Glycerol-based polymers and their pathway to industrial relevance

Michael John Forrester
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Glycerol-based polymers and their pathway to industrial relevance

by

Michael J Forrester

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Program of Study Committee:
Eric Cochran, Major Professor
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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2018
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DEDICATION

This collection of work is dedicated to my family. Their love and support give me the drive to continue the work even on the days when nothing seems to work the way I want.
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The work disclosed in this thesis is a discussion of the properties and implementation of glycerol-based materials with an emphasis on poly(acrylated glycerol). The first work discussed is the production and characterization of acrylated glycerol polymers. Because of the current abundance of glycerol, there is a large potential for materials and chemicals derived from glycerine. In this work we look at making and studying thermoplastic poly (glycerol-acrylate). In order to prevent these materials from rapidly producing thermosets, a type of polymerization chemistry known as reversible addition fragmentation chain transfer, or RAFT, is utilized. RAFT polymerization is a type of controlled radical polymerization that uses a small molecule called a chain transfer agent (CTA) to control the polymerization and to limit termination. As the CTA may not always be located at the end of the polymer chain it is of importance to know the stability of this molecule, especially when scale up is being considered.

This leads us to the second work in this thesis which is the study of the thermal stability of the CTA. This is important as many industrial processes use elevated temperatures in the processing of their materials. If these glycerine polymers are to be of industrial relevance the should ideally be compatible with existing polymer processing methods.

The third chapter of this thesis is the study of converting a living anionic polymer into a macro-chain transfer agent through a method known as atom transfer radical addition fragmentation reaction (ATRAF). The development of this method would open the door to efficiently producing glycerol, or other acrylics, that are block copolymers with styrenic or diene blocks. This work would give glycerol-acrylic polymers a strong competitive advantage against traditional petrochemical materials as it has properties that are difficult,
or impossible, to obtain through petrochemical monomers, are abundant, and cost effective.

Finally I will detail two ongoing projects. The first ongoing work is the development of a more scalable way of converting living anionic polymers into macro-chain transfer agents. This is done first by converting the anion into a macro-monomer and then doing a single insertion RAFT step to yield the macro-cta. I will detail what synthesis and characterization has been completed and what work is yet to be done. The second is the production of glycerol-acetal/acetate-acrylate polymers. These materials have glass transitions that are higher than that of glycerol-acrylate polymers. In this work I detail the initial synthesis and characterization that has been completed and the work that we are intending to complete.
CHAPTER 1. INTRODUCTION

The interest in materials derived from biologically derived sources is continually gaining momentum due to the cost, availability, and environmental impacts of petrochemical derived materials. This provides a unique challenge as most biologically derived chemicals tend to have a plethora of functional groups, and this makes the production of wide-scale industrially relevant materials somewhat challenging. In this work we not only look at polymers derived from an abundant and cheap bio-derived material, glycerol, but we show studies and develop methods that allow glycerol, and other biologically derived chemicals, industrially viable.

The first work discussed in this work, is the production and characterization of glycerol-acrylic thermoplastic polymers. Glycerol is widely produced, especially since the boom in the biodiesel industry, and the supply far exceeds the demand. Typically, glycerol has been seen in the food, beverage, cosmetic, and pharmaceutic industries with its primary purposes being a hydrating agent, a lubricant, or a sweetener. This gives glycerol a great opportunity to perform in new markets. There are some challenges to producing glycerol thermoplastics however. Because glycerol has three alcohols, it is very challenging to prevent the glycerol from becoming a multifunctional acrylic monomer. In turn this multifunctionality makes it difficult to produce polymers that are thermoplastics. This is due to the cross-linking that is common with multifunctional monomers. This cross-linking can be suppressed by use of the RAFT polymerization method, a type of controlled radical polymerization. This limits not only the rate of cross-linking, but also the rate of termination, allowing us to make large molecular weight thermoplastic materials. Once these materials have been synthesized we study the thermal, mechanical, and solubility
properties of the material at various levels of acrylic functionality as well as molecular weights.

While there have been a large variety of soft, low glass transition bio-derived polymers that have been described in literature, there have been very few high glass-transition polymers. These have typically been derived from sources such as lignin and have proved to be very challenging to make higher molecular weight thermoplastics. It is of particular interest to be able to produce affordable high molecular weight thermoplastic materials that are derived from biological sources, and in one of the ongoing works we are looking at two materials derived from glycerol that seek to accomplish this goal. It was discovered that the functionalization of the residual alcohols on glycerol-acrylic polymers led to a significant increase in glass transition. In this chapter we look at glycerol-acrylic polymers that are functionalized with acetal as well as acetyl functionality and study the properties of these materials.

It is our belief that these materials may one day be of industrial relevance as they have some very interesting and diverse properties. In order for these materials to have as much commercial viability as possible it is necessary that they are nearly "plug and play" with existing infrastructure. This not only cuts cost, but reduces the risk associated with producing a new product. One large concern about any RAFT based polymer is the thermal stability of the chain transfer agent (CTA). The CTA is a small molecule that controls the polymerization, and is susceptible to thermal degradation. This becomes particularly important if the CTA is located somewhere within the polymer chain rather than at the end of the chain. In this case, a degradation of CTA would cause a decrease in molecular weight, and would likely lead to a significant loss of mechanical and thermal performance. This thermal degradation is the focus of the second work discussed here. We study degradation of CTA as a function of temperature as well as position on the chain in order to make recommendations about not only what temperatures and durations can
be used to process the materials, but also to intelligently design where the CTA is located on the polymer.

Another step that can be taken to make these glycerine polymers as commercially attractive as possible is the ability to combine them with existing polymerization techniques. Anionic polymerization is one of the most extensively utilized polymerization methods for making block copolymers. It is not only extremely effective at polymerizing monomers such as styrene and dienes, it is also a very mild polymerization method. Anionic polymerization does have several limitations however. The polymerization of (meth)acrylics can only be done in sub ambient conditions with dry ice bath temperatures usually required. This becomes prohibitively expensive for all but the most high-value products. This is particularly disappointing considering the volatility of most diene prices and the relative stability of most acrylic prices. Radical polymerization is very well suited to polymerizing (meth)acrylates, but there are some significant drawbacks to RAFT polymerization. RAFT polymerization is abysmally sluggish at polymerizing styrenics and is almost completely inept at polymerizing diene polymers. This has led us to the next work that we will discuss which is a transformation of an anionically grown polymer into a RAFT macro-CTA. We utilize a reaction refered to as atom transfer radical addition-fragmentation (ATRAF) reaction. This is a process that yields efficiencies of 97% or greater in relatively short amounts of time. In addition, it utilizes a fairly simple method, with materials that are fairly inexpensive. The development of this method would potentially allow the anionic polymer industry to produce block copolymers made from any (meth)acrylic monomer, and could lead to further interest in bio-based acrylic polymers such as glycerol-acrylate.

Another method that we pursued for the conversion of an anionically grown polymer into a macro-CTA is the conversion of an anionic polymer first into a macromonomer. From this point we performed a single-insertion RAFT step to convert this macromonomer
into a macro-CTA. This is, what we hope to be, an improvement on the anionic to RAFT work utilizing the ATRAF reaction. The advantage to this method over the ATRAF reaction is that it utilizes the same method to produce the macro-CTA as is used for the polymerization. Additionally, thus far, reaction times have seemed to be much shorter and there is no need for the use of transition metals. Finally, this method can allow the creation of much more varied macro-CTAs. To date, we have been able to achieve conversions of 80%, and we believe that with some further study we can achieve conversions at least equal to the ATRAF method.
CHAPTER 2. GLYCEROL-ACRYLIC BIOPOLYMERS: A VERSATILE ELASTOMER WITH EXCELLENT MECHANICAL AND THERMAL PROPERTIES

Michael Forrester, Fang-Yi Lin, Nacu Hernandez, Chris Williams, and Eric Cochran.

2.1 Introduction

Due to the rising cost\(^1\) and environmental impact\(^2\) associated with the recovery and use of petroleum, bio-renewable chemicals have seen an extraordinary increase in interest as a chemical feedstock for both fuels and materials.\(^3\) Materials such as poly(lactic acid), soybean oil and cellulose are on the rise for a staggering number of applications that ranges from use in sutures\(^4\) to 3D printing\(^5\) to tires.\(^6\) Plant oil feedstocks are especially attractive due to their low cost and abundance. Typically, work has been dedicated to the production of various thermosetting materials;\(^7\) however, recent work has shown that soybean oil can be turned into a rubbery thermoplastic elastomer (TPE) by use of controlled radical polymerization techniques.\(^8-10\) This shows that it is feasible to make thermoplastics from a variety of biological sources including those that are highly functional.

This leads us to an interest in pursuing polymers derived from glycerol. Due to the boom in the biodiesel industry, there is a large amount of glycerol that is available for a very low price. Glycerol is one of the simplest and lowest costing biorenewable polyols currently available.\(^11-13\) Beyond the cost, glycerol-acrylic monomers would be significantly less flammable and toxic when compared to tradition petroleum acrylates.
The three hydroxyls present on glycerol make it an exciting building block for polymer production. This allows for the possibility of forming a wide variety of functional groups including: esters, ketones, aldehydes, ethers, silyl ethers, and acetals. This affords a material that has a high amount of tunability in mechanical, thermal, hydrophilicity, and other properties. One could imagine decreasing water solubility by adding a long chain ester, or decreasing flammability by adding a functional group that is flame retardant. The first challenge however, is to produce polymers made from glycerine. While there have been a wide variety of glycerol-derived polymers, most of these are thermosetting polymers, oligomers, or low molecular weight (<20kDa) polymers made through self-condensation, condensation with diacids, or condensation with diols.\textsuperscript{14–17} Any of the work being done with glycerol-acrylics seems to be done with mono glycerol methacrylate. While this should give a linear polymer, it would be difficult to produce glycerol mono-acrylate or glycerol mono-methacrylate cost effectively at a large scale. Achieving and characterizing high molecular weight glycerol thermoplastics using an economical method has not yet been accomplished and is the purpose of this work. We achieve this by using reversible addition fragmentation chain transfer, or RAFT. This is a form of controlled radical polymerization that uses a special reagent, known as a chain transfer agent (CTA), to control the polymerization and keep termination to a minimum. The chain transfer agent additionally keeps the branching to a more manageable level and inhibits cross-linking thereby allowing us to produce materials of substantial molecular weight (800kDa or higher) without forming thermosets.

2.2 Experimental

Glycerol, triphenylphosphine, hydroquinone, and acrylic acid were all purchased from Sigma Aldrich with purity of 99% or higher. Benzyl bromide, potassium phosphate tribasic, benzyl mercaptan, carbon disulfide, and azobisisobutyronitrile (AIBN) were pur-
Table 2.1. Table showing the ratios of reagents used for the acrylation of glycerol.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>1.2 Functionality</th>
<th>1.6 Functionality</th>
<th>2 Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>1 eq</td>
<td>1 eq</td>
<td>1 eq</td>
</tr>
<tr>
<td>Acrylic Acid</td>
<td>1.33 eq</td>
<td>1.78 eq</td>
<td>2.22 eq</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>.039 eq</td>
<td>.052 eq</td>
<td>.065 eq</td>
</tr>
<tr>
<td>Triphenyl Phosphine</td>
<td>.025 eq</td>
<td>.025 eq</td>
<td>.025 eq</td>
</tr>
</tbody>
</table>

Chased from Sigma Aldrich with purities of 98% or higher. Methanol was purchased from Fischer scientific with a purity of 99.8%.

2.2.1 Acrylation of Glycerol

Glycerol, Acrylic acid, hydroquinone, and triphenylphosphine were added together in a round bottom flask equipped with a stir bar and reflux condensor. The ratios of reagents used are shown in Table 2.1. This reaction mixture is heated at 125 °C for 36 hours at 500rpm. The monomer is then used without purification.

2.2.2 RAFT Agent-Dibenzyl Carbonotrithioate

The synthesis of dibenzyl carbonotrithioate (DBCTT) is well documented in literature, and there are multiple pathways available for this synthesis. We followed the route used by Gooch et al. Briefly, acetone, potassium phosphate (1.1 eq), and Benzyl Mercaptan (1eq) are mixed together and allowed to stir for 10 minutes. 1.7 eq of carbon disulfide is added and allowed to stir for 10 minutes. Finally 1.05 eq of benzyl bromide is added and allowed to stir for 10 minutes. The reaction mixture is then filtered and dried under reduced pressure to yield the product.

2.2.3 RAFT Polymerization of Acrylated Glycerol

The conditions of the reaction are shown in Table 2.2. The appropriate amount of each component are added to a flask with a magnetic stir bar. Then the material is sparged with
argon for a period of 15 minutes to an hour depending on the quantity of solution. The solution is then placed in an oil bath at 71°C for 8 hours at 500 rpm. The poly(acrylated glycerol), or PAG, is then precipitated in isopropanol and dried under reduced pressure at room temperature.

Table 2.2. Table showing the molar equivalents of each chemical used for the synthesis of each polymer.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>1.2-10k</th>
<th>1.2-100k</th>
<th>1.2-1M</th>
<th>1.6-10k</th>
<th>1.6-100k</th>
<th>2.0-10k</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG</td>
<td>70 eq</td>
<td>700 eq</td>
<td>7000 eq</td>
<td>60 eq</td>
<td>600 eq</td>
<td>50 eq</td>
</tr>
<tr>
<td>DBCTT</td>
<td>1 eq</td>
<td>1 eq</td>
<td>1 eq</td>
<td>1 eq</td>
<td>1 eq</td>
<td>1 eq</td>
</tr>
<tr>
<td>AIBN</td>
<td>.3 eq</td>
<td>3 eq</td>
<td>30 eq</td>
<td>.3 eq</td>
<td>3 eq</td>
<td>.3 eq</td>
</tr>
<tr>
<td>Methanol</td>
<td>312 eq</td>
<td>11000 eq</td>
<td>1100 eq</td>
<td>470 eq</td>
<td>9700 eq</td>
<td>610 eq</td>
</tr>
</tbody>
</table>

2.2.4 Analytics

The gel permeation chromatography (GPC) system used is a Malvern Viscotek high temperature GPC run in dimethylformamide. It is equipped with a refractive index detector, a UV-vis detector, a viscometer, and a light scattering detector. The equipment was equipped with Malvern CLM6210 high temperature columns that have a 10MDa cutoff. Samples were analyzed using the refractive index detector compared to a polymethylmethacrylate sample. Samples were run for 40 minutes through three columns in series.

The GCMS used is an Agilent 6890 GC coupled with an Agilent 5975C MS detector. Column used was a Agilent DB-1. The NMR is Bruker 600MHz. Samples were run for 32 scans with a 1 second delay. The DSC used is a TA instrument Q2000 DSC. DSC was run for three heating and cooling cycles from -70 °C to 30 °C. The data reported was the heating on the third cycle with the exotherm up.

Rheology was run on an Ares G2 rheometry using 8mm parallel plate geometry. The glass transition was determined by doing constant strain temperature sweeps and the master curve was generated by varying the frequency from 100 rad/s to 1 rad/s. The temperature range was from 40 °C to -80 °C with 10 °C increments.
We defined the solubility of the polymer to be a solution that had an average size less than 1 μm. This was done by use of a Malvern Zetasizer Nano ZS.

### 2.3 Results & Discussion

![Conversion of acrylic acid to glycerol acrylate over 39 hours](image)

**Figure 2.1.** Conversion of acrylic acid to glycerol acrylate over 39 hours

The results of acrylation are shown in Figure 2.1. As can be seen, this reaction follows a standard equilibrium reaction, reaching its equilibrium conversion of 80%. Additionally Figure 2.2 shows an example of NMR of glycerol having been reacted with acrylic acid. We can clearly see evidence of acrylic being converted to acrylate and glycerol being converted to esters.

Analysis of the monomer with GCMS indicates that the predominate materials present in the monomer are residual glycerol and acrylic acid, glycerol mono and di-acrylate, and glycerol dimer and trimers linked through their primary alcohols. Finally there is a small amount of glycerol triacrylate present in these samples. The residual acrylic acid will copolymerize into the glycerol chain; however, the rest of the impurities will not participate in the polymerization and will be removed upon precipitation of the polymer.
Due to the multifunctional nature of the monomer, as confirmed by GCMS and NMR, the polymers made from these monomers will be branchy, and the amount of branching goes up with the degree of functionality. This is supported by the experimental work, as we were unable to sufficiently inhibit cross-linking of the polymers when we attempted to polymerize the 1.6-1M, 2.0-100k, and 2.0-1M samples.

![AG 1.2 Functionality NMR](image)

**Figure 2.2.** NMR showing the result of reaction glycerol with acrylic acid.

NMR analysis on the solution after polymerization-Figure 2.3-shows that we can achieve extremely high monomer conversion. Table 2.3 shows that we were able to achieve above 85% conversion of acrylic functionality in all samples without the formation of gels.

GPC Analysis shown in Figure 2.4 and Table 2.3 show that the target molecular weight and the actual molecular weight are substantially different. The dispersities are also quite high; however, a trend can be clearly seen: molecular weight increases with decreasing concentration of CTA. The higher than targeted molecular weight and larger dispersities is often seen in other monomer systems such as with acrylated epoxidized soybean oil (AESO),\(^{19,20}\) and is likely affected by the branching of the system. Despite this, there is a clear increase in the molecular weight with increasing target molecular weight and this
shows that the CTA is actively controlling the polymerization. This is further supported by the fact that experiments without CTA gel almost immediately.

DSC and Isothermal Rheology Scans of these materials show the same general trend. Typically, as molecular weight increases the glass transition goes up, as functionality increases the glass transition also goes up and is evident in Figures 2.5 and 2.6 as well as summarized in Table 2.3. One observation about Figure 2.5 is that the temperature range of the glass transition is quite large. In the 1.2-10k sample the glass transition spreads
between -65°C and -5°C. We believe that the branching nature of the polymer is what causes the broadness in the glass transition. Additionally, the increase in glass transition with increasing molecular weight is something that is well known for polymers. Contrary to standard conventions however, is that as the functionality goes up, thereby increasing the branching, the glass transition is going up as well. The most likely explanation is that the reduction of hydrogen bonding associated with the conversion of alcohols to esters is causing an increase in the glass transition.

![Figure 2.5](image)

**Figure 2.5.** DSC that shows the onset of the glass transition and the end point of the glass transition for each PAG sample. The order from bottom to top is 1.2-10k, 1.2-100k, 1.2-1M, 1.6-10k, 1.6-100k, 2.0-10k

We also looked at the water compatibility of these materials. Table 2.3 shows the solubility of the various materials. Unsurprisingly, as we increase the acrylic functionality we decrease water solubility. What is slightly surprising is that increasing molecular weight of the 1.2 functionality polymers seems to improve solubility. At first this seems counter-intuitive; however, the use of the hydrophobic chain transfer agent seems to be strongly effecting the ability of the polymer to dissolve in water.

Finally we look at master-curves of these materials. Figure 2.7 and Table 2.3 show the overlayed results of the elastic modulus. What we find is that as molecular weight goes up the cross-over modulus increases and the cross-over frequency decreases. Addition-
Temperature sweep rheology that shows the peaks in Tan Delta for each PAG sample. The peaks in order: 1.2-10k is solid, 1.2-100k is dashed, 1.2-1M is dotted dashed, 1.6-10k is dotted, 1.6-100k is loosely dashed, and 2.0-10k is loosely dotted.

Table 2.3. Table summarizing analytics of PAG Polymerizations.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Conversion</th>
<th>DSC Tg(°C)</th>
<th>Rheology Tg (°C)</th>
<th>Terminal Regime Slope</th>
<th>Plateau Modulus (GPa)</th>
<th>Cross-over Modulus (MPa)</th>
<th>Cross-over Frequency (rad/s)</th>
<th>Water Solubility</th>
<th>Molecular Weight (kDa)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2-10k</td>
<td>97%</td>
<td>-22</td>
<td>5</td>
<td>.765</td>
<td>1</td>
<td>80</td>
<td>34000</td>
<td>Negligible</td>
<td>192</td>
<td>3.1</td>
</tr>
<tr>
<td>1.2-100k</td>
<td>89%</td>
<td>-10.88</td>
<td>16</td>
<td>.649</td>
<td>1.2</td>
<td>87</td>
<td>1337</td>
<td>20%</td>
<td>528</td>
<td>2.4</td>
</tr>
<tr>
<td>1.2-1M</td>
<td>94%</td>
<td>-14.99</td>
<td>4</td>
<td>.636</td>
<td>1.1</td>
<td>94</td>
<td>2487</td>
<td>30%</td>
<td>882</td>
<td>1.95</td>
</tr>
<tr>
<td>1.6-10k</td>
<td>97%</td>
<td>-14.75</td>
<td>16</td>
<td>.770</td>
<td>1.3</td>
<td>115</td>
<td>6700</td>
<td>Negligible</td>
<td>200</td>
<td>2.76</td>
</tr>
<tr>
<td>1.6-100k</td>
<td>94%</td>
<td>-0.33</td>
<td>30</td>
<td>.667</td>
<td>1.4</td>
<td>81</td>
<td>106</td>
<td>Negligible</td>
<td>645</td>
<td>2.47</td>
</tr>
<tr>
<td>2.0-10k</td>
<td>95%</td>
<td>-9.5</td>
<td>16</td>
<td>.740</td>
<td>1.6</td>
<td>100</td>
<td>3000</td>
<td>Negligible</td>
<td>194</td>
<td>2.85</td>
</tr>
</tbody>
</table>

ally as functionality goes up the cross-over modulus may increase slightly; however, the cross-over frequency goes down substantially. This implies that as we increase molecular weight and functionality the materials are behaving more elastic at lower frequencies. This very strongly matches the physical observations in which the 1.2-10k sample is incredibly soft and tacky, and the 1.2-1M is much more solid like and has significantly longer puddle times.
2.4 Conclusions

Thermoplastic glycerol acrylate polymers are a partially bioderived glycerol polymer. This meets the growing need for biorenewable alternatives to petroleum materials. But this material goes beyond just being an alternative, it offers interesting properties that are not obtained with petroleum based polymers. These materials can be water soluble with solubilities up to 30%. PAG seems to be a fairly tacky material and is something that our group is currently in the process of studying. The material has glass transitions below 30 °C, with some samples giving glass transitions below 0 °C. Given the high amount of residual hydroxy functionality, there is much opportunity to modify this material to suit various different needs. Given the ease with which these materials are produced, the abundance of the starting materials, and the properties that are achieved, these materials could be an exciting new contribution to the polymer industry.
References


CHAPTER 3. STABILITY OF POLYMER BOUND CHAIN TRANSFER AGENTS

Michael Forrester, Grant Johnson, Nicholas Bloome, William Bradley, and Eric Cochran.

3.1 Introduction

Reversible Addition Fragmentation Chain Transfer, or RAFT, polymerization is currently one of the most widely studied polymerization techniques.\textsuperscript{1–7} RAFT’s utilization of a small molecule chain transfer agent (CTA), allows for controlled polymerization of a great number of different monomers. Because of the easy tunability of the chain transfer agents and the versatility of polymerization there are a huge number of industries that RAFT polymers could be viable in. These include fields such as the medicine and drug delivery and medical fields,\textsuperscript{8–12} optics\textsuperscript{13,14} and coatings.\textsuperscript{15–17}

In order for these RAFT polymers to become more than just an academic interest, more information is needed in understanding the stability of the polymer-bound CTA. Because the CTA incorporates into the polymer chain, understanding the stability of the CTA is necessary in order to ensure the viability of these polymers. While there are several publications that address the intentional removal of CTAs\textsuperscript{18–20} there are very few that seem to address the thermal stability of the CTA\textsuperscript{21–23} and those that do either focus on the stability of the small molecule, or do not give a very detailed examination of the polymer-bound CTA stability.

The removal of the RAFT agent after polymerization can give a few benefits such as eliminating the color associated with the CTA. Additionally it can provide functional end
groups such as thiol, alkene and other functionality.\textsuperscript{22,24,25} Also, chemically removing the CTA can eliminate odors associated with thermal degradation of the CTA and may also improve cytotoxicity as well.

There are times, however, when removal of the chain transfer agent is undesirable. For instance, one could imagine the initial block of a block copolymer being synthesized via a different polymerization method, such as ATRP, and then being converted into a macro-CTA. If that conversion makes the initial block as part of the Z group, and the CTA were to break down thermally during processing of the polymer then the block copolymer would revert to two separated homopolymers. Additionally, telechelic and difunctional CTAs can be attractive as you can produce triblocks in 2 steps rather than three. The degradation of these CTAs would lead to diblocks instead of triblocks which would yield a substantial loss in properties. Finally, if it is desired to convert the CTA into some other functional group, such as a thiol via aminolysis, then the thermal degradation of the materials would prevent that.

This is particularly an issue as most industrial produced polymers are thermally processed. In order for RAFT polymers to truly have a widespread place in industry, it has to be compatible with the methods that industries currently utilize. To that end, the purpose of this work is to study the change in stability of the CTA as the molecular weight of the polymer goes up, as the polymer attached to the CTA is changed, as the type of CTA is changed, and as the location of the CTA is changed. The four CTAs used in this work are shown in Figure 3.1 and are referred to as CTA-DM, CTA-DD, CTA-TM, CTA-TD for monofunctional dithioester, difunctional dithioester, monofunctional trithiocarbonate and difunctional trithiocarbonate respectively. These CTAs are then polymerized with styrene and butyl acrylate and their thermal stability is then studied.
3.2 Materials and Methods

3.2.1 Materials

All materials were purchased from Sigma-Aldrich. CTA-DM (Benzyl-Benzodithioate) was purchased directly from Sigma-Aldrich. All other CTA’s were synthesized.

3.2.2 Analytic Methods

CTA Structure was verified via NMR. A Varian MR-400 was used with CDCl3 as a solvent. Molecular weights were calculated using an Waters Acquity GPC equipped with Acquity APC XT Columns. The molecular weight were calculated using an RI detector referenced against styrene or methyl methacrylate standards for styrene and butyl acrylate respectively. Steady shear and dynamic rheology were done using a Ares G2 Rheometer. Butyl acrylate samples were run at steady shear at 300 s\(^{-1}\) on a cone and plate (.1 rad, 25 mm) geometry. Styrene samples were run in dynamic mode at 100 rad/s and 1% and 3% strain on 8 mm parallel plate geometry for high and low molecular weights.
respectively. A Netzsch STA449 F1 was used to for TGA/MS and was run from 50 °C to 500 °C at a rate of 10 °C per minute.

3.2.3 Chain Transfer Agent Synthesis

CTA-TM and CTA-TD were synthesized using very similar methods. The reaction proceeds at room temperature. For CTA-TM 1 eq of thiol is mixed with a 4/1 ratio of water/acetone. .02 eq of tetrabutylammonium bromide and 1.1 eq of potassium phosphate tribasic are added and allowed to stir for 10 minutes. 2 eq of carbon disulfide are then slowly added and allowed to stir for 10 minutes. 1.1 eq of benzyl bromide is then added and allowed to stir for 10 minutes. Upon completion of the reaction acetone is removed under reduced pressure and the product is extracted into diethyl ether. $^1$H NMR: $\delta$ 7.3 (m,5H), $\delta$ 4.6 (s,2H), $\delta$ 3.3 (m,2H), $\delta$ 1.4 (t,3H).

For CTA-TD the reaction method is the same using 1 eq of thiol, 2.2 eq of potassium phosphate, 3 eq of carbon disulfide, and 2.2 eq of benzyl bromide. The product precipitates from solution. This solid is then collected and washed with water. It is then dried under reduced pressure to yield CTA-TD. $^1$H NMR: $\delta$ 7.3 (m,10H), $\delta$ 4.6 (s,4H), $\delta$ 3.4 (t, 4H), $\delta$ 1.7 (m,4H), $\delta$ 1.4 (m,4H).

CTA-DD was synthesized through a two step procedure. First 3 eq. of benzyl mercaptan are dissolved in toluene and mixed with 4 eq of triethylamine. 1 eq of terephthaloyl chloride is then slowly added to the solution and the reaction is allowed to proceed overnight at room temperature. Upon completion of the reaction the solvent is removed under reduced pressure. The product is then recrystallized in hot ethanol. $^1$H NMR: $\delta$ 8.1 (s, 4H), $\delta$ 7.3 (m, 10H), $\delta$ 4.4 (s, 4H).

The product is then mixed with toluene and 1.5 eq of Lawesson’s reagent. This reaction is heated to 110 °C and allowed to stir overnight. The solvent is then dried off at
reduced pressure and the product is purified via crystallization in hot ethanol to yield CTA-DD. $^1$H NMR: $\delta$ 8.1 (s, 4H), $\delta$ 7.3 (m, 10H), $\delta$ 4.7 (s, 4H).

### 3.2.4 Polymer Synthesis

The ratios of reagents used is shown in Table 3.1. For the butyl acrylate polymerization trithiocarbonates were polymerized at 80 °C . The dithioesters were polymerized at 100 °C . For styrene all polymerizations were carried out at 110 °C . All reactions were run for 20 hours.

### 3.3 Results and Discussion

We chose to focus our TGA-MS experiments on butyl acrylate samples. The reasoning for this is two fold. First, the TGA curves do not give particularly helpful data as the mass % of CTA is so small and thus we cannot utilize the mass analysis portion of this experiment. Secondly the polystyrene has overlapping mass fragments with the chain transfer agent, and thus isolating the CTA from the polymer becomes challenging. The MS of butyl acrylate gives some very useful information however. We chose to focus on
the 48, 50, 51, and 64 mass fragments. This is because these fragments were common across all CTAs as well as the polymer bound CTA. Additionally, the concentration of those fragments were on the right order of magnitude. In Figure 3.2 and 3.3 we can see the mass spec results as a function of temperature. Figure 3.4 compares the decomposition percentages, as calculated by integration of the curve, of the various samples and the chain transfer agent. Figure 3.5 shows the decomposition of the four common fragments for the PNBA-CTA-TM-65k sample.

Figure 3.2. TGA-MS of CTA-DM showing the main decomposition mass fragments.

Figure 3.3. TGA-MS of PNBA-CTA-DM-16kk showing mass fragments that are common with CTA-DM.
There are several conclusions that we can quickly draw from Figure 3.4. First, at low temperatures the dithioesters (DE) are significantly more stable than the trithiocarbonates (TC). As temperature increases the difference in decomposition becomes much smaller between the DEs and the TCs. The second observation we can make is that the low molecular weight polymers are generally less stable than the higher molecular weight polymers and in some cases even less stable than the CTA. This latter difference could likely be attributed to the change in the R group changing the stability of the chain. Additionally, we see that the difunctional (mid chain) CTAs are generally less stable than the monofunction (end chain) CTAs. Finally, we find that the CTA has minimal decomposi-
Figure 3.5. TGA-MS for PNBA-CTA-Dm-16k using channels 48, 50, 51, 64, blue, red, black, green respectively. The lines are linear fits that are meant to draw the attention of the eye.

Figure 3.6 and 3.7 show the changes in the GPC curves for styrene and butyl acrylate respectively, as the samples are subjected to progressively higher temperatures. Unsurprisingly, as the temperature increases the lower molecular weight up to 200 °C. This would imply that thermal processing at temperatures below 200 °C for short periods of time would have a minimal effect on the CTA.

A large motivation for doing this work was to determine the importance of CTA location. If the CTA is segregating blocks of a co-polymer and it is thermally degraded at low temperatures, this can pose a major issue for the performance of the material. To that end we subjected the sample to mechanical and thermal stress and tested what happened to the molecular weight and the viscosity of the material. We focused on the difunctional polymers, as these materials would have both a mechanical and molecular weight change as the CTA decomposed.
weight shoulder in the GPC becomes substantially more pronounced. We also find that the higher molecular weight polymers are generally a bit more stable. This change in molecular weight is summarized in Table 3.4. Also shown is the change in viscosity and the fraction of chain transfer agent that has decomposed. Tables 3.2 and 3.3 show the change in viscosity at various time points throughout the 1 hour experiment.

What we have found is that at 125 °C there is an almost trivial amount of decomposition for any of these materials. Additionally there is minimal decomposition in the samples at 150 °C; however, the molecular weight and choice of CTA seems to impact that stability. For example PS-CTA-DD-11k only has 84% of its original CTA content whereas the PS-CTA-DD-46k has 94%. Additionally it seems as though the Trithiocarbonates are somewhat less stable than the dithioesters when the polymer is n-butyl acrylate. When the temperature reaches 175 °C, we see significantly more decomposition, with as much as 30% of the initial CTA being decomposed.

This leads us to some important conclusions. First at temperatures less than 150 °C a material would be able to undergo long processing times or multiple processing times without losing substantial performance. Additionally this means that a CTA that is either difunctional or segregates two blocks of a copolymer could be used under these conditions. Secondly, Temperatures higher than 150 °C can be used; however, the processing time should be less than 10 minutes, and ideally fewer than 5 minutes. If higher processing temperatures are desired then it is important to understand that these materials will begin to decompose leading to a loss of properties if the polymer is segregated by the CTA. If these conditions are required a CTA that is located on the ends of the chain is preferred and would prevent the loss of material properties.
Figure 3.6. GPC done on polystyrene samples after dynamic rheology experiments showing decomposition of CTA. Black, blue, green, and red correspond to pre-rheology, 125 °C, 150 °C, and 175 °C respectively. From bottom to top correspond to PS-CTA-DD-11k, PS-CTA-DD-44k, PS-CTA-TD-11k, PS-CTA-TD-30k.

3.4 Conclusions

The stability of various CTAs and polymer-bound CTAs were studied to determine their thermal stability. In most cases the higher the molecular weight of the polymer, the better the stability of the molecule was. Also, generally monofunctional end-group CTAs are more stable than mid chain difunctional chain transfer agents. Polymer-bound
Figure 3.7. GPC done on poly(n-butyl acrylate) samples after steady shear rheology experiments showing decomposition of CTA. Black, blue, green, and red correspond to pre-rheology, 125 °C, 150 °C, and 175 °C respectively. From bottom to top correspond to PNBA-CTA-DD-11k, PNBA-CTA-DD-24k, PNBA-CTA-TD-19k, PNBA-CTA-TD-42k.

dithioesters are more stable than the polymer-bound trithiocarbonates as is the case with the bulk CTA. Polymer-bound CTA’s have very little decomposition at temperatures lower than 150 °C and thus CTAs that are difunctional or have two blocks segregated by a CTA would not see significant losses of properties at temperatures less than 150 °C. If higher
Table 3.2. Summary of styrene-CTA steady rheology experiments that shows the viscosity change in the samples as duration and temperature changes.

<table>
<thead>
<tr>
<th>time(min)</th>
<th>PS-CTA-DD-11k</th>
<th>PS-CTA-DD-46k</th>
<th>PS-CTA-TD-11k</th>
<th>PS-CTA-TD-30k</th>
</tr>
</thead>
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<tr>
<td>5 min</td>
<td>1.04 0.95 0.96</td>
<td>1.0 1.02 1.01</td>
<td>1.02 1.01 0.95</td>
<td>1.0 1.02 1.03</td>
</tr>
<tr>
<td>10 min</td>
<td>1.04 0.87 0.86</td>
<td>1.09 1.02 0.99</td>
<td>1.03 1.02 0.82</td>
<td>1.02 1.04 1</td>
</tr>
<tr>
<td>20 min</td>
<td>1.01 0.81 0.85</td>
<td>1.19 1.01 0.98</td>
<td>1.06 1.01 0.66</td>
<td>1.07 1.05 0.93</td>
</tr>
<tr>
<td>30 min</td>
<td>0.98 0.79 0.87</td>
<td>1.24 0.99 0.98</td>
<td>1.1 1 0.7</td>
<td>1.09 1.06 0.86</td>
</tr>
<tr>
<td>45 min</td>
<td>0.95 0.79 0.89</td>
<td>1.29 0.98 0.97</td>
<td>1.15 0.98 0.66</td>
<td>1.12 1.07 0.79</td>
</tr>
<tr>
<td>60 min</td>
<td>0.92 0.78 0.87</td>
<td>1.31 0.96 0.96</td>
<td>1.19 0.95 0.54</td>
<td>1.13 1.07 0.78</td>
</tr>
</tbody>
</table>

Table 3.3. Summary of butyl acrylate-CTA steady rheology experiments that shows the viscosity change in the samples as duration and temperature changes.

<table>
<thead>
<tr>
<th>time(min)</th>
<th>PNBA-CTA-DD-11k</th>
<th>PNBA-CTA-DD-24k</th>
<th>PNBA-CTA-TD-19k</th>
<th>PNBA-CTA-TD-42k</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min</td>
<td>1.02 1.01 1.02</td>
<td>1.01 1.01 1.01</td>
<td>1.01 1.02 1.01</td>
<td>1.04 1.02 1.01</td>
</tr>
<tr>
<td>10 min</td>
<td>1.01 0.98 0.98</td>
<td>1.01 1.01 1.01</td>
<td>1 1.02 1.03</td>
<td>1.07 1.03 1</td>
</tr>
<tr>
<td>20 min</td>
<td>0.98 0.94 0.95</td>
<td>1 1 0.99 1.03 1 0.98</td>
<td>1.11 1.05 0.97</td>
<td></td>
</tr>
<tr>
<td>30 min</td>
<td>0.97 0.92 0.95</td>
<td>0.99 0.99 0.99</td>
<td>1.04 1.03 0.98</td>
<td>1.13 1.05 0.94</td>
</tr>
<tr>
<td>45 min</td>
<td>0.95 0.91 0.94</td>
<td>0.99 0.99 0.98</td>
<td>1.05 1.03 0.95</td>
<td>1.16 1.04 0.91</td>
</tr>
<tr>
<td>60 min</td>
<td>0.94 0.91 0.94</td>
<td>0.99 0.99 0.97</td>
<td>1.05 1.02 0.92</td>
<td>1.18 1.03 0.88</td>
</tr>
</tbody>
</table>

processing conditions are desired or necessary, very short processing times, or an end-group CTA would have to be chosen in order to protect from the loss of molecular weight.

Table 3.4. Comparison of the viscosity and molecular weight changes after the 1 hour rheology experiment.

<table>
<thead>
<tr>
<th>sample</th>
<th>$\frac{\eta}{\eta_0}$</th>
<th>$\frac{M_n}{M_n,0}$</th>
<th>$\frac{[C-T-A]}{[C-T-A],0}$</th>
<th>$\frac{\eta}{\eta_0}$</th>
<th>$\frac{M_n}{M_n,0}$</th>
<th>$\frac{[C-T-A]}{[C-T-A],0}$</th>
<th>$\frac{\eta}{\eta_0}$</th>
<th>$\frac{M_n}{M_n,0}$</th>
<th>$\frac{[C-T-A]}{[C-T-A],0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-CTA-DD-11k</td>
<td>0.92 0.98 0.96</td>
<td>0.78 0.92 0.84</td>
<td>0.87 0.85 0.70</td>
<td>0.92 0.98 0.96</td>
<td>0.78 0.92 0.84</td>
<td>0.87 0.85 0.70</td>
<td>0.92 0.98 0.96</td>
<td>0.78 0.92 0.84</td>
<td>0.87 0.85 0.70</td>
</tr>
<tr>
<td>PS-CTA-DD-46k</td>
<td>1.31 1.02 1.04</td>
<td>0.96 0.97 0.94</td>
<td>0.96 0.88 0.76</td>
<td>1.31 1.02 1.04</td>
<td>0.96 0.97 0.94</td>
<td>0.96 0.88 0.76</td>
<td>1.31 1.02 1.04</td>
<td>0.96 0.97 0.94</td>
<td>0.96 0.88 0.76</td>
</tr>
<tr>
<td>PS-CTA-TD-11k</td>
<td>1.19 0.99 0.98</td>
<td>0.95 0.95 0.90</td>
<td>0.54 0.88 0.76</td>
<td>1.19 0.99 0.98</td>
<td>0.95 0.95 0.90</td>
<td>0.54 0.88 0.76</td>
<td>1.19 0.99 0.98</td>
<td>0.95 0.95 0.90</td>
<td>0.54 0.88 0.76</td>
</tr>
<tr>
<td>PS-CTA-TD-30k</td>
<td>1.13 0.98 0.96</td>
<td>1.07 0.97 0.94</td>
<td>0.78 0.87 0.74</td>
<td>1.13 0.98 0.96</td>
<td>1.07 0.97 0.94</td>
<td>0.78 0.87 0.74</td>
<td>1.13 0.98 0.96</td>
<td>1.07 0.97 0.94</td>
<td>0.78 0.87 0.74</td>
</tr>
<tr>
<td>PNBA-CTA-DD-11k</td>
<td>0.94 1.00 1.00</td>
<td>0.91 0.98 0.96</td>
<td>0.94 0.92 0.84</td>
<td>0.94 1.00 1.00</td>
<td>0.91 0.98 0.96</td>
<td>0.94 0.92 0.84</td>
<td>0.94 1.00 1.00</td>
<td>0.91 0.98 0.96</td>
<td>0.94 0.92 0.84</td>
</tr>
<tr>
<td>PNBA-CTA-DD-24k</td>
<td>0.99 1.00 1.00</td>
<td>0.99 1.00 1.00</td>
<td>0.97 0.98 0.96</td>
<td>0.99 1.00 1.00</td>
<td>0.99 1.00 1.00</td>
<td>0.97 0.98 0.96</td>
<td>0.99 1.00 1.00</td>
<td>0.99 1.00 1.00</td>
<td>0.97 0.98 0.96</td>
</tr>
<tr>
<td>PNBA-CTA-TD-19k</td>
<td>1.05 1.01 1.02</td>
<td>1.02 0.96 0.92</td>
<td>0.92 0.92 0.84</td>
<td>1.05 1.01 1.02</td>
<td>1.02 0.96 0.92</td>
<td>0.92 0.92 0.84</td>
<td>1.05 1.01 1.02</td>
<td>1.02 0.96 0.92</td>
<td>0.92 0.92 0.84</td>
</tr>
<tr>
<td>PNBA-CTA-TD-42k</td>
<td>1.18 0.99 0.98</td>
<td>1.03 0.93 0.86</td>
<td>0.88 0.86 0.72</td>
<td>1.18 0.99 0.98</td>
<td>1.03 0.93 0.86</td>
<td>0.88 0.86 0.72</td>
<td>1.18 0.99 0.98</td>
<td>1.03 0.93 0.86</td>
<td>0.88 0.86 0.72</td>
</tr>
</tbody>
</table>
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CHAPTER 4. BLENDING THE EFFECTIVENESS OF ANIONIC POLYMERIZATION WITH THE VERSITILITY OF RAFT BY USE OF THE ATOM TRANSFER RADICAL ADDITION-FRAGMENTATION TECHNIQUE

Michael Forrester, William Bradley, Fang-Yi Lin, Nacu Hernandez, Chris Williams, George Kraus, and Eric Cochran. Additionally, Bill and myself are co-first authors on this publication.

Anionic polymerization has been used industrially since the mid 20th century to produce many well-defined polymers with a variety of chain architectures.\textsuperscript{1} For example, poly(styrene-b-butadiene-b-styrene) (SBS) has been used extensively as a modifier for asphalt.\textsuperscript{2} Polybutadiene is commonly used to manufacture tire treads and carcasses.\textsuperscript{3} Anionic polymerization consistently produces well-defined polymers with dispersity (Ð) frequently less than 1.1, and is readily applied to diverse array of monomer types including vinyl aromatics, dienes, certain ring opening monomers, and others. It efficiently achieves conversions exceeding 99\% in fewer than four hours. Despite these advantages, anionic polymerization has its limitations. For instance, the carbanion active center will readily react with most electrophilic groups at rates competitive with monomer propagation. Significantly, many vinyl and (meth)acrylic compounds will not yield high molecular weight polymers without sub-freezing reaction temperatures,\textsuperscript{4} a prohibitively costly prerequisite for most commercial applications.

The dawn of reversible deactivation radical polymerization (RDRP, also commonly referred to as controlled radical polymerization) in the 1990s has opened some interesting doors for producing an array of new block copolymers. In general, these methods
drastically limit the free radical concentration, driving the rate of termination reactions to nearly negligible levels. For example, atom transfer radical polymerization (ATRP) is one of the most commonly researched RDRP techniques. ATRP is suitable for a wide variety of monomers including vinyl aromatics, (meth)acrylics, and vinylics. A well-designed ATRP will achieve good molecular weight control with dispersity values $1.1 < D < 1.5$. Some drawbacks include sluggish reaction kinetics with vinyl aromatics and an inability to control diene polymerization. Another undesirable aspect is the requirement of a homogeneous transition metal catalyst, commonly copper, that presents challenges with respect to separations, toxicity and environmental stewardship. ATRP is also particularly sensitive to oxidants and other contaminants. Progress continues in addressing these issues, for example with adaptations such as the ARGET (Activators ReGenerated by Electron Transfer) and ICAR (Initiators for Continuous Activator Regeneration) implementations. Nonetheless, with these adaptations number average molecular weights ($M_n$) greater than $M_n > 100$ kDa and $D < 1.5$ are difficult targets, requiring prohibitively long reaction times. Additionally, the ARGET/ICAR methods place restrictions on solvent selection, often forcing the use of expensive and nonvolatile candidates such as dimethylformamide or anisole. Thus, the reduction of transition metal use comes at the price of extended long reaction times, additional separations challenges and costly solvents. Widespread commercial adoption will require that these challenges be addressed.

The Reversible Addition Fragmentation Chain Transfer (RAFT) polymerization method was published three years after ATRP. It has since proven to be a reliable polymerization technique for producing block copolymers of controlled molecular weight and low dispersity. Like ATRP, RAFT is compatible with a large library of vinyl monomers. However, RAFT also suffers from sluggish kinetics with vinyl aromatic monomers. While RAFT can be used to control diene polymerization, temperatures greater than $120$ °C are required to achieve reasonable kinetics; under these conditions thermally tolerant chain
transfer agents must be used and crosslinking is problematic. Unlike ATRP, RAFT does not require the use of transition metals, rather relying on a chain transfer agent (CTA) that reversibly associates with chain ends to control the molecular weight. The CTA typically comprises a thiocarbonyl compound such as a dithioester, trithiocarbonate, xanthate, or dithiocarbamate. The activity and controllability of a CTA toward different functional monomers relies on functional groups that accompany the thiocarbonyl center. While the R group leaves as a free radical when activated, the Z group modifies the kinetics of RAFT process by stabilizing the intermediate radical-deactivated CTA structure. RAFT, in contrast to ATRP and anionic polymerization, has the advantage of being more compatible with functional groups, less sensitive to impurities, and more tolerant of solvent choice.

Accordingly, the advantages of the RAFT and anionic polymerization techniques are complementary: anionic polymerization efficiently produces vinyl aromatics and dienes, while RAFT polymerization offers access to a host of other vinyl-based monomers. For this reason, techniques for the sequential application of both methods would enable the construction of a much broader palette of heterogeneous copolymers. Styrene/diene based block copolymers, which are used extensively in various industries such as paving and construction, and paints and coatings, could be supplanted with styrene/butyl acrylate analogs. A natural strategy for the marriage of RAFT and anionic polymerization is the construction of CTA functionality from the terminus of a living polyanion. Zhang et al. achieved this by adding carbon disulfide to a diphenylethylene-capped polyisoprene. While this method was up to 95% efficient and offered a flexible selection of R groups, a number of drawbacks limit its reduction to commercial practice. Most notably, cryogenic temperatures are required to produce the macro-CTA. Additionally, the Z-group is restricted to the diphenylethylene end group of the terminated carbanion; accordingly, other desirable Z groups such as xanthate, phenyl dithioester, trithiocarbonanote, and dithiocarbamate are inaccessible through this method. Furthermore, the
anionic- and RAFT-based blocks are joined through the thioester linkage, potentially limiting the thermal and chemical stability of the final product.\textsuperscript{17} Yin et al. reported a macro-CTA produced through the esterification of a hydroxy-terminated polymer with an acid-functionalized CTA.\textsuperscript{18} While yields were not reported, our own experiments using this approach were roughly 50\% efficient. Nonetheless, these examples illustrate the utility of transforming anionically produced polymers into macro-CTAs.

In this work we illustrate the use of the atom-transfer radical addition-fragmentation (ATRAF) reaction that was developed by the Matyjaszewski group\textsuperscript{19} as a highly efficient and potentially scalable route to hybrid anionic/RAFT block copolymers. Various implementations of this process are shown in Schemes 4.1 and 4.2. Short reaction times, high conversion and yield, and mild reaction temperatures make this an appealing approach to macro-CTA fabrication. In addition to exemplifying the application of ATRAF to the marriage of anionic and RAFT polymerizations, we also investigate the practicality of reduced-copper/copper-free adaptations that would result in a more economical and scalable process. Additionally, we explore alternatives to ethylene oxide in building the intermediate ester linkage in this process, namely through acetal or silane functionalized capping agents. A list of materials that were made are summarized in Table 4.1; experimental details are provided in the Supporting Information.

Table 4.1 shows the results from the various steps of making macro-CTA from living anionic polymerization. Homopolymer molecular weights were determined by polystyrene-calibrated gel permeation chromatography (GPC); block copolymer molecular weights are estimated using that of the homopolymer precursor and composition measured by NMR. Efficiencies are determined by either NMR or GPC and are denoted in the table. Further details are available in the Supporting Information. In the first step, hydroxyl functionality is added to the living carbanion. In Scheme 1a, this is achieved through the addition of ethylene oxide followed by acidic methanol (1a). Alternatively, hydroxyl func-
Figure 4.1. Chemical scheme for various routes to hydroxyl terminated polystyrene: (a) Ethylene oxide termination with acidic workup ($R = -(\text{CH}_2)_2-$); (b) termination with 2-(3-chloropropoxy)-tetrahydro-2H-pyran followed by hydrolysis of the acetal ($R = -(\text{CH}_2)_3-$); and (c) (3-chloropropoxy)trimethylsilane termination followed by cleavage with TBAF ($R = -(\text{CH}_2)_3-$).

unctionality can be provided quantitatively with significantly less toxic reagents. For example, the carbanion can be quenched by a halogenated acetal that can be further hydrolyzed (1b). Halogenated silane-protected alcohol can also be used and subsequently cleaved with tetrabutylammonium fluoride (TBAF) to provide the alcohol (1c). GPC (Figure 1a) suggests chain-end modification through a subtle shift in the elution volume between PS-H and the corresponding PS-OH. $^1$H-NMR end group analysis (Figures S1–S5) definitively shows approximately 1 alcohol per chain, irrespective of the route chosen with near 100% molar conversion. Yields were nearly quantitative with slight losses (< 3%) due to handling during workup. Hydroxyl terminated polystyrene was converted to tert-bromine capped polystyrene with a stoichiometric excess of 2-bromo-2-methylpropanoyl bromide (2a), which proceeds to completion as supported by NMR (Figure S6) and GPC (Figure 1a). Bis(thiobenzoyl)disulfide (TBDS) provides the final macro-chain transfer agent functionality through the ATRAF method. Direct characterization of macro-CTA functionality proved to be difficult. Proton resonances in $^1$H-NMR from the thioate chain
ends overlap with those of the polymer, which compounded by their low prevalence as a chain-end moiety are undetectable; $^{13}$C-NMR experiments were also unable to discern the relevant carbon atoms. While GPC chromatograms show slight shifts in elution volume upon each chain-end modification, this provides only a weak qualitative indication of CTA attachment and no guarantee of activity. Accordingly, the most efficacious manner in which to quantify the macro-CTA activity is to produce a diblock copolymer. To judge the activity with multiple classes of radically polymerizable species, styrenic block copolymers were synthesized with $n$-butyl acrylate (3.a.i–iii.1), methyl methacrylate (3.a.i.2) and methyl acrylate (3.a.i.3) as demonstrated in Scheme 4.3. The detection of
the new polymeric species formed at 254 nm with UV detection is a strong indication that block copolymer was formed, as only the polystyrene block is detectable in this manner, as shown in Figure 1b. The ratio of the integrated value of the polystyrene homopolymer peak to the block copolymer peak yields the fraction of active macro-CTA. We recorded efficiencies as high as a 97% in this manner as shown in Table 4.1 for polymerization with methyl acrylate, n-butyl acrylate, and methyl methacrylate. These block copolymers under phase separation as expected; for example, differential scanning calorimetry, rheology and transmission electron microscopy data are provided in the Supporting Information and show a microphase separated lamellar morphology.

The “traditional” ATRAF (2a.i) method is evidently 97% efficient in producing active macro-CTA. Here we note that while phenyl is a robust choice for the Z-group, the use of TBDS is exemplary in nature and could easily be substituted for other disulfides as appropriate for other Z-groups. The ARGET methodology can be used to drastically reduce the requisite quantity of transition metal catalyst. This was illustrated using sub-stoichiometric quantities of copper (II) bromide and tin (II) ethylhexanoate (SnEtH) as the
### Table 4.1. Results of polymerization of PS-macro-CTA with various different monomer sources

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Scheme Code</th>
<th>$M_n$, kDa</th>
<th>PDI</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-OH-S</td>
<td>4.1a</td>
<td>10.0</td>
<td>1.11</td>
<td>100%(^a)</td>
</tr>
<tr>
<td>PS-OH-EO</td>
<td>4.1b</td>
<td>10.5</td>
<td>1.06</td>
<td>100%(^a)</td>
</tr>
<tr>
<td>PS-OH-A</td>
<td>4.1c</td>
<td>9.4</td>
<td>1.15</td>
<td>100%(^a)</td>
</tr>
<tr>
<td>PS-OH-TBB</td>
<td>4.2a</td>
<td>11.8</td>
<td>1.15</td>
<td>100%(^a)</td>
</tr>
<tr>
<td>PS-CTA-1</td>
<td>2a.i</td>
<td>12.3</td>
<td>1.17</td>
<td>— (^b)</td>
</tr>
<tr>
<td>PS-CTA-2</td>
<td>2a.ii</td>
<td>11.5</td>
<td>1.25</td>
<td>— (^b)</td>
</tr>
<tr>
<td>PS-CTA-3</td>
<td>2a.iii</td>
<td>13</td>
<td>1.1</td>
<td>— (^b)</td>
</tr>
<tr>
<td>PS-NBA-1L</td>
<td>3a.i.1</td>
<td>10,(^c) 33.3(^d)</td>
<td>1.30(^e)</td>
<td>95%(^f)</td>
</tr>
<tr>
<td>PS-NBA-1H</td>
<td>3a.i.1</td>
<td>10,(^c) 67(^d)</td>
<td>1.37(^e)</td>
<td>97%(^f)</td>
</tr>
<tr>
<td>PS-MMA</td>
<td>3a.i.2</td>
<td>10,(^c) 55.5(^d)</td>
<td>1.37(^e)</td>
<td>82%(^f)</td>
</tr>
<tr>
<td>PS-MA</td>
<td>3a.i.3</td>
<td>10,(^c) 37(^d)</td>
<td>1.31(^e)</td>
<td>93%(^f)</td>
</tr>
<tr>
<td>PS-NBA-2</td>
<td>3a.ii.1</td>
<td>10,(^c) 200</td>
<td>4(^e)</td>
<td>30%(^f)</td>
</tr>
<tr>
<td>PS-NBA-3</td>
<td>3a.iii.1</td>
<td>10,(^c) 140</td>
<td>2.6(^e)</td>
<td>30%(^f)</td>
</tr>
</tbody>
</table>

\(^a\)Molar conversion of chain end to -OH or -Br per \(^1\)H-NMR  
\(^b\)\(^1\)H-NMR CTA resonances overlap with polymer  
\(^c\)Polystyrene-CTA precursor  
\(^d\)Overall molecular weight computed from precursor molecular weight and \(^1\)H-NMR block copolymer composition  
\(^e\)Corresponding to the diblock copolymer peak extracted from the GPC chromatogram via peak deconvolution  
\(^f\)Fraction of RAFT-active chains per GPC peak deconvolution

Reducing agent. We noted that TBDS was susceptible to attack by the reducing agent, and were able to successfully afford (2a.ii) by alternating SnEtH and TBDS addition. While the efficiency of the macro-CTA was reduced to 30%, these experiments demonstrate ARGET-ATRAF is a viable approach that could be improved with further optimization of reaction conditions and the selection of reducing agent. The most ideal approach would be to completely remove the use of transition metal catalysts. To achieve this we utilized a method very similar to that described by Treat et al.\(^20\) in which a phenothiazine species activated by ultraviolet radiation was used as a photocatalyst to perform ATRP. While the Treat et al. team achieved the best balance of activation/deactivation rates using 10-phenylphenothiazine, we found that the readily available 10-methylphenothiazine was
Figure 4.4. The GPC chromatogram (a) shows the small shift from polystyrene aliquot (1o), to ethylene oxide capped (1a), to tert-butyl bromide capped (2a). The chromatogram (b) shows the growth of n-butyl acrylate using traditional ATRAF (3a.i.1), ARGET (3a.ii.1), and metal-free method (3.a.ii.1). The chromatogram (b) shows the growth of n-butyl acrylate (3a.i.1), methyl methacrylate (3a.i.2), and methyl acrylate (3a.i.3)

adequate since only a single activation/deactivation event is necessary. While the resultant macro-CTA produced block copolymer, the molecular weight distribution was quite broad and only 30% of the parent polystyrene was converted to diblock. We believe that a large factor of the lower conversion is that the particular wavelength of the UV radiation we used may damage the CTA species and further optimization of reaction conditions could render this method as an attractive candidate for producing metal-free RAFT CTA’s.

In this work we have shown that RAFT-active macro-CTAs can be efficiently produced from living polyanions under conditions that when optimized should be translatable to commercial practice. This process is done in solvents that are industrially common, as well as temperatures that are well within normal operating conditions for most industrial processes. To make this method as scalable as possible, it is desirable to reduce, replace, or remove the use of copper as the transition metal. We showed two examples working towards this end by demonstrating the ARGET method and also a photocatalytic reducing agent. While the efficiency of block-copolymer formation was low, both methods illustrated the reduction or even elimination of copper is possible with further
optimization. Alternatively, copper could be abandoned altogether by choosing a more environmentally friendly transition metal. While copper is usually preferred in ATRP reactions due to its nearly-ideal activation/deactivation rates, in the ATRAF method only the activation step is necessary. This means that a less-toxic/more environmentally benign transition metal with a fast activation rate such as tin, iron or titanium could potentially be substituted. If the transition metal utilization can be reduced to ppm levels while maintaining high levels of macro-CTA efficiency, we believe that ATRAF methods for producing RAFT-active materials from anionic polymerization processes could realize many of the requisite features for commercial success: high efficiency, short reaction times, and even one-pot synthesis. These features would allow for easier commercialization of RAFT polymers, and would lead toward a polymer market that is more diverse in both properties and application.

4.1 Supporting Information Available

Supporting information includes all experimental procedures as well as NMR, DSC, and rheology data.

References


CHAPTER 5. CONVERSION OF ANIONICALLY PRODUCED POLYSTYRENE TO MACRO-CTA BY SINGLE INSERTION OF A MACROMONOMER ONTO A CHAIN TRANSFER AGENT

Michael Forrester, William Bradley, Nacu Hernandez, Chris Williams, George Kraus, and Eric Cochran. Additionally, Bill and myself are co-first authors on this publication.

5.1 Introduction

The use of a macromonomer in order to produce a macro-cta is very similar to the work done by Houshyar who performed single insertion of monomers onto a RAFT chain transfer agent (CTA).\(^1\) This afforded a styrene-CTA that was a single repeat unit with no apparent dimerization. Additionally, the product was quite pure with the primary impurities being leftover CTA, and coupled initiator radicals. Using this approach we are able to insert a single macromonomer-polystyrene onto a CTA to create a macro-CTA. This method has some very attractive features: very rapid reaction time, scalable temperatures (<80°C), high conversions, and the ability to use any CTA compatible with the choice of monomer.

In this work we focus on the use of a methacrylic macromonomer-see Scheme 5.1; however, vinyls, styrenic, and acrylic are also viable options. These different monomers will influence which CTA is used and will affect the choice of additional blocks. For example, if it is desired to polymerize a methacrylate second block, a methacrylate macromonomer should be used as an acrylate, vinyl, or styrenic, will likely make control of the methacry-
late block difficult. Once these various macromonomers and various CTAs have been studied this will allow for a very versatile route for producing anionic-RAFT copolymers.

\[
\begin{align*}
\text{PS} & \quad \text{OH} \quad \text{PS} \\
\text{O} & \quad \text{AIBN} \quad \text{O} \\
\text{S} & \quad \text{S} \quad \text{CN} \quad \text{CN} \\
\text{S} & \quad \text{S} \quad \text{OH} \\
\text{PS} & \quad \text{Triethylamine} \quad \text{PS} \\
\end{align*}
\]

Figure 5.1. Schematic for single insertion of macromonomer to produce macro-CTA

5.2 Materials and Methods

5.2.1 Polymerization of Styrene

Styrene is polymerized with commonly used procedures. Styrene and sec-butyllithium are purchased from Sigma Aldrich. Sec-butyllithium (1.4M in cyclohexane) is used as received. Styrene is purified by inerting with Argon and passage through an activated alumina column. HPLC grade cyclohexane (CHX) was purchased from Fisher Scientific and purified by inerting with argon and then passing through an oxygen scavenging column (Engelhard q5) and an activated alumina column.
500mL of CHX is added to an argon-filled round bottom flask equipped with a stir bar. The flask is then heated to 40 °C in a water bath. 4.5 mL of sec-butyllithium solution (targeting an 8kDa polymer) is added. 50 grams of styrene is introduced slowly over the course of 30 minutes to limit the temperature increase due to the exothermic nature of the polymerization. Finally, an aliquot is taken in order to determine the molecular weight of the polymer prior to further modification.

5.2.2 Ethylene Oxide Capping

Next, living styrene is end capped with ethylene oxide to provide a primary alcohol at the end of the styrene chain. This is done according to established procedures. Ethylene oxide (EO) is purchased from Sigma Aldrich and triple purified: The ethylene oxide (minimum of 10 molar excess with respect to sec-butyllithium) is first distilled from its original storage vessel and transferred onto calcium hydride for a minimum of half an hour to remove moisture. EO is then distilled onto approximately .02 eq. of di-n-butylmagnesium and allowed to stir for a minimum of a half an hour, prior to transfer to a sealed buret. The purified EO is connected to the living PS- solution via a cannula, allowing its vapor phase diffusion to the living styrene solution. The reaction is allowed to proceed for a minimum of two hours and is then terminated with acidic methanol (1 mL fuming HCl/10 mL of methanol).

The PS-OH solution is repeatedly washed with saturated sodium bicarbonate solution and distilled water until pH neutral. The polymer is recovered by precipitation in methanol and washed until material becomes brittle and easily broken by impact with a spatula. The material is then dried under vacuum until all traces of cyclohexane and methanol have been removed. GPC analysis is used to determine the molecular weight distribution. NMR is used to determine a rough estimate of the number of chains that have been capped with ethylene oxide.
5.2.3 Macromonomer Production

To 10g of hydroxyl terminated polystyrene is added cyclohexane 200mL and triethy-  
lamine (10eq with respect to chain ends). Once dissolved methacryloyl chloride (10eq)  
is slowly added to the solution at room temperature. Upon completion of addition of  
methacryloyl chloride the solution is heated to 40°C and allowed to react for 12-16 hours.  

Methanol (100 eq) is then added and allowed to stir for 30 minutes. The solution is  
then taken and precipitated into methanol, collected and further washed with methanol  
until the solid turns brittle. The polymer is then dried under reduced pressure to re-  
move all traces of solvent. The polymer is then run through GPC to determine molecular  
weight, and NMR is used to determine the number of chains that have been converted to  
macromonomer.

5.2.4 Chain Transfer Agent-CYCART

2-cyano-2-propanyl ethyl carbonotrithioate (CYCART) is synthesized according to well  
established procedures. The precursor is first synthesized by taking ethanethiol, dis-  
solved in acetone and water, and deprotonating with sodium or potassium hydroxide.  
Carbon disulfide is then slowly added and allowed to react for about 15-30 minutes at  
room temperature. Finally tosyl chloride is added to produce the symmetric bis car-  
onotrithioate.

This precursor is then taken and reacted with an excess of AIBN using ethyl acetate  
as the solvent at reflux temperatures. The reaction is stirred overnight and excess AIBN  
and AIBN byproducts are removed by extraction and then crystallization of unwanted  
materials in hot hexanes.
5.2.5 Single Insertion onto CTA

To 1 gram of macromonomer dissolved in toluene (5 mL) is added 3 eq of CTA and 3 eq of AIBN. The solution is mixed and purged for 15 minutes before being heated to 80°C. Samples are taken in order to determine when the maximum macro-cta functionality has been achieved.

5.2.6 Macro-CTA Block Co-Polymer Production

To .1 grams of polymer is added 5 mL of toluene and 5 mL of butyl acrylate. .3:1 eq of AIBN:CTA is added. The solution is mixed and purged with argon for 15 minutes. The solution is then heated at 80°C for 1 hour and then the unreacted butyl acrylate and toluene are removed under reduced pressure. The block co-polymer is then run through GPC to determine the amount of active macro-CTA.

5.3 Results

Ethylene oxide was used to convert the living polystyrene carbanion to an alkoxide, and would be quenched with methanol for protonation to yield ethylene oxide capped PS. Characterization was done via NMR-Figure 1 and GPC, which showed a change in molecular weight-Figure 5.3.

Based on the molecular weight of the polymer, determined by GPC, the NMR says that we have quantitative amounts of alcohol functionality. Next we run NMR on the product after the reaction with the alkene source and we have a calculated value of 1 macromonomer per chain end-Figure 5.4.

Finally, upon reacting with a CTA and subsequently reacting into a block co-polymer we study the GPC-Figure 5.5- and find that we have a maximum of 80% conversion at 20 minutes. Table 5.1 shows the effect that time has on functionality.
Figure 5.2. NMR showing the integration of styrene range compared to the CH2 next to alcohol

Table 5.1. Results of macromonomer reacted with CTA over time

<table>
<thead>
<tr>
<th>Reaction Time</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>78%</td>
</tr>
<tr>
<td>40</td>
<td>72%</td>
</tr>
<tr>
<td>65</td>
<td>69%</td>
</tr>
<tr>
<td>120</td>
<td>54%</td>
</tr>
</tbody>
</table>

5.4 Proposed Work

We intend to do more work with optimizing the ratios of reagents. Ideally we wish to produce a macro-CTA without any purification steps. This means that we will attempt to run the reaction as close to stoichiometric amounts as possible. Next we want to take a
look at using different macromonomers. We’d like to study styrenic, vinyl, and acrylate as an alkene source to produce the macromonomer. Finally, proving that we can use multiple different Z groups (xanthate, dithioester, and dithiocarbamide) is a valuable endeavor and so that will be the last piece of this work.

5.5 Conclusions

The use of a macromonomer to do single insertion on a CTA is fairly effective and very rapid. We have been able to achieve conversions of 80%; if conversions can be increased into the upper 90% range, that makes this an exceedingly attractive method to producing anionic to RAFT block co-polymers, and could introduce some exciting new materials into
Figure 5.4. NMR showing the integration of styrene range compared to the alkene from the methacrylate group

the polymer market. This would lead to an increase in polymer applications, a reduction in cost, and an increase in viability for bio-based monomers.

References

Figure 5.5. GPC showing the growth of PS-NBA (solid line) and unmodified PS (dashed line)
CHAPTER 6. PRODUCTION AND CHARACTERIZATION OF FULLY FUNCTIONALIZED GLYCEROL-ACRYLIC POLYMERS

Michael Forrester, Shailja Goyal, Fang-Yi Lin, and Eric Cochran.

6.1 Introduction

Biobased glassy polymers, especially thermoplastics, have been elusive in literature. Few have ever been synthesized, especially when considering multifunctional molecules. While molecules like vanillan have seen some research and do offer somewhat glassy materials-Tg of 60-70-these are simple monofunctional monomers, and don’t have the scalability of glycerol\(^1\) as a monomer stock. Poly-lactic acid has seen significant interest recently; however, it has some less than desirable mechanical properties.

When glycerol acrylic esters have their residual alcohol functionalities converted to acetate/acetal functionality we find that the glass transition of these materials goes up. In this work we look at two different materials, the first is a glycerol acrylate that has roughly 2 acetyl groups and 1 acrylic group. The second is a acetal of glycerol that has 1 acrylic group. In this chapter we look at some of the thermal and mechanical properties of both of these materials.

The production of these two materials follows the schemes shown in Scheme 6.1 and 6.2.
6.2 Materials and Methods

Solketal, Methacrylic acid, methacrylic anhydride, triethylamine, Amberlyst 15, phenothiazine, and AIBN were purchased from Sigma Aldrich. DCC, DMAP, Glycerol, acetic anhydride, toluene, and methylene chloride were purchased from Fisher.

6.2.1 Glycerol-Acetate-Methacrylate Monomer

The monomer synthesis was done in two steps. First glycerol, methacrylic acid-1.3 eq, phenothiazine-200ppm, and Amberlyst 15-5% by weight- were mixed together in a round bottom flask with a magnetic stir bar. They are reacted together for 24 hours at 100°C. After the completion of the reaction, a sample is taken to run NMR and then the monomer proceeds to the next step without purification. To the previous solution is added acetic anhydride-3.5eq-over the course of one hour. Care is taken to monitor the temperature
as this reaction is very exothermic. Additionally, temperature should be maintained below 40°C to limit the amount of hydrolysis or transesterification that can occur with the methacrylic groups.

Once the monomer has been reacted it is filtered to remove amberlyst and then it is washed with saturated sodium bicarbonate solution and extracted into ether. A sample is taken and NMR is run in order to determine the final functionality of the monomer.

6.2.2 Solketal-Methacrylate Monomer for Making Thermosets

To a solution of solketal-1eq, phenothiazine-400ppm, and triethylamine-.1eq- is added 2eq of methacrylic anhydride over 30 minutes at room temperature. The reaction is then heated to 40°C for about 16 hours. The reaction is then extracted in ether and washed with saturated sodium bicarbonate solution.

6.2.3 Solketal-Methacrylate Monomer for Making Thermoplastics

DCC-2eq, DMAP-.1% by weight, methylene chloride, and phenothizine-400ppm are mixed together. Methacrylic acid-2 eq- is then added over 15 minutes. Finally solketal is added over 30 minutes. The reaction is then stirred at room temperature for about 16 hours. After the reaction is complete the organics are washed with saturated sodium bicarbonate solution. The excess DCC/DCU is crystallized out by dissolving the material in n-hexane and allowing to sit for several hours in a -28°C freezer.

6.2.4 Chain Transfer Agent-CYCART

2-cyano-2-ropanyl ethyl carbonotrithioate (CYCART) is synthesized according to well established procedures. The precursor is first synthesized by taking ethanethiol, dissolved in acetone and water, and deprotanating with sodium or potassium hydroxide. Carbon disulfide is then slowly added and allowed to react for about 15-30 minutes
at room temperature. Finally tosy chloride is added to produce the symetric bis carbonotrithioate.

This precursor is then taken and reacted with an excess of AIBN using ethyl acetate as the solvent at reflux temperatures. The reaction is stirred overnight and excess AIBN and AIBN biproducts are removed by extraction and then crystallization of unwanted materials in hot hexanes.

6.2.5 Polymerization and Characterization of GRAMA

The monomer is mixed with AIBN or another thermal initiator, it is poured into a mold with whatever the desired shape is and it is heated to above 100°C for about 4 hours. Upon completion the thermoset is then tested using DMA and a universal testing machine.

Due to the brittleness of the material, we chose to do three point bend instead of tensile testing for the universal testing machine. While this does not directly measure the properties that we are interested in, it does get us to the right order of magnitude. For DMA we chose a ramp rate of 5°C/min and a strain of .01%. For universal testing we chose a rate of 1mm/min.

6.2.6 Polymerization and Characterization of SMA

For thermosets, a portion of the clean monomer is mixed with AIBN-.1% weight- and are heated to 100°C for four hours in a mold of the desired shape. The sample is then tested on DMA to determine the glass transition.

For thermoplastics, a portion of the monomer is dissolved in toluene, and enough CYCART to achieve a 25kDa molecular weight are added. AIBN-.3 eq relative to CYCART is added. The solution is then purged with argon to remove dissolved oxygen. Finally the
solution is reacted at 80°C for four hours. The product is then precipitated into hexanes. GPC is then used in order to determine the molecular weight.

6.3 Results

6.3.1 GRAMA

NMR of the MAG shows a 60% conversion of the methacrylic acid to methacrylate. This would yield approximately 1 functional group based on the initial amount of methacrylic acid originally added (Figure 6.3). NMR clearly shows that the methacrylate and acetyl groups give a mostly monoacrylate diacetate glycerol molecule 6.4

![Figure 6.3. NMR of material after reaction with methacrylic acid.](image)

DMA shows a transition point in the Tan Delta of 88.5°C (Figure 6.5).

UTM gives a break modulus of 20MPa, a Young’s Modulus of 150MPa, and a ultimate tensile strength of about 2 MPa (Figure 6.6).

6.3.2 SMA

For the first method of producing monomer, NMR-Figure 6.7- shows that we have a functionalized solketal; however, it does not define how much multifunctional glycerol
molecules are present. GCMS however shows that about 10% of the monomer is difunctional glycerol.

DMA shows a glass transition point in the Tan Delta of 95°C for the thermoset material—Figure 6.8. Additionally, this material seems to be very resistant to thermal cracking or degradation even up to temperatures as high as 180°C.

For polymers produced with the monofunctional molecule—as verified by GCMS, the molecular weight control was superb with a dispersity of 1.1 and a molecular weight of 22kDa—with 25kDa as the target.
6.4 Discussion

6.4.1 GRAMA

The results that we achieved on GRAMA thermosets do have some interesting qualities. First, the Tg is fairly high. A glass transition of 80°C is similar to where a 7-10kDa polystyrene would be. GRAMA Thermoset has a break modulus of 20MPa which is about a third that of polystyrene. Young’s Modulus of polystyren is between 1.9-2.9 GPa compared to the 150MPa of GRAMA. Finally the ultimate tensile strength is around 32-44 MPa, compared to the 2 MPa of GRAMA. While there is clearly a difference between these two materials, it does seem to suggest that this material may have promise. It is
our belief that the properties may be able to be improved; however, due to imperfections in making the thermosets-bubbling, cracking, etc- that there is some weakening of the material that has to do with the geometry rather than the fundamentals properties of the materials. By adjusting the chemistry and improving the curing method, we believe that a much better performing material can be obtained.

6.4.2 SMA

These results seem to show a lot of promise. First, cross-linked SMA has a glass transition (90°C) rivaling that of polystyrene (100°C). Next, the fact that it doesn’t seem to crack or discolor as it is heated up beyond 180°C indicates that it is quite thermally stable. Finally it doesn’t seem to break down or swell with water even over weeks of being completely submerged in water. This makes SMA an appealing possible alternative to petroleum glassy materials such as styrene.

6.5 Conclusions and Future Work

Polymers made from GRAMA and Solketal Methacrylate show great promise as a way to make a higher glass transition temperature material that has decent mechanical properties. While these materials do not quite compare to styrene or other traditional
petrochemical glassy materials yet, they do provide a biorenewable alternative that with some optimization may have great potential. Currently, these materials may be able to be compounded with other glassy polymers to give good mechanical and thermal properties while replacing some of the material with a cheap biorenewable alternative.

In future work we seek to finish studying these two monomers and to find other monomers that can provide a higher glass transition as well as superior mechanical properties. One of the main methods that we will look at to accomplish this is the use of different functional groups—such as a glycerol-cyclohexyl or cyclopental acetal. Additionally, a large emphasis will be focused on improving our curing methods. It is our belief that this would allow us to make a material that could compete strongly with petrochemical thermoplastics.

References

CHAPTER 7. CONCLUSION

The synthesis of polymers derived from biological sources has become increasingly important due to the cost and availability of petroleum-derived chemicals. To help overcome this challenge we have developed a number of materials and techniques to help facilitate the transition to materials made from biologically-derived feedstocks. Glycerol has been shown to be a powerful building block for the production of both low glass transition, soft, tacky materials as well as higher glass transition, stiff, strong materials. Because of the studies done on the stability of these materials, we can design a product that not only has excellent properties, but that is also capable of being used in current polymer facilities with minimal modifications. Additionally, by studying a method to convert anionic polymers to RAFT macro-chain transfer agents we can not only allow for exciting development of new materials, but also provide a more economically attractive opportunity for commercializing these glycerol polymers.
APPENDIX . SUPPORTING INFORMATION FOR: BLENDING THE EFFECTIVENESS OF ANIONIC POLYMERIZATION WITH THE VERSITILITY OF RAFT BY USE OF THE ATOM TRANSFER RADICAL ADDITION-FragmentATION TECHNIQUE

A.1 Materials and Methods

A.1.1 Polymerization of Styrene

Polystyrene (PS) was produced via anionic polymerization according to commonly used procedures.\textsuperscript{1} Styrene and sec-butyllithium were purchased from Sigma Aldrich. Sec-butyllithium (1.4M in cyclohexane) was used as received. Styrene was purified by sparging with argon and passage through an activated alumina column. HPLC grade cyclohexane (CHX) was purchased from Fisher Scientific and purified by sparging with argon and then passing over columns packed with oxygen scavenger column (Engelhard Q5) and activated alumina.

In a typical polymerization, 500 mL of CHX was added to an argon-filled round bottom flask equipped with a stir bar and septum. The flask was then heated to 40 °C in a water bath. 4.5 mL (6.3 mmol) of sec-butyllithium solution (targeting an 8 kDa polymer) was added. 50 g styrene was introduced slowly over the course of 30 min to limit the temperature increase due to the exothermic nature of the polymerization. Finally, an aliquot was taken in order to determine the molecular weight of the polymer prior to further modification.
A.1.2 PS-OH: Hydroxylation of living polystyrene

PS-OH-EO: Ethylene Oxide Capping  Living polystyrene was end-capped with ethylene oxide (EO) to provide a terminal primary alcohol (PS-OH) according to established procedures. Ethylene oxide (EO) was purchased from Sigma Aldrich and triple-purified: EO in a 10:1 molar ratio with respect to PS chains was condensed in vacuo onto calcium hydride for a 30 min to remove moisture. EO was then vacuum distilled onto 0.02 eq. of di-n-butylmagnesium and allowed to stir for an additional 30 min; this step was repeated prior to vacuum distillation to a sealed buret. The purified EO is connected to the living PS solution via a cannula, allowing vapor phase diffusion of the EO to the polymer solution. The reaction was allowed to proceed for a 120 min and terminated with oxygen-free acidic methanol (1 mL fuming HCl:10 mL methanol).

The PS-OH solution was repeatedly washed with saturated sodium bicarbonate solution and distilled water until pH neutral. The polymer was recovered by precipitation in methanol and washed until material becomes brittle and easily broken by impact with a spatula. The material was then dried under vacuum until all traces of cyclohexane and methanol were removed. Gel permeation chromatography (GPC) analysis was used to determine the molecular weight distribution. 1H-NMR was used to determine the extent of -OH functionalization.

NMR analysis was done by comparing the integration between 3.2-3.5 and 6.1-7.4. GPC analysis was done by integrating the peak and comparing to a polystyrene calibration.

Silane Synthesis ((3-chloropropoxy)trimethylsilane)  All reagents were used as received. Chlorotrimethylsilane (TMSCl), 3-chloro-1-propanol and triethylamine are purchased from Sigma-Aldrich. Dichloromethane is purchased from Fisher Scientific. 1 eq of 3-chloro-1-propanol and 1.2 eq of triethylamine are mixed in DCM. 1.2 eq of TMSCl
is added dropwise. Upon completion of addition the solution is allowed to stir for four hours and then purified by first removing the excess reagents and solvent. Next the mixture is distilled to yield the final product, (3-chloropropoxy)trimethylsilane. The product is confirmed by integration of NMR peak between 3.6-3.85, 1.9-2.1, .1-.3.

PS-OH-S:Silyl Capping  Living polystyrene was end-capped with (3-chloropropoxy)trimethylsilane to provide a terminal TMS protected alcohol, which upon deprotection with tetrabutylammonium fluoride yields a primary alcohol. (3-chloropropoxy)trimethylsilane was purified by stirring over calcium hydride for several hours. A 3 eq. excess of the end terminator is added and allowed to stir for 4 hours. Upon completion of the reaction, the polystyrene is then precipitated in methanol then dried under reduced pressure. NMR is then performed to determine end group functionality. The polymer is redissolved into cyclohexane and a 10 eq. excess of tetrabutylammonium fluoride is then added and allowed to stir for approximately 16 hours. The polymer is then precipitated and dried to give the final product.

NMR analysis of silyl protected polymer was done by comparing the integration between 0.1–0.4 and 6.1–7.4. GPC analysis was done by integrating the peak and comparing to a polystyrene calibration. Analysis of the deprotected polymer (alcohol terminated) was done by observing the loss of peaks in the 0.1–0.4 region.

PS-OH-A:Acetal Capping  Living polystyrene was end capped with 2-(3-chloropropoxy)-tetrahydro-2H-pyran to provide a terminal acetal. The terminated is purified by stirring over calcium hydride. A 3 eq excess of the terminated is added to the living polymer solution and allowed to stir for four hours. The polymer is precipitated, dried, and NMR is used to determine end group functionality. The acetal terminated polymer is then deprotected with 1 M HCl in methanol at 65°C for 16 hours. Upon completion the polymer is precipitated, dried, and NMR is again used to determine removal of acetal functionality.
NMR analysis of acetal protected polymer was done by comparing the integration between 4.3–4.6 and 6.1–7.4. GPC analysis was done by integrating the peak and comparing to a polystyrene calibration. Analysis of the deprotected polymer (alcohol terminated) was done by observing the loss of peaks in the 4.3–4.6 region.

A.1.3 PS-Br: Tert-bromine capping

2-bromo-2-methylpropanoyl bromide was purchased from Sigma Aldrich and used as received. 10 g of PS-OH were added to a round bottom flask with 200 mL of cyclohexane and a stir bar. After complete dissolution of the PS-OH 10 eq (with respect to chain ends) of trimethylamine was added, followed by the addition of 10 eq of 2-bromo-2-methylpropanoyl bromide over 5 min. The mixture was heated to 40 °C and allowed to react 12 h prior to precipitation and washing in methanol until brittle. The polymer was then dried under reduced pressure to remove all traces of solvent. GPC analysis was used for molecular weight analysis and \(^1\)H-NMR was used to confirm tertiary bromine addition by integration between 3.7-4.1.

A.1.4 PS-CTA: ATRAF

**Traditional ATRAF**  Bis(thiobenzoyl)disulfide (TBDS) and N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA) were purchased from Sigma Aldrich and used as received. Copper (I) bromide (CuBr) and copper wire (Cu) were acquired from Fisher Scientific and used without further purification. 1 g of the PS-Br was dissolved in 5 g toluene and degassed with 15 min of argon sparging. 2 eq TBDS, 0.1 eq CuBr, 10 eq Cu filings, and 5 eq PMDTA were added to create the catalyst complex. The solution was bubbled with argon for 15 min before the PS-Br solution was added. The mixture was then heated to 80 °C for 12 h, cooled to room temperature, and passed through a silica column to remove most of the copper. The solution was then subjected to two precipitation/dissolution cycles in
methanol/toluene. The polymer was then washed with methanol until brittle and then dried under vacuum overnight.

**ARGET ATRAF**  Copper II bromide (CuBr$_2$) and tin (II) ethylhexanoate (SnEtH) were purchased from Sigma Aldrich and used without further purification. 1 g PS-Br was dissolved in 5 g toluene and degassed with 15 min of argon sparging. 0.3 eq CuBr$_2$ are dissolved in toluene and 5 eq PMDETA is added to create the copper complex. The solution was bubbled with argon for 15 min prior to the addition of the PS-Br solution. The solution is then heated to 80°C Next, 0.3 eq SnEtH was added and allowed to stir for 30 min, followed by the introduction of 0.3 eq TBDS and an additional 30 min stirring. The SnEtH/TBDS addition cycle was repeated three times. The purpose for the alternating SnEtH/TBDS addition strategy is that the SnEtH is a powerful enough reducing agent to have undesired side reactions with TBDS. Upon completion of the reaction, the polymer solution is passed through a silica column to remove most of the copper. The solution was then subjected to two precipitation/dissolution cycles in methanol/toluene. The polymer was then washed with methanol until brittle and then dried under vacuum overnight.

**Photocatalyzed, metal free ATRAF**  10-methylphenothiazine was purchased from Sigma Aldrich and used as received. At room temperature, 1 g PS-Br was dissolved in anisole, and then 5 eq TBDS and 5 eq of methylphenothiazine were added to the solution. The mixture was bubbled for 15 min with argon prior to stirring the reaction for 20 h at room temperature while being subjected to 254 nm wavelength light in a Southern New England Ultraviolet Company Photochemical Reactor with a RPR 3000A bulb.
A.1.5 PS-Acrylate block copolymers: PS-CTA mediated RAFT polymerization of acrylates

All acrylate monomers were purchased from sigma-aldrich and were used as received.

**N-Butyl Acrylate** 0.1 g of PS-CTA (8 kDa, 12.5 µmol), 1 g toluene, 0.4 g of \(n\)-butyl acrylate (3.13 mmol), and 0.492 mg of AIBN (3 µmol) were added to a flask and purged with argon for 10 min, and then heated to 80 °C for 1 h. The mixture was cooled, and the resultant poly(styrene-block-\(n\)-butyl acrylate) (PS-nBA) block copolymer was recovered by evaporation of toluene and unreacted butyl acrylate under vacuum. The polymer is then analyzed using GPC in order to determine the percent cross-over from PS to PS-CTA. This is done by integrating the UV signal of the grown polymer peak and integrating the residual original polymer peak. The ratio of the two yields the conversion.

The efficiency of the ATR reaction is determined by producing a block co-polymer of the styrene with NBA and using a UV detector to determine the amount of styrene that is present in the block-copolymer and comparing this to the residual original styrene peak.

**Methyl Methacrylate** 0.1 g of PS-CTA (8 kDa, 12.5 µmol), 1 g toluene, 0.4 g of methyl methacrylate (4 mmol), and 0.492 mg of AIBN (3 µmol) were added to a flask and purged with argon for 10 min, and then heated to 80 °C for 1 h. The mixture was cooled, and the resultant poly(styrene-block-methyl methacrylate) (PS-MMA) block copolymer was recovered by evaporation of toluene and unreacted methyl methacrylate under vacuum. The polymer is then analyzed using GPC in order to determine the percent cross-over from PS to PS-CTA. This is done by integrating the UV signal of the grown polymer peak and integrating the residual original polymer peak. The ratio of the two yields the conversion.

The efficiency of the ATR reaction is determined by producing a block co-polymer of the styrene with methyl methacrylate and using a UV detector to determine the amount of
styrene that is present in the block-copolymer and comparing this to the residual original styrene peak. This will allow for the calculation of end-capping efficiency.

**Methyl Acrylate** 0.1 g of PS-CTA (8 kDa, 12.5 µmol), 1 g toluene, 0.4 g of methyl acrylate(4.64 mmol), and 0.492 mg of AIBN (3 µmol) were added to a flask and purged with argon for 10 min, and then heated to 80 °C for 1 h. The mixture was cooled, and the resultant poly(styrene-block-methyl acrylate) (PS-MA) block copolymer was recovered by evaporation of toluene and unreacted methyl acrylate under vacuum. The polymer is then analyzed using GPC in order to determine the percent cross-over from PS to PS-CTA. This is done by integrating the UV signal of the grown polymer peak and integrating the residual original polymer peak. The ratio of the two yields the conversion.

The efficiency of the ATR reaction is determined by producing a block co-polymer of the styrene with NBA and using a UV detector to determine the amount of styrene that is present in the block-copolymer and comparing this to the residual original styrene peak.

**A.1.6 Gel permeation chromatography (GPC)**

GPC was done on a Waters Acquity APC System, equipped with a RI and UV detector. The columns used were XT 125, 200, 450, and 900. The system runs at 1 mL/min in tetrahydrofuran.

**A.1.7 Nuclear magnetic resonance spectroscopy (1H-NMR)**

Volume fraction of PS-PMA and the end group functionalization was calculated based on 1H NMR spectra recorded in deuterated chloroform with a Bruker Avance III spectrometer (600 MHz).
A.1.8 Differential scanning calorimetry (DSC)

The DSC measurement was taken from TA DSC Q2000 differential scanning calorimeter operating under nitrogen atmosphere. Samples underwent two cycles of heating and cooling process at 20 °C/min and 10 °C/min, respectively. The glass transition temperatures \( T_g \) were taken from the second heating cycle.

A.1.9 Transmission electron microscopy (TEM)

Before proceeding viscoelastic behavior and transmission electron microscope (TEM) micrographs, samples were annealed at 100 °C under vacuum for 3 days. To obtain ultrathin sections of sample for TEM imaging, PS-PMA was cut into 70 nm thick sections by cryomicrotome at -50 °C. The contrast of two blocks under TEM was enhanced by selective staining of osmium tetroxide which stained methyl acrylate only. TEM micrographs were then taken by FEI Tecnai G2-F20 scanning transmission electron microscope operating at 200 kV. The black and white regions were PMA and PS, respectively.

A.1.10 Dynamic shear rheology (DSR)

The viscoelastic behavior of PS-PMA was tested by a TA ARES-G2 rheometer. Sample was thermally pressed into 1 mm thick disk before testing. Both isochronal test and temperature frequency sweep were performed on 8 mm parallel plates. Data points shown in isochronal test were taken every 5 °C during heating under a constant 4% shear strain and 1 rad/s angular frequency oscillation. To acquire the master curve, temperature frequency sweep was performed between 40 and 160 °C and oscillated between 1 and 100 rad/s in the viscoelastic region of sample. Data points were then shifted corresponding to the principle of time-temperature superposition.
A.2 Results

Figure 1. NMR showing the integration of styrene range compared to the CH2 next to alcohol. The ratio of these peaks gives a rough estimate of the number of alcohol functional groups present.

Figure 2. 1H-NMR showing the region associated with the acetal proton. The ratio of this peak to the styrene peak gives a rough estimate of the number of acetal functional groups present.
Figure 3. 1H-NMR showing the lack of peaks in the acetal proton region. This is a strong indication that we have removed the acetal functionality and replaced it with a primary alcohol.

Figure 4. 1H-NMR showing the region associated with the silyl methyl proton. The ratio of this peak and the styrene peak gives a rough estimate of the number of silyl functional groups present.

Figure 5. 1H-NMR showing the lack of peaks in the silyl methyl proton region. This demonstrates that we were able to cleave the silyl functional group and leave behind a primary alcohol.
Figure 6. NMR showing the integration of styrene range compared to the CH2 next to the tert-butyl bromide ester. The ratio of these integrals gives a rough estimate of how many tertiary bromide functional groups are present.

Figure 7. DSC showing glass transition of both methyl acrylate as well as polystyrene blocks. While the polystyrene glass transition is weak, both the PS and the PMA glass transitions have shifted inward from where they would be for homopolymers. This is strong indication of the production of a block copolymer.
Figure 8. Isochronal rheology temperature ramp that shows an order to disorder transition at 165 °C. This is further evidence that the styrene was converted to a styrenic acrylate copolymer.

Figure 9. Rheology master curve done on block co-polymer showing a terminal slope of .55. This is typical of lamellar phase separated block copolymers and is a strong indication that the styrene was converted to a block copolymer.
Figure 10. TEM showing the phase separation between the methyl acrylate and styrene blocks. This shows very clear lamellar phase separation and is confirmation of the production of a block copolymer.
References
