Sustainable Cross-linked Polymers with Potential for Recyclability

A DISSERTATION
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF THE UNIVERSITY OF MINNESOTA
BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Marc A. Hillmyer, Advisor

August, 2017
Acknowledgements

There are many people which I need to acknowledge, but none more so than my advisor, Professor Marc Hillmyer. Throughout my graduate career, he always pushed me to new limits. He continuously supported me and often nominated me for awards which aided in my own growth as a research chemist. Even when I doubted my own abilities as a chemist, Marc never did, which was often a much needed boost. Without his guidance, I would not be where I am today.

I have had the opportunity to work with many other amazing scientists during graduate school. Dr. William Gramlich and Dr. Paula Delgado mentored me early in my career as a research scientist and their early guidance in the lab set the stage for my successes. I was also fortunate enough to mentor a graduate student, Guilhem De Hoe, as well as three undergraduates, Sonia Pollock, Truyen Le, and Isobel Jones. I believe I learned as much from them as they learned from me; perhaps I learned even more than they did.

I am also thankful to all the Professors who mentored me, whether through classes or other means, including, but not limited to, Professor Tim Lodge, Professor Ian Tonks, Professor William Dichtel, Professor Tom Hoye, and Professor Jane Wissinger.

A special acknowledgement also goes out to those involved in the Team Vitrimer Center for Sustainable Polymers collaboration, namely, David Fortman, Professor William Dichtel, and Professor Christopher Cramer. This collaboration was extremely beneficial to me, allowing me to learn how to not only perform research across disciplines, but to collaborate with researchers at a significant distance. I believe this experience will prove particularly valuable as I begin my career as an industrial chemist.

I had quite a few friends in the chemistry department, with whom I could always get an outside view from. In particular, (soon to be Dr.) Grant Frost and Dr. Andrew Urick, with whom I spoke on a weekly basis about anything and everything.

I would also like to thank the entirety of the Hillmyer group and the Center for Sustainable Polymers, especially those I collaborated with, including Dr. Debbie Schneiderman, Dr. David Guptil, Dr. Sebla Onbulak, and Dr. Yanzhao Wang. Frankly, there are too many people for me to thank them all directly, however, the helpful discussions I had with many of you were extremely beneficial. In some cases, it was as simple as helping me work up a reaction, in others, it was significantly more.

Last but not least, I would like to thank my fiancée, Courtney Olson. She did not help directly with my research, but I would not have remained nearly as sane as I am now without her. She is truly my better half; a caring and kind individual that made every day in graduate school a little bit easier, especially when I needed it the most.
Dedication

This thesis is dedicated to my parents, Neil Brutman and Megan Jobes. Without them, I would never have been born. Without their support, I would not have made it this far.
Abstract
Polymers are long chain molecules made up of repeat units called monomers linked end-to-end into giant molecules. A subset of these materials are cross-linked polymers, wherein the individual polymer chains are linked together into one continuous network. Unlike thermoplastics, cross-linked polymers are able to adopt a permanent shape and are stable under high temperature and solvent/chemically intensive conditions. Consequently, they are extremely useful for a multitude of applications, such as tires, insulation, adhesives, coatings, and various other products. Unfortunately, these favorable properties also prevent cross-linked polymers from being reprocessed to another shape or recycled through traditional means. Much research has been performed on producing cross-linked polymers that are capable of controllable reprocessing. However, most polymeric materials are derived from fossil fuel feedstocks and by virtue of their hydrocarbon backbones, are incapable of environmental degradation on reasonable timescales. Thus, there is still much to be developed in order to generate these materials sustainably. The overarching theme of my research was to produce cross-linked polymers that are both sustainable and recyclable.

The first section (Chapter 1) of this thesis is a Perspective on the future of sustainable, recyclable cross-linked polymers. This is followed by studies (Chapters 2-5) on potentially sustainable cross-linked polymers that are capable of dynamic cross-link exchange through urethane bond exchange. In the final section (Chapter 6), the production of chemically recyclable, sustainable cross-linked polyester elastomers is detailed.
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<td>five-membered cyclic carbonate</td>
</tr>
<tr>
<td>6CC</td>
<td>six-membered cyclic carbonate</td>
</tr>
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<td>ACPLA</td>
<td>aziridine cross-linked polylactide</td>
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<td>Activation energy</td>
<td>$E_a$</td>
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<td>B6CC</td>
<td>bis(six-membered cyclic carbonate)</td>
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<td>BDM</td>
<td>benzene dimethanol</td>
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<tr>
<td>BHT</td>
<td>butylated hydroxytoluene</td>
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<td>BPO</td>
<td>benzoyl peroxide</td>
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<td>bismuth(III) triflate</td>
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<td>calcium hydride</td>
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<td>CATSPLA</td>
<td>carboxylic acid terminated star-shaped polylactide</td>
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<td>FT-IR</td>
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<td>FurMal</td>
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<td>$G$</td>
<td>shear or stress relaxation modulus</td>
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<td>$G_0$</td>
<td>modulus at time = 0</td>
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<td>G2</td>
<td>Grubbs 2$^{nd}$ generation catalyst</td>
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<td>HTSPLA</td>
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<td>HTSPEO</td>
<td>hydroxyl-terminated star-shaped poly(ethylene oxide)</td>
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<td>IC</td>
<td>isocyanate</td>
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<td>MgSO$_4$</td>
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<td>$M_m$</td>
<td>mass-average molar mass</td>
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<tr>
<td>$M_n$</td>
<td>number-average molar mass</td>
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<td>$M_{n,\text{theo}}$</td>
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<td>tetrahydrofuran</td>
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<tr>
<td>TNPP</td>
<td>tris(nonylphenylphosphite)</td>
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<td>Abbreviation</td>
<td>Term</td>
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<td>--------------</td>
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<tr>
<td>TPE</td>
<td>thermoplastic elastomer</td>
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<td>TREN</td>
<td>tris(2-aminoethyl)amine</td>
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<tr>
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<td>$T_v$</td>
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<td>WLF</td>
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<tr>
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<td>density</td>
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<tr>
<td>$\sigma_{TS}$</td>
<td>tensile strength at break</td>
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<td>$\tau^*$</td>
<td>characteristic relaxation time</td>
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Chapter 1. Approaches to Sustainable and Continually Recyclable Cross-linked Polymers

Cross-linked polymers are ubiquitous in daily life, finding applications as tires, insulation, adhesives, automotive parts, and countless other products. The covalent cross-links in these materials render them more mechanically robust, chemically resistant, and thermally stable than their thermoplastic counterparts. Unfortunately, these covalent linkages also prevent recycling these materials into similar value goods. Furthermore, cross-linked polymers are typically produced from petroleum-based feedstocks and their hydrocarbon backbones render them non-degradable, making them unsustainable in the long-term. In recent years, much effort has focused on the development of recycling strategies for cross-linked polymeric materials. In the following Perspective, we discuss many of these recycling approaches, and highlight efforts to produce recyclable cross-linked polymers sustainably. We present our thoughts on future challenges that must be overcome enable widespread, viable, and more sustainable implementation of these materials.

Chapter 1.1 Introduction

Over the last century, plastics have become pervasive in most aspects of our lives, with applications ranging from consumer products to medical devices and industrial goods. The emergence of plastics is attributed to their high strength, low density, and remarkable affordability. However, most plastics used today, including polyethylene, polypropylene, poly(vinyl chloride), and polystyrene, are derived from non-renewable petroleum sources and persist in the environment long after their functional lifetimes. Though many plastics are recyclable, the current recycling systems are inefficient, and only 2% of plastic

* Preparing for submission as a perspective to ACS Sust. Chem. Eng., or similar journal.
packaging products are recycled into similar value products in the US (Figure 1.1). More alarmingly, approximately 40% of plastic packaging is landfilled and about 32% ends up dispersed in the environment, with current estimates suggesting that the weight of plastic in the ocean will surpass that of marine life by 2050. The best course of action for an immediate reduction in the environmental impact of plastic waste accumulation is to increase the amount of plastics recycled into similar value products as well as increasing the range of materials that are recyclable. However, this feat is not straightforward as traditional primary recycling techniques involve high-temperature melt-processing which often leads to deleterious chain-scission processes. Furthermore, the performance of recycled products are compromised if contaminants such as incompatible polymers, dyes, and plasticizers are present during reprocessing.

**Figure 1.1:** Flow of plastic packaging materials in 2013. Closed-loop recycling is the recycling of plastics into similar value products. If we extrapolate from plastic packaging to all polymeric materials, the problem intensifies as nearly all thermosets are not capable of closed-loop recycling. Ideally, the processes we discuss in this perspective will allow thermosets to be introduced into the closed-loop recycling process and those that do not, are capable of environmental degradation.

Even if a high rate of recycling can be achieved, current fossil fuel resources will become scarce in the long term. Although only about 8% of crude oil is required for annual
plastics production,\textsuperscript{4} we believe there is significant social and economic impetus to shift toward renewable feedstocks. Fossil fuel generation occurs over thousands to millions of years.\textsuperscript{5} Thus, the current rate of fossil fuel consumption is not sustainable and therefore, bio-based plastics have potential to ultimately dominate the market. Currently, however, only \textasciitilde{}1\% of plastics are produced from renewable resources. Polylactide (PLA) is the most common commercially available, bio-based plastic, as NatureWorks\textsuperscript{®} alone produced 140,000 tonnes of PLA in 2009.\textsuperscript{6} PLA offers improved sustainability because it is both industrially compostable and biocompatible; however, the need for industrial composting conditions (60 °C, high humidity) necessitates the requirement of specialized facilities. Various other plastics have been developed that can be environmentally degraded into benign products after disposal, and offer an alternative solution to modulating plastic waste.\textsuperscript{7,8,9,10,11,12} We believe that improving the sustainability of plastics will depend on both improving the efficiency of recycling processes and synthesizing novel plastics that degrade in the environment on reasonable timescales, while keeping in mind the ultimate benefits of bio-sourced starting materials.

Cross-linked polymers, often referred to as thermosets, are another ubiquitous class of materials comprising \textit{ca.} 15-20\% of polymers produced.\textsuperscript{13} Traditional recycling of cross-linked polymers via mechanical reprocessing is impractical due to the covalent bonds that connect the polymer chains into a network that does not flow at elevated temperature. Moreover, thermosets are insoluble and thus solution reprocessing techniques are also not viable. Although some of these materials are down-cycled into lower value products, nearly all thermosets are incinerated, landfilled, or otherwise unaccounted for, i.e. leakage (Figure 1). Still, the robust strength and chemical stability of thermosets renders them essential in
tires, engineering composites, foams, adhesives, and many other applications. Therefore, developing strategies to recycle these materials that do not compromise their performance represents a formidable challenge.

One of the earliest developed repair strategies for thermosets involves the incorporation of microcapsules containing healing agent that releases and cures upon fracture of the material.\textsuperscript{14} While this methodology is convenient in that many materials can be impregnated with microcapsules to enable healing, continual repair is impractical because the embedded monomers are consumed once the microcapsules rupture. Therefore, many efforts have been made to develop continually reprocessable cross-linked polymers by incorporating dynamic covalent bonds into polymer networks.\textsuperscript{3,15,16,17,18,19} Despite rapidly growing interest in reprocessable cross-linked polymers, relatively little effort has been made to combine other aspects of sustainability (\textit{i.e.} renewability and degradability) into the development of these polymers. In this Perspective, we will highlight promising approaches for continual recycling of cross-linked polymer materials via depolymerization strategies or dynamic exchange reactions. Furthermore, we hope to provide insight into the outstanding challenges these materials face towards replacing traditional non-recyclable thermosets and limiting the adverse environmental impacts of this important class of materials.

\textbf{Chapter 1.2 Depolymerization Strategies}

\textbf{Chapter 1.2.1 Thermal Depolymerization}

Pyrolysis is the process of breaking large molecules into smaller ones through high temperature treatment (typically $>600$ °C). The prototypical example is petroleum cracking, whereby larger hydrocarbons are cracked into small molecules that form the basis
of the petrochemical industry. Both thermoplastic and cross-linked polymers are capable of complete breakdown via pyrolysis,\textsuperscript{20,21,22} and various commodity plastics, including polyethylene,\textsuperscript{23} polypropylene,\textsuperscript{24} poly(methyl methacrylate),\textsuperscript{25} and polystyrene,\textsuperscript{26} undergo pyrolysis to yield a complex mixture of potentially valuable chemicals. The mixtures obtained from petroleum cracking are separated into highly desirable compounds and a similar process could be envisioned for recovery of high-value chemical feedstocks from complex mixtures of waste plastics. This method is of particular interest for cross-linked polymers, which typically have limited options for reprocessing. Unlike many of the chemistries we discuss below, pyrolysis is theoretically applicable to all polymers; however, the energy cost of high-temperature pyrolysis and complex separation techniques required for this approach are far from ideal. Therefore, the development of materials that selectively depolymerize to recover pure, reusable monomer feedstocks might be preferable to avoid expensive purifications and reduce excessive energy requirements.

Selective depolymerization to monomer at significantly lower temperatures than those required for pyrolysis (<200 °C) has been demonstrated for several polymers.\textsuperscript{27,28,29,30} These materials are generally lactone-based polyesters, but other polymers such as poly(phthalaldehyde),\textsuperscript{31} poly(tetramethylene oxide),\textsuperscript{32} poly(methyl methacrylate),\textsuperscript{25} certain polycarbonates,\textsuperscript{33} and poly(trimethylene urethane)\textsuperscript{34} have been shown to depolymerize directly to their respective monomers. In these materials, depolymerization is driven by the thermodynamic favorability for monomer above the ceiling temperature ($T_c$), the temperature at which the rate of polymerization and depolymerization are equal. Typical recovery processes yield high purity monomer, reducing the need for further purification. This strategy has been used to recycle cross-linked polymers; for example, cross-linked
poly(β-methyl-δ-valerolactone) was depolymerized to recover over 90% of the original monomer (Scheme 1.1).\textsuperscript{27,35} This strategy is applicable to any polymer with an appropriate $T_c$ and could become even more prevalent with the development of new monomer feedstocks capable of controlled thermal depolymerization to their monomers. We believe more research should be performed on the development of monomer feedstocks with optimized polymerization/depolymerization thermodynamics, as this could be a powerful chemical recycling strategy. We also stress that the scope of polymers with ceiling temperatures accessible for selective depolymerization extends beyond lactones, and developing strategies to incorporate other depolymerizable backbones into cross-linked resins could have major benefits for thermoset recycling.

**Scheme 1.1:** Poly(β-methyl-δ-valerolactone) backbone “unzipping” to monomer

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Chapter 1.2.2 Solvent-assisted Depolymerization

While almost all polymers can be subjected to pyrolysis, the compounds recovered cannot necessarily be used to manufacture similar value products. This is particularly true for polyurethanes\textsuperscript{36,37} and polyesters,\textsuperscript{38,39,40,41} which can be difficult to pyrolyze into useful small-molecules. Fortunately, the urethane and ester functional groups of these polymers are susceptible to reactions with nucleophiles such as water or methanol, allowing them to be depolymerized to compounds suitable for repolymerization. This strategy is amenable to any material in which the hydrolysable functional group is in the polymer backbone. The most common application of solvent-assisted depolymerization is the hydrolysis or alcoholysis of poly(ethylene terephthalate), a common commodity thermoplastic.\textsuperscript{38} Although polyurethane foams are traditionally considered non-recyclable, they can be
subjected to alcoholysis to obtain various urethanes or “blocked isocyanates” that can be used to produce materials of similar value.\textsuperscript{36} The development of efficient catalysts and optimization of engineering processes could make this strategy highly practical and the wide range of commodity plastics susceptible to solvolysis would allow for rapid implementation.

**Chapter 1.2.2.1 Hemiaminals/Hexahydrotriazines**

Developing thermoset materials that undergo solvolysis under milder conditions represents a promising route to improving the energy costs associated with solvent-assisted depolymerization. Hemiaminals and hexahydrotriazines are two functional groups recently reported to hydrolyze at ambient temperatures, while still displaying the excellent mechanical properties commonly observed in nitrogen-containing thermosets (Scheme 1.2).\textsuperscript{42} The condensation of three equivalents of primary amine with two equivalents of paraformaldehyde under mild conditions yields hemiaminal linkages, which display similar dissociation dynamics to the related acetal/hemiacetal linkages. Upon further heating, the hemiaminal groups condense to form hexahydrotriazines.\textsuperscript{43,44,45,46,47,48} These hexahydrotriazine moieties have been previously employed as cross-links in non-dynamic polymer systems,\textsuperscript{49,50} but Hedrick \textit{et al.} first demonstrated that these two sequential trifunctional moieties enable the synthesis of easily recyclable, high performance cross-linked polymers.\textsuperscript{42} These materials demonstrate superior mechanical performance to most thermosets as determined by tensile testing, but the hemiaminal and hexahydrotriazine linkages can be hydrolyzed in acidic conditions at room temperature to recover as much as 86\% of the amine monomer.
Building on this work, Li et al. synthesized a nanocomposite hemiaminal dynamic covalent network film with bacterial cellulose and reported materials that demonstrated improved mechanical strength without compromising their recyclability. Hemiaminal dynamic covalent organogels from amine-terminated, oligomeric poly(ethylene glycol) (PEG) were also synthesized by Hedrick et al., which heal in seconds at room temperature and are capable of complete reversion to monomer in water at room temperature (24 h). Hexahydrotriazine-based epoxy resins were reported using efficient epoxide-amine reactions to give fast curing, high-performance networks that degrade under mild conditions, illustrating that solvent-depolymerizable hexahydrotriazine networks can be applied to commercially-relevant materials.

Hemiaminal and hexahydrotriazine-linked networks couple facile synthesis and excellent mechanical properties with mild depolymerization to cleanly afford monomers. This facile degradation represents a sustainable approach to synthesis of high-performance polymer composites, as it allows for easy recycling of these typically intractable materials. However, the rapid degradation under acidic conditions must be taken into consideration for possible applications. Furthermore, solvent-free production would further improve the viability of these materials. Additionally, these materials could prove more useful if small scale repairs and/or direct reprocessing is demonstrated via this chemistry; this could potentially be achieved by selectively targeting fractures with aqueous media in a controlled fashion.
Chapter 1.2.3 Dissociative Depolymerization/Diels-Alder Cycloadducts

Moving beyond solvent-assisted and thermal depolymerization, another effective approach towards continually reprocessable cross-linked polymers is to control the reversible transformation between a cross-linked and uncross-linked state. Diels-Alder chemistry is the most prominently explored and promising example of this to date. Cross-linked polymer networks based on thermoreversible DA cycloadducts were first described in a U.S. patent from 1969. The patent describes polymers reversibly cross-linked by the cycloadduct formed between furan and maleimide (FurMal) moieties, which later became a common moiety used to produce reprocessable materials (Scheme 1.3). A comprehensive review published in 2013 on the use of FurMal linkages to produce reprocessable polymers indicates that this interest has persisted. Though not as widely studied as the FurMal system, the reversible dimerization of cyclopentadiene was introduced into reprocessable polymers in a 1974 US patent.

Scheme 1.3: Diels-Alder equilibrium of FurMal cycloadducts

The tunability and selectivity of reversible DA cycloadduct formation imparts many benefits in reprocessing cross-linked polymers. The kinetics and thermodynamics of the DA reaction can be tuned by choice of diene and dieneophile, as well as the steric bulk and regiochemistry of their substituents. The FurMal linkages are commonly studied because of their high rates of cycloadduct formation, and because their dissociation occurs within temperature ranges compatible with many polymer backbones. Still, the breadth of available diene/dienophiles and substitution patterns enables tuning of the
solubility of monomers, oxidative and hydrolytic stability of resins, and temperatures required for cross-linking/de-cross-linking, which is valuable for developing polymers for specific applications.

Furthermore, both the DA and RDA reactions are highly functional-group-tolerant, allowing DA adducts to serve as reversible cross-links for commodity polymers. FurMal linkages have been applied to reprocessable networks based on polyolefins, polyester, polyethers, polyurethanes, polyamides, polyoxazilines, polyketones, and polysiloxanes. DA linkages have also been incorporated into sustainable polymers, including poly(ε-caprolactone), poly(lactide), and hyaluronic acid, or into networks synthesized from biorenewable feedstocks including abietic acid, epoxidized soybean oil, and trehalose. Furan-based DA systems are partially renewable as furan derivatives can be obtained from hemicellulose, an abundant agricultural waste product. Maleimides can be produced renewably from succinic anhydride, though this is not the current industrial method for their production.

DA moieties can be incorporated into a variety of industrially relevant resins due to their functional group tolerance. While most reported DA-functionalized plastics and rubbers require specialized polymer synthesis and/or solvent casting methods to generate bulk materials, recent work from Magana et al. demonstrated that DA linkages can be incorporated into a commercially available polyethylene terpolymer via reactive extrusion with a FurMal cycloadduct-based monomer. More recent reports regarding poly(ε-caprolactone) networks show that extrusion and bulk mixing are feasible methods to obtain reprocessable DA networks. These are crucial developments towards the industrial viability of replacing conventional cross-linked materials with alternatives that
can be recycled using embedded DA linkages. The depolymerization of DA under relatively mild conditions without catalyst or solvent, in combination with the amenability to renewable substrates and polymers, indicate great potential in dynamic networks capable of reversible DA cycloadduct formation.

In some cases, the low temperatures at which RDA becomes relevant can compromise the cross-linked material at high temperatures and render them soluble as monomer dissolution shifts the equilibrium towards depolymerization. One promising proof of concept to overcome the thermal limitations was demonstrated by Fuhrmann, et al., who used a tetrafuryl-substituted diarylethene as the diene that allows for modulating the recyclability of the material via UV-Vis isomerization of the diarylethene moiety (Scheme 1.4). Additionally, many applications require cross-linked materials without requiring extreme temperature and solvent resistance (e.g., some adhesives and coatings). Thus, given the ease with which DA-based materials can be produced and reprocessed, we expect these materials will gain significant market value in the coming years.

**Scheme 1.4:** Modulating the recyclability of DA networks through light.
Chapter 1.3 Vitrimers and Related Materials

While thermal, solvent-assisted, and dissociative depolymerization strategies are amenable to the recycling of cross-linked networks, a more ideal processing strategy would avoid depolymerization and dissociative techniques in favor of direct reprocessing. A new approach allowing for direct recyclability was developed whereby dynamic bonds that undergo associative exchange-reactions are incorporated into polymer networks (Figure 1.2). These networks, termed vitrimers, show strong-glass forming behavior: when force is applied at reprocessing temperatures, vitrimers will relax stress over time in a manner that resembles silica-based glasses as opposed to typical thermoplastics, which have an abrupt drop in the viscosity just above their $T_g$. Some reactions discussed in this section may proceed through a dissociative transition state, but likely have a high association constant and therefore display vitrimer-like behavior (e.g., remain insoluble at high temperature). While vitrimer chemistry has been reviewed more extensively elsewhere,$^{75,76,77}$ we herein outline promising chemistries developed for vitrimer or vitrimer-like materials, and comment on their prospects for widespread, sustainable implementation.
Figure 1.2: Illustration of vitrimers, whereby a cross-linked polymer is broken and can be directly reprocessed into a similar value material. Transesterification is shown as an example of this type of reprocessing methodology.

Chapter 1.3.1 Transesterification

The most-commonly studied dynamic chemistry for producing vitrimers is the transesterification of esters in the presence of free alcohols, commonly catalyzed by Lewis acids or organocatalysts (Figure 1.2). In 2011, Montarnal et al. synthesized polyester-based epoxy networks containing a Zn(II) transesterification catalyst. These networks possess mechanical properties competitive with traditional epoxy resins but can be injection molded after curing and reprocessed to give materials with similar properties to the as-synthesized resins. The networks display gradual changes in viscosity related to the thermally-activated, associative exchange reactions. This unique capability allows for welding and processing of these polymers in a manner analogous to traditional silica glass, which has not been reported for dissociating networks. Capelot, et al. further showed that changing the catalyst structure and loading enabled control of the viscosity changes and reprocessing rates in these networks.
Due to the robustness of the transesterification reaction and the ease with which ester-based networks can be synthesized using common feedstocks, vitrimers based upon transesterification have been widely studied since their introduction. Commercially available epoxy/anhydride resins have enabled fundamental studies on the rheology of vitrimers with varying cross-link densities and glass transition temperatures,\textsuperscript{82,83} and this knowledge has been used to expand applications from rigid thermoset-like materials to cross-linked polyester elastomers.\textsuperscript{84} Further emerging applications that incorporate this chemistry include photocurable resins and coatings,\textsuperscript{85} carbon fiber-\textsuperscript{86} and silica-epoxy\textsuperscript{87} composites with enhanced mechanical properties, as well as shape memory materials\textsuperscript{88,89,90} that respond to various external stimuli.

Transesterification also represents an ideal chemistry for the large-scale implementation of sustainable materials with high-performance and recyclability. In fact, the first vitrimers reported were partially bio-based, comprising vegetable oil-based, oligomeric fatty acids as a primary component.\textsuperscript{79} Later, Williams \textit{et al.} reported fully bio-based polyester vitrimers via the reaction of epoxidized soybean oil and citric acid.\textsuperscript{91} These networks showed sufficient reprocessability using excess carboxylic acid groups to catalyze transesterification instead of transition metals. We believe these examples point the way toward fully sustainable polyester vitrimer systems. Most bio-derived/sustainable polymers are polyesters derived from sugar feedstocks,\textsuperscript{92} which provide a plethora of diverse monomers through which the properties of bio-based networks can be tuned for appropriate applications. Furthermore, significant research has focused on the development of fully sustainable epoxy networks,\textsuperscript{93} many of which could be made reprocessable by the incorporation of transesterification catalysts into the network.
In addition to improving the renewability of these networks, further investigation into the robustness of this exchange chemistry will enable widespread use of these networks. This includes exploring the ability to reprocess these materials multiple times and clear demonstrations of the reproducibility of reshaping and stress relaxation processes. There are also open questions about the long-term environmental stability of resins containing Lewis acid or organocatalysts. Thorough investigation into issues such as catalyst leaching, hydrolytic stability, and degradation mechanisms will help make these promising materials practical alternatives to traditional epoxy and polyester resins.

**Chapter 1.3.2 Sulfur Chemistries**

Dynamic sulfur-based chemistries are arguably the first reactions used in vitrimer-like reprocessable cross-linked networks and have the potential to significantly impact the recycling of many consumer products. The most common method of producing cross-linked elastomers is vulcanization of polyisoprene and polybutadiene—both of which can be renewably derived—with elemental sulfur, predominately used in the production of tires. While vulcanization is known to occur through a radical process, the average number of sulfur atoms in each link is difficult to elucidate. In 1946, Stern and Tobolsky showed that various vulcanized unsaturated polyolefin rubbers exhibit stress relaxation and creep at slightly elevated temperatures (≥ 60 °C), representing the first example of potential reprocessability in sulfur-containing networks. While it was suggested that a metathesis-type mechanism was responsible for relaxation, Tobolsky *et al.* later demonstrated that these vulcanized rubbers relaxed through homolytic S-S radical scission followed by rapid recombination (Scheme 1.5). This work was eventually confirmed by Nevajans *et al.*
through model compound studies, which also showed that the presence of a base enhances the rate of exchange and proceeds through thiolate anion mediated mechanism.\textsuperscript{96}

**Scheme 1.5: Radical disulfide exchange**

Disulfide linkages were first used to recycle cross-linked polymers in 1990\textsuperscript{97,98} when Tesoro \textit{et al.} recycled disulfide-containing epoxy resins by reducing the disulfide linkages into thiols and subsequently re-oxidizing the thiols to disulfides. Since this study, recycling of vulcanized rubbers using various chemistries has been investigated,\textsuperscript{99,100,101} with recent studies focusing on developing single step, catalyst-free disulfide exchange systems.\textsuperscript{102} In particular, use of aryl disulfides instead of alkyl disulfides significantly increases the rate of exchange, allowing for elastomers that heal at room temperature and high $T_g$ polymers that show excellent reprocessability.\textsuperscript{103,104} The library of sulfur-based monomers is quite large, enabling a high degree of tunability in the recycling conditions and mechanical properties of the materials. A recent study incorporated disulfide linkages into renewable epoxy resins, indicating that reprocessability of sulfur-based materials can be extended to bio-derived materials.\textsuperscript{105} Although most dynamic sulfur methodologies feature dissociative cross-links, one study demonstrated reprocessability through the reaction of thiols with disulfides.\textsuperscript{106} Unlike the aforementioned examples, these materials solely reprocess via associative cross-link exchange, which has several benefits over dissociative processes; however, thiols are prone to oxidation, which may limit the applications of these thiol-based reprocessable materials. Regardless, the environment would benefit greatly from recycling facilities for sulfur-based materials due to the sheer
volume of commercial sulfur cross-linked materials. We note that while bio-derived sulfur sources are rare, elemental sulfur is currently produced as an industrial-scale waste product in petroleum refining, and is therefore currently a valuable feedstock from a sustainability perspective.\textsuperscript{107}

Chapter 1.3.3 Olefin Metathesis

While unsaturated polyolefin rubbers are most commonly cross-linked via vulcanization, they are also commonly cross-linked through radical alkene polymerization.\textsuperscript{108,109} As these materials lack S-S bonds which allow for reprocessing of vulcanized rubbers, they are incapable of being reprocessed via the methods discussed above. However, these networks often contain residual alkene moieties that have potential for aiding in reprocessability via metal-catalyzed alkene metathesis.

In 2012, Lu et al. published two studies regarding alkene metathesis within radically cross-linked poly(butadiene) using Grubbs’ 2\textsuperscript{nd} generation ruthenium catalyst (G2) [Scheme 1.6].\textsuperscript{110,111} These materials rapidly relax stress and weld at room temperature. Furthermore, full recovery of tensile properties was observed after reprocessing materials that contained as little as 0.005 mol\% G2. In a recent study, Neal et al. addressed the less than ideal mechanical performance of these materials by incorporating amide groups into the network.\textsuperscript{112} These hydrogen bonding groups increased the toughness of these materials significantly. In our view, these promising systems would further benefit from 1) incorporation of the catalyst before cross-linking, or 2) a more efficient methodology to incorporate catalyst immediately before reprocessing, followed by subsequent recovery, 3) increasing the functional lifetime of the catalyst by preventing degradation,\textsuperscript{113} 4) using a latent metathesis catalyst\textsuperscript{114,115,116} such that the reaction can be (de)activated by external
stimuli, resulting in a more robust material, and 5) development of this technology for polyisoprene, which is capable of cross-metathesis, as well as for other renewable polymers.

**Scheme 1.6:** Cross alkene metathesis

![Scheme 1.6: Cross alkene metathesis](image)

**Chapter 1.3.4 Alkoxyamines**

Alkoxyamines have garnered interest for their ability to undergo reversible homolytic bond cleavage at mild temperatures (ca. 100 °C) to yield stable, nitroxyl/aminoxyl and carbon-centered radicals (Scheme 1.7). This reversible bonding has been used to develop nitroxide-mediated radical polymerizations, whereby the growth of radically-propagating polymers is modulated through an equilibrium activation-deactivation. Several cross-linked systems use these stable nitroxyl radicals to achieve reprocessability. In the earliest applications to repairable cross-linked polymers, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) moieties were incorporated via multiple synthetic steps as cross-linkers for polystyrene, poly(methyl methacrylate), or polyurethane resins. In all cases, these polymers display dynamic behavior at elevated temperatures and can be reprocessed to recover ca. 75% of tensile properties. In a more recent implementation, Jin et al. used commercially available TEMPO-substituted methacrylate to cross-link styrene-butadiene rubber in a one-step controlled curing process; these rubbers show near-quantitative reprocessing efficiencies over multiple compression molding cycles.
From our perspective, this approach has significant potential because it can be applied directly to any network based on controlled radical polymerization, and can be amended to traditional polymers based on (meth)acrylic, styrenic, and other olefinic monomers. This strategy should also be compatible with renewable feedstocks, especially as the syntheses of traditional petrochemical feedstocks from renewable resources are made more efficient. While networks reported to-date do not have mechanical properties comparable to traditional materials (perhaps due to cross-linking by the relatively weak alkoxyamine bond) and tend to show limitations in reprocessing efficiency (low recovery in mechanical properties after reprocessing) at higher cross-link densities, the toughening of these materials through additives and further developments in the chemistry of controlled radicals will likely overcome these present challenges.

Chapter 1.3.5 Imine and Vinylogous Urethane Exchange

Imines, or Schiff bases, are a classic example of a dynamic bond (Scheme 1.8A) and are commonly used to develop dynamic covalent molecular systems. The dynamic nature of the imine bond under relatively mild conditions (exchange can occur at ambient temperatures) and ability to control dynamics by stimuli such as heat, water content, and pH make these linkages intriguing for the synthesis of vitrimer-like systems. Taynton et al. demonstrated the synthesis of polyimine networks via the direct condensation of polyfunctional amines and aldehydes. These networks demonstrate very fast stress relaxation (which can be tuned by the presence of water) compared to most vitrimers and
maintain high reprocessing efficiencies. Additional studies demonstrated the reprocessing of polyimine-carbon fiber composites,\textsuperscript{126} the mechanical tuning of polyimine networks via aldehyde and amine selection,\textsuperscript{127} and their ultimate degradation under appropriate conditions.\textsuperscript{128} Further investigation should focus on understanding the long-term hydrolytic stability of these networks in environmental conditions.

**Scheme 1.8:** A) Imine exchange and B) Vinolygous urethane exchange.

Another promising chemistry exploiting the nucleophilicity of amines is the reversible conjugate addition of amines to vinolygous urethanes. Denissen, *et al.* synthesized vinolygous urethane vitrimers via the condensation of polyfunctional amines (an excess of amine functionality is required) and acetoacylesters (Scheme 1.8B).\textsuperscript{129} These vitrimers demonstrate exceptionally fast relaxation rates without external catalyst and near-quantitative reprocessing over five reprocessing cycles. Recently, Denissen *et al.* demonstrated various additives capable of catalyzing or inhibiting this exchange reaction, enabling tuning of the exchange reaction rate for desired applications.\textsuperscript{130} The practicality of water removal, as well as the long-term stability of the free-amines in these systems to oxidation, carbon dioxide exposure, and other environmental degradation-inducing conditions are opportunities for further study in these efficient systems. Imine or
vinylogous urethane materials could be quite promising as sustainable cross-linked materials, especially if the indefinite recyclability is practical under typical service conditions.

Chapter 1.3.6 Urea/Urethane Exchange

Polyurethanes (PUs) are a class of commodity polymers produced via the polyaddition of isocyanates and alcohols to produce foams, elastomers, sealants, coatings, and adhesives.\textsuperscript{131,132} Ranked sixth in terms of global production, PUs are among the most common polymers used in cross-linked polymer architectures; therefore, PUs are a prime target for cross-linked polymer recycling. While solvent-assisted depolymerization approaches have been developed for the chemical recycling of oligomers and small molecules, these approaches have many limitations (see above).\textsuperscript{36,37} Much work has focused on incorporating dynamic bonds into PU networks; however, we will focus on directly exploiting the dynamics of the urethane (or urea analogue) bond to enable reprocessing.

One promising approach takes advantage of the fact that the reaction of an alcohol and isocyanate is an equilibrium process, such that urethane linkages will dissociate at elevated temperatures into their constituent alcohol and isocyanate (Scheme 1.9). While this equilibrium has long been known as a source of stress relaxation in cross-linked PU materials,\textsuperscript{133,134} it has only recently been demonstrated that this property enables reprocessing and reshaping of cross-linked PUs. Zheng \textit{et al.} reported that PU elastomers containing dibutyltin dilaurate show rapid, Arrhenius-type stress relaxation behavior and plasticity at elevated temperatures.\textsuperscript{135} This behavior occurs even in the absence of free alcohol, suggesting the tin-catalyzed dissociation of urethanes as the dominant relaxation
mechanism. Further investigation on the dynamics and reprocessing of urethane cross-linked PLA and PEG has shown that, in the presence of tin(II), polyurethane dissociation occurs more appreciably than transesterification.\textsuperscript{136,137} Although this methodology proceeds through a dissociative mechanism, these PUs show vitrimer-like behavior, likely due to the high association constant between isocyanates and alcohols. For instance, the aforementioned cross-linked PUs are found to be insoluble at elevated temperatures which is more of typical of vitrimers than of dissociative networks. These findings demonstrate that any traditional cross-linked PU should show vitrimer-like in the presence of appropriate catalyst. Therefore, PUs synthesized from sustainable polycarbonate-\textsuperscript{138} and polyester-\textsuperscript{28,139,140} based polyols and bio-derived isocyanates can be explored for their direct recyclability. Further investigation should also focus on the development of non-toxic metal or organocatalysts for reprocessing.\textsuperscript{141} While many of these systems have been shown to relax stress and demonstrate plasticity, reprocessability has not been thoroughly investigated in most of these systems, and remains an area requiring further investigation.

**Scheme 1.9:** Urethane exchange

![Urethane exchange](image)

Another approach to enable dynamics at milder temperatures in urethane resins is the incorporation of more readily dissociative urethane analogues into PU networks, reminiscent of the blocked isocyanates commonly used for one-component curing of urethane adhesives and coatings.\textsuperscript{142} In a successful demonstration of this strategy, amino-alcohols containing sterically-hindered amines were reacted with isocyanates to generate
hindered urea bonds (Scheme 1.10). Bulkier amine substitution yielded faster dynamics, such that when a t-butyl-substituted amine is used, these hindered urea bonds undergo exchange at room temperature. Since this initial study, hindered ureas have been incorporated into elastomers that self-heal and rigid thermosets that show reproducible reprocessability at temperatures above the $T_g$. These networks can be synthesized by directly incorporating substituted amino-alcohols into traditional PU formulations, meaning that this strategy can be directly coupled with renewably-sourced polyols and isocyanates to develop more sustainable versions of these reprocessable materials. Currently, none of the aforementioned methodologies have been applied to the recycling of PU foams, which make up a large percentage of cross-linked PUs. We believe that demonstrating facile foam recyclability would be the next stage towards commercialization of this PU recycling process.

Scheme 1.10: Hindered urea exchange

Due to the harmful nature of isocyanates, regulatory bodies in both the United States and Europe are moving to reduce or remove the use of isocyanates in PU synthesis; therefore, developing alternate chemistries to synthesize cross-linked PU resins is imperative. We have studied the reprocessability of cross-linked PUs synthesized from bis(cyclic carbonates) and amines to produce polyhydroxyurethanes (PHUs). These networks display Arrhenius-type stress relaxation via the associative reaction of an
alcohol with a urethane, also known as transcarbamoylation, likely owing to the thermally stable \(N\)-alkyl-\(O\)-alkyl urethanes and stoichiometric equivalence of hydroxyl moieties. Excellent mechanical properties coupled with promising reprocessability make these materials an exciting strategy for producing isocyanate-free, reprocessable PUs. Although promising, PHUs have significantly slower curing times than isocyanate-based PUs and are not currently suitable for producing foams. Furthermore, 6-membered cyclic carbonates are preferred monomers because the resulting \(\gamma\)-hydroxyurethane linkage has improved stability compared to \(\beta\)-hydroxyurethanes\(^{148}\) and thus, the efficient synthesis of 6-membered cyclic carbonates should be targeted. Developments in 6-membered cyclic carbonate synthesis from feedstocks such as \(\text{CO}_2\)^{149} and urea,\(^{150}\) as well as the development of renewable amines, will profoundly impact the sustainability of these materials. Furthermore, efforts towards catalyzing the cross-linking reaction as well as transcarbamoylation should enable faster and more efficient (re)processing in these materials.

**Chapter 1.3.7 Siloxane Exchange**

Siloxane polymers, most notably polydimethylsiloxane (PDMS), have been explored since the 1940s.\(^{151}\) While linear PDMS is a liquid at room temperature, cross-linked PDMS is an elastomer typically used for non-structural applications such as coatings, though composites with silica fillers have more robust mechanical properties.\(^{152}\) The Si-O bond is stable to water, air, and radical coupling conditions, but can undergo exchange with nucleophiles, such as silonates (Scheme 1.11). As a result, siloxane exchange reactions are prominent in applications that require fast and efficient reactions, such as microencapsulated healing agents.\(^{153,154,155}\) Both acid and base-catalyzed siloxane
exchange was rigorously studied in the mid-1900s,\(^{151,156,157,158}\) and the reaction is thought to occur through an associative \(S_N2\)-like transition state. These studies demonstrated stress relaxation of cross-linked PDMS elastomers, suggesting their potential to serve as vitrimer-like materials.

**Scheme 1.11:** Siloxane-silonate exchange

\[
\begin{array}{c}
\text{Si-O-Si} \\
\Theta \\
\text{O-Si}
\end{array}
\quad \leftrightarrow 
\begin{array}{c}
\text{Si-O-Si} \\
\Theta \\
\text{O-Si}
\end{array}
\]

In 2012 Zheng *et al.* “rediscovered” this work and described reprocessable, cross-linked PDMS elastomers.\(^{159}\) Cross-linked networks synthesized via the catalytic ring-opening polymerization of octamethylcyclotetrasiloxane give clear, colorless elastomers that heal completely at 90 °C in 24 h via exchange of tetramethylammonium silonates with Si-O bonds. The authors showcased several reshaping experiments of the networks, and found this chemistry afforded quantitative recycling. Schmolke *et al.*\(^{160}\) expanded upon initial studies by probing the effects of both catalyst concentration and cross-linking density on the dynamics of the network. By increasing catalyst loading to 3.25 mol \%, networks are capable of rapid stress relaxation at temperatures as low as 5 °C. However, increased catalyst loading also decreased the mechanical integrity of the polymers, which was attributed to a reduction in viscosity due to increased reaction rates.

These dynamic siloxane systems are extremely promising because they demonstrate the fastest stress relaxation of any dynamic covalently cross-linked networks while maintaining quantitative reprocessing efficiencies. Furthermore, polysiloxanes are well known to be relatively non-toxic, having the same environmental impact as sand and
glass. To expand applications of these materials, the fast and selective silonate exchange must be coupled with more robust polymer backbones to prevent flow and depolymerization at service temperatures. We believe that incorporation of silyl ether bonds into hydroxyl-containing networks will combine the benefits of the robust exchange with enhanced mechanical properties, enabling wider application of this exchange chemistry.

Chapter 1.3.8 Boronic Ester Exchange

Boronic acid derivatives such as cyclic boronic and boronate esters have been implemented as dynamic covalent linkages in polymer networks. These two functional groups evolve from the reaction between a boronic acid and a 1,2- or 1,3-diol to form a cyclic boronic ester in anhydrous conditions or a cyclic boronate ester in basic aqueous media. To date, most reports incorporating dynamic bonds with anionic boronates focus on water-mediated self-healing of low-toxicity hydrogels for biomedical applications, but several vitrimer-like cross-linked systems with boronic esters have been reported.

In 2015, Cash et al. described networks synthesized via thiol-ene reactions between a tetrafunctional thiol and a difunctional vinyl monomer containing a boronic ester. These networks heal in the presence water at room temperature in 3 days. The use of water for successful healing implies that the primary mechanism for reprocessing is dissociative (i.e., hydrolysis and re-esterification) rather than associative. Although water aids the healing of these materials, it does not readily degrade them, likely due to the hydrophobic character of the network. A similar boronic-ester-based polysiloxane was later reported by Zuo et al., demonstrating compatibility with other polymer backbones.
Later, Cromwell et al. described the synthesis of reprocessable polyolefin networks containing 1,2-diol moieties and difunctional boronic ester cross-linkers. In tertiary amine-containing networks, healing occurs in the absence of water or alcohol; however, poor healing was observed in the absence of tertiary amines, suggesting an amine-catalyzed boronic ester metathesis mechanism. Recently, Rottger et al. demonstrated that boronic ester cross-links could be installed in commodity plastics such as polystyrene, high-density polyethylene (HDPE), and poly(methyl methacrylate) via functionalized monomers or post-polymerization modification. The authors demonstrated that model boronic esters undergo thermally-activated metathesis, allowing for the synthesis of materials with greater thermal and oxidative stability (Scheme 1.12). These vitrimers relax stress, can be reprocessed by heating (≥ 130 °C), and do not require water or catalyst to induce healing. The authors used industrially relevant techniques such as extrusion and injection molding to (re)process these materials. This promising application of boronic ester metathesis to conventional polymers demonstrates huge potential for modification of industrially ubiquitous thermoplastics into reprocessable, high performance vitrimers.

**Scheme 1.12: Boronic ester metathesis**

While boron-based polymers are not generally considered renewable, their hydrolysis product is non-toxic boric acid, which is a benefit from a sustainability standpoint. We believe there is an opportunity for future studies on boron-based
networks involving the optimization of their susceptibility to hydrolysis, allowing for tunable degradation of these materials in the environment after their functional lifetimes.

**Chapter 1.4 Summary**

We have highlighted many promising approaches towards addressing the lack of reprocessability and recyclability in traditional thermoset polymers. The methodologies vary from pyrolysis to the introduction of dynamic functional groups for traditional melt processing. We stress that the chemistries highlighted above are an incomplete list of strategies applied to this problem. All of the highlighted approaches have advantages and disadvantages in terms of reprocessing efficiencies, methods, cost, thermal stability, etc.; consequently, a combination of many of these chemistries will be developed to optimize materials for specific applications.

With that in mind, we believe that a continued understanding of the fundamental chemistry and physics governing these materials will be required to enable commercial implementation. For example, fundamental understanding of equilibrium thermodynamics will allow precise temperature control of depolymerization to monomers. Developments in dynamic covalent chemistry will enable a material’s design to be tailored towards exemplary reprocessability. Beyond this, further study of the behavior of these materials outside controlled laboratory conditions remains a hurdle towards the implementation of these systems. Since these polymers are inherently reactive/dynamic, factors such as long-term exposure to moisture, oxygen, and sunlight will ultimately determine their large-scale use.
More developments are required to improve the sustainability of reprocessable polymers reported to date. A common goal in the field of sustainable polymers is to create materials that are useful for precise amounts of time, before degrading rapidly to benign compounds. Therefore, developing materials that display both enhanced functional lifetimes and controlled degradation could have significant added value over current systems. Furthermore, developing extremely robust materials with recycling efficiencies comparable to thermoplastics could have large impacts in decreasing the amount of plastic waste generated, another crucial aspect to mitigating present socioeconomic issues related to polymer recycling.

Finally, we stress that many of these chemistries can and should be applied to sustainable polymer feedstocks, such as polylactide, saccharides, and cellulose derivatives, allowing plastics to begin decoupling from petroleum feedstocks. These same sustainable polymers are often capable of biodegradation to non-toxic small-molecules, which will further prevent significant environmental damage from the disposal of plastics. Although current recycling of polymers is inefficient at best, we believe that the strong research push to develop these continuously recyclable, high-performance polymers can only benefit our environment as we move forward, especially if researchers aim to make these materials truly sustainable in all facets of their life cycle.

Chapter 1.5 References


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Chapter 2. Polylactide Vitrimers

While much research has been aimed at new approaches to the healing of cross-linked polymers, there is a dearth of effort in the healing of renewable cross-linked polymers. In this study, the healing ability of renewable polylactide-based vitrimers containing stannous octoate \([\text{Sn(Oct)}_2]\) was investigated. The vitrimers were prepared from hydroxyl-terminated star-shaped poly((\pm)-lactide) samples that were cross-linked with methylenediphenyl diisocyanate. Cross-linked samples were prepared with isocyanate:hydroxyl (IC:OH) ratios of 0.6:1 to 1.1:1, and initial catalyst:hydroxyl (Sn(Oct)_2:OH) ratios ranging from 0.013:1 to 0.050:1. The plateau modulus and \(T_g\) values for the cross-linked samples decreased with decreasing IC:OH ratio. The materials were subjected to stress relaxation analyses, which confirmed that the materials were not only vitrimeric in nature, but exhibited remarkably short characteristic relaxation times of less than 50 s at 140 °C. Finally, vitrimers fractured in uniaxial tensile testing were healed by compression molding and exhibited up to 67% recovery of ultimate elongation, up to 102% recovery of tensile strength, and up to 133% recovery of tensile modulus values.

Chapter 2.1 Introduction

Cross-linked thermosets are a class of polymers that result from a typically irreversible bonding process, and are materials that can no longer flow or dissolve, rendering them practical for both high temperature and solvent intensive applications. Unfortunately, thermosets cannot be reprocessed by traditional means such as melt processing. Numerous methods involving thermally reversible physical cross-links, such

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as Diels-Alder cycloadducts, have been utilized to create reprocessable cross-linked polymers.\textsuperscript{1,2,3,4,5} However, these reactions do not conserve the number of cross-links in the network structure (i.e., the cross-link density is reduced in such non-degenerative bond cleaving processes) and thus the materials exhibit a loss in structural integrity upon heating.

Vitrimer, a new class of healing materials pioneered by Leibler and coworkers, are cross-linked polymers whose flow dynamics are reliant on the transient nature of their network structure.\textsuperscript{6,7,8} The intrinsic properties of vitrimers were originally demonstrated using polyester epoxy resins that incorporated a Zn(II) transesterification catalyst. Extraordinarily, interchain transesterification occurs upon heating and when stress is applied to the material, the bonds rearrange such that the stress is completely dissipated. Because transesterification is an isodesmic reaction, the materials do not exhibit a loss in structural integrity, even at elevated temperatures in solvents. The flow behavior of vitrimers relies on the rate of a chemical reaction in the melt state, and the viscosity ($\eta$) of vitrimers follows an Arrhenius relationship with temperature dependences similar to silica-based glasses, rather than the more typical Williams-Landel-Ferry (WLF) behavior.\textsuperscript{6,8} A freezing transition temperature, $T_v$, in vitrimers is defined as the temperature above which a reversible network topology can be achieved through bond exchange. In more quantitative terms, $T_v$ is the temperature at which $\eta = 10^{12}$ Pa·s, the traditionally defined solid to liquid transition viscosity.\textsuperscript{6,8,9,10,11} Since their discovery, vitrimers have been shown to be useful in a variety of practical applications, including adhesives and liquid-crystalline elastomers,\textsuperscript{12,13} and hold tremendous promise for a range of advanced material technologies. Vitrimers have also been produced utilizing olefin metathesis, and those materials exhibited healing properties at room temperature.\textsuperscript{14,15}
Recently, Altuna et al. developed a renewable vitrimer based on epoxidized soybean oil and citric acid. These vitrimeric materials were effective without the use of an extrinsic catalyst based on using low carboxylic acid:epoxide ratios, thus achieving a high concentration of hydroxyl (OH) moieties within the cross-linked system. These β-hydroxyester networks exhibited almost complete recovery in the mechanical properties after healing fractured samples at 150 °C. In these systems, the authors could achieve characteristic relaxation times ($\tau^*$) as small as 5.5 h at 150 °C. In comparison, Leibler et al. achieved a $\tau^*$ of approximately 1 h at 150 °C in the Zn(II) catalyzed transesterification reaction of the polyester epoxy resins, showing that the use of a catalyst, even at low concentrations, can significantly shorten the healing times.

Poly(lactide) (PLA), arguably the most studied bioderived thermoplastic, has a high tensile modulus and strength, making it a promising replacement for petroleum-based polymers such as poly(styrene) and poly(ethylene terephthalate). A variety of strategies have been adopted to broaden the range of PLA applicability. In particular, cross-linking has been used to create evenly degrading scaffolding for tissue regeneration applications and materials with significantly higher thermal stability as well as improved tensile and impact strengths.

Chapter 2.2 Results and Discussion

Chapter 2.2.1 Cross-linked Polymer Synthesis

Given the importance of PLA as a commercially viable sustainable thermoplastic, we sought to develop PLA vitrimers to achieve a system that is both easily processed (e.g., as in two-part thermosets) and reprocessed or healed post use or damage. Here we use a cross-linking reaction between hydroxyl-terminated 4-arm star-shaped poly((±)-lactide)
HTSPLA and methylenediphenyl diisocyanate (MDI), with stannous(II) octoate [Sn(Oct)$_2$] as both the cross-linking and transesterification catalyst. We reasoned that the concentration of ester groups in the resulting material would be much higher (one ester group per three backbone atoms) than the vitrimers previously developed and thus the materials should exhibit even faster relaxation rates, and consequently, faster healing characteristics. As the hydroxyl functionality will be consumed in the cross-linking reaction, and some remaining hydroxyl groups are necessary for the thermal and stress activated transesterification healing process, a range of isocyanate:hydroxyl (IC:OH) ratios were evaluated. Furthermore, Sn(Oct)$_2$ was selected as the catalyst due to its high catalytic activity in transesterification reactions, high stability in most media, low toxicity (FDA approved) and commercial relevance (Scheme 2.1). Two sets of urethane cross-linked poly((±)-lactide) (UCPLA) materials were produced; in set A, the IC:OH ratio was varied from 0.6:1 to 1.1:1 while maintaining a constant initial Sn(Oct)$_2$:OH loading of 0.025:1. In set B, the initial Sn(Oct)$_2$:OH loading was varied from 0.013:1 to 0.05:1 while maintaining a constant 0.75:1 IC:OH ratio (set B also included a control sample with no Sn(Oct)$_2$). The gel fractions (≥ 0.94) of all samples were determined by room temperature swelling tests (Table 2.1).

**Scheme 2.1 Synthesis of HTSPLA and UCPLA**
Chapter 2.2.2 Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis (DMTA) experiments were performed on set A. Figure 2.1 demonstrates a drop in modulus of more than two orders of magnitude while heating through the glass transition temperature ($T_g$). The subsequent appearance of a relatively constant plateau modulus (80–120 °C) was consistent with having a network structure. As the amount of MDI was increased from 0.6 to 1.1 IC:OH, the plateau modulus (at 100 °C), cross-linking density ($\nu_e$) and the $T_g$ of the materials increased from 1.1 to 4.5 MPa, 1.2 to 4.8 x 10$^{-4}$ mol cm$^{-3}$ and 55 to 65 °C, respectively (Figure 2.1, Table 2.1). Conversely, the molar mass between cross-links ($M_x$) decreased with increasing cross-link density, all indicative of a more constrained network as the result of an increase in the equivalents of MDI utilized. DSC analysis showed a similar trend in $T_g$ values (Table 2.1).

![Figure 2.1: A) Storage and B) loss modulus of UCPLA materials while varying IC:OH ratio. The amount of Sn(Oct)$_2$ was kept at a constant 0.025 to hydroxyls in HTSPLA. Data acquired from uniaxial tension deformation (30 to 120 °C at 5 °C min$^{-1}$, $\omega$=6.28 rad s$^{-1}$ and $\gamma$=0.05%) with a rectangular sample geometry.](image-url)
Table 2.1: Thermal and thermomechanical characterization of UCPLA materials with respect to IC:OH and Sn(Oct)$_2$ to initial OH ratios.

<table>
<thead>
<tr>
<th>Sample</th>
<th>IC:OH ratio</th>
<th>Sn(Oct)$_2$ to initial OH ratio</th>
<th>Gel %$^a$</th>
<th>$T_g$ DMTA (°C)$^b$</th>
<th>$T_g$ DSC (°C)</th>
<th>$E'$ (MPa) at 100 °C</th>
<th>$\nu_e$ ($10^{-4}$ mol cm$^{-3}$)$^c$</th>
<th>$M_x$ (kg mol$^{-1}$)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCPLA-0.60-0.025</td>
<td>0.60:1</td>
<td>0.025</td>
<td>94</td>
<td>55</td>
<td>50.</td>
<td>1.1</td>
<td>1.2</td>
<td>10.</td>
</tr>
<tr>
<td>UCPLA-0.70-0.025</td>
<td>0.70:1</td>
<td>0.025</td>
<td>96</td>
<td>57</td>
<td>51</td>
<td>1.6</td>
<td>1.7</td>
<td>7.3</td>
</tr>
<tr>
<td>UCPLA-0.80-0.025</td>
<td>0.80:1</td>
<td>0.025</td>
<td>97</td>
<td>60</td>
<td>55</td>
<td>2.3</td>
<td>2.5</td>
<td>5.1</td>
</tr>
<tr>
<td>UCPLA-0.90-0.025</td>
<td>0.90:1</td>
<td>0.025</td>
<td>98</td>
<td>62</td>
<td>57</td>
<td>3.3</td>
<td>3.6</td>
<td>3.5</td>
</tr>
<tr>
<td>UCPLA-1.00-0.025</td>
<td>1.0:1</td>
<td>0.025</td>
<td>98</td>
<td>64</td>
<td>57</td>
<td>3.7</td>
<td>4.0</td>
<td>3.1</td>
</tr>
<tr>
<td>UCPLA-1.10-0.025</td>
<td>1.1:1</td>
<td>0.025</td>
<td>97</td>
<td>65</td>
<td>57</td>
<td>4.5</td>
<td>4.8</td>
<td>2.6</td>
</tr>
<tr>
<td>UCPLA-0.75-0.013</td>
<td>0.75:1</td>
<td>0.013</td>
<td>99</td>
<td>59</td>
<td>56</td>
<td>1.1</td>
<td>1.2</td>
<td>11</td>
</tr>
<tr>
<td>UCPLA-0.75-0.025</td>
<td>0.75:1</td>
<td>0.025</td>
<td>99</td>
<td>58</td>
<td>52</td>
<td>1.3</td>
<td>1.4</td>
<td>9.0</td>
</tr>
<tr>
<td>UCPLA-0.75-0.050</td>
<td>0.75:1</td>
<td>0.050</td>
<td>99</td>
<td>58</td>
<td>56</td>
<td>1.3</td>
<td>1.4</td>
<td>9.0</td>
</tr>
</tbody>
</table>

$^a$Performed via solvent extraction after 48 h in methylene chloride.  
$^b$Determined by the peak temperature of the loss modulus after uniaxial tension deformation (30 to 120 °C at 5 °C min$^{-1}$, $\omega$=6.28 rad s$^{-1}$ and $\gamma$=0.05%) with a rectangular sample geometry; $^c$calculated using equation 2.1 at 100 °C and based on density of 1.25 g cm$^{-3}$.

The samples comprising set B with varying catalyst concentrations were also subjected to DMTA. This analysis indicated that there was a negligible difference in the plateau modulus (1.1 to 1.3 MPa) with respect to the amount of Sn(Oct)$_2$ (Figure 2.2, Table 2.1). Similarly, the calculated values of $\nu_e$ (1.2 to 1.4 x $10^{-4}$ mol cm$^{-3}$) and $M_x$ (9.0 to 11 kg mol$^{-1}$) did not change significantly with catalyst loading.
Figure 2.2: A) Storage and B) loss modulus of UCPLA materials while varying catalyst loading. The IC:OH ratio was kept at a constant 0.75:1. Data acquired from uniaxial tension deformation (30 to 120 °C at 5 °C min⁻¹, ω=6.28 rad s⁻¹ and γ=0.05%) with a rectangular sample geometry.

Chapter 2.2.3 Stress Relaxation Analysis

Stress relaxation analyses (SRA) were then performed on all of the materials in the linear viscoelastic regime until the samples had relaxed to 1/e of the initial stress relaxation modulus (i.e., after one mean lifetime, τ*) [Figure 2.3]. The control sample with negligible amount of Sn(Oct)₂ relaxed only about 3% of its initial relaxation modulus over 5000 s (the black curve in Figure 2.3B). Indeed, it has been shown previously that while thermally-activated transesterification in polyesters can occur, it does so at a much slower rate. The materials containing catalyst relaxed significantly faster, despite their high degree of cross-linking, giving evidence to their vitrimeric nature. Reduction in IC:OH ratios resulted in shorter relaxation times, likely due to an increase in number of unreacted hydroxyl groups (Figure 2.3A). Furthermore, materials with lower IC:OH ratios have lower plateau moduli allowing for the reactive dangling chain ends to move more freely in the material. Indeed, Altuna et al. attributed faster relaxation of their materials to this phenomenon.
Figure 2.3: Stress relaxation analysis with respect to A) varying IC:OH ratio (set A) at 120 °C, B) varying initial mol ratio of Sn(Oct)$_2$:OH (set B) at 120 °C and C) temperature with 0.75:1 IC:OH and initial 0.025:1 Sn(Oct)$_2$:OH ratios. The dashed line indicates 37% of the $G_0$. Data normalized and acquired at 9.3% strain.

At IC:OH ratios of 0.9:1 and above, the rate of stress relaxation no longer began to decrease but remained essentially constant. We suggest that at a perfect 1:1 IC:OH ratio, there would be little to no stress relaxation observed due to full consumption of hydroxyl groups. However, stress relaxation was observed in these materials and could be attributed to an incomplete conversion of the isocyanates in MDI. These remaining isocyanates would rapidly react with any moisture, releasing CO$_2$ and forming amines. The resulting amines can also react with esters forming amides and releasing hydroxyls capable of further transesterification.

Increasing the catalyst loading also accelerated the relaxation rate with a decrease in $\tau^*$ from 410 s to only 154 s at 120 °C (Figure 2.3C). An increase in the temperature also showed a direct correlation with the stress relaxation rate in agreement with Leibler and coworkers.$^{6,8}$ For example, $\tau^*$ for a sample with a 0.75:1 IC:OH ratio and an initial mol ratio of 0.025:1 Sn(Oct)$_2$:OH decreased from 4100 s at 100 °C to 33 s at 140 °C. In fact, at 140 °C, all nine of the materials containing catalyst exhibited $\tau^*$ values below 50 s. These results are significant when compared to previous work,$^{6,8}$ where the polyester epoxy resins containing 5 mol% Zn(II) to initial OH exhibited $\tau^* \approx 26$ s at 280 °C, while the UCPLA material with an initial mol ratio of 0.050:1 Sn(II):OH (approximately 5 mol% Sn(II) to
initial OH) achieved an average $\tau^* = 22 \pm 2$ s at a temperature 140 °C lower. We attribute this phenomenon to the high concentration of ester moieties in PLA-based materials and the high activity of Sn(II) catalysts, leading to an increase in the rate of transesterification. Despite having extremely fast relaxation rates at 140 °C, the materials still remain insoluble in hot 1,2,4-trichlorobenzene (Figure 2.4).

Figure 2.4: High temperature swell test with UCPLA-0.025-0.75 for 48 h at 140 °C in 1,2,4-trichlorobenzene.

To determine $T_v$ for UCPLA samples, the Maxwell equation (equation 2.3) was used to relate $\tau^*$ to $T_v$. The plateau modulus for each of these materials (see Figures 2.1 and 2.2) and $\eta = 10^{12}$ Pa·s at the solid to liquid transition temperature ($T_v$ for vitrimers) were inserted into equation 2.3 to yield a $\tau_v$ for each material (Table 2.2). The experimental $\tau^*$ values were then plotted vs. 1000/T and fit to the Arrhenius relationship (equation 2.2) in Figure 2.5. The curves in Figure 2.4 were then extrapolated to $\tau_v$, which gave $T_v$ for the UCPLA materials (Table 2.1). Remarkably, all of the systems had a $T_v$ within a few degrees of their $T_g$ values indicating that as soon as the materials reach the rubbery state, they are capable of transesterification and thus, flow. Furthermore, as the IC:OH ratio was decreased and the catalyst loading was increased, $T_v$ decreased in agreement with the literature.
Figure 2.5: Arrhenius analysis of \( \tau^* \) versus 1000/T with respect to A) IC:OH ratio and B) Sn(Oct)\(_2\) to initial OH ratio. Samples UCPLA-1.0 and UCPLA-1.1 not shown as their lines overlap with UCPLA-0.9.

An average activation energy, \( E_a \), of 156 ± 6 kJ mol\(^{-1}\) was extracted from the Arrhenius relationship (equation 2.2). The literature value of \( E_a \) for transesterification catalyzed by Sn(Oct)\(_2\) in the polylactide melt was reported as approximately 83 kJ mol\(^{-1}\),\(^{24}\) half of what was determined by stress relaxation. The inconsistency between these two values could be attributed to the presence of tris(nonylphenyl)phosphite (TNPP), which was added to thwart oxidative degradation, as it is an effective inhibitor of some transesterification catalysts.\(^{28,29,30,31,32}\) However, the same \( E_a \) was obtained for a sample similar to UCPLA-0.025-0.75 with no TNPP (Figure 2.5). Further investigation on the discrepancy in \( E_a \) is detailed in Chapter 3.
Table 2.2: Data extracted from SRA Arrhenius curves.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_v$ ($10^6$ s)$^a$</th>
<th>$E_a$ (kJ mol$^{-1}$)$^a$</th>
<th>$T_v$ (°C)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCPLA-0.60-0.025</td>
<td>2.7</td>
<td>146 ± 5</td>
<td>50</td>
</tr>
<tr>
<td>UCPLA-0.70-0.025</td>
<td>1.9</td>
<td>145 ± 8</td>
<td>54</td>
</tr>
<tr>
<td>UCPLA-0.80-0.025</td>
<td>1.3</td>
<td>147 ± 10</td>
<td>58</td>
</tr>
<tr>
<td>UCPLA-0.90-0.025</td>
<td>9.1</td>
<td>151 ± 11</td>
<td>63</td>
</tr>
<tr>
<td>UCPLA-1.00-0.025</td>
<td>8.1</td>
<td>159 ± 9</td>
<td>66</td>
</tr>
<tr>
<td>UCPLA-1.10-0.025</td>
<td>6.7</td>
<td>170 ± 6</td>
<td>70</td>
</tr>
<tr>
<td>UCPLA-0.75-0.013</td>
<td>2.7</td>
<td>156 ± 2</td>
<td>60</td>
</tr>
<tr>
<td>UCPLA-0.75-0.025</td>
<td>2.3</td>
<td>157 ± 4</td>
<td>58</td>
</tr>
<tr>
<td>UCPLA-0.75-0.050</td>
<td>2.3</td>
<td>176 ± 3</td>
<td>61</td>
</tr>
</tbody>
</table>

$^a$Calculated using equation 2.3. $^b$Calculated by extrapolating equation 2.2 to $\tau_v$.

Chapter 2.2.4 Tensile Testing and Reprocessing

All materials were subjected to uniaxial tensile testing and exhibited similar mechanical properties to the previously reported and related tolylene diisocyanate cross-linked polylactide samples ($\sigma_{TS} = 55$ MPa, $\varepsilon_b = 5\%$ and $E = 1.7$ GPa, Figure 2.6 and Table 2.3). The broken tensile bars were then reprocessed via compression molding at 140 °C and 4 MPa for 30 min [or approximately 35 to $85\tau^*$] (Figure 2.6). Remarkably, all of the samples with catalyst showed healing capability under these conditions (Figures 2.6 and 2.7). In stark contrast, the control sample showed a clear interface where it had been broken, and upon removal from the mold, broke into two separate pieces. Uniaxial tensile testing revealed a trend similar to that of SRA; samples containing lower IC:OH ratios and higher catalyst loadings showed a greater recovery of tensile properties (Figure 2.6 and Table 2.4). In particular, samples containing a 0.75:1 IC:OH ratio or lower and an initial mol ratio of 0.025:1 Sn(Oct)$_2$:OH or higher showed remarkable healing characteristics.
Figure 2.6: Uniaxial tensile testing of fresh UCPLA materials (solid lines) and after healing (dashed lines) with respect to A) varying the IC:OH ratio (set A) and B) varying the initial mol ratio of Sn(Oct)₂:OH (set B).

Table 2.3: Tensile testing of UCPLA materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon_b$ (%)</th>
<th>$\sigma_{TS}$ (MPa)</th>
<th>$E$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCPLA-0.60-0.025</td>
<td>5.5 ± 1</td>
<td>50 ± 4</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>UCPLA-0.70-0.025</td>
<td>4.8 ± 0.5</td>
<td>59 ± 1</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>UCPLA-0.80-0.025</td>
<td>5.1 ± 2</td>
<td>60 ± 4</td>
<td>1.8 ± 0.2</td>
</tr>
<tr>
<td>UCPLA-0.90-0.025</td>
<td>5.1 ± 0.8</td>
<td>60 ± 2</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>UCPLA-1.00-0.025</td>
<td>5.0 ± 0.4</td>
<td>56 ± 3</td>
<td>1.8 ± 0.2</td>
</tr>
<tr>
<td>UCPLA-1.10-0.025</td>
<td>5.5 ± 1</td>
<td>52 ± 2</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>UCPLA-0.75-0.013</td>
<td>4.5 ± 0.7</td>
<td>54 ± 2</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>UCPLA-0.75-0.025</td>
<td>4.5 ± 1</td>
<td>51 ± 4</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>UCPLA-0.75-0.050</td>
<td>5.4 ± 1</td>
<td>49 ± 4</td>
<td>1.5 ± 0.1</td>
</tr>
</tbody>
</table>

Tensile testing of the materials was performed after aging the samples at 25 °C in a desiccator for 48 hours.

Figure 2.7: UCPLA materials before (top) and after (bottom) healing via compression molding.
Table 2.4: Uniaxial tensile testing of UCPLA materials after healing

<table>
<thead>
<tr>
<th>Sample</th>
<th>ε_b (%)</th>
<th>Recovery (%)</th>
<th>σ_TS (MPa)</th>
<th>Recovery (%)</th>
<th>E (GPa)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCPLA-0.6-0.025</td>
<td>3.2 ± 0.9</td>
<td>58 ± 19</td>
<td>46 ± 6</td>
<td>92 ± 14</td>
<td>1.8 ± 0.2</td>
<td>120 ± 21</td>
</tr>
<tr>
<td>UCPLA-0.7-0.025</td>
<td>2.4 ± 0.4</td>
<td>50 ± 10</td>
<td>51 ± 8</td>
<td>86 ± 14</td>
<td>2.2 ± 0.2</td>
<td>122 ± 13</td>
</tr>
<tr>
<td>UCPLA-0.8-0.025</td>
<td>2.1 ± 0.8</td>
<td>41 ± 20</td>
<td>42 ± 17</td>
<td>70 ± 29</td>
<td>2.2 ± 0.1</td>
<td>122 ± 15</td>
</tr>
<tr>
<td>UCPLA-0.9-0.025</td>
<td>2.6 ± 0.5</td>
<td>51 ± 13</td>
<td>50. ± 8</td>
<td>83 ± 14</td>
<td>2.1 ± 0.2</td>
<td>124 ± 14</td>
</tr>
<tr>
<td>UCPLA-1.0-0.025</td>
<td>1.9 ± 0.9</td>
<td>38 ± 18</td>
<td>35 ± 15</td>
<td>63 ± 27</td>
<td>1.9 ± 0.1</td>
<td>106 ± 13</td>
</tr>
<tr>
<td>UCPLA-1.1-0.025</td>
<td>1.4 ± 0.5</td>
<td>25 ± 10</td>
<td>27 ± 9</td>
<td>52 ± 17</td>
<td>1.9 ± 0.1</td>
<td>106 ± 8</td>
</tr>
<tr>
<td>UCPLA-0.75-0.013</td>
<td>1.5 ± 0.5</td>
<td>33 ± 12</td>
<td>24 ± 7</td>
<td>44 ± 13</td>
<td>1.7 ± 0.1</td>
<td>106 ± 9</td>
</tr>
<tr>
<td>UCPLA-0.75-0.025</td>
<td>3.0 ± 0.7</td>
<td>67 ± 24</td>
<td>44 ± 7</td>
<td>86 ± 15</td>
<td>1.8 ± 0.2</td>
<td>113 ± 14</td>
</tr>
<tr>
<td>UCPLA-0.75-0.050</td>
<td>3.3 ± 0.8</td>
<td>61 ± 21</td>
<td>50. ± 6</td>
<td>102 ± 15</td>
<td>2.0 ± 0.5</td>
<td>133 ± 34</td>
</tr>
</tbody>
</table>

Tensile testing of the materials was performed after reprocessing at 140 °C for 30 min and then aging the samples at 25 °C in a desiccator for 48 hours.

Chapter 2.3 Conclusion

These PLA-based vitrimers were capable of relaxing stress at significantly higher rates than any other polyester-based vitrimer systems at moderate temperatures. DMTA evidenced that at temperatures well above the $T_g$ and $T_v$, under low stress and strain, the materials will also maintain their structural integrity. Furthermore, we demonstrated that by tuning the hydroxyl functionality and catalyst loading, an array of material properties can be achieved. Additionally, the $T_v$ of all the materials was within a few degrees of the $T_g$ and many of the materials were capable of a full recovery in their tensile strength.

Chapter 2.4 Experimental
Chapter 2.4.1 Materials

All chemicals were purchased from Sigma-Aldrich and were used as received unless otherwise specified. All solvents were purchased from Fisher scientific and purified by distillation over CaH$_2$ three times. Sn(Oct)$_2$ was purified via vacuum distillation (130-150 °C, 30 mTorr). Altasorb kindly provided (±)-lactide, which was also used as received. All chemicals were stored under N$_2$ unless otherwise specified.

Chapter 2.4.2 Synthetic Procedures

Synthesis of HTSPLA

Sn(Oct)$_2$ (0.005 eq., 0.028 g, 0.7 mmol) was dissolved in a minimal amount of toluene (ca. 0.5 mL) and charged in a pressure vessel, along with (±)-lactide (25 eq., 50 g, 350 mmol) and pentaerythritol (1 eq., 1.9 g, 14 mmol) (Scheme 2.1). The reaction mixture was heated to 160 °C for 3 h, then allowed to cool to room temperature and dissolved in an approximately equal volume of dichloromethane (DCM). The subsequent solution was precipitated in ethanol (ca. 10 times volume of product solution), redissolved in an approximately equal volume of DCM and reprecipitated in hexanes (10 times volume of DCM solution). The resulting polymer was then dissolved in DCM, transferred to a polypropylene container and dried with N$_2$ flow for approximately 24 h. The polypropylene container was then put in a vacuum oven at approximately 60 °C and 20 mTorr for 72 h, and subsequently cooled to room temperature. The resulting polymer was obtained in an 80% isolated yield. $^1$H NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 5.2 [bm, -COCH(CH$_3$)O-], 4.35 [m, -COCH(CH$_3$)OH end group], 4.16 [bs, C(CH$_2$)$_4$- PERYT], 1.56 [bm, -COCH(CH$_3$)O-], $M_n = 4000$ g mol$^{-1}$. LS-SEC (THF): $(dn/dc) = 0.049$ mL g$^{-1}$, $M_m = 5000$ g mol$^{-1}$, $D = 1.20$. DSC: $T_g = 35$ °C.
Chapter 2.4.3 Synthesis of UCPLA

HTSPLA (1 eq.), MDI (1 to 2.2 eq.), and TNPP (0.35 % by weight) were dissolved in an approximately equal volume of DCM. A stock solution of Sn(Oct)$_2$ in DCM was prepared (200 mg catalyst per mL solvent), at which point an aliquot of the catalyst solution, varying from 0.0050 to 0.10 initial mol ratio of Sn(Oct)$_2$:OH, was added to the HTSPLA and MDI solution. After complete mixing (ca. 30 s), the resulting solution was poured into a polypropylene mold (64 mm (D) x 74 mm (H)). The molds were covered with aluminum foil and left unperturbed for approximately 48 h. Tensile bars were then cut from the resulting films and placed under reduced pressure at approximately 80 °C and 20 mTorr for 48 h to ensure all solvent was removed and the curing reaction went to completion. A typical tensile bar was ca. 0.5 mm (T) × 3 mm (W) × 25 mm (L) and had a gauge length of 14 mm. Samples were named according to their isocyanate:hydroxyl (IC:OH) ratio and catalyst loading, e.g., a sample with 0.75:1 IC:OH ratio and a 0.025 initial mol ratio of Sn(Oct)$_2$:OH was named UCPLA-0.75-0.025.

Chapter 2.4.3 Characterization Methods

$^1$H-NMR spectroscopy

$^1$H-NMR spectroscopy was performed on a Varian Inova 500 MHz spectrometer (Santa Clara, CA). Solutions were prepared in CDCl$_3$ (Cambridge Isotope Laboratories). All spectra were acquired at 20 °C with 64 scans. Chemical shifts are reported in ppm with respect to the residual chloroform signal (7.26 ppm).

Uniaxial Tensile Testing

Uniaxial tensile testing was conducted using dog bone shaped tensile bars (ca. 0.5 mm (T) × 3 mm (W) × 25 mm (L) and a gauge length of 14 mm). The samples were aged
for 48 hours at 25 °C in a desiccator prior to testing. Tensile measurements were performed on a Shimadzu Autograph AGS-X Series tensile tester (Columbia, MD) at 25 °C with a uniaxial extension rate of 5 mm min\(^{-1}\). Young’s modulus (\(E\)) values were calculated using the Trapezium software by taking the slope of the stress-strain curve from 0 to 1% strain. Reported values are the average and standard deviations of at least five samples.

**Dynamic Mechanical Thermal Analysis**

DMTA and stress relaxation analysis (SRA) were performed on a TA Instruments RSA-G2 analyzer (New Castle, DE) using dog bone shape films (ca. 0.5 mm (T) × 3 mm (W) × 25 mm (L) and a gauge length of 14 mm). DMTA experiments were conducted in tension film mode, where the axial force was first adjusted to 0 N with a sensitivity of 0.05 N. The strain adjust was then set to 30%, with a minimum strain of 0.05%, a maximum strain of 5% and a maximum force of 1 N in order to prevent the sample from going out of the specified strain range. A temperature ramp was then performed from 30 °C to 120 °C at a rate of 5 °C min\(^{-1}\), with an oscillating strain of 0.05% and an angular frequency of 6.28 rad s\(^{-1}\). The \(T_g\) was calculated from the maximum value of the loss modulus. The crosslinking density (\(v_e\)) and the molar mass between crosslinks (\(M_x\)) were calculated using the storage modulus (\(E'\)) at 100 °C and equation 2.1.

\[
E'(T) = 3G'(T) = 3RTv_e = \frac{3\rho RT}{M_x}
\]  
(2.1)

Where \(E'\) and \(G'\) are the storage and shear modulus respectively, \(R\) is the universal gas constant, \(T\) refers to the absolute temperature in the rubbery region (ca. 373 K) and \(\rho\) is the density of the poly((±)-lactide (ca. 1.25 g cm\(^{-3}\)).

**Stress Relaxation Analysis**
SRA experiments were performed under strain control at specified temperature (100-140 °C). The samples were allowed to equilibrate at this temperature for approximately 15 minutes, after which the axial force was then adjusted to 0 N with a sensitivity of 0.05 N. Each sample was subjected to an instantaneous 9.3% strain. The stress decay was monitored, while maintaining a constant strain (9.3%), until the stress relaxation modulus had relaxed to at least 37% (1/e) of its initial value. This was performed three times for each sample.

The characteristic relaxation time ($\tau^*$) was defined as the time required for the stress relaxation modulus to reach 37% (1/e) of its initial value and determined via SRA at varying temperatures from 100 to 140 °C. These points were then plotted versus 1000/T and fit to the Arrhenius relationship in equation 2.2.

$$\tau^*(T) = \tau_0 e^{E_a/RT}$$  \hspace{1cm} (2.2)

Where $\tau_0$ is the characteristic relaxation time at infinite $T$, $E_a$ is the activation energy of the transesterification reaction (kJ mol$^{-1}$), $R$ is the universal gas constant and $T$ is the temperature at the SRA was performed (373-413 K).

$T_v$ is defined as the point at which a vitrimer exhibits a viscosity of $10^{12}$ Pa s, also known as the liquid to solid transition viscosity ($\eta$). Using Maxwell’s relation (equation 2.3) and $E'$ determined from DMTA, $\tau^*$ was determined to be ca. $1.4 \times 10^6$ s at $T_v$ (i.e., for these samples the relaxation time for a sample with modulus $E'$ at the defined liquid to solid transition viscosity of $10^{12}$ Pa s is estimated as $1.4 \times 10^6$ s for all temperatures since $E'$ is relatively invariant in the rubbery state). The Arrhenius relationship from equation 2.2 was then extrapolated to $\tau^*$ = $1.4 \times 10^6$ to determine $T_v$ for each sample.

$$\eta = \frac{1}{3} E' \ast \tau^*$$  \hspace{1cm} (2.3)
**Differential Scanning Calorimetry**

Differential scanning calorimetry (DSC) was conducted on a TA Instruments Discovery DSC (New Castle, DE). The instrument was calibrated using an indium standard. All samples were prepared using T-Zero hermetic pans (ca. 5 mg) under a N₂ purge of 50 mL min⁻¹. The thermal history of the samples was first erased by heating to 150 °C at a rate of 10 °C min⁻¹ and isothermally annealed for 1 min. The samples were then cooled at 10 °C min⁻¹ to -80 °C followed by a second heating cycle to 100 °C at 10 °C min⁻¹. Glass transition temperatures (T_g) were acquired at the mid-point of each transition using the Trios software and reported values are the average of at least three samples.

**Solvent Extraction**

Solvent extraction experiments were performed by placing a small amount of crosslinked polymer (ca. 20 mg) into a 20 mL vial filled with dichloromethane (DCM). The vial was then closed and stirred for 48 h before removing the solvent by gravity filtration. The recovered sample was dried under reduced pressure for 48 h at 60 °C and 20 mTorr, after which the sample was weighed and the gel percent was determined. A high temperature swell test was also performed with UCPLA-0.025-0.75 submerged in 1,2,4-trichlorobenzene at 140 °C for 120 h. Some yellowing, likely from oxidative degradation, was noticed about 9 h into the test, but the sample did not exhibit full dissolution during the entirety of the test. More yellowing was observed over this extended time period.

**Size Exclusion Chromatography**

Light scattering size exclusion chromatography (LS-SEC) was performed at 35 °C using three successive Phenomenex Phenogel-5 columns (Torrance, CA) and a Wyatt Technology DAWN DSP multiangle laser light scattering detector as well as a Wyatt
Optilab EX RI detector (Santa Barbara, CA); tetrahydrofuran was used as the mobile phase with an elution rate of 1 mL min\(^{-1}\). \(M_n\) was determined by calculating the \(dn/dc\) value of the polymer from the refractive index and the Agilent 1260LC data analysis software. \(M_n\) and \(D\) were determined based on a 10-point calibration curve using polystyrene standards purchased from Polymer Laboratories.

**Reprocessing Strategy**

Tensile bars broken via uniaxial tensile testing were placed in a dog bone shaped mold between two Teflon\textsuperscript{®} sheets. This was then placed in a press mold at 140 °C and allowed to equilibrate for 2 minutes. Approximately 4 MPa of pressure was then applied for 30 minutes, at which point the mold was removed from the press mold and allowed to cool to room temperature. The resulting tensile bars were ca. 0.5 mm (T) × 3 mm (W) × 25 mm (L) and a gauge length of 14 mm. The bars were then allowed to age at room temperature for 48 h in a desiccator, followed by uniaxial tensile testing to determine the recovery in their material properties.

**Chapter 2.5 References**

Chapter 3. A Mechanistic Study of the Polyurethane Stress Relaxation Reaction

Cross-linked polymers are used in many commercial products and are traditionally incapable of recycling via melt reprocessing. Recently, tough and reprocessable cross-linked polymers with have been realized by incorporating cross-links that undergo associative exchange reactions, such as transesterification, at elevated temperatures. Here we investigate how cross-linked polymers containing urethane linkages relax stress under similar conditions, which enables their reprocessing. Materials based on hydroxyl-terminated star-shaped poly(ethylene oxide) and poly((±)-lactide) were cross-linked with methylene diphenyldiisocyanate in the presence of stannous octoate [Sn(Oct)\(_2\)] catalyst. These polymer networks show rapid stress relaxation compared to most reported vitrimers. Polymers with lower plateau moduli exhibit faster rates of relaxation. Reactions of model urethanes suggest that exchange occurs through reversion of the urethanes to isocyanates and hydroxyl groups. Furthermore, Sn(Oct)\(_2\) appears to slow polymer dissolution at 140 °C in DMSO, which might arise from the formation of transient metal-coordination cross-links. These findings indicate that urethanes, which are straightforward to incorporate, impart dynamic character to polymer networks of diverse chemical composition.

Chapter 3.1 Introduction

Cross-linked polymer networks are prevalent in adhesives, composites, and other durable products. Unlike thermoplastics, cross-linked polymer networks are effectively irreparable and are non-recyclable through traditional means. Many studies have explored their reprocessing by incorporating dynamic cross-links.\(^1,2,3,4,5,6\) Early examples relied on

* Preparing for submission to *Macromolecules*, or similar journal.
thermally reversible moieties, such as Diels-Alder cycloadducts, which allow the materials to return to their pre-network state and be reshaped. These studies represent a significant conceptual advance for reprocessing cross-linked polymers; however, the materials often exhibit poor thermal stability and solvent resistance, limiting their potential applications.

A new class of reprocessable polymer networks, termed vitrimers, feature cross-links that undergo exchange through associative rather than dissociative processes. Vitrimers maintain their cross-linked nature at elevated temperature and/or in the presence of solvents, as demonstrated for polyester epoxy resins containing a Zn(II) transesterification catalyst. The cured resins are capable of reprocessing and injection molding at 280 °C, yet only swell in hot solvent (180 °C) rather than dissolving, as is typical for cross-linked polymers. The viscosity of vitrimers follows an Arrhenius relationship as a function of temperature, in contrast to the typical Williams-Landel-Ferry response observed for thermoplastics. This strong glass-forming behavior confers a topology freezing transition temperature (T_v). Below T_v the vitrimer behaves as a traditional thermoset, and above T_v the cross-links in vitrimers undergo dynamic exchange reactions that give rise to thermally activated stress relaxation.

Vitrimers and related materials have been developed based on dynamic chemistries including alkene metathesis, hindered urea exchange, disulfide/polysulfide metathesis, thiol-disulfide exchange, vinylogous urethane exchange, transcarbamoylation, siloxane equilibrium, and boronic ester exchange. We previously reported reprocessable materials based on poly((±)-lactide) (PLA) cross-linked with a diisocyanate in the presence of stannous octoate [Sn(Oct)_2] as a catalyst. We initially hypothesized that the high concentration of ester functionalities in the PLA
backbone was responsible for the rapid stress relaxation and efficient reprocessability of these materials. However, the Arrhenius activation energy ($E_a$) for stress relaxation (150 kJ/mol) was much higher than that determined for PLA transesterification (80 kJ/mol), indicating that other stress relaxation mechanisms were operative. We later showed that cross-linked polyhydroxyurethanes relax stress through transcarbamoylation, suggesting that the urethane linkages and free hydroxyl groups might also be responsible for stress relaxation in the PLA networks. Furthermore, stress relaxation of polyurethane networks lacking free hydroxyl groups was reported by Tobolsky in the 1950s.

Exploiting the dynamic nature of urethane bonds has recently become a promising approach for reprocessing polyurethane networks, although the chemical mechanism of these processes is not clear. For example, Zheng, et al. hypothesized that urethane reversion to alcohol and isocyanate was responsible for stress relaxation in polyurethane elastomers in the presence of dibutyltin dilaurate. Subsequent experiments demonstrated that networks based on N-aryl urethanes relax stress at elevated temperatures even in the absence of an external catalyst, although no explicit evidence for urethane reversion was presented in either case. Yang and Urban postulated that repair of cross-linked polyurethanes occurs through the generation of amines upon mechanical failure, which react further with urethanes to form ureas. Raman and IR spectroscopy were used to help substantiate these claims. While the modest spectral changes were consistent with this hypothesis, more definitive evidence was lacking. In light of these findings, a complete mechanistic understanding of stress relaxation for urethane-containing polymer networks remains unresolved.
Here we investigate the thermally activated stress relaxation of urethane-containing polymer networks as a function of temperature, catalyst presence, and polymer structure. The $E_a$ values for stress relaxation of PLA- and poly(ethylene oxide) (PEO)-based thermosets cross-linked with aryl isocyanates establish that urethane cross-link exchange is the dominant stress-relaxation mechanism in both networks. Transcarbamoylation of urethane model compounds at elevated temperature provides further insight into the mechanism responsible for stress relaxation. Variable-temperature NMR spectroscopy and polymer swelling experiments are also consistent with urethane reversion to isocyanate and alcohol groups being the predominant mechanism of stress relaxation in polymer networks cross-linked by $N$-aryl urethanes.

**Chapter 3.2 Results and Discussion**

**3.2.1 Synthesis of Urethane Cross-linked PEO and PLA**

In our previous study of urethane-cross-linked PLA,$^{33}$ the Arrhenius activation energy ($E_a$) of stress relaxation (150 kJ/mol) was far higher than that reported for Sn(Oct)$_2$-catalyzed transesterification in a PLA melt (80 kJ/mol).$^{34}$ To explore this discrepancy, we replaced the PLA component with a hydroxyl-terminated, star-shaped PEO (HTSPEO). If transesterification reactions are the dominant source of stress relaxation, our expectation is that the PEO-based materials would exhibit distinctly different stress relaxation behavior. Urethane-cross-linked PEO materials were prepared using similar conditions to those used for urethane-cross-linked PLA (Scheme 3.1).$^{33}$ The commercially available 4-arm hydroxyl-terminated PEO prepolymer was combined with MDI (NCO functionality of 2, 0.75 equiv. NCO groups per OH group) and Sn(Oct)$_2$ (2.5 mol% relative to initial OH groups) to give cross-linked networks. The cross-link density of these materials was varied
by using poly(methylene diphenyl diisocyanate) (PMDI, average NCO functionality of 3.2, 0.75 NCO groups per OH groups) as an alternate cross-linker. To make a direct comparison of these materials with PLA, we prepared 4-arm hydroxyl-terminated PLA prepolymer with $M_n$ of 1.0, 3.8, and 10 kg/mol and cross-linked them under the same conditions as the PEO prepolymer.

**Scheme 3.1:** Synthesis of urethane cross-linked PEOs and PLAs.

3.2.2 Dynamic Mechanical Thermal and Stress Relaxation Analysis

DMTA of the PEO-based materials reveals a plateau modulus of 3.7 MPa for the materials prepared using MDI cross-linker and a modulus of 6.6 MPa for the PMDI cross-linker, indicating that the higher isocyanate content of PMDI gives rise to higher cross-link density (Figure 3.1, Table 3.1). During the DMTA experiment, an uncharacteristic increase in the modulus of the materials was observed at 150 °C. However, materials that were swollen in MeOH for 48 h, no longer displayed this feature (Figure 3.1, dashed lines). Inductively coupled plasma mass spectrometry (ICP-MS) of the samples show that Sn is still present in the methanol swelled samples, suggesting that the methanol interacted with the material and/or catalyst in a manner such that this feature in DMTA disappeared. Varying the $M_n$ of the PLA prepolymer changed the plateau modulus. Although PLA-3.8-MDI and PLA-10-MDI have similar plateau moduli, which we attribute this behavior to
trapped entanglements (molar mass between entanglements ($M_c$) for PLA is 4 kg/mol)\textsuperscript{40} which become more prevalent as the prepolymer molar mass is increased (Figure 3.1)\textsuperscript{41}

Figure 3.1: DMTA of urethane cross-linked PEOs and PLAs; the dashed lines are for samples after being soaked in methanol for 48 h and subsequently vacuum dried. The analysis was run at 1 Hz and an oscillation strain of 0.05\%. PLAs were tested below 150 °C to avoid thermal decomposition and higher initial temperatures than PEOs to avoid transducer overload observed at lower temperatures.
### Table 3.1: Mechanical and Thermal Data of Urethane Cross-linked PEOs and PLAs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gel %</th>
<th>$E'$ (MPa)</th>
<th>$n_e \times 10^{-4}$ (mol mL$^{-1}$)</th>
<th>$M_x$ (kg mol$^{-1}$)</th>
<th>$T_{g,DMT}$ (°C)</th>
<th>$T_{g,DS}$ (°C)</th>
<th>$T_{A,DS}$ (°C)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$T_v$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-0.8-PMDI</td>
<td>99</td>
<td>6.6</td>
<td>8.9</td>
<td>1.6</td>
<td>3</td>
<td>294</td>
<td>142 ± 11</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>PEO-0.8-MDI</td>
<td>100</td>
<td>3.7</td>
<td>5.0</td>
<td>2.8</td>
<td>-1</td>
<td>-3</td>
<td>303</td>
<td>139 ± 5</td>
<td>76</td>
</tr>
<tr>
<td>PLA-1-MDI</td>
<td>99</td>
<td>2.4</td>
<td>3.2</td>
<td>4.8</td>
<td>57</td>
<td>55</td>
<td>189</td>
<td>155 ± 5</td>
<td>67</td>
</tr>
<tr>
<td>PLA-3.8-MDI</td>
<td>99</td>
<td>1.3</td>
<td>1.7</td>
<td>8.9</td>
<td>54</td>
<td>55</td>
<td>188</td>
<td>153 ± 3</td>
<td>56</td>
</tr>
<tr>
<td>PLA-10-MDI</td>
<td>99</td>
<td>1.3</td>
<td>1.7</td>
<td>8.9</td>
<td>58</td>
<td>53</td>
<td>202</td>
<td>165 ± 3</td>
<td>59</td>
</tr>
<tr>
<td>PEO-0.8-PMDI-SM</td>
<td>100</td>
<td>6.6</td>
<td>8.9</td>
<td>1.6</td>
<td>0</td>
<td>293</td>
<td>127 ± 31</td>
<td>108</td>
<td></td>
</tr>
<tr>
<td>PEO-0.8-MDI-SM</td>
<td>100</td>
<td>4.2</td>
<td>5.7</td>
<td>2.5</td>
<td>0</td>
<td>299</td>
<td>87 ± 27</td>
<td>81</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Samples are named as prepolymer type-molar mass (kg mol$^{-1}$)-cross-linker used. SM denotes the samples soaked in methanol. $^b$Determined as the ratio of the mass after a swell test to the mass before the swell test multiplied by 100. $^c$Determined by DMTA at 100 °C and 5 °C min$^{-1}$. $^d$Determined using equation 1. $^e$Defined as the temperature where the maximum of the loss modulus ($E''$) occurs in DMTA. $^f$Ascertained after erasing the thermal history at 150 °C for 1 min, cooling to -80 °C, and back to 150 °C at a rate 10 °C min$^{-1}$. $^g$Determined by heating from 20 °C to 550 °C at 10 °C min$^{-1}$. $^h$Determined from the Arrhenius fit from SRA (equation 2). Standard error is shown with these values. $^i$Determined by extrapolating the Arrhenius fit from SRA to $\tau_v^*$ for each individual sample, which is determined via equation 3.

SRA of the PEO-based materials reveals stress relaxation at similar rates to PLA-based materials (Figure 3.2A), suggesting that urethanes—not esters—are the dominant functional group contributing to stress relaxation. The characteristic relaxation time ($\tau_v^*$) was then plotted against 1000/T and subjected to an Arrhenius analysis (eq. 3.2), from which an $E_a$ of stress relaxation was extracted (Figure 3.2B, Table 3.1). The $E_a$ of stress relaxation did not vary significantly between the PEO- and PLA-based materials (the range of $E_a$ values is 145–162 kJ/mol, consistent with our previous work), providing further evidence that the urethane functionality dominates the stress relaxation behavior in all cases. FT-IR of all materials before and after SRA are indistinguishable, indicating that any changes in the functional groups of the network are minimal (Figures 3.3-3.5).
Figure 3.2: A) SRA for PEO and PLA-based materials at 130 °C and 5% strain. Samples were run until they reached $1/e$ (37%) of their original stress relaxation modulus ($G_0$). B) Arrhenius analysis while varying the $M_x$. Three experiments at each temperature are plotted; the temperature rounded to the nearest °C is shown below 1000/T. Dashed lines are for samples that were swelled in MeOH.

Figure 3.3: FT-IR spectra before and after stress relaxation analysis (SRA) at various temperatures on A) UCPEO-0.8-MDI and B) UCPEO-0.8-PMDI. Each spectra contains 16 scans and the intensities are normalized to the carbonyl stretch.
Figure 3.4: FT-IR spectra before and after stress relaxation analysis (SRA) at various temperatures on A) UCPLA-1.0-MDI B) UCPLA-3.8-MDI, and C) UCPLA-10-MDI. Each spectra contains 16 scans, was performed on a diamond ATR head, and the intensities are normalized to the carbonyl stretch. Due to the stiffness of these samples, it was difficult to obtain good contact with the ATR crystal.
Figure 3.5: FT-IR spectra before and after stress relaxation analysis (SRA) at various temperatures on A) UCPEO-MDI-NC and B) UCPEO-PMDI-NC. Each spectra contains 16 scans and the intensities are normalized to the carbonyl stretch.

While the $E_a$ values are very similar, the rates of relaxation are quite different among samples. We found that the relaxation rate increases dramatically with decreasing plateau modulus (Figure 3.6), consistent with previous studies performed in polyester vitrimers. Based on stoichiometry, PEO-0.8-PMDI and PEO-0.8-MDI have nearly identical residual hydroxyl group concentrations ([OH]$_{res}$), yet PEO-0.8-PMDI relaxed stress more slowly, suggesting that its lower modulus influenced the relaxation rate more than [OH] (Figure 3.6). Likewise, PLA-3.8-MDI and PLA-10-MDI have similar plateau moduli and vastly different residual [OH]$_{res}$ values, yet their rates of stress relaxation are essentially identical (Figure 3.6). This finding is consistent across all samples, both in this work and in our previous study.
Figure 3.6: Plots of characteristic relaxation time (τ*) at 130 °C vs. A) Storage/plateau modulus (E') at 130 °C and B) [OH]res, estimated from the cross-linking reaction stoichiometry. [OH]res is also shown in A) corresponding with the color associated with that material.

In our previous studies with PLA-based materials, we found that urethane-based stress relaxation occurred more rapidly in the presence of Sn(Oct)$_2$; however, we did not establish a value of $E_a$ in the absence of Sn(Oct)$_2$. This was in part due to the long times required for the experiment and the thermal sensitivity of PLA. Therefore, we explored the PEO-based materials after treatment with methanol. The rate of relaxation for PEO-based materials after methanol treatment was much slower, with τ* approximately 30 times longer at 150 °C, suggesting that methanol may deactivate the Sn(Oct)$_2$ catalyst (Figure 3.2B, dashed lines). The Arrhenius activation energies of these materials were inaccurate due to large deviations observed in τ*. Degradation was observed as an obvious browning at elevated temperatures for samples swelled in methanol.

3.2.3 Model Compound Studies

Model compound studies of the Sn(Oct)$_2$-catalyzed reactions of N-phenyl-O-octyl urethane were performed to test the urethane exchange hypothesis (Figure 3.7A). In the presence of excess 1-decanol and 2.5 mol% Sn(Oct)$_2$ at 150 °C, N-phenyl-O-octyl urethane reacts to give the O-decyl urethane, albeit slowly compared to the observed stress
relaxation. We therefore analyzed the reaction between two discrete urethanes in the absence of exogenous alcohol. Under these conditions, the formation of crossover products is observed more quickly and at similar time scales observed for stress relaxation, strongly suggesting that urethane reversion (not associative exchange) is the likely exchange mechanism (Figure 3.7B). It is possible that excess free alcohol coordinates to the Sn(II) ions, attenuating their ability to catalyze urethane exchange.\textsuperscript{43,44} Consistent with this explanation, when two discrete urethanes are heated in the presence of exogenous alcohol, only exchange with the free alcohol was observed at low conversions (and at a similar rate to urethane-hydroxyl exchange) (Figure 3.8A), demonstrating that the additional alcohol both slows the reaction and traps the isocyanate intermediates that would lead to urethane-urethane exchange. These results are also consistent with our observation that the rate of stress relaxation is dramatically reduced when the samples are swelled in an excess of methanol despite no loss in the loading of Sn in the samples as shown by ICP-MS.
Figure 3.7: GC-MS of model compound studies. A) Urethane-hydroxyl exchange conducted at 150 °C for 4 h (10:1 –OH to urethane) and B) Urethane-urethane exchange performed for 2 h at 150 °C (equimolar in both urethanes). Peak intensities are normalized to triphenylmethane (retention time = 13.7 min). Relative percentages of each compound are shown and while qualitatively significant, compound degradation on the GC column makes quantitative determination inconsistent.
**Figure 3.8:** Model compound studies. **A**) Urethane-urethane-hydroxyl exchange performed for 2 h at 150 °C (equimolar –OH to both urethanes) and **B**) urethane-urethane exchange with **N**-Methylated urethanes conducted at 150 °C for 4 h (equimolar in both urethanes). Peak intensities are normalized to triphenylmethane (retention time = 13.7 min). Relative percentages of each compound are shown and while qualitatively significant, compound degradation on the GC column makes quantitative determination inconsistent.

A urethane-urethane crossover experiment was also conducted on analogous **N**-methylated urethanes to explore the possibility of a different metathesis mechanism (Figure 3.8B), as **N**,**N**-disubstituted urethanes are incapable of reversion. Neither exchange products nor byproducts were observed, providing strong evidence for the dissociative mechanism. Unfortunately, the elevated temperature of the GC columns (>270 °C) is above the degradation temperature for **N**-aryl-**O**-alkyl urethanes (200 °C), making these results unreliable for a quantitative determination of reaction rates/activation energies.
Attempts to use $^1$H NMR spectroscopy to determine the rate of reaction of a free alcohol with a model urethane were complicated by observed byproduct formation under the higher temperature conditions required to observe sufficient exchange in the presence of excess free alcohol (see Figure 3.9 for more information).

![Chemical Structure]

**Figure 3.9:** $^1$H NMR spectrum of the neat reaction between $N$-phenyl-$O$-triethylene glycol and decanol at 180 °C. The reaction was allowed to proceed for the specified amount of time and then an aliquot was removed for analysis. The reaction progress was monitored by the protons of the $O$-methylene unit, whose peaks are shown above. Each spectrum was normalized to an external standard, 1,3,5-tribromobenzene. Byproduct formation in the vicinity of peak 2 muddles the determination of an $E_a$ for this reaction, indicating that more product is forming than reagent is diminishing. This byproduct is not consistent with typical side reactions that occur with urethanes as the $^1$H NMR spectrum does not indicate the formation of ureas and allophanates/biurets, whose $N$-aryl N-H peaks usually appear at ~8.5 and ~10.9 ppm in CDCl$_3$, respectively.$^{48,49,50}$

Although it appears that a urethane reversion pathway is operative in these systems, this mechanism is inconsistent with the insolubility of these networks in 1,2,4-trichlorobenzene (TCB) at 140 °C.$^{33}$ Other reprocessable cross-linked polymers based on
reversible bond forming reactions, such as Diels-Alder cycloadditions, are capable of full dissolution at elevated temperatures.\textsuperscript{9} Therefore, we hypothesized that the low polarity of TCB (dipole moment = 1.25)\textsuperscript{51} is too low to induce urethane reversion. If a polar aprotic solvent, such as DMSO (dipole moment = 3.96), \textsuperscript{52} is used, we hypothesized that the reactive moieties could be separated, allowing for full dissolution. Indeed, PEO-0.8-MDI, both before and after swelling in methanol, were insoluble in TCB but dissolved fully in anhydrous DMSO (Figure 3.10), again consistent with urethane reversion. The samples swelled in TCB were subsequently dried under vacuum and an FT-IR spectrum was obtained. While there are some minor detectable differences, no significant change in the carbonyl resonances are observed despite substantial discoloring (Figure 3.11). In contrast to our expectations based on rates of stress relaxation, the samples subjected to methanol treatment dissolved significantly faster (24 h vs. 36 h). Therefore, in addition to catalyzing urethane exchange, we hypothesize that Sn(Oct)\textsubscript{2} forms transient coordination cross-links with pendant alcohols, which slows dissolution in DMSO. The formation of these weak cross-links is consistent with the established combination mechanism between isocyanates and alcohols in the presence of tin catalysts.\textsuperscript{47,53} However, when the coordination site of the catalyst is saturated with methanol, these transient coordination cross-links are prevented from occurring, resulting in faster dissolution.
Figure 3.10: High temperature (140 °C) dissolution study on PEO-0.8-MDI in DMSO (top) and TCB (bottom). Samples are denser than DMSO, though less dense than TCB, explaining the difference in location in the pressure vessels. Eventually, the samples discolor, making them easier to visualize in the solvent. Both samples are completely dissolved within 36 h for DMSO; the sample without catalyst takes longer to dissolve. Meanwhile, the materials swell in TCB but do not eventually dissolve, even after 7 days.

Figure 3.11: FT-IR spectra of UCPEO samples before and after swelling in TCB for 7 days at 140 °C. Swelled samples were dried for 48 h under vacuum (ca. 30 mTorr) before the spectra were obtained.

As DMSO was capable of completely dissolving the PEO-based samples, we sought to visualize the formation of the isocyanate intermediates directly. We acquired a $^{13}$C NMR spectrum of the diethyl urethane adduct of MDI in DMSO-$d_6$ at 25, 120, and 140 °C (Figure 3.12). No peaks were observed in the $^{13}$C NMR spectrum that corresponded to
the isocyanate, suggesting that the equilibrium lies significantly toward the urethane at these temperatures. For further confirmation, a $^1$H NMR spectrum was also acquired; however, the only change observed was an upfield shift of the N–H peak due to loss of hydrogen bonding (Figure 3.13), further indicating that the isocyanate concentration at these temperatures is below the detection limit of NMR spectroscopy. This equilibrium strongly favoring the urethane form likely explains the Arrhenius-type dependence of SRA, as the cross-links never dissociate to an appreciable degree.

Figure 3.12: Partial $^{13}$C VT-NMR spectra (125 MHz, 100 mg mL$^{-1}$) of MDI and the diethyl urethane of MDI. A concentrated solution of the diethyl urethane of MDI in DMSO-$d_6$ (100 mg mL$^{-1}$) was used to obtain better signal to noise. The sample was run under N$_2$ in a sealed NMR tube with 2.5 mol% Sn(Oct)$_2$ to urethanes; once the desired temperature was attained, the solution was allowed to equilibrate for 10 min and then 128 scans were performed.
Figure 3.13: $^1$H VT-NMR spectra (500 MHz, 100 mg mL$^{-1}$) of MDI and the diethyl urethane of MDI in DMSO-$d_6$. The same solution from $^{13}$C VT-NMR was utilized for this experiment. The diethyl urethane of MDI was run under N$_2$ in a sealed high pressure NMR tube; once the desired temperature was attained, the solution was allowed to equilibrate for 10 min and then 16 scans were performed.

Despite being unable to directly detect the isocyanate intermediate by NMR spectroscopy, we sought additional evidence for a reversion mechanism by indirectly detecting isocyanate-derived species upon removal of alcohol. To do so, a mixture of the diethyl urethane of MDI and Sn(Oct)$_2$ (2.5 mol % to urethane) was heated in a distillation apparatus to force the formation of MDI by removal of ethanol. We found that no ethanol was recovered at 140 °C (24 h) or 150 °C (24 h). After 24 h at 160 °C, some ethanol was
recovered (18% of the theoretical amount) accompanied by the formation of an insoluble brown solid in the distillation pot. The FT-IR spectrum of the solid indicated the presence of isocyanurate moieties (1509, 1411, and 1171 cm\(^{-1}\), Figure 3.14), consistent with the formation of isocyanates followed by trimerization to isocyanurate during alcohol removal. This experiment confirms that the isocyanate species is highly transient at temperatures relevant to stress relaxation (140-150 °C), while also providing further evidence for a reversion-based mechanism.

![FT-IR spectra](image)

**Figure 3.14:** FT-IR spectra of diethyl carbamate of methylenediphenyldiisocyanate (MDI) before and after heating at 140 °C for 24 h, then 150 °C for 24 h, and finally 160 °C for 24 h. Each spectra contains 16 scans and the intensities are normalized to the carbonyl stretch.

### 3.2.4 Mechanism Proposal

From SRA, dissolution tests, model reactions, and literature precedents, we propose that two mechanisms of stress relaxation are possible in these materials (Scheme 3.2). In the presence of exogenous alcohol, the mechanism in Scheme 3.2A could predominate. Low conversion observed in the hydroxyl-urethane exchange reactions (10:1 –OH:urethane) could be due to strong coordination of the Sn(II) metal center by
alcohols, inhibiting the subsequent reversion of the urethane. However, rates would increase as the [OH] decreases, which is evidenced by a significant increase in the observed rate for urethane-urethane exchange. Furthermore, because the [OH] in the polymers is low, inhibition of the Sn(II) centers by excess alcohol is less likely to occur. Finally, at each step of the proposed mechanisms, some form of cross-link (covalent or metal-coordination) always remains, consistent with the higher resistance for Sn(II) containing materials to dissolve in DMSO, despite the significantly faster rate of urethane exchange based on SRA. Based on the dissolution experiments, we believe the mechanism for non-catalyzed urethane exchange is similar, excluding the transient Sn(II)-coordinated cross-link, resulting in dissolution occurring significantly faster in DMSO (Scheme 3.2B).

**Scheme 3.2:** Proposed stress relaxation mechanisms of A) hydroxyl-urethane exchange and B) urethane-urethane exchange.

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**Chapter 3.3 Conclusions**

We demonstrate that urethane cross-links are capable of reversion at elevated temperature, resulting in macroscopic stress relaxation. The modulus of the cross-linked polymers is the main factor controlling the relaxation time, whereby samples with lower moduli relax
faster. While the presence of hydroxyl moieties apparently lowers the $E_a$ of stress relaxation, their concentration does not appear to affect the overall rate of relaxation as significantly as the storage modulus. Urethane reversion is further suggested by model compound studies, in which rapid urethane exchange was observed in the absence of free hydroxyl groups and only when the urethane contains an N-H as opposed to N-Me. Remarkably, these urethane-based materials remain insoluble for longer times in hot DMSO when Sn(Oct)$_2$ is present, suggesting a transient metal-coordination cross-link. Meanwhile, a less polar solvent (TCB) swells the materials when heated (similarly to a typical cross-linked material) rather than dissolving them as would be expected for a thermoset based on reversible cross-links. While we are unable to observe the presence of isocyanates in VT-NMR at 140 °C, generation of isocyanurate moieties after distillation of ethanol from the same adduct provides further evidence for an isocyanate intermediate. These studies provide further insight into the vitrimer-like elevated temperature behavior of polyurethane networks, and suggest that further investigations of the reprocessability of commercially ubiquitous polyurethane thermosets will be a beneficial approach to the recycling of these materials.

**Chapter 3.4 Experimental**

**Chapter 3.4.1 Materials**

All reagents were purchased from Sigma-Aldrich (Milwaukee, WI) and were used as received unless otherwise stated. (±)-Lactide was kindly provided by Altasorb (Piedmont, SC) and used as received. Sn(Oct)$_2$ was purified by vacuum distillation (3x, ~130-150 °C, ca. 30-50 mTorr argon). DCM and methanol were purchased from Fisher Scientific (Hampton, NH); DCM was purified via a GC-SPS-4-CM glass contour 800-L
solvent purification system obtained from Pure Process Technologies (Nashua, NH). 4-Arm hydroxyl-terminated PLA and urethane cross-linked PLA were synthesized via a literature procedure. PLA samples are labeled as PLA-X-Y, where X is the $M_n$ of the prepolymer by $^1$H NMR spectroscopy and Y is the cross-linker used. Urethane cross-linked PEO was synthesized and labeled in the same manner as the PLA samples. All glassware was heated to 105 °C overnight prior to use unless otherwise specified.

**Chapter 3.4.2 Synthetic Procedures**

*Representative Synthesis of N-H Model Compounds*

To a flame-dried round-bottom flask under nitrogen atmosphere was added alcohol (16.8 mmol) and anhydrous THF (20 mL). A solution of stannous octoate (130 mg, 0.34 mmol, 2 mol%) dissolved in anhydrous THF (1 mL) was added, followed by addition of isocyanate (16.8 mmol) via syringe. The resulting solution was allowed to stir at room temperature for 24 h, and solvent was removed at reduced pressure to yield a white solid. The crude solid was chromatographed on silica gel in 20% EtOAc/Hexanes to yield the product.

*N-phenyl-O-octyl urethane:* White solid, 82% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 (d, $J = 8.0$ Hz, 2H), 7.35-7.23 (m, 2H), 7.05 (tt, $J = 7.1$, 1.2 Hz, 1H), 6.56 (br s, 1H), 4.16 (t, $J = 6.7$ Hz, 2H), 1.71-1.63 (m, 2H), 1.43-1.23 (m, 10H), 0.89 (t, $J = 7.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.7, 138.0, 128.9, 123.2, 118.5, 65.4, 31.7, 29.19, 29.15, 28.9, 25.8, 22.6, 14.0. IR (neat, ATR) 3304, 2956, 2920, 2853, 1698, 1599, 1544, 1444, 1236, 1055, 747 cm$^{-1}$.

*N-tolyl-O-decyl urethane:* White solid, 85% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28-7.22 (m, 2H), 7.10 (d, $J = 8.3$ Hz, 2H), 6.49 (br s, 1H), 4.14 (t, $J = 6.7$ Hz, 2H), 2.30 (s,
84

3H), 1.72-1.60 (m, 2H), 1.44-1.24 (m, 14H), 0.92-0.84 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.8, 135.4, 132.8, 129.4, 118.7, 65.3, 31.9, 29.51, 29.50, 29.27, 29.25, 28.9, 25.8, 22.6, 20.7, 14.1. IR (neat, ATR) 3327, 2919, 2851, 1696, 1596, 1531, 1314, 1235, 1071, 814 cm$^{-1}$.

$N$-tolyl-$O$-(triethyleneglycol monomethyl ether) urethane: Colorless oil, 57% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 (d, $J = 8.6$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.73 (br s, 1H), 4.35-4.28 (m, 2H), 3.78-3.71 (m, 2H), 3.73-3.62 (m, 6H), 3.59-3.52 (m, 2H), 3.38 (s, 3H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.5, 135.3, 132.7, 129.3, 118.7, 71.8, 70.42, 70.41, 70.40, 69.3, 63.9, 58.8, 20.6. IR (neat, ATR) 3306, 2873, 1727/1709, 1599, 1530, 1315, 1222, 1207, 1102, 1069, 816 cm$^{-1}$.

Representative Synthesis of $N$-CH$_3$ Model Compounds

To a flame-dried round-bottom flask under nitrogen atmosphere was added urethane (4 mmol) and anhydrous DMF (15 mL). The mixture was cooled in an ice bath, and sodium hydride (192 mg, 8.0 mmol, 320 mg dispersion in mineral oil) was added, resulting in gas evolution. The resulting mixture was allowed to stir for 10 minutes, then iodomethane (1.419 g, 10 mmol, 0.62 mL) was added via syringe. The resulting mixture was allowed to stir at room temperature for 18 h, then diluted with water (150 mL). This solution was extracted with diethyl ether (200 mL), which was washed with water (2 x 150 mL), dried over MgSO$_4$, and filtered. Solvent was removed at reduced pressure to yield a colorless oil. The crude oil was chromatographed on silica gel in 10% EtOAc/Hexanes to yield the product as a colorless oil.

$N$-methyl-$N$-phenyl-$O$-octyl urethane: Colorless oil, 65% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 (m, 2H), 7.27-7.15 (m, 3H), 4.09 (t, $J = 6.7$ Hz, 2H), 3.30 (s, 3H), 1.63-1.53
\[ (m, 2H), 1.33-1.22 \text{ (m, 10H)}, 0.88 \text{ (t, } J = 6.8 \text{ Hz, 3H}). \] 
\[ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{) } \delta 155.7, 143.4, 128.7, 125.8, 125.6, 65.8, 37.5, 31.7, 29.11, 29.08, 28.8, 25.8, 22.6, 14.0. \] 
IR (neat, ATR) 2925, 2855, 1703, 1598, 1498, 1346, 1154, 695 cm\(^{-1}\).

\textit{N-methyl-N-tolyl-O-decyl urethane:} Colorless oil, 55\% yield. \[ ^{1}\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.18-7.07 \text{ (m, 4H)}, 4.08 \text{ (t, } J = 6.7 \text{ Hz, 2H}), 3.27 \text{ (s, 3H)}, 2.34 \text{ (s, 3H)}, 1.64-1.54 \text{ (m, 2H)}, 1.35-1.23 \text{ (m, 14H)}, 0.89 \text{ (t, } J = 6.9 \text{ Hz, 3H}). \] 
\[ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{) } \delta 155.9, 140.8, 135.6, 129.3, 125.6, 65.8, 37.7, 31.9, 29.5, 29.4, 29.3, 29.1, 28.9, 25.8, 22.6, 20.9, 14.0. \] 
IR (neat, ATR) 2923, 2854, 1703, 1515, 1343, 1155, 1111, 820, 768 cm\(^{-1}\).

\textit{Model Alcohol-Urethane Exchange Reaction analyzed via GC-MS Analysis}

To a vial was added stannous octoate (11.9 mg, 0.03 mmol, 2.5 mol \% to urethane), \textit{N-phenyl-O-octyl urethane} (293 mg, 1.17 mmol), \textit{1-decanol} (1.86 g, 11.7 mmol), and triphenylmethane (27.0 mg, 0.11 mmol) as an internal standard. The resulting mixture was heated and stirred in an oil bath preheated to the desired temperature, aliquots were taken via syringe at various time points, diluted with DCM, and analyzed via GC-MS analysis. Concentrations of the transcarbamoylation product \textit{N-phenyl-O-decyl urethane} could not be determined quantitatively due to partial decomposition of the urethanes on the GC column at temperatures required to sufficiently volatilize them.

\textit{Model Alcohol-Urethane Exchange Reaction analyzed via NMR}

To a vial was added stannous octoate (11.6 mg, 0.03 mmol, 2.5 mol \% to urethane), \textit{N-tolyl-O-(triethyleneglycol monomethyl ether) urethane} (340 mg, 1.14 mmol), and \textit{1-decanol} (1.81 g, 11.4 mmol). The resulting mixture was heated and stirred in an oil bath preheated to the desired temperature; aliquots of \textit{ca.} 10 mg were taken via syringe at various time points, dissolved in CDCl\(_3\) (containing 10.0 mg/ml tribromobenzene as an
external standard) to a concentration of 50.0 mg/ml, and analyzed via $^1$H NMR analysis (the $-\text{CH}_2\text{O}$- peaks of the starting material and transcarbamoylation product are distinct). Concentrations of the transcarbamoylation product $N$-tolyl-$O$-decyl urethane could not be determined quantitatively due to overlap of the product resonance at ca. 4.1 ppm with a side product (the calculated amount of product formed is greater than the amount of starting material lost; running the reaction to high conversion clearly shows an overlapping resonance convoluting the product peak).

**Model Urethane-Urethane Crossover Reaction**

To a vial was added stannous octoate (23.9 mg, 0.059 mmol, 2.5 mol % to urethane), $N$-phenyl-$O$-octyl urethane (294 mg, 1.18 mmol), $N$-tolyl-$O$-decyl urethane (344 mg, 1.18 mmol), and triphenylmethane (30.5 mg, 0.12 mmol) as an internal standard. The resulting mixture was heated and stirred in an oil bath preheated to the desired temperature, aliquots were taken via syringe at various time points, diluted with DCM, and analyzed via GC-MS analysis. Concentrations of the transcarbamoylation product $N$-phenyl-$O$-decyl urethane could not be determined quantitatively due to partial decomposition of the urethanes on the GC column at temperatures required to sufficiently volatilize them.

**Synthesis of diethyl urethane adduct of MDI**

To a round-bottom flask was added MDI (10 g, 40 mmol), ethanol (9.3 mL, 160 mmol) and DCM (10 mL) under stirring. Once the solution was homogenous, it was cooled to 0 °C and Sn(Oct)$_2$ (0.81 g, 2 mmol, 2.5 mol% to $-\text{NCO}$) in DCM (10 mL) was added. The solution was then left at 0 °C for 10 min followed by room temperature for 20 h. The resulting solution was then concentrated via rotary evaporation, dried under high vacuum (~20 mTorr) for 48 h. The crude product was then dissolved in DMF (ca. 20 mL) and
precipitated into deionized water (ca. 200 mL) yielding a yellow solid that was dried under vacuum (20 mTorr) for 48 h (quantitative yield). $^1$H-NMR (500 MHz, DMSO-d$_6$; 25 °C):

$\delta$ (ppm) = 9.52 (s, 2H), 7.38 (d, 4H), 7.10 (d, 4H), 4.12 (q, 4H), 3.79 (s, 2H), 1.24 (t, 6H).

$^{13}$C-NMR (125 MHz, DMSO-d$_6$; 25 °C): $\delta$ (ppm) = 154, 138, 136, 129, 119, 60, 40, 15.

**Chapter 3.4.3 Characterization Methods**

$^1$H NMR spectroscopy was performed on a 500 MHz Bruker Avance III HD with SampleXpress spectrometer (Billerica, MA) or an Agilent DD MR-400 400 MHz spectrometer. Solutions were prepared in 99.8% CDCl$_3$ (Cambridge Isotope Laboratories). All spectra were acquired at 20 °C with at least 16 scans and a 1 s delay unless otherwise specified. Chemical shifts are reported in ppm with respect to residual CHCl$_3$ (7.26 ppm).

Variable temperature (VT) NMR was performed on a 500 MHz Bruker III at 120 °C and 140 °C. DMSO-d$_6$ (Cambridge Isotope Laboratories, 99.9%) purified via distillation over CaH$_2$ was kindly provided by the Lu Research Group at the University of Minnesota via Reed Eisenhart. The solution was prepared and sealed in a high-pressure NMR tube under N$_2$. The solution was allowed to equilibrate for 10 min at the desired temperature before acquiring the $^1$H NMR and $^{13}$C NMR spectra.

Gas chromatography/electron impact mass spectrometry was performed on an Agilent 6890N Network GC System with a JEOL JMS-GCmate II Mass Spectrometer (magnetic sector). Triphenylmethane was used as an internal standard.

Dynamic mechanical thermal analysis (DMTA) was performed on a TA Instruments RSA-G2 analyzer (New Castle, DE) using dog bone shape films (ca. 0.5 mm (T) × 3 mm (W) × 25 mm (L) and a gauge length of 14 mm). DMTA experiments were conducted in tension film mode, where the axial force was first adjusted to 0.2 N of tension...
(sensitivity of 0.01 N) to ensure no buckling of the sample. The proportional force mode was set to force tracking to ensure that the axial force was at least 100% greater than the dynamic oscillatory force. The strain adjust was then set to 30% with a minimum strain of 0.05%, a maximum strain of 5%, and a maximum force of 0.2 N to prevent the sample from going out of the specified strain range. A temperature ramp was then performed from –50 °C to 200 °C at a rate of 5 °C min⁻¹, with an oscillating strain of 0.05% and an angular frequency of 6.28 rad s⁻¹. PLA samples were subjected to a higher starting temperature due to transducer overload in the brittle regime (25 to 35 °C). The $T_g$ was calculated from the maximum value of the loss modulus. The cross-link density ($\nu_e$) and the molar mass between cross-links ($M_x$) were calculated using the storage modulus ($E'$) at 100 °C and equation 1.

$$E'(T) = 3G'(T) = 3RT\nu_e = \frac{3\rho RT}{M_x} \quad (3.1)$$

Where $E'$ and $G'$ are the storage and shear modulus respectively, $R$ is the universal gas constant, $T$ refers to the absolute temperature in the rubbery region (ca. 373 K) and $\rho$ is the density of the PLA (ca. 1.25 g cm⁻³) or PEO (1.13 g cm⁻³).

The SRA experiments were performed in a strain control at specified temperature (110-170 °C depending on the sample). The samples were allowed to equilibrate at this temperature for approximately 10 minutes, after which the axial force was then adjusted to 0 N with a sensitivity of 0.05 N. Each sample was subjected to an instantaneous 5% strain. The stress decay was monitored, while maintaining a constant strain (5%), until the stress relaxation modulus had relaxed to at least 37% ($1/e$) of its initial value. This was performed three times for each sample. The characteristic relaxation time ($\tau^*$) was defined as the time required for the stress relaxation modulus to reach 37% ($1/e$) of its initial value and
determined via SRA at varying temperatures. These points were then plotted versus $1000/T$ and fit to the Arrhenius relationship in equation 2.

$$\tau^*(T) = \tau_0 e^{1000E_a/RT} \tag{3.2}$$

where $\tau_0$ is the characteristic relaxation time at infinite $T$, $E_a$ is the activation energy of stress relaxation (kJ mol$^{-1}$), $R$ is the universal gas constant and $T$ is the temperature in K at which SRA was performed.

The topology freezing transition temperature, $T_v$, is defined as the point at which a material exhibits a viscosity of $10^{12}$ Pa s, also known as the liquid to solid transition viscosity ($\eta_v$). Using Maxwell’s relation (eq. 3) and $E'$ determined from DMTA at 100 °C, the $\tau^*$ at $T_v$ ($\tau_v^*$) was determined for each sample. The Arrhenius fit for each sample was then extrapolated to the corresponding $\tau_v^*$ to determine $T_v$ for each sample.

$$\eta_v = \frac{1}{3} E' * \tau_v^* \tag{3.3}$$

Differential scanning calorimetry (DSC) was conducted on a TA Instruments Discovery DSC (New Castle, DE). The instrument was calibrated using an indium standard. All samples were prepared using T-Zero hermetic pans (ca. 3–7 mg) under a N$_2$ purge of 50 mL min$^{-1}$. The samples were initially cooled to −80 °C and then heated to 150 °C at 10 °C min$^{-1}$. The samples were then cooled back to −70 °C at 10 °C min$^{-1}$ and heated again to 150 °C at the same rate. Values for $T_g$ were acquired at the mid-point of each transition in the second heating curve using the Trios® software. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 (New Castle, DE) under air at a heating rate of 10 °C/min to 550 °C. A typical sample size was between 8-15 mg.

Solvent extraction experiments were performed by placing a small amount of cross-linked polymer (ca. 20 to 100 mg) into a 20-mL vial filled with DCM. The vial was then
closed and stirred for 48 h before removing the solvent by gravity filtration. The recovered sample was dried under reduced pressure for 48 h at 20 mTorr, after which the sample was weighed and the gel percent was determined. A high temperature swell test was also performed with PEO-0.8-MDI (with and without catalyst) submerged in 1,2,4-trichlorobenzene (TCB) or anhydrous dimethylsulfoxide (DMSO) at 140 °C for 7 days or until full dissolution.

Chapter 3.5 References


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Clark, T.; Murray, J. S.; Lane, P.; Politzer, P. Why are dimethyl sulfoxide and dimethyl sulfone such good solvents? *J. Mol. Model.* **2008**, *14*, 689-697.


Chapter 4. Mechanically Activated, Catalyst-Free Polyhydroxyurethane Vitrimers

Vitrimers are polymer networks whose cross-links undergo associative exchange processes at elevated temperature, usually in the presence of an embedded catalyst. This design feature enables the reshaping of materials with mechanical properties similar to thermoset resins. Here we report a new class of vitrimers consisting of polyhydroxyurethanes (PHUs) derived from six-membered cyclic carbonates and amines. PHU networks relax stress and may be reprocessed at elevated temperature and pressure in the absence of an external catalyst. The as-synthesized networks exhibit tensile properties comparable to leading thermosets and recover ca. 75% of their as-synthesized values following reprocessing. Stress relaxation occurs through an associative process involving the nucleophilic addition of free hydroxyl groups to the carbamate linkages, and exhibits an Arrhenius activation energy (111 ± 10 kJ/mol) lower than that observed for molecular model compounds (148 ± 7 kJ/mol). These findings suggest that transcarbamoylation is activated by mechanical stress, which we attribute, based on DFT calculations, to the twisting of N lone pairs out of conjugation with the carbonyl π-orbitals. PHU vitrimers are a promising new class of repairable networks because of their outstanding mechanical properties, avoidance of toxic isocyanate monomers, and catalyst-free repair processes.

Chapter 4.1 Introduction

Thermosets are cross-linked polymer networks with outstanding mechanical strength and solvent resistance used in durable goods, adhesives, and composites. Their

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This work was a collaborative effort with the Dichtel and Cramer research groups.
static cross-links cause thermosets to be irreparable and difficult to recycle. Cross-links capable of dynamic exchange\textsuperscript{1,2,3,4,5,6,7,8,9,10} impart repair and reshaping capabilities but reduce toughness and shape persistence unless controlled precisely. A subset of dynamic cross-linked polymers, classified as vitrimers,\textsuperscript{1,2} combine excellent mechanical properties at service temperatures and malleability at elevated temperatures by employing cross-links that undergo associative, rather than dissociative, exchange reactions. This design results in gradual viscosity changes with respect to temperature, in contrast to the abrupt viscosity change observed just above the glass transition temperatures of thermoplastics, enabling vitrimers to be easily reprocessed.

Broadening the chemical scope of vitrimers beyond polyester resins (based on transesterification)\textsuperscript{11,12,13,14,15,16} and polybutadiene rubbers (based on alkene metathesis)\textsuperscript{17,18} provides a means to improve and expand both the performance and sustainability. Cross-linked polyurethanes (PU) are used extensively for cushioning and thermal insulation, yet the efficient reprocessing of PU thermosets is poorly established. Associative transcarbamoylation processes are sluggish for carbamates, and the dissociative reversion of carbamates to isocyanates and alcohols that typically occurs at high temperatures (>200 °C) can be associated with deleterious side-reactions. As such, existing healable cross-linked PUs either incorporate additional dynamic functional groups and/or are limited to elastomeric materials.\textsuperscript{19,20,21,22,23,24,25,26} Inspired by historic reports of enhanced stress relaxation in cross-linked polyurethanes containing free hydroxyl groups,\textsuperscript{27,28} we evaluated the vitrimeric properties of polyhydroxyurethane (PHU) networks whose synthesis from polyfunctional cyclic carbonates and amines provides one
hydroxyl group per carbamate linkage, avoids the use of toxic isocyanates, and is amenable to monomers derived from renewable sources.29,30

Here we report PHU networks derived from six-membered cyclic carbonates and polyfunctional amines as a new class of vitrimers that does not require the incorporation of an external catalyst. Stress relaxation in these polymers is consistent with an associative transcarbamoylation process, yet exhibits a lower Arrhenius activation energy in the polymer than that observed in molecular model compounds. We attribute this phenomenon to mechanical activation of the transcarbamoylation reaction and present supporting density functional theory (DFT) calculations. The combined thermal and mechanical activation of vitrimers represents a new and desirable reprocessing mechanism that will increase the utility of repairable polymer networks and the scope of chemical transformations available to these materials.

Chapter 4.2 Results and Discussion

Chapter 4.2.1 Synthesis of a Cross-linked Polyhydroxyurethane

A cross-linked PHU (4) was prepared through the reaction of bis(cyclic carbonate) 1 and tris(2-aminoethyl)amine 2 (Figure 4.1A) in CH2Cl2 at room temperature, after which the solvent was removed by heating to 90 °C under reduced pressure for 48 h. Polymer 4 was isolated as an orange solid that conformed to the shape of its mold. The FT-IR spectrum of 4 (Figure 4.2) exhibits a single peak in the carbonyl region at 1690 cm⁻¹, corresponding to a hydrogen-bonded carbamate C=O stretch. The spectrum also contains a new broad stretch at 3300 cm⁻¹, corresponding to the O-H stretch of hydroxyl groups, and no C=O stretch signals associated with residual cyclic carbonates. Swelling tests of the
polymer in THF (25 °C, 24 h) indicate gel fractions in excess of 0.98, consistent with a densely cross-linked network.

Figure 4.1: A) The reaction of bis(cyclic carbonate) 1 and triamines 2 and 3 provides PHUs 4 and 5, respectively. 6 is a hydroxyurethane model compound used for transcarbamoylation studies. B) Photograph of a ground sample of 4 (left), which was reprocessed into tensile bars (right) by heating to 160 °C at 4 MPa pressure for 8 h.

Figure 4.2: IR spectra of 1 (blue) and 4 (red). 16 scans were performed for each spectrum.
Chapter 4.2.2 Mechanical and Thermal Characterization

As-synthesized samples of 4 had average Young’s moduli ($E$) of 2.2 ± 0.4 GPa, strain-at-break ($\varepsilon_b$) of 6.9 ± 3.8%, and 72 ± 11 MPa tensile strength ($\sigma_b$), all competitive materials properties for typical thermosets.\textsuperscript{1,5,6,15} Also, 4 shows little weight loss up to 250 °C, as determined by thermogravimetric analysis (Table 4.1), and exhibits a glass transition temperature ($T_g$) of 54 °C, as determined by differential scanning calorimetry (Table 4.1). Dynamic mechanical thermal analysis (DMTA) revealed a precipitous drop in the modulus near 61 °C, similar to the $T_g$ determined by DSC. Above this temperature, the material has a constant plateau modulus of 7.5 MPa, corresponding to an estimated molar mass between cross-links of 1.2 kg/mol (Figure 4.3, Table 4.1). These combined observations indicate that 1 and 2 readily condense to provide a densely cross-linked, rigid PHU network.

<table>
<thead>
<tr>
<th>Table 4.1: Material Properties of Polyhydroxyurethanes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>4</td>
</tr>
</tbody>
</table>
Chapter 4.2.3 Stress Relaxation Analysis

The dynamic properties of 4 were characterized using tensile stress relaxation analysis (SRA) at elevated temperatures in the linear viscoelastic regime (Figure 4.4A). Samples were thermally equilibrated, subjected to a controlled strain of 5%, and the mean relaxation lifetime (τ* at G/G₀ = e⁻¹) was determined. SRA was performed at 170, 180 and 190 °C and was reproducible. The topology freezing transition temperature (Tᵥ), at which viscosity (η) crosses the traditionally defined solid-to-liquid transition of 10¹² Pa·s, was 111 °C (see Chapter 2.4.3); below Tᵥ, 4 behaves as a traditional thermo set. FT-IR spectra recorded after SRA performed at each temperature were unchanged relative to those of the as-synthesized networks, suggesting no significant change in the network functionality (Figure 4.5) and indicated the stability of 4 to the reprocessing conditions and stress relaxation through degenerate carbamate exchange reactions.

Figure 4.3: DMTA of 4 before and after reprocessing from 30 to 200 °C at 1 Hz, 0.05% oscillating strain, and a heating rate of 5 °C/min.
**Figure 4.4:** A) Normalized stress relaxation analysis performed on 4 at elevated temperature. The dashed-black line represents where $G/G_0 = e^{-1}$, defined as the characteristic relaxation time, $\tau^*$. B) Representative tensile tests of the as-synthesized (black) 4, samples reprocessed (See Figure 4.1B) for 3$\tau^*$ at 160 °C (blue), 170 °C (green), and 180 °C (red) and 4 MPa pressure, and an as-synthesized sample annealed for 3$\tau^*$ at 160 °C (dashed black).

**Figure 4.5:** FT-IR spectra of 4 before and after stress relaxation analysis as well as after healing. The regions where isocyanate and isocyanurate signals would be expected are highlighted in black and purple, respectively.
Chapter 4.2.4 Reprocessing of CPHUs

Uniaxial tensile testing was performed on both pristine and recycled dogbone samples to characterize the mechanical properties and reprocessability of polymer 4. The process of repairing and reshaping broken samples by compression molding was optimized with respect to reprocessing temperature and time. Reprocessing performed at 160 °C for $3\tau^*$ (ca. 8 h; Figure 4.1B) provided the maximum recovery of tensile properties relative to a tensile bar prepared directly from the polymerization (Figure 4.4B), with $E = 1.6 \pm 0.2$ GPa (76% recovery), $\varepsilon_b = 4.8 \pm 0.8\%$ (69% recovery), and $\sigma_b = 53 \pm 8$ MPa (74% recovery). We attribute the incomplete recovery of the tensile properties to minor decomposition in the network that occurs slowly at elevated temperature over long times, as evidenced by the discoloration of the materials and TGA isotherms showing modest mass loss (ca. 7% over 5 h at 190 °C, Table 4.1). Furthermore, tensile bars prepared directly from the polymerization that were heated to 160 °C for $3\tau^*$ prior to the analysis exhibited similarly reduced tensile properties (Figure 4.4B, Table 4.2), suggesting that the bond-formation process is efficient but that the polymers also undergo slight decomposition. Consistent with the FT-IR analysis after the SRA experiments (Figure 4.5), FT-IR spectra of reprocessed samples are identical to those of as-synthesized samples, corroborating isodesmic carbamate exchange reactions. A similar $T_g$ and an 80% recovery of the plateau modulus were observed by DMTA after reprocessing (Figure 4.3), further indicating that the dynamic bonds preserve the cross-linking density and mechanical properties of 4.
Table 4.2: Tensile properties of polyhydroxyurethane 4 before and after reprocessing at various temperatures, and attempted reprocessing of acetylated polyhydroxyurethane 8.

<table>
<thead>
<tr>
<th>Reprocessing Temp. (°C)</th>
<th>Reprocessing Time (min)</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
<th>$E$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Synthesized</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$72.1 \pm 11.1$</td>
<td>$6.93 \pm 3.78$</td>
<td>$2.17 \pm 0.37$</td>
</tr>
<tr>
<td>After Reprocessing, Polymer 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>480</td>
<td>$53 \pm 8$</td>
<td>$4.8 \pm 0.8$</td>
<td>$1.6 \pm 0.2$</td>
</tr>
<tr>
<td>170</td>
<td>320</td>
<td>$43 \pm 3$</td>
<td>$7.3 \pm 1.0$</td>
<td>$1.4 \pm 0.2$</td>
</tr>
<tr>
<td>170</td>
<td>240</td>
<td>$46 \pm 6$</td>
<td>$4.1 \pm 1.4$</td>
<td>$1.9 \pm 0.1$</td>
</tr>
<tr>
<td>170</td>
<td>160</td>
<td>$35 \pm 10$</td>
<td>$4.7 \pm 2.7$</td>
<td>$1.5 \pm 1.0$</td>
</tr>
<tr>
<td>180</td>
<td>120</td>
<td>$27 \pm 4$</td>
<td>$4.8 \pm 1.7$</td>
<td>$1.1 \pm 0.2$</td>
</tr>
<tr>
<td>After Reprocessing, Acetylated Polymer 8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>480</td>
<td>$3.2 \pm 0.9$</td>
<td>$6.9 \pm 2.2$</td>
<td>$0.2 \pm 0.1$</td>
</tr>
</tbody>
</table>

Chapter 4.2.5 Mechanistic Inquiries

The temperature dependence of the SRA experiments (Figure 4.6A) indicates that the PHU network 4 undergoes more rapid transcarbamoylation than model compounds under similar conditions. The temperature dependence of $\tau^*$ for 4 was fit to an Arrhenius relationship to determine the apparent activation energy ($E_a$, Figure 4.6A) of $111 \pm 10$ kJ/mol, which is significantly lower than that of uncatalyzed transcarbamoylation observed in model compound 6 ($148 \pm 7$ kJ/mol, Scheme 4.1, Figures 4.7 and 4.8) and similar to the lowest reported values of catalyzed transcarbamoylation in traditional urethanes [Bi(OTf)$_3$,}
$E_a = 112 \pm 9$ kJ/mol.\textsuperscript{32} We hypothesize that this phenomenon arises from the mechanical activation of the transcarbamoylation reaction, as model hydroxyurethane 6 shows relatively little conversion in the presence of excess alcohol at similar temperatures and timescales (Figure 4.7). Previous vitrimers have shown consistent $E_a$ values between their stress relaxation behavior and their catalyzed exchange reactions,\textsuperscript{1,6} with the notable exception of another urethane-containing material.\textsuperscript{15}

**Figure 4.6:** A) An Arrhenius plot for the thermal activation of stress relaxation in 4 (blue) and 5 (red) is consistent with vitrimeric behavior. B) Swelling in Ph$_2$O (180 °C, 24 h, top) does not dissolve 4, but 4 fully dissolves in tetraethylene glycol after 4 h (bottom). C) The similar activation energies for the stress relaxation 4 and 5 are suggestive of an associative transcarbamoylation mechanism.

**Scheme 4.1:** Transcarbamoylation in Model Compounds
Figure 4.7: Plots of transcarbomylation product 7 concentration versus time for transcarbamoylation of model compound 6 with 1-decanol as a function of temperature. Concentrations shown are the average of four independent trials at a given temperature; error bars indicate one standard deviation. Linear fits are shown for initial rates under pseudo-first order kinetic conditions.

Figure 4.8: Arrhenius plot for determination of activation energy of transcarbamoylation in model compound 6. Relative rates shown are the average of four independent trials; error bars indicate one standard deviation.

The decomposition of carbamates to isocyanates and alcohols, the most likely dissociative stress relaxation mechanism, generally occurs at much higher temperatures than those at which 4 exhibits rapid stress relaxation, particularly for urethanes derived from aliphatic isocyanates (>250 °C).\textsuperscript{33} Swell tests of 4 in Ph\textsubscript{2}O (180 °C, 24 h, Figure 4.6B) showed no evidence of dissolution, consistent with associative exchange in the presence of an unreactive solvent.\textsuperscript{34} On the other hand, the network dissolved completely in the reactive
tetraethylene glycol (TEG) within 4 h under identical conditions, consistent with transcarbamoylation being the dominant exchange mechanism. Stress relaxation experiments performed on 5, which is linked by N-methyl urethanes incapable of forming neutral isocyanates (Figure 4.6C), exhibited similar $E_a$ (101 ± 7 kJ/mol) for stress relaxation as 4. These experiments cast doubt that the reversion of carbamates to isocyanates is significant under the stress relaxation conditions, and demonstrate that alcohols significantly contribute to the stress relaxation. Stress relaxation rates of 5 were much slower than 4, indicating a difference in pre-exponential factor which may be associated with steric effects related to nucleophilic addition to the methyl-substituted carbamate. The absence of isocyanate or isocyanurate peaks in the FT-IR spectra of both 4 and 5 (Figures 4.5 and 4.9) after SRA is consistent with negligible isocyanate formation.

To further support an associative mechanism of reprocessing, the reprocessability of the polymer was characterized after the hydroxyl groups of ground polymer 4 were acetylated (Scheme 4.1, Figure 4.10). The acetylated polymers showed only a ca. 10 % recovery of mechanical properties, indicating the necessity of free hydroxyl groups for efficient reprocessing (Figure 4.11). These combined observations suggest that PHU stress relaxation and reprocessing occurs primarily through associative transcarbamoylation reactions, which is a key feature for accessing the desirable toughness, malleability, and creep resistance associated with vitrimers.
**Figure 4.9:** FT-IR spectra of 5 before and after stress relaxation analysis. The regions where isocyanate and isocyanurate signals would be expected are highlighted in black and purple, respectively.

**Figure 4.10:** FT-IR spectra of as-synthesized polymer 4, ground and acetylated polymer 8 before attempted reprocessing, and acetylated polymer 8 after attempted reprocessing.
Figure 4.11: Tensile testing of as-synthesized polymer 4 and reprocessed acetylated polymer 8, showing limited reprocessability in the absence of a large concentration of free hydroxyl groups.

The discrepancy in activation energy between PHU stress relaxation and model compound transcarbamoylation, along with dissociative exchange processes appearing to be inoperative, suggests that transcarbamoylation reactions are mechanically activated. Thermoplastic PUs previously exhibited decreased molar mass and increased dispersity when subjected to mechanical strain at high temperatures. These changes were attributed to the breaking of urethane bonds, whose rate increases with increased polymer size, a common trait of mechanically activated reactions in polymeric systems. We propose that transcarbamoylation is accelerated when mechanical strain causes the lone pair of the nitrogen atom to twist out of conjugation from the carbonyl π-electron system, thereby rendering the carbamate more susceptible to nucleophilic attack. The resulting orthocarbamate intermediate is most likely to reform the carbamate by expelling the alkoxy group so as to relieve the most stress.

Chapter 4.2.6 Computational Modelling of the Stress Relaxation Reaction

To assess this hypothesis, DFT calculations were undertaken (see Chapter 4.4.4) to predict $E_a$ values for the water catalyzed reaction of MeOH with $N,O$-dimethylcarbamate
to generate the product orthocarbamate. To address the potential influence of torsional strain, the energies of possible reactant and transition-state (TS) structures were computed for fixed OCNC dihedral angles of $\text{O} = \text{C}(\text{OCH}_3)\text{N}(\text{H})\text{CH}_3$. Interestingly, the $E_a$ values associated with many torsionally strained educt and TS structures were predicted to be much lower than for the analogous fully relaxed reaction (Figure 4.12). In particular, compared to the adiabatic $E_a$ of 70.7 kJ/mol that is predicted for fully relaxed structures in this model reaction, at an OCNC torsion angle of 90 degrees, the $E_a$ is predicted to drop to 35.5 kJ/mol (Figure 4.12 and 4.13). This reduction is quite similar to the difference in $E_a$ observed for the stress relaxation of 4 and transcarbamoylation processes of the model system. Importantly, computed TS-structure energies for water-catalyzed reversion of $N,O$-dimethylcarbamate were found to increase greatly due to torsional strain when compared with the educt, further consistent with the conclusion that isocyanate formation is not responsible for strain relief in the present system.

**Figure 4.12:** A) DFT calculated structures for $N,O$-dimethylcarbamate with their corresponding TS structures for water-catalyzed transcarbamoylation with methanol (above); H, C, N, and O atoms are shown as white, gray, blue, and red, respectively. B) The vertical $E_a$ to reach a constrained TS from a constrained educt as a function of the $\text{O} = \text{C}(\text{OCH}_3)\text{N}(\text{H})\text{CH}_3$ dihedral angle.
Figure 4.13: Enthalpies relative to global minimum separated reactant structures at the M06-2X/6-311+G(d,p) level of theory as a function of OCNC torsion angle in the N,O-dimethylcarbamate fragment. The educt enthalpies are represented by filled circles and TS-structure enthalpies are represented with crosses and open circles. Blue and red symbols refer to R and S local chirality at the nitrogen atom (the dots at torsion angles of 0 and 180 deg are arbitrarily colored as these structures have a planar N atom). Crosses and open circles refer to TS structures having ester groups with s-cis and s-trans stereochemistries, respectively.

Chapter 4.3

In conclusion, we have demonstrated that cross-linked PHUs derived from six-membered cyclic carbonates and amines display vitrimeric behavior in the absence of an embedded catalyst typically incorporated into such networks. Furthermore, we have posited that transcarbamoylation is the principal relaxation mechanism in PHU networks. These materials display mechanical properties competitive with traditional PU thermosets, yet enable reshaping and repair that will enhance their long-term utility. Moreover, these networks are prepared from readily accessible and general monomer classes, which will facilitate the full exploration and tuning of their properties.
Chapter 4.4 Experimental

Chapter 4.4.1 Materials

All reagents were purchased from Sigma-Aldrich. Tris(2-aminoethyl)amine (2) and tris[2-(methylamino)ethyl]amine (3) were stirred over CaH₂ and distilled prior to use; all other reagents were used without further purification. Dichloromethane (DCM), triethylamine (Et₃N), and tetrahydrofuran (THF) were purchased from commercial sources and purified using a custom-built alumina-column based solvent purification system. Other solvents were purchased from commercial sources and used without further purification.

Chapter 4.4.2 Synthetic Procedures

Synthesis of 1

To a flame-dried round-bottom flask under nitrogen atmosphere was added di(trimethylol)propane (10.0 g, 40 mmol) and 250 mL anhydrous THF. To the suspension was added ethyl chloroformate (25.2 g, 232 mmol) under stirring. The mixture was cooled to 0°C, triethylamine (24.6 g, 242 mmol) was added dropwise, and a white precipitate began to form. The mixture was warmed to room temperature and allowed to stir for 3 hours. The solid was removed via filtration, and solvent was removed at reduced pressure to yield a white solid. The solid was recrystallized from THF to obtain compound 1 as a white solid (8.6 g, 71%). ¹H NMR (400 MHz, CDCl₃) δ 4.29 (d, J = 10.1 Hz, 4H, -CH₂OCOOCH₂-), 4.17 (d, J = 10.5 Hz, 4H, -CH₂OCOOCH₂-), 3.50 (s, 4H, -CH₂OCH₂-), 1.50 (q, J = 7.5 Hz, 4H, -CH₃CH₂C-), 0.91 (t, J = 7.6 Hz, 6H, CH₃CH₂C-). ¹³C NMR (75 MHz, CDCl₃) δ 148.32 (-OCOO-), 72.76 (-OCH₂OCH₂O-), 70.71 (-CH₂OCH₂-), 35.36 (-[CH₂]₂C(CH₂)₂-), 23.55 (CH₃CH₂-), 7.34 (CH₃CH₂). IR (solid, ATR) 2972, 2918, 2881,
1732 (C=O stretch), 1463, 1412, 1165, 1106, 762 cm\(^{-1}\). The \(^1\)H and \(^{13}\)C NMR spectra match those previously reported in the literature.\(^{37}\)

**Synthesis of 6**

To a vial was added solid trimethylene carbonate (1.286 g, 12.6 mmol); the vial was heated to 60 °C, resulting in a clear melt. Butylamine (920 mg, 12.6 mmol) was added via syringe, and the mixture was heated at 60 °C for 12 hours. The resulting oil was chromatographed on silica gel in ethyl acetate to yield compound 6 as a colorless oil (2.09 g, 95%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.71 (br s, 1H, -NH-), 4.24 (t, \(J = 5.8\) Hz, 2H, -CH\(_2\)OH), 3.70-3.63 (m, 2H, -CH\(_2\)OH), 3.21-3.12 (m, 2H, -CH\(_2\)NH), 2.86 (br s, 1H, -OH), 1.85 (quintet, \(J = 6.1\) Hz, 2H, -CH\(_2\)CH\(_2\)OH), 1.52-1.42 (m, 2H, -CH\(_2\)CH\(_2\)NH), 1.41-1.25 (m, 2H, -CH\(_2\)CH\(_2\)CH\(_3\)), 0.93 (t, \(J = 7.3\) Hz, 3H, -CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.2, 61.5, 58.7, 40.7, 32.2, 31.9, 19.8, 13.6. IR (liquid, ATR) 3324, 2958, 2932, 2874, 1690 (C=O stretch), 1538 (N-H deformation), 1248, 1053 HRMS (ESI) calcd. for [C\(_8\)H\(_{17}\)NO\(_3\)+Na]\(^+\) 198.11006, found 198.10956.

**Synthesis of 7**

In a flame-dried round-bottom flask under nitrogen atmosphere, \(n\)-butylisocyanate (436 mg, 4.4 mmol) was dissolved in 5.0 ml anhydrous THF. Decanol (633 mg, 4.0 mmol) was added via syringe, followed by a solution of tin (II) octoate (32 mg, 2 mol %) in 0.2 ml anhydrous THF. The solution was allowed to stir at room temperature for 48 hours and solvent was removed at reduced pressure. The residue was chromatographed on silica gel in 20% EtOAc/Hexanes to yield 7 as a white solid (690 mg, 67%). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 4.59 (br s, 1H, -NH-), 4.03 (t, \(J = 6.7\) Hz, 2H, -OCH\(_2\)-), 3.21-3.11 (m, 2H, -NHCH\(_2\)-), 1.66-1.22 (m, 20H), 0.96-0.84 (m, 6H) \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 156.8,
64.8, 40.6, 32.0, 31.8, 29.5 (2C), 29.2 (2C), 29.0, 25.7, 22.6, 19.8, 14.0, 13.6 IR (solid, ATR) 3318 (N-H stretch), 2957, 2917, 2849, 1688 (C=O stretch), 1538 (N-H deformation), 1468, 1250, 1147, 1029, 1013 HRMS (DART) calcd. for [C_{15}H_{31}NO_2+H]^+ 258.24276, found 258.24355

**Synthesis of 4**

1 (798.0 mg, 2.639 mmol, 1 eq. cyclic carbonate) was dissolved in a minimal amount of anhydrous DCM (ca. 2.5 mL) along with tris(2-aminoethyl)amine 2 (257.3 mg, 1.760 mmol, 1 eq. amine to cyclic carbonate). Solutions were sonicated for one minute to ensure homogeneity, then poured into an aluminum mould (60 mm D x 10 mm H), and allowed to stand at room temperature for ca. 24 hours. Samples were cut from the resulting films, and placed under reduced pressure at 90 °C and 20 mTorr for ca. 48 hours to ensure complete cross-linking and removal of solvent. Swell tests were performed on the resulting materials in THF and a gel fraction of greater than 0.98 was found in all cases. IR (solid, ATR) 3297, 2962, 2880, 1689 (C=O stretch), 1527 (N-H deformation), 1460, 1257, 1105, 1020 cm⁻¹.

**Synthesis of 5**

1 (733 mg, 1 eq. cyclic carbonate) was dissolved in a minimal amount of anhydrous DCM (ca. 2.5 mL) along with tris[2-(methylamino)ethyl]amine 3 (304.5 mg, 1 eq. amine to cyclic carbonate). Solutions were sonicated for one minute to ensure homogeneity. The solutions were poured into an aluminum mould (60 mm D x 10 mm H), and allowed to stand at room temperature for ca. 48 hours. Samples were cut from the resulting films, and placed under reduced pressure at 90 °C and 20 mTorr for ca. 48 hours; due to the lower reactivity of the secondary amines, the materials were post-cured for 96 hours at 150 °C
and 20 mTorr to drive the reaction to higher conversion. IR (solid, ATR) 3427, 2931, 2879, 1677 (C=O stretch), 1459, 1402, 1186, 1111, 1039 cm$^{-1}$.

**Acetylation of 4 (8)**

4 was repeatedly ground in a burr coffee grinder and sifted until a fine powder was obtained. The fine powder of 4 (1.0 g, 5.0 mmol hydroxyl, 1 eq. hydroxyl) was then placed in a 250 mL round-bottom flask along with acetyl chloride (7.13 mL, 20 eq. to hydroxyl) and 100 mL of anhydrous THF. The heterogeneous mixture was cooled to 0 °C and triethylamine (13.9 mL, 20 eq. to hydroxyl) was added dropwise over 20 min while stirring and a white precipitate began to form. The mixture rapidly heated to 35 °C and then cooled to room temperature. It was allowed to stir for 24 h after which the solid was collected by filtration and rinsed with distilled water until the salts were removed. The remaining solid was further rinsed with an excess of acetone, then toluene and dried for 48 h under high vacuum (ca. 50 mTorr) yielding a yellow-orange solid (1.2 g). IR spectroscopy indicated full surface acetylation of –OH groups, as well as acetylation of urethane –NH groups; the obtained yield is indicative that functionalization is not quantitative due to limited swelling of the densely-cross-linked network. IR (solid, ATR) 2962, 2886, 1732 (acetyl C=O stretch), 1698 (urethane C=O stretch), 1682 (N-acetylated urethane C=O stretch), 1525 (N-H deformation, weak), 1462, 1366, 1227, 1158, 1111, 1034, 975, 771 cm$^{-1}$.

**Transcarbamoylation of 6 to 7**

To a vial was added hydroxyurethane model compound 6 (70 mg, 0.40 mmol), 1-decanol (632 mg, 4.0 mmol), and di-tert-butylbiphenyl (10 mg, 0.038 mmol) as an internal standard. The resulting mixture was heated in an oil bath preheated to the desired temperature (170-210 °C), aliquots were taken via syringe at various time points, and
analyzed via GC analysis with FID detection. Concentrations of the transcarbamoylation product 7 were determined from a calibration curve of independently synthesized 7.

**Chapter 4.4.3 Characterization Methods**

Infrared spectra were recorded on a Thermo Nicolet iS10 or a Bruker Alpha Platinum; both were equipped with a diamond ATR attachment and spectra were uncorrected.

Gas chromatography was performed on an Agilent 6890N Network GC System with a flame ionization detector. Concentrations were determined from a linear calibration of peak area to concentration relative to di-tert-butylbiphenyl as an internal standard.

NMR spectra were recorded on a Varian 400 MHz, a Varian 500 MHz or a Bruker ARX 300 MHz spectrometer using a standard $^1$H/X Z-PFG probe at ambient temperature with a 20 Hz sample spin rate.

Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 Thermogravimetric Analyzer. Samples were heated under a nitrogen atmosphere at a rate of 10 °C/min from 25 °C to 600 °C. Isotherms were taken by heating samples under nitrogen to the desired temperature at a rate of 20 °C/min, then maintaining constant temperature for five hours.

Differential scanning calorimetry (DSC) was performed on a TA instruments Q1000 Differential Scanning Calorimeter. Samples were heated at a rate of 10 °C/min to 175 °C to erase thermal history, cooled to -90 °C at 10 °C/min, and then heated to 175 °C at 10 °C/min. All data shown are taken from the second heating ramp.

Dynamic mechanical thermal analysis (DMTA) was performed on a TA Instruments RSA-G2 analyzer (New Castle, DE) utilizing dog bone shaped tensile bars (ca.
0.5 mm (T) × 3 mm (W) × 25 mm (L) and a gauge length of 16 mm). The axial force was adjusted to 0 N and a strain adjust of 30% was set with a minimum strain of 0.05%, a maximum strain of 5%, and a maximum force of 1 N in order to prevent the sample from buckling or going out of the specified strain. Furthermore, a force tracking mode was set such that the axial force was twice the magnitude of the oscillation force. A temperature ramp was then performed from 30 °C to 200 °C at a rate of 5 °C/min, with an oscillating strain of 0.05% and an angular frequency of 6.28 rad s⁻¹ (1 Hz). The $T_g$ was calculated from the maximum value of the loss modulus ($G''$). Estimated cross-linking density was determined as in the literature.¹⁵

Uniaxial tensile testing was conducted using dog bone shaped tensile bars (ca. 0.5 mm (T) × 3 mm (W) × 25 mm (L) and a gauge length of 16 mm). The samples were aged for at least 48 h at 25 °C in a desiccator prior to testing. Tensile measurements were performed on a Shimadzu Autograph AGS-X Series tensile tester (Columbia, MD) at 22 °C with a uniaxial extension rate of 5 mm/min. Young’s modulus ($E$) values were calculated using the Trapezium software by taking the slope of the stress-strain curve from 0 to 1 N of force applied. Reported values are the average and standard deviations of at least five samples.

Stress relaxation analysis (SRA) was performed on a TA Instruments RSA-G2 analyzer (New Castle, DE) utilizing rectangular films (ca. 0.5 mm (T) × 5 mm (W) × 10 mm (L)) or dog bone shaped tensile bars (ca. 0.5 mm (T) × 3 mm (W) × 25 mm (L) and a gauge length of 16 mm). The SRA experiments were performed in a strain control at specified temperature (150-210 °C). The samples were allowed to equilibrate at this temperature for approximately 10 minutes, after which the axial force was then adjusted to
0 N with a sensitivity of 0.05 N. Subsequently, each sample was subjected to an instantaneous 5% strain. The stress decay was monitored, while maintaining a constant strain (5%), until the stress relaxation modulus had relaxed to at least 37% (1/e) of its initial value. This was performed three times for each sample. The activation energy ($E_a$) and freezing transition temperature ($T_v$) were determined utilizing the methodology in literature.$^{12,15}$

In order to reprocess the materials, the polymer was ground in an electric coffee grinder and then placed into a dog bone shaped mold (ca. 0.5 mm (T) × 3 mm (W) × 25 mm (L) and a gauge length of 16 mm) between two thin Teflon® sheets. This assembly was placed in a Wabash-MPI compression mold (Wabash, IN), which was preheated to the desired temperature. The material was allowed to thermally equilibrate for two minutes, following a two minute period of rapidly increasing the pressure to 4 MPa then reducing back to 0 MPa in order to remove air bubbles. The pressure was then increased to 4 MPa and allowed to heat for varying periods of time and then rapidly cooled to room temperature over the course of 5 minutes using the water cooling function of the compression mold. The resulting tensile bars were then allowed to age for 48 h in a desiccator and subjected to uniaxial tensile testing in order to determine their recovery in mechanical properties. Reported values are the average and standard deviations of at least five samples.

**Chapter 4.4.4 Computational Methodology**

To assess whether direct elongation, as opposed to torsional variations, might play a role in lowering the activation free energies for transcarbamoylation, we consider the relative free energies of otherwise optimized reactant and TS structures in which the C-C distance between the two methyl groups on N,O-dimethylcarbamate were forced to
separations 5% greater than those found for fully relaxed structures (i.e., corresponding to the strain employed in the experimental studies). We found that relative to the fully relaxed structures, the free energies of the stretched reactant and TS structures both went up by about 16 kJ/mol, i.e., no rate acceleration would be expected in transcarbamoylation exclusively from this elongation strain (which is manifest as a combination of angle-bending strain and bond-stretching strain). It is of some interest to note that the same distortion energy — about 16 kJ/mol — is required to reach the most torsionally strained reactant structures. Thus, to the extent that strain will be distributed into different modes throughout the polymer depending on the details of local condensed-phase structure, one would expect more reactive torsionally strained structures to indeed be accessible.

Chapter 4.5 References


Chapter 5. Structural Effects on the Reprocessability and Stress Relaxation of Cross-linked Polyhydroxyurethanes*

Cross-linked polyhydroxyurethane (PHU) networks synthesized from difunctional six-membered cyclic carbonates and triamines are reprocessable at elevated temperatures through transcarbamoylation reactions. Here we study the structural effects on reprocessability and stress relaxation in cross-linked PHUs. Cross-linked PHUs derived from *bis*(five-membered cyclic carbonates) are shown to decompose at temperatures needed for reprocessing, likely via initial reversion of the PHU linkage and subsequent side reactions of the liberated amine and cyclic carbonate. Therefore, several six-membered cyclic carbonate-based PHUs with varying polymer backbones and cross-link densities were synthesized. These networks show large differences in the Arrhenius activation energy of stress relaxation (from 99 to 136 kJ/mol) that depend on the network structure, suggesting that transcarbamoylation reactions may be highly affected by both chemical and mechanical effects. Furthermore, all cross-linked PHUs derived from six-membered cyclic carbonates show mechanical properties typical of thermoset polymers, but recovered as much as 80% of their as-synthesized tensile properties after elevated temperature compression molding. These studies provide significant insight into factors affecting the reprocessable of PHUs and inform design criteria for the future synthesis of sustainable and repairable cross-linked PHUs.

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Chapter 5.1 Introduction

Thermosets are cross-linked polymer networks whose mechanically robust and solvent-resistant properties facilitate their use in demanding applications that require high dimensional stability. However, these desirable properties are no longer advantageous once thermosets are damaged or discarded, since their inability to dissolve or melt precludes reshaping or repair. The incorporation of covalent bonds capable of dynamic exchange into cross-linked polymers imparts self-healing to elastomeric materials and reprocessability to thermoset-like materials, yet compromises their toughness if not carefully controlled.\textsuperscript{1,2,3,4,5,6,7,8,9,10} Polymer networks termed vitrimers are a subset of repairable cross-linked polymers with outstanding mechanical properties that rely on associative, rather than dissociative, exchange reactions to relax stress and undergo repair.\textsuperscript{11,12} In their initial report, Montarnal et al. synthesized polyester-based epoxy resins containing free hydroxyl groups, which undergo catalyzed transesterification reactions at elevated temperatures that enable stress relaxation and reshaping.\textsuperscript{13} Nevertheless, these polymers have mechanical properties competitive with traditional epoxy resins at service temperatures. Another benefit of this design is that the viscosity of the polymer decreases gradually with temperature, because their flow relies on activated cross-link exchange, rather than the abrupt Williams-Landel-Ferry-type changes in viscosity observed in thermoplastic materials above the glass transition temperature (T\textsubscript{g}). This strong glass-forming behavior typically enables vitrimers to be reshaped, even without precise temperature control.

Early examples of vitrimers focused on polyester resins\textsuperscript{14,15,16,17,18} and polybutadiene rubbers.\textsuperscript{19,20,21} Other dynamic polymer networks have since emerged that
incorporate dynamic functional groups including disulfides, hindered ureas, vinylogous urethanes, alkylated triazoles, siloxanes, imines, and boronate esters, representing a significant expansion of dynamic chemistries that are compatible with the vitrimer concept. Yet developing vitrimeric materials with tunable mechanical properties that are economical and capable of efficient reprocessing remains an ongoing challenge. Polyhydroxyurethane (PHU) networks in particular show great potential as inexpensive, tunable, and sustainable vitrimers because their synthesis avoids toxic isocyanates and inherently provides a stoichiometric number of hydroxyl groups for cross-link exchange. Polyurethanes (PUs) are used as coatings, adhesives, foams, and thermosets, but are not typically reprocessed. Chemical recycling of cross-linked PUs has been explored as an effective approach to convert PUs into monomers or oligomeric molecules, but this approach is limited by the high energy requirements and multistep processing. Effective approaches for directly reprocessing cross-linked PUs have been developed, but most require specialized monomers containing other dynamic functional groups or have less desirable mechanical properties. Therefore, interest has arisen in controlling the dynamics of carbamate linkages themselves to enable reprocessing, inspired by seminal work on cross-linked PU stress relaxation by Offenbach and Tobolsky. We recently reported that PHU networks synthesized from polyfunctional six-membered cyclic carbonates (6CCs) and amines demonstrate vitrimeric behavior in the absence of external catalysts, and attributed this behavior to associative transcarbamoylation reactions that might be facilitated by mechanical effects. Here we analyze the effects of PHU structure on the thermal stability, stress relaxation behavior, and reprocessability of cross-linked networks. We establish that PHU networks based on five-membered cyclic carbonates
(5CCs) undergo thermal reversion and subsequent side reactions at elevated temperature, making them poor candidates for PHU vitrimers. Vitrimeric behavior is observed in networks derived from several \textit{bis}(6CCs), which inform design criteria for the development of thermally reprocessable PHUs.

**Chapter 5.2 Results and Discussion**

**5.2.1 Thermal Stability of Polyhydroxyurethanes Derived from 5CCs and 6CCs**

We previously described the stress relaxation and reprocessing of two similar PHU networks derived from 6CCs at elevated temperatures.\textsuperscript{34} Polyfunctional 5CCs are also attractive monomers because they are derived from inserting carbon dioxide into epoxides,\textsuperscript{45} typically through solvent-free protocols. Polyfunctional epoxides are easily derived from many renewable feedstocks, thus, the corresponding PHUs are promising sustainable alternatives to PUs synthesized from isocyanate precursors.\textsuperscript{46,47,48} However, 5CC-derived PHUs contain predominantly secondary hydroxyl groups,\textsuperscript{49,50} as compared to the primary hydroxyl groups found in 6CC-derived networks. Given the lower nucleophilicity of secondary alcohols (which may or may not undergo transcarbamoylation reactions under similar conditions) and the much smaller concentration of primary hydroxyl groups in these PHUs, these materials might require higher temperatures for stress relaxation. Therefore, we explored whether networks derived from 5CCs exhibit vitrimeric behavior.

We synthesized \textit{bis}(5CC) 1 via the insertion of carbon dioxide into 1,4-butane diol diglycidyl ether. Monomer 1 was reacted with TREN using a 1:1 molar ratio of amine:5CC to give cross-linked PHU networks via reaction in DCM at room temperature, followed by heating under vacuum to remove solvent and yield PHU 3 as an orange solid.
(Figure 5.1). FT-IR spectroscopy showed complete disappearance of the initial cyclic carbonate C=O stretch (1790 cm\(^{-1}\), Figure 5.2A), as well as the appearance of multiple absorbances associated with PHU structure: O-H stretch (3300 cm\(^{-1}\)), urethane C=O stretch (1690 cm\(^{-1}\)), and urethane N-H deformation (1530 cm\(^{-1}\)). Swelling tests of the polymers in DCM show gel fractions in excess of 0.97, further supporting that these monomers react to high conversion under the synthesis conditions to give densely cross-linked PHU networks. To determine whether these networks would behave as vitrimers at elevated temperatures, we analyzed their stability to sustained heating to temperatures greater than 170 °C, where stress relaxation occurred within a reasonable timeframe in 6CC-based PHUs.\(^{34}\) New peaks appear in the FT-IR spectra of polymer 3 after heating for either 15 min or 5 h, indicating side reactions occurring at elevated temperatures (Figure 5.2A). Within 15 min, a new peak appeared at 1790 cm\(^{-1}\), corresponding to partial reversion of the hydroxyurethane linkages to corresponding cyclic carbonate and amine. After extended heating, further decomposition was observed with the emergence of a new carbonyl peak associated with urea linkages (1640 cm\(^{-1}\)) and a shift in carbonyl absorbance from 1690 cm\(^{-1}\) to 1720 cm\(^{-1}\). Identical experiments were performed with a PHU network synthesized from \(\text{bis}(6\text{CC})\) 2 and TREN (Figure 5.1);\(^{34}\) this network (4) shows no detectable change in the IR spectra under identical conditions (Figure 5.2B) indicating that the 6CC-derived PHU linkages are more thermally stable than those derived from 5CCs.
Figure 5.1: A) Reaction of bis(five-membered cyclic carbonate) 1 or bis(six-membered cyclic carbonate) 2 with TREN to give cross-linked polyhydroxyurethane 3 and 4, respectively, highlighting the presence of secondary hydroxyl groups present in polymer 3. B) Transcarbamoylation is the proposed mechanism of stress relaxation and reprocessing in cross-linked PHUs.

Figure 5.2: A) FT-IR spectra of monomer 1 (black), polymer 3 (blue), and polymer 3 after heating at 180 °C for 15 min (green) and 5 h (red). B) FT-IR spectra of monomer 2 (black), polymer 4 (blue), and polymer 4 after heating at 180 °C for 15 min (green) and 5 h (red).

The difference in thermal stability between hydroxyurethanes derived from 6CCs and 5CCs was further explored using model compounds 5 and 6 (Figure 5.3). The 5CC model compound 5 was used as a mixture of secondary (5a) and primary (5b) hydroxyl-containing carbamates to most accurately model the likely structure of the PHU network. 5 and 6 were heated to 180 °C for up to 5 h and analyzed by GC-MS at
intermediate time points. After 60 min at 180 °C, 5 partially decomposes back to the 5CC from which it derives. This decomposition product is observed more prominently after 5 h, along with additional secondary decomposition products. These include di-\textit{n}-butylurea, which is presumably formed from the nucleophilic attack of liberated \textit{n}-butylamine on the carbamate linkage of the model compound. The presence of the cyclic carbonate upon sustained heating was confirmed by $^1$H NMR spectroscopy (Figure 5.4), providing further support of this decomposition mechanism. In contrast, no reversion is observed in the 6CC model carbamate 6 (Figures 5.3B and 5.5) under the same conditions; the only other detectable species is a small amount of a compound containing two carbamates, originating from the reaction of the free hydroxyl group with another molecule of 6. These observations are consistent with those of the polymer networks 3 and 4, and likely reflect the greater thermodynamic stability of 5CCs compared to 6CCs. 6CCs are estimated to have ring strain of about 3 kcal/mol greater than 5CCs.\textsuperscript{51}

**Figure 5.3:** GC-MS chromatograms of **A)** model compound 5 and **B)** model compound 6 as-synthesized (blue) and after heating to 180 °C for 1 h (green) and 5 h (red). An x was placed over each internal standard peak.
Figure 5.4: $^1$H NMR Spectra (400 MHz, CDCl$_3$) of model compound mixture 5 before (blue) and after heating at 170 °C for 5 hours (red). The sharp peaks from ca. 4.50-4.65 are characteristic of the parent cyclic carbonate.
Figure 5.5: $^1$H NMR Spectra (400 MHz, CDCl$_3$) of model compound 6 before (blue) and after heating at 170 °C for 5 hours (red). No cyclic carbonate is observed.

Based on these observations, the likely decomposition pathway for 5CC-derived PHUs first involves the reversion of the hydroxyurethane linkage to the 5CC and free amine (Figure 5.6A). Free amines may undergo several side reactions at elevated temperature. They can react with cyclic carbonates at higher temperatures via an undesired decarboxylative mechanism that gives linkages unable to undergo further exchange (Figure 5.6B). Amines also add to carbamates to form ureas (Figure 5.6C), thus impacting the network composition. Free hydroxyl groups in the network might also react with the cyclic carbonate moiety to give ether (Figure 5.6D) or carbonate (Figure 5.6E) linkages. Additional side reactions such as oxazolidone formation are also possible according to literature reports. We have no direct evidence for the formation of these species but
cannot rule out their presence at low concentrations in the decomposed networks. Given the propensity of 5CCs to undergo this deleterious decomposition process at temperatures needed for stress relaxation, strained cyclic carbonates, such as 6CCs, are more effective precursors for PHU networks that display vitrimer-like behavior.

![Proposed breakdown of hydroxyurethanes derived from 5CCs](image)

**Figure 5.6:** Proposed breakdown of hydroxyurethanes derived from 5CCs, labeled with the FT-IR frequency of the carbonyl species. **A)** At elevated temperatures, the hydroxyurethane reverts to cyclic carbonate and amine; **B)** subsequently, amine may react with cyclic carbonate in a decarboxylative manner, **C)** amine may react with urethane linkages to form ureas, or **D)** free hydroxyls may react with cyclic carbonate to form ether or **E)** carbonate linkages.

### 5.2.2 6CC-derived Polyhydroxyurethane Networks with Tunable Mechanical Properties

Having established the superior thermal stability of 6CC-based PHUs, we designed a modular approach to evaluate structure-property relationships related to their stress relaxation. Most reported 6CCs have been evaluated for controlled ring-opening polymerizations,\textsuperscript{53,54,55} and only a few examples have been incorporated into PHUs.\textsuperscript{56,57} Pratt *et al.* studied the ring-opening polymerization of 6CC monomers based on esterifying the pendant carboxylic acid of the 6CC 7, which is derived from bis(hydroxymethyl)propionic acid.\textsuperscript{58} Suitable monomers for PHU networks can be prepared by esterifying diols with 7 using the same approach. Diols based on oligoether chains of differing length provide materials with lower $T_g$’s, and branched aliphatic diols
provide higher $T_g$ materials. In all cases, carbodiimide-mediated esterifications between the diols and 7 provided monomers of high purity, which were readily reacted with TREN to give densely cross-linked networks (Figure 5.7). FT-IR analysis of all polymers was consistent with the expected PHU structure (Figure 5.8). Amidation at the sterically hindered ester was not observed in model compounds under similar reaction conditions, as only products corresponding to carbamate formation were observed. No amide resonances were observed in the FT-IR spectra of the PHUs, and gel fractions and DMTA indicated the formation of highly cross-linked networks (Table 5.1, Figure 5.9A). Stress relaxation experiments at elevated temperatures in the linear viscoelastic regime (Figure 5.9B) showed markedly differing behavior between the samples. All of the 6CC-based PHUs exhibited reproducible stress relaxation with no change in their FT-IR spectra after extended heating (Figures 5.8 and 5.10). The low $T_g$ PHUs 8 and 9 exhibit faster stress relaxation than the higher $T_g$ materials 10 and 11. The Arrhenius activation energies for the oligoether-based materials were markedly lower (99 ± 6 kJ/mol for 8, and 108 ± 11 kJ/mol for 9) than those of the aliphatic systems (136 ± 8 kJ/mol for 10, and 134 ± 4 kJ/mol for 11); this difference was unexpected, given that transcarbamoylation is expected to be responsible for stress relaxation in all cases. Although speculative, we hypothesize that these differences arise from the increased flexibility of the polymer chains in the oligoether-containing networks or differences in dielectric constants of the ether-containing networks lowering the reaction barrier for transcarbamoylation.
Figure 5.7: Synthesis of PHUs based on bis(hydroxymethyl)propionic acid. Diols were esterified with carboxylic acid-containing 6CC 7 in the presence of DCC and DMAP. The resulting bis(6CC)s are reacted with TREN via gelation in CH$_2$Cl$_2$ and heating under vacuum to yield cross-linked polyhydroxyurethanes 8–11.

Figure 5.8: FT-IR spectra of 8 (red), 9 (blue), 10 (green), and 11 (orange) before (solid) and after (dashed) stress relaxation analysis at 190 ºC.
Figure 5.9: A) Dynamic mechanical thermal analysis, B) Arrhenius plots of characteristic stress relaxation times, and C), D) tensile testing data of as-synthesized (solid) and reprocessed (dashed) polyhydroxyurethane 8 (red), 9 (blue), 10 (green), and 11 (orange).

Table 5.1: Material Properties of Cross-linked Polyhydroxyurethanes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Gel %</th>
<th>$T_d$ (°C; 5%)</th>
<th>$T_g$ (°C; DSC)</th>
<th>$T_g$ (°C; DMTA)</th>
<th>$E'$ at 100 °C (MPa)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$T_v$ (°C)</th>
</tr>
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<tbody>
<tr>
<td>4 Ref. 34</td>
<td>99</td>
<td>263</td>
<td>54</td>
<td>61</td>
<td>7.5</td>
<td>110 ± 3</td>
<td>111</td>
</tr>
<tr>
<td>8</td>
<td>96</td>
<td>265</td>
<td>7</td>
<td>0</td>
<td>3.6</td>
<td>99 ± 6</td>
<td>93</td>
</tr>
<tr>
<td>9</td>
<td>99</td>
<td>270</td>
<td>35</td>
<td>25</td>
<td>4.5</td>
<td>108 ± 11</td>
<td>98</td>
</tr>
<tr>
<td>10</td>
<td>98</td>
<td>280</td>
<td>48</td>
<td>41</td>
<td>3.3</td>
<td>136 ± 8</td>
<td>115</td>
</tr>
<tr>
<td>11</td>
<td>94</td>
<td>276</td>
<td>54</td>
<td>51</td>
<td>2.0</td>
<td>134 ± 4</td>
<td>108</td>
</tr>
<tr>
<td>12</td>
<td>98</td>
<td>278</td>
<td>45</td>
<td>41</td>
<td>2.4</td>
<td>132 ± 9</td>
<td>111</td>
</tr>
<tr>
<td>13</td>
<td>98</td>
<td>292</td>
<td>45</td>
<td>47</td>
<td>1.6</td>
<td>128 ± 13</td>
<td>105</td>
</tr>
<tr>
<td>14</td>
<td>98</td>
<td>299</td>
<td>42</td>
<td>44</td>
<td>1.2</td>
<td>117 ± 11</td>
<td>95</td>
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Figure 5.10: Representative normalized stress relaxation analysis curves for A) polymer 8, B) polymer 9, C) polymer 10, and D) polymer 11 at 190 °C (red), 180 °C (green), and 170 °C (blue). The dashed line represents the characteristic relaxation time, $\tau^*$. 

To further verify that this stress relaxation is the result of productive transcarbamoylation processes, rather than a result of degradation of the networks, we reprocessed damaged PHUs at elevated temperatures. In all cases, compression molding of crushed/broken samples provided fused, albeit discolored, cross-linked polymers. Compression molding of each material for three times its characteristic stress relaxation time ($\tau^*$, defined as the time required for an applied stress to relax to 1/e of its original value) at 160 °C led to materials with similar macroscopic behavior, but reduced mechanical properties as determined by tensile testing (Figures 5.9C and D, Table 5.2). The reprocessed oligoether-based polymers 8 and 9 recover only about 20 to 30% of their original tensile strength, but both show increased strain at break. The stiffer, aliphatic diol-based polymers 10 and 11 recover 50 to 75% of their original tensile strength and show
Young's moduli comparable to as-synthesized samples, similar to results obtained in our initial reports on polymer 4,\textsuperscript{34} indicating that the presence of ethers versus esters in the backbone does not have a dramatic effect on reprocessability. A second reprocessing cycle was performed on polymer 11, and a similar additional decrease in mechanical properties was observed (Figure 5.11D, Table 5.3), indicating that the materials as currently formulated are not indefinitely recyclable. The more elastomeric behavior of the lower glass transition polymers 8 and 9, as well as the decreased tensile properties of the higher glass transition polymers 10 and 11 are consistent with the reprocessed materials having lower cross-linking densities than the as-synthesized samples, similar to our initial study.\textsuperscript{34} Despite these diminished properties, we note that FT-IR spectroscopy does not show any evidence of the structural changes in these networks.
Table 5.2: Tensile Properties of PHUs

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
<th>$E$ (GPa)</th>
<th>Temp ($^\circ$C); Time (min) healed</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
<th>$E$ (GPa)</th>
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</thead>
<tbody>
<tr>
<td>4 Ref. 34</td>
<td>72 ± 11</td>
<td>6.9 ± 3.8</td>
<td>2.2 ± 0.4</td>
<td>160; 480</td>
<td>53 ± 8</td>
<td>4.8 ± 0.8</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td>8</td>
<td>1.9 ± 0.4</td>
<td>56 ± 8</td>
<td>(4.8 ± 0.5) x 10$^{-3}$</td>
<td>160; 280</td>
<td>0.57 ± 0.04</td>
<td>114 ± 9</td>
<td>(7.7 ± 0.6) x 10$^{-4}$</td>
</tr>
<tr>
<td>9</td>
<td>30 ± 6</td>
<td>198 ± 15</td>
<td>0.6 ± 0.5</td>
<td>160; 225</td>
<td>6.7 ± 2.4</td>
<td>216 ± 23</td>
<td>0.05 ± 0.04</td>
</tr>
<tr>
<td>10</td>
<td>66 ± 4</td>
<td>4.0 ± 0.5</td>
<td>1.9 ± 0.2</td>
<td>160; 570</td>
<td>34 ± 14</td>
<td>1.5 ± 0.5</td>
<td>2.5 ± 0.3</td>
</tr>
<tr>
<td>11</td>
<td>61 ± 6</td>
<td>2.2 ± 0.4</td>
<td>3.0 ± 0.4</td>
<td>160; 495</td>
<td>47 ± 4</td>
<td>2.1 ± 0.2</td>
<td>2.63 ± 0.05</td>
</tr>
<tr>
<td>12</td>
<td>82 ± 7</td>
<td>4.5 ± 0.4</td>
<td>2.3 ± 0.3</td>
<td>160; 580</td>
<td>37 ± 17</td>
<td>1.9 ± 0.8</td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td>13</td>
<td>82 ± 10</td>
<td>4.3 ± 0.6</td>
<td>2.5 ± 0.2</td>
<td>160; 545</td>
<td>32 ± 7</td>
<td>1.5 ± 0.4</td>
<td>2.42 ± 0.08</td>
</tr>
<tr>
<td>14</td>
<td>69 ± 7</td>
<td>3.5 ± 0.3</td>
<td>2.4 ± 0.3</td>
<td>160; 400</td>
<td>49 ± 6</td>
<td>2.2 ± 0.3</td>
<td>2.5 ± 0.1</td>
</tr>
</tbody>
</table>

To determine if the reduced mechanical properties are predominantly due to minor degradation processes or inefficient bond formation, we annealed as-synthesized tensile bars under N$_2$ for identical amounts of time. Annealed samples provided somewhat reduced tensile properties compared to as-synthesized samples (Figures 5.11 and Table 5.3), but perform better than the reprocessed samples. This observation suggests that moderate decomposition may be occurring under the reprocessing conditions, but that bond
formation has not reached the same extent as in as-synthesized samples. Therefore, further work is required to determine optimal reprocessing conditions for each PHU, which either balance the competing bond formation and degradation processes or accelerate transcarbamoylation to allow reprocessing at lower temperatures.

**Figure 5.11:** Representative stress-strain curves of as-synthesized (solid), annealed under nitrogen for 3τ* (dotted), and reprocessed via compression molding for 3τ* (dashed) A) polymer 8, B) polymer 9, C) polymer 10, and C) polymer 11. The results of a second reprocessing cycle on polymer 11 are shown in D), as a dashed-dotted line, which is offset by 1% strain for easier visualization.
Table 5.3: Tensile Testing Data of Annealed Samples and Multiply Reprocessed Samples

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
<th>$E$ (GPa)</th>
<th>Temp (°C); Time (min) annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 Ref. 34</td>
<td>72 ± 11</td>
<td>6.9 ± 3.8</td>
<td>2.2 ± 0.4</td>
<td>160; 480</td>
</tr>
<tr>
<td>8</td>
<td>1.37 ± 0.04</td>
<td>165 ± 12</td>
<td>(1.3 ± 0.1) x 10^{-3}</td>
<td>160; 280</td>
</tr>
<tr>
<td>9</td>
<td>16 ± 3</td>
<td>194 ± 7</td>
<td>0.5 ± 0.2</td>
<td>160; 225</td>
</tr>
<tr>
<td>10</td>
<td>70 ± 12</td>
<td>2.7 ± 0.4</td>
<td>3.0 ± 0.4</td>
<td>160; 570</td>
</tr>
<tr>
<td>11</td>
<td>63 ± 6</td>
<td>3.0 ± 0.4</td>
<td>2.5 ± 0.3</td>
<td>160; 495</td>
</tr>
<tr>
<td>12</td>
<td>78 ± 7</td>
<td>3.7 ± 0.3</td>
<td>2.5 ± 0.5</td>
<td>160; 580</td>
</tr>
<tr>
<td>13</td>
<td>76 ± 4</td>
<td>4.3 ± 0.4</td>
<td>2.4 ± 0.1</td>
<td>160; 545</td>
</tr>
<tr>
<td>14</td>
<td>69 ± 10</td>
<td>3.6 ± 0.7</td>
<td>2.5 ± 0.1</td>
<td>160; 400</td>
</tr>
<tr>
<td>Second Reprocessing Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>35 ± 8</td>
<td>1.5 ± 0.4</td>
<td>2.4 ± 0.1</td>
<td>160; 495</td>
</tr>
<tr>
<td>14</td>
<td>32 ± 10</td>
<td>1.7 ± 0.8</td>
<td>2.1 ± 0.2</td>
<td>160; 400</td>
</tr>
</tbody>
</table>

5.2.3 Effects of Cross-link density on Cross-linked Polyhydroxyurethane Stress Relaxation

To gain more insight into the factors that govern stress-relaxation phenomena in PHUs, we varied the cross-link density of the networks without significantly varying their chemical composition. Monomer 2 was reacted with varying ratios of HMDA and TREN (Figure 5.12A). FT-IR analysis of all polymers (Figure 5.13) showed complete disappearance of the initial cyclic carbonate C=O stretch (1740 cm^{-1}), and the appearance of an O-H stretch (3300 cm^{-1}) and urethane C=O stretch (1690 cm^{-1}), indicating high conversion of the polymerization. The $T_g$ of the networks, as determined by DSC, increased slightly with increasing cross-link density (from ca. 45–54 °C), consistent with limited change in the chemical structure of the network. DMTA indicated...
an expected increased rubbery plateau modulus/decreased molar mass between cross-links of these materials with increased cross-linker content (Figure 5.12B). Stress relaxation analysis performed from 170 to 190 °C in the linear viscoelastic regime shows a general trend of faster stress relaxation with lower cross-link density (Figures 5.12C and 5.14), as has been reported in other vitrimer systems. In all cases, FT-IR analysis after multiple stress relaxation experiments shows no detectable change in chemical functionality (Figure 5.13) indicating that the relaxation process is likely caused predominantly by transcarbamoylation reactions. The Arrhenius activation energy of stress relaxation is highest in samples with intermediate cross-link densities (132 ± 9 kJ/mol for 12 and 128 ± 13 kJ/mol for 13), while lower activation energies were measured at the lowest cross-link density (117 ± 11 kJ/mol for 14) and highest cross-link density (110 ± 10 kJ/mol for 4). While some of these activation energy values are essentially within error of the measurement, differences in relaxation behavior between the polymers of varying cross-link density are evident (Figure 5.15). While we are unsure of the exact cause of this change, we note that similar trends in activation energy have been observed when changing network structure in polyester vitrimers when stress relaxation was performed at temperatures close to the $T_g$. Given that the networks are of similar chemical composition, it is likely that chemical effects on transcarbamoylation dynamics are negligible, so we attribute this change in activation energy to differences in the stiffness of the materials. Although no clear trend is observed between the storage modulus and either the activation energy or pre-exponential factor of the Arrhenius model (Figure 5.15), it is possible that the urethane linkages may experience different levels of stress depending on the cross-link density. It is likely that the varying degree of stiffness for different PHUs might affect the
ability of reactive groups to adopt appropriate trajectories for transcarbamoylation. Further investigation is required to fully understand the degree to which these mechanical factors impact PHU stress relaxation.

Figure 5.12: A) Synthesis of cross-linked polyhydroxyurethanes of varied cross-linked density via reaction of monomer 2 with mixtures of hexamethylenediamine (HMDA) and TREN. B) Dynamic mechanical thermal analysis and C) Arrhenius plots of characteristic stress relaxation times of cross-linked polyhydroxyurethane 4 (black, Ref. 34), 12 (green), 13 (orange), and 14 (blue).
Figure 5.13: FT-IR spectra of 12 (green), 13 (orange), and 14 (blue), before (solid) and after (dashed) stress relaxation analysis at 190 °C.
Figure 5.14: Representative normalized stress relaxation analysis curves for A) polymer 12, B) polymer 13, and C) polymer 14 at 190 °C (red), 180 °C (green), and 170 °C (blue). The dashed line represents the characteristic relaxation time, $\tau^\ast$.

Figure 5.15: A) Arrhenius activation energy of stress relaxation and B) $\tau_0$, the pre-exponential factor of the Arrhenius relationship between $\tau^\ast$ and temperature as a function of rubbery storage modulus for polymers 4 and 12-14.

Reprocessing experiments were performed to determine how cross-link density affects reprocessability of the PHUs and further demonstrate that stress relaxation is caused
by productive transcarbamoylation reactions. Reprocessing of all samples at 160 °C for 3τ* yields macroscopically repaired samples. Interestingly, while all samples discolor upon reprocessing, the samples with lowest TREN loadings discolor the least (Figure 5.16A), consistent with an increase in decomposition temperature of ca. 35 °C observed with decreasing cross-linker content (Table 5.1). These observations suggest that tertiary amines are a source of decomposition in these materials. Tensile testing of the as-synthesized and reprocessed samples shows moderate reprocessing efficiencies (Figure 5.16B, Table 5.2), which are in agreement with expected trends in tertiary amine content. A second reprocessing cycle on polymer 14 yields similar reprocessing efficiency, resulting in further diminished mechanical properties (Figure 5.17). We note that these reprocessing conditions are not fully optimized for any particular sample; therefore, better reprocessing efficiency is likely possible given the very similar Young's moduli of the as-synthesized, annealed (Figure 5.17, Table 5.3), and reprocessed samples (Table 5.1). This behavior suggests that design of future PHU vitrimers could benefit from the design of higher functional cyclic carbonate cross-linkers or of aliphatic polyamines that lack tertiary amines within the network.
Figure 5.16: A) Photos of as-synthesized (left column) and reprocessed (right column) PHUs 12–14. Annealed samples have the same level of discoloration as the reprocessed samples. B) Tensile testing data of as-synthesized (solid) and reprocessed (dashed) polyhydroxy-urethane 12 (green), 13 (orange), and 14 (blue). Reprocessed samples are shifted right by 1% strain for easier visualization.
Figure 5.17: Representative stress-strain curves of as-synthesized (solid), annealed under nitrogen for $3\tau^*$ (dotted), and reprocessed via compression molding for $3\tau^*$ (dashed) A) polymer 12, B) polymer 13, and C) polymer 14. The annealed and reprocessed traces are shifted to the right by 1% strain for easier visualization. The results of a second reprocessing cycle on polymer 14 are shown in C) as a dashed-dotted line, which is also offset by 1% strain for easier visualization.

Chapter 5.3 Conclusions

We have evaluated PHU networks derived from 5CCs and 6CCs as reprocessable cross-linked networks. The higher thermodynamic stability of 5CCs leads to reversion and subsequent decomposition in 5CC-derived PHUs at temperatures required for reprocessing in densely cross-linked thermosets, while this decomposition is not observed in networks derived from 6CCs. We have further determined that the Arrhenius activation energy of stress relaxation in a variety of PHUs is highly dependent on the exact network structure, indicating that multiple processes may be possible for these relaxations or that
transcarbamoylation is impacted by the exact nature of the polymer network, either by chemical or mechanical factors. Furthermore, we demonstrate that these cross-linked materials can be reprocessed, although with somewhat diminished mechanical properties; despite the loss of performance, most reprocessed materials would be appropriate for similar structural applications as the pristine materials. We observed that the loss of mechanical properties is more pronounced with increased concentration of tertiary amines within the polymer networks. Therefore, we suggest that development of polyfunctional six-membered cyclic carbonates or polyfunctional aliphatic amines containing no tertiary amines may allow for the synthesis of PHU networks with improved reprocessing capabilities. Taken together, this work demonstrates the promise and design criteria for employing PHUs as sustainable and reprocessable thermoset-like materials.

**Chapter 5.4 Experimental**

**Chapter 5.4.1 Materials**

All reagents were purchased from Sigma-Aldrich or Fisher Scientific. Tris(2-aminoethyl)amine (TREN) was stirred over calcium hydride and distilled prior to use; all other reagents were used without further purification. Dichloromethane (CH₂Cl₂), tetrahydrofuran (THF), and dimethylformamide (DMF) were purchased from Fisher Scientific and purified using a custom-built alumina-column based solvent purification system. Other solvents were used without further purification. Di(trimethylolpropane)-based bis(cyclic carbonate) 2,⁶⁰ 6CC-based hydroxyurethane model compound 6,³⁴ and carboxylic acid functionalized 6CC (7)⁵⁸ were synthesized according to the literature procedures.

**Chapter 5.4.2 Synthetic Procedures**
Synthesis of 1

To a stainless steel pressure reactor was added 1,4-butanediol diglycidyl ether (11.95 g, 59.2 mmol), zinc iodide (180 mg, 0.5 mmol), and tetrabutylammonium iodide (180 mg, 0.5 mmol). The reactor was sealed and pressurized with 100 psi carbon dioxide, then heated to 100 °C for 36 h, while stirring the mixture. The reactor was allowed to cool and the residue was diluted with CH$_2$Cl$_2$ (300 mL), washed with H$_2$O (2 × 200 mL), dried over MgSO$_4$, filtered, and the solvent was removed at reduced pressure to yield an off-white solid. The solid was recrystallized from EtOH to yield 1 as a white solid (14.9 g, 87%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.85–4.77 (m, 2H), 4.60 (t, $J=8.4$ Hz, 2H), 4.44–4.37 (m, 2H), 3.74–3.47 (m, 8H), 1.68–1.61 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.0, 75.1, 71.3, 69.4, 66.0, 25.8. IR (solid, ATR) 2869, 1779 (C=O), 1396, 1101, 1073, 1043, 767, 713 cm$^{-1}$. The $^1$H and $^{13}$C NMR data match those previously reported.$^{61}$

Synthesis of 5CC Hydroxyurethane Model Compound (5)

In a round-bottom flask, 3-phenoxypropylenecarbonate (1.0 g, 5.13 mmol) and n-butylamine (413 mg, 5.64 mmol) were dissolved in anhydrous DMF (5.0 mL). The mixture was heated to 70 °C, and 1,8-diaza[5.4.0]undec-7-ene (DBU, 78 mg, 76 µL, 0.5 mmol) was added via syringe. The mixture was stirred at 70 °C for 12 h, then cooled to room temperature. The solution was partitioned between H$_2$O (50 mL) and EtOAc (50 mL), and the aqueous layer was washed with EtOAc (2 × 50 mL). The combined organic layers were dried over MgSO$_4$, filtered, and solvent was removed at reduced pressure to yield a yellowish oil. The resulting oil was chromatographed in EtOAc to yield the mixture of products as a colorless oil, which slowly solidified to a white, waxy solid (1.16 g, 85%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31–7.25 (m), 6.99–6.94 (m), 6.94–6.90 (m), 5.11–5.00
(m), 4.33–4.12 (m), 4.01 (d, J = 5.6 Hz, major), 3.89 (t, J = 5.2 Hz, minor), 3.50 (d, J = 4.0 Hz, minor), 3.17 (q, J = 6.5 Hz), 2.99 (t, J = 6.2 Hz, minor), 2.13 (s, major), 2.05 (s, major), 1.53–1.41 (m), 1.40–1.24 (m), 0.92 (t, J = 7.5 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.3, 156.8 (major C=O), 156.2 (minor C=O), 129.4, 121.1, 114.5, 73.4 (minor), 68.9 (major), 68.4 (major), 66.5 (minor), 65.9 (major), 62.2 (minor), 40.8, 31.8, 19.8, 13.6. IR (solid, ATR) 3337, 2957, 2871, 1689 (C=O stretch), 1540 (N-H deformation), 1232, 1059, 752 cm$^{-1}$. HRMS (ESI) calcd. for [C$_{14}$H$_{21}$NO$_4$+Na]$^+$ 290.1363 found 290.1369.

**Synthesis of a tetraethylene glycol-based bis(6CC)**

To a flame-dried round-bottom flask under nitrogen atmosphere was added 5-methyl-2-oxo-1,3-dioxane-5-carboxylic acid (4.00 g, 25 mmol), tetraethylene glycol (2.33 g, 12 mmol), and 25 mL anhydrous DMF. To the homogeneous solution was added 4-dimethylaminopyridine (DMAP, 300 mg, 2.5 mmol), and the solution was allowed to stir until the DMAP had fully dissolved. The solution was cooled to 0°C, solid N,N'-dicyclohexylcarbodiimide (5.30 g, 25.7 mmol) was added, and a white precipitate formed. The resulting mixture was allowed to stir and warm to room temperature for 18 hours. The mixture was filtered, and solid was washed with 200 mL EtOAc. The EtOAc was removed at reduced pressure, and 250 mL Et$_2$O was added; this mixture was allowed to stand until an oil separated from the Et$_2$O layer. The resulting oil was chromatographed on silica gel in 20% acetone/EtOAc to yield the desired product as a colorless oil (2.0 g, 35%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.71 (d, J = 10.9 Hz, 4H), 4.36 (m, 4H), 4.21 (d, J = 10.9 Hz, 4H), 3.70 (m, 4H), 3.63 (m, 8H), 1.32 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.6, 146.9, 72.3, 69.7, 67.9, 64.1, 39.5, 16.4. IR (neat, ATR) 2924, 1755, 1732, 1464, 1403, 1237, 1172, 1132, 1097, 1029 cm$^{-1}$. HRMS (ESI) calcd. for [C$_{20}$H$_{30}$O$_{13}$+H]$^+$ 479.1759 found 479.1769.
Synthesis of a diethylene glycol-based bis(6CC)

To a flame-dried round-bottom flask under nitrogen atmosphere was added 5-methyl-2-oxo-1,3-dioxane-5-carboxylic acid (4.00 g, 25 mmol), diethylene glycol (1.28 g, 12 mmol), and 25 mL anhydrous DMF. To the homogeneous solution was added DMAP (300 mg, 2.5 mmol), and the solution was allowed to stir until the DMAP had fully dissolved. The solution was cooled to 0°C, solid N,N’-dicyclohexylcarbodiimide (5.30 g, 25.7 mmol) was added, and a white precipitate formed. The resulting mixture was allowed to stir and warm to room temperature for 18 hours. The mixture was filtered, and solid was washed with 200 mL EtOAc. The EtOAc was removed at reduced pressure, 250 mL Et₂O was added, and the mixture was cooled, resulting in separation of a yellowish oil. The resulting oil was chromatographed on silica gel in 10% acetone/EtOAc to yield the desired product as a yellowish oil (2.37 g, 50%). ¹H NMR (400 MHz, CDCl₃) δ 4.71 (d, J = 10.8 Hz, 4H), 4.35 (m, 4H), 4.28 (d, J = 10.8 Hz, 4H), 3.69 (m, 4H), 1.33 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 171.0, 147.4, 72.8, 68.5, 64.7, 40.1, 17.2. IR (neat, ATR) 2962, 1747, 1728, 1463, 1403, 1236, 1170, 1131, 1096, 1031 cm⁻¹. HRMS (ESI) calcd. for [C₁₆H₂₂O₁₁+H]⁺ 391.1235 found 391.1245.

Synthesis of a neopentyl glycol-based bis(6CC)

To a flame-dried round-bottom flask under nitrogen atmosphere was added 5-methyl-2-oxo-1,3-dioxane-5-carboxylic acid (4.00 g, 25 mmol), neopentyl glycol (1.25 g, 12 mmol), and 25 mL anhydrous DMF. To the homogeneous solution was added DMAP (300 mg, 2.5 mmol), and the solution was allowed to stir until the DMAP had fully dissolved. The solution was cooled to 0°C, solid N,N’-dicyclohexylcarbodiimide (5.30 g, 25.7 mmol) was added, and a white precipitate formed. The resulting mixture was allowed
to stir and warm to room temperature for 18 hours. The mixture was filtered, and solid was washed with 200 mL EtOAc. The EtOAc was removed at reduced pressure, and 250 mL Et₂O was added, resulting in the formation of a white solid. The solid was recrystallized from 250 ml toluene to yield the desired product as a white, needle-like crystals (2.2 g, 47%). ¹H NMR (300 MHz, DMSO) δ 4.56 (d, J = 10.4 Hz, 4H), 4.37 (d, J = 10.4 Hz, 4H), 3.97 (s, 4H), 1.18 (s, 6H), 0.94 (s, 6H). ¹³C NMR (75 MHz, DMSO) δ 171.5, 147.2, 72.5, 69.4, 39.9, 34.7, 21.1, 16.3. IR (solid, ATR) 2965, 1741, 1725, 1469, 1397, 1237, 1172, 1133, 1095 cm⁻¹. HRMS (ESI) calcd. for [C₁₇H₂₄O₁₀+H]⁺ 389.1442 found 389.1451.

**Synthesis of a 2,2-diethylpropane-1,3-diol-based bis(6CC)**

To a flame-dried round-bottom flask under nitrogen atmosphere was added 5-methyl-2-oxo-1,3-dioxane-5-carboxylic acid (4.00 g, 25 mmol), 2,2-diethylpropane-1,3-diol (1.59 g, 12 mmol), and 25 mL anhydrous DMF. To the homogeneous solution was added 4-dimethylaminopyridine (300 mg, 2.5 mmol), and the solution was allowed to stir until the DMAP had fully dissolved. The solution was cooled to 0°C, solid N,N′-dicyclohexylcarbodiimide (5.30 g, 25.7 mmol) was added, and a white precipitate formed. The resulting mixture was allowed to stir and warm to room temperature for 18 hours. The mixture was filtered, and solid was washed with 200 mL EtOAc. The EtOAc was removed at reduced pressure, and 250 mL Et₂O was added, resulting in the formation of a white solid. The solid was recrystallized from 250 ml toluene to yield the desired product as white crystals (2.98 g, 60%). ¹H NMR (400 MHz, CDCl₃) δ 4.67 (d, J = 10.8 Hz, 4H), 4.22 (d, J = 10.8 Hz, 4H), 4.06 (s, 6H), 1.37 (q, J = 7.9 Hz, 4H), 1.32 (s, 6H), 0.96 (t, J = 7.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 170.9, 147.3, 72.9, 66.4, 40.4, 40.0, 22.8, 17.2, 6.8.
IR (solid, ATR) 2976, 1754, 1724, 1469, 1396, 1233, 1173, 1134, 1096 cm\(^{-1}\). HRMS (ESI) calcd. for \([C_{19}H_{28}O_{10}+H]^+\) 417.1755 found 417.1767.

**Synthesis of hydroxyurethane model compound 6**

To a vial was added solid trimethylene carbonate (1.286 g, 12.6 mmol); the vial was heated to 60 °C, resulting in a clear melt. Butylamine (920 mg, 12.6 mmol) was added via syringe, and the mixture was heated at 60 °C for 24 hours. The resulting oil was chromatographed on silica gel in ethyl acetate to yield compound 6 as a colorless oil (2.09 g, 95%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) 4.71 (br s, 1H), 4.24 (t, \(J = 5.8\) Hz, 2H), 3.67 (m, 2H), 3.18 (m, 2H), 2.60 (br s, 1H), 1.85 (quintet, \(J = 6.1\) Hz, 2H), 1.47 (m, 2H), 1.35 (m, 2H), 0.93 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) 157.2, 61.5, 58.7, 40.7, 32.2, 31.9, 19.8, 13.6. IR (liquid, ATR) 3324, 2958, 2932, 2874, 1690 (C=O stretch), 1538 (N-H deformation), 1248, 1053 HRMS (ESI) calcd. for \([C_8H_{17}NO_3+Na]^+\) 198.11006, found 198.10956. The characterization data match those previously reported in the literature.\(^{34}\)

**General Procedure for Synthesis of Cross-Linked PHUs**

**Bis**(cyclic carbonate) (ca. 800 mg), tris(2-aminoethyl)amine (**TREN**), and hexamethylenediamine (**HMDA**) (1 eq. total amine to cyclic carbonate) were dissolved in a minimum amount of CH\(_2\)Cl\(_2\) (ca. 3.0 mL). Solutions were sonicated for at least one minute to ensure homogeneity, then poured into an aluminum mold (60 mm (\(D\)) × 10 mm (\(H\))). Within less than 1 h, the samples formed homogeneous gels. The resulting gels were allowed to stand at room temperature for about 24 h. Samples were cut from the resulting transparent films, and subjected to reduced pressure at 90 °C and 20 mTorr for about 48 h to ensure complete cross-linking and removal of solvent. Samples containing HMDA were initially heated to 60 °C under vacuum for 24 h, followed by heating at 90 °C for 24 h under...
vacuum to avoid bubbling of the films upon CH$_2$Cl$_2$ evaporation. Gel fractions of the resulting samples were determined by swelling in CH$_2$Cl$_2$ for 48 h, then drying the polymers under 20 mtorr vacuum at 50 °C for 48 h. See below for further characterization data:

2: IR (solid, ATR) 3297, 2962, 2880, 1689 (C=O stretch), 1527 (N-H deformation), 1460, 1257, 1105, 1020 cm$^{-1}$.

3: IR (solid, ATR) 3316 (O-H stretch), 2940, 2866, 1688 (C=O stretch), 1530 (N-H deformation), 1456, 1247, 1104, 775 cm$^{-1}$.

8: IR (solid, ATR) 3360 (O-H stretch), 2880, 1716 (shoulder), 1695 (C=O stretch), 1530 (N-H deformation), 1456, 1242, 1121, 1047 cm$^{-1}$.

9: IR (solid, ATR) 3342 (O-H stretch), 2944, 1716 (shoulder), 1691 (C=O stretch), 1528 (N-H deformation), 1458, 1242, 1120, 1044 cm$^{-1}$.

10: IR (solid, ATR) 3366 (O-H stretch), 2962, 1720 (shoulder), 1694 (C=O stretch), 1529 (N-H deformation), 1463, 1241, 1126, 1045, 1019 cm$^{-1}$.

11: IR (solid, ATR) 3365 (O-H stretch), 2966, 1726 (shoulder), 1696 (C=O stretch), 1529 (N-H deformation), 1461, 1238, 1128, 1046 cm$^{-1}$.

12: IR (solid, ATR) 3317 (O-H stretch), 2930, 2880, 1687 (C=O stretch), 1531 (N-H deformation), 1461, 1250, 1110, 1031 cm$^{-1}$.

13: IR (solid, ATR) 3308 (O-H stretch), 2931, 2879, 1687 (C=O stretch), 1531 (N-H deformation), 1249, 1107, 1033 cm$^{-1}$.

14: IR (solid, ATR) 3298 (O-H stretch), 2929, 1688 (C=O stretch), 1532 (N-H deformation), 1462, 1250, 1107 cm$^{-1}$.
Chapter 5.4.3 Characterization Methods

Infrared spectra were recorded on a Thermo Nicolet iS10 or a Bruker Alpha Platinum; both were equipped with a diamond ATR attachment and spectra were uncorrected.

Gas chromatography/electron impact mass spectrometry was performed on an Agilent 6890N Network GC System with a JEOL JMS-GCmate II Mass Spectrometer (magnetic sector). Di-tert-butylbiphenyl or triphenylmethane were utilized as internal standards.

NMR spectra were recorded on a Varian 400 MHz or an Agilent DD MR-400 400 MHz spectrometer using a standard $^1$H/X Z-PFG probe at ambient temperature.

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo SDTA851 Thermogravimetric Analysis System. Samples were heated under a nitrogen atmosphere at a rate of 10 °C/min from 30 °C to 600 °C.

Differential scanning calorimetry (DSC) was performed on a TA instruments Q1000 Differential Scanning Calorimeter or a Mettler Toledo DSC822 Differential Scanning Calorimeter. Samples were heated at a rate of 10 °C/min to at least 130 °C to erase thermal history, cooled to at least −30 °C at 10 °C/min, and then heated to at least 130 °C. All data shown are taken from the second heating ramp. The glass transition temperature ($T_g$) was calculated from the maximum value of the derivative of heat flow with respect to temperature.

Dynamic mechanical thermal analysis (DMTA) was performed on a TA Instruments RSA-G2 analyzer (New Castle, DE) utilizing rectangular films (ca. 0.5 mm $(T) \times 5$ mm $(W) \times 10$ mm $(L)$). The axial force was adjusted to 0 N and a strain adjust of
30% was set with a minimum strain of 0.05%, a maximum strain of 5%, and a maximum force of 1 N in order to prevent the sample from buckling or going out of the specified strain. Furthermore, a force tracking mode was set such that the axial force was twice the magnitude of the oscillation force. A temperature ramp was then performed from 20 °C to 200 °C (−40 °C to 200 °C for low glass transition materials) at a rate of 5 °C/min, with an oscillating strain of 0.05% and an angular frequency of 6.28 rad s\(^{-1}\) (1 Hz). The glass transition temperature (\(T_g\)) was calculated from the maximum value of the loss modulus (\(G''\)).

Uniaxial tensile testing was conducted using dog bone shaped tensile bars (ca. 0.5 mm (\(T\) × 3 mm (\(W\) × 25 mm (\(L\) and a gauge length of 14 mm). The samples were aged for at least 48 h at 22 °C in a desiccator prior to testing. Tensile measurements were performed on a Shimadzu Autograph AGS-X Series tensile tester (Columbia, MD) at 22 °C with a uniaxial extension rate of 5 mm/min. Young's modulus (\(E\)) values were calculated using the Trapezium software by taking the slope of the stress–strain curve from 0 to 1 N of force applied. Reported values are the average and standard deviations of at least five samples.

Stress relaxation analysis (SRA) was performed on a TA Instruments RSA-G2 analyzer (New Castle, DE) utilizing rectangular films (ca. 0.5 mm (\(T\) × 5 mm (\(W\) × 10 mm (\(L\)). The SRA experiments were performed in a strain control at specified temperature (170–190 °C). The samples were allowed to equilibrate at this temperature for approximately 10 min, after which the axial force was then adjusted to 0 N with a sensitivity of 0.05 N. Subsequently, each sample was subjected to an instantaneous 5% strain. The stress decay was monitored, while maintaining a constant strain (5%), until the
stress relaxation modulus had relaxed to at least 37% (1/e) of its initial value. This was performed three times for each sample. The activation energy ($E_a$) and freezing transition temperature ($T_v$) were determined utilizing the methodology in literature.\textsuperscript{15,16}

To reprocess the materials, the polymer was broken into small pieces and then placed into a PTFE coated (Sprayon MR311) aluminum dog bone shaped mold (\textit{ca.} 0.5 mm ($T$) \times 3 mm ($W$) \times 25 mm ($L$) and a gauge length of 14 mm) between two thin Teflon\textsuperscript{®} sheets. This assembly was placed in a Wabash-MPI compression mold (Wabash, IN), which was preheated to the desired temperature. The material was allowed to thermally equilibrate for two min, followed by a 2 min period of rapidly increasing the pressure to 4 MPa then reducing back to 0 MPa in order to remove air bubbles. The pressure was then increased to 4 MPa and allowed to heat for varying periods of time and then rapidly cooled to room temperature over the course of 5 min using the water cooling function of the compression mold. A similar procedure was performed for rubbery samples, which were compression molded in a square mold ($5 \text{ cm} \times 5 \text{ cm}$), and tensile specimens were punched from the sheets after cooling. The resulting tensile bars were then allowed to age for 48 h in a desiccator and subjected to uniaxial tensile testing in order to determine their recovery in mechanical properties. Reported values are the average and standard deviations of at least five samples.

Annealed samples were prepared by heating as-synthesized tensile bars of the cross-linked polymers in an oven under a nitrogen atmosphere. The resulting tensile bars were aged for 48 h in a desiccator and subjected to uniaxial tensile testing to compare their mechanical properties to as-synthesized or reprocessed samples. Reported values are the average and standard deviations of at least five samples.
Chapter 5.5 References


Chapter 6. Renewable, Degradable, and Chemically Recyclable Cross-linked Elastomers*

Most commercial elastomers, typified by vulcanized natural rubber, are cross-linked polymers and as such cannot easily be reprocessed or recycled. While some are derived from renewable resources, the majority are produced from petroleum feedstocks and do not easily degrade. In this study, renewable elastomers based on β-methyl-δ-valerolactone were produced using two different methodologies: 1) tandem copolymerization/cross-linking with a bis(6-membered cyclic carbonate) and 2) cross-linking of a linear poly(β-methyl-δ-valerolactone) homopolymer with a free-radical generator. The mechanical properties of these materials were investigated; tensile strengths of up to 12 MPa and elongations up to 2000% were observed. Inclusion of a filler (fumed silica) was used to enhance the performance of the elastomers without significant loss of elasticity with some composites exhibiting tensile strengths nearly double the neat elastomer. Aqueous degradation studies indicated that the materials were capable of degradation in acidic and basic conditions at 60 °C. Moreover, these cross-linked elastomers can also be chemically recycled, yielding monomer in high purity and yield (>91% and 93%, respectively).

Chapter 6.1 Introduction

Cross-linked polymers (CPs) encompass almost a third of the synthetic polymer industry and are vital in a wide variety of products including tires, contact lenses, elastomers, adhesives, and foams. While cross-linking confers a number of advantages, including high thermal stability and solvent resistance, this structure also prevents these

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materials from being reprocessed. Postconsumer CPs are consequentially disposed of in landfills or by incineration, leading to significant loss of value.\textsuperscript{1} Additionally, the vast majority of synthetic polymers—including CPs—are petroleum-derived and non-degradable. Their production and disposal is therefore unsustainable in the long term. In recent years, considerable effort has been devoted to the development of CPs that are recyclable, some of which are also renewable.\textsuperscript{2,3,4,5,6,7,8}

Among the palate of renewable polymers, aliphatic polyesters are particularly attractive because they are easily synthesized and in many cases are also biodegradable and biocompatible.\textsuperscript{9,10,11} In numerous previous examples, aliphatic polyesters have been used to prepare thermoplastic elastomers (TPEs) that mimic styrenic block polymers in both design and performance.\textsuperscript{12,13,14,15,16,17,18,19,20,21,22} Conveniently, the thermal and mechanical properties of these TPEs can be easily tuned by altering the size and composition of the discrete polymer blocks. Unfortunately, TPEs typically have poor solvent resistance, low thermal stability, and often exhibit significant stress softening (known as the Mullins effect).\textsuperscript{23} Finally, polyester TPEs often require rigorous reaction conditions to ensure proper morphology; variations in dispersity and the presence of adventitious initiators can result in a dramatic reduction of toughness.

These issues are often resolved by the use of CPs, as they exhibit both high thermal stability and solvent resistance. A number of methods have been developed for cross-linking polyesters to improve their thermal, physical, and mechanical properties. These methodologies frequently employ hydroxy-multifunctional polyesters, or polyesterols, such as poly(lactide) (PLA) and poly(\(\varepsilon\)-caprolactone) (PCL). Polyesterols can be cross-linked using condensation reactions or further functionalized and subsequently cross-
As the polyesterols are synthesized by either step growth condensation or ring-opening transesterification polymerization (ROTEP), their reactive groups are generally terminal. In theory, the coupling efficiency should not be influenced by molar mass; in practice, low molar mass \(M_n \leq 5 \text{ kg mol}^{-1}\) to end group is often necessary to precisely target a balanced stoichiometry for the cross-linking reaction such that it reaches high conversion. As a result, the range of accessible molar masses between cross-links \(M_x\) is rather constrained. Improvements in the mechanical properties of CPs have been attributed to large \(M_x\) values. Most notably, ultimate elongation increases with \(M_x\). Furthermore, higher \(M_x\) allows entanglements to form, which behave as transient physical cross-links; a lower molar mass between entanglements \(M_e\) in the constituent polymer will increase the number of physical cross-links, also improving the mechanical properties.\(^{31}\)

Other strategies have been developed for polyesters to overcome these deficiencies. One method, tandem copolymerization/cross-linking, allows for direct conversion of monomers to CPs. Although this approach eliminates processing steps, it comes with its own challenges. For example, due to problems with solubility, high concentrations of bis(\(\varepsilon\)-caprolactone) cross-linkers (8 to 28 mol\%) are often required, rendering it difficult to tune the mechanical properties of the CPs in a controlled manner.\(^{32,33}\) Bis(6-membered cyclic carbonates) have been utilized at much lower loadings (1 mol\%) when copolymerized directly with \(\varepsilon\)-caprolactone (CL), but this system likely suffered from reactivity differences as well.\(^{34,35}\) The inclusion of trimethylene carbonate (50 mol\%) allowed for lower concentrations of cross-linker (0.05 mol\%) and resulted in an amorphous material; however, the mechanical properties of the resulting material are poor.
A second method that has been used to access tunable polyester elastomers is ROTEP of alkene-functionalized lactone comonomers with saturated aliphatic lactones (e.g., CL) to produce statistical copolymers. These copolymers can be cross-linked in subsequent steps using free radical or thiol-ene click reactions. While the properties of these CPs can be easily tuned, the alkene comonomers are often prohibitively expensive and/or challenging to synthesize on a large scale. Alkene functionalized macrolactones are more economical, however, their polymerization may also require the use of enzymatic polymerization catalysts, which can be limiting. Interestingly, free radical generators are capable of cross-linking fully saturated polyesters. Typically, this involves the thermal cross-linking of the polyester with an organic peroxide. Though this allows for facile tuning of the mechanical properties, these studies have been confined to high glass transition temperature ($T_g$) and/or semi-crystalline materials, which are not ideal for elastomers. In fact, there is a dearth of literature on tough, cross-linked amorphous, low $T_g$ polyesters; preceding examples have indicated poor tensile properties due to limits on $M_x$ dictated by the methodologies used. Those with competitive properties generally have a $T_g$ that is above –40 °C, limiting the scope of their potential applications.

We have demonstrated that β-methyl-δ-valerolactone (MVL) can be produced renewably on a large scale and can be polymerized in the bulk to afford poly(β-methyl-δ-valerolactone) (PMVL). The properties of amorphous PMVL ($T_g = -52 \degree C$ and $M_e = 4.3 \text{ kg mol}^{-1}$) make it an attractive polymer for use in a wide range of applications. For example, we have explored the use of PMVL in tough plastics, thermoplastic elastomers, soft polyurethane foams, and thermoplastic polyurethanes. Furthermore, PMVL has been
shown to depolymerize in the presence of catalyst, allowing for controlled recovery of pure monomer.\textsuperscript{45}

Herein, we report the production cross-linked elastomers prepared from PMVL. We use two different synthetic strategies: tandem copolymerization/cross-linking reaction of MVL with a bis(6-membered cyclic carbonate) and cross-linking of linear PMVL with a free-radical generator (Scheme 6.1). We investigate the impact of synthetic conditions and fumed silica incorporation on the mechanical properties of PMVL elastomers. Furthermore, we study the degradation of these materials in aqueous media. Finally, we show that these materials can be recycled to recover MVL in high purity and yield.

\textbf{Scheme 6.1: Synthesis of cross-linked PMVLs}
Chapter 6.2 Results and Discussion

Chapter 6.2.1 Synthesis and Characterization of Cyclic Carbonate Cross-linked PMVL (CC)

We first investigated PMVL elastomers synthesized using a tandem methodology (Scheme 6.1A). A bis(6-membered cyclic carbonate) was chosen as a cross-linker due to its high solubility in neat MVL, and also because it was anticipated that MVL and B6CC would have similar reactivity. The equilibrium monomer concentration of MVL is 90% at room temperature, thus we removed residual monomer post-polymerization prior to testing the material properties.17

As PMVL is able to depolymerize in the presence of catalyst, we scanned a variety of methodologies to deactivate TBD so that any residual monomer could be removed under reduced pressure and the material could operate at elevated temperatures without uncontrollable depolymerization. Guanidine-based organocatalysts are most commonly deactivated using a large excess of benzoic acid, yet we observed that the excess benzoic acid sublimed under vacuum and that the films depolymerized in these conditions. We posit that there remained an acid adduct of TBD that was capable of depolymerizing PMVL, as similar acid adducts of organocatalysts are capable of transesterification.46 Additionally, deactivation of TBD through exposure to air generally took up to two weeks at ambient conditions, suggesting that diffusion of oxygen and carbon dioxide into the polymer is slow.

† Samples prepared using this method are named as CC-X-Y, where X and Y represent the mol% B6CC and the theoretical molar mass (kg mol⁻¹) if no cross-linking were to occur, respectively. For example, a sample with 1.00 mol% B6CC and a theoretical molar mass of 100 kg/mol based on the amount of BDM added (assuming 100% monomer conversion and no cross-linker added) would be denoted CC-1.00-100.
Therefore, we developed a method to convert the hydroxyl end-groups of PMVL to acetate groups; we suspected that acetylation chemistries would also deactivate the residual TBD. To accomplish this, we applied a solution of acetic anhydride and triethylamine in DCM (5 equivalents with respect to hydroxyl moieties or TBD if no added initiator was added) to the surface of the film. After allowing the solution to diffuse through the film for 20 h, we subjected the material to reduced pressure to remove residual monomer. We found that this could be accomplished with mild heating (80 to 90 °C) without significant depolymerization. We observed that this end-capping strategy also increased the decomposition temperature ($T_d$) of the polymers by 10–15 °C when compared with CC samples in which we deactivated TBD with two weeks of air exposure. The significant increase in the $T_d$ can be attributed to the lack of hydroxyl groups, which are required for depolymerization of PMVL to occur via an “unzipping” mechanism. The amount of cross-linker did not appear to affect the mass recovery after excess monomer removal, nor was there a significant difference in their $T_d$’s. On the other hand, the yield of an elastomer produced with no initiator was significantly lower (76%), likely owing to a slower polymerization rate; if the polymerization had been allowed to proceed, higher conversion would be likely. This indicates that some initiator is necessary to attain high monomer conversion in a reasonable period of time.

Once the monomer removal protocol was established, two sets of CC samples were investigated. At a fixed ratio of MVL to added BDM initiator (specifically, 876:1), we first varied the concentration of B6CC from 0.25 to 2.0 mol% relative to MVL. All of the materials with B6CC concentrations greater than or equal to 0.25 mol% gelled within 10 min. To ensure conversion of MVL monomer reached equilibrium, the films were allowed
to cure overnight (ca. 20 h). After monomer removal, extraction experiments revealed high gel percentages that increased slightly with cross-linker content (Table 6.1). Next, we fixed the ratio of MVL to B6CC (specifically at 100:1) and varied the amount of added initiator. No clear trend in gel percentage was observed when the concentration of initiator was varied. Furthermore, the $T_g$ of all the materials was between –47 and –49 °C compared to –52 °C for PMVL homopolymer, this observation suggests that the molecular structure and amount of cross-linker did not significantly contribute to the thermal properties of the material. These results are summarized in Table 6.1, below.

**Table 6.1:** Tandem Cross-linking of PMVL with B6CC

<table>
<thead>
<tr>
<th>CC-$X$-$Y$</th>
<th>Mass recovery (%)</th>
<th>Gel %</th>
<th>$E'$ at 25 °C (MPa)</th>
<th>$M_{x,eff}$ (kg mol$^{-1}$)</th>
<th>$M_{x,\text{theo}}$ (kg mol$^{-1}$)</th>
<th>$T_g$ DMTA (°C)</th>
<th>$T_g$ DSC (°C)</th>
<th>$T_d$ (°C)</th>
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<tbody>
<tr>
<td>CC-0.25-100</td>
<td>88</td>
<td>89</td>
<td>1.2</td>
<td>6.8</td>
<td>40</td>
<td>–49</td>
<td>–48</td>
<td>274</td>
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<tr>
<td>CC-0.50-100</td>
<td>91</td>
<td>95</td>
<td>1.8</td>
<td>4.5</td>
<td>21</td>
<td>–48</td>
<td>–48</td>
<td>262</td>
</tr>
<tr>
<td>CC-0.75-100</td>
<td>89</td>
<td>98</td>
<td>1.9</td>
<td>4.3</td>
<td>13</td>
<td>–48</td>
<td>–47</td>
<td>266</td>
</tr>
<tr>
<td>CC-1.0-100</td>
<td>89</td>
<td>99</td>
<td>2.1</td>
<td>3.9</td>
<td>10</td>
<td>–48</td>
<td>–48</td>
<td>269</td>
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<tr>
<td>CC-2.0-100</td>
<td>89</td>
<td>100</td>
<td>2.7</td>
<td>3.0</td>
<td>5.1</td>
<td>–47</td>
<td>–46</td>
<td>269</td>
</tr>
<tr>
<td>CC-1.0-NI</td>
<td>76</td>
<td>98</td>
<td>2.8</td>
<td>2.9</td>
<td>10</td>
<td>–47</td>
<td>–47</td>
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<td>97</td>
<td>1.8</td>
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<td>262</td>
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<tr>
<td>CC-1.0-75</td>
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<td>1.6</td>
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<td>–48</td>
<td>–47</td>
<td>263</td>
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<td>CC-1.0-150</td>
<td>89</td>
<td>99</td>
<td>2.2</td>
<td>3.7</td>
<td>10</td>
<td>–48</td>
<td>–47</td>
<td>266</td>
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<tr>
<td>CC-1.0-200</td>
<td>89</td>
<td>100</td>
<td>1.7</td>
<td>4.8</td>
<td>10</td>
<td>–48</td>
<td>–47</td>
<td>262</td>
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</table>

$X$ = mol% B6CC to MVL and $Y$ = theoretical $M_n$ (kg mol$^{-1}$) assuming no cross-linker was added and 100% monomer conversion. $^b$Recovery of mass after heating in a vacuum oven for 48 h at 80 °C. $^c$Determined after removing residual monomer. $^d$Determined using $E'$ from DMTA in equation 6.1. $^e$Calculated by dividing the mass of the polymer recovered by the mol of B6CC and assuming no contribution from entanglements. $^f$Calculated from the maximum of the loss modulus. $^g$NI stands for no initiator; $M_n$ in the presence of no B6CC with high purity monomer is >200 kg mol$^{-1}$ relative to polystyrene standards in RI-SEC with CHCl$_3$ as the mobile phase. $^h$Taken on the second heating ramp at a rate of 10 °C min$^{-1}$. $^i$Taken under air, defined as the temperature at which 5% mass loss is observed.

With the materials in hand, we sought to determine their tensile properties and compare them to those of a conventional elastomer, specifically vulcanized natural rubber (generic rubber band, Universal®, Deerfield, IL). Remarkably, CC-0.25-100 and CC-0.50-
100 both exhibited significantly higher tensile strength and elongation than rubber bands as well as a substantial strain hardening effect (Figure 6.1A). Interestingly, CC-0.75-100 and CC-1.00-100 both showed uniaxial extension properties very similar to that of a rubber band, although their tensile strength drops significantly compared to the samples with lower cross-linker content. A second batch of analogous materials exhibited nearly identical properties, indicating this behavior is reproducible. As expected, increasing the amount of cross-linker resulted in a reduction of the strain at break while slightly increasing Young’s modulus. However, there was no clear correlation between cross-linker content and ultimate tensile strength. Cross-linked rubbers often show a maximum in tensile strengths at intermediate cross-link densities which would initially explain this trend. However, the increase in tensile strength for CC-2.0-100 does not correlate, suggesting other undeterminable factors may be involved. Data summarizing mechanical characteristics as a function of cross-linker content are available in Figure 6.2.
Figure 6.1: A) Representative tensile data for CC elastomers cross-linked with varying amounts of B6CC and keeping BDM constant. B) Representative hysteresis data for a cross-linked elastomer (CC-1.0-100).

Figure 6.2: Tensile properties of PC while varying mol% of B6CC. The amount of initiator was kept at a constant amount such that $M_n$ of PMVL would be 100 kg/mol if 100% conversion were achieved and no cross-linking occurred. A) Stress at break, B) strain at break, and C) Young’s modulus.
Hysteresis experiments revealed that the energy loss and residual strain per cycle decreased monotonically with B6CC content, with the sample containing 2.0 mol% B6CC exhibiting the least amount of hysteresis loss over 20 cycles (Figure 6.1B, Figure 6.3, Table 6.2). The results obtained via DMTA indicated a similar trend in the stiffness of the elastomers; samples with more cross-linker exhibited a higher plateau modulus (Figure 6.4). Samples with the least amount of cross-linker displayed a slightly negative sloping plateau modulus at temperatures above the $T_g$. This effect is likely due to dangling chain ends as this phenomenon has been seen previously in materials with high levels of this network defect.\(^{48}\) The effective molar mass between cross-links ($M_{x,\text{eff}}$) of the materials was much lower than expected (Table 6.1); as the $M_e$ of linear PMVL is 4.3 kg/mol, this result is likely due to inherent entanglements contributing to $M_{x,\text{eff}}$.\(^ {49}\) Therefore, it is also possible that the relaxation of transient entanglements within the network are also contributing to the negatively sloping modulus exhibited by samples with low cross-linker content.
Figure 6.3: Cycles 1, 2, and 20 of the hysteresis of CC while varying B6CC. The amount of initiator was kept at a constant amount such that $M_{n,\text{theo}}$ of PMVL would be 100 kg/mol if 100% conversion were achieved and no cross-linking occurred. The hysteresis of a rubber band is also shown. Samples were run for 20 cycles at a rate of 50 mm min$^{-1}$. 
### Table 6.2: Hysteresis data

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 20</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 20</th>
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<td>12</td>
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*a* Calculated by dividing the area under the contraction by the area under the extension.

*b* Determined as the point at which the contraction reaches a plateau stress.
Figure 6.4: DMTA of CC while varying the mol% of B6CC. The amount of initiator was kept at a constant amount such that $M_{n,\text{theo}}$ of PMVL would be 100 kg/mol if 100% conversion were achieved and no cross-linking occurred. A) Storage modulus ($E'$) and B) loss modulus ($E''$). Samples were measured from –70 to 200 °C at a strain rate of 0.05% and a frequency of 1 Hz.

We next tested the set of materials prepared at fixed B6CC content with varying amounts of initiator (indicated in the bottom half of Table 6.1). Uniaxial extension tests revealed that increasing the amount of initiator caused the material to lose significant toughness (Figure 6.5, Figure 6.6, Table 6.3), though no significant change in hysteresis loss was observed (Figure 6.7). We hypothesize that the loss of toughness is due to an increase in network defects from a higher amount of active initiation sites; network defects can cause a significant reduction in mechanical properties because the applied stress will be localized rather than equally divided among the strands in the network.\(^{30}\) Furthermore, the absence of initiator did not produce a more desirable material, thus, the addition of some initiator is preferred to obtain higher mass recovery after monomer removal high conversion of monomer.
Representative tensile data showing the influence of varying amounts of BDM, while keeping B6CC constant, on tensile properties.

Table 6.3: Tensile properties of CC materials

<table>
<thead>
<tr>
<th>CC-mol% B6CC-Target $M_n$</th>
<th>Stress at break (MPa)</th>
<th>Strain at break (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC-0.25-100</td>
<td>4.9 ± 0.9</td>
<td>1800 ± 100</td>
<td>0.80 ± 0.07</td>
</tr>
<tr>
<td>CC-0.50-100</td>
<td>7 ± 1</td>
<td>1200 ± 90</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>CC-0.75-100</td>
<td>3.6 ± 0.4</td>
<td>530 ± 20</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>CC-1.0-100</td>
<td>3.1 ± 0.7</td>
<td>360 ± 30</td>
<td>1.9 ± 0.3</td>
</tr>
<tr>
<td>CC-2.0-100</td>
<td>6.9 ± 0.6</td>
<td>270 ± 9</td>
<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>CC-1.0-NF</td>
<td>4 ± 1</td>
<td>350 ± 40</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>CC-1.00-50</td>
<td>1.8 ± 0.1</td>
<td>300 ± 20</td>
<td>1.5 ± 0.3</td>
</tr>
<tr>
<td>CC-1.0-75</td>
<td>1.5 ± 0.2</td>
<td>220 ± 40</td>
<td>1.4 ± 0.1</td>
</tr>
<tr>
<td>CC-1.0-150</td>
<td>4 ± 1</td>
<td>390 ± 50</td>
<td>1.8 ± 0.2</td>
</tr>
<tr>
<td>CC-1.0-200</td>
<td>5 ± 1</td>
<td>390 ± 40</td>
<td>2.1 ± 0.3</td>
</tr>
</tbody>
</table>

aTheoretical $M_n$ (kg mol$^{-1}$) assuming no cross-linking were to occur. bCalculated from the slope of the stress-strain data from 0-10% strain. cNI stands for no initiator; $M_n$ in the presence of no B6CC with high purity monomer is >200 kg mol$^{-1}$.

Figure 6.6: Tensile properties of CC while varying target $M_n$ while keeping mol% of B6CC fixed. Target $M_n$ is determined by calculating the theoretical $M_n$ of the polymer assuming no cross-linker were added and 100% conversion of monomer. A) Stress at break, B) strain at break, and C) Young’s modulus.
Figure 6.7: Cycles 1, 2, and 20 of the hysteresis of CC while varying amount of BDM and keeping a constant 1 mol% B6CC. Samples were run for 20 cycles at a rate of 50 mm min⁻¹.
Neglecting the impact of reactivity ratio differences, if the ratio of MVL to BDM is fixed, $M_x$ should increase with a decreasing amount of B6CC in the initial feed because less tetrafunctional junctions will be formed. On the other hand, $M_x$ should not vary significantly if the ratio of MVL to BDM is varied as BDM is difunctional and will not introduce cross-link junctions. Indeed, the plateau modulus and $M_{x,\text{eff}}$ increase as the amount of B6CC is decreased, whereas no clear trend is seen when varying the amount of BDM (Figures 6.4A and 6.8A, Table 6.1).

![Figure 6.8: DMTA of CC while varying the initiator loading and maintaining a 1 mol% B6CC. A) $E'$ and B) $E''$. Samples were measured from –70 to 200 °C at a strain rate of 0.05% and a frequency of 1 Hz.](image)

**Chapter 6.2.2 Synthesis and Characterization of Peroxide Cross-linked PMVL (PC)**

In addition to the tandem copolymerization/cross-linking strategy, we also explored a sequential approach where linear PMVL homopolymer was synthesized and cross-linked using a free radical generator (Scheme 6.1B). This was accomplished by melt blending linear PMVL with BPO in a twin-screw extruder at 70 °C and cured in a press mold at 150 °C. We fixed the initial molar mass of the PMVL prepolymer ($M_n = 162$ kg mol$^{-1}$) and

---

‡ Samples are named as PC-Z-FSQ where Z represents the wt% BPO relative to PMVL and Q represents wt% FS fed into the extruder. For instance, a sample with 1 wt% BPO and 0 wt% FS would be denoted PC-1.0-FS0.
varied the mass percent of BPO in the blend. In some cases, a hydrophobic FS filler, Aerosil R 812, was also added. The characteristics of these samples and blends are summarized in Table 6.4, below.

**Table 6.4:** Post Polymerization Cross-linking of PMVL with BPO

<table>
<thead>
<tr>
<th>PC-Z-FSQ(^zx)</th>
<th>Gel %</th>
<th>FS (%)</th>
<th>(E') at 25 °C (MPa)</th>
<th>(M_{x,\text{eff}}) (kg mol(^{-1}))(^b)</th>
<th>(T_{\text{g,DMTA}}) (°C)(^c)</th>
<th>(T_{\text{g,DSC}}) (°C)(^d)</th>
<th>(T_d) (°C)(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-1.0-FS0</td>
<td>76</td>
<td>0</td>
<td>1.4</td>
<td>5.8</td>
<td>-50</td>
<td>-50</td>
<td>264</td>
</tr>
<tr>
<td>PC-2.0-FS0</td>
<td>93</td>
<td>0</td>
<td>1.7</td>
<td>4.8</td>
<td>-49</td>
<td>-50</td>
<td>244</td>
</tr>
<tr>
<td>PC-3.0-FS0</td>
<td>95</td>
<td>0</td>
<td>1.8</td>
<td>4.5</td>
<td>-50</td>
<td>-49</td>
<td>246</td>
</tr>
<tr>
<td>PC-4.0-FS0</td>
<td>96</td>
<td>0</td>
<td>2.1</td>
<td>3.9</td>
<td>-50</td>
<td>-49</td>
<td>242</td>
</tr>
<tr>
<td>PC-5.0-FS0</td>
<td>97</td>
<td>0</td>
<td>2.1</td>
<td>3.9</td>
<td>-49</td>
<td>-48</td>
<td>241</td>
</tr>
<tr>
<td>PC-2.0-FS10</td>
<td>96</td>
<td>9</td>
<td>2.4</td>
<td>3.4</td>
<td>-49</td>
<td>-50</td>
<td>256</td>
</tr>
<tr>
<td>PC-2.0-FS20</td>
<td>95</td>
<td>16</td>
<td>2.9</td>
<td>2.8</td>
<td>-50</td>
<td>-51</td>
<td>259</td>
</tr>
<tr>
<td>PC-2.0-FS30</td>
<td>95</td>
<td>25</td>
<td>5.0</td>
<td>1.6</td>
<td>-48</td>
<td>-51</td>
<td>256</td>
</tr>
</tbody>
</table>

\(^x\)Z = wt% BPO with respect to PMVL and FSQ = wt% FS with respect to PMVL; all samples produced with 162 kg mol\(^{-1}\) PMVL relative to polystyrene standards in RI-SEC with CHCl\(_3\) as the mobile phase.  

\(^b\)Calculated using \(E'\) from DMTA in equation 6.1.  

\(^c\)Determined from the maximum of the loss modulus from DMTA.  

\(^d\)Taken on the second heating ramp at a rate of 10 °C min\(^{-1}\).  

\(^e\)Taken under air, defined as the temperature at which 5% mass loss is observed.

To our knowledge, the exact mechanism by which saturated polyesters cross-link in the presence of radicals has not been studied. Hermans and Eyk suggest that the reaction of cyclohexane with BPO produces carbon radicals capable of a variety of reactions, most commonly resulting in dimers and other oligomers.\(^{50}\) The tertiary carbon within the backbone of PMVL is the most stable position for carbon radicals, and thus, we assume that the longer-lived radicals at the tertiary carbons allow for a more efficient reaction than at the methylene units along the backbone. Indeed, the PC elastomers exhibited higher gel fractions when compared to PCL cross-linked with BPO, which contains no tertiary carbons.\(^{41}\)
The reaction of PMVL with BPO did not afford a high degree of cross-linking at 0.1 and 0.5 wt% of BPO. PC elastomers prepared with 2 and 3 wt% BPO exhibited very desirable tensile properties (Figure 6.9, Table 6.5, Figure 6.10A) and outperformed all CC samples. At BPO loadings of 4 and 5 wt%, the materials began to drastically lose toughness, exhibiting significant decreases in tensile strength and elongation; furthermore, these samples no longer exhibited significant strain hardening. Indeed, this phenomenon has previously been observed with vulcanized rubber and has been attributed to variations in the viscoelastic properties of the material rather than a reduction in its inherent strength.\textsuperscript{47} However, Smith and Chu posit that no simple correlation can be attributed to this occurrence as tensile failure depends on a variety of factors.\textsuperscript{51} All of the PC samples exhibited a grayish yellow discoloration. We surmise that the yellow discoloration in the absence of FS is due to slight oxidative degradation while the gray discoloration is due to impurities present in the extruder. Indeed, samples prepared by solvent casting in DCM also had a yellow discoloration, however, no gray discoloration was observed. No significant difference in mechanical or thermal properties were observed between samples prepared by solvent casting and extrusion.

Table 6.5: Tensile properties of PC and PC-FS materials

<table>
<thead>
<tr>
<th>PC-wt% BPO-wt% FS\textsuperscript{a}</th>
<th>Stress at break (MPa)</th>
<th>Strain at break (%)</th>
<th>Young's modulus (MPa)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-1.0-FS0</td>
<td>6 ± 1</td>
<td>2000 ± 100</td>
<td>1.13 ± 0.07</td>
</tr>
<tr>
<td>PC-2.0-FS0</td>
<td>12 ± 2</td>
<td>1400 ± 100</td>
<td>1.40 ± 0.08</td>
</tr>
<tr>
<td>PC-3.0-FS0</td>
<td>10 ± 4</td>
<td>1170 ± 80</td>
<td>1.44 ± 0.06</td>
</tr>
<tr>
<td>PC-4.0-FS0</td>
<td>4 ± 2</td>
<td>700 ± 200</td>
<td>1.56 ± 0.04</td>
</tr>
<tr>
<td>PC-5.0-FS0</td>
<td>2.4 ± 0.7</td>
<td>400 ± 100</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>PC-2.0-FS10</td>
<td>18 ± 2</td>
<td>1300 ± 80</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td>PC-2.0-FS20</td>
<td>19 ± 2</td>
<td>1400 ± 100</td>
<td>1.8 ± 0.3</td>
</tr>
<tr>
<td>PC-2.0-FS30</td>
<td>22 ± 5</td>
<td>1400 ± 100</td>
<td>2.2 ± 0.2</td>
</tr>
</tbody>
</table>
All samples produced with 162 kg mol\(^{-1}\) PMVL. Calculated from the slope of the stress-strain data from 0-10% strain.

Figure 6.9: Tensile properties of PC while varying wt% of BPO. A) Stress at break, B) strain at break, and C) Young’s modulus.

Figure 6.10: A) Representative tensile data for PC elastomers and a commercially available generic rubber band. The 1 wt% BPO sample (black line) begins to tear near the grip above 1500% strain, making the observable tensile strength at break lower than its
Tensile data for PC-FS composites prepared with 2 wt% BPO relative to the mass of PMVL.

Similarly to the CC elastomers, the radically cross-linked materials exhibited higher plateau moduli and better hysteresis recovery when the loading of BPO was increased (Figures 6.11 and 6.12). At low BPO loading, we also observe a negatively sloping plateau modulus, similar to CC samples with low B6CC loading, which we attributed to dangling chain ends and the relaxation of transient entanglements within the network. The large increase in tensile strength from CC to PC was not entirely expected. We hypothesize that the difference in reactivity ratios between MVL and B6CC may have resulted in more network defects and a less uniform distribution of cross-links than in the PC elastomers. The radicals formed in the production of PC samples should theoretically have an equal probability of reacting with each repeat unit, which would result in a more uniform distribution of cross-links. As previously discussed, an applied force is more evenly dispersed in materials with evenly distributed cross-links, than in those with more network defects; as a result, the more uniform materials should be significantly stronger.

Figure 6.11: DMTA of PC while varying BPO wt%. A) $E'$ and B) $E''$. Samples were measured from –70 to 200 °C at a strain rate of 0.05% and a frequency of 1 Hz.
Figure 6.12: Cycles 1, 2, and 20 of the hysteresis of PC while varying the amount of BPO. Hysteresis of a rubber band is also shown. Samples were run for 20 cycles at a rate of 50 mm min⁻¹.
Chapter 6.2.3 PC-Fumed Silica Composites

In an attempt to further improve the properties of the PMVL elastomers and to reduce the total cost of the elastomer, we prepared composites containing fumed silica, Aerosil R 812.\(^5\) We recently demonstrated that this FS could be homogenously dispersed in cross-linked hydrogenated polyolefins and also impart dramatic improvements in the mechanical properties.\(^6\) Although we also attempted to produce filler reinforced materials using both the tandem cross-linking strategy, we observed that TBD catalyst used for the copolymerization reaction was intolerant of the FS. However, we found that FS reinforced elastomers could easily be prepared using the sequential radical melt blending route. For all samples, the BPO loading was fixed at 2 wt% with respect to PMVL, and blends containing 10 to 30 wt% FS were prepared. The TGA data indicated that in all cases the incorporation of FS into the polymer matrix during twin-screw extrusion was slightly lower than the feed amount (Table 6.4). Since the TGA of Aerosil R 812 exhibited no mass loss up to 550 °C, we believe this minor discrepancy is due to inefficient extrusion rather than FS degradation, loss of water, or volatile small molecules adsorbed to the surface of the filler.

As expected, the mechanical properties of the PC elastomers improved dramatically when blended with FS (Figure 6.10B, Table 6.5, Figure 6.13). The tensile strengths of the composites were improved by 50 to 83% relative to the neat elastomer and the elongation at break remained nearly constant at all filler loadings. Furthermore, the Young’s modulus increased from 1.4 to 2.2 MPa when 25 wt% FS was incorporated. This significant stiffening effect from the FS was also observed by DMTA; the plateau modulus rose from 1.7 to 5.0 MPa when 25 wt% FS was incorporated (Figure 6.14, Table6.5). As we anticipated, increasing the amount of FS filler also increased the extent of the Mullins effect
observed during hysteresis (Figure 6.15, Table 6.2). Even at 9 wt% incorporation of FS, the appearance of the resulting elastomer was colorless and translucent in contrast to the samples in the absence of FS which were a grayish yellow color. It is likely that the FS behaves as a white dye in the materials.

![Figure 6.13: Tensile properties of PC-FS composites. A) Stress at break, B) strain at break, and C) Young’s modulus.](image)

![Figure 6.14: DMTA of PC-FS composites. A) $E'$ and B) $E''$. Samples were measured from –70 to 200 °C at a strain rate of 0.05% and a frequency of 1 Hz.](image)
Figure 6.15: Cycles 1, 2, and 30 of the hysteresis of PC-FS composites. All samples contained 2 wt% BPO with respect to PMVL. Hysteresis of a rubber band is also shown. Samples were run for 20 cycles at a rate of 50 mm min$^{-1}$. 
Chapter 6.2.4 Chemical Recyclability

To demonstrate the recyclability of the PMVL elastomers, we determined the percentage of monomer that was recoverable via chemical depolymerization of CC-0.50-100 and PC-2.0-FS0. While CC should be easily depolymerizable, the backbones of the PC materials are chemically altered by the radical cross-linking reaction. We were therefore unsure as to whether the covalent linkages formed during the radical reactions would inhibit the depolymerization. To facilitate MVL recovery via depolymerization, we added stannous octoate and pentaerythritol ethoxylate (a high boiling tetraol) to the elastomers and heated them to 150 °C overnight under vacuum. Both CC and PC elastomers were both capable of depolymerization. We were able to recover 91% of pure MVL from CC-0.50-100 and 93% from PC-2.0-FS0 (Figure 6.16).

**Figure 6.16:** $^1$H-NMR in CDCl$_3$ of pure MVL and MVL recovered from the depolymerization of CC-0.50-100 and PC-2.0-FS0.
Chapter 6.2.5 Aqueous Degradation

Finally, we investigated the hydrolytic degradation of the elastomers in aqueous media. Samples were placed in PBS (pH = 7.4), 1 M hydrochloric acid, and 1 M sodium hydroxide (Figure 6.17). The elastomers proved to be resilient to degradation in PBS solutions at physiological conditions (37 °C) and in acidic solutions at room temperature, though PC-2.0-FS0 exhibited slight degradation in the basic solutions at room temperature (Figure 6.17A). The poor hydrolytic degradability is likely due to the hydrophobic nature of the materials. Increasing the temperature to 60 °C dramatically improved the degradation of the samples in both acid and base (Figure 6.17B). As hydrochloric acid can behave as a polymerization catalyst for MVL, it is also capable of depolymerizing PMVL at elevated temperature and therefore, capable of degrading the samples. We hypothesize that the increased temperature improved the penetration of polar moieties into the network, allowing accelerated basic degradation of PC-2.0-FS0. Interestingly, CC-0.50-100 appeared to be highly resistant to the basic solution, even at 60 °C; this is somewhat counterintuitive given that esters are easily cleaved in the presence of hydroxide ions. The Young’s modulus, plateau modulus, and gel content of PC-2.0-FS0 and CCP-0.50-100 are almost identical, suggesting that either the carbonate moieties lend chemical resistance or that peroxide cross-linking may alter the chemical structure of PMVL in a way that leaves it more susceptible to degradation in basic conditions.
Figure 6.17: Degradation studies of CC-0.50-100 and PC-2.0-FS0 in aqueous PBS (37 °C), 1 M hydrochloric acid (aqueous), and 1 M sodium hydroxide (aqueous). Samples were studied at A) room temperature (excluding PBS buffer) and at B) 60 °C. Degradation was not performed in PBS buffer at 60 °C as we sought to mimic physiological conditions.

Chapter 6.3 Conclusions

We have demonstrated that elastomers with a wide range of mechanical properties can be produced from PMVL. Tandem and radical cross-linking methodologies can both be successfully implemented depending on the desired processing conditions and physical/mechanical properties of the material. The mechanical properties of the reported materials were far superior to similar low \( T_g \), amorphous polyester elastomers reported in the literature, and the toughness could be improved further by incorporating FS. The Young’s modulus and tensile strength were improved by 57% and 83%, respectively,
without sacrificing the elongation at break by incorporating up to 25 wt% FS in PC. Furthermore, PC-FS materials were produced with similar tensile strength and elongation at break compared to synthetically challenging thermoplastic elastomers based on MVL and lactide.\(^{17}\) The ability to produce tough composite elastomers facilely with PC will greatly improve its viability as a commodity rubber. Moreover, the recyclability of CC and PC was successfully demonstrated, as they were both able to depolymerize in the presence of catalyst to provide up to 93% recovery of MVL. Finally, both polymers showed the ability to degrade under acidic conditions at 60 °C, while only PC was capable of degradation in basic conditions; this apparent degradation is promising towards the sustainability of these materials.

**Chapter 6.4 Experimental**

**Chapter 6.4.1 Materials**

All reagents were purchased from Sigma-Aldrich (Milwaukee, WI) and were used as received unless otherwise stated. 1,5,7-triazabicyclodec-5-ene (TBD) was purified by vacuum sublimation (70 °C, 30 mTorr). DCM, THF, and methanol were purchased from Fisher Scientific (Hampton, NH); DCM and THF were purified via a GC-SPS-4-CM glass contour 800-L solvent purification system obtained from Pure Process Technologies (Nashua, NH). 3-Methyl-1,5-pentanediol was obtained from TCI (Portland, OR) and used without further purification. MVL was produced by one of two methods as described in previous studies and purified by fractional distillation (3X) over calcium hydride (72 °C, 1 Torr).\(^{45,54}\) 5,5'-(oxybis(methylene))bis(5-ethyl-1,3-dioxan-2-one) (B6CC), a bis(6-membered cyclic carbonate), was also produced as described in a previous study and recrystallized from THF (3X).\(^7\) Aerosil R 812 was kindly provided by Evonik Industries.
(Parsippany, NJ). Rubber bands were purchased from the University of Minnesota chemistry stockroom; they were manufactured in Thailand for Universal® (Deerfield, IL). All glassware was heated to 105 °C overnight prior to use.

**Chapter 6.4.2 Synthetic Procedures**

*Modified synthesis of MVL from 3-methyl-1,5-pentanediol*[^54]

3-Methyl-1,5-pentanediol (1 L, 974 g, 8.24 mol) and copper chromite (50 g, 0.16 mol, 2 mol%) were charged into a 2-L 3-neck round bottom flask fitted with a Dean-Stark apparatus, a thermometer, and a glass stopper. The apparatus was then attached to a bubbler filled with silicon oil. A heating mantle was used to heat the round bottom flask to 240 °C under vigorous stirring. The temperature of the reaction rapidly rose to 170 °C, followed by collection of water (*ca.* 5 mL) and an unknown organic liquid (*ca.* 5 mL). Following removal of these impurities, the reaction temperature rose rapidly to *ca.* 210-220 °C followed by evolution of H₂ gas. The reaction was allowed to continue for 20 h and then cooled. At this time the ¹H-NMR spectrum of the solution indicated *ca.* 95% conversion of the diol. The crude product, a mixture of MVL monomer and PMVL polymer, was then purified by fractional distillation under reduced pressure.

First, a forerun was removed (1 Torr, 55-72 °C, 50 g) followed by a second fraction (1 Torr, 72-75 °C, 850 g). The higher boiling fraction was a clear, colorless liquid containing a minor amount of 4-methyl-3,4,5,6-tetrahydro-2H-pyran-2-ol. The concentration of this impurity in MVL was estimated to be ~0.2 mol% using the ¹H-NMR signal corresponding to the methine proton at δ 5.3 ppm. To remove the lactol, the crude MVL was stirred with phosphorous pentoxide (5 g) at 120 °C for 12 h; this resulted in the dehydration of the lactol impurity and polymerization of the MVL (~60% conversion of...
MVL was observed) presumably with water or lactol as the initiating species. The solution of polymer in monomer was then distilled under the conditions previously described until ca. 10% of the liquid remained in the pot. Analysis of the resulting MVL via $^1$H-NMR spectroscopy indicated that it no longer contained any lactol impurity, within the detection limit of the instrument used. To obtain high purity monomer, the MVL was then distilled two more times under reduced pressure from calcium hydride, each time discarding the first 5% of distillation liquid, to yield a clear a colorless liquid (65-75% yield).

To evaluate the monomer purity, test polymerizations were conducted in the bulk at room temperature using 0.1 mol% TBD as a catalyst in the absence of exogenous initiator. The molar mass of the resultant polymer is expected to depend on the concentration of adventitious initiators which can be roughly estimated via size-exclusion chromatography. For this work we classified the MVL as low purity if polymerization results in PMVL with $M_n < 100$ kg/mol, moderate purity if $M_n > 100$ kg/mol, and high purity if $M_n > 200$ kg/mol. The copper chromite residue after the first distillation has been used in up to four successive reactions without noticeable decrease in activity. $^1$H-NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 4.40 [m, -O-CH$_2$-CH$_2$-, 1H], 4.25 [m, -O-CH$_2$-CH$_2$-, 1H], 2.66 [m, -CO-CH$_2$-CH(CH$_3$)-, 1H], 2.20 [m, -CO-CH$_2$-CH(CH$_3$)-, 1H], 2.03-2.13 [m, CO-CH$_2$-CH(CH$_3$)-CH$_2$- and -CO-CH$_2$-CH(CH$_3$)-, 2H], 1.9 [m, -CH(CH$_3$)CH$_2$-CH$_2$-O, 1H], 1.55 [m, -CH(CH$_3$)-CH$_2$-CH$_2$-, 1H], 1.05 [d, -CH$_2$-CH(CH$_3$)-CH$_2$-, 3H].

**Synthesis of a cyclic carbonate cross-linked PMVL (CC)**

Under a nitrogen atmosphere, MVL (7.00 g, 61.4 mmol, high purity) was charged into a 20-mL scintillation vial along with varying amounts of B6CC (46 to 371 mg, 0.15 to 1.23 mmol, 0.25 to 2 mol% to MVL) and 1,4-benzenedimethanol (BDM, 0 to 19 mg, 0
to 0.14 mmol). The mixture was stirred until completely homogenous, then a solution of TBD in DCM (100 mg/mL, 85 μL solution, TBD = 0.1 mol% relative to MVL) was injected using a gastight syringe. The polymerization solution was allowed to stir for ca. 10 s and then poured into a Pyrex® petri dish (inner diameter = 90 mm). The contents of petri dish were allowed to cure overnight at room temperature under nitrogen (ca. 20 h) to ensure maximum conversion. The resulting elastomer was then removed from the dish and a 1 M solution of acetic anhydride and triethylamine in DCM (0.35 to 1.40 mL, ca. 5 eq relative to hydroxyl moieties or TBD if no BDM was used) was dripped over the top of the film via a syringe. The elastomer was allowed to sit in air for another 20 h and then placed in an oven under reduced pressure at 80–90 °C for 48 h to remove DCM, acetic anhydride, triethylamine, and residual MVL monomer. This process afforded a clear, colorless, and odorless cross-linked PMVL film (88 to 91% mass yield). Samples prepared using this method are named as CC-X-Y, where X and Y represent the mol% B6CC and the theoretical molar mass (kg mol⁻¹) if no cross-linking were to occur, respectively. For example, a sample with 1.00 mol% B6CC and a theoretical molar mass of 100 kg/mol based on the amount of BDM added (assuming 100% monomer conversion and no cross-linker added) would be denoted CC-1.00-100.

**Synthesis of MVL homopolymer**

Under a nitrogen atmosphere, MVL (100.00 g, 875 mmol, moderate purity) was charged into a 1-L round bottom flask with a Teflon® coated magnetic stir bar. A solution of TBD in DCM (1.22 mL, 100 mg TBD/mL DCM, 0.1 mol% TBD to MVL) was added to the monomer, then the flask was sealed with a rubber septum and the mixture was stirred for 16 hours. Following this, a 1 M benzoic acid solution in DCM was added (9 mL, 10 eq. benzoic acid to TBD) and the polymer solution was diluted with additional DCM to ca.
500 mL. Once the polymer was fully dissolved, the solution was precipitated into methanol (5 L), then dried over a stream of nitrogen for 2 days, dried under vacuum at room temperature for 3 days, and finally dried in an oven under reduced pressure at 60–70 °C for 2 days. The resulting PMVL was a highly viscous, clear and, colorless (85-88% yield).

$^1$H-NMR (500 MHz, CDCl$_3$; 25 °C): $\delta$ (ppm) = 4.13 [m, -O-CH$_2$-CH$_2$-, 2H], 2.34 [m, -CO-CH$_2$-CH(CH$_3$)-, 1H], 2.20 [m, -CO-CH$_2$-CH(CH$_3$)-, 1H], 2.10 [m, -CH$_2$-CH(CH$_3$)-CH$_2$-, 1H], 1.72 [m, -CH(CH$_3$)-CH$_2$-CH$_2$-, 1H], 1.55 [m, -CH(CH$_3$)-CH$_2$-CH$_2$-, 1H], 1.00 [d, -CH$_2$-CH(CH$_3$)-CH$_2$-, 3H]. RI-SEC (CHCl$_3$): $M_n$ = 162 kg mol$^{-1}$, $D$ = 1.29. DSC: $T_g$ = –52 °C. TGA: $T_d$ (5% mass loss, Air) = 240 °C.

Production of peroxide cross-linked PMVL (PC) and PC-fumed silica composites (PC-FS)

PMVL homopolymer (2.00 g) and benzoyl peroxide (BPO, 20 to 100 mg, 1 to 5 wt%) were loaded into a twin-screw extruder (DSM Xplore 5 mL micro compounder; Geleen, Netherlands) at 70 °C (10 h half-life for BPO) and allowed to mix for 10 min before extruding a grayish yellow material (ca. 80% recovery). Composites were also prepared with 10, 20, or 30 wt% fumed silica (FS) fed into the extruder (2 wt% BPO relative to PMVL was used for all composites), yielding a colorless and translucent material. The homogenous polymer mixture was placed in a 5 cm (W) × 5 cm (L) × 0.05 cm (T) aluminum mold that was placed between two 12 cm x 12 cm aluminum plates with a thin Teflon® sheet (0.05 mm thick) over each plate. This was then placed in a press mold (Wabash MPI; Wabash, IN) at 150 °C and 3 tons of pressure for 10 min and rapidly cooled to room temperature over 5 min, affording a translucent, grayish yellow elastomer. In the presence of FS, the materials appeared colorless and translucent. Samples are named as
PC-Z-FS\(Q\) where \(Z\) represents the wt\% BPO relative to PMVL and \(Q\) represents wt\% FS fed into the extruder. For instance, a sample with 1 wt\% BPO and 0 wt\% FS would be denoted PC-1.0-FS0.

*Depolymerization of CC-0.50-100 or PC-2.0-FS0*

CC-0.50-100 or PC-2.0-FS0 (*ca.* 1.00 g cut into small pieces), stannous octoate (1 drop, *ca.* 20 mg), and pentaerythritol ethoxylate (1 drop, *ca.* 20 mg, \(M_n = 797\) g/mol) were placed in a 10-mL round bottom flask equipped with a simple vacuum distillation apparatus. The mixture was heated to 150 °C overnight at 1 Torr, yielding a clear and colorless liquid (91% recovery for CC-0.50-100 and 93% for PC-2.0-FS0 after a mass correction for cross-linker was performed). The \(^1\)H-NMR spectrum of the distillate was identical to that of pure MVL (Figure 6.16).

*Chapter 6.4.3 Characterization Methods*

\(^1\)H-NMR spectroscopy was performed on a 500 MHz Bruker Avance III HD with SampleXpress spectrometer (Billerica, MA). Solutions were prepared in 99.8% CDCl\(_3\) (Cambridge Isotope Laboratories). All spectra were acquired at 20 °C with 64 scans and a 2 s delay. Chemical shifts are reported in ppm with respect to CHCl\(_3\) (7.26 ppm).

Uniaxial tensile testing and hysteresis measurements were conducted using dogbone-shaped tensile bars (*ca.* 0.5 mm (T) × 3 mm (W) × 25 mm (L) and a gauge length of 14 mm for PC samples or 0.5 mm (T) × 5 mm × 38 mm (L) and a gauge length of 22 mm for CC samples). The samples were aged for 48 hours at 25 °C in a desiccator prior to testing. Tensile measurements were performed on a Shimadzu Autograph AGS-X Series tensile tester (Columbia, MD) at 25 °C with a uniaxial extension rate of 50 mm min\(^{-1}\). Young’s modulus \((E)\) values were calculated using the Trapezium software by taking the
slope of the stress-strain curve from 0 to 10% strain. Reported values are the average and standard deviations of five replicates from the same sample. Twenty cycles were performed during hysteresis measurements to 67% strain at 50 mm min\(^{-1}\) and the energy loss was calculated by subtracting the area under the curve of the contraction from the area under the curve of the extension in each cycle. The residual strain was taken as the point at which the return cycle reached its minimum stress. All graphical representation of hysteresis data was smoothed using a 100-point adjacent-averaging smoothing function in Origin® data analysis software in order to remove noise.

Dynamic mechanical thermal analysis (DMTA) was performed on a TA Instruments RSA-G2 analyzer (New Castle, DE) using dog bone shape films (ca. 0.5 mm (T) × 3 mm (W) × 25 mm (L) and a gauge length of 14 mm). DMTA experiments were conducted in tension film mode, where the axial force was first adjusted to 0.2 N of tension (sensitivity of 0.01 N) to ensure no buckling of the sample. The proportional force mode was set to force tracking to ensure that the axial force was at least 100% greater than the dynamic oscillatory force. The strain adjust was then set to 30% with a minimum strain of 0.05%, a maximum strain of 5%, and a maximum force of 0.2 N in order to prevent the sample from going out of the specified strain range. A temperature ramp was then performed from –70 °C to 200 °C at a rate of 5 °C min\(^{-1}\), with an oscillating strain of 0.05% and an angular frequency of 6.28 rad s\(^{-1}\). The \(T_g\) was calculated from the maximum value of the loss modulus. The effective molar mass between cross-links (\(M_{x,\text{eff}}\)), which consists of contributions from cross-links and entanglements, was calculated using the storage modulus (\(E'\)) at 25 °C and equation 6.1.

\[
E'(T) = 3G'(T) = 3RT \nu_e = \frac{3 \rho RT}{M_{x,\text{eff}}} 
\]  

(6.1)
Where $E'$ and $G'$ are the storage and shear modulus respectively, $R$ is the universal gas constant, $T$ refers to the absolute temperature in the rubbery region (ca. 298 K), $v_c$ is the cross-link density, and $\rho$ is the density of PMVL\textsuperscript{17} (ca. 1.1 g cm\textsuperscript{-3}).

Differential scanning calorimetry (DSC) was conducted on a TA Instruments Discovery DSC (New Castle, DE). The instrument was calibrated using an indium standard. All samples were prepared using T-Zero hermetic pans (ca. 5 mg) under a N\textsubscript{2} purge of 50 mL min\textsuperscript{-1}. The samples were initially cooled to –80 °C and then heated to 100 °C at 10 °C min\textsuperscript{-1}. The samples were then cooled back to –80 °C at 10 °C min\textsuperscript{-1} and heated again to 100 °C at the same rate. Values for $T_g$ were acquired at the mid-point of each transition in the second heating curve using the Trios® software. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 (New Castle, DE) under air at a heating rate of 10 °C/min to 550 °C. A typical sample size was between 8-15 mg.

Solvent extraction experiments were performed by placing a small amount of cross-linked polymer (ca. 20 to 100 mg) into a 20-mL vial filled with DCM. The vial was then closed and stirred for 48 h before removing the solvent by gravity filtration. The recovered sample was dried under reduced pressure for 48 h at 20 mTorr, after which the sample was weighed and the gel percent was determined.

The hydrolytic degradation of the elastomers was investigated in accelerated conditions using 1 M aqueous solutions of NaOH or HCl at 60 °C as well as in biologically relevant conditions by using an aqueous PBS (pH = 7.4) solution at 37 °C. Nine replicates of each cross-linked polymer sample were prepared (50 mg each). The replicates were immersed in triplicate in the aforementioned aqueous solutions in separate 20-mL scintillation vials and heated to their respective temperatures. The insoluble mass was
recorded after removing each sample from the solution and patting it dry with a Kimwipe™, after which the sample was re-immersed in the same solution. Solutions were checked weekly with litmus paper to ensure their pH remained stable; none of the solutions showed pH variance by this method. The data presented in the plots of insoluble mass % (percentage of original mass) over time includes the averages and standard deviations of the triplicate samples in their respective medium.

Refractive index size exclusion chromatography (RI-SEC) was performed on an HP/Agilent 1100 series SEC at 35 °C using three successive PLgel Mixed C Columns and a PLgel 5 μm guard column with an HP 1047A RI detector (Santa Clara, CA). CHCl₃ was used as the mobile phase with an elution rate of 1 mL min⁻¹. The $M_n$ and $D$ were determined based on a 10-point calibration curve using EasiCal™ polystyrene standards purchased from Agilent.

Chapter 6.5 References


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Appendix A. Epoxy Cross-linked Poly(4-methylcaprolactone) and Aziridine Cross-linked Polylactide Vitrimers

Appendix A.1 Introduction

The revelation that urethane cross-linked PLA and PEO (Chapter 3) went through a dissociative mechanism led us to pursue other avenues of cross-linking to produce polyester-based vitrimers which relax stress via transesterification. Furthermore, we sought to use isocyanate-free, renewable cross-linkers due to the relatively high toxicity of isocyanate precursors. For this study, a tris(aziridine) and a tris(epoxide) were chosen as cross-linkers. Due to the poor reactivity of aziridines and epoxides with hydroxyls, a method for efficient carboxylic acid functionalization of hydroxyl-terminated polyesters was developed. 4-arm PLA and later, 4-arm poly(4-methylcaprolactone) [P4MCL] were chosen as prepolymers. While the cross-linking of carboxylic acid-terminated PLA with aziridines proved rather facile at room temperature, obtaining defect free materials when cross-linking PLA with epoxides proved rather difficult due to defect formation as a result of cross-linking occurring near the glass transition temperature ($T_g$). Thus, we chose to produce epoxide cross-linked materials from P4MCL, whose $T_g$ ($-60 \degree C$) is far lower than for PLA ($ca. 60 \degree C$).

Appendix A.2 Aziridine Cross-linked PLA

For the initial part of this study, we produced polyester vitrimers that relied on aziridine-based cross-linkers, as aziridines are known to react in a facile manner at room temperature with carboxylic acid-terminated polyesters. Furthermore, the reaction of aziridines with carboxylic acids produces an amine which we hypothesized would then react with an ester at elevated temperature to form an amide and a hydroxyl, allowing for transesterification. With that in mind, we immediately set out to produce a carboxylic acid-
terminated PLA and were able to optimize this functionalization procedure to a one-pot procedure with very little succinic anhydride (Scheme A.1). With this new procedure, carboxylic-acid terminated star-shaped PLA (CATSPLA) was synthesized and purified more easily with higher yields when compared with previous literature reports.\textsuperscript{1,2} With CATSPLA in hand, we were able to cross-link this material using a tris(aziridine) in a reproducible fashion to form aziridine cross-linked PLA (ACPLA). Cross-linking was performed with three different catalysts: stannous octoate, scandium(III) triflate, and lanthanum(III) triflate as well as a catalyst-free control sample (Scheme A.1). Furthermore, gel fractions of these materials were typically in excess of 0.90, showing that these materials were highly cross-linked.

\textbf{Scheme A.1}

With ACPLA in hand, we immediately began to evaluate its vitrimeric ability through stress relaxation analysis (SRA) at various temperatures (Figure A.1A). Interestingly, the rare earth metal triflates were capable of relaxing the ACPLA at significantly faster rates than stannous octoate, which showed almost no appreciable increase in relaxation rate when compared to the control sample with no catalyst. This is in stark contrast to our original study with urethane cross-linked PLA and PEO (see
Chapters 2 and 3), which relaxed over 200 times faster at 140 °C in the presence of Sn(Oct)$_2$ than ACPLA with Sn(Oct)$_2$. From this data, we were able to extract activation energies ($E_a$) of 120 ± 0.6, 120 ± 4.7, and 111 ± 2.2 kJ/mol for Sc(OTf)$_3$, La(OTf)$_3$, and Sn(Oct)$_2$, respectively. Oddly, a lower $E_a$ was obtained in the absence of catalyst (89 ± 2.2 kJ/mol) and we are unable to explain this discrepancy nor why Sn(Oct)$_2$-containing samples are slower but have a lower $E_a$ than the rare earth metal triflate catalysts. We hypothesized that the presence of amines might interfere with our study as multiple reactions would increase the $E_a$ determine by SRA. Thus, we chose to evaluate the ability of an epoxide-based cross-linker which would create a hydroxyl functionality when reacted with a carboxylic instead of producing an amine.

![Figure A.1](image)

**Figure A.1:** A) SRA of ACPLA with various catalysts at 160 °C and 9.3% strain and B) Arrhenius plots of ACPLAs.

<table>
<thead>
<tr>
<th>PLA $M_n$ (kg/mol)</th>
<th>Catalyst</th>
<th>mol% catalyst to OH</th>
<th>Gel %</th>
<th>$E^*$ at 100 °C (MPa)</th>
<th>$M_x$ (kg/mol)</th>
<th>$T_g$ (°C, DMTA)</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.9</td>
<td>None</td>
<td>N/A</td>
<td>98</td>
<td>6.6</td>
<td>1.2</td>
<td>45</td>
<td>89 ± 2.2</td>
</tr>
<tr>
<td>3.9</td>
<td>Sc(OTf)$_3$</td>
<td>2.5</td>
<td>100</td>
<td>6.0</td>
<td>1.4</td>
<td>57</td>
<td>120 ± 0.6</td>
</tr>
<tr>
<td>3.9</td>
<td>La(OTf)$_3$</td>
<td>2.5</td>
<td>100</td>
<td>5.8</td>
<td>1.4</td>
<td>56</td>
<td>120 ± 4.7</td>
</tr>
<tr>
<td>3.9</td>
<td>Sn(Oct)$_2$</td>
<td>2.5</td>
<td>100</td>
<td>3.5</td>
<td>2.3</td>
<td>47</td>
<td>111 ± 2.2</td>
</tr>
</tbody>
</table>
Appendix A.3 Epoxide Cross-linked P4MCL

Triglycidyl isocyanurate (TGIC) was chosen as the epoxide-based cross-linker due to its high boiling point, thermal stability, and potential for renewability. We initially began these studies using CATSPLA as the prepolymer, but decided to switch the prepolymer to carboxylic acid-terminated star-shaped P4MCL (CATSP4MCL) as it was significantly easier to produce cross-linked materials using the same methodology (Scheme A.2). Unlike the aziridine cross-linker, TGIC cross-linking required elevated temperature to achieve appreciable reaction at reasonable time scales (~8 h at 80 °C). We opted to evaluate Sn(Oct)$_2$ and Sc(OTf)$_3$ as the catalysts, excluding La(OTf)$_3$ as it showed similar catalytic ability to Sc(OTf)$_3$ and was often more difficult to solubilize into the polymer. We found that in the presence of Sn(Oct)$_2$ or no catalyst, the resulting epoxide cross-linked PMCL (ECP4MCL) had gel fractions greater than 0.90, but it was often hard to achieve higher than 0.80 with Sc(OTf)$_3$.

Scheme A.2
With these materials in hand, we began to explore ECP4MCL’s ability to relax via SRA as with the previous materials. We found that due to the ductile nature of these materials, we had to pull them to 20% elongation in SRA in order to get an appreciable signal from the rheometer. Remarkably, the materials containing Sc(OTf)₃ relaxed stress on similar time scales as urethane cross-linked PLA (see Chapters 2 and 3), though with a much lower $E_a$ of 105 kJ/mol (Figure A.2). As with ACPLA, Sn(Oct)₂ exhibited very little catalytic activity when embedded in ECP4MCL. Even after 10000 s, these materials had relaxed no more than 15% of their stress at 120 °C. From these results, we were able to conclude that Sn(Oct)₂ was most likely not catalyzing appreciable transesterification. Although Sc(OTf)₃ showed fantastic catalytic ability for stress relaxation of these polyester networks, we began to notice the materials containing Sc(OTf)₃ would slowly degrade at room temperature and after 1-2 weeks exposed to atmosphere, ECP4MCL had reverted back to a viscous liquid. We hypothesized this was due to reaction of esters with atmospheric water which was drawn into the material by the hygroscopic nature of Sc(OTf)₃ and exacerbated by the catalyst’s high activity. Despite prior knowledge of the catalyst’s hygroscopic nature, P₄MCL is a relatively hydrophobic material, and made up over 90 wt% of the material, thus, this degradation was unexpected. Later, it became obvious that rare earth metal triflates also contributed to significant hydrolysis of ACPLA as well. Consequently, we chose to forego further examination of Sc(OTf)₃ as a vitrimer catalyst.
Figure A.2: A) SRA of ECP4MCL at 20% strain and B) Arrhenius plot of ECP4MCL with 2.5 mol% Sc(OTf)$_3$.

Table A.2: Mechanical and Thermal Properties of ECPMCL.

<table>
<thead>
<tr>
<th>PMCL</th>
<th>$M_n$ (kg/mol)</th>
<th>Catalyst</th>
<th>mol% catalyst to OH</th>
<th>Gel %</th>
<th>$E'$ at 100°C (MPa)</th>
<th>$M_x$ (kg/mol)</th>
<th>$T_g$ (°C, DMTA)</th>
<th>$T_g$ (°C, DSC)</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 Sn(Oct)$_2$</td>
<td>2.5</td>
<td>95</td>
<td>1.2</td>
<td>6.9</td>
<td>-54</td>
<td>-53</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 Sc(OTf)$_3$</td>
<td>2.5</td>
<td>75</td>
<td>0.3</td>
<td>28.3</td>
<td>-54</td>
<td>-54</td>
<td>109 ± 5.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Appendix A.4 Experimental

Appendix A.4.1 Materials and Methods

All chemicals were purchased from Sigma-Aldrich and were used received unless otherwise specified. All solvents were purchased from Fisher scientific and purified by distillation over CaH$_2$ three times. Sn(Oct)$_2$ was purified via vacuum distillation (130-150 °C, 30 mTorr). Altasorb kindly provided (±)-lactide, which was also used as received. All chemicals were stored under N$_2$ unless otherwise specified. HTSPLA was synthesized as with HTSPLA in Chapter 2, except that succinic anhydride (1.3 eq to OH) was added at the end of the polymerization and further stirred for 1 h at 160 °C.
Appendix A.4.2 Synthetic Procedures

Synthesis of ACPLA

CATSPLA (1.5 g, 1 eq –OH) and a tris(aziridine) (1 eq aziridine) were mixed in 2 mL DCM (Sn(Oct)$_2$ or no catalyst) or ethyl acetate (rare earth metal catalysts) along with the corresponding catalyst (2.5 mol% to –OH). The resulting solution was poured into a polypropylene container and allowed to sit for 24 h at room temperature and then 48 h at 80 °C under vacuum.

Synthesis of 4-methylcaprolactone

To a 2-L erlenmeyer was added $m$-chloroperbenzoic acid (105 g) and DCM (800 mL) under stirring. Once dissolved, the solution was dried over MgSO$_4$ and filtered into a 2-L, 3-neck round bottom flask equipped with a septum, addition funnel, and thermometer. The MgSO$_4$ was then rinsed with 200 mL DCM, which was then filtered into the 2-L round bottom flask. The resulting solution was cooled to 0-5 °C in an ice bath and 4-methylcaprolactone (46.5 mL) in DCM (50 mL) was added dropwise over 30 min. The ice bath was then removed and the reaction was allowed to stir for another 3 hours at room temperature, followed by vacuum filtration to remove precipitated $m$-chlorobenzoic acid. The filtrate was then washed with 10% aqueous sodium sulfite (3x) and brine (2x) followed by drying over MgSO$_4$. The resulting solution was concentrated via rotovap to give a crude yellow product (49.7 g) which was allowed to sit over CaH$_2$ for approximately 2 days before distilling (2x) to yield a clear liquid (84-86 °C at 1 Torr, 31.3 g, 66% yield). $^1$H NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 4.33-4.24 (m, 1H), 4.24-4.13 (m, 1H), 2.72-2.56 (m, 2H), 2.00-1.85 (m, 2H), 1.85-1.72 (m, 1H), 1.56-1.44 (m, 1H), 1.39-1.26 (m, 1H), 1.00 (d, 3H).
Synthesis of 4-arm carboxyl-terminated P4MCL

Sn(Oct)$_2$ (4 mg, 0.025 mol%) was dissolved in a minimal amount of toluene (ca. 0.1 mL) and charged in a pressure vessel, along with 4-methylcaprolactone (5 g, 39 mmol) and pentaerythritol (0.073 g, 0.54 mmol). The reaction mixture was heated to 160 °C for 3 h, then succinic anhydride (0.3 g, 3 mmol) was added under N$_2$ and stirred for 1 h. The mixture was then allowed to cool to room temperature and dissolved in an approximately equal volume of dichloromethane (DCM). The subsequent solution was precipitated in methanol (ca. 10 times volume of product solution), redissolved in an approximately equal volume of DCM and reprecipitated in hexanes (10 times volume of DCM solution). The resulting polymer was then dissolved in DCM, transferred to a polypropylene container and dried with N$_2$ flow for approximately 24 h. The polypropylene container was then put in a vacuum oven at approximately 60 °C and 20 mTorr for 72 h, and subsequently cooled to room temperature. The resulting polymer was obtained in a 76% isolated yield. $^1$H NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 4.20-4.01 (m, 158 H), 2.64 (m, 16 H), 2.42-2.23 (m, 150 H), 1.74-1.39 (m, 390 H), 0.97-0.87 (m, 240 H). $M_n = 10.1$ kg mol$^{-1}$. DSC: $T_g = -60$ °C.

Synthesis of ACPLA

CATSP4MCL (1.5 g, 1 eq –OH) and triglycidyl isocyanurate (1 eq aziridine) were mixed in 2 mL DCM [Sn(Oct)$_2$ or no catalyst] or ethyl acetate [Sc(OTf)$_3$] along with the corresponding catalyst (2.5 mol% to –OH). The resulting solution was poured into a polypropylene container and allowed to sit for 24 h at room temperature. In the presence of Sn(II) or no catalyst, the film was allowed to further cure under N$_2$ at 120 °C for 3 h. In
the presence of Sc(III), the film was allowed to further cure under vacuum at 80 °C for 12 h.

Appendix A.4.3 Characterization

Please refer to Chapter 2 for characterization methodologies for these materials.

Appendix A.5 References


Appendix B: Olefin Metathesis VitrimerS from 3-Methylcyclooctene

Appendix B.1 Introduction

Studies performed in the Guan research group revealed the potential for vitrimers via olefin metathesis utilizing cross-linked polybutadiene with Grubbs 2nd generation catalyst (G2). Unfortunately, these materials suffered a number of drawbacks: 1) catalyst was added via solvent at fairly low temperatures (−42 °C), adding an additional step to production, and 2) the incredibly fast stress relaxation of the resulting materials at room temperature reduced their mechanical robustness. Thus, we sought to produce these materials in one step from monomer via ring-opening metathesis polymerization (ROMP) of 3-methylcyclooctene (3-MeCOE) with two bis(cyclooctene) cross-linkers (Scheme B.1) and then attempt to utilize a literature-reported UV-activated metathesis catalyst to control when stress relaxation occurs (Scheme B.2).

Scheme B.1 Synthesis of a cross-linked poly(3-MeCOE)

Scheme B.2 Synthesis of a UV-activated metathesis catalyst
Appendix B.2 Synthesis of Cyclooctene-based Cross-linkers

Two possible cyclooctene-based (COE) cross-linkers were synthesized in this study, bis(COE) and pentamethylene-bis(COE) [PM-bis(COE)] as shown in Scheme B.3. The synthesis of bis(COE) was rather facile, occurring readily when dripped over elemental magnesium in anhydrous ether to give a decent yield after purification (68%). The production of PM-bis(COE) was not quite as facile as a large portion of bis(COE) was recovered in the process, presumably occurring via Mg transfer to 3-bromocyclooctene. Furthermore, the distillation of PM-bis(COE) is fairly difficult due to a high boiling point, and thus, fairly low yields were typical (10%). Furthermore, the resulting materials are identical in mechanical and thermal properties and thus, this study will solely focus on the use of bis(COE) as a cross-linker.

Scheme B.3 Synthesis of BCOEs

Appendix B.3 ROMP of 3-MeCOE with COE-based Cross-linkers

The synthesis of cross-linked poly(3-MeCOE) is rather facile with G2 (0.025 mol%) when performed under N\textsubscript{2} at 60 °C for 3 h, giving a nearly 80% yield of polymer after vacuum drying. The loss of mass in these materials is presumably due to evaporation of monomer due to its volatility and the poor seal of the polypropylene jars utilized in the cross-linking reaction. Indeed, 3-MeCOE will proceed to nearly 99% conversion under similar conditions when no cross-linker is present. In the first experiments, 1 mol% of
cross-linker was used with 0.025 mol% G2, and was fairly successful. Stress relaxation was extremely promising and showed rather fast relaxation with activation energies nearly identical to literature values for G2-catalyzed alkene metathesis (Figure B.1).

![Stress relaxation Arrhenius plot of the characteristic relaxation time ($\tau^*$).](image)

**Figure B.1:** Stress relaxation Arrhenius plot of the characteristic relaxation time ($\tau^*$). Samples were run between 40-60 °C and 10% strain.

Still, we found that the gel fractions of the materials are rather poor when using below 1 mol% of cross-linker (0 to 0.7) and maintaining a constant 0.025 mol% G2. When varying the amount of cross-linker, the gel fractions did not necessarily correspond to the amount of cross-linker present (Table B.1). We began to question why this may be the case and soon realized that results become extremely inconsistent when air exposure is not minimized. Indeed, stress relaxation of two samples produced under nearly identical situations show that short term exposure to oxygen (3 days) can slow stress relaxation by an order of magnitude, though not nearly as slow as a sample treated with ethyl vinyl ether (Figure B.2). Being more careful to prevent air exposure, we made another material with the same amount of cross-linker and catalyst and ran stress relaxation (Figure B.2, sample
C) and found that this material relaxed stress significantly faster, presumably due to less G2 degradation.

Table B.1: Cross-linked poly(3-MeCOE) thermal and mechanical properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cross-linker (mol%)</th>
<th>Catalyst (mol%)</th>
<th>Gel fraction</th>
<th>$T_d$ (5%)</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25</td>
<td>0.025</td>
<td>0.688</td>
<td>318</td>
<td>−64</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.025</td>
<td>0</td>
<td>341</td>
<td>−64</td>
</tr>
<tr>
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<td>0.025</td>
<td>0.541</td>
<td>317</td>
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</tr>
<tr>
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<td>0.025</td>
<td>0.778</td>
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<td>−63</td>
</tr>
<tr>
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<td>2</td>
<td>0.025</td>
<td>0.863</td>
<td>332</td>
<td>−63</td>
</tr>
</tbody>
</table>

Figure B.2 Stress relaxation at for three identical samples containing 1 mol% bis(COE) and 0.025 mol% G2. Samples run at 10% strain and 50 °C. The blue line denotes a sample that has been exposed to ethyl vinyl ether in order to deactivate the G2 present in the material.

Regardless of the instability seen in the other materials, we still sought to make the UV-activated catalyst and try to produce cross-linked polymers with it. After producing the catalyst (Scheme B.2), we found that even at 0.05 mol% of the catalyst, we were unable to get it to polymerize 3-MeCOE with UV-light and heat, which is likely due to its insolubility on the monomer. Based on this result and the poor oxidative stability of the polymers above, we chose to discontinue this project.
Appendix B.4 Experimental

Appendix B.4.1 Materials

All chemicals were purchased from Sigma Aldrich and used as received unless otherwise stated. 2-thiollnaphthaene was purified via vacuum sublimation. 3-bromoCOE and 3-MeCOE were produced via a literature procedure. The UV-activated metathesis catalyst was also produced via a literature procedure, though 2-chlorobenzaldehyde was used in place of 2-fluorobenzaldehyde. All solvent were purchased from Fisher Scientific (Hampton, NH), except DMF which was purchased from Sigma Aldrich; DCM was purified via a GC-SPS-4-CM glass contourt 800-L solvent purification system obtained from Pure Process Technologies (Nashua, NH).

Appendix B.4.2 Synthetic Procedures

Synthesis of bis(COE)

Mg turnings (6.5 g, 159 mmol) were added to a RBF equipped with a thermometer, septum, and reflux condenser. The flask was evacuated and refilled with argon (3x) and anhydrous THF (50 mL) was added via cannulated to the addition funnel. Then, 3-bromocyclooctene (10 g, 7.52 mL, 53 mmol) was added dropwise; the reaction mixture was then allowed to stir overnight. The next morning, the reaction was cooled to 0 °C and a saturated NH₄Cl solution (5 mL) was added dropwise. The resulting suspension was then poured over DI water. The aqueous layer was then extracted with ether (3 x 50 mL), neutralized with saturated NaHCO₃, and dried with brine followed by MgSO₄. The solvent was then evaporated to yield a colorless wax (6 g, 68% yield). The product is further purified by a Kugelrohr distillation (50-100 mTorr and oven at 100 °C). ¹H NMR (500 MHz, CDCl₃; 25 °C): δ (ppm) = 5.68 (m, 2 H), 5.34 (m, 2 H), 2.44 (m, 1 H), 2.36 (m, 1
H), 2.23 (m, 2 H), 2.03 (m, 2 H), 1.66 (m, 6 H), 1.50 (m, 4 H), 1.32 (m, 4 H), 1.17 (m, 1 H), 1.05 (m, 1 H).

**Synthesis of PM-bis(COE)**

To a solution of 3-bromo-1-cyclooctene (20 g, 15 mL, 106 mmol) and CuI (200 mg, 1.1 mmol) in anhydrous THF (100 mL), pentamethylenebis(magnesium bromide) in THF solution (0.5 M, 48 mL, 24 mmol) in additional anhydrous THF (50 mL) was added dropwise at 0 °C over 15 min under nitrogen flow. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was carefully quenched by adding ice water slowly at 0 °C and then neutralized slowly with saturated NH₄Cl. The organic layer was separated, and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was dried over anhydrous MgSO4 and concentrated via rotovap to afford crude 1,5-bis(cyclooctenyl)pentane as a light yellow oil. The product was then purified by distillation, yielding first bis(cyclooctene) [ca. 2 g] followed by 1,5-bis(cyclooctenyl)pentane (3 g, 10% yield, 150 °C at 50 mTorr). Alternatively, a Kugelrohr distillation can be performed, first at 100 °C to remove bis(cyclooctene) and then 170 °C to obtain the desired product. ^1H NMR (500 MHz, CDCl₃; 25 °C): δ (ppm) = 5.63 (q, 1 H), 5.20 (t, 1 H), 2.50-2.34 (m, 1 H), 2.23 (m, 1 H), 1.68 (m, 3 H), 1.52 (m, 2 H), 1.19-1.04 (m, 3H).

**Representative synthesis of crosslinked poly(3-MeCOE)**

To a 20-mL vial was added bis(COE) [70 mg, 1 mol%], butylatedhydroxytoluene (0.02 g) and 3-MeCOE (2 g). The resulting solution was stirred until homogenous and then G2 catalyst solution (3 mg, 0.12 mL in 25 mg/mL solution in DCM, 0.025 mol%) was added via syringe. The solution was allowed to stir for 30 s and then poured into a
polypropylene jar. The jar was promptly sealed and placed in an oven under N$_2$ at 60 °C for 3 h. The oven was then allowed to slowly cool to room temperature, after which the material was placed under vacuum for 24-72 h.

**Appendix B.4.3 Characterization**

Please refer to chapter 2 for characterization techniques.

**Appendix B.5 References**