Post polymerization Modification and Preparation of Dynamic Polymer Networks via Guanylation of Aryl Carbodiimides

Conner J. Klingler

Western Washington University, cjklingler@outlook.com

Follow this and additional works at: https://cedar.wwu.edu/wwuet

Recommended Citation


https://cedar.wwu.edu/wwuet/1300
Post polymerization Modification and Preparation of Dynamic Polymer Networks via Guanylation of Aryl Carbodiimides

By

Conner J. Klingler

Accepted in Partial Completion of the Requirements for the Degree Master of Science

ADVISORY COMMITTEE

Dr. Michael B. Larsen, Chair

Dr. Amanda R. Murphy

Dr. David A. Rider

GRADUATE SCHOOL

David L. Patrick, Dean
Master’s Thesis

In presenting this thesis in partial fulfillment of the requirements for a master’s degree at Western Washington University, I grant to Western Washington University the non-exclusive royalty-free right to archive, reproduce, distribute, and display the thesis in any and all forms, including electronic format, via any digital library mechanisms maintained by WWU.

I represent and warrant this is my original work and does not infringe or violate any rights of others. I warrant that I have obtained written permissions from the owner of any third party copyrighted material included in these files.

I acknowledge that I retain ownership rights to the copyright of this work, including but not limited to the right to use all or part of this work in future works, such as articles or books.

Library users are granted permission for individual, research, and non-commercial reproduction of this work for educational purposes only. Any further digital posting of this document requires specific permission from the author.

Any copying or publication of this thesis for commercial purposes, or for financial gain, is not allowed without my written permission.

Conner J. Klingler
Post polymerization Modification and Preparation of Dynamic Polymer Networks via Guanylation of Aryl Carbodiimides

A Thesis
Presented to
The Faculty of
Western Washington University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
Conner J. Klingler
Abstract

Styrenic carbodiimide (CDI) polymers have shown an interesting ability to form reversible polymer networks, known as covalent adaptable networks (CANs), through an uncatalyzed reaction with multifunctional amines. CANs have been a topic of interest in polymer chemistry due to their ability to be reprocessed, which is not found in classic thermoset polymer networks. However, not much is known about the capabilities of the nucleophilic addition of amines to aryl CDI repeat unit structures that goes into making these networks due to the understudied reactions involved. This thesis aims to develop a better understanding of the chemistry involved through various post polymerization modification (PPM) reactions and adjustments to the CDI polymer structure used in these specific CANs. The synthesis of polymer chains containing aryl CDI repeat unit structures and the reactions performed on said structures with full characterization will be presented. Rheological studies comparing various CANs generated from both sterically hindered CDI polymer structures and CDI polymers with differing comonomer compositions will be compared.
Acknowledgements

I would like to thank Dr. Larsen for all the support and time he has given me during my time as his master’s student. In the process of learning polymer chemistry, he has been an incredible resource. His genuine passion for chemistry and ability to instill that same passion in new chemists is inspiring. I have no doubts that he will continue to foster amazing chemists during his tenure at WWU.

I would also like to give thanks to all of my lab mates that I have worked with these last two years. My experience as a master's student wouldn’t be nearly as memorable or fulfilling without them. Every day in the lab has been such a fun and happy experience with them. I have no doubts that they will all go on to do incredible things in their respective fields.

All the help and support I have received from Kyle Mikkelsen, Sarina Kiesser, and Alyssa Tsukada in AMSEC and SciTech should be acknowledged as well. They are not only incredible people, but also extremely knowledgeable in the instruments key to both my and many others' research here at WWU.

Finally, I would like to thank my incredible friends and family who have been supporting me through all the ups and downs of these last two years. I would not have been able to make it through grad school without all of you.
Table of Contents

Abstract.................................................................................................................................iv
Acknowledgements................................................................................................................v
List of Figures.........................................................................................................................viii
List of Schemes......................................................................................................................viii
List of Tables.........................................................................................................................viii
List of Equations...................................................................................................................viii
Chapter 1. Introduction........................................................................................................1
  1.1 Polymers.........................................................................................................................1
  1.2 CDI..................................................................................................................................3
  1.3 Covalent Adaptable Networks (CANs)........................................................................6
  1.4 PPM...............................................................................................................................10
  1.5 Future Outlook of the Research.....................................................................................13
Chapter 2. CDI Repeat Unit Modifications........................................................................14
  2.1 Introduction...................................................................................................................14
  2.2 Experimental................................................................................................................15
    2.2.1 Materials................................................................................................................15
    2.2.2 Methods..................................................................................................................15
    2.2.3 Synthesis of 1-(p-tolyl)-3-(4-vinylphenyl) thiourea (thiourea1)...........................16
    2.2.4 Synthesis of N-p-tolyl-N-(4-vinylphenyl)methanediimine (monomer1)..............17
    2.2.5 General procedure for the polymerization of monomer1..................................17
    2.2.6 Synthesis procedure for the 1:10 copolymerization of monomer1 and styrene....18
    2.2.7 General procedure for PPM of Poly(1).................................................................18
    2.2.8 RAFT copolymerization of monomer1 and styrene general procedure..............29
    2.2.9 General procedure for the block polymer formation using the RAFT poly1 polymer..20
  2.3 Results and Discussion................................................................................................20
    2.3.1 Synthesis and Polymerization of Monomer1.........................................................20
    2.3.2 PPM of The CDI Repeat Unit................................................................................25
    2.3.3 Method for Determining The mmol of CDI Repeat Unit to mg of Copolymer....28
    2.3.4 PPM of Poly(1)........................................................................................................29
    2.3.5 RAFT Copolymerization of monomer1 and Styrene............................................34
  2.4 Conclusions..................................................................................................................36
Chapter 3. Research Into Different CDI CAN Structures..................................................38
  3.1 Introduction...................................................................................................................38
  3.2 Experimental................................................................................................................39
    3.2.1 Materials................................................................................................................39
    3.2.2 Methods..................................................................................................................40
    3.2.3 General procedure for the synthesis of 1-(2,6-dimethylphenyl)-3-(4-vinylphenyl)thiourea (thiourea2).........................................................................................40
    3.2.4 General procedure for the synthesis of N-(2,6-dimethylphenyl)-N-(4-vinylphenyl)methanediimine (monomer2).................................................................41
3.2.5 Synthesis procedure for the 1:10 copolymerization of N-(2,6-dimethylphenyl)-N-(4-vinylphenyl)methanediimine and styrene (poly2) ........................................................................................................42
3.2.6 Synthesis procedure for the 1:10 copolymerization of N-(2,6-dimethylphenyl)-N-(4-vinylphenyl)methanediimine and butyl methacrylate (poly3) ........................................................................................................42
3.2.7 General procedure for the piperazine-containing CAN of Poly2 (CAN1) .........................43
3.3 Results and Discussion .......................................................................................................44
3.3.1 Synthesis and polymerization of monomer2 ....................................................................44
3.3.2 Copolymerization of styrene and monomer2 ..................................................................45
3.3.3 The 10:1 Copolymerization of Butyl Methacrylate and Monomer2 .................................46
3.3.4 Preparation of CANs made from Poly2 ........................................................................48
3.3.5 Synthesis and characterization of CANs made from Poly3 .............................................52
3.4 Conclusions .......................................................................................................................56
Appendix Figures ..................................................................................................................58
Citations .............................................................................................................................83
List of Figures
Figure 1.1 Three common polymerization methods.................................................................1
Figure 1.2 How thermoplastics and thermosets respond to heat............................................2
Figure 1.3 General structure of CDI.......................................................................................3
Figure 1.4 Diels-Alder thermoreversible CAN.......................................................................8
Figure 1.5 PPM polymer synthesis of a unpolymerizable monomer example.........................10
Figure 1.6 Bottle brush polymer synthesis using PPM..........................................................12
Figure 1.7 Examples of PPM of styrene-CDI statistical copolymers......................................12
Figure 2.1 The PPM of 10:1 styrene:CDI statistical copolymer.............................................15
Figure 2.2 Purposed mechanism for the formation of monomer1 from thiourea1................22
Figure 2.3 1H NMR of the homopolymer..............................................................................23
Figure 2.4 MALDI-TOF data of the homopolymer..............................................................25
Figure 2.5 IR spectrum comparison of the unmodified and modified homopolymer.............26
Figure 2.6 MALDI-TOF mass spectrometry data comparison of the PPM of the homopolymer..27
Figure 2.7 Example 1,3,5-trimethoxybenzene standardized sample.....................................28
Figure 2.8 All PPM reactions and the resulting isolated yields.............................................31
Figure 2.9 GPC results of the block polymer formation using the 198:1 RAFT copolymer.......35
Figure 3.1 Kinetics study of the TGM reaction....................................................................38
Figure 3.2 The CAN structures that will be discussed in the chapter..................................39
Figure 3.3 GPC chromatogram of poly(2)...........................................................................46
Figure 3.4 GPC chromatogram of poly(3)...........................................................................48

List of Schemes
Scheme 1.1 Synthesis of CDI using Mukaiyama’s reagent......................................................4
Scheme 1.2 General guanidine synthesis without catalyst.....................................................6
Scheme 2.1 Synthesis of monomer1.......................................................................................21
Scheme 2.2 Polymerization of monomer1...............................................................................22
Scheme 3.1 Synthesis of thiourea2.......................................................................................44
Scheme 3.2 Synthesis of monomer2.....................................................................................45
Scheme 3.3 Synthesis of CAN1 and CAN2...........................................................................49

List of Tables
Table 2.1 RAFT copolymerization results............................................................................36
Table 3.1 CAN characterization data tabulation................................................................54

List of Equations
Equation 2.1 Determining the mmol CDI repeat unit to mg of copolymer.........................29
Chapter 1. Introduction

1.1 Polymers

The word polymer comes from the Greek word polimeres meaning “having many parts”. This is an apt description considering that polymers consist of many repeating structures. The chain-growth polymerization of monomers, the starting structures that combine to make a polymer, can occur through three common methods: cationic, anionic, and free radical. The method that is used is determined based on the structure of the monomer used in the polymerization. The free radical polymerization method uses a radical initiator that breaks apart forming a radical and bonds to the polymerizable functional group (commonly a double bond) on the monomer and initiates it by transferring the radical to the monomer. This initiated monomer then bonds with an uninitiated monomer growing the polymer chain and moving the radical to the end of the chain. This process continues until all the monomer is used up or until a termination event occurs (Figure 1.1).

Figure 1.1. Three common polymerization methods.
A similar process occurs in the other two methods, but the radical initiator is replaced with a positively charged initiator in the case of cationic polymerization and a negatively charged initiator in anionic polymerizations (Figure 1.1).\textsuperscript{3,4} The monomers used in this thesis have a polymerizing site that resembles styrene, so the free radical method is employed since this is the most common method of polymerizing styrene.

Once the polymer chain is made, the polymer then falls under two main classes based on how the polymer chains interact with each other in a bulk material (Figure 1.2).

\textbf{Figure 1.2} How thermoplastics and thermosets respond to heat.
The first class of a polymer material is called thermoplastic. The polymer chains in these materials are not covalently bonded to each other and instead interact through intermolecular forces. Due to there being no bonds between polymer chains, thermoplastics are able to be reprocessed using heat. The second class of polymer materials is thermoset. The polymer chains are bonded together through covalent bonds (known as crosslinks) between two polymer repeat units on separate polymer chains. These covalent bonds form using functional groups in the repeat units or when reagents are added to the polymer sample initiating a reaction with the repeat units. The polymer chains then form a structure from these crosslinks called a network. After these crosslinks are formed the network is no longer able to change shape through thermal means, no matter how much heat is added and instead starts to degrade. Reactive functional groups need to be present in the repeat units to form these networks. Thus, specific functional groups are chosen so they only react when the crosslinks are intentionally made. In this thesis polymers that use carbodiimide (CDI) as a reactive functional group for crosslink synthesis and other polymer modifications will be discussed.

1.2 CDI

CDI is an unsaturated functional group (Figure 1.3) and has been a structure of interest since the 1950s.

\[ \text{R\-N\(=\text{C}\=\text{N}\)\-R'} \]
R = alkyl or aryl
R' = alkyl or aryl

**Figure 1.3** General structure of CDI.
There are a variety of methods used to synthesize this functional group depending on the overall structure of the final compound. The formation of CDI classically involved catalytic conversions of starting material or some sort of oxidation reaction. In reactions where a catalyst is used, isocyanates are directly converted into CDIs. The catalyst commonly used was a phosphorous-based catalyst which greatly improved the yields of the reaction and allowed for a variety of R groups to be present on the isocyanate. In cases where oxidation-like reactions occur, metal oxides (such as mercuric oxide) were used in the synthesis of CDI structures. In these reactions R group containing thioureas underwent a desulfurization reaction to form the CDI. Instead of using a metal oxide, another method is using Mukaiyama’s reagent (2-chloro-1-methylpyridinium iodide) to produce CDI structures directly from thioureas. This method of synthesizing CDI is ideal since it does not produce any water as a byproduct like when metal oxides are used. (Scheme 1.1).

![Scheme 1.1 Synthesis of CDI using Mukaiyama’s reagent.](image)

CDI has uses in various fields of chemistry such as biochemistry, synthetic chemistry, and polymer chemistry. In the field of biochemistry, CDIs have several uses in relation to proteins. One example of this is the ability of a water-soluble CDI to inactivate α-chymotrypsin through a reaction on the active site serine that transforms it to an oxazoline. In synthetic organic
chemistry, the CDI functional group is a helpful starting point for building useful and interesting compounds. A common use of CDI in synthetic chemistry is the formation of guanidine structures. An example of this is the catalytic guanylation of CDIs with primary aromatic and secondary amines reported by Zhang and Hou. In their synthesis they report using a half-sandwich yttrium alkyl complex as the catalyst.\(^{12}\) There has been many reported uses of CDI in the field of polymer chemistry as well. In the late 1960s it was found that cross-linked organosilicon CDI polymers were useful for high temperature paints and electrical insulating coatings.\(^{10}\) CDI polymers are also useful as a reinforcement material due to the rigid nature of the polymer chains. Specifically, poly(4,4’-diphenylmethanecarbodiimide), when used as an additive to nylon, increases the relative melt strength and viscosity of the material.\(^{10}\) Another classical use of the CDI functional group in polymer chemistry is post polymerization modification (PPM) of polymers. An example of this is the coupling of glycine ester with poly(acrylic acid) using water soluble CDI.\(^{10}\)

The research that will be covered in this thesis will use the ability of CDIs to form the guanidine functional group. By reacting diamines with the CDI group on the repeat units of the polymer chains, diguanidine crosslinks can be formed or new structures can be introduced through the formation of functionalized guanidine groups. These guanidines can form readily without the need of a catalyst or harsh conditions due to the R groups of the CDI being aryl structures which promote the nucleophilic addition of amines to the CDI structure \(\text{(Scheme 1.2)}\). The networks formed with the diguanidine crosslinks are also unique due to the crosslink formation being reversible at elevated temperatures.\(^{13}\)
This type of polymer network is called a covalent adaptable network (CAN) and is another aspect of the research being discussed in this thesis.

### 1.3 Covalent Adaptable Networks (CANs)

As previously mentioned, there are two main classes of polymer materials, thermoplastic and thermoset. CANs lay outside either class due to their unique ability to change shape like thermoplastics while still containing the crosslinks that are found in thermoset materials. This is due to the networks having enough covalently bonded crosslinks that reversibly bond together under specific stimulus to allow for a degree of flow in polymer chains sufficient for the material to change shape. Polymer materials that respond to stimuli, known as “smart materials”, are a new and interesting field of study with potential to solve many current issues. Since the overall structure of CANs is that of a thermoset, under ambient conditions they benefit from the physical properties of that structure type. Thermoset materials are useful due to their robustness and ability to resist degradation from environmental conditions. However, by developing a material that contains crosslinks that are thermally reversible it is possible to make a material that is reprocessable. The adaptable covalent bonds in the material also allow for reversible adhesives or self-healing materials to be developed.
The formation of polymers and the reactions that take place on the macromolecule scale follow the principle of equal reactivity. This principle states that the size of the molecule used in the reaction has no effect on the reactivity of the functional groups present. Using this principle, common reactions used at the small molecule scale can be applied to polymer chains to introduce useful functional groups or to react specific groups. To make a CAN, functional groups that can create reversible linkages are strategically placed along the polymer chain during polymerization. This is so that the reversible crosslinks that give CANs their unique properties can easily form. An example of this is the incorporation of furan and maleimide into the polymer chain which allows for thermoreversible crosslinks to form based on Diels-Alder reactions (Figure 1.4). It is also possible to generate CANs that have photochemically reversible crosslinks. With this method, specific wavelengths of light can be used to initiate a cyclization reaction. One of the structural motifs that make this reaction type possible is coumarin, which can form different isomers through a [2+2] dimerization.
Figure 1.4 Diels-Alder thermoreversible CAN

Since CANs have the structure of a thermoset while still being able to be reprocessed, they can be used in a variety of ways. Thermally reversible CANs are used as hot melt adhesives, in which the materials are manipulated at elevated temperatures then allowed to cool into the final networked material. There are uses for thermally reversible CANs in the field of electronics as well, since electronic components often require a strong protective material due to their delicate nature. When said parts break or no longer function, it is extremely helpful to be able to remove the protective covering to work on them. Thermally reversible CANs also boast an ability to be easily “healed” due to the fact that heat beyond a certain threshold is all that is needed for the material to bond back together after cracking. With extra care taken to prevent any unwanted irreversible side reactions, the mechanical integrity of the material can remain nearly unchanged as well. Photoreversible CANs have a variety of applications and are particularly useful when
light irradiation is preferred to alter the material as opposed to heat. Hydrogels, commonly used to encapsulate cells, can be made as photoreversible CANs allowing them to reversibly exhibit different mechanical properties depending on the wavelength of light used. Photoreversible CANs can also be used as shape memory materials. When these materials are exposed to a specific wavelength of ultraviolet light, they can be formed into a new shape and retain it but revert to the original shape when exposed to a different wavelength of ultraviolet light. Similar to thermally reversible CANs, photoreversible CANs can undergo crack healing as well. By incorporating cinnamate groups into the materials, cracks can be easily repaired through slight heating to allow for better interaction between polymer chains, followed by specific wavelengths of light fixing the broken bonds.

The CANs that will be discussed in this thesis are thermoreversible CANs that undergo a reversible metathesis reaction. Specifically, the unique guanidine structures that form the crosslinks of the polymer networks undergo a reversible reaction at elevated temperatures allowing the CAN to flow. When the material cools back down, the guanidine crosslinks reform, regenerating the polymer network. This thesis aims to explore how changing the structure of the guanidine crosslinks and the CDI repeat units used to make these crosslinks affect the chemical and physical properties of the resulting CAN.
The research that will be discussed in this thesis centers around PPM. This is the process of modifying reactive sites on the polymer to add new functional groups or change the polymer architecture. One classic example of PPM that is still used today is the vulcanization of natural rubber, in which natural rubber polymer chains are crosslinked with sulfur to make a network. PPM is beneficial in research for a variety of reasons, one of which is the ability to generate large libraries of functionalized polymer samples from a single large polymer batch. It is also possible to use PPM to synthesize polymer chains that could not otherwise be generated from the corresponding monomer (Figure 1.5) due to that monomer having other reactive sites that act as synthetic traps when polymerizing.

PPM can be used in a variety of ways when it comes to polymer chemistry. Some basic examples of this include modifying either end groups or repeat units of the polymer to change functional groups or produce networks. Just like in the synthesis of CANs, PPM follows the principle of equal reactivity, meaning as long as the proper functional groups are present most reactions are possible. Some of the key reaction types used in PPM include addition, substitution,
elimination and isomerization. These reaction types are generally performed to change functional groups on the repeat units which result in changing the properties of the polymer. A classic example of this is the modification of cellulose (a natural polymer) with nitric acid which transforms benign cellulose into the explosive material nitrocellulose. It is also possible to change the physical properties of a polymer through these repeat unit reactions as well. An example of this is the Diels-Alder cycloaddition reaction in which a furan or anthracene group on the polymer repeat units undergo an addition reaction with a pyrrole dione. This cycloaddition reaction would likely result in an increase in the glass transition temperature \( T_g \) of the polymer due to an increase in side chain size and intermolecular forces from additional \( \pi \)-stacking of the new aromatics. PPM reactions on the end groups of polymers are how many changes in polymer architecture occur. The changes in the architecture can range from compositional changes to morphological changes. For example, a compositional change would occur when a polymer consisting of a single repeat unit becomes a block copolymer consisting of two or more different repeat units. This occurs by reinitiating the growth of the polymer with another different monomer to produce a copolymer with different repeat unit sections called a block copolymer. In these cases, the PPM reaction occurs with a polymer produced using a controlled polymerization method which results in a polymer that can be reinitiated. Morphological changes using PPM can also be accomplished by incorporating end groups on the polymer chain that are able to be polymerized. An example of this is the formation of bottlebrush polymers. First, small polymer chains are produced using a controlled polymerization method. Then, the end groups are polymerized together using a different, orthogonal method to generate the bottle brush shape (Figure 1.6).
As previously mentioned, PPM is the backbone of the research that will be discussed in this thesis. PPM was used to generate a library of functionalized copolymer samples from a single large batch of styrene-CDI statistical copolymers. The CDI functional group on the polymer repeat units were reacted with a variety of primary and secondary amine-containing structures with different functional groups, some of which included competing nucleophiles. Using the same reaction but with secondary diamines, copolymer networks were formed as well. Examples of these PPM reactions can be seen in Figure 1.7.
These reactions have proven to be reversible at elevated temperatures and are the basis of the thermally reversible CANs that will be discussed in this thesis.

1.5 Future Outlook of the Research

CDI polymers have shown to be highly adaptable and have the desirable ability to form CAN networks. The structure of the CDI repeat units in the polymer allows for an extremely simple guanidine formation reaction which is reversible at elevated temperatures. Further studies into the scope of possible reaction partners should be explored, as there is potential for more synthetically useful structures to be developed using this chemistry. The biological and environmental safety of the materials should also be explored as well if they are to be used in commercial products.
Chapter 2. CDI Repeat Unit Modifications

2.1 Introduction

The research presented in this chapter explores the polymerization of monomers containing aryl CDI functional groups and the reactivity of the corresponding polymers. The study specifically focused on the CDI functional group’s capacity within the polymer repeat units to form guanidine structures through nucleophilic addition of amines. The aryl substituents of the repeat units increases the reactivity of the CDI functional group, allowing for an extremely mild guanidine formation not commonly seen in literature. This guanidine formation reaction occurs at room temperature with no catalyst in open atmosphere with only amines and the styrenic CDI copolymers in solvent. The fully modified polymers can then be isolated by simply removing the solvent.

The aim of the research presented in this chapter is to explore the limitations of this guanidine formation chemistry. To accomplish this, a variety of PPM reactions were performed on specific polymer samples. The end goal of this research was to develop a library of polymer samples modified using various amines. The amines used in this study contain a variety of structures and functional groups that could pose some synthetic challenges in other methods of guanidine formation.
Figure 2.1 The PPM of a 10:1 styrene:CDI statistical copolymer.

Note: some portions of the data and procedures were reproduced with permission from the publication: Postpolymerization Modification by Nucleophilic Addition to Styrenic Carbodiimides. Copyright 2023, American Chemical Society.25

2.2 Experimental

2.2.1 Materials.

All chemicals were purchased from commercial sources and used as received. Poly(N-p-tolyl-N-(4-vinylphenyl)methanediimine-co-styrene)$_{10}$ (poly1) used in the PPM reactions was synthesized as previously described.25 The dry solvents were dispensed from an Inert PureSolv solvent purification system. Triethylamine was dried using 4 Å molecular sieves and distilled under nitrogen.

2.2.2 Methods.

The $^1$H NMR spectra were collected using a Bruker Avance III 500 MHz FT-NMR spectrometer. IR spectra were collected using a Thermo iS10 FT-IR with single-bounce diamond ATR. Matrix Assisted Laser Desorption/Ionization time of flight (MALDI-TOF) mass spectrometry was performed on a Bruker autoflex maX MALDI-TOF/TOF spectrometer using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malonitrile (DCTB) as the matrix for an unmodified
homopolymer sample and 2,5-dihydroxybenzoic acid (DHB) for the modified homopolymer sample silver trifluoroacetate was used for the ion source. Polymer degradation temperatures were determined via thermogravimetric analysis (TGA) using a TA Instruments Q500 with platinum pans. GPC chromatograms were obtained with a Malvern Viscotek GPCMax equipped with Phenomenex Phenogel 5 µm 104 Å column, a SEC- MALS 9 multiangle light scattering detector, viscometer, and differential refractive index detector.

2.2.3 Synthesis of 1-(p-tolyl)-3-(4-vinylphenyl) thiourea (thiourea1):25

In a dry 100 mL flask under N₂, dry THF (30 mL) was added while stirring followed by 4-aminostyrene (5.00 mL, 42.7 mmol, 1.0 equiv.) and p-tolyl isothiocyanate (6.69 g, 44.8 mmol, 1.05 equiv.). The reaction mixture was stirred for 2 h at 20 °C. The thiourea was then precipitated out of the reaction mixture with hexanes (20 mL). The precipitate was isolated through vacuum filtration and allowed to dry in the filter resulting in a white powder (8.7 g, 76%). ¹H NMR (500 MHz, CDCl₃) δ 7.77 (s, 1H), 7.72 (s, 1H), 7.43 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.25 – 7.20 (m, 4H), 6.69 (dd, J = 17.6, 10.9 Hz, 1H), 5.73 (dd, J = 17.6, 0.8 Hz, 1H), 5.27 (dd, J = 10.8, 0.8 Hz, 1H), 2.36 (s, 3H).
2.2.4 Synthesis of N-p-tolyl-N-(4-vinylphenyl)methanediimine (monomer1):²⁵

In a dry 100 mL flask, 2-chloro-1-methylpyridinium iodide (4.00 g, 15.7 mmol, 1.2 equiv.) and thiourea¹ (3.50 g, 13.0 mmol, 1.0 equiv.) were added. The head space was then evacuated and backfilled with N₂. Dry DCM (30 mL) was then added while stirring, dissolving the solids. Triethylamine (5.43 mL, 39.0 mmol, 3.0 equiv.) was then added to the reaction mixture and it was stirred at room temperature. After the 30 min, the solvent was removed from the reaction mixture via rotary evaporation. The remaining residue was redissolved using a minimal amount of a 2:1 hexanes/DCM solution. The redissolved residue was purified via elution through a silica plug with 2:1 hexanes/DCM solution resulting in a clear light-yellow oil (2.6 g, 74%). ¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, J = 8.4 Hz, 2H), 7.16 – 7.11 (m, 4H), 7.07 (d, J = 8.4 Hz, 2H), 6.68 (dd, J = 17.6, 10.9 Hz, 1H), 5.71 (dd, J = 17.6, 0.8 Hz, 1H), 5.23 (dd, J = 10.8, 0.8 Hz, 1H), 2.34 (s, 3H).

2.2.5 General procedure for the polymerization of monomer1:

THF (5.0 mL) was added to a dry Schlenk flask followed by monomer¹ (1.89 mL, 8.54 mmol, 1.0 equiv.) and Azobisisobutyronitrile (AIBN) (0.140 g, 0.854 mmol, 0.1 equiv.). The reaction mixture was then subjected to three freeze-pump-thaw cycles to degas the solution. The flask was then backfilled with N₂ following the final thaw then heated to 60 °C and stirred for 16 h. The reaction was then stopped by exposing the reaction mixture to air. The polymer was then isolated through a dropwise precipitation into a methanol + 1% deionized water (10x reaction volume) solution. Vacuum filtration was used to recover the precipitated polymer. The polymer was then
redissolved in minimal THF for a second precipitation. The polymer was then precipitated dropwise again into chilled hexanes (10x the volume of the redissolved polymer solution) and filtered again. The polymer was then dried on a Schlenk line at 60 °C under vacuum resulting in a white powder (0.85 g, 42%). \( M_n = 29,000 \text{ Da} \) and dispersity = 3.3.

2.2.6 Synthesis procedure for the 1:10 copolymerization of monomer1 and styrene:\textsuperscript{25}

THF (40 mL) was added to a dry 250 mL Schlenk flask followed by styrene (12.82 mL, 111.0 mmol, 9.0 equiv.), monomer1 (2.45 mL, 11.1 mmol, 0.9 equiv.), and AIBN (2.02 g, 12.3 mmol, 1.0 equiv.). The Reaction proceeded as outlined in the general procedure 2.2.5. The polymer was then dried on a Schlenk line at 40 °C under vacuum resulting in a white powder. The Reaction proceeded as outlined in the general procedure 2.2.5. \( M_n = 11,000 \text{ Da} \) and dispersity = 1.5.

2.2.7 General procedure for PPM of Poly(1):

Poly(1) (0.100 g, 0.083 mmol CDI repeat unit, 1.0 equiv.) was dissolved in 0.4 mL CH\(_2\)Cl\(_2\) in a 20 mL scintillation vial. The amine (0.083 mmol, 1.0 equiv.) was then added, and the reaction mixture was allowed to stir under ambient conditions for 1 h. The reaction mixture was then analyzed by ATR FT-IR spectroscopy to confirm the absence of the CDI stretching frequency at \(~2100 \text{ cm}^{-1}\). The fully modified copolymer was isolated by removing the volatiles under vacuum at 60 °C.
When poly(monomer1) (the homopolymer) was used the reaction conditions and equivalents described above were used with THF as the solvent used instead of CH$_2$Cl$_2$.

When 2-methylpiperidine was the amine used in the reaction, 1.5 equiv. of amine was used. The modified polymer was then isolated by precipitation in 10 mL of hexanes, then filtered.

When L-alanine methyl ester hydrochloride was the amine used in the reaction, 1.5 equiv. of amine and 1.0 equiv. of triethylamine was added to the reaction mixture. The modified polymer was then isolated by precipitation in 10 mL of hexanes and filtered. The collected solids were then triturated with water to remove residual hydrochloride salts.

2.2.8 RAFT copolymerization of monomer1 and styrene general procedure:

Stock solutions of AIBN (100 mg/mL) and 2-cyano-2-propyl dodecyl trithiocarbonate (100 mg/mL) were first prepared in dry THF. To a dry Schlenk flask under N$_2$, THF (2.0 mL) was added followed by AIBN (58 µL, 0.035 mmol, 0.3 equiv.), 2-cyano-2-propyl dodecyl trithiocarbonate (0.41 mL, 0.12 mmol, 1.0 equiv.), monomer1 (0.25 g, 1.07 mmol, 9.0 equiv.), and styrene (1.23 mL, 10.67 mmol, 90 equiv.). The Reaction proceeded as outlined in the general procedure 2.2.5. The polymer was then dried on a Schlenk line at 60 °C under vacuum resulting in a white powder.

Three variations of monomer:CTA ratios were examined; 99:1 (above), 198:1, and 297:1. The three ratios were acquired by adjusting the amount of CTA added in the above procedure.
2.2.9 General procedure for the block polymer formation using the RAFT poly1 polymer:

A stock solution of AIBN (50 mg/mL) was prepared using dry THF prior to the start of the reaction. To a dry Schlenk flask with a stir bar the 200:1 RAFT copolymer (100 mg, 0.018 mmol trithiocarbonate endgroup, 1.0 equiv.) was added and the headspace was evacuated and backfilled with N₂. The polymer was dissolved in dry THF (1 mL) followed by the addition of styrene (0.41 mL, 3.54 mmol, 200 equiv.) and the AIBN solution (5.81 µL, 0.0018 mmol, 0.1 equiv.). The reaction proceeded as outlined in the general procedure 2.2.5. The polymer was then dried on a Schlenk line at 60 °C under vacuum resulting in a white powder (0.13 g, 28%). Mₙ = 30,000 Da and dispersity = 1.2.

2.3 Results and Discussion

2.3.1 Synthesis and Polymerization of Monomer1

The preparation of the monomer1 was accomplished through a two-step process (Scheme 2.1). The first step consisted of a nucleophilic addition of 4-aminostyrene to p-tolyl isothiocyanate which yielded the intermediate thiourea1. The structure of the thiourea was then confirmed using ¹H NMR spectroscopy. The identifying peaks of the structure are from the vinyl
benzene and tolyl groups on either side of the thiourea group in the center (Appendix Figure A.1). After confirming the structure of the thiourea the collected product was then used in the second step of the monomer synthesis.

Scheme 2.1 Synthesis of monomer1.

The thiourea intermediate then underwent a dehydrosulfurization using Mukiyama's reagent to generate the CDI monomer monomer1. This transformation was accomplished through mechanism that can be seen in Figure 2.2. The structure was confirmed using a combination of $^1$H NMR and IR spectroscopy. The $^1$H NMR spectrum was used to confirm the vinyl benzene and tolyl groups attached to the CDI group in the center (Appendix Figure A.2). The IR spectrum was then used to confirm the formation of the CDI functional group which appears $\sim2100$ cm$^{-1}$ (Appendix Figure A.3).
Figure 2.2 Purposed mechanism for the formation of monomer1 from thiourea1.

The monomer was then polymerized using the free radical polymerization method with AIBN as the radical initiator (Scheme 2.2). Once AIBN initiated the polymerization, the polymer grew via chain growth, meaning the polymer chain grew by one repeat unit at a time. This process results in high molecular weight polymer chains being produced early on in the reaction when monomer concentration was the highest. The average molecular weight ($M_n$) and dispersity of the polymer chains were then determined using GPC. In one instance the measured $M_n$ was roughly 29,000 Da and the dispersity was 3.3 (Appendix Figure A.4).

Scheme 2.2 Polymerization of monomer1.
The structure of polymer, like the monomer, was confirmed using a combination of $^1$H NMR and IR spectroscopy. The NMR spectrum can be seen in Figure 2.3. The $^1$H NMR spectrum is consistent with what was expected for the polymer.

![Figure 2.3 $^1$H NMR of the homopolymer](image)

Note: not all signals in the green and orange highlighted regions are magnetically equivalent.

There is a clearly defined aromatic region and the methyl group of polymer repeat unit is also present at an expected chemical shift of 2.27 ppm. The ratio of the integration values of these two regions was also consistent with the number of hydrogens present in these functional groups. Like the monomer, IR spectroscopy was used to confirm the presence of the CDI functional group. The IR spectrum ([Appendix Figure A.5](#)) showed a prominent peak at ~2100 cm$^{-1}$ consistent with the C=N stretching frequency of the CDI functional group.
The degradation temperature ($T_d$), determined at the point when the sample had lost 5% of its mass, was determined to be 208 °C (Appendix Figure A.6). This $T_d$ is much lower than that of pure polystyrene (324 °C) showing that the introduction of the CDI repeat unit lowers the overall thermal stability of the polymer. MALDI-TOF mass spectrometry was used to confirm the molecular weight of the repeat units and the end groups of the polymer chain, which gives insight into the most common termination event. The MALDI data seen in Figure 2.4 had spacing between the adjacent mass peaks that was consistent with the purposed structure of the repeat unit. The end group structure was determined by plotting the degree of polymerization of the polymer vs the mass of the polymer at the corresponding mass peak. This was done for each of the separate polymer species found in the MALDI data. A linear line of best fit was generated for each polymer species and the y-intercept corresponded to the mass of the end groups which was used to determine the end group structure. Through this analysis the most common termination of event of the polymerization was found to be recombination. Recombination is where the radical ends of two separate polymer chains come together to form a bond which ends the growth of the polymer chain.
Figure 2.4 MALDI-TOF Data of the homopolymer  

a) MALDI mass spectrometry data for the polymer with labels corresponding to populations derived from two different termination events (blue-recombination, red-disproportionation).  
b) Scatter plot of the mass peaks and the corresponding degree of polymerization of the two polymer species found in the MALDI data.

2.3.2 PPM of The CDI Repeat Unit

To test the viability of the PPM of the CDI repeat units within poly1, a modification reaction was first performed using the homopolymer. The modification of the homopolymer proceeded through the nucleophilic addition of 4-methylbenzene to the CDI functional group within the repeat units. Once one hour had passed to allow for the full modification of the polymer, the reaction mixture was tested on an IR spectrometer. The peak at ~2100 cm⁻¹
associated with the CDI functional group was no longer present (Figure 2.5) showing full modification of the polymer sample.\textsuperscript{31}

![Figure 2.5 IR Spectrum comparison of the unmodified and modified homopolymer]

The solvent and volatiles were then removed from the reaction flask, first by rotary evaporation then followed by a high vacuum while the vial was heated to 60 °C. The resulting isolated yield was greater than 95%. The structure of the modified polymer was then confirmed using a \textsuperscript{1}H NMR spectroscopy (Appendix Figure A.7). The \textsuperscript{1}H NMR spectrum showed an increase in the integration value (from 8.00 to 12.00) of the aromatic region consistent with the addition of the aromatic ring from the nucleophilic addition of 4-methylbenzyl amine to the CDI functional groups. The appearance of the benzylic peak at \(~4.3\) ppm in the \textsuperscript{1}H NMR spectrum confirmed the success of the repeat unit modification. Another indication of the modification succeeding was the increase in integration of the methyl group peak (from 3.00 to 6.34) associated with the methyl group attached to the benzene ring of the repeat unit. This is due to the methyl group of the 4-methylbenzylamine group having a similar chemical shift resulting in the peaks overlapping. To
further confirm the modification of the CDI repeat units of the homopolymer, an unmodified sample of the homopolymer and the same sample modified with 4-methylbenzyl amine were analyzed using MALDI TOF mass spectrometry. A comparison of the two samples can be seen in Figure 2.6.

**Figure 2.6 MALDI-TOF mass spectrometry data comparison of the PPM of the homopolymer.**

The distance between two adjacent mass peaks of a single polymer species in the MALDI data directly corresponds to the molecular weight of the repeat unit. By comparing the modified sample to the unmodified sample, we found that the difference between two adjacent peaks in the modified sample directly correlates to the added mass from the repeat unit modification.
2.3.3 Method for Determining The mmol of CDI Repeat Unit to mg of Copolymer

Before any reaction with the 10:1 styrene to monomer copolymer took place, the ratio of mmol of CDI present to total copolymer mass was determined. By knowing the mmol of the CDI repeat units we were able to add reagents at amounts relative to the repeat units rather than the copolymer as a whole. This method uses reference peaks and their integration values from $^1$H NMR spectrum with 1,3,5-trimethoxybenzene used as an internal standard. (Figure 2.7).

![Figure 2.7 Example 1,3,5-Trimethoxybenzene Standardized Sample.](image)

The peak at ~6.00 ppm associated with the hydrogens on the aryl ring of 1,3,5-trimethoxybenzene were integrated and normalized to 3.00.$^{32}$ The peak associated with methyl
group of the CDI repeat unit (at ~2.30 ppm) was integrated and the value recorded. **Equation 2.1** was then used to determine the mmol of CDI repeat unit to mg of copolymer ratio using the information found in the $^1$H NMR spectrum. The calculated ratio of the mmol of CDI repeat unit to mg copolymer of the copolymer sample (poly1) used in all PPM reactions discussed in this chapter was 8.83E-4 mmol CDI/ mg poly.$^{25}$

**Equation 2.1 Determining the mmol CDI repeat unit to mg of copolymer.**

\[
\left( \frac{\text{Carbodiimide Methyl Group Peak Integral}}{\text{Number of Protons from Methyl Group}} \right) \left( \frac{\text{mg 1,3,5 - Trimethoxybenzene}}{168.19 \text{ mg/mmol}} \right) = \text{mmol CDI/ mg Poly}
\]

### 2.3.4 PPM of Poly(1)

The next step was to explore modifying a single large batch of copolymer sample to determine the sensitivity and scope of this reaction with various functional groups. A single polymer sample was used for all the PPM reactions to maintain a consistent benchmark in which to compare the results. The polymer used was poly(1) made by an undergraduate in the Larsen research group.$^{25}$ The structure of the polymer was confirmed using $^1$H NMR and IR spectroscopy (Appendix Figures A.8 and A.9) before being used in the PPM reactions. The solvent used in the PPM reactions of the copolymer was switched from THF to DCM to allow for easier removal of the volatiles when isolating the modified polymer. A series of differently functionalized amines were used to develop a library of functionalized polymer samples. **Figure 2.8**.
For all amines used other than 2-methylpiperidine and L-alanine methyl ester hydrochloride, the same procedure was used to modify the 10:1 copolymer. The reaction was accomplished with each of the amines through the nucleophilic addition of an equimolar amount of the amine to the CDI containing repeat unit. After an hour of reaction time, the reaction mixture was then tested using an IR spectrometer to confirm the success of the modification reaction. The full modification of the copolymer, like the homopolymer, was confirmed through the disappearance of the peak at ~2100 cm\(^{-1}\) from the N=C=N stretching frequency of the CDI functional group.\(^{31}\) As previously mentioned, some modifications to the PPM procedure were required when L-alanine methyl ester hydrochloride and 2-methylpiperidine were used. In the case where 2-methylpiperidine was used, the only changes to the procedure were an increase of the amine’s molar equivalents to 1.5 and a precipitation into hexanes to fully isolate the modified copolymer. Due to the need to precipitate the modified copolymer, the yield percent from this PPM was much lower at 36.2%. When L-alanine methyl ester hydrochloride was the amine used, an increase of amine equivalents to 1.5 was also required. In addition to the increase in amine loading, triethylamine was also added at 1.0 equivalents relative to the CDI repeat units. The modified copolymer was then isolated through precipitation into hexanes. The collected solids were then tritiated with water to remove the remaining hydrochloride salts. Similar to the PPM reaction with 2-methylpiperidine, this PPM reaction had a lower percent yield than a majority of the PPM reactions at 51.5%. The structures of the amines used in the PPM reactions along with the resulting percent yields of the reactions can be seen in Figure 2.8.
The structures of the modified copolymers were confirmed using $^1$H NMR spectroscopy. This was accomplished by comparing the spectrum of the unmodified copolymer to the spectra of the modified copolymers. In most cases there were clear additions of functional groups in the NMR spectra from the nucleophilic addition of the amines to the CDI functional group. In addition, peaks that are spread out and are no longer sharp are a good indicator that the functional groups have been added to the polymer. This change in shape occurs in polymers due to the functional groups of each repeat unit having slightly different chemical shifts since they are not all in the same exact position on the polymer. In the case of the copolymer modified with piperidine, a spread-out signal at 3.29 ppm with a relative integration value of 3.68 was the noted change.

**Figure 2.8 All PPM reactions and the resulting isolated yields.**
These reported values supported the assignment of this peak as the protons adjacent to the nitrogen on the cyclic ring of the piperidine group which was added (Appendix Figure A.10). When 4-methylbenzyl amine was used, an additional p-tolyl methyl group signal at 2.29 ppm confirmed the modification. This peak was slightly lower in chemical shift than one at 2.34 ppm associated with the p-tolyl methyl group of the repeat unit structure (Appendix Figure A.11). When 2-aminoethanol was used, two peaks at 3.77 and 3.47 ppm were used to confirm the modification of the copolymer. These peaks correspond to the protons of the carbon chain of the newly added ethanol group (Appendix Figure A.12). When allylamine was the amine used three peaks at 3.96, 5.17, 5.96 ppm showed the successful modification of the copolymer. Using integration values and the predicted ppm of the chemical shifts the peaks 5.17 and 5.96 ppm were confirmed to be from the alkene group added by the addition of allylamine (Appendix Figure A.13). In the case where methyl 4-piperidinecarboxylate was used the appearance of a peak at 3.68 ppm indicated the successful addition of the amine. This peak at 3.68 ppm corresponds to the newly added ester group from the nucleophilic addition (Appendix Figure A.14). The peak shape in the $^1$H NMR spectrum also helps to identify if the peaks are from the addition of the amines to the CDI repeat units. When 5-norbornene-2-methylamine was the amine used, peaks at 6.13, 5.94, and 2.79 ppm were used to confirm the success of the PPM reaction. By integrating and normalizing the p-tolyl methyl peak of the CDI repeat unit structure to 3.00 the relative integration value of the peaks at 6.13 and 5.94 ppm was obtained. The combined integration value (2.13) and chemical shifts of these two peaks affirmed that the peaks were from the hydrogens of the alkene group in the cyclohexene ring of the norbornene group (Appendix Figure A.15). In the case of dibenzylamine, a broad peak at 4.36 ppm was used to
confirm the addition of the amine to the carbodiimide repeat units. This peak can be associated with the protons on each side of the tertiary nitrogen formed through the nucleophilic addition of dibenzylamine (Appendix Figure A.16). While it was not possible to assign unique peaks to the polymer modified with propargyl amine, the IR spectrum was solely used to confirm the modification of the polymer sample through the disappearance of the peak at ~2100 cm\(^{-1}\) associated with the unmodified CDI functional group (Appendix Figure A.17). The success of the modification was further supported by the appearance of a stretching peak around 3300 cm\(^{-1}\), indicative of the bond involving the terminal hydrogen and carbon of the alkyne group. The lack of unique peaks is due to the overlap of chemical shifts from the added propargyl group, and the alkyl functional groups present in the carbon backbone of the polymer chain. In the \(^1\)H NMR spectrum of the 2-methylpiperidine modified copolymer the unique peak associated with the successful modification of the copolymer appears at 2.98 ppm. This peak is associated with the hydrogen attached to the tertiary carbon atom in the ring of the 2-methylpiperidine group. This assignment was confirmed with the integration (a value of 1.09) of the peak matching up with the expected number of hydrogens present at this point (Appendix Figure A.18). In the case when L-alanine methyl ester hydrochloride was the amine used for the PPM reaction a single peak at 3.68 ppm was the identifying peak in the \(^1\)H NMR spectrum. This peak at 3.68 ppm was determined to be the protons of the methyl group on the ester functional group added by the nucleophilic addition of L-alanine methyl ester hydrochloride. This assignment was confirmed by the integration value (2.86) of the peak matching the expected number of hydrogens (Appendix Figure A.19).
2.3.5 RAFT Copolymerization of monomer1 and Styrene

In an attempt to further explore the capabilities of monomer1 a series of controlled polymerizations were performed. The controlled polymerization method used was reversible addition-fragmentation chain transfer (RAFT) method. This method employs a chain transfer agent (CTA) that limits the growth of the polymer chain by reversibly bonding to the end of the growing polymer chain. Three ratios of monomer to CTA were explored: 99:1, 198:1, and 297:1. The ratio of CDI monomer to styrene monomer was kept constant at 10:1 for each monomer:CTA ratio. These three ratios were used to determine how lowering the concentration of CTA in the polymerization would effect the size of the resulting polymer. In each iteration of monomer:CTA ratio stock solutions of AIBN and 2-cyano-2-propyl dodecyl trithiocarbonate (the CTA) were prepared using dry THF for ease of use. The three ratios of monomer:CTA were prepared by maintaining the amount of monomer used and adjusting the amount of CTA delivered to match the ratios. Once the controlled 10:1 copolymers were fully isolated, they were tested using $^1$H NMR spectroscopy and gel permeation chromatography (GPC). $^1$H NMR spectroscopy was used to confirm the structure of the copolymer and the addition of the CTA end group (Appendix Figure A.20). The presence of a monomodal curve with a narrow dispersity in the GPC chromatogram indicated a single polymer species produced from the reaction and confirmed that the polymerization was controlled. (Appendix Figures A.21-A.23). By adjusting the monomer:CTA ratio we found that the average molecular weight of the copolymers could be controlled while maintaining low dispersity of the polymer’s molecular weight (Table 2.1).
Table 2.1 RAFT copolymerization results.

<table>
<thead>
<tr>
<th>Mono:CTA Ratio</th>
<th>$M_n$ (Average Molecular Weight)</th>
<th>Dispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>99:1</td>
<td>3,000 Da</td>
<td>1.1</td>
</tr>
<tr>
<td>198:1</td>
<td>5,600 Da</td>
<td>1.1</td>
</tr>
<tr>
<td>297:1</td>
<td>14,000 Da</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Polymers produced with this method of controlled polymerization can be reinitiated post polymerization and continue to grow.\(^{33}\) This is accomplished through the addition of a radical initiator to the polymer along with additional monomer. To show that this was possible with the RAFT copolymers that were produced, the 198:1 RAFT copolymer was reinitiated in the presence of styrene. The resulting polymer was then analyzed on the GPC to determine the outcome of the polymerization. The GPC data showed an increase in average molecular weight of the polymer sample from 5,300 Da to 30,000 Da while maintaining a monomodal curve in the GPC data. The data also showed that there was little to no change in the dispersity of the polymer chain lengths. (Figure 2.9).

![Figure 2.9 GPC results of the block polymer formation using the 198:1 RAFT copolymer](image.png)
*Peaks > 10.8 mL retention volume are associated with solvent breakthrough

2.4 Conclusions

The ability to modify the CDI functional group within the repeat units of polymer chains was studied. The reactivity of the CDI functional group was explored through PPM reactions with variously functionalized amines. The functional groups present on the amines included ester, alkene, alkyne, norbornene, and alcohol groups. The successful addition of the amine 4-aminoethanol which contained an alcohol group was especially interesting, as it shows that the nucleophilic addition of the amine to the CDI group is highly selective even in the presence of competing nucleophiles such as an alcohol group. The structures of the amines also varied, with both primary and secondary amines successfully reacting with the CDI functional group. The secondary amines used contained both cyclic and acyclic structures. All the PPM reactions between the amines and the CDI functional group occurred at room temperature open to ambient conditions within an hour. The mild reaction conditions and speed of the reaction shows that the copolymer is highly modifiable with a variety of functional groups. In a majority of the reactions the calculated yield was greater than 95% showing that the products were easily isolatable with high purity. Functional groups such as norbornene which was added by the addition of 5-norbornene-2-methylamine could lead to additional PPM reactions allowing for changes to the polymer architecture. The controlled copolymerization of the CDI monomer and styrene shows the reliability of the CDI monomer in polymerizations. Both the dispersity of the chain lengths and the molecular weight of the copolymers produced indicated that the
polymerizations were reliably controlled using the RAFT polymerization method. The formation of the block polymer from the 198:1 RAFT copolymer confirmed that the produced RAFT copolymers had the ability to reinitiate. By employing PPM reactions at the CDI functional group within the repeat units and in conjunction with RAFT copolymer reactions, a deeper understanding of these polymers was achieved.
Chapter 3. Research Into Different CDI CAN Structures

3.1 Introduction

The research presented in this chapter involves the exploration of new covalent adaptable network (CAN) structures. The crosslinks that will be discussed are reversible due to the diguanidine crosslinks that form the network structures. These diguanidine crosslinks are able undergo an exchange reaction under elevated temperatures known as thermal guanidine metathesis (TGM) which allows for flow of the material.

The aim of the research presented in this chapter is to explore how changing the structure of the CDI copolymers affects the properties of resulting CANs. Previous kinetic studies of small molecule analogs of monomer1 showed that increasing steric hindrance of the amine used to form the guanidine structure increased the rate of the dissociation of the amine (Figure 3.1). By increasing the rate in which the guanidine structures dissociate, the Eₐ of the analogous CANs should also decrease.

![Figure 3.1 Kinetics study of the TGM reaction.][13]

<table>
<thead>
<tr>
<th>Guanidine</th>
<th>Temperature (°C)</th>
<th>$K \times 10^4$ (relative rate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>160</td>
<td>1.0</td>
</tr>
<tr>
<td>G2</td>
<td>160</td>
<td>2.3</td>
</tr>
</tbody>
</table>

[13] Figure 3.1 Kinetics study of the TGM reaction.
It was hypothesized that this effect would compound when steric hindrance was also applied to the CDI repeat unit. To test this hypothesis, a more sterically hindered monomer was produced and used in two different 10:1 copolymerizations with styrene and butyl methacrylate. Styrene and butyl methacrylate were used as comonomers to determine if polarity and a lower glass transition temperature ($T_g$) in the comonomer would affect the properties of the CAN as well. To form the networks, two separate diamines were used as well (piperazine and 2,5-dimethylpiperazine) to determine if increasing steric hinderance on the repeat unit and the crosslink would have a compounding effect in the networks (Figure 3.2).

![Figure 3.2 The CAN structures that will be discussed in the chapter.](image)

3.2 Experimental

3.2.1 Materials.

All chemicals were purchased from commercial sources and used as received. The dry solvents were dispensed from an Inert PureSolv solvent purification system. Triethylamine was dried using 4 Å molecular sieves and distilled under nitrogen.
3.2.2 Methods.

The $^1$H NMR spectra were collected using a Bruker Avance III 500 MHz FT-NMR spectrometer. IR spectra were collected using a Thermo iS10 FT-IR with single-bounce diamond ATR. Degradation temperatures were determined via thermogravimetric analysis (TGA) using a TA Instruments Q500 with platinum pans. GPC chromatograms were obtained on a Malvern Viscotek GPCMax equipped with Phenomenex Phenogel 5 µm 104 Å column, a SEC- MALS 9 multiangle light scattering detector, viscometer, and differential refractive index detector. Dynamic mechanical analyses (DMA) were performed using a TA Instruments Q800 in tension mode. Rheometry data was obtained using a TA Instruments DHR-2 Discovery Hybrid Rheometer with 25 mm parallel plates.

3.2.3 General procedure for the synthesis of 1-(2,6-dimethylphenyl)-3-(4-vinylphenyl) thiourea (thiourea2):

To a dry flask containing a stir bar under N$_2$, dry THF (24 mL) was added while stirring followed by the addition of 4-aminostyrene (4 mL, 34.1 mmol, 1.0 equiv.) and 2,6-dimethyl phenyl isothiocyanate (5.4 mL, 35.8 mmol, 1.05 equiv.). The reaction mixture was then heated to 50°C using an oil bath and allowed to stir overnight under N$_2$. The reaction mixture was then removed from heat and the solvent was fully removed via rotary evaporation. The crude solids were recrystallized in toluene (8 mL / g crude solid). The resulting product was an off-white powder and was then heated on a Schlenk line under a high vacuum at 60°C overnight to remove any remaining toluene (7.4 g, 77%). $^1$H NMR (500 MHz, DMSO) δ 9.89 (d, J = 35.2 Hz, 1H), 9.00 (s, 1H),
3.2.4 General procedure for the synthesis of N-(2,6-dimethylphenyl)-N-(4-vinylphenyl)methanediimine (monomer2):

To a dry flask containing a stir bar, thiourea2 (1.00 g, 3.54 mmol, 1.0 equiv.) and 2-chloro-1-methylpyridinium iodide (1.08 g, 4.25 mmol, 1.2 equiv.) were added. The headspace of the flask was then evacuated and backfilled with N₂, followed by the addition of dry DCM (10 mL). To the reaction mixture, dry triethylamine (1.48 mL, 10.6 mmol, 3.0 equiv.) was then added while stirring. The reaction mixture was then heated to 40°C and allowed to react for 3 hours. After 3 hours the reaction flask was removed from heat and the solvent was removed using rotary evaporation. The remaining residue was redissolved using a minimal amount of a 2:1 hexanes/DCM solution. The redissolved residue was purified via elution through a silica plug with the 2:1 hexanes/DCM solution resulting in a clear light-yellow oil (0.77 g, 93%). ¹H NMR (500 MHz, CDCl₃) δ 7.41 – 7.35 (m, 2H), 7.16 – 7.11 (m, 2H), 7.08 – 7.04 (m, 2H), 7.00 (dd, J = 8.5, 6.3 Hz, 1H), 6.69 (dd, J = 17.5, 10.9 Hz, 1H), 5.70 (dd, J = 17.6, 0.9 Hz, 1H), 5.23 (dd, J = 10.8, 0.9 Hz, 1H), 2.40 (s, 6H).
3.2.5 Synthesis procedure for the 1:10 copolymerization of monomer2 and styrene (poly2):

To a dry Schlenk flask, AIBN (367 mg, 2.24 mmol, 1.0 equiv.) was added and the headspace was then evacuated and backfilled with N₂. THF (5 mL) was then added followed by styrene (2.33 mL, 20.1 mmol, 9.0 equiv.) and monomer2 (0.50 mL, 2.01 mmol, 0.9 equiv.). The reaction mixture was then put through three freeze-pump-thaw cycles to degas the solution. The flask was then backfilled with N₂ following the final thaw then heated to 60 °C and stirred for 16 h. The reaction was then stopped by exposing the reaction mixture to air. The polymer was then isolated through a dropwise precipitation into a methanol + 1% deionized water (60 mL) solution. Vacuum filtration was used to recover the precipitated polymer. The polymer was then dried on a Schlenk line at 60 °C under vacuum resulting in a white powder (12 g, 65%). $M_n = 9,600$ Da and dispersity = 1.4.

3.2.6 Synthesis procedure for the 1:10 copolymerization of monomer2 and butyl methacrylate (poly3):

To a dry Schlenk flask, AIBN (367 mg, 2.24 mmol, 1.0 equiv.) was added and the headspace was then evacuated and backfilled with N₂. THF (8 mL) was then added followed by butyl methacrylate (3.20 mL, 20.1 mmol, 9.0 equiv.) and monomer2 (0.50 mL, 2.01 mmol, 0.9 equiv.). The reaction mixture was then put through three freeze-pump-thaw cycles to degas the solution. The flask was then backfilled with N₂ following the final thaw then heated to 60°C and stirred for 16 h. The reaction was then stopped by exposing the reaction mixture to air. The polymer was then isolated through a dropwise precipitation into a methanol + 1% deionized water (100 mL) solution. The
polymer was then isolated through decanting and had a gum-like consistency before drying. The polymer was then dried on a Schlenk line at 60 °C under vacuum resulting in a brittle off white solid (18 g, 81%). $M_n = 8,000$ Da and dispersity = 3.8.

3.2.7 General procedure for the piperazine-containing CAN of Poly2 (CAN1)

The mmol of CDI to mg of polymer used in this procedure was determined via the method outlined in section 2.3.3 of chapter 2.

In a dry beaker containing a stir bar, Poly2 (9.97 x $10^{-7}$ mmol CDI/mg poly, 96.0 mg, 0.957 mmol, 2.0 equiv. CDI functionality) was dissolved in minimal THF. After the polymer was fully dissolved, dioctyl phthalate (0.051 mL, 0.128 mmol, 5 wt.% relative to the combined weight of the polymer and amine) was added to the mixture. In a separate dry beaker containing a stir bar, anhydrous piperazine (42.3 mg, 0.491 mmol, 1.025 equiv. amine functionality) was dissolved in minimal THF. Both beakers were then heated to 50°C and the anhydrous piperazine solution was poured into the beaker containing the polymer. The mixture was allowed to stir for 30 s before being poured into a Petri dish heated to 50°C. The mixture in the petri dish was heated until it became solid then was allowed to dry in the fume hood overnight with a perforated tin foil covering. The solids were then removed from the Petri dish, dried in a vacuum oven at 100°C for 2 h, and ground into a fine powder using a mortar and pestle. They were then placed on a high vacuum system overnight at 60°C for the final drying step.
The procedure above was used unchanged with piperazine swapped with 2,5-dimethylpiperazine to produce a CAN crosslinked with 2,5-dimethylpiperazine (CAN2).

CANs produced using poly3 used the same procedure outlined above when both piperazine (CAN3) and 2,5-dimethylpiperazine (CAN4) were used to crosslink poly3.

3.3 Results and Discussion

3.3.1 Synthesis and polymerization of monomer2

To make the new monomer, the starting thiourea (thiourea2) was produced seen in Scheme 3.1.

Scheme 3.1 Synthesis of thiourea2.

To produce thiourea2 the nucleophilic addition of 4-aminostyrene to 2,6-dimethyl phenyl isothiocyanate was performed. Unlike in the synthesis of thiourea1, the produced thiourea was unable to be isolated through precipitation into hexanes. Instead, the solvent was removed from the reaction mixture and thiourea2 was recrystallized using toluene (8 mL / g of crude solid). The
structure of the thiourea in both cases was confirmed using $^1$H NMR spectroscopy (Appendix Figure A.24). The isolated thiourea was then used in the next step seen in Scheme 3.2 to generate the new sterically hindered CDI monomer (monomer2).

![Scheme 3.2 Synthesis of monomer2.](image)

As in the synthesis of monomer1, the thiourea intermediate thiourea2 was reacted with Mukiyama’s reagent and underwent dehydrosulfurization to produce monomer2. The monomer isolated by elution through silica was a clear light-yellow oil. This oil was confirmed to be the intended monomer free of impurities through $^1$H NMR and IR spectroscopy (Appendix Figures A.25 and A.26). Similar to monomer1, the IR spectrum is used to confirm the formation of the CDI functional group which can be seen by the peak at $\sim$2100 cm$^{-1}$ in the spectrum.

### 3.3.2 Copolymerization of styrene and monomer2

The copolymerization of styrene and monomer2 was accomplished via a free radical polymerization. Styrene and monomer2 were initiated using AIBN as a radical source to begin the polymerization. For this copolymerization styrene and monomer2 had a stoichiometric ratio of 10:1 (styrene:monomer2). Following the completion of the reaction, the polymer sample was
isolated via precipitation followed by vacuum filtration. The polymer sample was characterized using $^1$H NMR spectroscopy (Appendix figure A.27) along with GPC to determine the outcome of the polymerization. $^1$H NMR spectroscopy (Appendix figure A.28) was used to confirm the mmol of CDI repeat unit relative to 1 mg of polymer sample (see Section 2.3.3). The GPC chromatogram of the polymer sample was used to confirm that there was a single polymer distribution produced in the reaction along with the average molecular weight and dispersity of the polymer chains (Figure 3.3).

![Figure 3.3 GPC chromatogram of Poly(2).](image)

**3.3.3 The 10:1 Copolymerization of Butyl Methacrylate and Monomer2**

*Peaks > 10.8 mL retention volume are associated with solvent breakthrough*

The copolymerization of butyl methacrylate and the sterically hindered CDI monomer (monomer2) also used the free radical polymerization method to polymerize the two monomers.
Just like in the previously mentioned copolymerization of styrene and \textit{monomer2}, the monomers (butyl methacrylate and \textit{monomer2}) were reacted in a 10:1 stoichiometric ratio. The radical initiator used to polymerize the two monomers was also AIBN. Once the reaction was complete, the finished copolymer was isolated via precipitation. During the precipitation the precipitate compiled together into a single mass which had the consistency of chewed gum. Due to this, the polymer was easily isolated through decanting the solution and manually moving the polymer sample into vials with a spatula. The isolated polymer was then heated to 60°C on a high vacuum system overnight to fully remove the solvent. As before, the combination of GPC and \textsuperscript{1}H NMR spectroscopy was used to determine the outcome of the polymerization along with the properties and structure of the polymer. The GPC chromatogram indicated that a single molar mass distribution produced in the polymerization, as the refractive index trace appeared as a monomodal curve. The average molecular weight of the polymer along with the dispersity of the polymer chain lengths was also determined by the chromatogram (seen in Figure 3.4). \textsuperscript{1}H NMR spectroscopy was used to confirm the structure of the polymer along with the mmol of the CDI repeat unit relative to one milligram of polymer sample \textit{(Appendix figures A.29 and A.30, Section 2.3.3)}. 
Figure 3.4 GPC chromatogram of Poly(3)

*Peaks > 10.8 mL retention volume are associated with solvent breakthrough

3.3.4 Preparation of CANs made from Poly2

Piperazine and 2,5-dimethyl piperazine were used in the synthesis of CANs using Poly2 (Scheme 3.3). CAN1 and CAN2 were formed through the nucleophilic addition of the crosslinking diamines (piperazine for CAN1 and 2,5-dimethyl piperazine for CAN2) to CDI repeat units.
Scheme 3.3 Synthesis of CAN1 and CAN2.

These nucleophilic additions occurred between the repeat units of separate polymer chains at the CDI functional group. Through repeated nucleophilic additions of the diamines to many different polymer chains the polymer networks CAN1 and CAN2 were formed. The network formation was accomplished in a matter of seconds by combining a diamine dissolved in solvent with Poly2 plus a plasticizer dissolved in solvent into a petri dish. The plasticizer was added to the reaction to later help with chain movement when the CANs reversibly form crosslinks to allow for easier processing and data collection. The success of the formation of the CANs was confirmed by the complete disappearance of the CDI functional group as seen in IR spectra (Appendix figures A.31 and A.32). Any remaining solvent from the formation of the CANs was fully removed though the combined use of a vacuum oven and high vacuum set up before any further characterization was performed. Finally, the dried CANs (CAN1 and CAN2) were ground down into fine powders during the drying process in preparation of further processing.
**CAN1** and **CAN2** were then characterized by TGA to determine the 5% mass loss degradation temperature ($T_d$) of the polymer networks, which identifies the upper limit for melt pressing and subsequent characterization. The $T_d$ of the CAN samples was found to be 240 °C for **CAN1** and 230 °C for **CAN2** ([Appendix figures A.33 and A.34](#)). The CANs were then placed into molds to shape them into disks and bars. These molds were placed into a heated hydraulic press to form the shapes needed for characterization on a rheometer and DMA (disk and bar respectively). When the disk mold was used the samples **CAN1** and **CAN2** were first heated to 330 °F (165 °C) from room temperature (25 °C) in the mold using the press with no pressure applied from for a duration of 30 min. Directly following the first 30 min a pressure of 5000 psi was applied to the mold while maintaining the temperature at 330 °F for an additional 30 min. Once the final 30-min duration had passed, the mold was removed from the press and cooled using a continuous stream of air. The disk was then removed from the mold and set aside for characterization on a rheometer. The process of producing bars from **CAN1** and **CAN2** was similar, with the only difference being the applied pressure (1000 psi).

The bars produced from **CAN1** and **CAN2** were characterized using a temperature ramp procedure on a DMA with a tension clamp fixture. The procedure measures the storage and loss modulus of the material so that the glass transition ($T_g$) of the material can be determined. The $T_g$ of a material represents the temperature in which a polymer material transitions from stiff and glassy to soft and rubbery. From the storage and loss modulus curves, the tan $\delta$ curve was derived. The tan $\delta$ is the ratio of loss modulus to storage modulus and peaks at $T_g$. The DMA determines these values by applying a sinusoidal force to the material as the temperature is ramped. The $T_g$
of CAN1 crosslinked with piperazine was 136 °C and CAN2 crosslinked with 2,6-dimethyl piperazine was 139 °C (Appendix figures A.35 and A.36). These temperatures were considered when determining the parameters for the following rheological studies.

The previously formed disks of CAN1 and CAN2 were then used in a stress relaxation procedure using shear rheology between 25 mm plates on a rheometer. In this procedure, the sample is heated well above $T_g$ and a rotational shear force is applied by the top rotating plate and the bottom plate is fixed in place. The rheometer then measures how a material relaxes the strain applied, reporting the results in megapascals (MPa) over the duration of the experiment. For CAN1 and CAN2 the temperatures used were 160, 165, 175, 180, 185, and 190 °C with a 1-minute soak time before each data collection. For each temperature a 1% strain was applied during the 20-minute run during which a constant downward force of 5N was applied. From these parameters a step overlay of the stress relaxation curves was produced (Appendix figures A.37 and A.38). An exponential decay fitting function \( y = G \times e^{-\left(\frac{x}{t}\right)^B} \) was then applied to each stress relaxation curve to determine the relaxation time (\(t\)) of the materials at each temperature. An Arrhenius plot was then produced, using the calculated relaxation times and the temperatures they were acquired at, so that activation energies (Ea) could be calculated for the materials. (Appendix figures A.39 and A.40). This quantity relates to the energy required for the both the crosslinks to reversibly dissociate and the polymer chains to flow.

The Ea of CAN1 was calculated to be 96.7 +/- 2.56 kJ/mol and CAN2 had a calculated Ea of 161.0 +/- 1.59 kJ/mol. These values were counter to the hypothesized effect of steric hindrance.
when present at both the crosslink and CDI repeat unit. The $E_a$ required for flow increased when steric hindrance from the methyl groups of the CDI repeat unit and amine crosslink were both present. This finding was also present in the relaxation times of CAN1 and CAN2 at 175 °C. The relaxation times of these systems at 175 °C were 2702 s and 10203 s respectively. The longer relaxation time and higher activation energy of CAN2 when compared to CAN1 shows that having sterically hindering groups on the CDI repeat unit does not improve the dissociation of the reaction pairs.

3.3.5 Synthesis and characterization of CANs made from Poly3

The amines piperazine and 2,5-dimethyl piperazine were used to produce CAN3 and CAN4 respectively from Poly3. These CANs were produced to determine how changing the comonomer to one with a lower $T_g$ and greater polarity would affect the physical properties of the resulting CAN. CAN3 and CAN4 were produced in the same fashion as the CANs outlined in section 3.3.3 of this chapter. This was done to allow for a direct comparison of the two system sets. The successful formation of these CANs was confirmed by disappearance of the CDI stretching frequency at ~2100 cm$^{-1}$ using IR spectroscopy. The CANs were then fully dried of any remaining solvent and ground down into a powder for further characterization.

The $T_d$ of CAN3 and CAN4 was determined using a TGA and was found to be 248 °C and 242 °C respectively (Appendix figures A.41 and A.42). These temperatures were used to determine the possible temperature range for melt pressing these CANs. The $T_d$ of CAN3 and
**CAN4** have shown that there was no significant change in structural integrity when compared with the same CAN systems produced from **Poly2**. As previously discussed, the powdered CANs were then placed separately into the two mold types. The CANs were first pressed into the bar shape using the bar mold. This process consisted of first heating the mold in the melt press from room temperature (25 °C) to 315 °F with no pressure applied for 30 min. Once the 30 min had passed 1000 psi was applied to the mold and the temperature was maintained for an additional 20 min. Similar process was used to make the disk shape with both materials. To produce the disks the CANs were heated in the mold from room temperature to 330 °F with no pressure applied for 30 min. Following the first 30-minute interval a pressure of 5000 psi was applied to the mold for an additional 30 min while maintaining the heat applied at 330 °F.

The bars produced from **CAN3** and **CAN4** were characterized by DMA with the same parameters as **CAN1** and **CAN2**. This was done to determine if there was any change in the $T_g$ of the CANs through the introduction of butyl methacrylate into the polymer chains compared to when styrene was used. The $T_g$ of **CAN3** with piperazine as the crosslinking amine was 99 °C (Appendix figure A.43) which was significantly lower than the comparable CAN system **CAN1** (136 °C). **CAN4** which was crosslinked with 2,5-dimethyl piperazine had a $T_g$ of 103 °C (Appendix figure A.44) which also showed a lower $T_g$ than its comparable CAN system **CAN2** (139 °C). Similar to the previously mentioned CAN systems **CAN3** and **CAN4** showed no significant change in $T_g$ between the two different crosslink types as well. The difference in $T_g$ between the two different CAN system types shows that the introduction of a comonomer with a low homopolymer $T_g$ can in fact lower $T_g$ of the overall system.
The next point of comparison was the rheological data collected from **CAN3** and **CAN4** using the same stress relaxation procedure parameters as CANs 1 and 2. The stress relaxation curves of both **CAN3** and **CAN4** were collected at 160, 165, 175, 180, 185, and 190 °C. The curves were all fitted using a nonlinear exponential decay function like the one used for CANs 1 and 2 (**Appendix figures A.45 and A.46**). From this fitting function the relaxation times were plotted using the same Arrhenius plot format outlined in section 3.3.3 of this chapter. From these plots the $E_a$ of **CAN3** and **CAN4** were determined to be 124.0 +/- 4.13 kJ/mol and 246.0 +/- 75.1 kJ/mol respectively (**Appendix figures A.47 and A.48**). When comparing the two systems together with their analogous counterpart (**CAN1** to **CAN3** and **CAN2** to **CAN4**) there were greater $E_a$ values for the CANs that used butyl methacrylate as the comonomer. There is also an increase in relaxation times of the butyl methacrylate CANs in the 175 °C stress relaxation run. **CAN3** had a stress relaxation time of 3176 s which was much longer than **CAN1** (2702 s). The relaxation time of **CAN4** at this temperature point was also much longer with a duration of 181964 s when compared to **CAN2** (10203 s). The characterization data of the four CAN materials was tabulated in **Table 3.1**.

**Table 3.1 CAN characterization data tabulation.**

<table>
<thead>
<tr>
<th>CAN</th>
<th>$T_i$ (°C)</th>
<th>$T_f$ (°C)</th>
<th>$E_a$ (kJ/mol)</th>
<th>Relaxation time @ 175 °C (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CAN1</strong></td>
<td>240</td>
<td>136</td>
<td>96.7 +/- 2.56</td>
<td>2703</td>
</tr>
<tr>
<td><strong>CAN2</strong></td>
<td>230</td>
<td>139</td>
<td>161.0 +/- 1.59</td>
<td>10203</td>
</tr>
<tr>
<td><strong>CAN3</strong></td>
<td>248</td>
<td>99</td>
<td>124.0 +/- 4.13</td>
<td>3176</td>
</tr>
<tr>
<td><strong>CAN4</strong></td>
<td>242</td>
<td>103</td>
<td>246.0 +/- 75.1</td>
<td>181964*</td>
</tr>
</tbody>
</table>

*Fitting was not ideal*
Both the $E_a$ and relaxation times of CANs 3 and 4 when compared to CANs 1 and 2 show that the introduction of a lower $T_g$ and more polar comonomer increases the energy and time required for network flow. This was contrary to expectations; it was hypothesized that increasing the gap between the $T_g$ of the material and the temperature at which stress relaxations were performed would result in decreased relaxation times and $E_a$.

### 3.4 Conclusions

The effects of the sterically hindered monomer monomer2 and the comonomer butyl methacrylate on the physical properties of CANs were studied. The synthesis of monomer2 proved to be straightforward with only slight alterations to the original synthesis method being required. The intermediate thiourea2 was easily isolated with high yields following the optimization of the crystallization method used to isolate and purify it. Monomer2 was then produced through the dehydrosulfurization of thiourea2 and isolated. The synthesis of copolymers using monomer2 was then accomplished through free radical polymerization analogous to that used previously. The success of these copolymerizations was then confirmed though the monomodal distribution of chain lengths in the GPC chromatograms. Which showed dispersity values and molar masses consistent with expected values from free radical polymerizations.
The copolymers known as poly2 and poly3 which used styrene and butyl methacrylate respectively as the comonomer were then networked into CANs 1-4. The CANs were produced through the crosslinking poly2 and poly3 with both piperazine (produced CAN1 and CAN3) and 2,5-dimethylpiperazine (produced CAN2 and CAN4). These CANs were then characterized using IR spectroscopy, TGA, DMA, and rheology to determine the success of the network formation and to compare their physical properties. Between the different polymers and crosslinks, there was no appreciable difference in the T_d of the CAN systems. This showed that the steric hindrance of the crosslink and comonomer type had little to no effect on the thermal stability of the CANs. When comparing the crosslinking amine (piperazine and 2,5-dimethylpiperazine), there seems to be little to no effect on the T_g. However, a lower T_g was observed when butyl methacrylate was used as the comonomer in the copolymer. The stress relaxation results revealed a contradiction in the case of the CANs produced using poly2, deviating from expectations established by prior small molecule kinetics studies. These studies suggested that more sterically hindered guanidines dissociated faster than their unsterically hindered counterparts. However, not only was this not observed in the case of CAN1 and CAN2, but the opposite effect occurred.

The effects that a lower T_g comonomer has on the physical properties of CANs were explored through the comparison of CANs produced from poly2 and poly3. When CAN3 and CAN4 which contained butyl methacrylate as the commoner were compared to CAN1 and CAN2 some interesting results occurred. Although CANs produced from poly3 exhibited lower T_g than those produced from poly2, both CAN3 and CAN4 showed higher E_a and relaxation times compared to their poly2 CAN counterparts. Through changing the structure and composition of
the polymers used in the CAN formation a better understanding of how the structural motifs
effect the physical properties of these CANs was accomplished.
Appendix Figures

Note: not all signals in the green and orange highlighted regions of the $^1$H NMR spectrums are magnetically equivalent.

Figure A.1 $^1$H NMR of thiourea1
Figure A.2 $^1$H NMR of monomer1

Figure A.3 IR Spectrum of monomer1
Figure A.4 GPC chromatogram of homopolymer

*Peaks > 10.8 mL retention volume are associated with solvent breakthrough

Figure A.5 $^1$H NMR of homopolymer

$M_n = 29,000$ Da
Dispersity: 3.3
Figure A.6 TGA of homopolymer

![TGA graph]

$T_d = 208^\circ C$

Figure A.7 $^1$H NMR of 4-Methylbenzyl Amine Modified homopolymer

![NMR spectrum]
Figure A.8 $^1$H NMR of Poly(1)

Figure A.9 IR Spectrum of Poly(1)
Figure A.10 $^1$H NMR of Piperidine Modified Poly(1)

Figure A.11 $^1$H NMR of 4-Methylbenzyl Amine Modified Poly(1)
Figure A.12 $^2$H NMR of 2-Aminoethanol Modified Poly(1)

Figure A.13 $^3$H NMR of Allylamine Modified Poly(1)
Figure A.14 $^1$H NMR of Methyl 4-Piperidinecarboxylate Modified Poly(1)

Figure A.15 $^1$H NMR of 5-Norbornene-2-methylamine Modified Poly(1)
Figure A.16 $^1$H NMR of Dibenzylamine Modified Poly(1)

Figure A.17 IR of Propargyl amine Modified Poly(1)

No peak at 2100 cm$^{-1}$
Figure A.18 $^1$H NMR of 2-Methyl Piperidine Modified Poly(1)

Figure A.19 $^1$H NMR of L-Alanine Methyl Ester Hydrochloride Modified Poly(1)
Figure A.20 $^1$H NMR of The RAFT Polymerization of Poly(1)

Figure A.21 GPC of The 99:1 Monomer to CTA RAFT Polymerization of Poly(1)

*Peaks > 10.8 mL retention volume are associated with solvent breakthrough*
Figure A.22 GPC of The 198:1 Monomer to CTA RAFT Polymerization of Poly(1)
*Peaks > 10.8 mL retention volume are associated with solvent breakthrough

![Graph](image1)

$M_n = 5,600$ Da
Dispersity: 1.1

Figure A.23 GPC of The 297:1 Monomer to CTA RAFT Polymerization of Poly(1)
*Peaks > 10.8 mL retention volume are associated with solvent breakthrough

![Graph](image2)

$M_n = 14,000$ Da
Dispersity: 1.1
Figure A.24 $^1$H NMR of Thiourea2

Figure A.25 $^1$H NMR of Monomer2
Figure A.26 IR Spectrum of Monomer2

Figure A.27 $^1$H NMR of poly2
Figure A.28 $^1$H NMR of poly2 for CDI mmol/mg poly calculation

Figure A.29 $^1$H NMR of poly3
Figure A.30 $^1$H NMR of poly3 for CDI mmol/mg poly calculation

Figure A.31 IR spectrum of CAN1
Figure A.32 IR spectrum of CAN2

Figure A.33 TGA data of CAN1
Figure A.34 TGA data of CAN2

Figure A.35 Tan delta curve from DMA data of CAN1
Figure A.36 Tan delta curve from DMA data of CAN2

Figure A.37 Stress relaxation curves of CAN1
Figure A.38 Stress relaxation curves of CAN2

Figure A.39 Arrhenius plot of relaxation times relative to their temperatures of CAN1

\[ Y = 11634.6x - 18.083 \]

\[ E_a = 96.7 \pm 2.56 \text{ kJ/mol} \]
Figure A.40 Arrhenius plot of relaxation times relative to their temperatures of CAN1

\[ Y = 19449.3x - 34.197 \]

\[ E_a = 161.0 \pm 1.59 \text{ kJ/mol} \]

Figure A.41 TGA data of CAN3

\[ T_d = 248 \, ^\circ C \]

at 95 wt%
Figure A.42 TGA data of CAN4

$T_d = 242 \, ^\circ C$

at 95 wt%

Figure A.43 Tan delta curve from DMA data of CAN3

$T_g = 99 \, ^\circ C$
Figure A.44 Tan delta curve from DMA data of CAN4

Figure A.45 Stress relaxation curves of CAN3
Figure A.46 Stress relaxation curves of CAN4

Figure A.47 Arrhenius plot of relaxation times relative to their temperatures of CAN3

\[ Y = 14928.8x - 25.257 \]

\[ E_a = 124.0 \pm 4.13 \text{ kJ/mol} \]
Figure A.4.8 Arrhenius plot of relaxation times relative to their temperatures of CAN4

$Y = 29647.8x - 55.472$

$E_a = 246.0 \pm 75.1 \text{ kJ/mol}$
Citations


(30) Li, Y.; Hoskins, J. N.; Srerama, S. G.; Grayson, M. A.; Grayson, S. M. The Identification of Synthetic Homopolymer End Groups and Verification of Their Transformations Using


(32) An Alternative Synthesis of 2,6-Dimethoxy-1,4-Benzochinone. https://doi.org/10.3184/174751917X14894997017379.