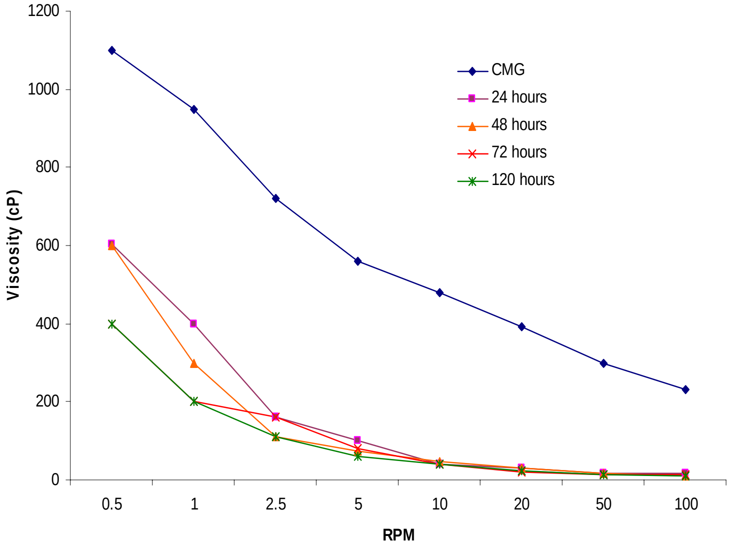


Figure 3.11 Comparison of viscosities for the copolymer CMG-poly-n-butyl acrylate (0.5% (wt) solution concentration) produced from DEPN mediated CRP, [I] 0.4mmol *

***CMG-poly-n-butyl acrylate solutions were measured at pH 4; CMG solution was measured at pH 6.**

Table 3.3 Trends in molecular weight and DP of DEPN mediated CRP of poly-n-butyl acrylate as a function of reaction time and initiator concentration

Molarity of DEPN/ Ce(IV) (mmol)	Reaction Time (hours)	*Molecular Weight	DP of fragments	Solubility of Graft in Water
0.836	24	600	3	Swells
0.836	72	851	5	Swells
0.418	24	686	4	Water Soluble
0.418	48	604	2	Water Soluble
0.418	72	1322	9	Swells
0.418	120	815	5	Swells
0.212	24	558	3	Water Soluble
0.212	48	686	4	Water Soluble
0.212	72	815	5	Swells
0.212	120	1,017	7	Swells

*** Molecular weight of enzymatically cleaved side chains from CMG, poly-n-butyl acrylate copolymers**

Chapter 4 Graft Copolymerization of Derivatized Guar Gum Through the Free Radical RAFT Process

4.1 Introduction

The aim of this project is to hydrophobic modify carboxymethyl guar gum (CMG) in order to produce water soluble polymers that would be used in hydraulic fracturing fluids for enhanced oil recovery (EOR) in the oil industry. The hydrophobically modified polysaccharides are projected to facilitate enhanced well productivity, while introducing less damaging completion and stimulation fluids. Better cleaning performance is attained through the aggregation of the nonionic hydrophobically modified polysaccharide (that is similar to that for surfactant micelle formation), which will lead to better cleaning performance.[3,16,33,43] The hydrophobically modified CMG grafts were synthesized through the RAFT (reversible addition fragmentation chain transfer) process as an alternative controlled radical process (CRP) to the previous mentioned methods of utilizing either Barton esters or nitroxide mediation.

The success of living free radical polymerizations achieved through the RAFT process has been reported by several groups. RAFT polymerization is different from other controlled free radical polymerizations mainly because it can be used with a wide range of monomers and reaction conditions, while producing controlled molecular weight polymers with very narrow polydispersities (less than 1.2).[74] RAFT incorporates a chain transfer agent that reacts with an initiating radical. A conventional initiator, such as azo or peroxy initiators, may be used to initiate the chains. The reversible reaction is between a dormant chain and an active radical. The end group originating from the transfer agent is exchanged between the two chains. The RAFT free radical process occurs in the presence of reagents such as dithioesters; an addition fragmentation process is used to exchange the dithioester between the two chains. [The transfer agent is then activated by the radicals originating from initiator decomposition (**Figure 4.1**).][75]

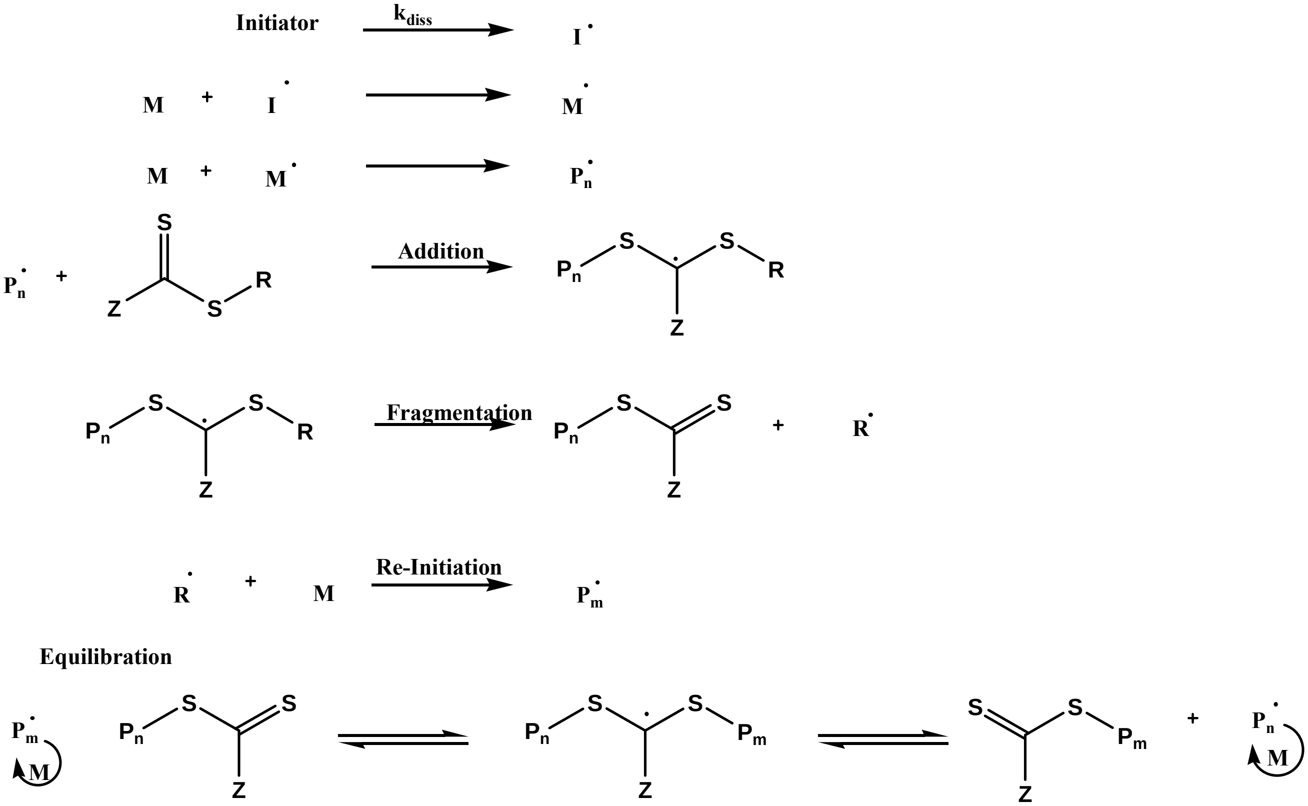


Figure 4.1 Reversible addition fragmentation transfer polymerization

Synthesis of carboxyl terminated trithiocarbonates (RAFT agents) has made obtaining low polydispersed polymers from a variety of monomers possible. Water soluble RAFT agents, such as S, S – bis(α,α' –dimethyl-α''-acetic acid) trithiocarbonate (**1**), have extremely high chain transfer efficiency. [76-78] Because the carbon attached to the labile sulfur atom is tertiary and bears a radical stabilizing carboxyl group, the RAFT agent is able to control the radical polymerization. Homopolymerization or copolymerization of alkyl acrylates, acrylic acid, and styrene are well controlled in either bulk or solution.[75]

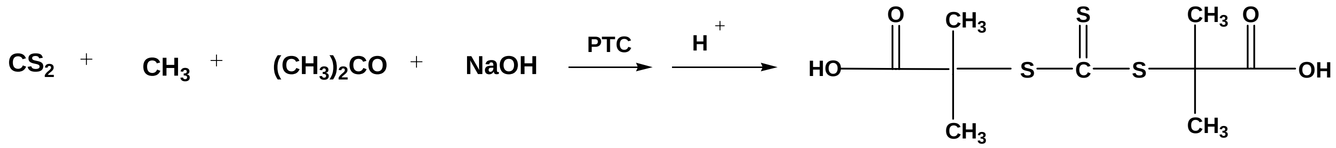


Figure 4.2 Synthesis of the water soluble RAFT agent S, S – bis(α,α’ –dimethyl-α”-acetic acid) trithiocarbonate (1)

1

The total number of chains in the system is the sum of transfer agent and primary radical molecules. To maximize the living nature of the free radical polymerization, there should be a large excess of transfer agent to initiator. An extremely active transfer agent is rapidly consumed (within a few percent monomer conversion), while it takes a less active transfer agent more time for consumption. For rapid consumption, a few dead chains may result from irreversible termination, creating a narrow molecular weight distribution. A broader distribution and more dead chains result from slow transfer agent consumption. Conventional initiators are used; therefore new chains are continually being created as long as initiator remains. Initiator decomposition is accelerated at higher reaction temperatures, which allow for all chains to be created within a narrow time frame, providing a narrow molecular weight distribution.[79-81] The average degree of polymerization is given by **equation 4.1**, DP is the degree of polymerization; $[M]_0$, the initial monomer concentration; [M], the monomer concentration at any given time; $[AB]_0$, the initial transfer agent concentration; [AB], the concentration of transfer agent at any given time; $[I]_0$, the initial concentration of initiator; [I], the initiator concentration at any given time; ε is the initiator efficiency.[82]

Equation 4.1

$$DP = \frac{[M]_0 - [M]}{([AB]_0 - [AB] + \varepsilon([I]_0 - [I])}$$

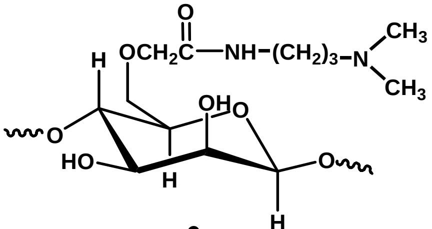
In RAFT free radical polymerizations, the reversible step is transfer and not termination (which is the reversible step in ATRP, atom transfer radical polymerization, and nitroxide-mediated free radical polymerizations); the concentration of radicals is not affected compared to a conventional free radical polymerization. As with reversible termination, some irreversible termination occurs, resulting in a broader molecular weight distribution. Unlike reversible termination, the rate is not consequently suppressed.[83,84]

The most notable difference between reversible termination and reversible transfer mechanisms is observed in how each type of polymerization behaves in emulsion/miniemulsion polymerization. With reversible termination, the radical concentration is lower than in bulk. In addition, the deactivation step of a growing radical is very fast (close to diffusion controlled) and is comparable to termination rate coefficients. However, deactivation dominates over irreversible termination due to the higher concentration of deactivating species compared to available radicals. Many of the advantages of emulsion/miniemulsion polymerization (increased rate and higher molecular weight) are not expected to be realized in reversible termination systems. In reversible transfer, the radical concentration is not affected.[75,84,85]

4.1.1 RAFT in an Aqueous Dispersed System

The water soluble hydrophobically modified polysaccharides in this project are produced in an aqueous system. An emulsion polymerization, in which the two phases are immiscible liquids, is used to produce the aliphatic polymers. A water soluble stabilizer, surfactants such as soap or detergent, is necessary to maintain the emulsion. Usually the initiator system is located in the aqueous phase and the free radicals which it generates cross into the organic droplets where they give rise to the polymer chains. The emulsion polymerization is a heterogeneous process, with active species crossing phase boundaries. The monomer resides mainly in other droplets of relatively large size, which behave as a reservoir of monomer rather than as reaction volumes. A small fraction of the monomer molecules is contained within the micelles where the polymer chains are synthesized. Free radicals coming in from the aqueous phase penetrate the micelles to encounter monomer and start polymerization. As polymer chains form, more monomer enters the micelle from the large droplets after diffusing through the aqueous phase. The monomer reservoir shrinks as time passes in a batch reaction system, while the micelles swell as the polymer chains grow. Since the number of micelles per unit volume of the aqueous phase far exceeds the number of large monomer droplets, a propagating radical is far more likely to encounter a micelle than a droplet of monomer as it diffuses through the water.[31,53,61,86,87]

The CMG modified with a tertiary amine, 3-dimethylaminopropylamine (DMAPA) carboxymethyl guar gum (**2**), gives rise to micelle like structures, such as those formed by a detergent, in an emulsion polymerization.[13,16,30,44] The use of RAFT in emulsion polymerization was first reported by Lai et al[76]. It was noted that the transfer agent should partition primarily into the aqueous phase, while having sufficient water solubility to diffuse through the aqueous phase from monomer droplets to particles. Since RAFT polymerization is a reversible transfer process, the addition of a RAFT agent to a polymerization is not expected to affect the polymerization rate.[81,88]



2

4.2 Experimental

Materials. All reagents were purchased from Aldrich or Acros. Inhibitor was removed from the monomer using Aldrich inhibitor remover packing resin (for HQ and HEQ removal). All other reagents were used without further purification. All solvents were dried using standard laboratory procedures. S, S – bis(α,α' –dimethyl-α''-acetic acid) trithiocarbonate (RAFT agent, **1**) was synthesized according to a procedure cited in literature.[76-78] The polystyrene, acrylic acid RAFT block copolymer was synthesized in house by Ahmad Bahamdam and Codrin Daranga.[78]

Instrumentation. ^{1}H NMR (250MHz) spectra were obtained on a Bruker DPX 250. FT-IR results were obtained from a Bruker Tensor 27. A Bruker Proflex was used to obtain MALDI data. Elemental Analysis samples were submitted to Huffman Laboratories, Golden, CO 80403. Viscosities were measured on the Brookfield PVS003 rheometer.

4.2.1 Preparation of Methylated Carboxymethyl Guar Gum (A)

Guar gum (70g) was slurried in 400mL of 2-propanol in a N_2 atmosphere, for 30 minutes. A NaOH solution, 24.8g, (40% wt/wt) was added over 20 minutes and the reaction was allowed to stir at room temperature for 30 minutes. Sodium chloroacetate, 60g, (40% wt/wt) was added to the reaction slowly over 30 minutes and allowed to react for 1 hour at room temperature.

The temperature was increased to 70ºC for 2 hours. The reaction mixture was cooled and filtered; the filtered product was washed twice with 400mL of 80% (v/v) methanol/water solution, and washed once with acetone. The resulting sodium-CMG was vacuum dried at 60ºC for 12 hours.

The Na-CMG (40g) was slurried in dimethyl sulfate (50mL) at 60ºC under nitrogen for 6 hours. Methylated carboxymethyl guar gum was filtered, soaked in methanol (450mL), washed with acetone (450mL), and dried 12 hours at 60ºC. FT-IR (cm^{-1}): 3393(w-OH), 2913 (w-C-H), 1732, (s, ester carbonyl), and 1026(vs, CO).

4.2.2 Synthesis of 3-Dimethylaminopropylamine (DMAPA) Carboxymethyl Guar Gum (B)

Methylated CMG (9.772g) and 3-dimethylaminopropylamine (80mL) were heated to 70ºC for 4 hours. After the reaction mixture cooled, the grafted polymer product was precipitated in acetone, filtered, and vacuum dried at room temperature for 12 hours. 8.740g of the amino amide (DMAPA-CMG) was synthesized. ^1H NMR ($CDCl_3$), δ: 3.88 and 3.69 ppm.

4.2.3 Controlled Radical Grafting of a Copoly(Styrene-B-acrylic Acid) RAFT Terminated Polymer[78] onto Carboxymethyl Guar Gum (C)

Combined CMG (2.5g), the block copolymer (3.0g), and water (900mL) in an industrial blender was mixed vigorously for 20 minutes. The mixture was poured into a three neck round bottom flask equipped with a condenser, stir bar, and thermocouple in an inert environment (N_2) and heated at 95ºC for 10 minutes. The reaction was controlled by the RAFT agent on the block copolymer. A 7% molar solution of ceric ammonium nitrate (CeIV) (0.24g) in 1M nitric acid (HNO_3) was added to the reaction mixture to initiate the grafting process. The reaction mixture was refluxed for 24 hours at 95ºC. The reaction mixture was cooled, concentrated by rotary evaporation, and the concentrated product mixture was freeze dried for 24 hours to remove the remaining water. The grafted polymer produced weighed 4.464g for a weight gain of 93.6%. ^1H

NMR ($CDCl_3$), δ: 1.56, 1.26, 0.87. ^1H NMR of aqueous (D_2O), δ: 7.16, 4.0, 3.69, 2.31, 1.58, 1.02.

4.2.4 The Photolytic Polymerization of n-Butyl Acrylate onto 3-Dimethylaminopropylamine Carboxymethyl Guar Gum (D)

The DMAPA-CMG (**2**), (2g), n-butyl acrylate (5mL), and water (75mL) were combined in an industrial blender and mixed on high speed 20 minutes. RAFT agent (S-1-dodecyl-S-dimethylacetic)thiocarbonate), 0.172g , was added and blended on high speed 5 minutes. The reaction mixture was poured into a jacketed flask equipped with a stir bar, condenser, thermometer, and a cold water flow, so that the reaction temperature was maintained at 27ºC. The reaction was exposed to UV-B light (285 – 315 nm) at a distance of 1.5 ft, and irradiated for 24 hours. The reaction mixture was concentrated, by rotavap, and the n-butyl acrylate, CMG copolymer (2.025g) precipitated in acetone. ^1H NMR ($CDCl_3$), δ: butyl acrylate oligomers (5.56, 5.53, 1.38, 1.05 ppm), CMG backbone (4.12, 3.85, 3.62 ppm)

4.2.5 The Photolytic Polymerization of Lauryl Acrylate onto 3-Dimethylaminopropylamine (DMAPA) Carboxymethyl Guar Gum (E)

DMAPA-CMG (2.462g), lauryl acrylate (3mL), and water (150mL) were combined in the industrial blender and mixed at maximum speed for 20 minutes. The RAFT agent (S-1-dodecyl-S-dimethylacetic) thiocarbonate (0.126g) was blended 5 min (maximum speed). The reaction mixture was poured into a jacketed flask equipped with a stir bar, condenser, thermometer, and a cold water flow, so that the reaction temperature was maintained at 27ºC. The reaction was exposed to a UV-B light (fluorescent 10.0) (300 nm) at a distance of 1.5 ft, and irradiated for 24 hours.

The product mixture was concentrated *in vacu* and the grafted polymer precipitated out in acetone. The DMAPA-CMG-g-lauryl acrylate product (2.528g) had a weight gain of 11.66%. The grafted polymer was analyzed by elemental analysis for sulfur content, which confirms the presence of sulfur groups from the RAFT agent. The average molecular weight achieved for the lauryl acrylate side chains was 825 with an average DP of 2. ^{1}H NMR ($CDCl_3$), δ: 0.88(3H), 1.272(22H), 1.6(1H), 4.0(2H). FT-IR (KBr, cm^{-1}): 3384(w, OH), 2924(CH), 1736(carbonyl).

4.2.6 The Photolytic Grafting of a Copoly(Styrene-B-acrylic Acid) RAFT Terminated Polymer[78] onto 3-Dimethylaminopropylamine Carboxymethyl Guar Gum (F)

DMAPA-CMG (2.5g), copoly(styrene-b-acrylic acid) (2.0g), and water (150mL) were blended at maximum speed for 20 minutes. The reaction mixture was poured into a jacketed flask equipped with a condenser, stir bar, thermometer, and a cool water flow to allow the reaction to remain at 27ºC. The reaction was exposed to UV light (300nm) at a distance of 1.5 feet for 24 hours. The DMAPA-CMG-g-poly(styrene-b-acrylic acid) (3.867g, 71.87% weight gain) product was precipitated from acetone as an off white powder. ^{1}H NMR ($CDCl_3$), δ: 6.96(ArH), 4.0(O-CH_2, 2H), 1.57(t, 2H), 1.26(d, 4H), 0.88(m, 6H)

4.3 Results and Discussion

Incorporating RAFT agents into the CRP of hydrophobic monomers onto the backbone of DMAPA-CMG (**2**) resulted in the synthesis of water soluble amphipathic polymers. The CRP RAFT process proceeds by means of a quasi-emulsion. Surfactant is not incorporated into the polymerizations; the resulting micelle formation during the course of the RAFT process may be attributed to the ionic nature of the CMG. An added benefit of the RAFT CRP process is that it may proceed under thermal or photolytic conditions.

Under thermal conditions, the CRP RAFT process of a hydrophobe group onto CMG takes place in aqueous media at moderate temperatures, as low as 65ºC. An external initiator, Ce(IV), was used to generate an alkyl radical directly onto the backbone of CMG. The RAFT agent S, S – bis(α,α'-dimethyl-α"-acetic acid) trithiocarbonate, **1**, is implemented to control the addition of monomer to the polysaccharide backbone through a mechanism of reversible transfer. The polystyrene, acrylic acid (AA) RAFT block copolymer was grafted onto the CMG backbone, producing a water soluble polymer (**C**). The block copolymer (poly(styrene-b-AA)) was synthesized utilizing a RAFT agent, **1**. The RAFT agent was left attached to the block copolymer, so that the pre-existing block copolymers could be grafted directly onto the CMG backbone. Although the CMG, poly(styrene-b-AA) copolymer produced under thermal conditions was water soluble, the grafted polymer did not produce a gel material upon treatment with zirconium ammonium acetate. The long chain grafts produced in this process appear to initiate the complexing efficiency of the zirconium crosslinking agent.

To analyze the structure of (**C**) by NMR the spectra of the compound dissolved in aqueous and organic deuterated solvents must be compared. The ^{1}H NMR of (**C**) in D_2O reveals the CMG backbone, as a broad range of peaks (4.0 – 3.5 ppm) and the alkyl groups of acrylic acid. A brief comparison of the ^{1}H NMR of CMG and the ^{1}H NMR of (**C**), **Figure 4.4**, clearly illustrates the functionalization of the modified polysaccharide. Since the hydrophobically modified CMG copolymer is water soluble, it is not surprising to have the polystyrene moiety of the block copolymer side chains show up in the spectrum (7.16 ppm). For the ^{1}H NMR of (**C**) in toluene-d8, acetone, or $CDCl_3$ (**Figure 4.5**) the guar protons can not be seen in the resulting spectra; however, the alkyl region from the side chains of the block copolymer is detected. It is important to note that the ^{1}H NMR in acetone-d6 of the copoly(styrene-b-acrylic acid) RAFT terminated polymer have a signal in the aromatic region (7.19 ppm) from the polystyrene of the block copolymer.

The functionalization of CMG with a tertiary amine, DMAPA, provides the added benefit of the RAFT free radical polymerizations being able to proceed under photolytic conditions without the use of an external initiator[89]. The RAFT agent, **1**, in combination with the tertiary amine behaves as a type II photosensitizer and undergoes a bimolecular reaction, when it absorbs UV light (300nm) and forms a triplet state that abstracts a hydrogen from the amine moiety of DMAPA-CMG. [Type I photosensitizers undergo a unimolecular bond cleavage upon irradiation to yield free radicals.]

This is analogous to the photolysis of a tertiary amine activated by benzophenone isopropylthioxanthone and N-methyl maleimide.[90] This is also illustrated in the model reaction scheme in which benzophenone behaves as a type II photosensitizer in the production of carbon-centered free radicals, **Figure 4.6**. The resulting radical is an efficient polymer initiator.[91,92] **Figure 4.7** has the RAFT agent behaving as the photosensitizer abstracting a hydrogen from the amino amide moiety of the DMAPA-CMG backbone, leaving a carbon-centered radical on the amino moiety of the CMG backbone. To better analyze the structural composition of compound (**D**), the copolymer was enzymatically cleaved (with a mixture of pyrolases), and the organic side chains of poly-n-butyl acrylate were extracted from the aqueous mixture with toluene.

^{1}H NMR (D_2O) CMG

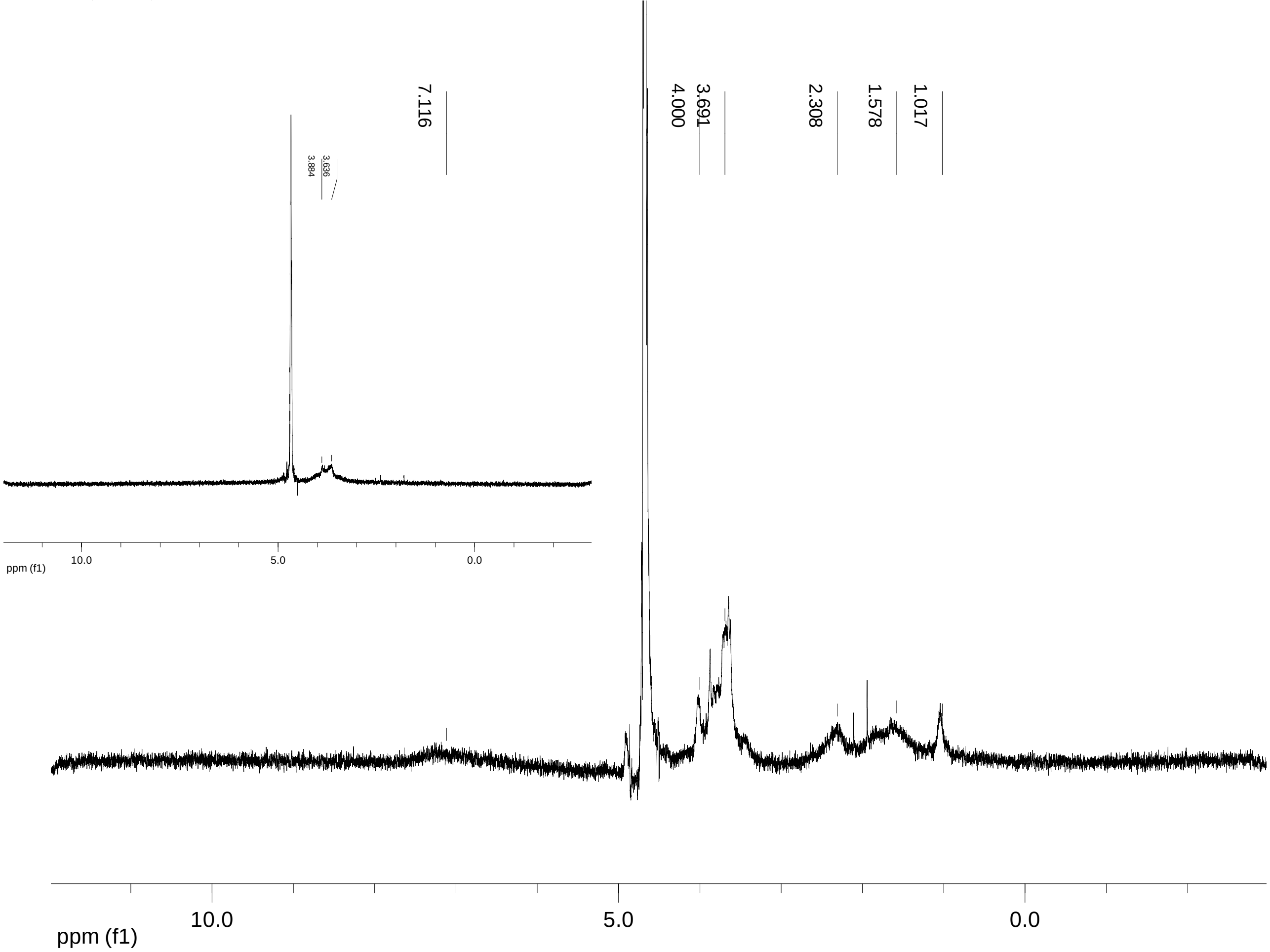


Figure 4.3 ^{1}H NMR (250MHz, D_2O) of poly(styrene-b-acrylic acid) RAFT terminated polymer grafted to CMG (C); upper left corner, ^{1}H NMR (250MHz, D_2O) of CMG

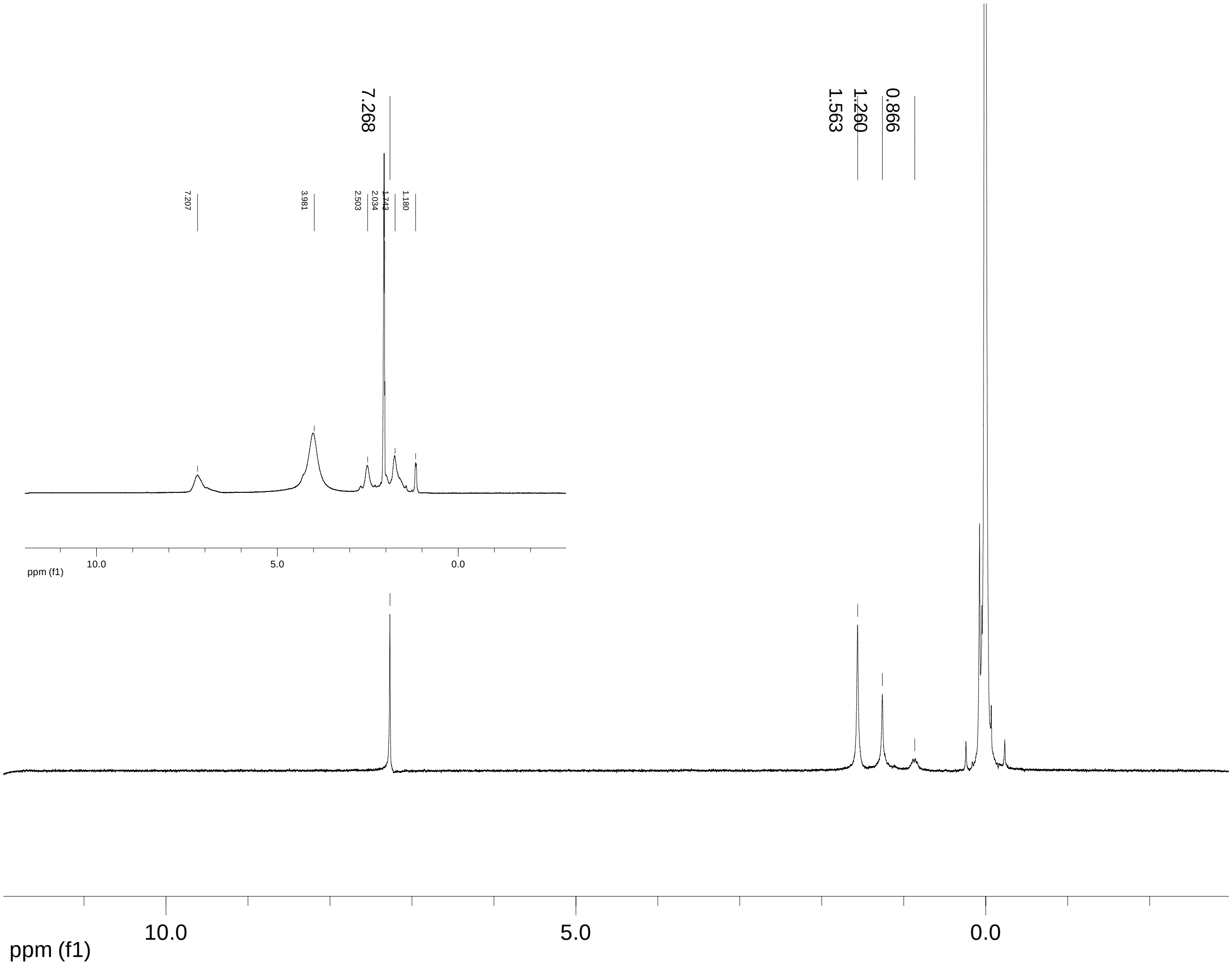


Figure 4.4 ^{1}H NMR (250MHz, $CDCl_3$) of poly(styrene-b-acrylic acid) RAFT terminated polymer grafted to CMG (C); Upper left corner, ^{1}H NMR (250MHz, acetone-d6) for the poly(styrene-b-acrylic acid) RAFT terminated polymer

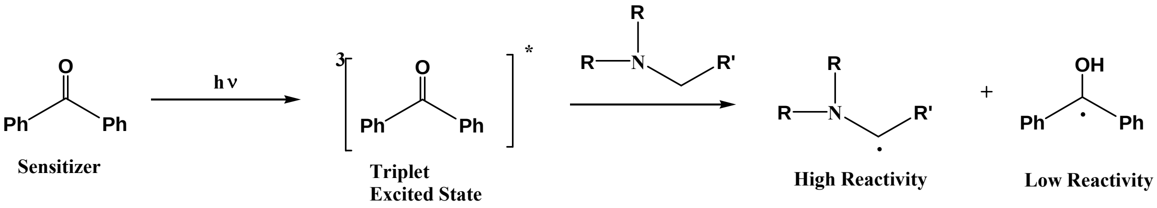


Figure 4.5 Photoinitiation with triplet sensitizers and tertiary amines

The cleaved polysaccharide backbone with a mono- or di-saccharide with the occasional unit of butyl acrylate grafted remained in the aqueous solution, as evident in **Figure 4.8**. The ^{1}H NMR largely represents the CMG backbone, but a peak from the alkyl groups on n-butyl acrylate is present at 1.8 ppm. The ^{1}H NMR, **Figure 4.9**, of the toluene extraction from the cleaved copolymer (**D**) clearly represents the poly-n-butyl acrylate side chains, while the attached sugar unit is visible at 3.8 ppm.

The controlled radical polymerizations of the hydrophobes n-butyl acrylate (**D**), lauryl acrylate (**E**), and copoly(styrene-b-acrylic acid) (**F**) were respectively grafted onto DMAPA-CMG with the mediation of **1** as a photosensitizer. **Figure 4.7** is the reaction scheme for the photoinduced polymerization of lauryl acrylate onto DMAPA-CMG. **Figure 4.10** is the photoinduced polymerization of the poly(styrene-b-acrylic acid) block copolymer onto the DMAPA-CMG backbone; the source of RAFT agent, **1**, is from the terminal ends of the block copolymer chains.

The FT-IR (KBr) of the polylauryl acrylate side chains from the copolymer DMAPA-CMG, lauryl acrylate (**E**), **Figure 4.11**, clearly displays the spectra of lauryl acrylate. The ^{1}H NMR for the copolymer **E** in D_2O only has peaks resolved for the DMAPA-CMG backbone, **Figure 4.12**. When copolymer **E** was dissolved in d_8-toluene, the ^{1}H NMR (**Figure 4.13**) revealed the alkyl groups from polylauryl acrylate (1.39, 0.96 ppm) and the DMAPA-CMG backbone (4.12 ppm).

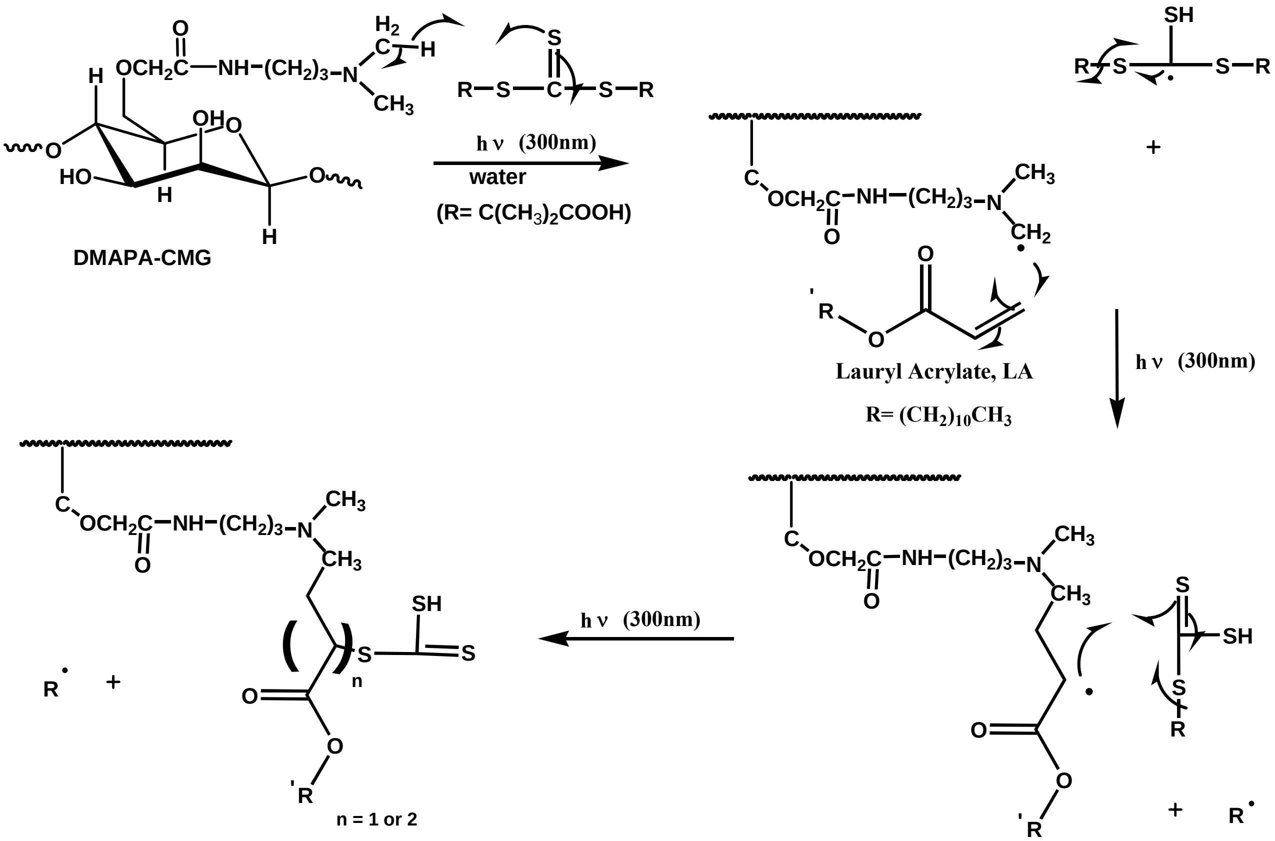
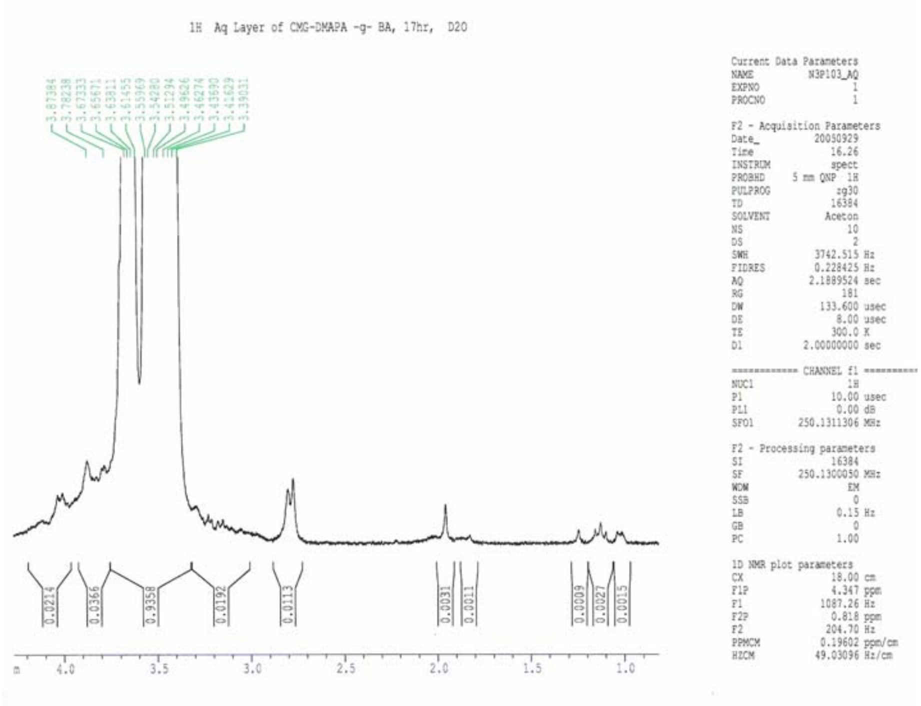


Figure 4.6 Photo-initiated reaction of DMAPA-CMG with lauryl acrylate in the presence of RAFT agent (E)



```
Current Data Parameters
NAME          N3P103_AQ
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20050929
Time              16.26
INSTRUM           spect
PROBHD     5 mm QNP  1H
PULPROG            zg30
TD                16384
SOLVENT          Aceton
NS                   10
DS                    2
SWH            3742.515 Hz
FIDRES         0.228425 Hz
AQ            2.1889524 sec
RG                  181
DW              133.600 usec
DE                 8.00 usec
TE                300.0 K
D1           2.00000000 sec

============ CHANNEL f1 ==========
NUC1                 1H
P1                10.00 usec
PL1                0.00 dB
SFO1        250.1311306 MHz

F2 - Processing parameters
SI                16384
SF          250.1300050 MHz
WDW                  EM
SSB                   0
LB                 0.15 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                18.00 cm
F1P               4.347 ppm
F1              1087.26 Hz
F2P               0.818 ppm
F2               204.70 Hz
PPMCM           0.19602 ppm/cm
HZCM           49.03096 Hz/cm
```

Figure 4.7 ^{1}**H NMR (250MHz, D_2O) of aqueous segment of the enzymatically cleaved poly-n-butyl acrylate, DMAPA-CMG (D)**

Then enzymatic cleavage of the grafted copolymer (**E**) allows for isolating the polylauryl acrylate side chains of the copolymer from the mono- or di-saccharide units without any hydrophobic modification (or with minimal monomer addition, one lauryl acrylate unit). The hydrophobic side chains were extracted from the aqueous solution by toluene. The ^{1}H NMR (D_2O) of the aqueous layer, **Figure 4.14**, reveals the structure of the DMAPA-CMG unit (4.17, 3.14 ppm) and the alkyl groups of lauryl acrylate (1.23, 0.99 ppm). The ^{1}H NMR ($CDCl_3$) of the polylauryl acrylate side chains, **Figure 4.15**, has the peaks of lauryl acrylate well resolved (2.36, 1.61, 1.27, 0.89 ppm) and the sugar monomer, which remains attached to the side chain after enzyme cleavage, is resolved at 4.02 ppm.

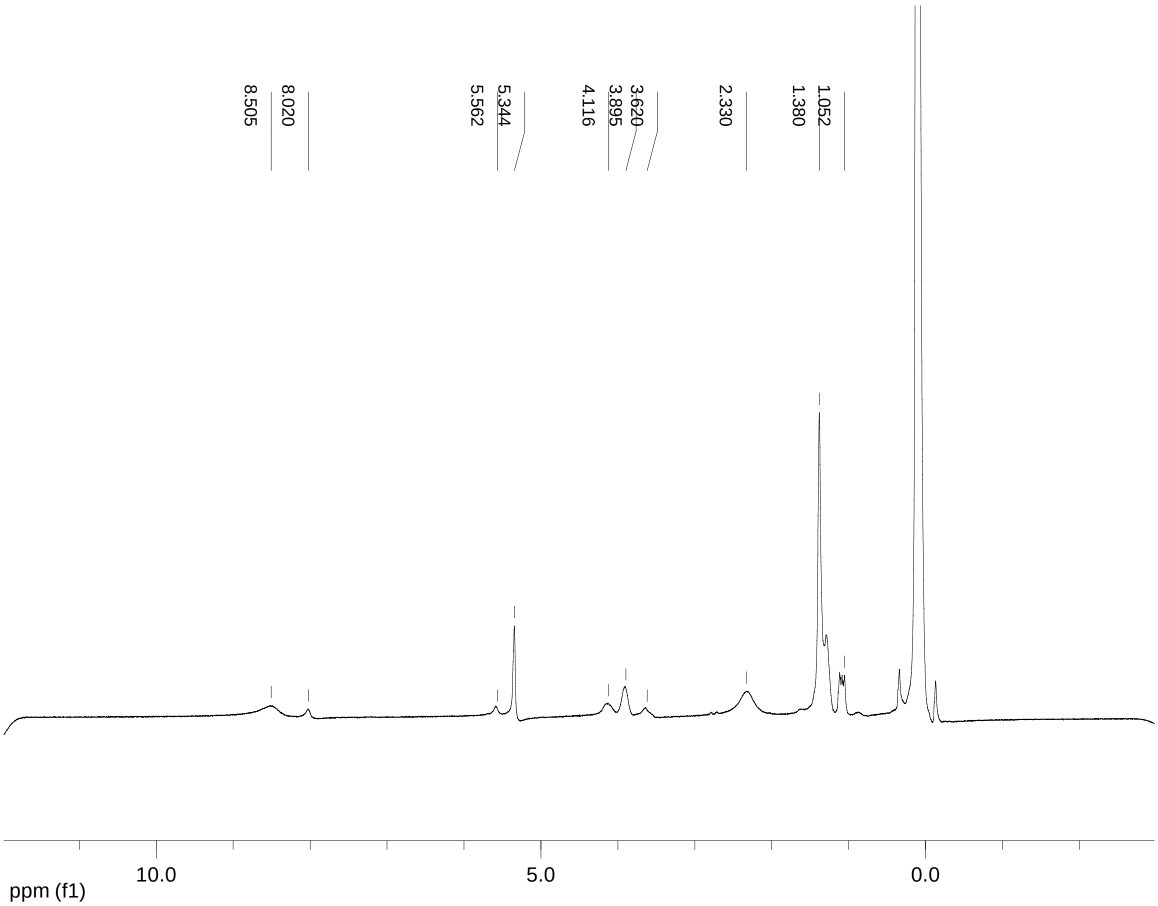


Figure 4.8 ^{1}H NMR (250MHz, $CDCl_3$) of organic segment of the enzymatically cleaved poly-n-butyl acrylate, DMAPA-CMG copolymer (D)

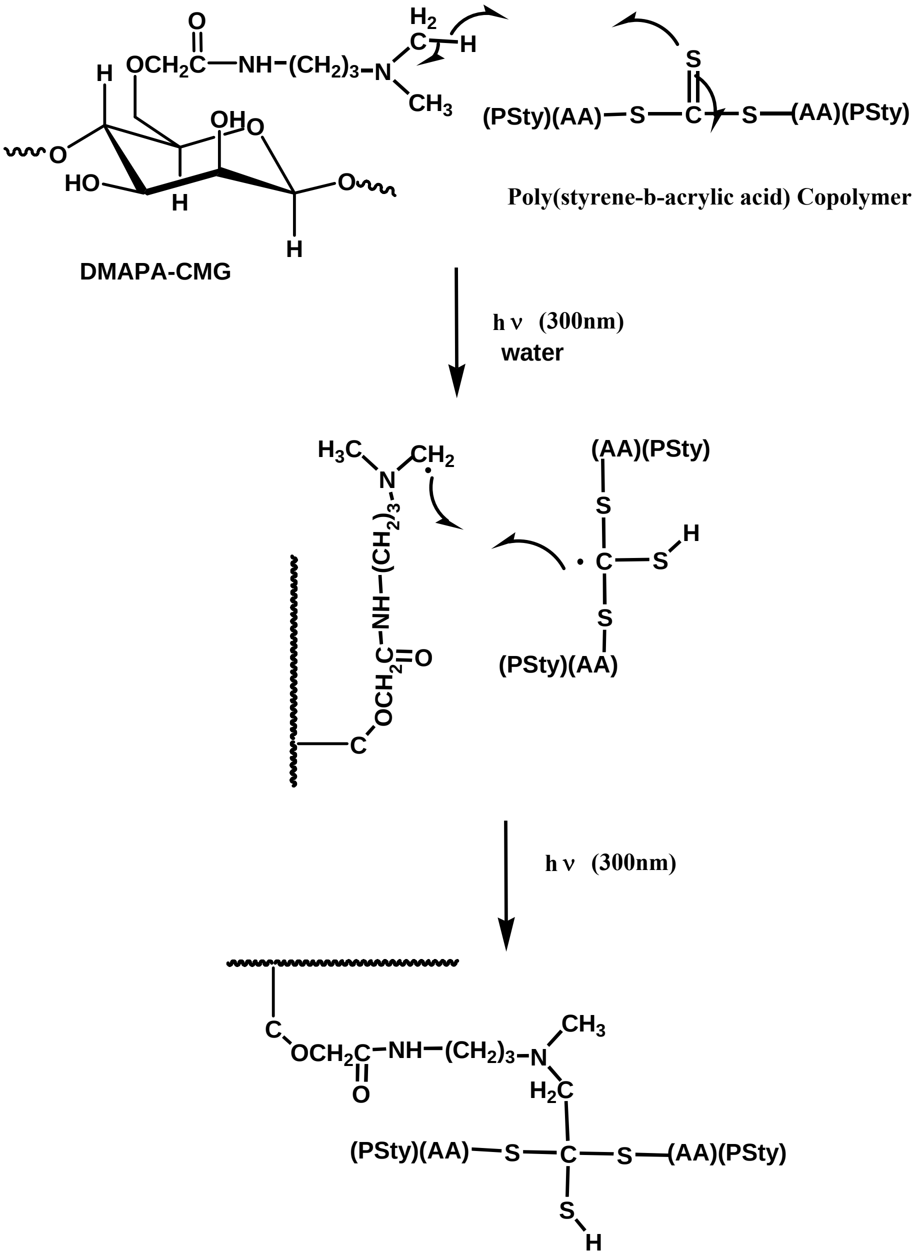


Figure 4.9 Graft of copoly(styrene-b-acrylic acid) to modified CMG (F)

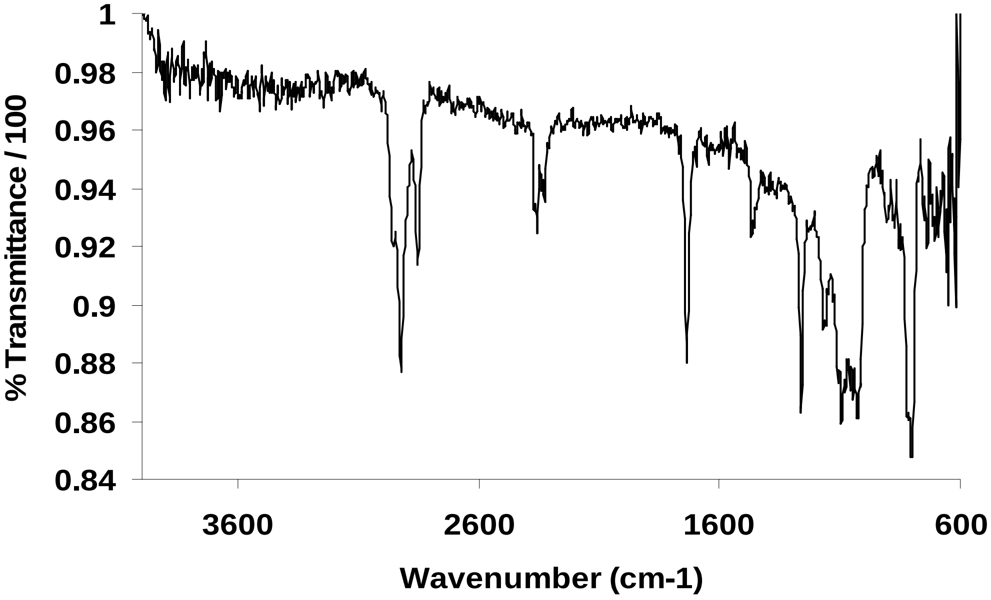


Figure 4.10 FT-IR (KBr) of the organic segment of the enzymatically cleaved DMAPA-CMG, lauryl acrylate copolymer (E)

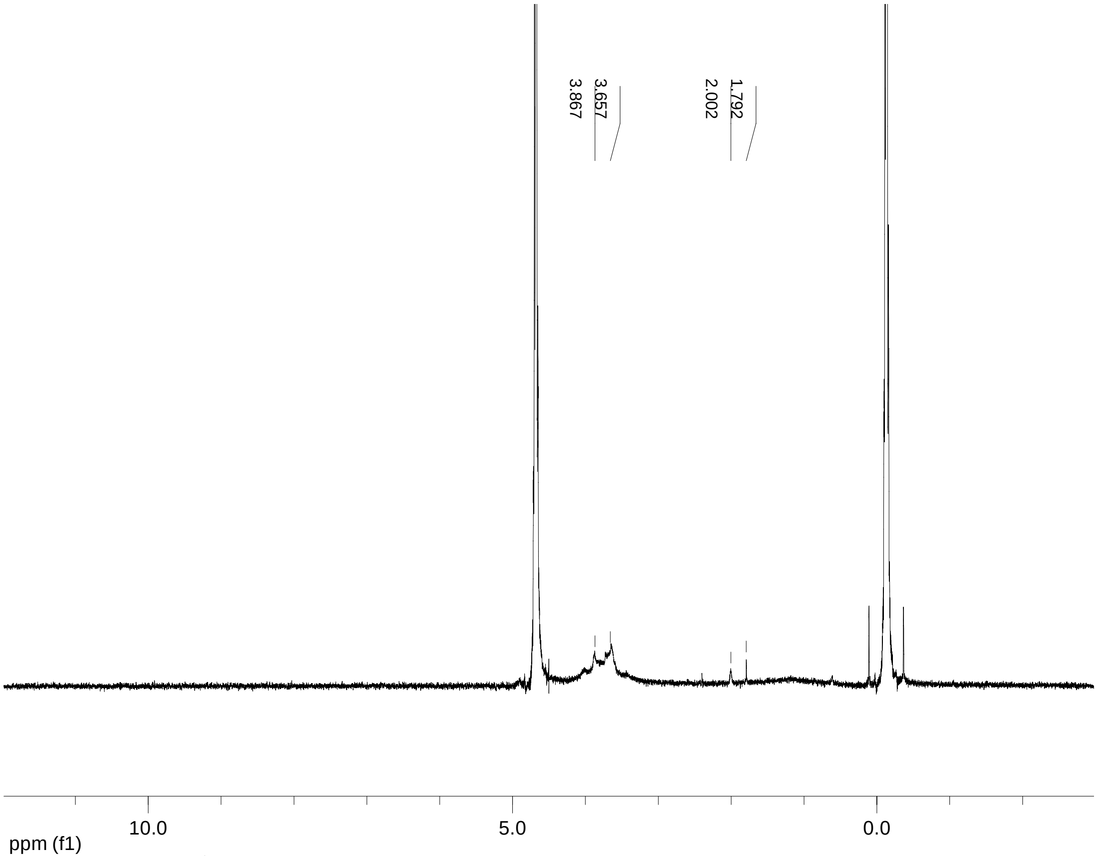


Figure 4.11 ^{1}H NMR (250MHz, D_2O) of the lauryl acrylate, DMAPA-CMG copolymer (E)

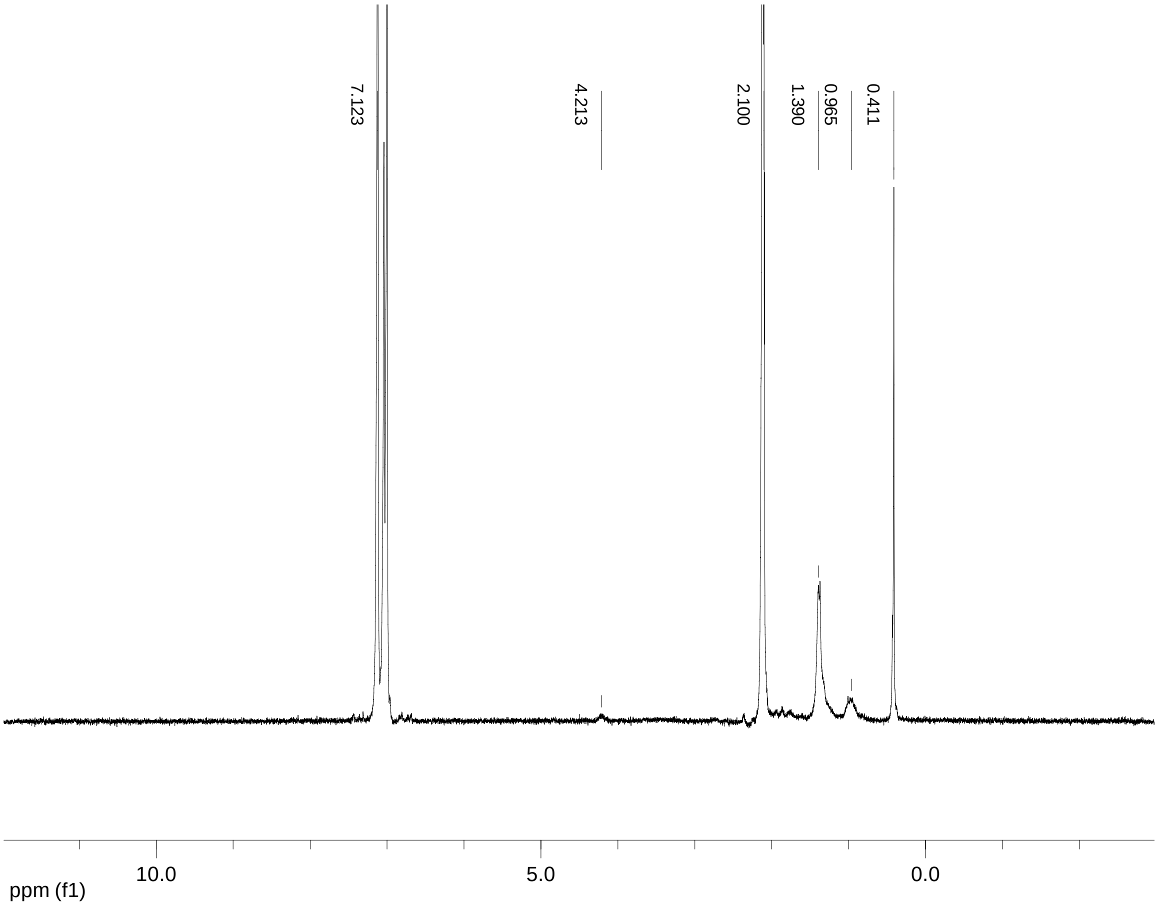


Figure 4.12 ^{1}H NMR (250MHz, d_8-toluene) of the lauryl acrylate, DMAPA-CMG copolymer (E)

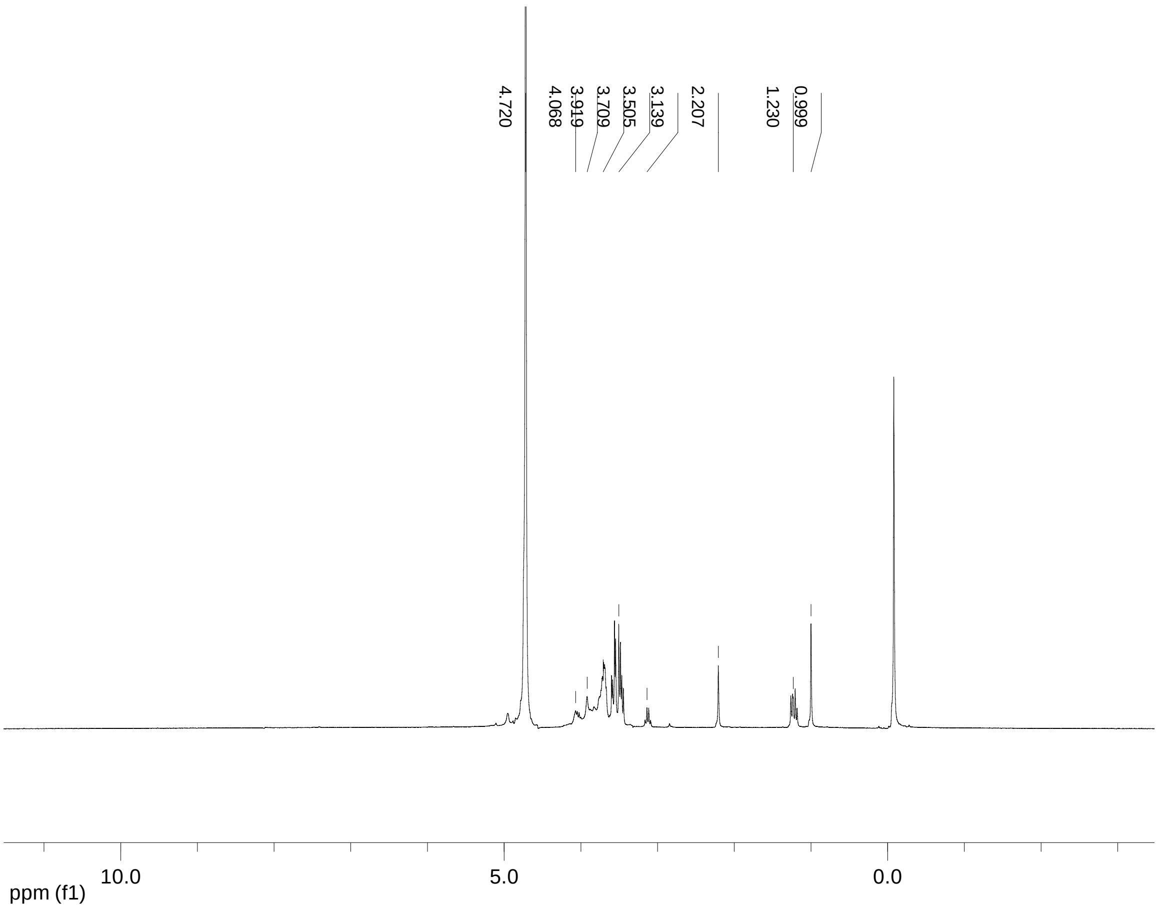


Figure 4.13 ^{1}H NMR (250MHz, D_2O) of aqueous segment of the enzymatically cleaved lauryl acrylate, DMAPA-CMG copolymer (E)

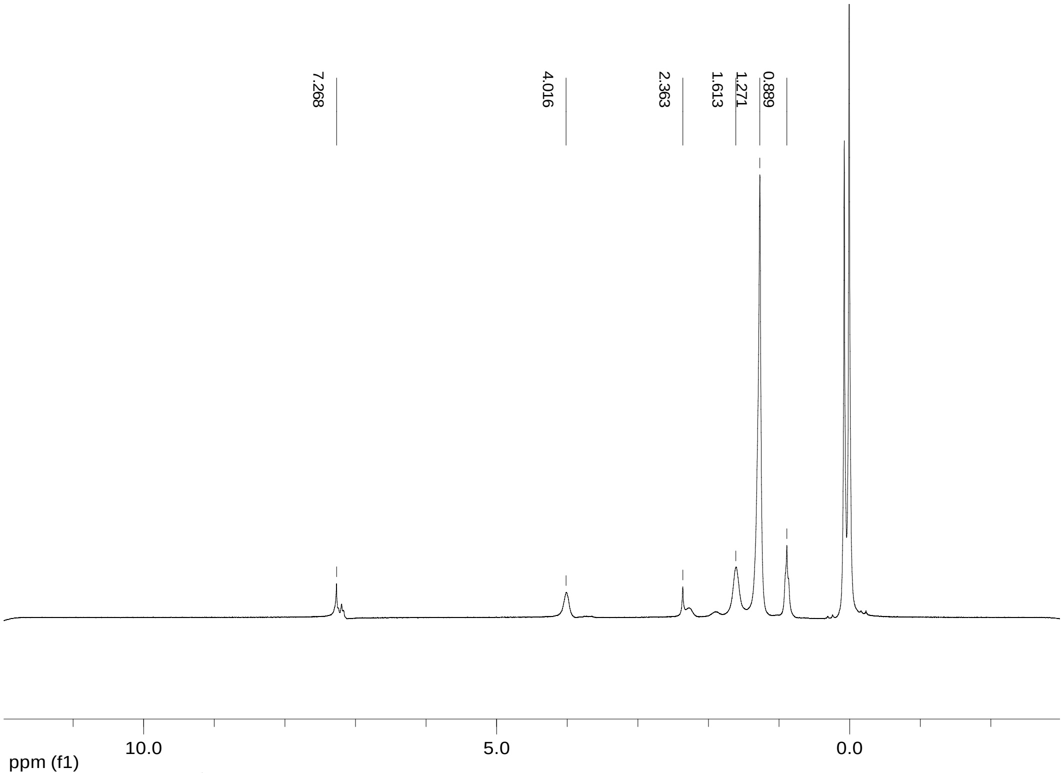


Figure 4.14 ^{1}H NMR (250MHz, $CDCl_3$) of organic segment of the enzymatically cleaved lauryl acrylate, DMAPA-CMG copolymer (E)

The poly(styrene-b acrylic acid)block copolymer terminated with RAFT agent (**1**) was grafted onto the DMAPA-CMG backbone (**F**), unlike growing the polymer chain from the polysaccharide backbone, the block copolymer was pre-constructed. The resulting photolytic reaction (**Figure 4.7**) proceeded through the mediation of the RAFT agent, **1**. The poly(styrene-b acrylic acid)block copolymer side chains were extracted by toluene after being enzymatically cleaved from the DMAPA-CMG backbone. Comparing the ^{1}H NMR($CDCl_3$) of the isolated side chains with the ^{1}H NMR (d6-acetone) of the poly(styrene-b acrylic acid)block copolymer (**Figure 4.16**) allows for easy identification of the peaks resolved from the block copolymer; the aromatic peaks from the polystyrene side chains have shifted slightly up field to 6.95 ppm. The peaks for protons of the saccharide unit attached to the side chain of the block copolymer are observed at 3.33 and 4.07 ppm.

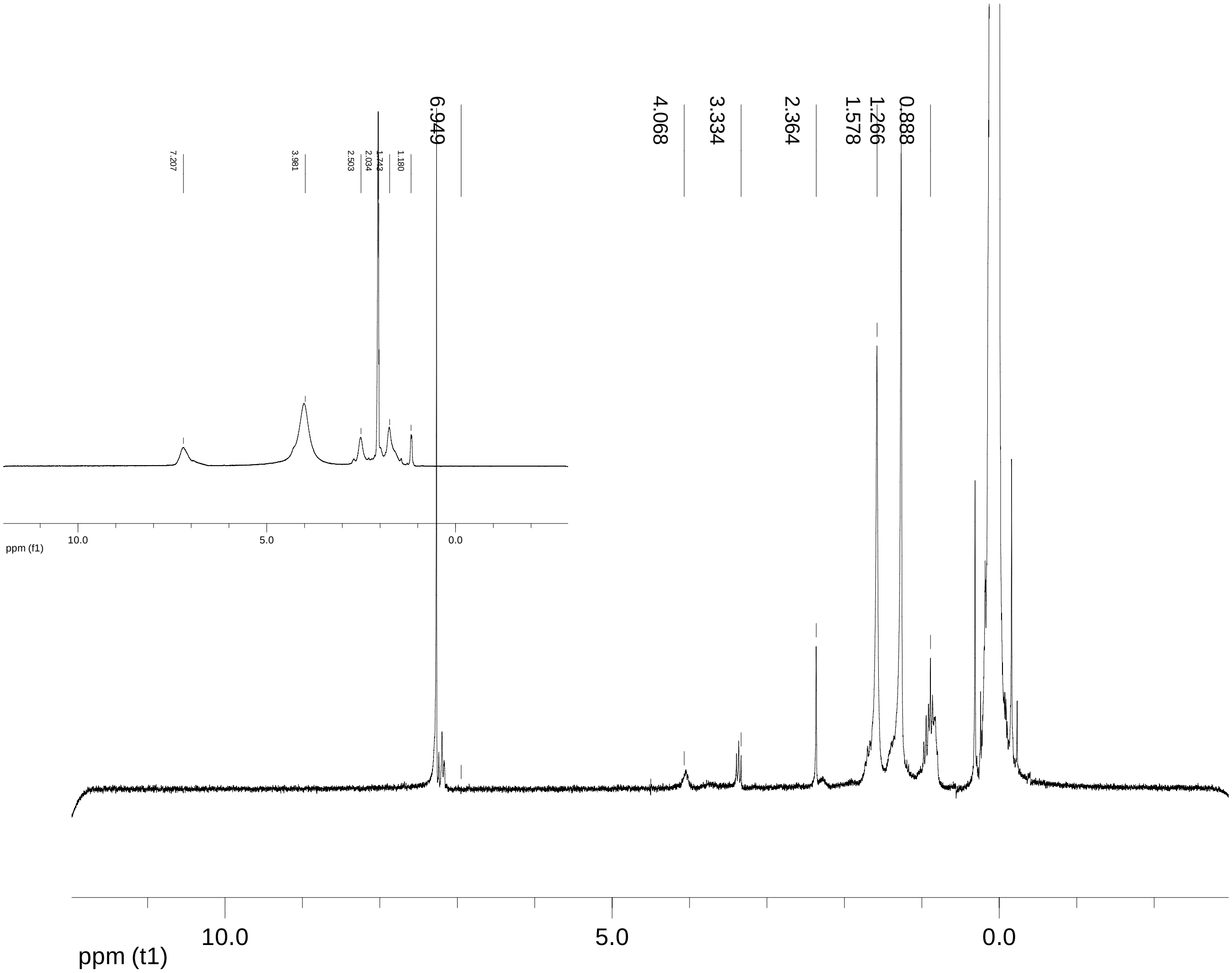


Figure 4.15 ^{1}H NMR (250MHz, $CDCl_3$) of organic side chains of enzymatically cleaved polystyrene, acrylic acid RAFT block copolymer grafted to CMG (F); upper left corner, ^{1}H NMR (250MHz, acetone-d6) of polystyrene, acrylic acid RAFT block copolymer

Chapter 5 Characterization of the Rheology of Crosslinked Gels

5.1 Introduction

The demands for greater oil well productivity require developing less damaging completion and stimulation fluids for enhanced oil recovery (EOR). It is imperative that the intended volume of proppant be transported to the newly created fracture. An essential aspect of carrier fluids in EOR is that the gel is properly degraded and flows efficiently from the fracture back to the surface lowering damage and maintaining a conductive pathway. A high-viscosity fluid is required to carry the proppant and maintain the proppant in solution down hole to the fracture. A low concentration of the thickener polymer may be crosslinked to achieve high viscosity. Once the proppant is placed in the created fractures, breakers chemically cleave the polymer backbone to oligomers which results in a drop in viscosity. The viscosity of the fluid must be easily reduced to that of water so that the broken gel may flow back easily between the grains of the sand (propping open the fractures) to allow for easy clean-up.[13,41,42]

This body of work has examined hydrophobically modified guar gum and hydrophobically modified CMG for use as carrier fluids in EOR efforts. The samples were degraded by an enzyme based breaker system which selectvively cleaves the guar backbone from a pH range of 5 to 9 (temperature ranges 45 – 105 ºC). Toluene was used to extract the degraded samples, which simulates the clean up process. Many of the modified CMG copolymers produced in chapters 3 and 4 exhibit improved rheological properties over guar gum and CMG. Measuring viscosity is a well accepted method for evaluating fracturing fluids in the oil industry. The evaluation of viscosity includes linear and the corresponding crosslinked fluids at different concentrations over an extended period of time.[29]

5.2 Experimental

5.2.1 Instrumentation

Gel viscosities of the non-crosslinked copolymers were measured at room temperature using a Brookfield dial reading viscometer with an electric drive. A number 4 spindle was used to determine the viscosity of the solutions prepared. The Brookfield manual stated that no calibration was necessary if the number 4 spindle was used in a 400mL beaker for the viscosity measurements. The polymer solutions were prepared using deionized water, and the samples were allowed to hydrate for at least one hour. Five revolutions of the spindle were allowed to pass before each dial reading was recorded. Several readings were taken at each RPM (rotation per minute), readings were taken in both increasing and decreasing order of RPM, an average of the readings recorded at each RPM was multiplied by the K value in order to obtain the viscosity (cP). **Table 5.1** displays the K values that correspond to each RPM (for spindle 4).

For the crosslinked copolymers, the higher viscosities were measured using a Brookfield PVS rheometer equipped with a B5 bob. This instrumentation is equipped to hold pressures of up to 1000 psi and temperatures over 250ºC. The device functions as a coquette coaxial cylinder rotational viscometer. When the outer cylinder rotates at a known velocity, this causes a viscous drag to be exerted by the fluid which will create a torque on the bob, the measurement recorded allows for calculating the viscosity. Deflection is measured when the torque is transmitted to a spring. The relationship between the deflection and the fluid viscosity is determined by calibration with standard fluids. The viscosity as measured by this apparatus is a measure of the shear stress caused by given shear rate. For Newtonian fluids, the relationship is a linear function (plot of shear rate versus shear stress is a straight line).

Table 5.1 K values for viscosity measurements for the Brookfield dial reading viscometer

Speed	Factor K
0.5	4000
1	2000
2.5	800
5	400
10	200
20	100
50	40
100	20

5.2.2 Viscosity Measurements

The samples were prepared according to industrially recommended concentrations 4.8g/L (40lb/1000 gal) and at lower concentrations of 2.4g/L (20lb/1000gal). The polymer samples were dispersed in deionized water and allowed to hydrate at least 30 minutes. Sodium thiosulfate (1.2g/L, 10lb/1000gal) was added as gel stabilizer. The viscosity of the polymer fluids before crosslinking was measured at different RPM's using the Brookfield dial reader, with spindle number 4.

The uncrosslinked polymer solutions were transferred to a Waring blender. The pH of the solutions was adjusted to 10, by adding a 5% KOH solution dropwise. Under excess shear, 0.2 – 0.4mL of zirconium carbonate crosslinking agent (Benchmark, 8.3%

zirconium carbonate) was added. The solutions were blended until the vortex disappeared, an indicator of gel formation. The resulting gel was transferred to the PVS Brookfield rheometer. The viscosity of the crosslinked polymers was measured at different shear rates. After the samples were loaded, the system was pressurized to 150psi. The specified shear rates for each of the shear rate ramps were 25, 50, 75, and 100 s^{-1} (a ramp refers to a single cycle of measuring the viscosities at each shear rate in increasing and decreasing order). The fluids were allowed to equilibrate for 40 seconds before any readings were taken. Three reading were collected for each shear rate. The fluids were sheared at a constant 100 s^{-1} initially and between shear rate ramps. All of the viscosity measurements were taken at room temperature.

5.2.3 Gel Hydrolysis

One percent aqueous solutions were prepared from the control (CMG) and the modified samples. The samples were previously crosslinked with zirconium carbonate at pH 10. After the pH of the fluids were reduced to pH 5 – 7, the enzyme breaker (pyrolase$^{\text{TM 200}}$), 0.3mL, was added to approximately 100mL of the gel solution and allowed to react for 2 hours at 60 C. To study the effectiveness of the break and to evaluate the hydrophobic fragments, 20mL aliquots were extracted with an equal amount of toluene. The solvents were evaporated from both the aqueous and organic fractions, and the samples were analyzed by FT-IR, NMR, and MALDI (matrix assisted laser desorption ionization mass spectrometry). An example of the cleaved gel separated into two layers is pictured in **figure 5.1**.

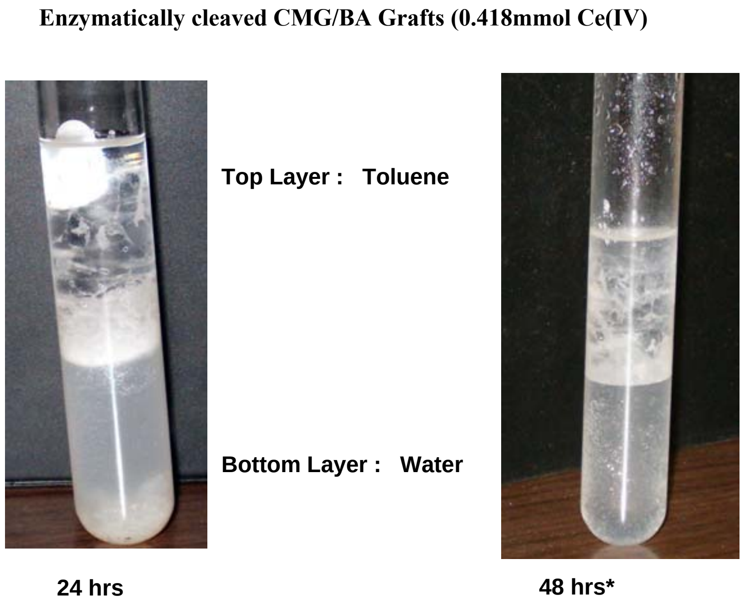


Figure 5.1 Enzymatically cleaved CMG, poly-n-butyl acrylate copolymer gel separated into aqueous and organic fractures

5.3 Results and Discussion

This chapter explores the rheology of the hydrophobically modified CMG copolymers that were able to be crosslinked by zirconium carbonate to form gels. **Table 5.2** is a summary of the gels produced from the selected copolymers. Strong gels with high viscosities were produced from the RAFT process of a photolytic induced system involving a CMG backbone modified with a tertiary amine, and the lauryl acrylate (**B**) or the poly(styrene-acrylic acid) block (**A**) grafted in this system produced. The copolymers A and B have gel viscosities higher than that of the CMG gel. The copolymers CMG-g-lauryl acrylate (**C**) and CMG-g-poly-n-butyl acrylate (**D**) prepared through a nitroxide-mediated CRP process; the resulting grafted copolymers produced strong gels with high viscosities comparable to the viscosity of CMG gel.

The poly(n-butyl acrylate)-g-CMG copolymers (**D**) were prepared using different reaction times. The 12 hour reaction time from the CRP process produced the only copolymer that formed a strong gel. The 18, 24, 48, and 72 hour reaction times for the graft copolymerization of poly-n-butyl acrylate produced water soluble polymers. The copolymers produced from the CRP of 18 and 24 hour reaction times formed weak gels that upon increasing shear broke down in viscosity irreversibly. The 48 and 72 hour reaction times for the poly-n-butyl acrylate copolymerization produced polymers that did not crosslink to form a gel.

Figure 5.2 examines the rheology of the CMG-g-poly-n-butyl acrylate gel (**D**) after a 12 hour reaction time. The viscosity for gel **D** is five times lower than the viscosity of CMG gel. Over the given time range of measuring the viscosity, shear degradation was minimal. As shear was reduced, the viscosity of the copolymer was virtually restored to its initial measurements (at low shear).

Table 5.2 Comparison of gels produced from CMG copolymers

Copolymer	Mediator	% Weight Gain	Gel Strength	Max. Viscosity (cP) (shear rate 25 s-1)
CMG	**-------**	**-------**	**Strong**	**5,800**
DMAPA-CMG-g-Poly(Styrene-Acrylic Acid) Block (A)	**RAFT**	**67.6**	**Strong**	**6,000**
DMAPA-CMG-g-Lauryl Acrylate (B)	**RAFT**	**14.8**	**Strong**	**6,800**
CMG-g-Lauryl Acrylate (C)	**DEPN**	**44.8**	**Strong**	**4,000**
CMG-g-Poly-n-Butyl Acrylate, 12hr (D)	**DEPN**	**17.8**	**Strong**	**1,000**
CMG-g-Poly-n-Butyl Acrylate, 18hr (D-2)	**DEPN**	**22.1**	**Weak**	**----------**
CMG-g-Poly-n-Butyl Acrylate, 24hr(D-3)	**DEPN**	**26.5**	**weak**	**-----------**

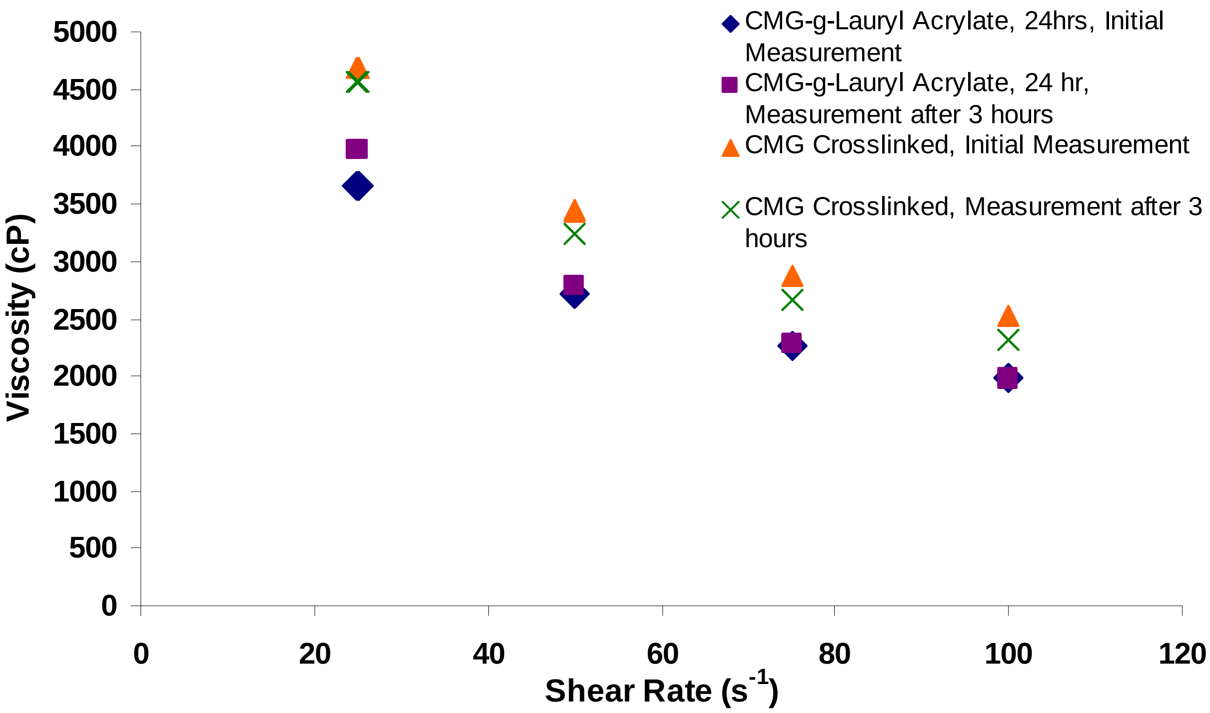


Figure 5.2 **Viscosity of DEPN mediated CMG-g- poly-n-butyl acrylate crosslinked copolymer under cyclic stress conditions (D)**

Lauryl acrylate grafted to the CMG backbone in both the DEPN (nitroxide) mediated CRP process (**C**) and the RAFT free radical process (**B**) produced a copolymer that would crosslink to form a gel. **Figure 5.3** is the comparison of the viscosities for the crosslinked and non-crosslinked lauryl acrylate, CMG copolymer (**C**). The plot illustrates a higher viscosity (measured with the Brookfield dial reading viscometer) for the crosslinked gel than for both non-crosslinked copolymer and the non-crosslinked CMG. **Figure 5.4** is a plot of the viscosities for the crosslinked lauryl acrylate copolymer (**C**) measured with the Brookfield PVS rheometer. The viscosity of the copolymer **C** gel is high, approaching that of the CMG gel. Although the viscosities drop with increasing shear, they are restored to initial viscosity (for that time range). The measurements were taken over three hours, revealing very little change in viscosity of copolymer **C** over time.

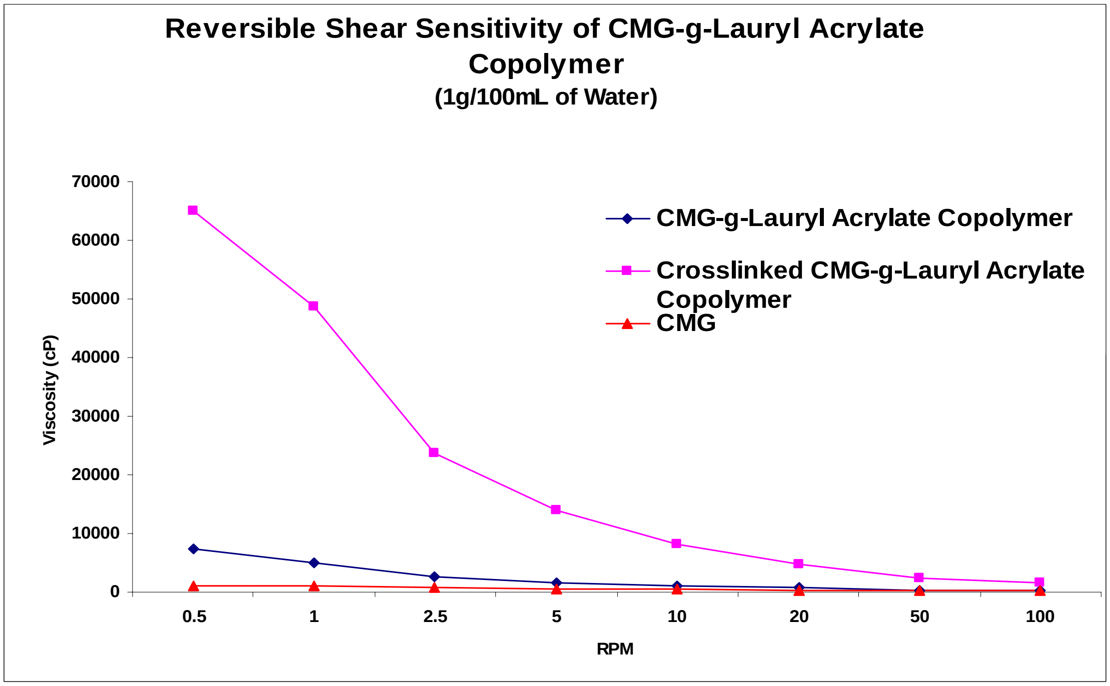


Figure 5.3 Viscosity comparison between the crosslinked and non-crosslinked CMG-g-lauryl acrylate copolymer (C)

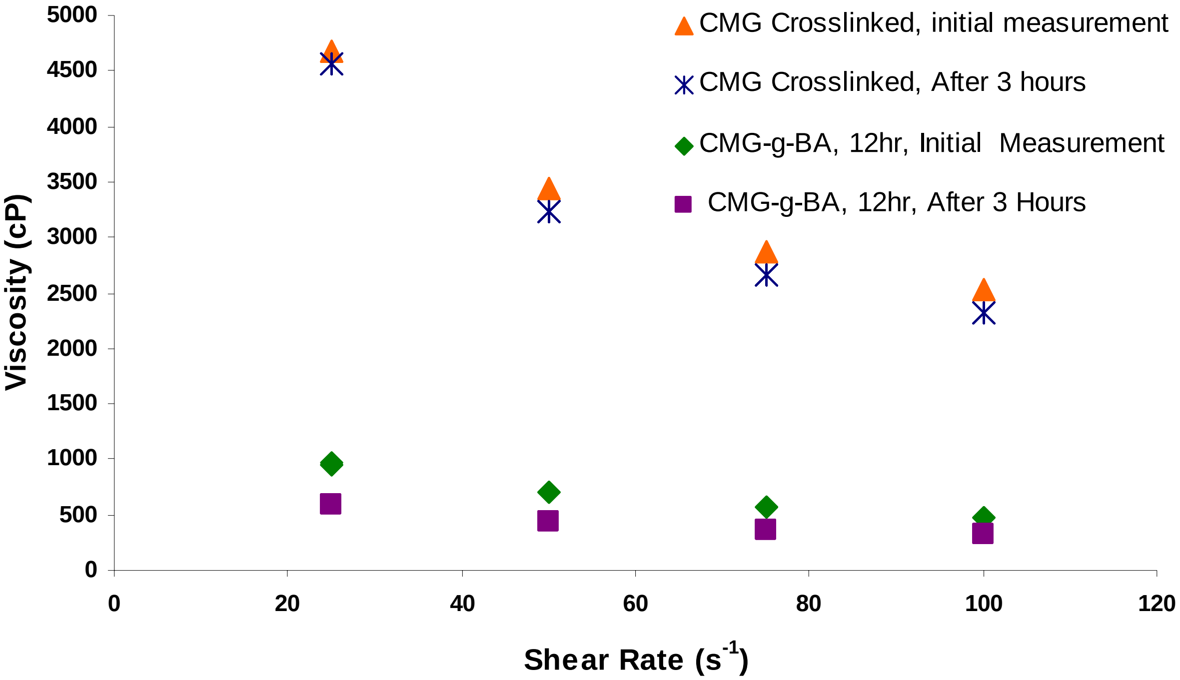


Figure 5.4 Viscosity of DEPN mediated CMG-g-lauryl acrylate crosslinked copolymer under cyclic stress conditions (C)

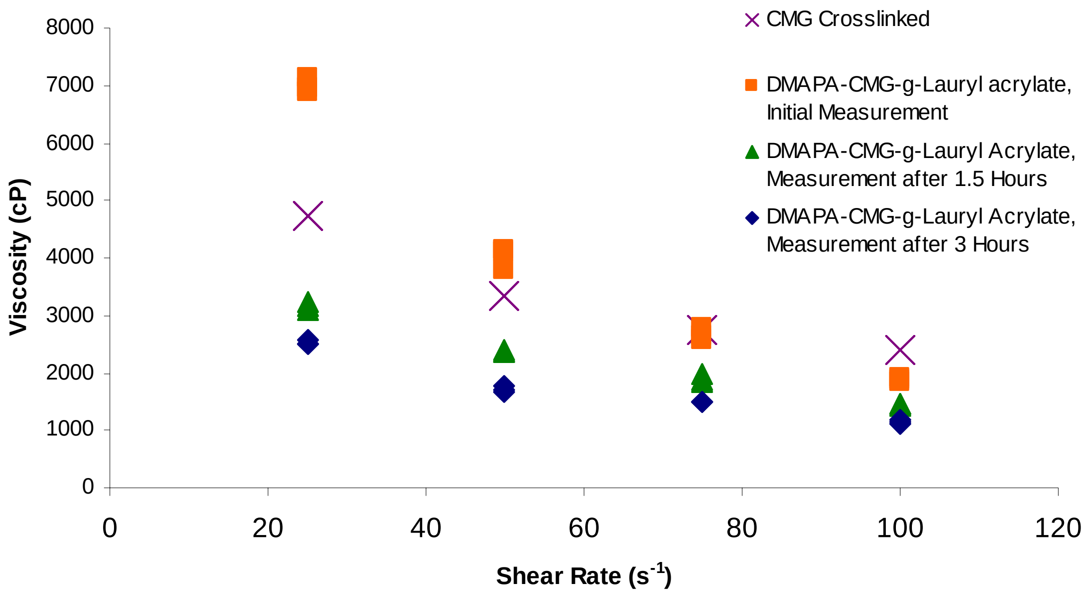


Figure 5.5 Viscosity of DMAPA-CMG-g-lauryl acrylate crosslinked copolymer under cyclic stress conditions (B)

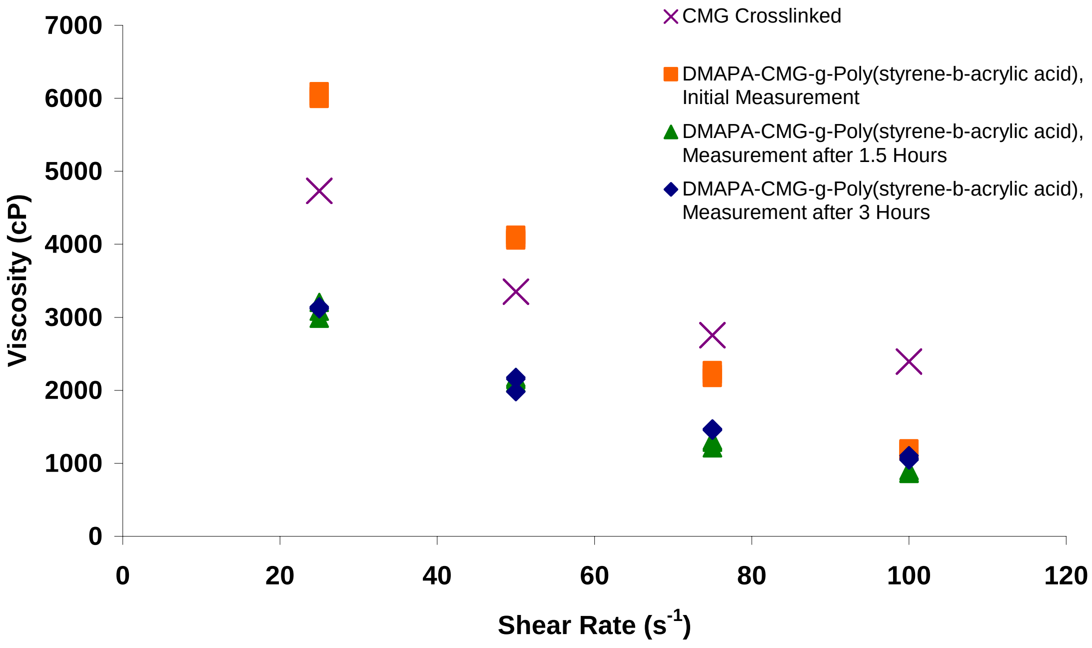


Figure 5.6 Viscosity of DMAPA-CMG, poly(styrene-acrylic acid) graft crosslinked copolymer under cyclic stress conditions (A)

A look at the gel viscosity measurements of the hydrophobically modified copolymers produced from the RAFT free radical process indicates that the materials are high viscosity shear thinning. **Figure 5.5** illustrates that the viscosities of the crosslinked lauryl acrylate, DMAPA-CMG copolymer (**B**) gel are higher than the viscosity for crosslinked CMG. After 1.5 hours of measuring the viscosity of copolymer **B**, the viscosity dropped two fold, but the viscosity was maintained for an additional 1.5 hours. **Figure 5.6** is a plot of the viscosity of the DMAPA-CMG, poly(styrene-acrylic acid) block graft copolymer gel under cyclic stress conditions (**A**) in which the copolymer has a higher viscosity than the CMG gel at under low shear. After 1.5 hours of cycling the shear (ranging form 25 – 100 s^{-1}) of gel **A**, the viscosity of the copolymer dropped by as much as half at low shear to viscosity lower than that of the CMG gel and remained constant for another 1.5 hours. Under high shear (100 s^{-1}), the viscosity of gel **A** has the same value for three hours under cyclic shear conditions.

Chapter 6 Summary and Future Work

6.1 Conclusions

Water soluble copolymers produced from the hydrophobic modification of guar gum and CMG were successfully synthesized through controlled radical polymerization (CRP) methods described in this work. The most successful materials are not only water soluble but were able to be crosslinked (with zirconium carbonate) to produce gels; these grafts were produced through nitroxide-mediated CRP process and through the RAFT radical polymerization of hydrophobic moieties onto the backbone of CMG. The grafting process was verified and monitored by FT-IR and ^{1}H NMR.

The grafted derivatives were evaluated for hydraulic fracturing application in the oil industry. The rheological properties of the grafted derivatives were compared with the polysaccharide backbone guar gum and CMG. Aqueous solutions of the graft copolymers exhibit viscosities one or two orders of magnitude lower than solutions of the corresponding polysaccharide. Aqueous solutions of the graft copolymers crosslinked with a zirconium crosslinking agent at high pH displayed rheological properties surpassing that of the polysaccharide. The crosslinked fluids were degraded by treatment with an enzyme breaker system, to facilitate the clean up process. The degraded parts of some of these derivatives created emulsions when extracted with organic solvent. It is important to note that the side chains grafted to the backbone of guar gum (as well as CMG) have different degrees of hydrophobicity which imparts different degrees of surfactancy to the gel fragments. The low viscosity and the surfactant behavior of the fragments make them less damaging materials to the formation and they can be removed easily from the formation either by flow back of oil or water. The clean up process should be facilitated by the surfactant behavior of degraded guar adducts.

The viscosity of the hydrophobically modified polymers increases with increasing hydrophobe addition and alkyl chain length provided the hydrophobe incorporation does not the exceed the maximum amount allowed to maintain aqueous solubility of the polymer. The viscosities of the hydrophobically modified copolymers are high at low shear rates. The hydrophobically modified polymers over come the problem of shear degradation, because the intermolecular associations, broken down by high shear conditions, will reform when the shear stress return to lower values. The results obtained from this research indicate that improved flow properties and greater viscosities may be achieved by incorporating hydrophobically modified guars into the EOR process.

6.2 Future Work

Future experimental study should be carried out on the rheological properties of the hydrophobically modified CMG copolymers in order to confirm the suitability of these products for use as fracturing fluids.

1. The compatibility of these materials with the fluids of the formations must be studied (each formation has different types of fluids used in EOR). This may be achieved by preparing the samples using brines or fluids from the formation and study their behavior.
2. The long term rheological behavior of these fluids at the reservoir high pressure and temperature must be assessed more thoroughly. This may be simulated with the Brookfield instrument which may operate at temperatures of up to 200ºC and pressures up to 1000psi.

3. Solid state NMR may provide a means to give a more accurate assessment of graft content. Using solid samples would eliminate the effect of solvents, solubility or high viscosity problems that were observed when preparing the samples in solution.
4. Other candidates for the hydrophobe moiety of the grafted copolymer may offer improved rheology properties. The poly(styrene-acrylic acid) block copolymer grafted onto the modified CMG backbone (functionalized with a tertiary amine) displayed the most promising rheological traits (water soluble, shear thinning, high viscosities); this system should be studied more in the future. The block moiety could also be optimized and other blocks could be considered for preparing water soluble grafted copolymers.
5. The chemistry of binding with RAFT copolymers to form grafted materials should be examined further. The process may provide a facile method for introducing grafts with controlled chain lengths.

References

(1) Harris, PC *Journal of Petroleum Technology* **1988**, *SPE 17112*, 1277 - 1278.

(2) Dawson, J, Kesavan , S, Lee, HV, USA Patent, 6387853B1, 2002.

(3) Ely, JW *Stimulation Engineering Handbook*; 2nd ed.; Penn Wells Publishing Company: Tulsa, OK, 1994.

(4) Dantas, T, Santana, VC, Neto, AA, Moura, MC *Journal of Dispersion Science and Technology* **2005**, *26*, 1 - 4.

(5) Cheng, Y, Brown, KM, Prud'homme, RK *Biomacromolecules* **2002**, *3*, 456.

(6) Kruijf, A, Roodhart, LP, Davies, DR *Society of Petroleum Engineers* **1983**, SPE25206, 525.

(7) Gidley, J, Holdtich, SA, Nierode, DE, Veatch, RW *Society of Petroleum Engineers* **1989**, *12*, 1 - 38.

(8) Shah, S, Lord, DL, Rao, BN *Society of Petroleum Engineers* **1997**, SPE37487, 751.

(9) Wang, X, Quu, Q, McCarthy, S, Null, J, Bowen, K *Society of Petroleum Engineers* **2002**, SPE73789, 1.

(10) Much, M, Franklin, V *Society of Petroleum Engineers* **1998**, SPE3978, 273.

(11) Stahl, G, Schulz, DN, Water-Soluble Polymers for Petroleum Recovery, American Chemical Society Proceedings, Plenum Press, Anaheim, California, 1986.

(12) Flippen, M, Yang, B *Society of Petroleum Engineers* **1997**, 38305, 433.

(13) Seaman, J *Handbook of Water Soluble Gums and Resins*; McGraw Hill, 1980.

(14) Trade India http://www.trade-india.com, 2006.

(15) Gitting, M, Cipelletti, L, Trappe, V, Weitz, DA-M, Marques, C *Journal of Physical Chemistry, B* **2000**, *104*, 4381.

(16) Parija, S, Misra, M, Mohanty, AK *Journal of Macromolecular Science - Polymer Reviews* **2001**, *C41*, 3, 175 - 197.

(17) Moorehouse, R, Harry, DN, and Merchant, U *Society of Petroleum Engineering* **1998**, *SPE 39531*, 253 - 269.

(18) *Reservoir Stimulation*; 3rd ed.; Economides, M, Nolte, K, Ed.; Wiley: New York, 2000.

(19) Lapasin, R, DeLorenzi, L, Priel, S *Carbohydrate Polymers* **1995**, *28*, 195.

(20) Dawson, J *Society of Petroleum Engineers* **1991**, SPE21230, 203.

(21) Ainley, B, Nimerick, KH, Card, RJ *Society of Petroleum Engineers* **1993**, 25463, 517.

(22) Rosene, R, Shumaker, EF *Society of Petroleum Engineers* **1971**, 33471, 1.

(23) Putzig, DE, European Patent Application, 1989:26480, 1988.

(24) Farnworth, F, Jones, SL, McAllpine, I *In Specialty Inorganic Chemicals*; RSC: London, 1981.

(25) Moles, P, MEL Chemicals http://www.zrchem.com.

(26) Raval, D, Patel, MV, Patel, RG, Patel, VS *Starch/Staerke* **1991**, *43*, 12, 483 - 487.

(27) Weaver, JD, Slabaugn, Billy F, Halliburton, USA Patent Application, 20050065038, 2003.

(28) Grattoni, CA, Al-Sharji, HH, Yang, C, Muggeridge, AH, Zimmerman, RW *Journal of Colloid and Interface Science* **2001**, *240*, 601 - 607.

(29) Bock, J, Siano, DB, Valint, PL Jr., Pace, SJ *Advances in Chemistry Series, American Chemical Society* **1989**, *223*, 411 - 424.

(30) Klucker, R, Candau, F, Schosseler, F *Macromolecus* **1995**, *28*, 6416 - 6422.

(31) Bahadur, P, Sastry, NV *Principles of Polymer Science*; Alpha Science International Ltd: Pangbourne, England, 2002.

(32) Beihoffer, T, Lundberg, DJ, Glass, JE, **Influence of polarity in water - soluble polymer synthesis.** Advances in Chemistry Series **1989**, 223(Polym. Aqueous Media), 51-64.

(33) Evani, S, Rose, GD *Polymeric Materials, Science and Engineering* **1987**, *57*, 477-481.

(34) Audibert, A, Argillier, JF, Ladva, H, Way, P, Hove, A, Netherlands *Society of Petroleum Engineers* **1999**, SPE54767.

(35) Kruljf, A, Roodhart, LP, Davies, DR *Society of Petroleum Engineers* **1983**, 25206, 525.

(36) Peiffer, D, Kaladas, JJ, USA Patent, 4,894,422, 1990.

(37) Schulz, D, Kaladas, JJ, Maurer, JJ, Bock, J *Polymer* **1984**, *28*, 12, 2110 - 2115.

(38) Maurer, J, Schulz, DN, Bock, J, USA Patent, 4,579,926, 1986.

(39) Schulz, D, Maurer, JJ, Bock, J, USA Patent 4,463,151, 1984.

(40) Biggs, S, Hill, A, Candau, F *Journal of Physical Chemistry* **1992**, *96*, 1505 - 1511.

(41) Flynn, C, Goodwin, *JW, Polymers as Rheology Modifiers*, ACS Symposium Series, American Chemical Society **1991**, *462*, 2 - 17.

(42) McCormick, C, Hester, RD, Davis, DL, Middleton, JC, Polymers for Mobility Control in Enhanced Oil Recovery, DOE/BC/10844-20, 1990.

(43) McCormick, C, Johnson, CB Water Soluble Polymers for Petroleum Recovery; Stahl, G., Schulz, D.N, Ed.; Plenum Press: New York, 1988.

(44) Valint, P, Brock, J, Schulz, DN Polymers in Aqueous Media: Performance through Association Glass, J. E., Ed.; American Chemical Society: Washington, D.C., 1989.

(45) Evenson, T Dissertation, Louisiana State University, 1994.

(46) Jasinski, R, Redwine, D, Rose, G *Journal of Polymer Science: Part B: Polymer Physics* **1996**, *34*, 1477 - 1488.

(47) Subhash, NG, Shah, N, Yuan, W-L, O'lear, E, A *Journal of Applied Polymer Science* **2001**, *82*, 6, 2978 - 2990.

(48) Chowdhury, S, Kundu, N *Journal of Organic Chemistry* **2001**, *82*, 3520.

(49) Taunk, K, Behari, K *Journal of Applied Polymer Science* **2000**, *77*, 39.

(50) Thimma, R, Tammishetti, S *Advanced Technology in Polymers* **2003**, *14*, 663.

(51) Szwarc, M *Nature (London)* **1956**, *78*, 1168.

(52) Szwarc, M, Levy, M *Journal of the American Chemical Society* **1956**, *78*, 2675.

(53) Odian, G *Principles of Polymerization*; 3rd ed., 1991.

(54) Georges, M, Veregin, RPN, Kazmaier, PM, Hammer, GK *Macromolecules* **1993**, *26*, 2987.

(55) Georges, M, Veregin, RPN, Kazmaier, PM, Hammer, GK *Journal of Physical Organic Chemistry* **1995**, *8*, 301 - 305.

(56) Greszta, D, Matyjaszewski, K *Macromolecules* **1996**, *29*, 7661.

(57) Hawker, C, Barclay, GG, Orellana, A, Dao, J, Devonpor, W *Macromolecules* **1996**, *29*, 5245.

(58) Hawker, C, Elce, E, Dao, J, Volksen, W, Russell, TP, Barclay, GG *Macromolecules* **1996**, *29*, 2686.

(59) Wang, J, Matyjaszewski, K *Macromolecules* **1995**, *28*, 7901.

(60) Gray, M K, Zhou, H, Nguyen, ST, Torkelson, JM *Macromolecules* **2003**, *36*, 5792.

(61) Bisht, H, Chatterjee, A *Journal of Macromolecular Science - Polymer Reviews* **2001**, *C41(3)*, 139 - 173.

(62) Solomon, D, H, Rizzardo, E, Cacioli, P, USA Patent, 4,581-429, 1986.

(63) Hawker, C *Accounts of Chemical Research* **1997**, *30*, 373.

(64) Baldovi, T, Mohtat, MV, Scaiano, JC *Tetrahedron Letters* **1996**, *37*, 4919.

(65) Fukuda, T, Terauchi, T, Goto, A, Tsujii, Y, Miyamoto, T, Shimizu, Y *Macromolecules* **1996**, *29*, 3050.

(66) Benoit, D *Journal of the American Chemical Society* **1999**, *121*, 16, 3904 - 3920.

(67) Benoit, D *Polymer Preprints* **1997**, *38*, 651.

(68) Farcet, C *Macromolecules* **2000**, *33*, 23, 8559 - 8570.

(69) Guerret, O, USA Patent, 0077873 A1, 2004.

(70) Grimaldi, S *Macromolecules* **2000**, *33*, 4.

(71) Hawker, C *Journal of the American Chemical Society* **1994**, *116*, 11185.

(72) Sharma, B, Kumar, Vineet, Soni, PL *Journal of Macromolecular Science: Part A-Pure and Applied Chemistry* **2003**, *40*, 49 - 60.

(73) Barton, D, Kretzschmar, G *Tetrahedron Letters* **1983**, *24*, 5889.

(74) Chiefari, J, Chong, YK, Ercole, F, Kristina, J, Jeffery, J, Le, T-N, Toshan, Moad, G, Moad, Moad, C, Rizzardo, G, Thang, ES *Macromolecules* **1998**, *31*, 5559 - 5562.

(75) Cunningham, MF *Progress in Polymer Science* **2002**, *27*, 1039 - 1067.

(76) Lai, JT, Filla, D, Shea, R *Polymer Preprints* **2002**, *43*, 2, 122

(77) Monteiro, M, Hodgson, M, De Brouwer, H *Journal of Polymer Science* **2000**, *38*, 3864 - 3874.

(78) Bahamdam, A Dissertation, Louisiana State University, 2005.

(79) Moad, G, Solomon, DH *The Chemistry of Free Radical Polymerization* Pergamon, Oxford, 1995.

(80) Monteiro, MJ, Sjoberg, M, Van der Vlist, J, Gottgens, CM *Journal of Polymer Science A: Polymer Chemistry* **2000**, *38*, 4206 - 4217.

(81) Monteiro, MJ, Hodgson, M, De Brouwer, H *Journal of Polymer Science A: Polymer Chemistry* **2000**, 38, 3864 - 3874.

(82) Lansalot, M, Farcet, C, Charleux, B, Bairon, JP, Pirri, R *Macromolecules* **1999**, *32*, 7354 - 7360.

(83) Lee, TP, Moad, G, Rizzardo, E., European Patent, WO 9801478, 1998.

(84) Matyjeszewski, K *Controlled radical polymerization*; American Chemical Society: Washington, D.C., 1998.

(85) Ganachaud, F, Monteiro, M, Gilbert, R, Dourges, M-A, Thang, S, Rizzardo, E *Macromolecules* **2000**, *33*, 6378 - 6745.

(86) Campbell, I *Introduction to Synthetic Polymers*; 2nd ed.; Oxford University Press: New York, 2000.

(87) Lee, DI, The control of structure in emulsion polymeriazation, Macromolecular Symposia, Huthig and Wepf Publishers, Zug, Switerzerland, 33, 1990.

(88) Starnes, WH, Jr., Zaikov, Chung *Macromolecules* **1998**, *31*, 1508 -1517.

(89) Waldermar, A, Moorthy, J, Nau, W, Scaiano, JC *Journal of the American Chemical Society* **1997**, *119*, 6749 - 6756.

(90) Viswanathan, KH, Joensson,CE, Nason, S, Lindgren, C *Macromolecules* **2002**, *35*, 21, 7963 - 7967.

(91) Dyer, D, Feng, J, Schidt, R, Wong, VN, Zhao, T, Yagci, Y *Macromolecules* **2004**, *37*, 7072 - 7074.

(92) Feng, J, Haasch, R, Dyer, D *Macromolecules* **2004**, *37*, 9525 - 9537.

Vita

Veronica K. Holmes is a native of Bayou Goula, Louisiana. She graduated from White Castle High School in White Castle, Louisiana, in Spring,1995. She received a Bachelor of Science degree from Southern University A&M, Baton Rouge, Louisiana in Spring,1999. She received a Doctor of Philosophy in chemistry from Louisiana State University and Agricultural and Mechanical College in Spring, 2007. She intends to pursue a career in industry as a research and development chemist.