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UNIVERSITY OF CALIFORNIA, IRVINE

Design, Synthesis and Testing of a Zinc Amide Self-healing System and a Boronic Ester Vitrimer System

THESIS

submitted in partial satisfaction of the requirements for the degree of

MASTER OF SCIENCE

in Chemistry

by

Hongkai (Eddy) Zhao

Thesis Committee: Professor Zhibin Guan, Chair Assistant Professor Allon Hochbaum Assistant Professor Shane Ardo

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DEDICATION

То

my parents and friends

in recognition of their tremendous support

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ABSTRACT OF THE THESIS

Design, Synthesis and Testing of a Zinc Amide Self-healing System and a Boronic Ester Vitrimer System

By

Hongkai (Eddy) Zhao Master of Science in Chemistry University of California, Irvine, 2016 Professor Zhibin Guan, Chair

Dynamic materials including self-healing polymers and vitrimers have huge potential for improving current material's performance, lifetime and processability. In this thesis, we have synthesized a self-healing system by incorporating zinc amide interaction and a vitrimer system via transesterification of boronic esters. Chapter 1 provides a brief introduction to the background of self-healing polymers and vitrimers. Chapter 2 details the design and development of a zinc amide self-healing polymer system. Chapter 3 discusses attempts to synthesize a catalyst free, tunable boronic ester vitrimer.

Chapter 1: Introduction to Self-healing Polymers and Vitrimers

1.1 Background of Self-healing Polymers and Vitrimers

Materials that can heal themselves after damage can improve their service time and safety. The field of self-healing polymers has been burgeoning rapidly in the past two decades^{1,2} and a typical damage repair cycle of self-healing polymers¹ is illustrated in Figure 1.1.



Evolution of Damage and Repair

Figure 1.1: Damage repair cycle of self-healing polymers. Reprinted from ref. 1

After physical damage is incurred because of chain cleavage or chain slippage, reactive chain ends are generated. Reactive chain ends can then come into contact with each other due to segmental mobility and conformational changes or diffusion of low molecular weight segments. They will then react with each other and reform bonds that repair the network. Various chemistries including covalent bonding,^{3,4} ionic interactions,^{5,6} hydrogen bonding⁷⁻⁹ and $\pi \pi$ stacking^{10,11} have been explored to synthesize such materials. One of the self-healing system in the Guan lab uses zinc imidazole metal ligand interaction in a polystyrene backbone.¹² As hydrogen bonding was also shown before to induce self-healing, the Guan lab attempted to incorporate hydrogen bonding by introducing amide groups into the previous zinc imidazole system to synthesize a two-tier self-healing system. However, this new two tier system showed very poor self-healing efficiency which led us to hypothesize that zinc and amide group might interact with each other to disturb zinc imidazole interaction and amide amide hydrogen bonds. The Guan lab decided to look into this new zinc amide interaction and the following work details the design, synthesis and characterization of this new self-healing polymer.

Vitrimer was a new type of polymer material invented by Leibler in 2011.¹³ Crosslinked polymer networks that are able to exchange their cross-links are called Covalent Adaptable Networks (CANs) and vitrimers are CANs following an associative mechanism.¹⁴ (Figure 1.2) The stimulus for cross-link exchange is usually



Figure 1.2: Exchange Mechanisms of CANs: a) dissociative mechanism b) associative mechanism. *Reprinted from ref. 13.*

heat. Due to the cross-linked nature of the network, at low temperature vitrimers are insoluble in organic solvents and mechanically robust, behaving like thermosets. At elevated temperature, the cross-linked covalent bonds start to exchange with each other. Because the exchange mechanism is associative, an old cross-link is broken only after a new one has formed. This maintains the overall cross-link density and renders the material insoluble in organic solvent. However, due to the dynamics in the network because of cross-link shuffling, the material becomes malleable and can be reprocessed into different shapes with ease. Further investigation shows vitrimer was the

first organic polymer material that has similar viscosity behavior as silica glass. Various chemistries including transesterification,¹³ transamination¹⁵ and transalkylation¹⁶ have been incorporated into the vitrimer systems.

Problems with previous vitrimer systems include catalyst incorporation, toxic starting materials, inability to tune material properties. Wulff and coworkers showed that the rate of transesterification of boronic esters can be tuned by neighboring groups over many orders of magnitude.¹⁷ The Guan lab decided to incorporate transesterification of boronic esters in a vitrimer system, which would be catalyst free and have tunable properties.

1.2 Summary and Outlook

Both self-healing polymers and vitrimers are at the forefront of current material research and will have a tremendous impact on the industry of new materials. Although various chemistries have been incorporated in polymeric materials to achieve self-healing, there remain a great number of dynamic interactions to be explored. As we have noticed that zinc amide interaction existed in a previously studied two-tier system, we tried to study this interaction and incorporate it in a polymer system to achieve self-healing. Vitrimer is another type of dynamic materials that behave as thermoset at service temperature and can be reprocessed at elevated temperatures. Since the rate of transesterification of boronic ester can be tuned over many orders of magnitude by a neighboring group, we have incorporated this in a polymer to synthesize a catalyst free, tunable boronic ester vitrimer system. Efforts in the Guan lab are ongoing to optimize both systems.

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Chapter 2: Zinc Amide Self-healing Polymer System

2.1 Introduction

The human body and many biological materials are able to self-heal after mechanical damage. In contrast, most synthetic materials cannot self-repair and must be replaced after functional failure. If the self-healing power from nature can be mimicked and applied to synthetic materials, their lifetime would be lengthened, propensity to mechanical failure would be reduced, and cost of maintenance or replacement would be minimized. For reasons above, research in dynamic materials has burgeoned since the early 2000s.¹

The field of self-healing polymers started in 2001, when White et al. developed a self-healing system embedded with catalyst and encapsulated monomers.² Microcapsules will break and release monomers which polymerize to heal after mechanical damage. Since then, a wide range of materials using reversible covalent³⁻⁶ and non-covalent bonds⁷⁻⁹ have been used to promote self-healing.

Material combining good healing efficiency and robust mechanical properties is one of the main goals of self-healing polymers. Guan and coworkers have shown incorporating sacrificial bonds in a self-healing polymer system can dramatically improve its mechanical properties such as strain at break and toughness.¹⁰ Specifically, secondary amide side chains were used to create dynamic energy diss linked polymer network, which can self-heal via o



Figure 2.1: Design concept for (a) reversible, energy dissipative rupture of sacrificial hydrogen bonds in a (b) G2-mediated olefin-containing network. *Reprinted from ref. 10.*

chains were used to create dynamic energy dissipative hydrogen bonds in a covalently crosslinked polymer network, which can self-heal via olefin metathesis (Figure 2.1). Following the same strategy, the Guan group proceeded to introduce sacrificial hydrogen bonds into another highly efficient self-healing system with zinc imidazole motif.¹¹ This zinc imidazole self-healing system was very efficient because zinc imidazole interaction was very

dynamic. However, after secondary amide side chains were incorporated into this imidazole containing polymer, the material became very brittle and hard and did not achieve self-healing after zinc incorporation. It was hypothesized that zinc and amide might have interacted strongly enough to disturb zinc imidazole interaction.

Thus if we can probe and tune the strength and dynamics of zinc



Figure 2.2: Design concept for a self-healing polymer with zinc amide motif

amide interaction, this might prove to be another self-healing motif. Herein described is my effort to synthesize self-healing amide containing polymers (ACPs) with zinc amide motif (Figure 2.2).

2.2 Results and Discussion

Part I. Synthesis and Characterization of N-ethylisobutyramide and ACPs



Scheme 2.1 a) Synthesis of N-ethylisobutyramide b) Synthesis of ACMs c) Synthesis of ACPs by RAFT

Synthesis of N-ethylisobutyramide and ACPs is shown in Scheme 2.1. Nethylisobutyramide was synthesized by reacting amine with acid chloride.¹² This amide molecule was used in the NMR spectroscopy study shown below. All monomers follow a simple two step synthesis.¹³ First, **1** is reacted with **2** via N-terminal acetylation to form **3**, which is then coupled with acrylic acid through EDC coupling to make amide containing monomers (ACMs) with different steric bulk and electron density near the amide group. We hypothesized that zinc would bind to the oxygen in the amide functional group, thus by changing the steric bulk and electronic density on the adjacent functional group, we should be able to tune ACPs' binding affinity with zinc. ACMs were copolymerized with n-butyl acrylate (BA) to form ACPs (ACP-CH₃, ACP-CF₃ ,ACP-isopropyl and ACP-t-butyl) by reversible addition-fragmentation chain transfer polymerization (RAFT), a living polymerization technique which offers control on rate of polymerization and polydispersity (PDI).¹¹ BA was incorporated to increase solubility in organic solvents and thus improve processability. ACM to RAFT initiator molar ratio was 200:1. Polymerization was stopped at 50% conversion to get a target average chain length of 100 with low PDI. ACM to BA molar ratio was 35 : 65, this ratio was adopted from previous work in the Guan lab.¹² All ACPs were characterized by ¹H NMR and gel permeation chromatography (GPC) (Table 2.1). Due to time constraint and a change of project, ACP-isopropyl was not made.

% conversion	% amide	Mn from NMR	GPC Results	PDI	Mw	Mn from GPC		
49.0	36.0	15000	R = methyl	1.33	9900	7500		
47.3	33.6	16000	R = t-butyl	1.29	9500	7400		
55.0	34.0	19000	$R = CF_3$	1.28	10000	7800		
	% conversion 49.0 47.3 55.0	% conversion% amide49.036.047.333.655.034.0	% Mn conversion % amide Mn 49.0 36.0 15000 47.3 33.6 16000 55.0 34.0 19000	% Mn GPC Results 49.0 36.0 15000 R = methyl 47.3 33.6 16000 R = t-butyl 55.0 34.0 19000 R = CF ₃	$\frac{\%}{conversion}$ $\frac{Mn}{from}$ NMRGPC ResultsPDI49.036.015000R = methyl1.3347.333.616000R = t-butyl1.2955.034.019000R = CF_31.28	$\frac{9}{6}$ conversion $\frac{Mn}{from}$ NMRGPC ResultsPDIMw49.036.015000R = methyl1.33990047.333.616000R = t-butyl1.29950055.034.019000R = CF31.2810000		

 Table 2.1: Characterization of ACPs

The number averaged molecular weight (Mn) determined by ¹H NMR does not match those determined by GPC because GPC uses polystyrene standard, which has a very different structure from polyacrylate. This caused GPC results to be off from real values. However, GPC yielded correct relative values. It was concluded that three ACPs with similar chain lengths and % amide were synthesized.

Part II. NMR Study

A model amide molecule, N-ethylisobutyramide, was studied by NMR to determine the rate of exchange of zinc and amide. By taking the NMR of amide with zinc in solution at low temperatures, we expected to see coalescence of the bound and unbound peaks of amide with





zinc and then proceed to calculate the rate of exchange. N-ethylisobutyramide was added to deuterated acetone to have a concentration of 0.232 M, the highest concentration we could get without precipitating amide or zinc di[bis(trifluoromethylsulfonyl)-imide], $Zn(NTf_2)_2$, out of solution. $Zn(NTf_2)_2$ was added so that Amide/Zn molar ratio = 10 to achieve similar populations of bound/unbound amides. ¹H NMR of amide with zinc was taken at 4 various temperatures: 298

K, 273 K, 223 K and 183 K and ¹H NMR of only amide was taken at 298 K (Figure 2.3). Coalescence of bound and unbound amide peaks were not observed so kinetics calculations could not be carried out. However, all the peaks (a, c, d, f) near the amide groups shifted further down field as the temperature went down. This was because at low temperature there were a higher percentage of amides bound to zinc. Zinc binding to carbonyl would cause the neighboring hydrogens to be deshielded, as the exchange time scale was faster than NMR time scale, NMR peaks were a statistical average of amides bound and unbound which would show a downfield shift. NMRs of three ACMs, with different zinc amide ratio were also taken to further confirm this zinc amide interaction. ¹H NMR at 298 K of three ACMs were taken with amide/Zn molar ratio = 12, 4, 2, 1 along with only ACM and only Zn(NTf₂)₂ (Figure 2.4).



Figure 2.4: Kinetic NMR study of three ACM with different zinc amide molar ratio. Three peaks shift in each graph but only one peak is highlighted in orange square to show the trend.

Zn(NTf₂)₂ only shows a solvent peak and another peak around 6.0 ppm which we first attributed to water. The peak still existed after drying with abderhalden's pistol and was not taken into account in NMR analysis. NMRs of all three ACMs show that different zinc loading lead to different peak shifts. All results above do show that zinc amide interaction can be a dynamic and tunable interaction which was then studied in polymers samples by rheology experiments.

Part III. Rheology Experiments

Rheology is the study of flow of materials. In this study, dynamic viscosity, storage modulus and loss modulus were measured. Polymer samples were divided into halves, half of polymer is without Zn and the other half has amide/Zn molar ratio = 20:1. This low concentration of Zn was chosen because preliminary investigation showed that high incorporation of zinc (amide/zinc molar ratio = 4 : 1) resulted in hard material unable to be characterized by rheology. A frequency sweep at room temperature (25 °C) from 0.1 Hz to 100 Hz was carried out and % strain was fixed at 25% following literature protocol.¹¹



Figure 2.5: a) Storage (dashed) and loss (solid) modulus of three ACPs with Zn b) Storage (dashed) and loss (solid) modulus of three ACPs without zinc c) dynamic viscosity of three ACPs with/without Zn.

Dynamic viscosity measures the resistance of material to shear stress. All ACPs showed increased dynamic viscosity as zinc is added at any specific frequency, which corroborated that zinc amide interaction exists. ACP-CH₃ showed higher viscosity at any frequency than ACP-CF₃ or ACP-t-butyl. This result can be explained as follows. Placing a very electron withdrawing CF₃ next to the carbonyl reduces electron density on oxygen, which then binds weaker to zinc. t-butyl group is bulkier than CH₃ and its increased steric bulk next to the carbonyl of amide hinders the oxygen from interacting with zinc. Both of these two reasons above lead to lower dynamic viscosity in polymer samples and this also showed that zinc amide interaction was tunable via modifying the functional group next to amide. Storage modulus G' measures the stored energy and loss modulus G'' measures energy dissipated. Frequency at which G' and G'' cross-over measures the rate of bond exchange. We saw no cross-over of storage and loss modulus before 100 Hz and could not determine their rates. In order to observe G' and G'' cross-over point, another frequency sweep at elevated temperature can be carried out.

2.3 Conclusions and Future Work

Coalescence of bound and unbound peaks of amide with zinc were not observed due to faster exchange time scale than the NMR time scale, however, small amide molecules at different temperatures and with different zinc amide ratios showed peak shifts for hydrogens next to the amide group, which supported zinc amide interaction exists. Amides with various functional groups of different steric bulk and electron density were incorporated in polymers and tested by rheology, which showed different strengths of interaction. Future works include incorporating zinc amide in two-tier multiphasic polymers and test for mechanical and selfhealing properties.

2.4 Experimental

General Experimental Information Unless otherwise noted, reactions were carried out with stirring with a magnetic stir bar at room temperature. Anhydrous solvents were purified through a column of alumina according to the method described by Grubbs et al¹⁴ before use. All commercial reagents were used as received unless otherwise noted. Flash column chromatography was performed by forced flow of indicated solvent systems over 32 - 63u silica gel from Dynamic Adsorbants (Norcross, GA). ¹H NMR and ¹³C NMR spectra were recorded at 500 and 125 MHz, respectively, on Bruker GN-500 or CRYO-500 spectrometers. ¹H NMR and ¹³C NMR chemical shifts are reported as δ values in ppm relative to TMS or residual solvent: CDCl₃ (7.26 ppm; 77.0 ppm), or CD₂Cl₂ (5.30 ppm; 54.0 ppm). ¹H NMR data are reported as follows: chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), coupling constants in Hz, and relative integration in number of protons. Multiplets (m) are reported over the range of chemical shift at which they appear. For ¹³C NMR spectra, only chemical shift values are reported. Mass Spectra were obtained on Micromass LCT (ES-MS, low resolution), Micromass Autospec (ES-MS and GC-MS, high resolution), and Perseptive Biosystems DE STR (MALDI-TOF) instruments. Gel Permeation Chromatography (GPC) traces were obtained on an Agilent 1100 SEC system using a PLGel Mixed-C column from Polymer Labs (Amherst, MA). THF or DMF was used as eluting solvent at a flow rate of 1.0 mL/min. Number averaged and weight averaged molecular weight distributions (M_n and M_w, respectively) of samples were measured with respect to polystyrene (PS) standards purchased from Aldrich (Milwaukee, WI). ¹H NMR, ¹³C NMR, and HRMS are reported for any new compounds or compounds following a new procedure. For all published compounds, only ¹H NMR is reported.

Synthesis of N-ethyllsobutyrylamide: The synthesis was adapted from a previously reported procedure.¹² Solution of sodium hydroxide (0.4904g, 12.26mmol) in 1.5mL of water was slowly added to ethylamine hydrochloride (0.500g, 6.13mmol) in 1.05mL of water. The mixture was cooled for 10 minutes in ice bath. Isobutyryl chloride (0.654g, 6.13mmol) was slowly added dropwise over 10 minutes to make sure temperature of mixture is below 10°C. Mixture was then allowed to go back to room temperature overnight. The amide layer was decanted. Aqueous layer was extracted with 0.3mL of diethyl ether 3 times. Amide and diethyl ether extracted were combined and dried with anhydrous sodium sulfate. It was then condensed by rotary evaporation to yield a colorless oil(0.1195g, 16.9%). ¹H NMR(500 MHz, CDCl₃) δ 6.92 (s, 1 H), 3.17 (dq, *J* = 7.0 Hz, 5.0 Hz, 2 H), 2.35 (septet, J = 7.0 Hz, 1 H), 1.07-1.03 (m, 9 H).

General Procedure for Synthesis of N-(5-hydroxypentyl)acetamide, N-(5-hydroxypentyl)isobutyramide, N-(5-hydroxypentyl)pivalamide: The synthesis was from a previously reported procedure.¹³ 5-aminopentanol (10g, 96.9mmol) was added to 150mL ethyl acetate and cooled in ice bath for 10 minutes. Acetic anhydride (10.92g, 106.6mmol)/isobutyric anhydride (16.90g, 106.6mmol)/pivalic anhydride (19.85g, 106.6mmol) was added dropwise slowly. The reaction reacted under nitrogen and was allowed to slowly go back to room temperature overnight. 20 hours later, 10mL of methanol was added to the mixture. After 30 minutes. Mixture was then condensed by rotary evaporation.

For synthesis of N-(5-hydroxypentyl)acetamide, the condensed mixture was put under high vacuum at 80°C overnight to yield a colorless oil(14.98g, 106% yield). The identity was confirmed by ¹H NMR with a small amount of impurity. ¹H NMR(500 MHz, CDCl₃) δ 6.65 (s, 1 H), 4.40 (br. s, 1 H) 3.55 (t, *J* = 7.0 Hz, 2 H), 3.15 (q, J = 7.0 Hz, 2 H), 1.91 (s, 3 H), 1.56 – 1.42 (m, 4 H) 1.38 – 1.29 (m, 2 H).

For synthesis of N-(5-hydroxypentyl)isobutyramide, 150 mL of dichloromethane was added to the mixture and was then washed sequentially with equal volume of saturated sodium bicarbonate and brine and dried with anhydrous sodium sulfate. Mixture was then condensed by rotary evaporation to yield a yellow, viscous oil (6.90g, 41.1% yield). The identity of product was confirmed by ¹H NMR, ¹³C NMR, and HRMS. ¹H NMR (500 MHz, CDCl₃) δ 5.80 (s, 1 H), 3.63 (t, *J* = 6.5 Hz, 2 H), 3.23 (q, J = 6.5 Hz, 2 H), 2.39-2.29 (m, 2 H), 1.64-1.48 (m, 4 H), 1.42-1.35 (m, 2 H), 1.13 (d, J = 6.8 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 177.3, 62.5, 39.2, 35.7, 32.2, 29.4, 23.0, 19.7. HRMS (CI): m/z calcd [M+Na]⁺: 196.1313; found: 196.1312.

For synthesis of N-(5-hydroxypentyl)pivalamide, 150mL of Dichloromethane was added to the mixture and was then washed sequentially with equal volume of saturated sodium bicarbonate and brine and dried with anhydrous sodium sulfate. Mixture was then condensed by rotary evaporation to yield a yellow, viscous oil (14.08g, 77.6% yield). The identity of product was confirmed by ¹H NMR, ¹³C NMR and HRMS. ¹H NMR (500 MHz, CDCl₃) δ 5.85 (s, 1 H), 3.59 (t, *J* = 8.2 Hz, 2 H), 3.20 (q, J = 8.5 Hz, 2 H), 2.62 (s, 1 H), 1.58-1.45 (m, 4 H), 1.40-1.33 (m, 2 H), 1.15 (s, 9 H). ¹³C NMR (125 MHz, CDCl₃) δ 178.7, 62.4, 39.4, 38.6, 32.1, 29.4, 27.6, 23.1. HRMS (CI): m/z calcd [M+Na]⁺: 210.1470; found: 210.1462.

Synthesis of 2,2,2-trifluoro-N-(5-hydroxypentyl)acetamide: The synthesis is adapted from a previously reported procedure.¹⁵ 5-amino-pentanol (5.0g, 48.45mmol) and triethylamine (TEA) (20.77mL, 145.35mmol) were dissolved in 100mL dry DCM and cooled in ethylene glycol with dry ice, temperature was kept at -10°C. Trifluoroacetic anhydride (11.19g, 53.3mmol) was added dropwise slowly to make sure temperature stay below 0°C. The reaction

reacted under nitrogen and was allowed to slowly go back to room temperature overnight. 20 hours later, 20mL of DI water was added to the mixture. After 20 minutes, organic mixture was condensed by rotary evaporation to a syrup. The syrup was then purified by column chromatography (silica, gradient 100% DCM to 80% DCM/20% Acetone). It was then condensed by rotary evaporation to yield a colorless, nonviscous oil (6.26g, 62.9% yield). The identity of product was confirmed by ¹H NMR, ¹³C NMR and HRMS. ¹H NMR (500 MHz, CDCl₃) δ 6.90 (s, 1 H), 3.65 (t, *J* = 6.5 Hz, 2 H), 3.35 (q, J = 7.0 Hz, 2 H), 2.04 (s, 1H), 1.67-1.55 (m, 4 H), 1.45-1.35 (m, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 157.5, 116.5 (q), 62.5, 39.6, 30.1, 28.2, 22.8. HRMS (CI): m/z calcd [M+Na]⁺: 222.0718 ; found: 222.0721.

Synthesis of 5-acetamidopentyl acrylate: The synthesis was from a previously reported procedure.¹³ EDC·HCl(30.62g, 159.7mmol) was added to a solution of N-(5-hydroxypentyl)acetamide (14.07g, 96.8mmol), acrylic acid(10.50g, 145.4mmol), DIPEA(20.63g, 159.7mmol) and DCM(264.5mL). The mixture was stirred at room temperature for 24 hours. Another 264.5mL of DCM was added. Mixture was sequentially washed with 529mL of 1M NaOH, 1M HCl, saturated NaHCO₃ and brine. The organic phase was dried with anhydrous Na₂SO₄. It was then condensed by rotary evaporation. Crude product was purified by column chromatography (silica, gradient 100% DCM to 95% DCM/5% Methanol) to yield a colorless oil. (6.43g, 33.3% yield) The identity of product was confirmed by ¹H NMR. ¹H NMR (500 MHz, CDCl₃) δ 6.39-6.26 (m, 2 H), 6.13-6.04 (m, 1 H), 5.83-5.76 (m, 1 H), 4.24 (t, J = 4.5 Hz, 2 H), 3.19 (q, J = 7.25 Hz, 2 H), 1.85(s, 3 H) 1.69-1.61 (m, 2 H), 1.55-1.45 (m, 2 H), 1.41-1.32 (m, 2 H).

Synthesis of 5-isobutyramidopentyl acrylate: The synthesis was from a previously reported procedure.¹³ EDC·HCl (12.60g, 65.7mmol) was added to a solution of N-(5-

hydroxypentyl)isobutyramide (6.90g, 39.8mmol), acrylic acid (4.30g, 59.7mmol), DIPEA (8.49g, 65.7mmol) and DCM (108.9mL). The mixture was stirred at room temperature for 24 hours. Another 108.9mL of DCM was added. Mixture was sequentially washed with 219.8mL of 1M NaOH, 1M HCl, saturated NaHCO₃ and brine. The organic phase was dried with anhydrous Na₂SO₄. It was then condensed by rotary evaporation. Crude product was purified by column chromatography (silica, gradient 100% DCM to 95% DCM/5% Methanol) to yield a colorless oil. (4.20g, 46.4% yield) The identity of product was confirmed by ¹H NMR, ¹³C NMR and HRMS. ¹H NMR (500 MHz, CDCl₃) δ 6.39-6.26 (m, 1 H), 6.13-6.04 (m, 1 H), 5.83-5.76 (m, 1 H), 5.65 (s, 1 H) 4.24 (t, J = 6.5 Hz, 2 H), 3.21 (q, J = 7.0 Hz, 2 H), 2.30(s, 1 H) 1.72-1.64 (m, 2 H), 1.55-1.45 (m, 2 H), 1.41-1.32 (m, 2 H), 1.14 (d, J = 7.0 Hz, 6 H). ¹³C NMR (125 MHz, CDCl₃) δ 177.5, 166.7, 130.9, 128.5, 64.3, 39.1, 35.5, 29.5, 28.2, 23.5, 19.8. HRMS (CI): m/z calcd [M+Na]⁺: 250.1419; found: 250.1412.

Synthesis of 5-pivalamidopentyl acrylate: The synthesis was from a previously reported procedure.¹³ EDC·HCl (23.79g, 124.1mmol) was added to a solution of N-(5-hydroxypentyl)pivalamide (14.08g, 75.2mmol), acrylic acid (8.13g, 112.8mmol), DIPEA (16.03g, 124.1mmol) and DCM (205.8mL). The mixture was stirred at room temperature for 24 hours. Another 205.8mL of DCM was added. Mixture was sequentially washed with 411.6mL of 1M NaOH, 1M HCl, saturated NaHCO₃ and brine. The organic phase was dried with anhydrous Na₂SO₄. It was then condensed by rotary evaporation. Crude product was purified by column chromatography (silica, gradient 100% DCM to 95% DCM/5% Methanol) to yield a colorless oil. (6.04g, 33.3% yield) The identity of product was confirmed by ¹H NMR, ¹³C NMR and HRMS. ¹H NMR (500 MHz, CDCl₃) δ 6.39-6.26 (m, 1 H), 6.13-6.04 (m, 1 H), 5.83-5.76 (m, 1 H), 5.75 (s, 1 H) 4.24 (t, J = 6.8 Hz, 2 H), 3.25 (q, J = 7.0 Hz, 2 H), 1.72-1.64 (m, 2 H), 1.55-1.45

(m, 2 H), 1.41-1.32 (m, 2 H), 1.19 (s, 9 H). ¹³C NMR (125 MHz, CDCl₃) δ 179.2, 166.7, 130.9, 128.5, 64.1, 39.1, 38.1, 29.8, 29.1, 28.1, 23.5. HRMS (CI): m/z calcd [M+Na]⁺: 264.1576; found: 264.1570.

Synthesis of 5-(2,2,2-trifluoroacetamido)pentyl acrylate: The synthesis was from a previously reported procedure.¹³ EDC·HCl (11.43g, 59.62mmol) was added to a solution of 2,2,2-trifluoro-N-(5-hydroxypentyl)acetamide (7.20g, 36.12mmol), acrylic acid (3.73mL, 54.18mmol), DIPEA (10.4mL, 59.60mmol) and DCM (98.8mL). The mixture was stirred at room temperature for 24 hours. Another 98.8mL of DCM was added. Mixture was sequentially washed with 200mL of 1M NaOH, 1M HCl, saturated NaHCO₃ and brine. The organic phase was dried with anhydrous Na₂SO₄. It was then condensed by rotary evaporation. Crude product was purified by column chromatography (silica, gradient 100% DCM) to yield a colorless oil. (5.32g, 58.2% yield) The identity of product was confirmed by ¹H NMR, ¹³C NMR and HRMS. ¹H NMR (500 MHz, CDCl₃) δ 6.87 (s, 1H), 6.40-6.29 (m, 1 H), 6.15-6.07 (m, 1 H), 5.89-5.79 (m, 1 H), 4.15 (t, J = 6.8 Hz, 2 H), 3.39 (q, J = 7.0 Hz, 2 H), 1.72-1.55 (m, 4 H), 1.45-1.35 (m, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 166.5, 157.5 (q), 131.1, 128.2, 116.5 (q), 64.1, 39.6, 28.5, 28.2, 23.1. HRMS (CI): m/z calcd [M+Na]⁺: 276.0823; found: 276.0825.

General Procedure for RAFT Polymerization: The synthesis was adapted from a previously reported procedure.¹¹ Benzyl ethyl carbonotrithioate (a chain transfer agent) (1 eq.), acrylate monomer (70 eq.), butyl acrylate (130 eq.) AIBN (0.2 eq.), anisole (0.5mL as internal standard) and DMF (volume which makes the total acrylate concentration to be 1.5M) was added to a dried schlenk flask. It was purged with nitrogen for 1 hour and then put in oil bath at 65 °C. The reaction was monitored by ¹H NMR by the ratio of acrylate peaks between 5.80ppm to 6.50ppm to the anisole peak at 3.73ppm. A typical polymer ¹H NMR (between 3.5ppm and

6.5ppm) is shown. The reaction was stopped at 50% conversion by opening to air, adding 4methoxy phenol and cooling in ice bath. Mixture was then condensed by rotary evaporation. The residue was then dissolved in minimal acetonitrile and transferred to a Nalgene centrifuge tube. The polymer was precipitated twice in Et₂O/hexane (1:3 v/v) followed by centrifugation at 8500 rpm, for 10 minutes at 4 °C. It was then precipitated two more times in Et₂O/hexane (2:3 v/v) and then characterized by GPC in DMF. Polymer was dissolved in acetonitrile and kept as stock solution. To quantify the mass of polymer measured, some amount of stock solution would be transferred to a pre-weighed vial. The solution would be completely dried in oven at 80 °C for 12 hours under reduced pressure (< 1 torr).

Incorporation of zinc in ACPs: $Zn(NTf_2)_2$ was first dissolved in acetonitrile to make a solution. This $Zn(NTf_2)_2$ solution was added to a vial containing polymer stock solution. The mixture was vortexed for 30 seconds and then transferred to a Teflon mold to air dry in the hood overnight. It was heated to 80°C under house vacuum (150 torr) overnight then followed by high vacuum (<1 torr) at 80°C overnight.

Rheology Procedure: Rheology data were collected on an AR-G2 rheometer from TA Instruments (20 mm Peltier plate with no solvent trap, stainless steel, 2800 µm gap width). The instrument was equipped with Peltier temperature control system. Frequency sweep experiments were performed at 25% strain by varying the frequency between 0.1 and 100 Hz at 25 °C for each polymer system.

Thermal Characterization Procedure: Differential scanning calorimetry (DSC) was performed using a TA Q1000. Polymer samples (5-10 mg) were placed in a non-hermetic pan and scanned against an empty reference. A heat-cool-heat cycle was used. The sample was ramped to 180 °C at a rate of 10 °C/min to remove thermal history. Next, the sample was cooled to -80 °C at a rate of 20 °C/min. After an isotherm at -80 °C for 10 min, the sample was ramped to 200 °C at 5 °C/min.

Representative NMR Spectra

¹H NMR Spectrum



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¹H NMR Spectrum



¹H NMR Spectrum



Normalized Intensity Date Stamp File Name Sweep Width (Hz) Owner S Receiver Gain Nucleus Acquisition Time (sec) ω N 0.1-0.2 0.7 0.8 0.9 1.0 0.3 0 (ppm) 19.70 23.03 29.43 EZ-1-010.004.esp 230 220 210 200 190 180 170 160 150 140 130 120 110 100 (Hz) 2478.2 2897.1 3701.7 21 Apr 2015 1 C:\Users\ProE guest 7298.20 30302.11 13C .0813 0.9344 1.0000 0.8088 VerticalScaleFactor = 1 18:18: 00 No 6 4 U 55 Number of Transients 1024 Points Count 32768 SW(cyclical) (Hz) 30303.03 Temperature (degree C) 25.000 Comment (ppm) 32.18 35.70 39.23 -177.27 sionalpc\Desktop\Edd 4934.4 (Hz) 4047.6 4490.5 Ö 0.7195 0.6543 0.5028 Z-restored spin-echo 13C spectrum with 1H decoupling Masters life/NMF HO 9 S α Z N-(5-hydroxypentyl)isobutyramide (ppm) 53.49 62.46 76.84 Chemical Shift (ppm) Origin Pulse Sequence Solvent 1-010\4\fid (Hz) 6728.5 7857.6 9666.5 0.8335 Height 0.0748 90 80 70 60 50 40 30 cnyo500 SpinEchopg30gp.prd CHLOROFORM-d Spectrum Offset (Hz) 77.35 12 10 No. (ppm) 77.10 77.35 177.27 62.46 Date Original Points Count Frequency (MHz) 22299.9 (Hz) 9698.9 9730.3 -53.49 Height 0.3224 0.1773 -39.23 -35.70 -32.18 -29.43 -23.03 125.79 13835.8457 21 Apr 2015 18:18:56 8 19.70 10 0 -10

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¹³C NMR Spectrum

¹H NMR Spectrum



¹³C NMR Spectrum










8029

.12561786

1.42099264e+8



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34





Generic ¹H NMR of acrylate peaks(5.74ppm to 6.33ppm) and anisole peak(3.73ppm) to monitor percentage conversion of polymerization.

Representative GPC Trace



rid1A

Mn :	4.6811e4	g/mo
Mw:	5.9844e4	g/mo
Mz:	7.1551e4	g/mo
My :	0.000000	g/mo
D :	1.2784e0	
[n]:	0.000000	ml/g
Vp:	7.6895e0	ml
Mp:	7.7434e4	g/mo
A :	2.3081e4	ml*V
10%	2.5961e4	g/mo
30%	4.1786e4	g/mo
50%	5.7604e4	g/mo
70%	7.4954e4	g/mo
90%	9.7444e4	g/mo

Data File : C:\HPCHEM\1\DATA\EDDY\EZ-1-106.D Print Date : Wednesday 12/02/15 17:18:36

Sign :

Representative DSC Thermogram

Sample: EZ-1-113-2 Size: 9.5000 mg Method: Heat/Cool/Heat Comment: 75% diol 25% slow-crosslinker run2 File: C:\TA\Data\DSC\Eddy\EZ-1-113.002 Run Date: 17-Dec-2015 16:29 Instrument: DSC Q2000 V24.4 Build 116 DSC 0.0 -0.1 Heat Flow (W/g) -0.2 75.76min 11.28°C -0.2384W/g 78.76min 26.25°C -0.2810W/g -0.3 --50 -100 ò 50 100 150 200 Exo Up Universal V4.5A TA Instruments Temperature (°C)





2.5 References

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Chapter 3: Tunable Boronic Ester Vitrimers

3.1 Introduction

Polymer materials are classically subdivided into two main classes, thermosets and thermoplastics, according to their thermal behavior. Thermosets are irreversibly cross-linked and thus tolerant to both high temperature and most solvents. This unique property of thermosets renders them the material of choice for many high performance materials.¹⁻³ However, thermosets must be polymerized in a mold having the shape of the desired object because they cannot be reshaped or reprocessed once fully cured. On the other hand, thermoplastics are easily reprocessed⁴ but cannot withstand high temperatures and many solvents. An ideal material would have its network fixed at service temperature and its bonds break and reform at elevated temperature or by a convenient stimulus so as to be reprocessed.

Polymer networks with exchangeable chemical bonds, covalent adaptable networks or CANs,⁵⁻¹¹ have been synthesized in the hope of combining high performance with processability. Various chemistry have been used in cross-linking polymer chains and they can be categorized as dissociative and associative CANs by their exchange mechanism.¹² Dissociative CANs, such as those using Diel-Alder cycloadducts as cross-links, exchange bond by first breaking it and then forming it again at another place. This partial depolymerization process causes dissociative CANs to lose their structural integrity during bond exchange. Associative CANs only break their cross-link when a new one has been formed, therefore maintaining their network integrity by keeping a constant cross-link density.

Associative CANs were also later coined as vitrimers and pioneered by Leibler et al¹³ in 2011. A few types of associative exchange motifs have been used to make vitrimer systems including catalyzed transesterification in epoxy resins, transalkylation of triazolium salts,

transamination of vinylogous urethanes, etc.¹²⁻²¹ Vitrimers were shown to be as strong as thermosets at room temperature, insoluble in organic solvents even at high temperatures, and also reprocessable without losing network integrity. In addition, the viscosity behavior of conventional polymers such as polystyrene follows the William-Landel-Ferry (WLF) model but vitrimer viscosity behavior is similar to those of silica glass, following the Arrhenius model. Thus the name was coined to be vitrimer, which means strong glass former. These properties of vitrimers will very likely impact industries that rely on thermosets and elastomers.

Previously in the Guan lab it was reported that by incorporating boronic cross-linkers of ester different exchange rates in a 1,2-diol containing polymer (DCP), materials self-healing with different efficiencies were made (Figure 3.1).²² Polymer chains cross-linked by fast exchange cross-linker showed



Figure 3.1: Design concept of polymer system. Reprinted from ref. 22.

much better self-healing property than those cross-linked by slow exchange cross-linker. This idea of tuning bulk material property by tuning small molecule kinetics can also be applied to vitrimer systems. Previously samples were made with low diol percentage of 20 mol% and low cross-link density of 0.5-1 mol% to facilitate self-healing. If we increase the diol percentage and dynamic boronic ester cross-linker percentage to create a highly cross-linked network, a tunable boronic ester vitrimer system could be made. Furthermore, it was shown that a library of boronic esters with exchange rates over many orders of magnitude²³ are available, making fine tuning of

vitrimer properties possible. This difference in the exchange rate of various boronic ester crosslinkers should give rise to a difference in the temperature at which they can be reprocessed. Additionally, mechanical properties can be tuned by varying cross-link density and polymer chain length. Herein is my initial effort towards synthesizing and characterizing this new vitrimer system. Two cross-linkers of different exchange rate, various cross-link density and different polymer chain lengths were explored.

3.2 Results and Discussion

Synthesis and Characterization of Fast Cross-Linker (FCL), Slow Cross-Linker (SCL), 1,2-diol containing polymers (DCPs) and Cross-linked DCPs

Synthesis of FCL **2**, SCL **4**, and DCP is outlined in scheme 3.1. A double reductive amination of 2-formylphenyl boronic acid with N,N-dimethylethylenediamine was carried out to make precursor 1^{24} , which was esterified with propane-1,2-diol to form FCL **2**.²² Double nucleophilic substitution of 2-bromobenzyl bromide with ethylene glycol formed a diphenyl bromide,²⁵ which was converted to a pinacol diboronic ester **3** by Miyaura borylation.²⁶ Cleavage of pinacol ester in **3** by sodium periodate followed by hydrochloric acid gave a diboronic acid²⁶ which was esterified by propane-1,2-diol to yield SCL **4**. Epoxidation of 1,5-cyclooctadiene (COD) with mCPBA gave epoxide **5**,²⁷ which was ring opened by water to yield a 1,2-diol containing monomer **6**.²² Cyclooctene was copolymerized with **6** by ring opening metathesis polymerization (ROMP) to make DCPs.²² Two DCP diol percentage were chosen to be 50 mol%



Scheme 3.1: a) Synthesis of FCL, b) Synthesis of SCL, c) Synthesis of DCP.

and 75 mol% to have high cross-link density potential. The properties of both 50% DCPand 75%

DCP are summarized in table 1. With FCL, SCL and DCPs at hand, cross-linked samples were made for vitrimer property tests. In the boronic ester vitrimer system, free diols are needed for bond exchange. As each cross-linker connects two diols, 50% DCP was cross linked with 15 mol% FCL/SCL, which means 30% out of 50% diols were cross-linked and 20% diols remained free. To achieve a similar cross-link density, 75% DCP was

Table 3.1: Characterization of DCPs

	50%DCP	75%DCP
Diol% ^a	52	73
PDI ^b	1.74	1.27
Mn ^c	48000	46000
Mw^d	85000	60000

^aEstimated from ¹H NMR, ^{b,c,d}Determined by gel permeation chromatography using polystyrene standards in THF.

cross-linked with 25 mol% FCL/SCL, which meant 50% out of 75% diols were cross-linked and 25% diols remained free. 50% DCP cross-linked with 15 mo% FCL will be referred as 50%DCP-15%FCL and other cross-linked samples will be similarly named. All samples were

cross-linked in solution and the concentrations of DCP, FCL and SCL were explored to make sure gelation occurred after mixing. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were run to determine thermal properties of cross-linked samples. The glass transition temperature (Tg) of all four sample ranged between 15°C to 25°C and initial degradation temperature ranged from 174°C to 208°C. A temperature window of 25°C to 174°C was therefore determined for subsequent stress relaxation (SR) experiment to ensure chain mobility and no degradation.

Stress Relaxation (SR) Experiments on cross-linked DCPs

Due to the dynamic nature of their cross-links, vitrimers should relax stress completely at elevated temperatures. Furthermore, vitrimer viscosity should follow the Arrhenius model. Both above properties can be tested by SR experiments. In a SR experiment, a step strain is incurred on the sample by either pulling, pressing or shearing depending on the physical properties of the



Figure 3.2: a) Tension mode SR experiment of 50% DCP with 15% FCL under 2% strain at 60°C, 70°C, 80°C, and 110°C over 10 hours. b) Tension mode SR experiment of 50% DCP with 15% FCL and only 50% DCP under 2% strain at 70°C over 10 hours.

material. The strain is held constant throughout the experiment and stress of the sample is measured by a detector. Tension mode (strain is incurred by pulling the sample) SR experiment was first tested on 50% DCP-15% FCL at different temperatures, under varying percent strain and a relaxation time of up to 10 hours. No samples relaxed completely and 40%-50% residual

stress was still observed on all cross-linked samples. (Figure 3.2a) In fact, SR experiment on uncross-linked 50%DCP showed almost identical percent residual strain as the 50%DCP with 15%FCL (Figure 3.2b). This inability to relax stress completely with dynamic cross-links was attributed to entanglement of long polymer chains. To avoid long chain entanglement which prevents full relaxation, shorter chain 1,2-diol containing oligomers (DCOs) were proposed for vitrimer formation.

Synthesis and Characterization of DCOs

To synthesize short chain DCOs, a chain transfer agent (CTA) styrene²⁸ was added to the ROMP procedure. By going through cross metathesis with an active chain end, styrene caps the chain end with a methylene group while regenerating the active Grubbs 2nd generation catalyst.



Scheme 3.2: Synthesis of DCO

DCO diol percentage was first chosen to be 50%. The properties of 50% DCO are summarized in table 3.2. The chain length of 50% DCO was shown by NMR to be about 11 units long and about one tenth that of DCPs.

 Table 3.2: Characterization of DCO

	Diol % ^a	Chain length (monomer unit) ^b	PDIc	Mn ^d	Mw ^e
50% DCO	43	11	1.85	1100	2000

^{a,b}Estimated from ¹H NMR, ^{c,d,e}Determined by gel permeation chromatography using polystyrene standards in DMF.

Stress Relaxation (SR) Experiments on cross-linked DCOs

With a shortened chain length for DCO, we hoped to see that SR of cross-linked DCOs would show complete relaxation at elevated temperatures. Similar to cross-linked DCPs, four samples were synthesized to be 50%DCO-15%FCL/SCL and 50%DCO-20%FCL/SCL. Samples cross-linked with SCL were fairly brittle and would break when clamped and samples cross-linked with FCL were too soft to be clamped. SR experiment was switched from tension mode to



Figure 3.3: a) Compression mode SR experiment of 50%DCO-20%FCL under 3% strain at -5°C, 0°C, 5°C, 10°C and 15°C. b) Compression mode SR experiment of 50%DCO-15%SCL under 3% strain at 30°C, 35°C, 40°C, 45°C, 50°C, 60°C and 70°C.

compression mode (strain is incurred by pressing on the sample) to better characterize crosslinked DCOs. However, because 50%DCO-20%SCL was too brittle to be shaped into a testable sample and 50%DCO-15%FCL showed relaxation time that were too small to be differentiated, only 50%DCO-20%FCL and 50%DCO-15%SCL were tested by compression mode SR (Figure

3.3). Both showed complete relaxation.

Data fitting using Arrhenius Equation

Since relaxation time depends on bond exchange rate and bond exchange rate determines viscosity of vitrimers, relaxation time of vitrimers also follows the Arrhenius model. The characteristic



Figure 3.4: Plot of $ln(\tau)$ vs. 1000/T

relaxation time τ^* is defined to be the time it takes for a sample to relax from 100% to 1/e (about 37%) of initial stress and can be related to temperature as $\tau^*(T) = \tau_0 e^{Ea/RT}$ where τ_0 is the characteristic relaxation time at infinite temperature, E_a is the activation energy of bond exchange, R is the universal gas constant and T is temperature. Although 50%DCP-20%FCL showed complete relaxation but the SR curves of different temperatures intersect each other at random points and indicated that it did not follow Arrhenius model during relaxation and thus was not a vitrimer. However, the SR curves of 50%DCP-15%SCL showed nonintersecting curves which indicated possible Arrhenius behavior. The characteristic relaxation time τ^* was fitted with temperature T. Taking the natural log of both side of original equation we have $\ln[\tau^*(T)] = E_a/RT + \ln(\tau_0)$ which shows that plot of $\ln(\tau^*)$ vs. 1/T should be linear. The plot of $\ln(\tau^*)$ vs. 1000/T is shown in Figure 3.4 (coefficient of 1000 is to convert unit from joules to kilojoules). The value of R^2 was very close to 1 and showed a very good Arrhenius behavior. From the slope of the fitted linear equation the activation energy of bond exchange E_a was found to be 57.9 kJ/mol (13.83 kcal/mol) for SCL.

Solubility Tests

All previous vitrimer systems showed insolubility in solvents at even elevated temperatures, showing a robust, highly cross-linked and complete network. Both 50%DCP-20%FCL and 50%DCP-15%SCL were submerged in scintillation vials with different solvents with stirring for a few days at room temperature (Table

Table 3.3	: Solut	oility '	Test
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	DCM	Toluene
50%DCO-15%SCL	Soluble	Soluble
50%DCO-20%FCL	Soluble	Soluble

Solubility tests of 50%DCO-20%FCL and 50%DCO-15%SCL in DCM and toluene.

3.3). It was shown that both samples dissolved in DCM and toluene over 1 day. Since both solvents do not react with the boronic ester vitrimer, this indicated that complete network was not formed and the sample that were tested could have been clusters of partially formed network.

3.3 Conclusions and Future Work

In pursuit of a tunable boronic ester vitrimer system, various cross-linked DCPs and DCOs were synthesized and tested. Long chain DCPs were first cross-linked with both FCL and SCL at various cross-link densities and then subjected to SR experiment. Although SR experiments were conducted at elevated temperatures over relaxation time of up to 10 hours, residual stress was still noted. As complete relaxation was not achieved, it was concluded that vitrimers were not made and the residual stress was due to long chain entangle. This was confirmed by SR experiment of cross-linked and uncross-linked 50%DCP. To avoid chain entanglement, short chain 50%DCOs were made and cross-linked. Although cross-linked 50%DCO showed complete relaxation and one possible Arrhenius behavior, further solubility tests showed that a complete robust network was not formed. Future work includes first finding a procedure to fully form the vitrimer network by tuning the concentration of stock solutions of both cross-linkers and oligomers, changing the composition of solvents, or varying cross-linking temperatures. After complete vitrimer network formation is confirmed, tunability of vitrimer properties by tuning the cross-linker dynamicity, cross-link density and oligomer chain length will be tested by SR experiment, solubility tests and tensile tests.

3.4 Experimental

General Experimental Information Unless otherwise noted, reactions were carried out with stirring with a magnetic stir bar at room temperature. Anhydrous solvents were purified through a column of alumina according to the method described by Grubbs et al²⁹ before use. All

commercial reagents were used as received unless otherwise noted. ¹H NMR and ¹³C NMR spectra were recorded at 500 and 125 MHz, respectively, on Bruker GN-500 or CRYO-500 spectrometers. ¹H NMR and ¹³C NMR chemical shifts are reported as δ values in ppm relative to TMS or residual solvent: CDCl₃ (7.26 ppm; 77.0 ppm), or CD₂Cl₂ (5.30 ppm; 54.0 ppm). 1 H NMR data are reported as follows: chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), coupling constants in Hz, and relative integration in number of protons. Multiplets (m) are reported over the range of chemical shift at which they appear. For ¹³C NMR spectra, only chemical shift values are reported. Mass Spectra were obtained on Micromass LCT (ES-MS, low resolution), Micromass Autospec (ES-MS and GC-MS, high resolution), and Perseptive Biosystems DE STR (MALDI-TOF) instruments. Gel Permeation Chromatography (GPC) traces were obtained on an Agilent 1100 SEC system using a PLGel Mixed-C column from Polymer Labs (Amherst, MA). THF or DMF was used as eluting solvent at a flow rate of 1.0 mL/min. Number averaged and weight averaged molecular weight distributions (Mn and Mw, respectively) of samples were measured with respect to polystyrene (PS) standards purchased from Aldrich (Milwaukee, WI). ¹H NMR, ¹³C NMR, and HRMS are reported for any new compounds or compounds following a new procedure. For all published compounds, only ¹H NMR is reported.

Synthesis of (((ethane-1,2-diylbis(methylazanediyl))bis(methylene))bis(2,1phenylene))diboronic acid (1): The synthesis was adapted from a previously reported procedure.³⁰ A solution of 2-formylphenyl boronic acid (12.48g, 83.2mmol), N,Ndimethylethylenediamine (3.667g, 41.6mmol) and anhydrous MgSO₄ (10g) in 100mL dry methanol was heated under reflux for 5h. The solution was then cooled to 0°C and NaBH₄ (6.77g, 179mmol) was added in small portions to prevent overfoaming. Mixture was then allowed to equilibrate to room temperature overnight. Mixture was then filtered and condensed to a syrup. To the syrup was added 100mL of saturated NaHCO₃, 100mL of DI water, 200mL of chloroform. Organic layer was collected and aqueous layer were extracted twice with 100mL of chloroform each, which were combined with organic layer. This organic layer was dried over anhydrous MgSO₄, filtered, and concentrated to yield a brown crystal. Brown crystal is recrystallized as follows. To 2g of brown crystal was added a mixture of 21mL acetonitrile and 75mL DI water. Mixture was heated to 60°C for 10 minutes till all brown crystals dissolved. This mixture was then sonicated for 20 minutes, it was then let sit overnight to precipitate out a white solid. Total white solid collected was 3.76g, 25.4% yield. The identity of the product was confirmed by ¹H NMR. ¹H NMR(500 MHz, CD₃OD) δ 7.48 (s, 2H), 7.23 (s, 4H), 7.13 (s, 2H), 3.95 (s, 4H), 3.23 (s, 4H), 2.45 (s, 6H).

Synthesis of N1,N2-dimethyl-N1,N2-bis(2-(4-methyl-1,3,2-dioxaborolan-2-yl)benzyl)ethane-1,2-diamine (2): The synthesis was adapted from a previously reported procedure.³¹ In a flame (2 d round bottom flask, 1 (1.30 g, 3.65 mmol) and MgSO4 (5.0 g) were suspended in anhydrous toluene (140 mL) and heated to 100 °C. Once the reaction mixture was warm, propylene glycol (0.555 g, 0.536 mL, 7.30 mmol) was added dropwise and allowed to react for two hours. The solids were then removed via vacuum filtration and the filtrated was concentrated in vacuo yielding a light brown oil with some impurities (1.038g, 65.2%). The identity of the product was confirmed by ¹H NMR. ¹H NMR(500 MHz, CDCl₃) δ 7.48 (s, 2H), 7.21 (m, 4H), 7.06 (m, 2H), 4.35 (s, 2H), 4.08 (s, 2H), 3.85 (s, 4H) 3.55 (s, 2H), 3.03 (s, 4H), 2.45 (s, 6H), 1.30 (s, 6H).

Synthesis of 1,2-bis((2-(4-methyl-1,3,2-dioxaborolan-2-yl)benzyl)oxy)ethane (4): The synthesis was adapted from a previously reported procedure.³¹ (((ethane-1,2-

diylbis(oxy))bis(methylene))bis(2,1-phenylene))diboronic acid **4'** was made and provided by a fellow lab mate Jaeyoon Chung. In a flame dried round bottom flask, **4'** (0.40 g, 1.21 mmol) and MgSO4 (5.0 g) were suspended in anhydrous toluene (140 mL) and heated to 100 °C. Once the reaction mixture was warm, propylene glycol (0.184 g, 0.178 mL, 2.42 mmol) was added dropwise and allowed to react for two hours. The solids were then removed via vacuum filtration and the filtrated was concentrated in vacuo yielding a light brown oil (0.485g, 97.7%). The identity of the product was confirmed by ¹H NMR. ¹H NMR(500 MHz, CDCl₃) δ 7.70 (m, 2H), 7.39 (m, 2H), 7.30 (m, 2H), 7.15 (m, 2H), 4.73 (s, 4H), 4.55 (m, 2H), 4.25 (m, 2H) 3.74 (m, 2H), 3.60 (s, 4H), 1.25 (s, 6H).

Synthesis of (Z)-9-oxabicyclo[6.1.0]non-4-ene (5): The synthesis was from a previously reported procedure.³² A solution of mCPBA (5.50 g, 31.9 mmol) in 90mL of chloroform was added dropwise to 1,5-cyclooctadiene (4.28g, 39.6 mmol). This mixture was allowed to stir at room temperature for 12h and subsequently filtered to remove the mCPBA. Chloroform layer was then washed with aqueous NaHSO₃, NaHCO₃ and NaCl. Organic layer was then condensed and purified by column (90/10 hexane/ethyl acetate) to yield a clear oil (2.60g, 65.7%). The identity of the product was confirmed by ¹H NMR. ¹H NMR(500 MHz, CDCl₃) δ 5.55 (m, 2H), 3.05 (m, 2H), 2.42 (m, 2H), 2.15 (m, 2H) 2.00 (m, 4H).

Synthesis of (Z)-cyclooct-5-ene-1,2-diol (6): The synthesis was from a previously reported procedure.³¹ In a round bottom flask, 6 (2.32 g, 18.71 mmol) was dissolved in 37 mL of water with rapid stirring. To the reaction mixture, 3 drops of concentrated H_2SO_4 was added and allowed to react for 12 hours at room temperature. In a separatory funnel, the reaction mixture was added to 60 mL diethyl ether followed by 12 mL of saturated aqueous NaHCO3 solution. The ether layer was then extracted with brine, dried over Na2SO4 and was concentrated in vacuo

yielding a pure, clear and colorless liquid. Yield: 1.69 g (82 %) The identity of the product was confirmed by ¹H NMR. ¹H NMR(500 MHz, CDCl₃) δ 5.59 (m, 2H), 3.65 (m, 2H), 3.23 (s, 2H), 2.35 (m, 2H), 2.10 (m, 4H), 1.55 (m, 2H).

Ring-Opening Metathesis Polymerization (ROMP) of 50% DCP: This was modified from a previous procedure.³¹ In a round bottom flask at room temperature, Grubbs' second generation catalyst (4.8 mg, 0.00564 mmol) was dissolved in 70 mL of (IPA/PhMe = 1:1). In a separate flask, cyclooctene (1.55 g, 14.08 mmol) and (Z)- cyclooct-5-ene-1,2-diol (2.00 g, 14.08 mmol) were combined with 5 mL of (IPA/PhMe = 1:1). The catalyst solution was charged with the monomer mixture and allowed to react for four hours at room temperature. The reaction mixture was quenched with trace amounts of ethyl vinyl ether. The polymer was precipitated from MeOH and characterized by NMR in CDCl₃. GPC was run in THF (dissolving reaction mixture in THF directly and filter). ¹H NMR of 50% DCP:

Ring-Opening Metathesis Polymerization (ROMP) of 75% DCP: This was modified from a previous procedure.³¹ In a round bottom flask at room temperature, Grubbs' second generation catalyst (4.8 mg, 0.00564 mmol) was dissolved in 70 mL of (IPA/PhMe = 1:1). In a separate flask, cyclooctene (0.91mL, 7.04 mmol) and (Z)- cyclooct-5-ene-1,2-diol (3.00 g, 21.12 mmol) were combined with 5 mL of (IPA/PhMe = 1:1). The catalyst solution was charged with the monomer mixture and allowed to react for fifteen hours at room temperature. The reaction mixture was quenched with trace amounts of ethyl vinyl ether. The polymer was precipitated from hexane and characterized by NMR in CD₃OD. GPC was run in THF (dissolving reaction mixture in THF directly and filter). ¹H NMR of 75% DCP: **Ring-Opening Metathesis Polymerization (ROMP) of 50% DCO:** This was modified from a previous procedure.¹⁷In a round bottom flask at room temperature, Grubbs' second generation catalyst (12 mg, 0.01413 mmol) was dissolved in 30 mL of (IPA/PhMe = 1:1). In a separate flask, cyclooctene (0.91mL, 7.04 mmol), (Z)- cyclooct-5-ene-1,2-diol (1.00 g, 7.04 mmol) and styrene (0.163mL, 1.408 mmol) were combined with 10 mL of (IPA/PhMe = 1:1). The catalyst solution was charged with the monomer and styrene mixture and allowed to react for four hours at room temperature. The reaction mixture was quenched with trace amounts of ethyl vinyl ether. The reaction mixture was concentrated in vacuo and then dissolved in methanol. It was then filtered through silica and celite. The oligomer was then concentrated in vacuo and dissolved in (IPA/PhMe = 1:1) to make a stock solution of 0.0365g/mL. It was characterized by NMR in D₆ DMSO and CDCl₃. GPC was run in DMF. ¹H NMR of 50% DCO

Representative procedure for preparing cross-linked bulk samples: DCP was dissolved in (IPA/PhMe = 1:1) to have a concentration of 0.01g/mL as stock solution. DCO had a concentration of 0.0365g/mL. Both cross-linkers also dissolved in (IPA/PhMe = 1:1). FCL was made to have a concentration of 0.01g/mL and SCL 0.04g/mL as stock solution. To the stirring polymer solution, desired amount of cross-linker solution was added. The cross-linked polymer network was then cast into a Teflon mold and allowed to slowly evaporate at room temperature for 8h on the bench top. The polymer films were then placed in a vacuum oven at 80 °C overnight to remove any residual solvent.

Representative Stress Relaxation (SR) procedure: All samples were measured by a TA Q800 dynamic mechanical analysis instrument (DMA). For tension mode SR, samples were hot pressed into a rectangular shape (l,w,t: 12.0 x 3.4 x 0.20 mm) and percent strain of 2% and 4.5% were used. For compression mode SR, samples were hot pressed into a round disk shape (d,t: 10

x 3 mm) and percent strain of 3% was used. All samples were preheated/precooled to set temperature, isotherm for 5 minutes and then subjected to a constant strain. Relaxation time varied from 1 minute to 10 hours.

DSC procedure: Differential scanning calorimetry measurements were performed using a TA Q2000 instrument. ~10 mg of polymer sample was placed in a non-hermitic pan and scanned against an empty reference pan. The DSC experiment was performed in a heat-cool cycle (25 to 180 °C, 20 °C/min; 180 to -80 °C, 10 °C/min; isothermal -80 °C, 30 min; -80 to 200 °C, 5 °C/min), wherein the thermal transitions for the last heating cycle were recorded.

TGA procedure: The thermal stability of the polymers was probed by TGA. The samples were heated from 25 °C to 850 °C at 10 °C/min and mass loss was plotted versus temperature. For clarity, the derivative of the mass loss is shown as well.

Representative NMR Spectra

¹H NMR Spectrum



6

1716

7.601

1.92541146

1305 9731

7.234.3031444 7.092.15453243

4.73362688e+8

4.30314445

2.15453243 1.92541146

2.11802784e+8 2.37006992e+8









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¹H NMR Spectrum of 50% DCP



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¹H NMR Spectrum of 50% DCO
Representative GPC Trace



rid1A

Mn :	4.6811e4	g/mo
Mw:	5.9844e4	g/mo
Mz:	7.1551e4	g/mo
My :	0.000000	g/mo
D :	1.2784e0	
[n]:	0.000000	ml/g
Vp:	7.6895e0	ml
Mp:	7.7434e4	g/mo
A :	2.3081e4	ml*V
10%	2.5961e4	g/mo
30%	4.1786e4	g/mo
50%	5.7604e4	g/mo
70%	7.4954e4	g/mo
90%	9.7444e4	g/mo

Data File : C:\HPCHEM\1\DATA\EDDY\EZ-1-106.D Print Date : Wednesday 12/02/15 17:18:36

Sign :

Representative DSC Thermogram

Sample: EZ-1-113-2 Size: 9.5000 mg Method: Heat/Cool/Heat Comment: 75% diol 25% slow-crosslinker run2 File: C:\TA\Data\DSC\Eddy\EZ-1-113.002 Run Date: 17-Dec-2015 16:29 Instrument: DSC Q2000 V24.4 Build 116 DSC 0.0 -0.1 Heat Flow (W/g) -0.2 75.76min 11.28°C -0.2384W/g 78.76min 26.25°C -0.2810W/g -0.3 --50 -100 ò 50 100 150 200 Exo Up Universal V4.5A TA Instruments Temperature (°C)





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