ABSTRACT
KENNEMUR, JUSTIN GLENN. Synthesis and Investigation of Chiral Polycarbodiimides with Reversible Dynamic Properties. (Under the direction of Bruce M. Novak.)

“If atoms are letters and words are molecules, then chemistry can just claim to know phrases. Paragraphs are beyond us – chapters a dream, and books perhaps centuries away.”

~ Sir Fraser Stoddart

Ever since the pioneering idea of macromolecules was introduced by Staudinger in the 1920’s, the interdisciplinary field of synthetic polymer chemistry has grown tremendously and has now emerged into the mature subject that it is today. During this maturation, polymers have globally incorporated themselves into the everyday lives of humanity. Although, in most instances, polymers have been reveled for being lightweight, strong, chemically inert, flexible, and relatively inexpensive materials, a new breed of functional polymers are now being synthesized by polymer chemists and creating frontline attention within peer-reviewed journals. These new polymers are specialty materials designed to perform a function and otherwise interact in some way with their surroundings. The breadth of functionality being investigated is too long to list, ranging from something as complicated as biomimetic or conductive polymers to something as simple as improved degradation or “green” polymers. Along with these new functionalities comes new challenges faced by polymer chemists with regards to the synthesis and characterization of such systems and although many significant advances have been made, this field is generally considered to be within the early stages of discovery. This manuscript will discuss a particular class of functional polymers known as polycarbodiimides and their application as specialty materials will be outlined as well as significant advances made to the synthesis and characterization of these polymers. Focus is placed on particular types of helical
polycarbodiimides containing polyarene and aliphatic pendant groups. Through chiro-optical analysis, these polymers display a low energy solvo- and thermo-controllable conformational switching which is believed to arise from reorientation of the polyarene pendant groups fixed to the helical polycarbodiimide backbone scaffold. In essence, these polymers act as molecular shutters and, through their chirality, can greatly alter the polarization of light under very mild conditions. Structure activity relationships were performed and a library of over twenty new polymers was created to further understand the limitations and driving forces behind this unique phenomenon. In addition, synthetic optimization and property relationships of a new hallmark polymer, N-(1-naphthyl)-N’-(n-octadecyl) polycarbodiimide, is explored with the inclusion of solvation, molecular weight, regioregularity, and enantiomeric studies and their effect on this switching behavior.

In addition to the reversible dynamic properties of these polycarbodiimides, this manuscript will also explore new approaches towards better understanding and controlling fundamental properties of polycarbodiimides in general. Regioregularity of asymmetric carbodiimide polymers will be discussed and select polymers from within this new library reveal evidence of potentially controlling regioselectivity of these polymer systems through pendant group substituent effects. New improvements to and clarification of analytical techniques for determination of the amount of regioirregularity within these polymer systems are also discussed.
Synthesis and Investigation of Chiral Polycarbodiimides with Reversible Dynamic Properties

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

Chemistry

Raleigh, North Carolina

2010

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DEDICATION

This manuscript is dedicated to my mother, Mary Kennemur, who taught me that hard work and dedication will one day pay off and whose love, guidance, and encouragement laid the path for the person that I am today. I also wish to dedicate this to my father, Johnnie Glenn Kennemur (1939-2008) who I lost during my time in graduate school and I know was watching over throughout.
BIOGRAPHY

Justin Glenn Kennemur was born at Shaw A.F.B, Sumter, South Carolina in July of 1979. At the age of two he moved to Yorktown, Virginia where he was raised. After graduating from Tabb High School in 1997, he attended Radford University in Radford, Virginia. It was during his first year there when his general chemistry professors encouraged and helped him realize his potential in the subject of chemistry and in 1998 he won the CRC Press LLC Freshman Chemistry Achievement Award. With his new found passion for the subject of chemistry he decided to stay at Radford and in May of 2002 he graduated from Radford University with a B.S. Emphasis Degree in Chemistry and a Minor in Math. During his tenure at Radford he received the Dale Snead Boxley Scholarship in 1998 and the Dr. Roger F. Lambert Scholarship in Chemistry in 1999 along with becoming an active member of The American Chemical Society and The Delta Chi Fraternity. After graduating from Radford he immediately began working as a Chemical Technician at Polymer Solutions Incorporated in Blacksburg, Virginia. After three years he had been promoted three times and obtained the position of Senior Chromatography Analyst before leaving in 2005 when he was accepted into the Ph.D. Program in Chemistry at North Carolina State University. Later that year, he joined the research group of Dr. Bruce M. Novak. In 2006 he won an award for Outstanding Research Accomplishments in Chemistry at the NCSU Chemistry Department Poster Session. In 2009 he took 2nd Place in the PAMS Division Poster Award at the NCSU Graduate Student Symposium and later that year won the ACS Richard D. Gilbert Award in Polymer Science, Best Poster.
ACKNOWLEDGEMENTS

Out of all the sections in this manuscript, I wrote this one last and truly believe it is the toughest section to write because I can not begin to put into words how truly blessed I have felt for all the people that have been a part of my life. My mother is one of the strongest and most inspirational people I have ever met and I can’t thank her enough for all of the support and love that she has shown me throughout my life. Together, she and I have overcome a lot of adversity and I am truly thankful to her and dedicated to make her proud. To my sisters, Dawn and Teresa, and their husbands, Lee and Duane, I wish to thank them for always being there and providing enrichment to my life in their own ways. I have been blessed with incredible friends, too many to name, and I want to thank them all collectively for their support.

I wish to thank Dr. Cindy Burkhardt and Dr. Francis Webster, two chemistry professors at Radford University who turned my eye towards this field and supported me throughout. At Polymer Solutions Incorporated I matured as a chemist and a person through the guidance of Dr. James Rancourt, Dr. Sue Mecham, and Jason Todd and am thankful for all the opportunity, knowledge, and constructive criticism they gave me. Although I didn’t know it at the time, they truly prepared me for the transition to graduate school.

I am indebted to Dr. Bruce Novak for taking me into his research group and allowing me to pursue my own ideas. Coming from an industry job, I was a little nervous at first about having an advisor with such a hands-off approach. Suddenly, five years later I find myself developed into the self-motivated, well prepared, and independent chemist that I am
today. Bruce was there with words of encouragement and advice along the way and I look forward to his advice for years to come.

To the Novakians who have fought in the trenches with me over the years, I am truly thankful to all of you for making this such a great experience. Every first year graduate student hopes to have a great teacher and friend in the new lab that he is working in and I was blessed to have Keitaro Seto as this person. Thanks Keitaro for everything you taught me and I have never met anyone so selfless and willing to go out of their way to help. To the senior members, Yoko, Hyun-Su, Haibo, Ying, and J.B., and our newest member Januka, thanks for all of your support and advice. A special thanks to Chris Kilgore, Anna Croom, Vanessa Porter, and all of the other undergraduates who helped along the way. And finally, clam, to my partner in crime Joey Dorito DeSousa, thanks for all the great talks over napkins at Sammys, the random facts over lunch while fighting the Dragon, and the new found respect for Connecticut. I look forward to our continued friendship.

I wish to thank my committee members Dr. Chris Gorman, Dr. Christian Melander, and Dr. Alan Tonelli, all of which I was lucky to have as a professor for one of my graduate classes and have become friends with. Thank you for agreeing to be on my committee and for your combined support.

Finally, to my fiancé, soon to be wife, and best friend Vanessa Walker who unexpectedly came into my life during this journey and has enriched it with laughter and love. I want to thank you for all your patience during those late nights and for all the encouragement and love you have provided.
TABLE OF CONTENTS

LIST OF TABLES.................................................................................................................. x
LIST OF SCHEMES................................................................................................................ xi
LIST OF FIGURES.................................................................................................................. xii
LIST OF ABBREVIATIONS.................................................................................................... xxvi

CHAPTER 1: INTRODUCTION TO HELICAL POLYMERS................................................. 1
  1.1 History of Helical Polymers...................................................................................... 1
  1.2 Chemistry of Helical Polymers.............................................................................. 5
  1.3 References............................................................................................................. 11

CHAPTER 2: A REVIEW OF POLYCARBODIIMIDES................................................... 15
  2.1 Background........................................................................................................... 15
  2.2 Carbodiimides.................................................................................................... 17
  2.3 Catalysts............................................................................................................. 24
  2.4 Polycarbodiimides.............................................................................................. 29
    2.4.1 Introduction.................................................................................................... 29
    2.4.2 Polycarbodiimides as Dynamic Helical Polymers........................................ 33
    2.4.3 Polycarbodiimides as Static Helical Polymers............................................. 40
    2.4.4 Properties of Polycarbodiimides................................................................. 49
  2.5 References........................................................................................................... 56

CHAPTER 3: SWITCHING HELICAL POLYCARBODIIMIDES.................................... 59
  3.1 Discovery.............................................................................................................. 59
3.2 Optical Rotation and Circular Dichroism ........................................ 61
3.3 Early Investigations of the Switching Phenomenon .......................... 65
3.4 Initial Investigations of New Switching Polycarbodiimides ................. 73
3.5 Discovery of a New and More Versatile Switching Polycarbodiimide..... 76
3.6 Enantiomeric Switching Behavior of M versus P Helices ................... 86
3.7 Solvent Effects on Switching Behavior ............................................ 87
3.8 Effects of Polymer Properties on Switching Behavior ....................... 92
3.9 Effects of Alkyl Pendant Group Size on Switching Behavior .......... 102
3.10 Effects of Size and Spatial Arrangement of Aromatic Pendant Groups on
      the Switching Behavior ............................................................ 104
3.11 Modifying Switching Behavior through Substituent Effects on
      Naphthalene ................................................................. 113
3.12 Miscellaneous Studies (Odds and Ends)......................................... 125
      3.12.1 Solvation Investigations Using Charge Transfer Complexation with Iodine............................................................. 125
      3.12.2 Investigation of Solvation Using a Mixed Solvent System ......... 133
      3.12.3 Attempts at Synthesizing Switching Polycarbodiimides from
            Chiral Monomers............................................................. 134
      3.12.4 Induction of Excess Helical Sense on Poly-39 through Chiral
            Acid................................................................................ 137
      3.12.5 Attempts at Synthesizing Fluorescent Carbodiimide Copolymers... 140
LIST OF TABLES

Table 2.1  Backbone activation energy barriers of imine carbons of several polycarbodiimides obtained by $^{13}$C CP/MAS NMR spectroscopy…………  43

Table 3.1  Polymerization parameters and polymer properties for previously reported anthracene pendant group containing polycarbodiimides…………………. 72

Table 3.2  Physical constants of various solvents tested compared to temperature of switching…………………………………………………………………... 89

Table 3.3  Experimental parameters for molecular weight study of Poly-39 using Cat-4……………………………………………………………….. 94

Table 3.4  Experimental parameters for variable temperature polymerization study of Poly-39 using Cat-4……………………………………………….. 100

Table 3.5  Experimental setup for chiral acid (-)CSA molecular chaperone study on achiral Poly-39…………………………………………………………….. 139

Table 4.1  Thermal decomposition products of various asymmetric polycarbodiimides analyzed by GC/MS following decomposition……………………………. 182

Table 4.2  GC-FID analysis of decomposition monomers from Poly-6 and Poly-62 solutions in CHCl$_3$…………………………………………………………… 196
LIST OF SCHEMES

Scheme 3.1  Total synthesis of Mono-50 and Mono-51.................................118
Scheme 3.2  Synthesis (R)-2,6-dimethylheptyl isocyanate from (R)-Pulegone.................137
LIST OF FIGURES

Figure 1.1 Various types of helical polymers…………………………………………………..2

Figure 1.2 Opposite handed polymer helices comprised from achiral monomers are enantiomers of one another. Their designation of M (for minus) and P (for plus) can be assigned by looking down the helical axis. If the helix travels away from the viewer in a clockwise direction it is designated as P and oppositely, if it travels in a counter-clockwise direction it is an M helix…..7

Figure 1.3 (a) Energy plot of helical polymers from achiral monomers. Such polymers are comprised of equal-energy enantiomeric helical segments separated by higher-energy helical inversions. (b) Helical polymers from homochiral monomers form diastereomeric helices that are not equal in energy (ΔE), resulting in a helical sense that is thermodynamically preferred…………………8

Figure 1.4 (a) The Sergeants and Soldiers effect; Less than 1% (molar ratio) of chiral sergeant units induce a preferred helical excess comparable to a polymer of 100% homochiral units. (b) Majority Rules; a slight enantiomeric excess of chiral isocyanate monomers induces a highly preferred helical excess………..10

Figure 1.5 Helical induction of poly((4-carboxyphenyl)-acetylene) through acid-base interactions with chiral amines. The dynamic PPA backbone adopts a preferred helical sense through the use of molecular chaperones…………. 11
Figure 2.1  Initially discovered titanium(IV) catalysts, Cat-(1-3), shown to polymerize carbodiimides in a living fashion……………………………………………………16

Figure 2.2  Polycarbodiimides combine the salient features of the static polyisocyanide and the dynamic polyisocyanate helical polymers………………………………………17

Figure 2.3  Synthesis of carbodiimides by the reaction of a primary amine and an isocyanate followed by subsequent dehydration of the 1,3-disubstituted urea using dibromotriphenylphosphorane and an acid scavenger triethylamine...19

Figure 2.4  Application of heat to asymmetric carbodiimides results in dimerization followed by an exchange of pendant groups. This metathesis yields a mixture of the original asymmetric and two symmetric carbodiimides………………..21

Figure 2.5  Carbodiimides are unstable in the presence of acid which catalyses a series of reactions based on the nucleophiles present. The presence of acid alone catalyzes the formation of dimers and trimers……………………………………22

Figure 2.6  Positive ion HRMS-ESI of pure N-(1-naphthyl)-N’-(n-dodecyl) carbodiimide injected in the presence of formic acid, water, and methanol……………..23

Figure 2.7  List of catalysts capable of polymerizing carbodiimides…………………………25

Figure 2.8  Initiation and propagation mechanism for the polymerization of carbodiimides using a titanium(IV) catalyst……………………………………………………26

Figure 2.9  Initially attempted monomers revealed that steric crowding around the carbodiimide center plays a large role on the efficacy of successful polymerization…………………………………………………………..31
Figure 2.10 Molecular mechanics and modeling results of a simplistic polycarbodiimide backbone reveals a 6/1 helical sense with a helical pitch of 13.8 Å and a dihedral angle of approximately 60° between repeat units………………… 33

Figure 2.11 The chiral Mono-12 is polymerized kinetically by Cat-25 resulting in a polymer with no excess helical sense and an optical rotation equivalent to that of the starting monomer……………………………………………………. 34

Figure 2.12 Annealing of Poly-12 at 85, 80, 75 °C allows the polymer to adopt the thermodynamically preferred helical sense and results in a large increase in optical rotation………………………………………………………………………... 35

Figure 2.13 Annealing Poly-13 results in a redirection in optical rotation by evolving from its KCC to its TCC at various temperatures in toluene……………………………………36

Figure 2.14 Sergeant-Soldier experiments performed by (a) Schlitzer, (b) Lu, and (c) Blackburn using various chiral and achiral monomers…………………..37

Figure 2.15 Majority rules experiment using various ratios of (R) vs. (S) Mono-13. A cooperativity is seen and using 60% enantiomeric excess of the (R) unit which leads to an optical rotation close to that of a homopolymer from (R) units alone………………………………………………………………………... 38

Figure 2.16 (a) Chiral acids can function as molecular chaperones and induce an excess helical sense to a racemic mixture of polycarbodiimides containing no chiral pendant groups. (b) Mirror image behavior is seen by using enantiomeric acids……………………………………………………………………………... 40
Figure 2.17  Achiral carbodiimide monomers designed to induce a large racemization barrier on resulting polymers………………………………………………………42

Figure 2.18  Annealing of Poly-22 in chloroform at 50 °C results in initial racemization but not complete racemization. The optical rotation values plateau at -360° showing a permanent asymmetry related to this polymer system………………46

Figure 2.19  Chiral and achiral carbodiimides containing 1-anthryl pendant group polymerized using chiral (Cat-4) or achiral (Cat-15) catalysts…………………47

Figure 2.20  Annealing Poly-23(R) and Poly-23(S) at in (a) THF, 50°C, (b) CHCl₃, 50°C, and (c) toluene, 80°C results in no significant change in optical rotation suggesting their KCC and TCC are the same.

Figure 2.21  Polycarbodiimides studied for liquid crystalline properties…………………49

Figure 2.22  Optical polarizing microscope images of LC (a) smectic Poly-6, 20% w/w in toluene at 45 °C (200x), (b) cholesteric Poly-2(R), 12% w/w in CHCl₃ at r.t. (500x), and nematic Poly-27, 21.4% w/w in 1,1,2,2-tetrachloroethane at 65 °C (200x)…………………………………………………………………………………51

Figure 2.23  Differential scanning calorimetry (DSC) thermogram of Poly-24…………54

Figure 2.24  Copolymerizing a dicarbodiimide crosslinker with chiral Mono-2(R) results in a “locked-in” cholesteric gel……………………………………………………………..54

Figure 2.25  Polycarbodiimides containing high polarity pendant groups enabling water solubility……………………………………………………………………………55
Figure 3.1  Polymerization of Mono-21 using Cat-7 was found to result in a highly regioregular Poly-21……………………………………………………………………59

Figure 3.2  Monitoring specific optical rotation over a low temperature range resulted in a large reversible change in optical rotation in toluene (c= 0.1 g/100mL)………60

Figure 3.3  Optical rotation viewed as the difference between left and right circularly polarized light before and after movement through a chiral analyte.......... 62

Figure 3.4  Preferential absorption of one direction (E_L) of circularly polarized light over the other (E_R) results in elliptically polarized light when passed through a chiral analyte. The arc-tangent of the minor to major axis of the ellipse is known as the ellipticity (θ)…………………………………………………………63

Figure 3.5  Variable temperature ECD (top) and UV-Vis (bottom) of Poly-21 in toluene over repeated heating and cooling cycles……………………………………66

Figure 3.6  (a) Variable temperature g_{abs} (top) and UV-Vis (bottom) of Poly-21 in CHCl_3. (b) Variable temperature g_{abs} of Poly-21 in THF……………………………………66

Figure 3.7  g_{abs} values at 385 nm for Poly-21 when dissolved in various mixtures of toluene/THF……………………………………………………………………67

Figure 3.8  Molecular motions of Poly-21 capable of causing conformational changes and effecting optical rotation………………………………………………68

Figure 3.9  Annealing of Poly-21 in toluene at 80 °C requires more than 100 hours for full racemization…………………………………………………………68
Figure 3.10 (a) The experimental vibrational absorbance. (b) VCD of Poly-21 in CHCl$_3$ at 25 °C (c = 10.0 mg/mL, l = 300 µm). (c) VCD of Poly-21 in toluene at 25 °C (c = 20.1 mg/mL, l = 200 µm). (d) The optimized P helix model of Poly-21 and its VCD spectrum calculated by density functional theory using B3 LYP functional and 6-31G(d) basis sets.

Figure 3.11 Theoretical models for the two anthracene pendant group rotational states.

The geometries of both states were determined by optimization of the repeat unit at the semiempirical level (AM1) and then optimization of the 18-mer at the molecular mechanics level (MMFF94).

Figure 3.12 Variable temperature ECD (top) and UV-Vis (bottom) performed on previously synthesized Poly-21 from (a) Cat-4 and (b) Cat-5 in toluene.

Spectrum (b) shows the switching behavior.

Figure 3.13 Initial newly synthesized polycarbodiimides for switching behavior investigations.

Figure 3.14 Variable temperature polarimetry studies of (a) Poly-36 in toluene (c = 0.104 g/100mL) and CHCl$_3$ (c = 0.132 g/100mL). (b) Poly-38 in toluene (c = 0.108 g/100mL) and CHCl$_3$ (c = 0.108 g/100mL). path length = 0.5 dm for all tests.

Figure 3.15 Polymerization of Mono-39 using Cat-4 resulting in a new, more versatile, switching polycarbodiimide.
Figure 3.16 Variable temperature polarimetry of Poly-39 in (a) CHCl₃, (b) THF, and (c) toluene

Figure 3.17 Variable temperature ECD of Poly-39 in THF (top) and UV-Vis at r.t. (bottom)

Figure 3.18 VT-¹H NMR of Poly-39 in THF-d₈. Changes in aryl proton chemical shifts are seen as a result of anisotropic differences during the switching process of the naphthyl groups

Figure 3.19 Specific optical rotation of Poly-39 in THF held isothermal at four different temperatures during 4 h increments (c = 0.200 g/100mL). Slight drifting in cell temperature is evident; however, the specific optical rotation remains constant at isothermal conditions

Figure 3.20 Annealing of Poly-39 in toluene at 65, 70, 75, and 80 °C

Figure 3.21 Linear plot for determination of rate constants (k₁obs) for racemization of Poly-39 in toluene at various temperatures

Figure 3.22 Arrhenius plot for determination of energy barrier to racemization (E_r) for Poly-39 in toluene

Figure 3.23 Annealing of Poly-39 in decalin at 65, 70, 75, and 80 °C

Figure 3.24 Linear plot for determination of rate constants (k₁obs) for racemization of Poly-39 in decalin at various temperatures

Figure 3.25 Arrhenius plot for determination of energy barrier to racemization (E_r) for Poly-39 in decalin
Figure 3.26  Polarimetry analysis of Poly-39(R) ((a) in CHCl$_3$, (c) in toluene) and Poly-39(S) ((b) in CHCl$_3$, (d) in toluene). Polymerizing identical achiral monomers into opposite helices results in enantiomeric switching behavior……………86

Figure 3.27  Variable temperature polarimetry of Poly-39 in (a) CHCl$_3$, (b) ethylbenzene, (c) THF, (d) DCM, (e) toluene, (f) chlorobenzene, (g) xylenes, (h) 1,2-dichlorobenzene, (i) cyclohexane, (j) decalin…………………………………………………………….89

Figure 3.28  Variable temperature polarimetry of Poly-39 in (a) Toluene, (b) Ethylbenzene, (c) Propylbenzene, (d) Butylbenzene, (e) Cumene, and (f) Benzene…….. 90

Figure 3.29  Extreme switching differences between toluene and butylbenzene may be caused by different solvation at the interface between the aromatic and aliphatic corona……………………………………………………………………………………………………………….91

Figure 3.30  Variable temperature polarimetry of Poly-39 in CHCl$_3$ polymerized with different monomer to catalyst ratios of Cat-4 .................................94

Figure 3.31  Variable temperature polarimetry of Poly-39 in toluene polymerized with different monomer to catalyst ratios of Cat-4.................................95

Figure 3.32  IR spectra overlay of Poly-39 with various molecular weights.................96

Figure 3.33  Duplicate polymerization of Mono-39 using Cat-7 revealed both polymers Poly-39(Cat-7)a and Poly-39(Cat-7)b to have regioirregularity.............98

Figure 3.34  IR spectra overlay of Poly39(80K), Poly-39(Cat-7)a and Poly-39(Cat-7)b. Polymerization of Mono-39 with Cat-7 reveals no significant improvement in regioregularity……………………………………………………………..98
Figure 3.35  IR spectra overlay of Poly-39 from Cat-4 polymerized at various
temperatures................................................................. 101
Figure 3.36  Variable temperature polarimetry of Poly-39 polymerized at (a) 10 °C, (b)
25 °C, (c) 35 °C, (d) 45 °C, and (e) 55 °C in CHCl₃......................... 102
Figure 3.37  Polymerization of Mono-40 results in a soluble switching polymer with
slightly less aliphatic pendant group size........................................ 103
Figure 3.38  Variable temperature polarimetry of (a) Poly-40 in CHCl₃ (c = 0.21 g/100mL,
1 = 0.5 dm) and (b) Poly-39 in CHCl₃ (c = 0.23 g/100mL, 1 = 0.5 dm)…… 104
Figure 3.39  Synthesis of two new polycarbodiimides for investigation of (a) spatial
arrangement (Poly-41) and (b) size (Poly-42) of the polyarene pendant
group..................................................................................... 105
Figure 3.40  (a) Variable temperature polarimetry of Poly-41 in toluene (c = 2.13 g/100mL,
1 = 0.5 dm). (b) Variable temperature ECD of Poly-41 in THF at 9.5, 25, and
40 °C ...................................................................................... 106
Figure 3.41  (a) Variable temperature polarimetry of Poly-42 in toluene (c = 0.212 g/100
mL, λ = 589 nm, 1 = 0.5 dm) and (b) ethylbenzene (c = 0.204 g/100 mL, λ =
589 nm, 1 = 0.5 dm).................................................................. 106
Figure 3.42  IR spectra and regioregularity comparison of Poly-39(80K), Poly-41, and
Poly-42.................................................................................... 108
Figure 3.43  New carbodiimide monomers designed to probe size and spacing effects on
the switching phenomenon......................................................... 108
Figure 3.44 Molecular model of amidinate complex of Mono-43 with Cat-4 revealing the 2-methyl substituent to potentially block the path of monomer insertion and preventing propagation…………………………………………………….. 109

Figure 3.45 Synthesis of (a) Poly-44 and (b) Poly-45…………………………………. 111

Figure 3.46 Synthesis of Poly-46………………………………………………………… 112

Figure 3.47 New carbodiimide monomers designed to alter the electronics of the naphthalene π-ring system…………………………………………………. 114

Figure 3.48 Polymerization of Poly-49 required one month using Cat-4………………. 116

Figure 3.49 Variable temperature polarimetry of Poly-49 in (a) CHCl$_3$ (c = 0.215 g/100mL) (b) THF (c = 0.206 g/100mL), and (c) toluene (c = 0.212 g/100mL)………………………………………………………. 116

Figure 3.50 Polymerization of Mono-50 and Mono-51. Polymerization of Mono-51 resulted in an insoluble solid……………………………………………… ..118

Figure 3.51 Variable temperature polarimetry of Poly-50 in (a) CHCl$_3$ (c = 0.200 g/100mL), (b) toluene (c = 0.206 g/100mL), and (c) propylbenzene (c = 0.200 g/100mL). Changes in [α] are reversible upon cooling………………………….. 119

Figure 3.52 Polymerization of Mono-52 and Mono-53…………………………………… 120

Figure 3.53 Variable temperature polarimetry of Poly-52 in (a) CHCl$_3$ (c = 0.218 g/100mL), (b) THF (c = 0.202 g/100mL), and (c) toluene (c = 0.213 g/100mL)………………………………………………………. 122
Figure 3.54  Normalized specific optical rotation data of Poly-52 with bromine mass subtracted from the concentration…………………………………………. 122

Figure 3.55  Variable temperature polarimetry of Poly-53 in (a) CHCl$_3$ (c = 0.205 g/100mL), (b) THF (c = 0.219 g/100mL), and (c) toluene (c = 0.206 g/100mL)…………………………………………………………………… 123

Figure 3.56  Polymerization of Moly-54……………………………………………… 124

Figure 3.57  Variable temperature polarimetry of Poly-54 in (a) CHCl$_3$ (c = 0.203 g/100mL), (b) THF (c = 0.209 g/100mL), and (c) toluene (c = 0.214 g/100mL)…………………………………………………………………… 124

Figure 3.58  Charge-transfer complexation of iodine and various solvents…………….. 127

Figure 3.59  Iodine doped benzene, toluene, and THF without (left) and with (right) Poly-39. A color change can be seen from pink to orange in benzene and toluene as a result of CT complexation with the polymer………………………………. 129

Figure 3.60  Visual reference of toluene solution with Poly-39 with no iodine added. The polymer solution alone is colorless………………………………………… 129

Figure 3.61  (a) Picture of (from left to right) Poly-39 in CHCl$_3$ (2 mg/mL), CHCl$_3$ only, I$_2$ in CHCl$_3$ (0.1 mg/mL), Poly-39 (2 mg/mL) + I$_2$ (0.1 mg/mL) in CHCl$_3$. (b) UV-Vis spectra of Poly-39 in CHCl$_3$ (44 ppm) and I$_2$ in CHCl$_3$ (106 ppm)……………………………………………………………………….. 131
Figure 3.62 Overlay of UV-Vis spectra for (a) I$_2$ in CHCl$_3$ (106 ppm), and solutions of Poly-39 (1.09 mg/mL) with additive amounts of I$_2$ (b) 25:1, (c) 12:1, (d) 8:1, (e) 6:1, and (f) 5:1 ratio of moles of polymer repeat unit to iodine. For (b-f), the polymer absorption was subtracted from the spectrum revealing the charge transfer band at 368 nm.

Figure 3.63 Overlay of ECD spectra of (a) Poly-39 (101 ppm) in CHCl$_3$ and mixtures of 4:1, 2.3:1, and 1:1 moles polymer repeat unit to moles iodine added. (b) Same iodine solutions in (a) but with polymer absorbance subtracted. No Cotton effects in the 368 nm range are observed.

Figure 3.64 Variable temperature polarimetry of Poly-39 in (a) CHCl$_3$, ((b) 80%, (c) 60%, (d) 30% CHCl$_3$ in toluene), and (e) toluene.

Figure 3.65 Newly synthesized chiral carbodiimide monomers containing a potentially switching pendant group.

Figure 3.66 Copolymerization of Mono-6 and Mono-42 for potential fluorescent polycarbodiimide studies.

Figure 4.1 Stereoregular outcomes for monosubstituted vinyl monomer polymerizations.

Figure 4.2 Regioregular outcomes for asymmetric carbodiimide monomer polymerizations.

Figure 4.3 Mechanism for carbodiimide monomer initiation and propagation on titanium(IV) amidinate complexes and the resulting regioisomers.
Figure 4.4 Decomposition of symmetric polycarbodiimides results in a clean return to monomer through homolytic cleavage of the polymer chain followed by a radical unzipping process.............................................................. 178

Figure 4.5 For regioregular asymmetric polycarbodiimides, the resulting decomposition product is the original asymmetric monomer regardless of where homolytic chain cleavage originates................................................................. 179

Figure 4.6 For regioirregular asymmetric polycarbodiimides, the resulting decomposition products depend on the location of homolytic chain cleavage and could result in two symmetric metathesis monomers in addition to the original asymmetric monomer................................................................. 180

Figure 4.7 Previously reported IR and $^{13}$C data for asymmetric polycarbodiimides containing various aromatic and aliphatic substituents. Poly-23 is reported incorrectly and should have the chiral stereocenter on the $\gamma$-position of the aliphatic pendant group................................................................. 184

Figure 4.8 Calibration curve of poly-2-vinylpyridine $M_w$ standards and their elution by GPC in THF with 5 % DMAEA................................................................. 188

Figure 4.9 GPC elution overlay of regioirregular Poly-39 ($M_w = 78$K, PDI = 4.2) and regioregular Poly-41 ($M_w = 13$K, PDI = 1.3) and Poly-42 ($M_w = 12.6$K, PDI = 1.7)......................................................................................................... 189

Figure 4.10 Monomers and polymers designed for a new regioregularity study.......... 192
Figure 4.11  GC-FID calibration curves of Mono-6, Mono-16, and Mono-62 at known injection concentrations in CHCl$_3$…………………………………………. 193

Figure 4.12  Sample injection showing all three monomer elutions and internal standard (IS) heptadecane…………………………………………………………….194

Figure 4.13  IR spectra of Poly-62 polymerized at various temperatures……………….195

Figure 4.14  Newly synthesized polycarbodiimides designated with their preferred regioisomers……………………………………………………………….. 198

Figure 4.15  Asymmetric aryl-alkyl monomers with no aryl substituents show no favored mode of monomer insertion as a result of no significant bias to amidinate nitrogen coordination on the titanium metal center…………………….. 200

Figure 4.16  Asymmetric aryl-alkyl monomers with electron withdrawing (EW) aryl substituents will show a favored mode of monomer insertion as a result reduced aryl-nitrogen coordination on the titanium metal center………………201

Figure 4.17  Asymmetric aryl-alkyl monomers with electron donating (ED) aryl substituents will show a favored mode of monomer insertion as a result enhanced aryl-nitrogen coordination on the titanium metal center……….. 201
LIST OF ABBREVIATIONS

List of Monomers – Polymers discussed are derived from monomers of the same number.

Mono-1  \(N\)-methyl-\(N'\)-(n-hexyl) carbodiimide
Mono-2  \(N\)-methyl-\(N'\)-((R)-(+)1-phenylethyl) carbodiimide
Mono-3  \(N\)-methyl-\(N'\)-benzyl carbodiimide
Mono-4  \(N\)-methyl-\(N'\)-phenyl carbodiimide
Mono-5  \(N\)-ethyl-\(N'\)-(n-hexyl) carbodiimide
Mono-6  Di-n-hexyl carbodiimide
Mono-7  \(N\)-ethyl-\(N'\)-((R)1-phenylpropyl) carbodiimide
Mono-8  Diphenyl carbodiimide
Mono-9  Di-(2-ethylhexyl) carbodiimide
Mono-10 Diisopropyl carbodiimide
Mono-11 \(N\)-methyl-\(N'\)-(tert-butyl) carbodiimide
Mono-12 \(N\)-(R)-2,6-dimethylheptyl-\(N'\)-(n-hexyl) carbodiimide
Mono-13 \(N\)-(R)-2,6-dimethylheptyl-\(N'\)-phenyl carbodiimide
Mono-14 \(N\)-phenyl -\(N'\)-(n-hexyl) carbodiimide
Mono-15 \(N\)-methyl -\(N'\)-(S)-(−)-1-phenylethyl) carbodiimide
Mono-16 Di-(4-butylphenyl) carbodiimide
Mono-17 Di-(4-butoxycarbonylphenyl) carbodiimide
Mono-18 Di-(3-methylphenyl) carbodiimide
Mono-19 Dibenzyl carbodiimide
Mono-20 \( N\)-methyl-\( N'\)-(2-isopropyl-6-methylphenyl) carbodiimide
Mono-21 \( N\)-(1-anthryl)-\( N'\)-(n-octadecyl) carbodiimide
Mono-22 \( N\)-methyl-\( N'\)-(2-isopropyl-6-methylphenyl) carbodiimide
Mono-23 \( N\)-(1-anthryl)-\( N'\)-((R/S)-3,7-dimethyloctyl) carbodiimide
Mono-24 Di-n-dodecyl carbodiimide
Mono-25 \( N\)-12-(4'-Methoxybiphenyl-4-oxy)dodecyl-\( N'\)-n-dodecyl carbodiimide
Mono-26 \( N\)-12-(4'-Methoxybiphenyl-4-oxy)dodecyl-\( N'\)-n-hexyl carbodiimide
Mono-27 \( N\)-6-(4-(4-Methoxyphenyloxy)hexyl-\( N'\)-n-hexyl carbodiimide
Mono-28 1,6-di(\( N'\)-methylcarbodiimido) hexane
Mono-29 Di-((2-\( N\),\( N\)-dimethylamino)ethyl) carbodiimide
Mono-30 Di-((2-\( N\),\( N\)-dimethylaminoethoxy)ethyl) carbodiimide
Mono-31 Di-(2-morpholinoethyl) carbodiimide
Mono-32 \( N\)-(\( N\)-methyl-\( N\),(\( N\),\( N\)-dimethylamoethyloxy)ethylaminoethyl)-\( N'\)-((S)-1-methoxy-2-propyl) carbodiimide
Mono-33 \( N\)-(3-bromophenyl)-\( N'\)-(n-hexyl) carbodiimide
Mono-34 \( N\)-(3-cyanophenyl)-\( N'\)-(n-hexyl) carbodiimide
Mono-35 \( N\)-(3-nitrophenyl)-\( N'\)-(n-hexyl) carbodiimide
Mono-36 \( N\)-(3-bromophenyl)-\( N'\)-(n-octadecyl) carbodiimide
Mono-37 \( N\)-(3-cyanophenyl)-\( N'\)-(n-octadecyl) carbodiimide
Mono-38 \( N\)-(3-nitrophenyl)-\( N'\)-(n-octadecyl) carbodiimide
Mono-39  \( N\-(1\text{-naphthyl})-N'\-(n\text{-octadecyl}) \) carbodiimide
Mono-40  \( N\-(1\text{-naphthyl})-N'\-(n\text{-dodecyl}) \) carbodiimide
Mono-41  \( N\-(2\text{-naphthyl})-N'\-(n\text{-octadecyl}) \) carbodiimide
Mono-42  \( N\-(1\text{-pyrenyl})-N'\-(n\text{-octadecyl}) \) carbodiimide
Mono-43  \( N\-(2\text{-methyl-1-naphthyl})-N'\-(n\text{-octadecyl}) \) carbodiimide
Mono-44  \( N\-(4\text{-indanyl})-N'\-(n\text{-dodecyl}) \) carbodiimide
Mono-45  \( N\-(2\text{-fluorenyl})-N'\-(n\text{-octadecyl}) \) carbodiimide
Mono-46  \( N\-(1\text{-naphthylmethyl})-N'\-(n\text{-dodecyl}) \) carbodiimide
Mono-47  Di-1-naphthyl carbodiimide
Mono-48  \( N\-(5\text{-quinolyl})-N'\-(n\text{-octadecyl}) \) carbodiimide
Mono-49  \( N\-(5\text{-quinolyl})-N'\-(n\text{-dodecyl}) \) carbodiimide
Mono-50  \( N\-(4\text{-methyl-1-naphthyl})-N'\-(n\text{-dodecyl}) \) carbodiimide
Mono-51  \( N\-(4\text{-methyl-1-naphthyl})-N'\-(n\text{-hexyl}) \) carbodiimide
Mono-52  \( N\-(4\text{-bromo-1-naphthyl})-N'\-(n\text{-dodecyl}) \) carbodiimide
Mono-53  \( N\-(4\text{-chloro-1-naphthyl})-N'\-(n\text{-dodecyl}) \) carbodiimide
Mono-54  \( N\-(4\text{-methoxy-1-naphthyl})-N'\-(n\text{-dodecyl}) \) carbodiimide
Mono-55  \( N\-(1\text{-S)-(1,2,3,4-tetrahydonaphthyl)})-N'\-(n\text{-dodecyl}) \) carbodiimide
Mono-56  \( N\-(1\text{-S)-(1,2,3,4-tetrahydonaphthyl)})-N'\text{-ethyl} \) carbodiimide
Mono-57  \( N\-(1\text{-naphthyl})-N'\-(R)-1\text{-phenylethyl}) \) carbodiimide
Mono-58  \( N\-(1\text{-naphthyl})-N'\-(S)-1\text{-cyclohexylethyl}) \) carbodiimide
Mono-59  \( N\-(1\text{-naphthyl})-N'\-(S)-2\text{-methylbutyl}) \) carbodiimide
Mono-60 \( N\)-(1-naphthyl)-N'-(S)-2,6-dimethylheptyl) carbodiimide

Mono-61 \( N\)-isopropyl-N'-n-hexyl) carbodiimide

Mono-62 \( N\)-(4-butylphenyl)-N'-(n-hexyl) carbodiimide

**List of Catalysts**

Cat-1 trichloro titanium(IV) \( N,N'\)-(di-trimethylsilyl) phenyl amidinate

Cat-2 \( \eta^5\)-cyclopentadienyl-dichloro-ethoxy titanium(IV)

Cat-3 \( \eta^5\)-cyclopentadienyl-dichloro-\( N,N\)-dimethylamino titanium(IV)

Cat-4 (R)-BINOL-diisopropoxy titanium(IV)

Cat-5 (S)-BINOL-diisopropoxy titanium(IV)

Cat-6 (R)-BINOL-di-\( t\)-butoxy titanium(IV)

Cat-7 (R)-(3,3’-dibromo-BINOL)-di-\( t\)-butoxy titanium(IV)

Cat-8 (R)-(3,3’-di(trimethylsilyl)-BINOL)-diisopropoxy titanium(IV)

Cat-9 (R)-(3,3’-di(trimethylsilyl)-BINOL)-di-\( t\)-butoxy titanium(IV)

Cat-10 (R)-(3,3’-di(triphenylsilyl)-BINOL)-diethoxy titanium(IV)

Cat-11 (R)-(3-(2-hydroxyphenyl)-BINOL)-\( t\)-butoxy titanium(IV)

Cat-12 (R)-(3-(2-hydroxy-3-biphenyl)-BINOL)-\( t\)-butoxy titanium(IV)

Cat-13 (R)-(3-(2-hydroxy-3-biphenyl)-3’-bromo-BINOL)-\( t\)-butoxy titanium(IV)

Cat-14 (R)-(3-(2-hydroxy-3,5-dimethylphenyl)-BINOL)-\( t\)-butoxy titanium(IV)

Cat-15 trichloro-(2,2,2-trifluoroethoxy) titanium(IV)

Cat-16 Copper(I) chloride
<table>
<thead>
<tr>
<th>Cat-17</th>
<th>Copper(II) chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-18</td>
<td>Copper(II) monochloride methoxide</td>
</tr>
<tr>
<td>Cat-19</td>
<td>Copper(I) (N,N')-trimethysilyl-phenylamidinate</td>
</tr>
<tr>
<td>Cat-20</td>
<td>Copper(I) (N,N')-diphenylamidinate</td>
</tr>
<tr>
<td>Cat-21</td>
<td>Copper(II) chloride (N,N')-trimethysilyl-phenylamidinate</td>
</tr>
<tr>
<td>Cat-22</td>
<td>Nickel(II) di-COD phenyl bromide</td>
</tr>
<tr>
<td>Cat-23</td>
<td>Nickel(II) triphenylphosphoryl phenyl</td>
</tr>
<tr>
<td>Cat-24</td>
<td>Dicyclopentadienyl-methyl zirconium (IV) with counter anion tris(tetrachlorobenzenediolato)phosphate(V)</td>
</tr>
</tbody>
</table>

**Other Abbreviations Used**

- **BINOL**: 1,1’-binaphth-2,2’-ol
- **COD**: 1,5-cyclooctadiene
- **PMA**: polymethylacrylate
- **PMMA**: polymethylmethacrylate
- **PPA**: polyphenylacetylene
- **HPLC**: high performance liquid chromatography
- **CSP**: chiral stationary phase
- **TEA**: triethylamine
- **HRMS**: high resolution mass spectrometry
- **ESI**: electrospray ionization
- **THF**: tetrahydrofuran
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEE</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>KCC</td>
<td>kinetically controlled conformation</td>
</tr>
<tr>
<td>TCC</td>
<td>thermodynamically controlled conformation</td>
</tr>
<tr>
<td>ORD</td>
<td>optical rotatory dispersion</td>
</tr>
<tr>
<td>CSA</td>
<td>camphorsulfonic acid</td>
</tr>
<tr>
<td>CP/MAS</td>
<td>cross polarized/magic angle spinning</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>LC</td>
<td>liquid crystal</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>CD</td>
<td>circular dichroism</td>
</tr>
<tr>
<td>ECD</td>
<td>electronic circular dichroism</td>
</tr>
<tr>
<td>VCD</td>
<td>vibrational circular dichroism</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>ultraviolet-visible</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methylpyrrolidinone</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>VT</td>
<td>variable temperature</td>
</tr>
<tr>
<td>PTFE</td>
<td>polytetrafluoroethylene</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
</tr>
</tbody>
</table>
IR  infrared (or infrared spectrometer)
CT  charge transfer
HOMO  highest occupied molecular orbital
LUMO  lowest unoccupied molecular orbital
ISC  intersystem crossing
GC/MS  gas chromatography/mass spectrometry
GC-FID  gas chromatography – flame ionization detector
BHT  butylated hydroxytoluene
AIBN  azobisisobutyronitrile
DMAEA  $N,N$-dimethylaminoethylamine
P2VP  poly-2-vinylpyridine
PDI  polydispersity
RF  response factor
EW  electron withdrawing
ED  electron donating
Chapter 1: Helicity in Macromolecules

1.1 History of Helical Polymers

The helix is a ubiquitous chiral macrostructure that is found throughout nature. Complex biological systems and their components such as proteins, polypeptides, genes, and DNA all utilize the helical structure as a means of performing complex chemical tasks such as information storage, support of tissue, molecular transportation, and localized chemical transformations.\(^1\) Synthetically, polymer chemists have been invested in the creation of macromolecules with an excess helical conformation due to their potential application as biomimetic materials to perform tasks such as those mentioned above and also because of their potential use as molecular recognition or sensory materials, stationary phases for chiral chromatography, sites for selective chemical reactions and asymmetric catalysis, polarizers in optical display technology, and liquid crystalline materials.\(^1-4\)

To date, a relatively small class of synthetic polymers have been characterized and shown to exhibit a helical sense. Such polymers include: polymethacrylates (PMAs), polymethacrylamides, polyisocyanides, poly(quinoxaline-2,3-diyl)s, polyisocyanates, polysilanes, polychlorals, polyacetylenes (such as cis-polyphenylacetylenes or PPAs), and, the focus of this manuscript, polycarbodiimides (Figure 1.1).\(^2\) Although a complete summary of the advances in helical polymer chemistry lies outside the scope of this thesis, the following will serve as a brief introduction spanning some of the more
prominent advances. Okamoto, Yashima, Maeda and colleagues have written multiple reviews on the current advances in synthetic helical polymer chemistry and these are recommended as comprehensive manuscripts for in-depth knowledge of this topic.\textsuperscript{2-4}

In the early 1950’s, Pauling, Watson, and Crick discovered that nature had already found advanced potentials though use of the helical motif and was utilizing a right handed \( \alpha \)-helical structure for proteins\textsuperscript{5} and a double-stranded helix for DNA.\textsuperscript{6} It was soon after when the field of synthetic helical polymers was initiated by Natta in 1955 as he discovered that, through the use of his own catalyst system, stereoregular isotactic polypropylene exhibits a helical structure in the solid state.\textsuperscript{7} This helical conformation was only obtained in the crystalline structure of the polymer and loss of helicity occurred during its dissolution. The persistence of helical conformation in solution was discovered by Pino and Lorenzi in 1960.
through synthesis of highly isotactic helical vinyl polymers containing configurationally chiral substituents. Polyisocyanides bearing tert-butyl pendant groups were successfully resolved into opposite handed helices through chiral chromatography by Nolte and Drenth in 1974, opening the door to the idea that bulky pendant groups may lead to asymmetry of a polymer backbone comprised from achiral monomers. Okamoto and Yuki et al. took this idea a step further in 1979 when they synthesized a fully isotactic, stable, single-handed helical vinyl polymer, (Figure 1.1(a)), from the achiral monomer triphenylmethyl methacrylate via anionic asymmetric polymerization using optically active organolithium initiators. This polymer’s large, sterically restricting trityl pendant groups were found to highly improve the stability of the helix by preventing rotation of the main chain bonds and keeping the helix “locked-in” to its excess helical sense even at higher temperatures. This robust chiral polymer was one of the first synthetic helical polymers to be used commercially as a chiral stationary phase (CSP) in high performance liquid chromatography (HPLC) columns. To date many close analogs of this polymer have been introduced, providing a catalog of CSPs that are highly useful in the pharmaceutical and natural product industry due to their ability to separate enantiomers from racemic mixtures of small molecules.

While Okamoto’s polymer utilizes a stiff or rigid helical backbone, in the late 1980’s Green and co-workers began pioneering a new breed of helical polymers, polyisocyanates. In an initially proposed calculation by Troxell and Scheraga, which was further confirmed and improved by Tonelli, the polyalkylisocyanate backbone retains a lowest energy helical structure of approximately 8 residues per 3 helical turns in the solid state and solution with a
translation distance of each residue along the helix of just over 20 nm. The rigidity of the polyisocyanate is dependant upon the molecular weight and the increased amount of existing helical reversals for higher molecular weight polymers. Unlike the aforementioned vinyl polymers, polyisocyanates are more dynamic in the sense that their backbone has a low energy barrier to helix inversion, rendering it more flexible. This flexibility allows the polymer to easily interconvert between left and right handed helical segments and therefore can adopt a preferred helical sense through use of a small chiral perturbation. This bias can be controlled by configurationally chiral pendant groups (sergeant – soldier, majority rules)\textsuperscript{11, 14, 15} or by chiral influence through non-covalent interactions with the backbone (molecular chaperones)\textsuperscript{16} which will be discussed in more detail vide infra. These general principles for helical polymers containing low helical inversion energy barriers were found to be universal and applicable to other dynamic helical backbones such as polyacetylenes\textsuperscript{17-19} and polysilanes\textsuperscript{20, 21} which have received much attention over the last few decades.

Due to the increasing variety of helical polymers now being researched and discovered, it is necessary to begin organizing the different characteristics of these polymers. As such, most helical polymers can be separated into two main categories; static helical polymers and dynamic helical polymers. Static helical polymers are those containing a high barrier to helical inversion and are typically formed into a preferred helical sense kinetically during polymerization. Polymethacrylates, polymethacrylamides, polyisocyanides, poly(quinoxaline-2,3-diyl)s, and polycarbodiimides fall into this category of helical polymer. Oppositely, helical polymers with a low barrier to helix inversion such as polyisocyanates,
polysilanes, polyacetylenes, and polycarbodiimides fall into the class of dynamic helical polymers since their backbones are more fluxional and can be influenced into an excess helical sense during or after polymerization through the use of chiral influence. It is not a mistake that polycarbodiimides were included in the lists of both categories. Some types of helical polymers are capable of exhibiting behavior associated with both classes depending on the overall properties of the polymer. As will be shown later in this thesis, polycarbodiimides are recognized as a hallmark example of this type of hybrid helical polymer. Recently, a new class of helical polymers known as foldamers has emerged; however, since the properties associated with this type of helical polymer do not generally apply to polycarbodiimides, further discussion of them will not be included. Moore et al has published a nice review of foldamers which can be referenced for those seeking additional information on this particular subject.

1.2 Chemistry of Helical Polymers

In addition to common characteristics that typically affect polymer properties such as molecular weight, polydispersity, regioregularity, tacticity, and the style of polymerization such as living, anionic, cationic, radical, or step-growth, etc., there are a variety of other factors that can play a large role on the resulting behavior and properties of synthetic helical polymers. These factors include the use of chiral vs. achiral monomers, the resulting energy barrier to helical inversion (static vs. dynamic backbone), polymerizing using kinetic vs. thermodynamic control, the excess helical sense (or enantiomeric excess) of the resulting
polymer, and a few associative terms specific to helical polymers such as helical pitch, persistence length, cooperativity, and chiral amplification. The nature of the catalyst used also plays a role in the resulting polymer, however, since a large variety of catalysts are used to produce different helical polymers, a description of catalysts pertaining specifically to polycarbodiimides will be discussed later in this text.

Achiral or prochiral monomers are typically polymerized into helical macromolecules through the use of a chiral catalyst or chiral initiator. During polymer initiation and propagation, this initial chiral stimulant (if the using a chiral end group) or continuous chiral influence (if the chirality is governed by continual transfer to the active propagation site) creates a bias towards the propagating direction of the helix and therefore leads to a preferred and excess helical sense. This type of polymerization, known as helix-sense-selective polymerization, produces a helix that is solely responsible for the resulting chirality of the polymer. Opposite handed helices of this nature behave as enantiomers such that they are mirror images of one another and all of their physical properties are identical with the exception of the direction in which they rotate plane polarized light. Much like configurationally chiral carbon stereocenters that are designated R or S through the Cahn-Ingold-Prelog system, helices are conformationally chiral structures and are designated M or P by viewing down the helical axis (Figure 1.2). If the helix travels away from the viewer in a clockwise direction it is designated as a P or right-handed helix. Oppositely, if it travels in a counter-clockwise direction it is designated an M or left-handed helix. It is an entropically and thermodynamically favorable process for these enantiomeric helices to
racemize into an equal mixture of these helical segments. Therefore, achiral monomers are typically polymerized under kinetic control into polymers with sufficiently high helical inversion barriers ($E_i$, Figure 1.3(a)) to prevent racemization of the helix at ambient temperatures following polymerization. In most cases, the use of bulky sterically restricting pendant groups such as the previously mentioned triphenylmethyl group (Figure 1.1(a)) provides the polymer with an improved helical inversion barrier.

The use of chiral monomers is also an interesting way to induce a preferred helical sense. A small molecule with multiple stereocenters results in isomers called diastereomers. Unlike enantiomers, diastereomers do not have the same physical properties and are not

**Figure 1.2** – Opposite handed polymer helices comprised from achiral monomers are enantiomers of one another. Their designation of M (for minus) and P (for plus) can be assigned by looking down the helical axis. If the helix travels away from the viewer in a clockwise direction it is designated as P and oppositely, if it travels in a counter-clockwise direction it is an M helix.
equivalent in energy.\textsuperscript{26} Similarly, a helical polymer composed of homochiral monomer segments adopts a diastereomeric relationship between opposite handed helices and results in a helical sense having a lower energy than the other (Figure 1.3(b)). Due to this bias in energy, this polymer is now thermodynamically driven to adopt the helical sense of lower energy. Successful sense-selective polymerizations have been reported for both static and dynamic backbones; however, due to the fluxional nature of the dynamic helical polymers, this thermodynamically preferred diastereomer is necessary to retain an excess helical sense.

Figure 1.3 – (a) Energy plot of helical polymers from achiral monomers. Such polymers are comprised of equal-energy enantiomeric helical segments separated by higher-energy helical inversions. (b) Helical polymers from homochiral monomers form diastereomeric helices that are not equal in energy ($\Delta E$), resulting in a helical sense that is thermodynamically preferred.

Helical inversions or reversals are anomalies that occur along a helical polymer chain, at which, the direction of helical sense changes. For helices comprised from achiral monomers, the presence of disfavored higher-energy helical inversions is validated by the entropic desire to create racemic disorder in the system. Therefore, it is expected that heat
favors an increase of helical reversals along a helical chain comprised of achiral monomers. For helices derived from homochiral monomer units, the application of heat allows progression towards the thermodynamically favored helical diastereomer. Helical inversions can be eliminated by forcing them off of the chain ends or by a synergistic termination of two helical inversions coming together. For dynamic helical backbones, helical reversals move readily along the polymer backbone, allowing better induction of excess helical sense through chiral stimulant. The term “Sergeants and Soldiers” was first introduced by Green and co-workers through careful experiments performed on dynamic helical polyisocyanates. It was discovered that only a small amount (1 mol %) of chiral isocyanate monomer was necessary to co-polymerize achiral aliphatic polyisocyanates into an excess helical sense.\textsuperscript{14,27} The chiral “sergeant” units receive a high cooperativity from the achiral “soldier” units allowing their relatively small inflection of chirality to transverse the entire polymer chain (Figure 1.4(a)). Cooperativity, as it applies to helical polymer chemistry, is generally defined as the amount of excess helical-sense induced per some arbitrary unit of chiral influence. Due to the rarely occurring helical reversals on the polyisocyanate chain and their ability to move rapidly along it, the otherwise indifferent achiral isocyanate co-polymer units are easily persuaded to adopt the preferred helical sense dictated by the chiral sergeant co-polymer units. Another elegant example of cooperativity, also performed by Green et al, demonstrated that a high excess helical sense can be achieved by using only a 12% enantiomeric excess (6% molar difference) of one isocyanate monomer over its enantiomer (Figure 1.4(b)).\textsuperscript{15} This phenomenon known as the “majority rules” effect is a prime example
of the delicate nature of dynamic helical systems and how a small excess in chiral influence can cause a large chiral amplification through cooperation of the helix.

![Diagram of Sergeant and Soldier Effect and Majority Rules](image)

**Figure 1.4** – (a) The Sergeants and Soldiers effect: Less than 1% (molar ratio) of chiral sergeant units induce a preferred helical excess comparable to a polymer of 100% homochiral units. (b) Majority Rules; a slight enantiomeric excess of chiral isocyanate monomers induces a highly preferred helical excess.

Induction in helicity can also be caused by non-covalent interactions between the polymer and a chiral perturbation such as a chiral solvent or chiral guest molecule. Okamoto, Yashima, and co-workers reported a *cis-transoidal* poly(4-carboxyphenyl)-acetylene capable of adopting a preferred helical sense through acid-base interactions between the carboxylic acid pendant group and their complexation with chiral amines (Figure 1.5). Since polyphenylacetylenes are a dynamic class of helical polymers, the chiral amines behave as a “molecular chaperone” and induce a preferred helical sense. These PPA systems can function as molecular sensors capable of probing the chirality of amines through the observation of chiral amplification induced upon the helix.
These discoveries exemplify current fundamental methodologies available for manipulation of polymer backbones capable of adopting a preferred helical-sense. For a more in-depth look at specific synthesis and analytical techniques this thesis will now turn focus on polycarbodiimides and the direct chemistry that affects them.

Figure 1.5 – Helical induction of poly((4-carboxyphenyl)-acetylene) through acid-base interactions with chiral amines. The dynamic PPA backbone adopts a preferred helical sense through the use of molecular chaperones.

1.3 References


Chapter 2: A Review of Polycarbodiimides

2.1 Background

In 1964, Robinson first reported anionic polymerization of low molecular weight polycarbodiimides using organolithium catalysts. However, due to the lack of control over the polymerizations and the relatively low molecular weight obtained, future work was halted. Radical and cationic polymerization attempts were deemed unsuccessful and thermal polymerizations only led to oligomers. It wasn’t until 1994 when Goodwin and Novak reported the ability to polymerize carbodiimides in a living fashion through the use of organotitanium(IV) catalysts (Figure 2.1). Patten and Novak had previously proven these catalysts to be successful for controlled living polymerizations of isocyanates. It was later determined that copper(I/II), nickel(II), and zirconium(IV) based catalyst systems could also effectively polymerize carbodiimides. The discovery of synthesizing polycarbodiimides in a living fashion was monumental due to the potential properties that these polymers may obtain. The polycarbodiimide backbone can be viewed as a hybrid between polyisocyanates (a dynamic helical polymer) and polyisocyanides (a static helical polymer), (Figure 2.2). As mentioned in Part 1, very prominent research has been carried out in the field of polyisocyanates and polyisocyanides, however, both of these polymer systems have positive and negative attributes. For polyisocyanides, steric hindrance caused by the bulky imine substituents and the constricted rotation of the sp² hybridized carbon backbone results
in stable static helices. Poly(t-butylisocyanide) has a helical inversion barrier of >27 kcal/mol.\textsuperscript{6} The disadvantage of polyisocyanides is their relatively short persistence length (approx. 30 Å for poly (1-phenylethylisocyanide)).\textsuperscript{7} The persistence length is defined as the average projection of the end-to-end vector on the tangent to the chain contour at the chain end in the limit of infinite chain length.\textsuperscript{8} In other words, it is the average distance over which the direction of the chain persists and is directly related to a polymer’s stiffness. Therefore, the helices of polyisocyanides will not racemize appreciably at room temperature but the lack of persistence length causes them to adopt random-coil geometry instead of the more desired rigid-rod geometry. Polyisocyanates, on the other hand, have much larger persistence lengths of almost 600 Å, making them stiff polymers which is attributed to the carbonyl moiety and the partially conjugated nature of the nylon-1 backbone.\textsuperscript{9} Consequently,
Figure 2.2 – Polycarbodiimides combine the salient features of the static polyisocyanide and the dynamic polyisocyanate helical polymers.

Polyisocyanates exhibit low helical inversion barriers (12 kcal/mol for n-hexyl isocyanate).\textsuperscript{10, 11} As will be discussed, polycarbodiimides combine the salient features from both of these polymer systems and can be synthesized to obtain static and/or dynamic helical properties.

2.2 Carbodiimides

Before discussing polycarbodiimides, it is first important to gain a fundamental understanding of their monomer precursors. Carbodiimides are the diimides derived from carbon dioxide and have a heterocumulene structure that is isoelectronic with isocyanates.\textsuperscript{12} The two nitrogen-attached pendant groups can be identical (symmetric carbodiimides) or different (asymmetric carbodiimides) and may be of a wide range of functionalities including alkyl, aryl, acyl-, trimethylsilyl-, thioacetyl-, imidoyl-, or even halogens. Commercially, only a
small set of carbodiimides are available and these reagents are often used as mediators in peptide, nucleotide, and, more recently, proteomics chemistry. They are also valuable dehydration agents due to their ability to form stable and often insoluble ureas which can easily be removed by filtration. Other uses for carbodiimides include polymer additives, heterocycle synthesis, permease inhibition, and cycloaddition reactions. All of the carbodiimide monomers used in this manuscript are not commercially available and therefore continual synthesis and purification improvements, as well as the understanding of the stability of this particular class of molecules, are necessary.

Due to their allene structure, carbodiimides can exist as stereoisomers in theory, but only a few carbodiimides have ever been resolved into their existing enantiomeric forms. One such example, bisferrocenylcarbodiimide, has been partially resolved and it is claimed that a stabilizing interaction between the ferrocenyl groups and the carbodiimide moiety is reason for this resolution. However, most carbodiimides are not resolvable due to a very low energy barrier to racemization of the carbodiimide through imine inversion and rotation which has been calculated to be <10 kcal/mol by a semiempirical method. Symmetric carbodiimides are generally easier to synthesize over asymmetric derivatives. Traditionally, primary amines can be combined with a coupling agent such as phosgene, triphosgene, or bis-(4-nitrophenyl) carbonate followed by dehydration of the subsequent 1,3-disubstituted urea. Due to the toxicity of most coupling agents, an alternative preparation of symmetric carbodiimides from isocyanates using a phospholene oxide catalyst requires no solvent and this method generally produces good yields due to the production of carbon dioxide, which
drives the reaction. Alternatively, thioureas can be synthesized followed by desulfurization using mercuric oxide.

For most cases, our research employed asymmetric carbodiimides. The synthesis of choice involves the reaction of a primary amine and an isocyanate to form a 1,3-disubstituted urea (Figure 2.3). The solubility of the urea depends highly on the nature of the pendant groups chosen. Dehydration of the urea using dibromotriphenylphosphorane, a salt adduct that can be made in-situ by the addition of molar equivalents of triphenylphosphine and

Figure 2.3 – Synthesis of carbodiimides by the reaction of a primary amine and an isocyanate followed by subsequent dehydration of the 1,3-disubstituted urea using dibromotriphenylphosphorane and an acid scavenger triethylamine.
bromine, and an acid scavenger such as triethylamine (TEA) yields the carbodiimide product along with triphenylphosphine oxide and triethylaminium bromide by-products. Optimal purification of the carbodiimides following dehydration is an ongoing process and needs to be adjusted depending on the nature of the nitrogen-attached pendant groups. Purchase of a pre-made dibromotriphenylphosphorane salt has eliminated some of the more persistent contaminants which are believed to originate from uncomplexed bromine reagent. Other creative ways of synthesizing asymmetric carbodiimides include; reacting isothiocyanates with amines followed by desulfurization of the thiourea using mercuric oxide, reaction of isocyanates with iminophosphoranes via the aza-Wittig reaction or with phosphoramidates, and the use of amidoximes via the Tiemann rearrangement. For symmetric carbodiimides, final purification by vacuum distillation is the preferred method provided that the monomer has a low enough boiling point. This method is not recommended for asymmetric carbodiimides due to their ability to thermally metathesize, a process by which two carbodiimides dimerize and exchange pendant groups leading to a mixture of symmetric and asymmetric carbodiimides (Figure 2.4). Our work has found that this metathesis is more favorable with asymmetric carbodiimides containing an aryl and an alkyl pendant group. Instead, we have achieved success purifying asymmetric carbodiimides through column chromatography using neutral pH silica gel.

The storage and stability of carbodiimides can fluctuate depending on the nature of the pendant groups. Bulky tertiary alkyl pendant groups typically provide the best stability for carbodiimides due to their size and the relatively inert induction effects of hydrocarbons
Figure 2.4 – Application of heat to asymmetric carbodiimides results in dimerization followed by an exchange of pendant groups. This metathesis yields a mixture of the original asymmetric and two symmetric carbodiimides.

on the carbodiimide moiety. Later, it will be later shown that bulky tertiary and secondary alkyl groups are not ideal for the synthesis of polycarbodiimides. Aryl groups tend to lend instability to carbodiimides especially if they contain electron donating groups in the ortho- or para-position. This instability is not necessarily a bad thing because it is directly correlated to their reactivity and, therefore, their ability to be polymerized quickly. Other trends state that solid carbodiimides are more stable than liquids and that diarylcarbodiimides are more stable than N-alkyl-N'-aryl carbodiimides. Most of the carbodiimides monomers discussed herein can be dried and stored under nitrogen atmosphere at cold temperatures and remain stable for at least a few weeks prior to polymerization. Carbodiimides that are a solid at the storage temperature have been stored for months without any appreciable degradation.
Carbodiimides will react rapidly in the presence of acid to form cyclic dimers and trimers (Figure 2.5). Protonation of the basic carbodiimide nitrogen catalyzes their reactivity allowing the electrophilic carbon center to be highly susceptible. In the presence of water and acid, carbodiimides will convert back to their stable urea precursors. Without water, other nucleophiles such as alcohols, thiols, and amines will react to form isoureas, isothioureas, and guanidines respectively. High resolution mass spectrometry (HRMS) with cationic electrospray ionization (ESI) is a good technique for observing some of the potential side reactions of carbodiimides in the presence of acid. A sample of pure $N$-(1-naphthyl)-$N'$-(n-dodecyl) carbodiimide diluted in water:acetonitrile (5:95 v/v) with 0.1% formic acid was

![Figure 2.5 – Carbodiimides are unstable in the presence of acid which catalyzes a series of reactions based on the nucleophiles present. The presence of acid alone catalyzes the formation of dimers and trimers.](image-url)
tested. The analysis report reveals four major ions detected (Figure 2.6). These ions match the original protonated carbodiimide (337 m/z, z =1), N-(1-naphthyl)-N’-(n-dodecyl) urea (355 m/z, z = 1), N-(1-naphthyl)-N’-(n-dodecyl) methoxyisourea (369 m/z, z = 1), and dimer of the original monomer (673 m/z, z =1). The major presence of isourea was later determined to be caused by methanol in the instrument system due to an incomplete flush from methanol to acetonitrile as the mobile phase prior to injection.

![Figure 2.6](image)

**Figure 2.6** – Positive ion HRMS-ESI of pure N- (1-naphthyl)-N’-(n-dodecyl) carbodiimide injected in the presence of formic acid, water, and methanol reveals transformation of the carbodiimide (337 M⁺ + H⁺) to urea (355 M⁺ + H⁺), methoxy-isourea (369 M⁺ + H⁺) and dimer (673 M⁺ + H⁺).

With this in mind, it is important for our monomers to be void of any acidic protons prior to polymerization. Care must be taken when purifying monomers using column chromatography on silica gel due to residual acid and water that is adsorbed on the silicon oxide surface. Although resulting ureas are usually insoluble in the mobile phase and are
retained on the column, neutral silica gel (pH = 7.0) is recommended to minimize loss of carbodiimide product.

2.3 Catalysts

Since the discovery of **Cat-1-3** (Figure 2.1) and their ability to polymerize carbodiimides in a living fashion, a variety of titanium, copper, nickel, and zirconium catalysts have been synthesized (Figure 2.7). The titanium (IV) catalysts are air and moisture sensitive requiring the use of a Schlenk apparatus under an inert nitrogen blanket or an inert dry box system for synthesis and polymerizations. The amine and alkoxide ligands are known as the initiation or transfer ligands. Upon initial nucleophilic attack of the first carbodiimide nitrogen onto the electron deficient d⁰ titanium metal center, this ligand transfers onto the electrophilic center carbon of the carbodiimide (Figure 2.8). As the polymerization progresses and sequential carbodiimides insert, the transfer ligand remains on the polymer as an end group while the rest of the catalyst carries along the propagating chain end. The retained ligands on the metal center can be chiral or achiral and their size and inductive effects can greatly alter the kinetics of polymerization. The 1,1′-binaphth-2,2′-ol (BINOL) ligand was employed as a chiral ligand for titanium catalysts to induce helix-sense-selective polymerization of achiral carbodiimides. Due to the atropisomeric nature of the BINOL ligand, they can be designated as R (**Cat-4,6**) or S (**Cat-5**) and racemization of the ligand by rotation of the aryl-aryl bridging bond does not occur at modest temperatures due to steric inhibition. (R)-BINOL titanium diisopropoxide (**Cat-4**) and its (S) enantiomer
(Cat-5) have been shown to successfully polymerize many different symmetric and asymmetric carbodiimides into an excess helical sense.\textsuperscript{18-23} Due to known aggregation of these plain BINOL based titanium catalysts,\textsuperscript{24} many of the bulkier BINOL based catalysts (Cat 7-10)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{catalysts.png}
\caption{List of catalysts capable of polymerizing carbodiimides}
\end{figure}
were synthesized to reduce aggregation.\textsuperscript{18, 19} This is also the reasoning behind using bulkier alkoxide ligands such as isopropoxy (\textbf{Cat-4,5,8}) or tert-butoxy (\textbf{Cat-6,7,9}). Of the catalysts made, only \textbf{Cat 7}, \textbf{9}, and \textbf{10} were found to be monomeric as a solid crystal, the most notable

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.8}
\caption{Initiation and propagation mechanism for the polymerization of carbodiimides using a titanium(IV) catalyst.}
\end{figure}

being \textbf{Cat-7} due to its moderate activity and good yields of resulting polymer.\textsuperscript{18, 19} Even though these catalysts are shown to be monomeric in the solid crystal, aggregation behavior may be different when dissolved in various solvents. The monoalkoxy titanium (IV) catalysts (\textbf{Cat-11-14}) were made in an effort to maximize helix-sense-selective polymerization however reaction times were very slow and resulting polymers were of low yield ($\leq 36\%$) and probably low in molecular weight. The general trend is that bulky ligand based titanium catalysts are less aggregated but, as a consequence, polymerize carbodiimides much slower. Additionally, if the carbodiimides themselves have bulky pendant groups,
polymerization may not occur at all. The achiral trichlorotitanium(IV) trifluoroethoxide catalyst (Cat-15) is a highly active catalyst. The three chloride ligands are less bulky than BINOL ligands and they also increase the activity of the titanium center by inductively withdrawing electron density. As a result, Cat-15 results in fast, kinetically controlled, polymerizations and high polymer yields. Consequently, since there is no chiral influence from this catalyst, it is not a candidate for helix-sense-selective polymerization of achiral monomers.

Hyun Su-Lee successfully synthesized a cationic dicyclopentadienyl-methyl zirconium (IV) catalyst with a large chiral tris(tetrachlorobenzenediolato)phosphate(V) counter anion (Cat-24). The larger zirconium metal center belongs to the same periodic group as titanium and was shown to also successfully polymerize achiral symmetric and asymmetric carbodiimides such as N-(methyl)-N’-(phenyl) carbodiimide (92 % yield of polymer reported). The large chiral anion was designed to govern the direction of insertion and propagation of the polymer chain and achieve helix-sense-selective polymerizations but this was deemed unsuccessful.

Due to the difficulty of handling air and moisture sensitive catalysts, copper (I/II) catalysts, having late transition metal centers, were synthesized to be a more robust way of creating polycarbodiimides. Initial experiments using common copper (I) (Cat-16) and copper (II) (Cat-17,18) salts showed promise for polymerizing carbodiimides under normal atmosphere with the copper (II) salts showing greater activity. Further improvements to the design yielded copper (II) amidinate complexes (Cat-19-21) and resulted in yields equivalent
to those observed for titanium (IV) complexes. These catalysts have good tolerance in air and in minimally wet solvents, although using excessive water was shown to reduce the yield of polymer. These systems were also shown to be living due to the absence of chain transfer and chain termination side-reactions.\textsuperscript{4} Drawbacks to the copper catalyst systems include stubborn solubility of the copper salt complexes in most solvents and the absence of chiral ligands capable of helix-sense-selective polymerization. The same can be reported for the nickel based catalyst systems (\textbf{Cat-22,23}) which were also found to tolerate oxygen and moisture and reasonably high yields of polycarbodiimide were obtained but without the ability for chiral induction.

To date, titanium catalysts have provided the bulk of carbodiimide polymerizations reported. Different polymerization conditions using different monomers and a variety of the aforementioned catalysts have shown improvements to specific polymerization systems. Collectively, there is still much to learn about the behavior of these polymerizations. As a result of the equilibrium process, monomer reversibly coordinates and inserts during propagation. For this reason many polymerization trials were performed neat (no solvent) using various liquid monomers. Le Chatelier’s principle suggests that increasing monomer concentration drives the equilibrium towards polymer formation. The use of solvent would decrease monomer concentrations and therefore polymer yields would suffer. Although this is true in theory, it is found that higher yields and better solubility are obtained from polymers that were created in the presence of a small amount of solvent such as chloroform. Neat polymerizations can be wrought with other inconsistencies; the most prominent being
the potential inability for monomer to act as a proper solvent for the catalyst. Pre-dispersing the catalyst in a small amount of solvent prior to polymerization can provide a better homogeneity of the polymer initiation process. Additionally, solvent must be used if the monomer is a solid. Other fluctuating experimental conditions such as the purity of the monomer, the polymerization temperature, and the monomer to catalyst ratio can collectively affect the polymer outcome as well. Many reports for the new catalysts have not taken into account these other variables that may play a large role on the properties of the resulting polymers. Conducting a series of experiments that systematically takes into account every one of these variables would be a very large task; however, it is important moving forward that one keeps awareness of these variables. As will be shown vide infra, unexpected results can occur from slight changes in polymerization conditions.

2.4 Polycarbodiimides

2.4.1 Introduction

The purpose of this section will be to take into account most of the relevant advancements and discoveries pertaining to polycarbodiimide chemistry since our research group began to focus on them. The name of these polymer systems has fluctuated from polyguanidines to polycarbodiimides throughout and arguments can be made for both cases since the resulting backbone of these polymers resembles that of a repeating guanidine unit. However, it is typical for polymer systems to adopt the name of their monomer precursors preceded by “poly”, such as polystyrene. For consistency, we will refer to all of these
polymer systems as polycarbodiimides throughout this document regardless of how they were previously reported. To keep organized, carbodiimide monomers will be given sequential numeric abbreviations such as Mono-1, 2, 3… etc. in the order they are discussed throughout this thesis. Additionally, polymers will be designated Poly-1, 2, 3… etc. and it is to be assumed throughout that Poly-X is derived from Mono-X.

Initial studies by Goodwin on the efficacy of titanium catalysts (Cat-1-3) on a variety of carbodiimide monomers revealed some initial generalizations that can be made about the plausibility of successful polymerization. Figure 2.9 shows some of the initially attempted monomers and their resulting success when polymerization was attempted using sterically free and highly active Cat-1 versus the more crowded and moderately active Cat-2. The most important trend lies with the connectivity of the α-carbons directly attached to the nitrogen on the carbodiimide center. Most carbodiimides containing a methyl pendant group (Mono-1-4) were found to polymerize successfully with both catalysts, the exception being Mono-11 which was unsuccessful due to the bulky tert-butyl substituent. It is therefore safe to assume that no carbodiimides containing a sterically hindered α-tertiary pendant group will polymerize. Predictions become a little grey when dealing with α-primary, α-secondary and aryl pendant groups. Generally, an α-secondary carbon can be polymerized if the other pendant group is a methyl group (Mono-2), however, when the methyl group is changed to an ethyl group (Mono-7), only the less bulky Cat-1 will work. Two α-secondary carbons, such as Mono-10, will not polymerize. Carbodiimides with two primary α-carbons generally polymerize rapidly (Mono-5,6) but when both groups contain β-branching (Mono-9),
Figure 2.9 – Initially attempted monomers revealed that steric crowding around the carbodiimide center plays a large role on the efficacy of successful polymerization.

polymerization ceases. Aryl groups (Mono-4,8) can be generally polymerized but are limited by the bulk of the catalyst and the other monomer pendant group. These general trends can be taken into consideration when designing new monomers for polymerization. Additionally, Cat-1 and 2 were found to display catalytic activity in a variety of solvents including chloroform, benzene, toluene, hexanes, tetrahydrofuran (THF), diethyl ether (DEE),
and pyridine although substantially slower polymerization was observed for pyridine due to strongly coordinating nature of the heterocyclic nitrogen lone pair.²

The polycarbodiimide structure contains a repeating amidine unit through which steric repulsions caused by the imine and amine nitrogen substituents prohibit the polymer backbone from adopting the preferred planar conjugated arrangement (Figure 2.10). Through molecular mechanics and modeling of these systems, the dihedral angle between repeat units is approximately 60°, however this is likely to fluctuate depending on the bulk of the pendant groups. For example, di-n-hexyl polycarbodiimide (Poly-6) is calculated to have a 55° dihedral angle while N-methyl-N’-((R)-1-phenylethyl) polycarbodiimide (Poly-2) is calculated to have a dihedral angle of 74°. Additionally, the helical pitch, or the distance between identical places on neighboring helical turns, can fluctuate with more bulky pendant groups but is generally calculated to be around 13.7 Å. It takes approximately six repeat units to make one complete helical turn, hence polycarbodiimides adopt a 6/1 helix. Another interesting feature of the polycarbodiimide backbone is its polarity. Due to the imine lone pairs along the backbone and their ability to form an all syn structure with bulky substituents, this polarity aligned in a vector that travels down the center of the helix can have an additive dipole of up to 1.7 debyes/repeat unit as calculated at the semi-empirical AM1 level.
Figure 2.10 – Molecular mechanics and modeling results of a simplistic polycarbodiimide backbone reveals a 6/1 helical sense with a helical pitch of 13.8 Å and a dihedral angle of approximately 60° between repeat units.

2.4.2 Polycarbodiimides as Dynamic Helical Polymers

To begin understanding the nature of the polycarbodiimide backbone, experiments involving induction of an excess helical sense were initiated. In 1998, Schlitzer reported an experiment of helical induction by polymerizing the chiral N-(R)-2,6-(dimethylheptyl)-N-(n-hexyl) carbodiimide (Mono-12) using cyclopentadienyl-dichloro-titanium(IV) isopropoxide catalyst (Cat-25) (Figure 2.11). The catalyst was found to polymerize Mono-12 into a kinetically controlled conformation (KCC) as evidenced by the polymer adopting no more optical rotation than that observed from the monomer. By annealing the polymer at temperatures of 75, 80, and 85 °C, a large amplification in optical rotation from
Figure 2.11 – The chiral Mono-12 is polymerized kinetically by Cat-25 resulting in a polymer with no excess helical sense and an optical rotation equivalent to that of the starting monomer.

\[ [\alpha]_{365}^{20} = +7.6^\circ \]

\[ [\alpha]_{365} = +7.5^\circ \text{ to } [\alpha]_{365} = -157.5^\circ \text{ in hexane (} c = 0.24 \text{ g/100mL) occurred which eventually plateaus off (Figure 2.12). This change in optical rotation can be explained by the fact that the initial KCC of the polymer was an equal mixture of left and right handed helical segments with a diastereomeric relationship due to the homochiral pendant group. Upon heating at higher temperatures, inversions of the backbone became possible and Poly-12 was able to adopt a thermodynamically controlled conformation (TCC) with a preferred excess helical-sense. The process was not reversible and the energy barrier to helical inversion was initially reported inaccurately as 6.4 kcal/mol\(^{26}\) but was later determined to be approximately 21.6 kcal/mol by Gonglu Tian. This polymer is an example of how polycarbodiimides can behave as dynamic helical polymers when the pendant groups are relatively free from steric crowding. Tian and Lu later performed a similar experiment using \( N\)-(R)-2,6-dimethylheptyl-\( N\)'-phenyl polycarbodiimide Poly-13 from Cat-15 and discovered that even greater changes are seen when using a chromophoric aromatic pendant group (Figure 2.13).\(^{20}\)
Figure 2.12 – Annealing of Poly-12 at 85, 80, 75 °C allows the polymer to adopt the thermodynamically preferred helical sense and results in a large increase in optical rotation. (Copyright 1998 American Chemical Society, reprinted with permission)

Interestingly, the initial polymer prior to annealing is already found to have a large optical rotation $[\alpha]_{435} = -209^\circ$ and during the annealing process the optical rotation permanently changes to a large value in the opposite direction $[\alpha]_{435} = +255^\circ$. This was also ascribed to be a transition from the KCC to TCC and the energy barrier to helical inversion was reported as 29.2 kcal/mol. Another unmentioned and interesting observation is that the final specific optical rotations after annealing of Poly-12 (-157.5°) and Poly-13 (+255°) are in opposite rotatory directions which means the thermodynamically preferred helical sense may be opposite for these polymers even though the chiral pendant group for both is the same.

Many experiments have been performed to determine polycarbodiimide cooperativity such as sergeants-soldiers, majority rules, and molecular chaperones (vide supra). Many of these experiments have lead to mixed but interesting results.
Figure 2.13 – Annealing Poly-13 results in a redirection in optical rotation by evolving from its KCC to its TCC at various temperatures in toluene (c = 0.2 g/100mL). (Copyright 2004 American Chemical Society, reprinted with permission)

Sergeant-Soldier experiments have been performed by Schlitzer, Lu, and Blackburn, each of which investigate the cooperativity of different chiral (sergeant) groups on achiral (soldier) groups along the polymer chain. Schlitzer’s Poly-12-co-6 set of polymers was found to increase almost linearly as the mol % of chiral Mono-12 was increased (Figure 2.14a). This behavior describes a lack of cooperativity in the system, however, it was deduced that these copolymers were blocky due to kinetically different monomers insertion rates caused by the difference in steric hindrance between Mono-12 and Mono-6. Therefore, all of the sergeants were grouped together and not effectively inducing chirality to the soldiers. Lu’s Poly-13-co-14 showed that copolymers with more chiral units display lower optical rotations after annealing (Figure 2.14b). Additionally, a higher mol % of chiral units required longer times to reach the TCC and the net change in optical rotation before and after annealing was less. This behavior is opposite of that shown for polyisocyanates and was
attributed to differences and variations of the inversion barriers and conformations between the two co-polymer units. Blackburn’s study using Poly-15-co-14 reached a maximum optical rotation when 30 mol % of the chiral unit was used. Using more or less chiral monomer resulted in a drop in the optical rotation observed after annealing. This study did show cooperativity when using a low ratio of chiral unit but the sudden drop of optical
rotation at higher concentrations is a unique observation that testifies to the complexity of conformational differences possible in polycarbodiimide systems.

Schlitzer also attempted a majority rules experiment by polymerizing various molar ratios of Mono-12(R) and Mono-12(S) with Cat-25 (Figure 2.15). After annealing of the various copolymer derivatives a non-linear increase in optical rotation was observed. A 60% enantiomeric excess (ee) of the Mono-12(R) resulted in a final optical rotation close to that observed for a homopolymer of Mono-12(R). Although cooperativity in this system is evident, it is not as profound as those observed for polyisocyanates (vide supra).

Another property associated with the repeating amidine backbone unit is the relative basicity of the nitrogens. Therefore one can expect the addition of acid to protonate the backbone of these polymers if the pendant groups are not too bulky and the counter anion can be electrostatically held in proximity of the protonated backbone. Taking advantage of this

Figure 2.15 – Majority rules experiment using various ratios of (R) vs. (S) Mono-12. A cooperativity is seen and using 60% enantiomeric excess of the (R) unit leads to an optical rotation close to that of a homopolymer from (R) units alone.
property, another experiment reported by Schlitzer was done on di-n-hexyl polycarbodiimide (Poly-6) which was polymerized into a racemic KCC using achiral Cat-25. Unlike Poly-12, this polymer has no configurationally chiral pendant group and therefore a TCC will not promote the formation of an excess helical sense. Instead, a molecular chaperone experiment was performed to induce a diastereomeric excess helical sense by protonation of the backbone with chiral (S)-camphorsulfonic acid ((S)-CSA) (Figure 2.16a). As the molar equivalents of (S)-CSA was increased, a non-linear increase in specific optical rotation was observed for Poly-6 (Figure 2.16b). (R)-CSA caused mirror image behavior and ORD to increase in the opposite direction. Mild heating and changing the polarity of solvent was also found to increase the effectiveness of this induction. Although protonation with a chiral acid can induce an excess helical sense, the cooperativity of polycarbodiimides requires a 4:1 (mol. repeat unit : mol. acid) ratio before significant increases in specific optical rotation is observed. It is speculated that a large expansion of the helical pitch of the polycarbodiimide backbone occurs when protonated due to electrostatic repulsions of the positively charged nitrogens and this may account for the general lack of cooperativity.

From these studies we can gather a few conclusions about polycarbodiimides; (1) they can behave as dynamic helical polymers when using relatively non-bulky pendant groups, (2) evidence of cooperativity is seen in these systems with sergeant-soldier, majority rules and molecular chaperones experiments but due to differences in polymerization kinetics
conformational restrictions, and regioregularity between co-polymer units these systems are currently unable to exhibit high cooperativity, (3) configurationally chiral stereocenters in the β-position are of adequate proximity to influence the helical sense of the backbone, (4) arene pendant groups can often lead to enhanced optical rotations, and (5) the basicity of the polymer backbone allows sufficient protonation from organic acids. These experiments are worth revisiting once better control and understanding of the polymer macrostructure is obtained.

2.4.3 Polycarbodiimides as Static Helical Polymers

The use of chiral pendant groups to obtain an excess helical sense can be costly and difficult to synthesize. New focus was placed on creating polycarbodiimides through helix-
sense-selective polymerizations using chiral catalysts with achiral monomers from cheaper and more readily available precursors. As previously stated in Section 2.3, chiral BINOL titanium(IV) catalysts allow achiral monomers to be polymerized into a preferred excess helical sense. The goal is to synthesize monomers that will incorporate sufficient steric hindrance around the backbone and yield robust helical polymers with an appreciably high energy barrier to racemization. An initial problem becomes apparent when observing Goodwin’s initial polymerizations that show increasing the bulk of the pendant group too much will result no polymerization (Mono-9-11). However, when compared to the aliphatic pendant group containing Poly-12 (Ea = 21.6 kcal/mol), a higher energy barrier was observed for Poly-13 (Ea = 29.2 kcal/mol) which contained a phenyl pendant group. Building upon this observation, the idea of adding restrictive substituents to the phenyl group led to a new family of polycarbodiimides that were designed with the intention of creating static helical polycarbodiimides.

Lim and Kim synthesized a series of polymers using Mono-6,16-19 (Figure 2.17) with Cat-3 and observed their 13C spin-lattice relaxation times in the rotating frame as a function of temperature using solid state 13C cross-polarized / magic angle spinning (CP/MAS) NMR spectroscopy.27,28 From these experiments they were able to calculate the relative rigidity of the backbone by determining the activation energies of the imine carbons for each polymer (Table 2.1). When comparing the results to the base di-n-hexyl Poly-6 (19.76 kcal/mol), the di-aryl pendant polymers Poly-16 and Poly-18 had a higher energy
Figure 2.17 – Achiral carbodiimide monomers designed to induce a large racemization barrier on resulting polymers.

barrier (23.20 and 23.12 kcal/mol). Interestingly, the di-aryl polymer Poly-17 was calculated to have a lower energy barrier of 18.63 kcal/mol. The di-benzyl polymer derivative Poly-19 had the lowest energy barrier of them all (12.64 kcal/mol). Since the imine carbon along the polymer backbone has no directly attached protons, their relaxation times can be very slow and reported to be significantly broadened at higher temperatures. Coupling this with the fact that these carbons only comprise half of the backbone composition (the other half being the amine nitrogen), these results may not be a direct representation of the full dynamics involved in the racemization process.
Table 2.1 – Backbone activation energy barriers of imine carbons of several polycarbodiimides obtained by $^{13}$C CP/MAS NMR spectroscopy

<table>
<thead>
<tr>
<th>Polymer</th>
<th>R1</th>
<th>R2</th>
<th>$E_a$ kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-6</td>
<td>n-hexyl</td>
<td>n-hexyl</td>
<td>19.76</td>
</tr>
<tr>
<td>Poly-16</td>
<td>4-butylphenyl</td>
<td>4-butylphenyl</td>
<td>23.20</td>
</tr>
<tr>
<td>Poly-17</td>
<td>4-butoxy carbonylphenyl</td>
<td>4-butoxy carbonylphenyl</td>
<td>18.63</td>
</tr>
<tr>
<td>Poly-18</td>
<td>3-methylphenyl</td>
<td>3-methylphenyl</td>
<td>23.12</td>
</tr>
<tr>
<td>Poly-19</td>
<td>benzyl</td>
<td>benzyl</td>
<td>12.64</td>
</tr>
</tbody>
</table>

A more inclusive way to determine the energy barrier to helix racemization ($E_r$) is by annealing the polymer and observing the loss of optical rotation through the use of polarimetry. This system was modeled after the equation representing the two helical senses in a reverse equilibrium, Eq. (1), where $[M]_0$ represents the initial concentration of the excess helical sense, $[M]_\text{eq}$ is its concentration at equilibrium, $[M]$ is the concentration being observed as a function of time “$t$”, and $k_{\text{obs}}$ is the rate constant. Since we cannot directly measure the concentration of excess helical sense, we can replace it with the observed specific optical rotation, $[\alpha]$, which yields Eq (2).

$$\ln\left(\frac{[[M]_0 - [M]_\text{eq}]}{([M] - [M]_\text{eq})}\right) = k_{\text{obs}} t$$

$$\ln\left(\frac{[[\alpha]_0 - [\alpha]_\text{eq}]}{([\alpha] - [\alpha]_\text{eq})}\right) = k_{\text{obs}} t$$
As discussed, it is thermodynamically favorable for the helix to completely racemize when polymerized from achiral monomers, we can assume the specific optical rotation at equilibrium, $[\alpha]_{eq}$, to be zero since all the helical segments rotating in the positive direction are being cancelled by an equal amount being rotated in the negative direction. Hence, Eq. (2) can be further distilled down to Eq. (3). A linear plot using this equation will yield $k_{obs}$ as the slope. By performing these experiments at different temperatures we can obtain multiple rate constants and use them in the Arrhenius equation (4) to determine the energy barrier to racemization ($E_r$) where $T$ is the temperature in Kelvin, $R$ is the molar constant (8.31 J K$^{-1}$ mol$^{-1}$ or 1.99 cal K$^{-1}$ mol$^{-1}$). To obtain $E_r$ in kcal/mol it is often typical that the x-axis be plotted as $1 / (T \times 1000)$.

$$\ln\left(\frac{[\alpha]_0}{[\alpha]}\right) = k_{obs}t$$  \hspace{1cm} (3)$$

$$\ln(k_{obs}) = \left(\frac{E_r}{R}\right)\frac{1}{T} + \ln(A)$$  \hspace{1cm} (4)$$

By using this method, Lu determined the $E_r$ for **Poly-6** polymerized from **Cat-5** to be 22.8 kcal/mol, which is 3 kcal/mol higher than that reported by Lim and Kim using $^{13}$C CP/MAS NMR.** Poly-14** was also synthesized using **Cat-5** and its $E_r$ determined as 25.6 kcal/mol. This result reconfirms that aryl pendant groups result in improved helical stability when compared to primary aliphatic groups.
Further steric hindrance was induced by incorporating alkyl substituents on the ortho-positions of the phenyl pendant group. \( N\)-methyl-\( N'\)-(2-methyl-6-isopropylphenyl) polycarbodiimide (Poly-22) was the most successful of these derivatives due to the polymerizability of the monomer (resulting from the non-bulky methyl substituent) and the solubility of the polymer. Poly-22 exhibited very large specific optical rotations ([\( \alpha \)]\textsubscript{435} = -867° in toluene, -1034° in CHCl\(_3\)) and when annealed the specific optical rotation did not approach zero (Figure 2.18).\textsuperscript{20} Initially, the specific optical rotation began to decrease but the value plateaus off at -360°. The \( E_r \) for the initial process was calculated to be 23 kcal/mol but the more interesting observation is the permanent asymmetry that is exhibited by the polymer. It was concluded that a higher level of non-racemizable asymmetry is built into the polymer system as a result of the bulky substituted phenyl pendant groups. Their close packing along the polymer chain prohibits the ability to undergo concerted rotations which removes a level of cooperativity required for full racemization. It is of note that the regioregularity and molecular weight of Poly-22 were never determined and could reveal some very interesting insight to this unique behavior.

As will be discussed in Chapter 4, the determination and understanding of regioregularity has been an ongoing issue for unlocking some of the unusual behavior of polycarbodiimides. Another prime example was shown during continuing attempts to create robust helical polymers. Keeping focus placed on using asymmetric aryl pendant groups, a series of polymers incorporating a 1-anthryl pendant group were polymerized under
Figure 2.18 – Annealing of Poly-22 in chloroform (c = 0.33 g/100mL) at 50 °C results in initial racemization but not complete racemization. The optical rotation values plateau at -360° showing a permanent asymmetry related to this polymer system. (Copyright 2004 American Chemical Society, reprinted with permission)

a variety of conditions. Figure 2.19 shows many of the variables that can affect the outcome of a polycarbodiimide including; the solvent used, the temperature of polymerization, the monomer to catalyst ratio, and the yield of the resulting polymer. Since gel permeation chromatography (GPC) often leads to varying and inconclusive results on the true molecular weight of these polymer systems, a good way to generalize the anticipated molecular weight is by the monomer to catalyst ratio combined with the resulting polymer yield. Since these polymerization systems have been shown to be living, a 100% polymer yield theoretically implies a low polydispersity of polymers with a number of repeat units equal to the monomer to catalyst ratio. Therefore, a low polymer yield could imply that many of the monomer units never propagated and the molecular weight of the polymers is much less than originally
anticipated. In Figure 2.19 most of the polymerization variables were kept similar and this allows different polymer properties to be attributed to the behavior of the catalyst and monomer. The most prominent outcome from these polymers is the resulting regioregularity of the Poly-23(R) and Poly-23(S) when compared to Poly-21 which is determined by infrared spectroscopy (IR) (vide infra). Poly-23(R) and Poly-23(S) were found to have a single C=N imine stretch absorption at 1622 cm\(^{-1}\) and Poly-21 was observed to have two imine stretch absorptions at 1641 and 1622 cm\(^{-1}\), which is indicative of regioirregularity.
These differences were reportedly caused by the nature of the catalysts used and the likely aggregation of the BINOL containing Cat-4. Since Mono-21 is achiral, using the faster and less aggregated achiral Cat-15 catalyst would not result in an excess helical sense but could be playing a role in polymerizing the kinetically preferred regioisomer. The incorporation of a chiral stereocenter in the γ-position of Poly-23(R) and Poly-23(S) may allow induction of excess helical sense through annealing. Using a chiral stereocenter in the β-position, as done for Poly-12, resulted in no polymerization likely due to confliction between the bulkier anthracene unit and the spatial constriction of having the β-stereocenter within certain proximity of the carbodiimide moiety. Instead of having to anneal the KCC of Poly-23(R) and Poly-23(S) into an excess helical sense (TCC), it was discovered that the KCC and TCC are the same for these polymer systems. In other words, the virgin polymers exhibited a large specific optical rotation prior to annealing and it remained stable even at higher temperatures (Figure 2.20). Therefore these polymers adopt the thermally preferred helical diastereomer as it is polymerized even though the catalyst used is achiral. Poly-21 requires a chiral catalyst to obtain an excess helical sense and racemization through annealing revealed the \( E_r \) to be 36 kcal/mol, the highest \( E_r \) reported for a polycarbodiimide from an achiral monomer to date. Although the best helical thermal stability is achieved by using chiral pendant groups, Poly-22 and Poly-21 reveal that very robust or static helical polycarbodiimides from achiral monomers can be obtained.
Figure 2.20 – Annealing Poly-23(R) and Poly-23(S) at (a) THF, 50°C, (b) CHCl₃, 50°C, and (c) toluene, 80°C results in no significant change in optical rotation suggesting their KCC and TCC are the same.

2.4.4 Properties of Polycarbodiimides

Polycarbodiimides have a remarkable advantage over polyisocyanates and polyisocyanides due to the incorporation of two pendant groups per repeat unit. As discussed, these pendant groups do not have to be the same and this allows our research to employ a number of synthetic strategies when deciding on the pendant groups used. For example, one pendant group can be chosen to perform a function while the other pendant group can be used solely to improve the desired solubility of the polymer. Due to this synthetic freedom, a number of polycarbodiimides have been synthesized to fully utilize this advantage and obtain desired properties of the polymer system.

One of the interests in creating rigid stable helical polycarbodiimides is the application that rigid-rod like polymers have in the field of liquid crystalline (LC) materials. Chiral helices that behave as rigid rods can form cholesteric liquid crystals capable of
exhibiting brilliant colors. Kim first synthesized a variety of polycarbodiimides to better understand their LC behavior. Initial investigations were performed on racemic, homochiral and achiral monomers polymerized by Cat-3 (Figure 2.21). A lyotropic LC of Poly-6 was found to exhibit a layered, smectic mesophase at critical concentration, 20% w/w in toluene (Figure 2.22a). The smectic order of these LC systems is greater than the nematic mesophase shown for poly-hexylisocyanate and was attributed to the increased density of identical hexyl pendant groups which provide a uniform corona of aliphatic spacing between polymer chains. When disrupting the uniformity of the side chains, such as Poly-2(rac), the lyotropic LC (20% w/w in toluene) retains an orientation order but loses the positional order, resulting in a nematic LC phase. Due to the homochirality of the side chains of Poly-2(R), this helix was capable of adopting an excess helical sense and exhibited a cholesteric mesophase from a 12.5% w/w solution in chloroform (Figure 2.22b). Since Poly-2(R) requires less concentration of polymer to obtain the LC phase, this is an indication that this polymer is stiffer than its racemic counterpart Poly-2(rac). The addition of mesogenic biphenyl (Poly-26) and azo-biphenyl (Poly-27) side chains could allow the observation of smectic ordering from polycarbodiimides comprised of dissimilarly sized pendant groups. Poly-26 was found, through X-ray diffractometry, to be a very ordered crystal structure in the solid state with interchain distances less than those observed for Poly-6. This indicates that the mesogenic side chain actually promotes interpenetration of the coronas surrounding the
polymer backbones. As a consequence, LC properties of **Poly-26** were unable to be performed due to poor solubility. **Poly-27** has significantly less order in the solid state and the azo-biphenyl mesogen was soluble and capable of forming a lyotropic LC at 21.4% w/w in 1,1,2,2-tetrachloroethane at 65°C. It was discovered that the LC of **Poly-27** still retained a nematic structure, concluding that the backbone dominates the phase behavior over the mesogenic side chains (Figure 2.22c).\(^{31}\) The larger dodecyl pendant group containing polymers, **Poly-24** and **Poly-25** were synthesized to investigate any thermotropic LC properties that may be associated with these systems. Polycarbodiimides do not have a high
thermal stability and will decompose back into carbodiimides at temperatures upwards of 150 °C. Therefore the idea of surrounding the polycarbodiimide chains in a paraffin-like sea of pendant groups, which show melting around 33 °C, may allow the observation of thermotropic LCs at relatively low temperatures. Differential scanning calorimetry (DSC) of Poly-24 reveals a second endothermic transition around 102 °C which was found to be the formation of a thermotropic mesophase formation (Figure 2.23). Poly-25, which contains a mesogenic side chain, was found to form a smectic mesophase at 130 °C. Therefore, oppositely to a lyotropic LC, thermotropic ordering is governed more by the mesogenic side chains over the backbone. Zhang was able to synthesize remarkably colorful birefringent cholesteric polycarbodiimide gels by doping Poly-2(R) with a small amount of dicarbodiimide crosslinker (Mono-28) (Figure 2.24). Since this polymer contains no chromophores capable of absorbing in the visible spectrum, the colors are produced solely by the Bragg reflection of light from the pitch of the frozen cholesteric domains. Solubility is a constant synthetic challenge when designing polycarbodiimides. The incorporation of long aliphatic chains onto carbodiimides often relieves some of the interchain packing that would otherwise render a polycarbodiimide insoluble in most organic solvents. A majority of the polycarbodiimides discussed up to this point, unless otherwise noted, have exhibited solubility in organic solvents ranging from mid-polarity (THF, CHCl₃) to low-polarity (toluene, cyclohexane).
Figure 2.22 – Optical polarizing microscope images of LC (a) smectic Poly-6, 20% w/w in toluene at 45 °C (200x), (b) cholesteric Poly-2(R), 12% w/w in CHCl₃ at r.t. (500x), and nematic Poly-27, 21.4% w/w in 1,1,2,2-tetrachloroethane at 65 °C (200x).
Figure 2.23 – Differential scanning calorimetry (DSC) thermogram of Poly-24.

Figure 2.24 – Copolymerizing a dicarbodiimide crosslinker with chiral Mono-2(R) results in a “locked-in” cholesteric gel.
Very few polycarbodiimides have been synthesized and found to be soluble in higher polarity solvent such as methanol and water. Li was capable of synthesizing a small group of polycarbodiimides which exhibited solubility in such solvents (Figure 2.25). Since biological systems are almost always aqueous, the fruition of hydrophilic polycarbodiimides is important, allowing potential future research pathways, such as biomimetic applications, to be plausible.

![Figure 2.25](image)

**Figure 2.25** – Polycarbodiimides containing high polarity pendant groups enabling water solubility.

Although many properties have been discussed for polycarbodiimide systems thus far, the remainder of this text involves a unique property which was accidentally discovered during the challenge of creating static helical polycarbodiimides. These “switching” helical polycarbodiimides are very intriguing and behave unlike anything ever reported for synthetic helical polymer systems. In addition to this switching phenomenon, further emphasis will be placed on implementing regioregularity on polycarbodiimide systems and discovering new ways to analytically determine regioregularity.
2.5 References


Chapter 3: Switching Helical Polycarbodiimides

3.1 Discovery

The previously discussed success in creating polycarbodiimides containing a high energy barrier to helical racemization resulted in a particular polymer (Poly-21) that displayed a very high energy barrier of 36 kcal/mol. During the process of characterizing this polymer some very unusual and interesting behavior was observed. By polymerizing Mono-21 with the dibromo-BINOL-Ti(IV)-di-t-butoxide catalyst, Cat-7, a highly regioregular Poly-21 was obtained (Figure 3.1). It was discovered that optical rotations for this polymer changed dramatically and quickly when dissolved in toluene and heated between 30 and 45 °C (Figure 3.2). The total change in specific optical rotation is approximately 500° and, more interestingly, changes in the direction of rotation from positive to negative occurred as temperature is increased. After repeated heating and cooling, this process was observed to be reversible and revealed that unexpected conformational changes were occurring with this polycarbodiimide system.

Figure 3.1 – Polymerization of Mono-21 using Cat-7 was found to result in a highly regioregular Poly-21.
The development of synthetic helical polymers capable of exhibiting conformational changes through the influence of external forces, such as solvent, pH, and temperature, has been a growing area of interest. Of this class of polymers, some have been reported to exhibit large changes and reversals in direction of optical rotation and circular dichroism (CD) Cotton effects. To date, most of these conformational changes reported by synthetic helical polymers such as polyisocyanates, poly(phenylacetylene)s, and polysilylenes have been attributed to helix-helix transitions of their relatively flexible backbone through the influence of chiral pendant groups and/or chiral guest molecules. Potential applications of such systems include; optical sensors, optical displays, chemo-sensors, biomimetic materials, data storage devices, and chiral separations, to name a few. In light of this, it will be shown that Poly-21 is unique in the sense that it is polymerized with an excess helical sense using achiral monomers and similar optical rotation and CD changes are observed without the influence of chiral perturbations and without the inversion of the helical backbone.
3.2 Optical Rotation and Circular Dichroism

Dr. Hong-Zhi Tang provided insight into the mechanism of these low energy conformational changes by performing a series of experiments using optical rotation and circular dichroism (CD). It is important to understand the differences between these two analytical techniques and the information they provide when analyzing macromolecular systems.

Optical rotation or circular birefringence uses plane polarized light at a specific wavelength and is the measurement of the concerted physical rotation of this plane of light by a chiral analyte. This rotation results from the left and right circularly polarized components of the plane polarized light. When passing through a chiral medium with an enantiomeric excess, one circularly polarized direction of the light travels at a different speed than the other. This velocity difference causes an overall rotation of the plane of light (Figure 3.3). The optical rotation ($\alpha$) in degrees is defined as:

$$\alpha = \frac{\pi d}{\lambda} \left( n_L - n_D \right)$$  \hspace{1cm} (3.1)

where $d$ is the distance which the light travels through the analyte, $\lambda$ is the wavelength, and $n$ is the refractive index of circularly left ($n_L$) and right ($n_D$) polarized light.\(^{14}\) Since this is a physical rotation, the wavelength chosen should not be absorbed by the analyte or the solvent within which the analyte is dissolved. Optical rotation is typically normalized and reported as specific optical rotation ($[\alpha]$) defined by:
where \( c \) is the concentration of the analyte in grams per milliliter and \( l \) is the sample path length in decimeters. It is necessary to report the temperature \( (T) \) in Celsius and wavelength \( (\lambda) \) in nanometers as well as the solvent used since these variables can play a large role on the optical rotation observed. Dilute solutions are often used for optical rotation experiments to ensure good separation of the chiral species and eliminate false readings that may result from intermolecular aggregation. Optical rotation is typically measured using a polarimeter, an instrument which hosts the analyte solution on a stage and measures the degree of rotation of plane polarized light which is shined through it.

**Figure 3.3** – Optical rotation viewed as the difference between left and right circularly polarized light before and after movement through a chiral analyte. The degree of rotation from the initial plane axis \((z)\) is the optical rotation \((\alpha)\).15

Circular dichroism has become an increasingly popular way to determine macrostructural information of chiral polymers. CD is the measurement of unequal absorption of left and right circularly polarized light and is usually measured over a range of wavelengths.14 There are many terms used in the expression of these analyses therefore I
Electronic circular dichroism (ECD) couples the utility of a polarimeter with a UV-Vis spectrometer. Circularly polarized UV-Vis radiation is swept through a sample cell containing a chiral analyte that has chromophores capable of absorbing this radiation. As a result, the chromophoric groups positioned on a chiral macrostructure preferentially absorb one direction of circularly polarized light over the other. This preferential absorption distorts the circularly polarized light into elliptically polarized light (Figure 3.4). The angle of ellipticity (θ) is the arc-tangent of the minor to major axis of the ellipse and is defined by:

$$\theta = \frac{\pi}{\lambda} (A_L - A_R)$$

(3.3)

where $A_L$ and $A_R$ are the absorption coefficients of the left and right polarized light by the analyte. The difference between these coefficients ($\Delta A$) is more commonly referred to as the
circular dichroism. Ellipticity ($\theta$) is generally a small value and therefore is typically seen expressed as millidegrees or (mdeg). The molar ellipticity ([\theta]) is defined by:

$$[\theta]^T_{\lambda} = \frac{100\theta}{cl}$$  \hspace{1cm} (3.4)

where $c$ is the concentration in moles per liter (otherwise known as molarity ($M$)) and $l$ is the path length in centimeters. The molar ellipticity ([\theta]) is hence reported in the units ($M^{-1}m^{-1}$). For polymers, the molecular weight of the repeat unit is used to calculate $M$. As mentioned, units reported for CD experiments can sometimes be confusing and are seen reported as molar circular dichroism ($\Delta\varepsilon$), which is the difference between the extinction coefficients in the left $\varepsilon_L$ and right $\varepsilon_R$ direction. The molar ellipticity and molar circular dichroism can be easily interconverted by

$$[\theta]^T_{\lambda} = 3300(\Delta\varepsilon)$$ \hspace{1cm} (3.5)

therefore they have the same units ($M^{-1}m^{-1}$). Circular dichroism observed from a chiral analyte over a range of wavelengths results in peaks known as Cotton effects and is the most common data presented when performing such experiments.

Vibrational circular dichroism (VCD) combines the utility of an infrared (IR) spectrometer with a polarimeter. This instrument performs on the same CD theory discussed above but instead of absorption through electronic transitions (ECD) this analysis measures the differential absorption of left and right circularly polarized infrared or near-infrared radiation through bond vibrational modes.\textsuperscript{17} This is a powerful technique and can often be
combined with molecular modeling programs and density functional theory calculations to determine chiral structure information of synthetic and biological macromolecules.

3.3 Early Investigations of the Switching Phenomenon

When observing the switching phenomenon of Poly-21 in toluene over the respective temperature range using ECD, large changes in Cotton effects were observed (Figure 3.5). In addition to reversal of ellipticity from a positive to a negative direction, there is also a change in the shape of the Cotton effects. Although a large change in optical rotation and ECD Cotton effects was observed for Poly-21 in toluene, this was the only solvent tested that was found to display this unique switching phenomenon. As shown in Figure 3.6, dissolving the polymer in chloroform (CHCl₃) and tetrahydrofuran (THF) revealed a constant negative ECD Cotton effect between 25 and 50 °C. Figure 3.6 reveals another way of reporting ECD data. The Kuhn’s Dissymmetry Ratio (gabs) is defined as the molar circular dichroism (Δε) divided by the molar extinction coefficient (ε) which is obtained from UV-Vis spectroscopy using the Beer-Lambert law:

\[
A = \varepsilon cl
\]

(3.6)

where A is absorbance of a sample of path length l (in cm) and concentration c (in mol/L). The units for ε are typically \( M^{-1}cm^{-1} \) and care should be taken to convert Δε to the same units before calculating gabs. It was decided that the more polar solvents, CHCl₃ and THF, caused Poly-21 to greatly favor the conformation exhibited at higher temperatures in toluene. Interestingly, THF could be doped into a toluene/Poly-21 solution and the switching could be
Figure 3.5 – Variable temperature ECD (top) and UV-Vis (bottom) of Poly-21 in toluene (c = 2.1 x 10^{-4} M, l = 10 mm) over repeated heating and cooling cycles. (Copyright 2005 American Chemical Society, reprinted with permission)\(^1\)

Figure 3.6 – (a) Variable temperature gabs (top) and UV-Vis (bottom) of Poly-21 in CHCl\(_3\) (c = 2.1 x 10^{-4} M, l = 10 mm). (b) Variable temperature gabs of Poly-21 in THF (c = 2.1 x 10^{-4} M, l = 10 mm). (Copyright 2005 American Chemical Society, reprinted with permission)\(^1\)
observed at room temperature (Figure 3.7). Therefore, not only is this switching thermo-controlable but also solvo-controlable as well.

![Graph](image)

**Figure 3.7** – $g_{abs}$ values at 385 nm for Poly-21 when dissolved in various mixtures of toluene/THF. (Copyright 2005 American Chemical Society, reprinted with permission)

Three possible mechanisms to explain the conformational changes observed with Poly-21 were investigated (Figure 3.8). In order to better understand what is happening, it is important to be able to eliminate some of these mechanisms as contributors to these changes. Rotations of main chain bonds ($\phi$) are directly involved in helical racemization and are considered to be the highest in energy of the three mechanisms. Although it is likely that main chain rotations do not contribute to full racemization of the polymer alone, when Poly-21 was annealed in toluene at 80 °C, full racemization required over 100 hours (Figure 3.9). The calculated mid-point temperature of this reversible switching process in toluene was determined to be 38.5 °C making it considerably lower in energy than the racemization process. This implies that helix inversions ($\phi$) are likely not involved in the
Figure 3.8 – Molecular motions of Poly-21 capable of causing conformational changes and effecting optical rotation. (Copyright 2005 Wiley InterScience, reprinted with permission)

Figure 3.9 – Annealing of Poly-21 in toluene at 80 °C requires more than 100 hours for full racemization. (Copyright 2005 American Chemical Society, reprinted with permission)

switching. Furthermore, due to the absence of diastereomeric helices, helical inversions would be a thermodynamically and entropically favorable process and would not exhibit complete reversibility like this switching process does. For further experimental evidence to exclude helical inversions, collaboration with Polavarapu et al allowed analysis of these two different conformations using VCD spectroscopy. By focusing on the imine stretch infrared absorption at 1641 cm\(^{-1}\) it would be expected that visual changes in the imine VCD
would be seen if backbone inversions were occurring. To visualize both switching
conformations, VCD was performed in toluene at room temperature (where ECD cotton
effects were positive) and CHCl₃ at room temperature (where ECD cotton effects were
negative). No difference in the imine VCD was observed between these two samples, only a
slight variation in intensity of the bisignate couplet peak at 1641 cm⁻¹ (Figure 3.10). This
experiment is conclusive evidence that backbone helical inversions are not occurring.
Comparison of this VCD data to a calculated VCD spectrum by density functional theory
using B3 LYP functional and 6-31G(d) basis sets reveals **Poly-21** to have a P-helical sense.

![Figure 3.10](image)

*Figure 3.10* – (a) The experimental vibrational absorbance. (b) VCD of **Poly-21** in CHCl₃ at
25 °C (c = 10.0 mg/mL, l = 300 µm). (c) VCD of **Poly-21** in toluene at 25 °C (c = 20.1
mg/mL, l = 200 µm). (d) The optimized P helix model of **Poly-21** and its VCD spectrum
calculated by density functional theory using B3 LYP functional and 6-31G(d) basis sets.
(Copyright 2005 Wiley InterScience, reprinted with permission)¹⁸
Imine inversions ($\omega$) are a little more complicated to rule out. The energy barrier to imine inversion in small molecules has been determined to be approximately 20-26 kcal/mol, which is equivalent to 50-180 °C. Once again, these temperatures are above the thermal switching temperature of 38.5 °C and well above the solvent induced switching performed at room temperature by doping with THF. Of the three mechanisms, the one lowest in energy is the $N$-anthracene bond rotations ($\theta$). Due to the asymmetry and size of the anthracene groups, free rotation of the $N$-anthracene bond is constricted. When visualizing rotation around this bond, two relative conformations of the anthracene units are seen (Figure 3.11). In one position, the anthracene groups are pulled in close to the helical backbone and in the other they are splayed outward away from the helical director. From computational modeling it was determined that there is a difference in energy associated with these two conformations that evolves from the dipole moments of the anthracene units and their alignment with or against the inherent dipole of the polycarbodiimide backbone. The difference in dipole moment between these states is 0.8 debyes. This could explain why these transitions require such low energy and why polar solvents such as CHCl$_3$ and THF are shown to exhibit no switching. The polar solvents stabilize the more polar, higher energy conformation. It was therefore concluded that this polymer system behaves as a low energy solvo- and thermocontrollable nano-shutter and exhibits synchronous rearrangement of the anthracene units around the helical backbone scaffold. This discovery could have great application in the advancements of optical display, sensory, and storage technologies.
Before my research can build upon and improve these findings, it is important to point out a few summaries about Poly-21. To better organize these points, Table 3.1 shows a collection of characterization results and polymerization parameters from polymers similar to Poly-21 that have been previously reported in publications by our group. Poly-23(R) and Poly-23(S) were included in this table because they also contain an anthracene pendant group but neither showed any switching behavior in toluene. This may be attributed to the (R/S)-3,7-dimethyoctyl pendant group which contains a bulky stereocenter close enough to the polymer backbone to possibly interfere with anthracene realignments. It is noteworthy that both of these polymers were reported as highly regioregular with a single imine IR absorption at 1620 cm\(^{-1}\) meaning their dominant regioisomer is opposite of that reported for the switching Poly-21 (1642 cm\(^{-1}\)) polymerized from Cat-7. According to initial reports of
Table 3.1 – Polymerization parameters and polymer properties for previously reported anthracene pendant group containing polycarbodiimides.

<table>
<thead>
<tr>
<th>Polymer ID</th>
<th>Catalyst used</th>
<th>Ref</th>
<th>Polym. solvent *</th>
<th>IR – Imine cm(^{-1})</th>
<th>Mono: Cat Ratio</th>
<th>Yield %</th>
<th>(M_w) (PDI)</th>
<th>([\alpha]_D) in tol. (° C)</th>
<th>Switches in tol.?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-21</td>
<td>Cat-4</td>
<td>1,18</td>
<td>CHCl(_3)</td>
<td>1641, 1620</td>
<td>50:1</td>
<td>77</td>
<td>234K‡ (19.3)</td>
<td>+130° (20)</td>
<td>No†</td>
</tr>
<tr>
<td>Poly-21</td>
<td>Cat-5</td>
<td>18</td>
<td>CHCl(_3)</td>
<td>1641, 1620</td>
<td>96:1</td>
<td>80</td>
<td>NR</td>
<td>-51° (20)</td>
<td>Yes†</td>
</tr>
<tr>
<td>Poly-21</td>
<td>Cat-7</td>
<td>1,16</td>
<td>Tol.</td>
<td>1642</td>
<td>NR**</td>
<td>NR</td>
<td>16K‡ (2.7)</td>
<td>+300° (31)</td>
<td>Yes</td>
</tr>
<tr>
<td>Poly-23(R)</td>
<td>Cat-15</td>
<td>18</td>
<td>CHCl(_3)</td>
<td>1620</td>
<td>59:1</td>
<td>60</td>
<td>NR</td>
<td>+791° (25)</td>
<td>No</td>
</tr>
<tr>
<td>Poly-23(S)</td>
<td>Cat-15</td>
<td>18</td>
<td>CHCl(_3)</td>
<td>1620</td>
<td>58:1</td>
<td>80</td>
<td>NR</td>
<td>-778° (25)</td>
<td>No</td>
</tr>
</tbody>
</table>

* All polymerizations were performed at room temperature and worked up in methanol
** NR = Not Reported
† Shown on ECD spectra in supporting information document of ref. 18
‡ GPC Universal calibration using PS standards in CHCl\(_3\) and RI detector only

this switching process,\(^1\) it would seem that a highly regioregular polymer was necessary in order for this system to display the switching phenomenon; but this is not the case. In the supplemental information of a prior publication,\(^20\) Poly-21 was synthesized using the aggregated (S)-BINOL Cat-5 and shown to have regioirregularity by multiple imine stretches in its IR spectrum. A variable temperature ECD analysis of this polymer between 10 and 80 °C shows a reversal in Cotton effect as well (Figure 3.12(b)). Although they weren’t looking for it at the time, this polymer did switch. This may indicate that regioregularity alone may not be responsible for the switching process. The question then becomes; why didn’t Poly-21 polymerized from the (R)-BINOL Cat-4 show any switching behavior (Figure 3.12(a))? Speculations could be made involving molecular weight (\(M_w\))
since the monomer to catalyst ratio used was less and also a lack of excess helical sense since the specific optical rotation in toluene is considerably low. It is obvious that more investigations are needed.

3.4 Initial Investigations of New Switching Polycarbodiimides

Based on the conclusions made about the mechanism of switching, new potentially switching polycarbodiimides will require arene pendant groups with enough restriction to prevent free-rotation of $N$-aryl bonds and sufficient dipole moment to create a difference in energy states between conformations. With this in mind, our initial design of polycarbodiimides that may meet these criteria involved phenyl pendant groups with various substituents on the meta-position (Figure 3.13). The 3-bromo-, 3-cyano-, and 3-nitroaniline precursors are inexpensive, readily available, and may be capable of providing all of the
Figure 3.13 – Initial newly synthesized polycarbodiimides for switching behavior investigations.

criteria necessary as well as diversify the polarity of the arene groups. Our initial set of polymers (Poly 33-35) contained a hexyl chain as the other pendant group. Syntheses of Mono-33-35 were performed by combining the aniline precursors with n-hexyl isocyanate then dehydration of the resulting urea using bromine, triphenylphosphine, and TEA (Refer to Figure 2.3). Neat polymerizations of Mono-33-35 using Cat-4 yielded solid polymer after one day. Work up of these polymers revealed major solubility issues preventing full characterization. Solvents attempted include: CHCl₃, pyridine, benzene, N-methylpyrrolidinone (NMP), dimethylsulfoxide (DMSO), nitromethane, THF, dichloromethane (DCM), chlorobenzene, and dimethylformamide (DMF). Furthermore,
none of these polymers were soluble in toluene which is needed for switching investigations. Subsequently, the decision was made to increase the aliphatic character of the polymers by increasing the alkyl pendant group from n-hexyl to n-octadecyl (Poly-36-38). The solubility issues were overcome and each of these polymers exhibited solubility in CHCl₃ and toluene. Variable temperature polarimetry experiments on Poly-36 and Poly-38 revealed no significant changes in specific optical rotations in toluene or chloroform (Figure 3.14). The conclusion was made that the meta-substituted phenyl pendant groups may not have enough size to prevent free-rotation of the N-aryl bonds and therefore eliminate synchronous realignments necessary for switching. A reassessment of the design was needed.

**Figure 3.14** – Variable temperature polarimetry studies of (a) Poly-36 in toluene ($c = 0.104$ g/100mL) and CHCl₃ ($c = 0.132$ g/100mL). (b) Poly-38 in toluene ($c = 0.108$ g/100mL) and CHCl₃ ($c = 0.108$ g/100mL). path length = 0.5 dm for all tests.
3.5 Discovery of a New and More Versatile Switching Polycarbodiimide

Our next course of action was to increase the arene pendant group size and move to a larger 1-naphthyl pendant group, Poly-39 (Figure 3.15). Prior to discovery of the switching phenomenon, Gonglu Tian previously synthesized a similar polymer and found it to form highly opalescent films due to frozen cholesteric domains.\textsuperscript{21} Mono-39 was synthesized from 1-naphthylamine and n-octadecyl isocyanate according to Figure 2.3. Polymerization of Mono-39 was performed at room temperature using Cat-4 pre-dissolved in minimal CHCl\textsubscript{3} at a 215:1 monomer to catalyst ratio. Initiation and formation of the amidinate complex with Cat-4 was seen by a change in polymerization solution color from orange to dark red within 15 minutes and the polymerization solidified within 3 days. Workup of the polymer was performed in n-butanol after discovering that methanol was immiscible with the residual monomer. Although this may seem trivial, it has been widely reported for all polycarbodiimide work-up procedures thus far, including Poly-21, that methanol was used for precipitation of the polymer. The fact that Mono-39 (and likely Mono-21 as well) is not miscible in methanol causes residual monomer to stick to the precipitated polymer and may interfere with proper purification.

During polarimetry analysis, it was soon discovered that Poly-39 not only undergoes reversible optical switching in toluene, but for the first time we observe unique thermally induced switching profiles in other solvents such as CHCl\textsubscript{3} and THF (Figure 3.16).\textsuperscript{22} Resulting effects from switching in these different solvents include a change in the switching
Figure 3.15 – Polymerization of Mono-39 using Cat-4 resulting in a new, more versatile, switching polycarbodiimide.\textsuperscript{22}

![Chemical structure and reaction scheme]

Figure 3.16 – Variable temperature polarimetry of Poly-39 in (a) CHCl\textsubscript{3}, (b) THF, and (c) toluene.\textsuperscript{22}

![Graph showing optical rotation vs. temperature]

Temperature (~ 0.5 °C in CHCl\textsubscript{3}, 19.5 °C in THF, and 36 °C in toluene, taken at the $\Delta[\alpha]$ midpoint) and a shift in the min/max of the optical rotation plateaus. The net change in specific optical rotation for this polymer reaches 1700° and changes in rotational direction. Since Poly-39 contains a significant amount of $\pi$-character, it is worth noting that we are confident these observed changes are not due to aggregation of the polymer chains. Large
conformational changes observed by ECD due to supramolecular aggregation of chiral polythiophenes based on interchain \( \pi-\pi \) interactions and solvation efficiency have been reported.\(^{23}\) Our confidence towards the absence of such aggregation is based upon four observations: (1) Aggregation is very sensitive to concentration and the optical switching properties observed do not change at various concentrations. (2) The polymers are easily passed through a 0.2 \( \mu \)m PTFE syringe filter (where aggregates would stick) in all reported solvents, most notably \( \text{CHCl}_3 \) and toluene which exhibit opposite switching positions at room temperature. (3) The optical rotation outputs are stable which would not be the case if aggregates of the polymer were crossing in and out of the path of plane polarized light. (4) The large n-octadecyl pendant groups surrounding the \( \pi \)-rich polymer backbone provide a “sheath” of aliphatic character, allowing good solvation between chains and a dampening of interchain interactions. To our knowledge, this is the first polymer system that undergoes a thermally induced conformational change in multiple solvents that doesn’t involve helical inversion and without supramolecular aggregation or the influence of chiral pendant groups and/or chiral perturbations. It is also the largest change in specific optical rotation observed for these polycarbodiimide systems thus far.

Many heat-cool cycles can be performed with repeatable switching and without significant racemization of the helix. This is especially true in \( \text{CHCl}_3 \) and THF where the switching occurs at lower temperatures and further supports previously made conclusions that these transitions are too low in energy to involve imine or helix inversions.\(^{18}\) Quick heating of the polymer solution with a preheated circulation bath shows evidence that these
changes will occur very rapidly, however, accurate kinetic studies are hampered by the speed of solution heating and the time between polarimetry readings. Unlike Poly-21, the blue-shifted naphthyl group permits optical rotation experiments at 435 nm which benefits the amplification in optical rotations observed. ECD experiments of Poly-39 were performed at various temperatures in THF (Figure 3.17). As a result of the switching process, observed Cotton effects move from a positive to a negative direction and are reversible. In addition, blue/red shifts of the peak maxima are observed during this process, especially at the E$_2$ band (301$\leftrightarrow$293 nm) absorption of the naphthyl group, suggesting that the polymer backbone induces an auxochromic effect on the naphthalene units during their repositioning.$^{24}$

![Figure 3.17 – Variable temperature ECD of Poly-39 in THF (top) and UV-Vis at r.t. (bottom). (c = 40 $\mu$g/mL). The solution was heated from 11 °C to 40 °C and then cooled back to 9 °C.$^{22}$](image)
It should be noted that the imine on the helical backbone exhibits a Cotton effect that is hidden beneath the larger amplitude chromophoric pendant group absorption. UV-Vis absorption of di-n-hexyl polycarbodiimide (Poly-6) which has no arene chromophores has a λ_max of 239 nm in THF.

To further support that these observed changes are a result of realignment of the polyarene pendant groups, variable temperature (VT) ¹H-NMR was performed on Poly-39 by J.B. Clark, IV in THF-d₈. Spectra were taken in 10 °C intervals that cover the thermal range where optical switching is observed for this solvent (Figure 3.18). Between the temperatures of 20 and 30 °C, the appearance of two new chemical shifts near 6.5 ppm along with the emergence and sharpening of the broad peak at 7.0 ppm is seen. This observation falls in line with expected changes in anisotropic behavior that would be experienced by the aryl protons from the repositioning of the arene pendant groups relative to one another and the polymer backbone.

Another interesting, and never before reported, property of these polymer systems is that the specific optical rotation can be tuned and held to any value within the range of optical switching under isothermal conditions. This permits the polymer system to function as a tunable polarizer capable of spanning the full arc values ±359° and maintaining the desired optical rotation output without significant racemization of the helical backbone. Figure 3.19 shows an isothermal study performed on Poly-39 in THF. Over the course of 16 h, the polymer solution temperature was changed every 4 h and the resulting optical rotation exhibited was held with relative stability. The gradual drift of the first three
Figure 3.18 – VT-$^1$H NMR of Poly-39 in THF-$d_8$. Changes in aryl proton chemical shifts are seen as a result of anisotropic differences during the switching process of the naphthyl groups.\textsuperscript{22}

![NMR Spectra of Poly-39 in THF-$d_8$](image)

Figure 3.19 – Specific optical rotation of Poly-39 in THF held isothermal at four different temperatures during 4 h increments ($c = 0.200$ g/100mL). Slight drifting in cell temperature is evident; however, the specific optical rotation remains constant at isothermal conditions.\textsuperscript{22}

![Specific Optical Rotation of Poly-39 in THF](image)
increments are due to slow deviations in solution temperature resulting from changes in ambient temperature competing with the circulation bath throughout the day. During the last 4 h of the experiment, the solution temperature held constant at 19.6 °C and the resulting optical rotation also remained constant. The spike at just over 12 h is from an overshoot caused by the cooling process of the circulation bath.

Determination of the energy barrier to helical racemization (E_r) was performed by annealing Poly-39 at higher temperatures and measuring loss of optical activity. Initially this analysis was performed in toluene to stay consistent with previously reported Poly-21. After annealing Poly-39 in toluene at various temperatures (Figure 3.20), calculation of the rate constants (k_obs) for each temperature (Figure 3.21), and calculation of E_r using an Arrhenius plot (Figure 3.22), the racemization energy was determined to be 22.7 kcal/mol which is decent but admittedly less than expected. After reevaluation, it was decided that toluene may not be an ideal solvent for determination of E_r due to the fact that most of the optical rotation of Poly-39 is lost at high temperatures as a result of the switching process (See Figure 3.16(c)). Another annealing study was then performed in decalin, a solvent in which Poly-39 was not found to switch but was found to exhibit high optical rotations at higher temperatures. Figures 3.23, 3.24, and 3.25 show the results of annealing in decalin and the resulting E_r was calculated to be 24.3 kcal/mol, which is 1.6 kcal/mol higher than originally determined in toluene. Both racemization studies prove the energy barrier to helical racemization to be much higher than the observed switching temperatures and although this barrier is not as high as the 36 kcal/mol reported for Poly-21, the fact that
switching can now be observed at much lower temperatures in THF and CHCl₃ overcomes this slight loss in helical stability.

**Figure 3.20** – Annealing of Poly-39 in toluene at 65, 70, 75, and 80 °C.

**Figure 3.21** – Linear plot for determination of rate constants (k_{obs}) for racemization of Poly-39 in toluene at various temperatures.
Figure 3.22 – Arrhenius plot for determination of energy barrier to racemization ($E_r$) for Poly-39 in toluene.

Figure 3.23 – Annealing of Poly-39 in decalin at 65, 70, 75, and 80 °C.
Figure 3.24 – Linear plot for determination of rate constants \( (k_{\text{obs}}) \) for racemization of Poly-39 in decalin at various temperatures.

Figure 3.25 – Arrhenius plot for determination of energy barrier to racemization \( (E_r) \) for Poly-39 in decalin.
3.6. Enantiomeric Switching Behavior of M versus P Helices

When previously reviewing the data in Table 3.1, it was discussed that Poly-21 exhibited variable temperature ECD switching behavior when polymerized from the Cat-5 but that no switching was seen from Poly-21 catalyzed from the enantiomeric catalyst Cat-4 (Figure 3.12). Although there are multiple reasons that could explain the failed switching behavior of Poly-21 with Cat-4, these results did not sit well with us since the polymer helices from each catalyst should behave as enantiomers. Although we have already seen profound switching behavior for Poly-39 from Cat-4, we wanted to recreate two identical side-by-side polymerizations, the only difference between them being the chirality of catalyst used (Cat-4 vs. Cat-5) and test to see if the switching behavior behaves equally but in

![Graph showing polarimetry analysis](image)

**Figure 3.26** – Polarimetry analysis of Poly-39(R) ((a) in CHCl₃, (c) in toluene) and Poly-39(S) ((b) in CHCl₃, (d) in toluene). Polymerizing identical achiral monomers into opposite helices results in enantiomeric switching behavior. ($\lambda = 435$ nm, $c = 0.20 – 0.22$ g/100 mL).²²
opposite directions (Figure 3.26). To ensure that these polymers would be as similar as possible (with the exception of the catalyst chirality), a new batch of Poly-39(R) was prepared at the same time as Poly-39(S) using the same batch of monomer, amount of monomer, dilution solvent (CHCl₃), monomer to catalyst ratio (250:1), temperature (r.t.), polymerization time (5 days), and work up. The Poly-39(R) data in Figure 3.26 has slightly less amplitude in specific optical rotation than shown for previously reported Poly-39 in Figure 3.16. This is sometimes seen between polymer samples that are prepared during different runs, allowing the possibility of slightly different variables in the polymerization process to lend slightly different properties (excess helical sense, regioregularity, Mₘ, etc.) to the resulting polymers. Poly-39(R) and Poly-39(S) were tested by variable temperature polarimetry in CHCl₃ and toluene and found to exhibit nearly identical and opposite switching behavior (Figure 3.26). This study confirms opposite handed helices of these polymers behave enantiomerically throughout the switching process.

3.7. Solvent Effects on Switching Behavior

Since Poly-21 was not found to switch in CHCl₃ or THF and it was concluded that these polar solvents helped stabilize the higher energy conformation of the helix.¹ Now that we can observe the switching phenomenon in multiple solvents using Poly-39, it is important to reassess how the polarity and other properties of the solvent affect the switching behavior for these systems. A range of solvents were chosen based on dipole moment, density, and boiling point and their ability to adequately solvate Poly-39. A solvent was deemed adequate
if the polymer solution was not turbid and passed through a 0.45 µm PTFE syringe filter without issues. Much to our surprise, Poly-39 exhibited a switching fingerprint in most of these solvents and at different temperatures (Figure 3.27). When comparing all of the solvent properties with the approximate switching temperature (Table 3.2), no discernable trend is realized. One conclusion made possible is that solvents with close to zero dipole moments, such as cyclohexane and decalin, did not exhibit any switching behavior. Solvents with the highest dipole moments, 1,2-dichlorobenzene (2.5 D), CHCl₃, (1.04 D), and THF (1.75 D) showed no relationship between dipole moment and the resulting switching temperatures of 60 °C, 0.5 °C, and 19.5 °C respectively. Of all of the solvents tested, ethylbenzene is the most intriguing. When compared to toluene, ethylbenzene is very similar in dipole moment (0.59 D vs. 0.37 D) and identical in density (0.87 g/cm³). Remarkably, the addition of one methylene unit to toluene is discovered to lower the switching temperature almost 20 °C.

Building upon this discovery, a new set of aromatic solvents with varying aliphatic character was tested. Poly-39 was dissolved in benzene, toluene, ethylbenzene, propylbenzene, isopropylbenzene (cumene), and butylbenzene for variable temperature polarimetry analysis of solvent effects on switching behavior (Figure 3.28). Benzene, being relatively non-polar, exhibited no switching just like cyclohexane and decalin did in the previous study. However, a discernable trend is seen with the other aromatic solvents. Increasing the length of the aliphatic chain on the solvent molecule results in a decrease of the switching temperature and a decrease of the switching amplitude for Poly-39.
Figure 3.27 – Variable temperature polarimetry of Poly-39 in (a) CHCl₃, (b) ethylbenzene, (c) THF, (d) DCM, (e) toluene, (f) chlorobenzene, (g) xylenes, (h) 1,2-dichlorobenzene, (i) cyclohexane, and (j) decalin. (c = 0.20 – 0.25 g/100mL, l = 0.5 dm)

Table 3.2 – Physical constants of various solvents tested compared to temperature of switching.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>~Switching Temp (°C)*</th>
<th>bp (°C)</th>
<th>µ (debyes)</th>
<th>δ (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane†</td>
<td>---</td>
<td>81</td>
<td>-0</td>
<td>0.78</td>
</tr>
<tr>
<td>Decalin</td>
<td>---</td>
<td>190</td>
<td>-0</td>
<td>0.88</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>---</td>
<td>40</td>
<td>1.60</td>
<td>1.33</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>0.5</td>
<td>61</td>
<td>1.04</td>
<td>1.48</td>
</tr>
<tr>
<td>THF</td>
<td>19.5</td>
<td>65</td>
<td>1.75</td>
<td>0.89</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>20</td>
<td>136</td>
<td>0.59</td>
<td>0.87</td>
</tr>
<tr>
<td>Toluene</td>
<td>36</td>
<td>111</td>
<td>0.37</td>
<td>0.87</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>40</td>
<td>132</td>
<td>1.69</td>
<td>1.11</td>
</tr>
<tr>
<td>Xylenes‡</td>
<td>50</td>
<td>140</td>
<td>0.21</td>
<td>0.87</td>
</tr>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>60</td>
<td>180</td>
<td>2.50</td>
<td>1.31</td>
</tr>
</tbody>
</table>

*Approximated switching temperatures taken at mid. pt. of [a] plateaus (small bias in temp. readings are likely due to an old method of temp. reading from cooling bath and not with an “in cell” thermocouple)
‡values are an average of cis and trans values
†values are an average of o-, m-, and p-xylene
Figure 3.28 – Variable temperature polarimetry of Poly-39 in (a) toluene, (b) ethylbenzene, (c) propylbenzene, (d) butylbenzene, (e) cumene, and (f) benzene. \(c = 0.20 – 0.22 \, \text{g}/100\text{mL}, \, l = 0.5 \, \text{dm}\)

The decrease in switching amplitude seems to affect the positive optical rotation conformation more than the negative. For Butylbenzene, the optical switching is almost lost completely and the mid-point of the switch is below -10 °C. This is a very interesting discovery and is an extreme example of the importance solvation plays in this switching process. So the question now becomes, what is it about an aliphatic “tail” on the benzene solvent molecule that causes this behavior? A possible explanation may be visualized when thinking about the how Poly-39 is solvated. When looking at a cross-section of this polymer, there are two coronas that solvent molecules must penetrate in order to completely solvate the polymer (Figure 3.29). The outer corona is a large aliphatic “sheath” caused by the long octadecyl pendant groups. This large aliphatic corona is responsible for reducing interchain packing and allowing good solubility of Poly-39 in a wide range of solvents. We are
Figure 3.29 – Extreme switching differences between toluene and butylbenzene may be caused by different solvation at the interface between the aromatic and aliphatic corona (red circle).

confident that the outer regions of this corona are well solvated. When approaching the inner corona, things begin to get a little more interesting. The density of the aliphatic groups increase and a new \( \pi \)-rich corona caused by the naphthalene pendant groups is found. The answer for the extreme difference in switching behavior between toluene and butylbenzene may lie with the solvation of this aliphatic-aromatic coronal interface. This seems fitting since a mixture of aliphatic and aromatic character is what is being adjusted on the solvent and this is the same as the character as this interface. Further solvation studies found later in this text (Section 3.12.1 and 3.12.2) offer conclusion that efficient solvation of these polymer
chains is occurring throughout the aromatic corona; leaving the notion that there may be some other reason for this observed trend. Since non-polar solvents consistently show no switching behavior, it is safe to assume that polarity of the solvent does play some role but it may not be a major contributor as once thought before these studies.

3.8. Effects of Polymer Properties on Switching Behavior

Although we now know that solvent can play a large role on the potential switching properties of Poly-39, we also wanted to determine what the affects of different polymer properties are on the switching process. The most common characteristic that can affect the properties of almost all polymer systems is the molecular weight. As previously discussed absolute molecular weight determination of these polymer systems is complicated due to extreme broadening of the polymer elution through GPC columns. Viscosity measurements have also been attempted but it was found that the viscosity of these polymer solutions continually fluctuate as the rigid rod nature of the chains become aligned in the viscometer. A more general way to study the effects of molecular weight on the switching properties of Poly-39 is to alter the monomer to catalyst ratio of the polymerizations. Assuming the polymerizations to be living, a theoretical molecular weight ($M_w$) for these polymerizations can be determined by:

$$
M_w = X_m \left( \frac{w_m}{w_p} \right) M_m
$$

(3.7)
where $\chi_{mc}$ is the number of monomer moles per mole of catalyst (i.e. the monomer to catalyst ratio), $w_m$ is the initial weight of monomer, $w_p$ is the final weight of the polymer, and $M_m$ is the formula weight of the monomer. The monomer formula weight is equal to the formula weight of the polymer repeat unit. Polymerizations of Mono-39 were setup using Cat-4 according to Table 3.3. The yields of the anticipated higher molecular weight polymers were low, causing the calculated $M_w$ of the largest three polymers to be similar.

Variable temperature polarimetry was performed in CHCl$_3$ (Figure 3.30) and toluene (Figure 3.31). All of the polymers, regardless of molecular weight, seemed to undergo the switching process around the same temperature in CHCl$_3$ and toluene however, the lower molecular weight Poly-39(17K) shows significantly less amplitude. Poly-39(80K) shows much higher switching amplitude than the other two polymers of similar $M_w$ (Poly-39(81K) and Poly-39(71K)). The remaining polymer, Poly-39(36K), shows similar switching to the 81K and 71K polymers in toluene and CHCl$_3$. From this experiment we can conclude polymers that are too low in molecular weight will have much less switching amplitude. This may answer the question of why the previously discussed Poly-21 was not found to undergo switching in toluene (Figure 3.12(A)) since the monomer to catalyst ratio used for this polymer was comparatively low (Table 3.1). Poly-39(80K) has a much higher switching amplitude than the rest, leading us to believe that other traits of this polymer are playing a large role on the switching properties.
Table 3.3 – Experimental parameters for molecular weight study of Poly-39 using Cat-4.

<table>
<thead>
<tr>
<th>Wt. Mono-39 (g)</th>
<th>(mmol) Mono-39</th>
<th>(µmol) Cat-4</th>
<th>Mono: Cat Ratio</th>
<th>Vol. CHCl₃ (mL)</th>
<th>Rxn Time (days)</th>
<th>% Yield</th>
<th>Theo. Mₙ</th>
<th>Yield Corrected Mₙ</th>
<th>Polymer ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.02</td>
<td>2.41</td>
<td>5.7</td>
<td>421:1</td>
<td>2</td>
<td>7</td>
<td>46</td>
<td>177K</td>
<td>81K</td>
<td>Poly-39(81K)</td>
</tr>
<tr>
<td>1.05</td>
<td>2.48</td>
<td>8.0</td>
<td>309:1</td>
<td>2</td>
<td>7</td>
<td>55</td>
<td>130K</td>
<td>71K</td>
<td>Poly-39(71K)</td>
</tr>
<tr>
<td>1.04</td>
<td>2.46</td>
<td>11.5</td>
<td>215:1</td>
<td>2</td>
<td>7</td>
<td>88</td>
<td>90K</td>
<td>80K</td>
<td>Poly-39(80K)</td>
</tr>
<tr>
<td>1.05</td>
<td>2.48</td>
<td>22.9</td>
<td>108:1</td>
<td>2</td>
<td>7</td>
<td>80</td>
<td>45K</td>
<td>36K</td>
<td>Poly-39(36K)</td>
</tr>
<tr>
<td>1.07</td>
<td>2.53</td>
<td>45.9</td>
<td>55:1</td>
<td>2</td>
<td>7</td>
<td>73</td>
<td>23K</td>
<td>17K</td>
<td>Poly-39(17K)</td>
</tr>
</tbody>
</table>

Figure 3.30 – Variable temperature polarimetry of Poly-39 in CHCl₃ polymerized with different monomer to catalyst ratios of Cat-4. (c = 0.20-0.22 g/100mL, l = 0.5 dm)
Figure 3.31 – Variable temperature polarimetry of Poly-39 in toluene polymerized with different monomer to catalyst ratios of Cat-4. (c = 0.20-0.22 g/100mL, l = 0.5 dm)

Another major property associated with polycarbodiimides is the regioregularity. This concept will be touched on briefly and is explained in more detail in chapter 4. Essentially, when an asymmetric carbodiimide monomer is inserted into the polymer chain during propagation, two possible regio-outcomes are possible. The regioisomers are identified by which of the two pendant groups ends up on the imine nitrogen versus the amine nitrogen. Up until this point, IR has been used to qualitatively determine the regioregularity of the polymer systems since the C=N imine bond absorption energy is different if the nitrogen is attached to an aryl pendant group (~1640 cm\(^{-1}\)) or an alkyl pendant group (~1620 cm\(^{-1}\)). When looking at an overlay of the IR spectra for the polymers used in the molecular weight study of Poly-39, you can see various qualitative amounts of regioregularity. Figure 3.32 reveals very interesting information when compared to the
Figure 3.32 – IR spectra overlay of **Poly-39** with various molecular weights

observed switching amplitudes of Figures 3.30 and 3.31. Although it is believed that molecular weight is the leading cause of such a low switching amplitude observed for **Poly-39(17K)**, Figure 3.32 reveals this polymer to be the only one that favors the C=N-alkyl regioisomer represented by the 1620 cm$^{-1}$ absorption. Furthermore, **Poly-39(80K)**, which was observed to have the highest switching amplitude, seems to highly favor the C=N-aryl regioisomer represented by the 1640 cm$^{-1}$ absorption. This implies that, although the polymers will switch if regioirregularity is present, one regioisomer may be causing
amplification in the observed switching properties and may even be the sole contributor to the switching process.

The next experiments were designed to try and induce preferred regioregularity of Poly-39. The most obvious way would be to use the previously synthesized Cat-7 which was claimed to polymerize Poly-21 into a regioregular polymer due to the non-aggregated state of the catalyst. However, the same results were not reproducible when polymerizing Mono-39 in duplicate using Cat-7 (Figure 3.33). Poly-39(Cat-7)a and Poly-39(Cat-7)b were both analyzed in the thin film by IR. When compared to the previously discussed Poly-39(80K) derived from the more aggregated Cat-4, neither of these polymerizations exhibited any significant improvement to the regio-outcome of the polymers (Figure 3.34). Furthermore, the resulting yield of polymers derived from Cat-7 are considerably less (Figure 3.33) after 7 days due to the increased steric around the propagating active chain end. Although Cat-7 may have been responsible for the regioregular Poly-21 we are now learning that there may have been other variables which were not taken into account that may have led to the regio-preference of this polymer. It was decided that no improvements to the polymer switching properties or regioregularity of Poly-39 were seen to justify the increased price of starting materials needed for the synthesis of Cat-7 and the use of Cat-4 would be continued for the remainder of this research.
Figure 3.33 – Duplicate polymerization of Mono-39 using Cat-7 revealed both polymers Poly-39(Cat-7)a and Poly-39(Cat-7)b to have regioirregularity.

Figure 3.34 – IR spectra overlay of Poly39(80K), Poly-39(Cat-7)a and Poly-39(Cat-7)b. Polymerization of Mono-39 with Cat-7 reveals no significant improvement in regioregularity.
In another effort to synthesize regioregular Poly-39, a series of polymerizations were performed using different polymerization temperatures summarized in Table 3.4. Since the mechanism of monomer insertion is a reversible process, this experiment could elucidate the possibility of a thermodynamically favorable regioisomer. Effort was made to keep the polymerization variables such as monomer to catalyst ratio and dilution of CHCl₃ as similar as possible. Polymerizations at lower temperatures were allowed to react longer before workup than polymerizations at higher temperatures in order to obtain similar polymer yields. The initial polymerization at 45 °C failed, likely due to contamination in the reaction flask and this reaction was successfully redone using the same monomer batch, catalyst, and CHCl₃ solution. When performing IR on thin films of Poly-39 polymerized at different temperatures, an immediate trend in regioisomer preference is realized (Figure 3.35). For Poly-39(10°C) and Poly-39(25°C), no preference in regioisomer is seen and the two imine absorptions are almost equivalent in size. However, once polymerization temperature reaches 35°C, a predominant regioisomer (C=N-aryl, 1640 cm⁻¹) begins to emerge. For Poly-39(45°C) and Poly-39(55°C), the preference for the C=N-aryl regioisomer is so great that the other imine absorption at 1620 cm⁻¹ reduces to a small shoulder on the larger imine absorption at 1640 cm⁻¹. From this experiment it is evident that the polymerization temperature can dictate a preferred regioisomer for the resulting Poly-39. A duplicate set of polymers was synthesized by an REU student, Vanessa Porter, under my tutelage and similar results were obtained. The potential reasoning behind this selective regioisomer preference will be further discussed in Chapter 4. Variable temperature polarimetry in CHCl₃ was performed
on these polymers to compare the switching amplitude against their determined regioregularity (Figure 3.36). Interestingly, **Poly-39(35°C)** exhibited the most switching amplitude even though IR shows this polymer to be less regioregular than **Poly-39(45°C)** and **Poly-39(55°C)**. A possible explanation for this result is the potential for the polymerizations at higher temperatures to slowly racemize the polymer during the polymerization. Therefore, although the polymers from higher temperatures have more regioregularity, they have less excess helical sense and therefore less switching amplitude than **Poly-39(35°C)** which gets the best of both worlds; a slight regio preference and gentle polymerization temperature to prevent helical racemization. **Poly-39(10°C)** and **Poly-39(25°C)** both had considerably

### Table 3.4 – Experimental parameters for variable temperature polymerization study of Poly-39 using Cat-4.

<table>
<thead>
<tr>
<th>Wt. Mono-39 (g)</th>
<th>Mono-39 (mmol)</th>
<th>Cat-4 (µmol)</th>
<th>Mono:Cat Ratio</th>
<th>Vol. CHCl₃ (mL)</th>
<th>Rxn Temp. (°C)</th>
<th>Rxn Time (days)</th>
<th>% Yield</th>
<th>Polymer ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
<td>2.40</td>
<td>9.6</td>
<td>250:1</td>
<td>0.43</td>
<td>10</td>
<td>18</td>
<td>73</td>
<td>Poly-39(10°C)</td>
</tr>
<tr>
<td>1.04</td>
<td>2.47</td>
<td>9.6</td>
<td>257:1</td>
<td>0.43</td>
<td>25</td>
<td>12</td>
<td>78</td>
<td>Poly-39(25°C)</td>
</tr>
<tr>
<td>1.00</td>
<td>2.38</td>
<td>9.6</td>
<td>248:1</td>
<td>0.43</td>
<td>35</td>
<td>11</td>
<td>77</td>
<td>Poly-39(35°C)</td>
</tr>
<tr>
<td>1.05</td>
<td>2.50</td>
<td>9.6</td>
<td>260:1</td>
<td>0.43</td>
<td>45</td>
<td>8</td>
<td>76*</td>
<td>Poly-39(45°C)</td>
</tr>
<tr>
<td>0.99</td>
<td>2.35</td>
<td>9.6</td>
<td>245:1</td>
<td>0.43</td>
<td>55</td>
<td>7</td>
<td>72</td>
<td>Poly-39(55°C)</td>
</tr>
</tbody>
</table>

* - initial 45 °C polymerization failed and was redone successfully
lower switching amplitude than the rest of the polymers and, consequently, also had the highest regioirregularity. Therefore we can conclude that the C=N-aryl regioisomer seems to promote the amplitude of optical rotation switching. Until we can obtain highly regioregular Poly-39 using a low polymerization temperature, we cannot conclude that a polymer comprised solely of this regioisomer will yield the best switching results.

**Figure 3.35** – IR spectra overlay of Poly-39 from Cat-4 polymerized at various temperatures
Figure 3.36 – Variable temperature polarimetry of Poly-39 polymerized at (a) 10 °C, (b) 25 °C, (c) 35 °C, (d) 45 °C, and (e) 55 °C in CHCl₃ (c = 0.20 – 0.23 g/100mL, l = 0.5 dm).

3.9. Effects of Alkyl Pendant Group Size on Switching Behavior

It is important to eliminate any role that the large aliphatic groups may be playing on the switching process for these polymer systems. An ideal study would be to chop off the aliphatic chain completely and use a methyl group opposite the 1-naphthyl group, but this polymer would exhibit very poor solubility. Since reducing the alkyl chain too much can also cause problems in solubility, it may be possibly to reduce the octadecyl pendant group down to a dodecyl pendant group without consequence. Mono-40 was synthesized and polymerized using Cat-4 to obtain Poly-40 in good yield (Figure 3.37). Mono-40, having less aliphatic character, is miscible in ethanol (EtOH) and therefore work-up of Poly-40 was performed by dissolution in wet CHCl₃ and precipitation in EtOH. Poly-40 was found to be regioirregular by IR with a slight preference towards the C=N-aryl imine regioisomer which
Absorbs at 1639 cm$^{-1}$. Theoretically, Poly-40 should have a larger amplification in specific optical rotation when compared to Poly-39 due to the loss of six methylene units per repeat unit of the polymer. This loss in mass will cause a similar concentration of Poly-40 solution to contain more naphthalene units when compared to Poly-39. Figure 3.38 shows a variable temperature polarimetry comparison of Poly-40 and Poly-39(Cat-7)a in CHCl$_3$. Although only a slight amplification in switching can be observed for Poly-40, the more important information derived from this overlay is that the switching profiles are almost identical. These results fall in agreement with our conclusions that the aliphatic pendant groups provide good solubility for these polymer systems but do not play a role in the switching process.
Figure 3.38 – Variable temperature polarimetry of (a) Poly-40 in CHCl₃ (c = 0.21 g/100mL, l = 0.5 dm) and (b) Poly-39 in CHCl₃ (c = 0.23 g/100mL, l = 0.5 dm).

3.10. Effects of Size and Spatial Arrangement of Aromatic Pendant Groups on the Switching Behavior

Synthetic investigation was performed focusing on the effects of size and geometry of these polyarene pendant groups. The repeat unit of Poly-41 is constitutionally the same as Poly-39, the only difference being the attachment of the 2-naphthyl versus the 1-naphthyl pendant group (Figure 3.39(a)). As a consequence of this difference, the spatial arrangement of the naphthalene groups around the helical scaffold is altered. Interestingly, this spatial alteration caused Poly-41 to exhibit no significant changes in specific optical rotation as a function of temperature in toluene, $[\alpha]^{10}_{435} = +247^\circ$, $[\alpha]^{70}_{435} = +180^\circ$, (Figure 3.40(A)). The slight decrease in optical rotation at higher temperatures was not reversible, making it likely due to partial racemization of the helix. Variable temperature ECD was also performed on Poly-41 in THF and no significant changes in observed Cotton effects were seen
(Figure 3.40(b)). This discovery elucidates the necessity for these polyarene pendant groups to have a sufficient “kink” in their geometry relative to the helical director, making them more prone to restricted rotation through “shutter-like” interactions.

**Figure 3.39** – Synthesis of two new polycarbodiimides for investigation of (a) spatial arrangement (Poly-41) and (b) size (Poly-42) of the polyarene pendant group.

**Poly-42** was created to further understand the upper-size limit of these polyarene flaps and the 1-pyrenyl pendant group is the largest polyarene pendant group synthesized thus far (Figure 3.39(b)). When testing the switching capabilities of **Poly-42** in toluene (Figure 3.41(a)), a large reversible change in optical rotation was observed, however, the
switching behavior was broadened and occurs at much higher temperature than seen for Poly-21 and Poly-39. Due to concerns with toluene vapor pressure within the cell at temperatures higher than 80 °C, we decided to perform another polarimetry test in...
ethylbenzene. Just like observed for Poly-39, the switching process in ethylbenzene occurs at a much lower temperature than that observed for toluene (Figure 3.41(b)). In this case, the addition of a single methylene carbon to the side chain of the aromatic solvent lowers the switching temperature by approximately 40 °C. Overall, the larger 1-pyrenyl pendant groups provide a greater optical rotation at the sodium-D line (589 nm) when compared to Poly-21, but they also behave more cumbersome, requiring relatively higher temperatures, and resulting in broadening of the switching profile.

Characterization of Poly-41 and Poly-42 by IR surprisingly revealed them both to be highly regioregular. For Poly-41, the dominant imine absorption was observed at 1618 cm\(^{-1}\) with a small shoulder at 1633 cm\(^{-1}\) (Figure 3.42). This preferred regioisomer places the arene pendant group on the amine nitrogen which is the opposite regioisomer previously discussed to promote switching amplitude in Poly-39. From this standpoint, it may be likely to conclude that Poly-41 does not switch due to this preferred regioisomer, however, Poly-42 also favors this regioisomer with a single sharp imine stretch at 1614 cm\(^{-1}\). Although conflicting, this observation implies that some degree of switching can occur regardless of the regioposition of the polyarene pendant group.

Figure 3.43 reveals more carbodiimide monomers that were synthesized in an effort to create potentially switching polycarbodiimides and uncover more answers towards the necessary requirements of their design. Mono-43 is very similar to Mono-39 with the exception of the methyl substituent on the 2-position of the 1-naphthyl pendant group. The inclusion of this methyl group was for two purposes: (1) the hydrogens of the methyl group
Figure 3.42 – IR spectra and regioregularity comparison of Poly-39(80K), Poly-41, and Poly-42.

Figure 3.43 – New carbodiimide monomers designed to probe size and spacing effects on the switching phenomenon.

will have a unique $^1$H-NMR chemical shift that may be observed during the switching process without interference and overlap from other hydrogens. (2) The methyl group
provides a “kick-stand” on the naphthalene unit and may in some way alter the observed switching process. Although Mono-43 was synthesized successfully and in good yield, polymerization using Cat-4 at room temperature and at 45 °C yielded no polymer. Complexation of Mono-43 with Cat-4 was observed as indicated by the polymerization solution adopting a deep red color but somehow this new methyl substituent was preventing propagation. When constructing a lowest energy conformation molecular model of the initiation amidinate complex of Mono-43 with Cat-4 (Figure 3.44), it was found that the 2-methyl substituent extends directly over the titanium-nitrogen amidinate bond, potentially preventing propagation through steric effects. This failed polymerization is a good example of the sensitive ballet of steric hindrance necessary for the propagation of these polymer systems.

Figure 3.44 – Molecular model of amidinate complex of Mono-43 with Cat-4 revealing the 2-methyl substituent to potentially block the path of monomer insertion and preventing propagation.
Mono-44 and Mono-45 contain a 4-indanyl and 2-fluorenyl pendant group instead of the 1-naphthyl polyarene group. These monomers were designed to determine if the “shutters” require a fully aromatized system or if a bulky hybrid of aromatic and aliphatic character would suffice. Due to the aliphatic character of the indanyl group, we were confident that a shorter dodecyl chain could be used as the other pendant group without solubility issues. Mono-44 was successfully polymerized into Poly-44 using Cat-4 with good yield (Figure 3.45(a)). IR indicated Poly-44 to be highly regioregular favoring the C=N-alkyl regioisomer absorption at 1616 cm\(^{-1}\). Variable temperature polarimetry testing in CHCl\(_3\) revealed Poly-44 to have a large optical rotation but no reversible switching of optical rotation at higher temperatures \([\alpha]^{5.0}_{435} = 1043^\circ\), \([\alpha]^{40}_{435} = 862^\circ\). The slight decrease in specific optical rotation is reversible but this is a typical drift associated with heating polarimetry solutions and not likely due to conformational switching. It is concluded that switching polycarbodiimides require a fully aromatized polyarene flap and not just a pendant group large enough to prevent free N-aryl bond rotations. This discovery could indicate some form of \(\pi-\pi\) interactions, such as slip-stacked \(\pi\)-stacking,\(^ {27}\) are taking place between the polyarene flaps and explain why a fully aromatized pendant group is necessary. Mono-45 was also successfully polymerized into Poly-45 using Cat-4 (Figure 3.45(b)), however, the resulting yield was low. As a consequence, the specific optical rotation of Poly-45 in CHCl\(_3\) was also low \([\alpha]^{15}_{435} = 29^\circ\) and the polymer exhibited no significant change in optical rotation as a function of temperature. Given what we know about the required spatial arrangements of the flaps (from Poly-41) and the necessity of a fully
aromatized pendant group (from Poly-44), it was decided that no further investigations of this polymer would be pursued.

**Figure 3.45** – Synthesis of (a) Poly-44 and (b) Poly-45.

Mono-46 presents an interesting case by separating the naphthalene pendant group from the backbone by one methylene unit. Will giving the polyarene shutter an “elbow” and more degrees of freedom still cause observed conformational changes on the polymer? If the main driving forces behind these conformational changes are from intershutter π-π interactions, then the methylene unit may allow the polyarene groups to move more freely into positions that maximize these interactions. Poly-46 was synthesized in decent yield from Mono-46 and Cat-4 (Figure 3.46). The resulting polymer was extremely tacky and adhered to itself during precipitation in ethanol. Final drying required lyophilization from benzene. Since both the nitrogens on Poly-46 are directly attached to a methylene unit, the IR spectra
reveals only one sharp imine absorption at 1645 cm\(^{-1}\) and this may constitute an overlap of both regioisomer absorptions. When performing variable temperature polarimetry of Poly-46 in CHCl\(_3\) it was discovered that this polymer has a very small specific optical rotation \([\alpha]\)\(_{435}^\circ\) = -11.2°, \([\alpha]\)\(_{435}^\circ\) = -18.7° (c = 0.23 g/100mL) which remains relatively stable over the full range of temperatures. Although Poly-46 did not switch, these results exemplify the extreme amplification of specific optical rotations exhibited by polycarbodiimides containing a directly attached aryl pendant group. Furthermore, direct aryl attachment to the backbone is deemed necessary for observing the switching phenomenon.

For solubility reasons, the polymerization of di-1-napthyl carbodiimide (Mono-47) was not expected to be successful, and we were right. Any oligomers that may have been forming immediately became insoluble, preventing further propagation. However, the idea of obtaining a polycarbodiimide with two potentially switching pendant groups per repeat unit was worth the effort of trying, but unfortunately to no avail.

Through the synthesis and analysis of all of these polymers, although most of them failed to switch, we were able to gain a testament to the careful balance of spatial
requirements, size, connectivity, and degree of aromaticity necessary for this unique switching phenomenon to take place. We have determined that the most ideal pendant group for observing this switching behavior so far requires a fully aromatic, fused two-ring, 1-naphthyl pendant group directly attached to the backbone. In addition care must be taken when placing any substituents onto the naphthalene group since they may sterically interfere with a monomer’s ability to be polymerized.

3.11. Modifying Switching Behavior through Substituent Effects on Naphthalene.

A new library of monomers was synthesized with the goal of altering the electronics of the aromatic naphthalene π-system (Figure 3.47). Through the use of substituent effects on the ring system we may be able to alter the energy required to undergo conformational switching and the observation of these changes may lead to some further clues towards the main driving forces behind this behavior. The use of a 5-quinolyl pendant group (Mono-48, Mono-49) was immediately a favorite choice among these derivations since we can retain a 2-fused ring π-system without the spatial addition of pendant groups to the ring and also, the incorporation of the heterocyclic nitrogen will diversify the electronics on the arene pendant group. When synthesizing Mono-48 it became apparent that the purification process for this monomer was not as efficient as observed for previously discussed monomers. A persistent brown coloration to the monomer was not separable by column chromatography and polymerization attempts using Cat-4 in CHCl₃ were unsuccessful. Since, Mono-48 results in a solid monomer at room temperature, the decision was made to change the n-octadecyl
Figure 3.47 – New carbodiimide monomers designed to alter the electronics of the naphthalene π-ring system.

pendant group to a n-dodecyl pendant group which would make Mono-49 an oil at room temperature. In our experience, oil based monomers are easier to purify through column chromatography and they can be polymerized more effectively since additional solvent is not required to dissolve the monomer. It was during the attempted synthesis of Mono-49 when the benefit of using purchased pre-made dibromotriphenylphosphorane salt became apparent. The persistent brown coloration of Mono-48 and Mono-49 was likely caused by free bromine that had not complexed with the triphenylphosphine reagent in-situ. Although this was never a problem with previously synthesized monomers, the introduction of a heterocyclic nitrogen lone pair allows complexation with bromine. By using the pre-made salt, we eliminate free bromine in the process and clear light yellow Mono-49 oil was obtained in good yield. Goodwin reported that using pyridine as a polymerization solvent would result in much slower polymerizations and this was attributed to the complexation
ability of the heterocyclic nitrogen on the pyridine ring with the titanium(IV) center.\textsuperscript{29}

Therefore we can expect that this monomer, which also has a heterocyclic nitrogen, will polymerize at a reduced rate when compared to previous polymerizations. Successful polymerization of \textbf{Mono-49} with \textbf{Cat-4} required almost one month of polymerization time to obtain a 41\% yield (Figure 3.48). The heterocyclic nitrogen makes \textbf{Mono-49} polar enough to become miscible with methanol and this was the solvent chosen for purification and precipitation of the polymer. IR of \textbf{Poly-49} reveals a preference for the C=N-aryl regioisomer at 1637 cm\textsuperscript{-1} creating optimism that any lack of switching amplitude will not be a result of regioregularity. When variable temperature polarimetry was performed on \textbf{Poly-49} in CHCl\textsubscript{3}, THF, and toluene, some remarkably interesting results were uncovered (Figure 3.49). \textbf{Poly-49} exhibits reversible switching in CHCl\textsubscript{3} but not in THF and toluene. The mid-point temperature of switching in CHCl\textsubscript{3} is 22.5 °C which is 22 °C higher than \textbf{Poly-39} in the same solvent. The net change in specific optical rotation is approximately 350° and considerably less than \textbf{Poly-39}, however, this may be due to the potentially low molecular weight of the polymer as a result of low yield. The disappearance of switching in both THF and toluene was not anticipated and the reasoning for such behavior is unknown. The fact that switching occurs near room temperature in CHCl\textsubscript{3} provides good utility for these polymer systems. \textbf{Poly-49} presents a potentially new use for these switching polycarbodiimides as a result of having a heterocyclic nitrogen lone pair in a reversibly chiral environment. This polymer system may be used as a site for asymmetric catalysis and possibly alter the stereoselectivity.
of a reaction in one switching position versus another. Research in our group is currently underway to investigate such reactions.

Figure 3.48 – Polymerization of Poly-49 required one month using Cat-4.

Figure 3.49 – Variable temperature polarimetry of Poly-49 in (a) CHCl₃ (c = 0.215 g/100mL) (b) THF (c = 0.206 g/100mL), and (c) toluene (c = 0.212 g/100mL).
The remaining monomers from Figure 3.47 all contain different substituents with varying degrees of electron donating and electron withdrawing behavior. Decision was made to place these substituents on the naphthalene 4 position since this lies on the same axis as the N-aryl bond rotation and points away from the carbodiimide moiety which will hopefully minimize any interference sterically during the polymerization process. To obtain Mono-50 and Mono-51 a few additional synthetic steps were necessary to obtain 4-methyl-1-aminonaphthalene from purchased 1-methylnaphthalene (Scheme 3.1).\textsuperscript{30} Polymerization of Mono-50 and Mono-51 using Cat-4 yielded Poly-50 and Poly-51 (Figure 3.50). Previously synthesized polymers from our group, such as Poly-22, have shown greatly improved solubility through the simple addition of alkyl substituents to phenyl pendant groups and it was hoped that such benefit would allow Poly-51 to be soluble with a shorter n-hexyl chain, but this polymer was determined insoluble in a wide range of organic solvents. Poly-50, on the other hand, was soluble in a wide range of organic solvents typically used for variable temperature polarimetry. Figure 3.51 displays the observed specific optical rotation as a function of temperature of Poly-50 in CHCl\textsubscript{3}, toluene, and propylbenzene. Initial studies in CHCl\textsubscript{3} and toluene revealed that the polymer might be switching and that the switching temperature has now exceeded the upper temperature limit for the solvent where the vapor pressure may become too high for the sample cell. A third study was done using propylbenzene, a solvent previously shown to lower the switching temperature for Poly-39, and a very broad but reversible switching occurs with a midpoint close to 50 °C. In all three solvents, the specific optical rotation returns to a high value upon cooling ($\{\alpha\}_{21435} = 1503^\circ$ in
Scheme 3.1 – Total synthesis of Mono-50 and Mono-51.

**Figure 3.50** – Polymerization of Mono-50 and Mono-51. Polymerization of Mono-51 resulted in an insoluble solid.
Figure 3.51 – Variable temperature polarimetry of Poly-50 in (a) CHCl$_3$ ($c = 0.200$ g/100mL), (b) toluene ($c = 0.206$ g/100mL), and (c) propylbenzene ($c = 0.200$ g/100mL). Changes in $[\alpha]$ are reversible upon cooling.

CHCl$_3$, $[\alpha]^{24}_{435} = 1327^\circ$ in toluene, and $[\alpha]^{24}_{435} = 1135^\circ$ in propylbenzene, after heating). A slight loss in initial optical rotation does occur due to minor helical racemization at higher temperatures. It seems as though the addition of a 4-methyl substituent on the 1-naphthyl pendant group has significantly increased the switching temperatures in each solvent. Poly-39 was found to switch at approximately 4 °C in propylbenzene while Poly-50 could have a switching midpoint as high as 55 °C in the same solvent, a difference of nearly 50 °C. Poly-50 has a remarkably high specific optical rotation and IR spectroscopy reveals this polymer to be highly regioregular favoring the C=N-alkyl regioisomer absorption at 1614 cm$^{-1}$. Essentially, Poly-50 has broken through a barrier of many previously seen trends. It is seen to switch at high specific optical rotation amplitude even though it has a high preference of the C=N-alkyl regioisomer and was recovered in somewhat low yield (50%)
using a 140:1 monomer to catalyst ratio. For these reasons Poly-50 merits further investigation in the future.

Mono-52 and Mono-53 have adopted bromine and chlorine, respectively as substituents on the 4 position of the 1-naphthyl pendant group. 4-bromo-1-aminonaphthalene and 4-chloro-1-aminonaphthalene were found available for purchase from Aldrich, making them convenient candidates for further studies. Halogens are an interesting choice since they instill mixed inductive effects by being σ-withdrawing through their electronegativity and π-donating due to their lone pairs. Poly-52 and Poly-53 were obtained using Cat-4 in good yields (Figure 3.52). Poly-52 was worked up in EtOH and determined to be regioirregular by IR with two equal sized imine absorptions at 1633 and 1618 cm⁻¹. Variable temperature

![Chemical structures and reaction schemes for Mono-52 and Mono-53.](image)

**Figure 3.52** – Polymerization of Mono-52 and Mono-53.
polarimetry of Poly-52 in CHCl₃, THF, and toluene reveals completely altered switching profiles for these solvents (Figure 3.53). Instead of having a global effect of switching behavior for each solvent, Poly-52 has increased the CHCl₃ and toluene switching temperature while decreasing the THF switching temperature when compared to Poly-39. Solubility issues prevented temperatures below 8 °C from being analyzed in CHCl₃ and THF, but a clear switching transition can be seen around this temperature. The estimated switching midpoints for Poly-52 in CHCl₃ and THF by extrapolating the switching transition are ~10 °C and ~13 °C respectively. The switching midpoint in toluene is approximately 54 °C and the switching profile is slightly broadened by comparison. Additionally, Poly-52 exhibits much less amplitude when compared to Poly-39 and Poly-50. Part of this reason could be explained by the increased molecular mass of the polymer repeat unit through the addition of a heavy bromine atom. Removing the 19 % bromine weight from the repeat unit and normalizing the specific optical rotation results in the normalized plot shown in Figure 3.54, where the specific optical rotation increases approximately 100° in toluene at 25 °C. The chlorine substituent also has an effect on the switching profiles for Poly-53 (Figure 3.55). In this case it seems the more electronegative chlorine atom has reduced the CHCl₃ and THF switching temperature even further and below the polymer’s solubility range and also reduced the toluene switching by approximately 7 °C when compared to Poly-52. Also, Poly-53 is found to be highly in favor of the C=N-aryl regioisomer by the appearance of a dominant imine absorption at 1635 cm⁻¹ when analyzing its IR spectrum. Although the mixed inductive effects associated with halogens complicate definite conclusions, it seems
**Figure 3.53** – Variable temperature polarimetry of **Poly-52** in (a) CHCl$_3$ ($c = 0.218$ g/100mL), (b) THF ($c = 0.202$ g/100mL), and (c) toluene ($c = 0.213$ g/100mL).

**Figure 3.54** – Normalized specific optical rotation data of **Poly-52** with bromine mass subtracted from the concentration in (a) CHCl$_3$ ($c = 0.218$ g/100mL), (b) THF ($c = 0.202$ g/100mL), and (c) toluene ($c = 0.213$ g/100mL).
that the more electronegative chlorine substituent causes a decrease in switching temperatures compared to bromine. When you combine this observation with the increases in switching temperatures observed for the slightly donating methyl substituent on Poly-50, a trend may be developing.

![Graph showing variable temperature polarimetry of Poly-53 in different solvents](image)

**Figure 3.55** – Variable temperature polarimetry of Poly-53 in (a) CHCl₃ (c = 0.205 g/100mL), (b) THF (c = 0.219 g/100mL), and (c) toluene (c = 0.206 g/100mL).

To further investigate if electron donating substituents attached to the naphthyl pendant group will increase the observed switching temperatures, Poly-54 was synthesized from Mono-54 using Cat-4 at a 200:1 monomer catalyst ratio (Figure 3.56). After workup and precipitation in EtOH, Poly-54 was obtained in good yield (77 %) as a fluffy light yellow solid. IR spectroscopy revealed Poly-54 to be highly regioregular favoring the C=N-alkyl regioisomer with a single sharp absorption at 1620 cm⁻¹. Variable temperature polarimetry revealed even more interesting results (Figure 3.57). Instead of increasing the switching
Figure 3.56 – Polymerization of Mono-54.

Figure 3.57 – Variable temperature polarimetry of Poly-54 in (a) CHCl$_3$ ($c = 0.203$ g/100mL), (b) THF ($c = 0.209$ g/100mL), and (c) toluene ($c = 0.214$ g/100mL).

temperature in CHCl$_3$, and toluene compared to Poly-39 as seen for Poly-50, the temperature of switching was greatly reduced for toluene ($\sim$5 °C taken at the extrapolated mid-point) and increased for CHCl$_3$ ($\sim$24 °C). Continued investigation in THF revealed a switching temperature similar to CHCl$_3$ ($\sim$26 °C) in addition to a sharpening of the switching profile.
**Poly-54** breaks the previous record set for **Poly-39** by having the highest amplitude difference in specific optical rotation with a total change of 1850° in THF. A very interesting result considering that the high regioregularity of **Poly-54** is the opposite shown to promote switching amplitude for **Poly-39**. Even though the trend that electron donating substituents increase the switching temperature profiles in all solvents is broken by these observations, this polymer holds a new standard for switching amplitude and, in addition, further reconfirms that these naphthyl reorientations can occur regardless of the regioposition offered by the polymer. It is safe to say that each new switching polymer synthesized seems to break working hypotheses that are developed towards trends in this switching behavior. Although the results can often be disconcerting for those eagerly awaiting answers as to why switching occurs, these polymers and their behavior are highly intriguing and we are just scratching the surface of their potential. This research has provided a broad foundation which can be built upon for research moving forward and has unlocked some of the full potential of these polymer systems. It is with hope that future synthetic studies in addition to advances in polymer instrumentation to probe kinetics and solvation can provide more clues towards the driving forces behind this unique behavior.

### 3.12 Miscellaneous Studies (Odds and Ends)

#### 3.12.1 Solvation Investigations Using Charge Transfer Complexation with Iodine

Of the variety of non-covalent binding interactions possible between molecules, a π-donor-acceptor complex is unique because it can often lead to visual color changes
indicative to the human eye. A donor-acceptor interaction is possible between two molecules where one has an unoccupied low energy orbital (acceptor) and another has an occupied high energy orbital (donor). When these two molecules are brought together in proper alignment, these two orbitals are capable of mixing and stabilizing each other, creating a new orbital of lower energy. In the ground state, this new stabilized mixing of orbitals can be excited by radiation (in this case UV-visible light) allowing the transfer of the electron from the donor to the acceptor of the complex. This new complex, known as a charge-transfer (CT) complex results in new light absorption known as a CT band which is completely unique for these types of non-covalent interactions and is not observed for the donor or acceptor complex alone. Iodine has a very intense purple color in the vapor phase caused by the promotion of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (Figure 3.58). However, iodine can also act as a Lewis acid type acceptor when mixed with a variety of solvents, especially those with good Lewis base donor features such as \( \pi \)-bonds or lone pairs. If the Lewis base strength of the solvent is weak, such as a saturated alkane, any resulting CT complex is also weak and iodine solutions retain the purple color due to the lack of CT formation and the high energy UV light necessary to promote electrons within any minor CT complexes that are formed. If the Lewis base strength of the solvent is too strong, such as the oxygen lone pairs in methanol, then a dissociative complexation occurs resulting in the formation of \( \text{I}_3^- \) and an intense yellow solution. However, a solvent with Lewis basicity in between these two extremities can result in a very good CT complex with noticeable color changes in the visible spectrum.
Such is the case for $\pi$-rich systems such as benzene, which results in an iodine color change from purple to red when dissolved. As shown in Figure 3.58, this red (or pink when dilute) color is due to the combined absorption of the new CT band and the adduct absorption band of iodine.

![Figure 3.58 – Charge-transfer complexation of iodine and various solvents. (Special thanks to Professor James Martin for use of this figure)](image)

Building off of the idea that molecules might be solvating Poly-39 differently depending on their ability to penetrate the aliphatic and aromatic coronas around the polymer, we wanted to investigate solvation by doping these solvents with iodine. If the
solvent is capable of penetrating to the aromatic corona of the polymer, it should carry the iodine molecules with it and we can visualize the formation a charge transfer complex with the naphthalene units or the nitrogen lone pairs on the polymer. Figure 3.59 shows some initial experiments of iodine doped benzene, toluene and THF with and without dissolved Poly-39. The concentration of iodine in each solution is 55 µg/mL (or ppm) and the concentration of Poly-39 in the polymer containing samples is approximately 4.8 mg/mL. A CT complexation with Poly-39 can be seen for the benzene and toluene solutions resulting in a color change from pink to orange. To ensure this color change is not an inherent discoloration by the polymer alone, Figure 3.60 shows the color of a blank toluene solution and a solution of Poly-39 in toluene of equal concentration as used for the solutions in Figure 3.59. It can be seen that the polymer solution is colorless and therefore this new orange color must be the result of a CT complex formation between iodine and the polymer. No color change can be seen in the THF solutions and this can be explained by the preferential CT complex formation between the THF solvent oxygen and iodine over the polymer. Through these trial runs it was determined that the solvent used must not interfere by forming preferential CT complexes with iodine. Therefore THF is not suitable for these experiments due to strong complexation. When moving forward to spectroscopy studies with benzene and toluene, although a visual color change can be seen, UV-Vis and ECD experiments will be dampened by absorption of these aromatic solvents in the wavelengths of interest. Additionally, these solvents will have competing CT complexation with iodine. CHCl₃, on the other hand, does not form a good CT complex with iodine as evidenced by the
Figure 3.59 – Iodine doped benzene, toluene, and THF without (left) and with (right) Poly-39. A color change can be seen from pink to orange in benzene and toluene as a result of CT complexation with the polymer.

Figure 3.60 – Visual reference of toluene solution with Poly-39 with no iodine added. The polymer solution alone is colorless.
retention of a deep purple color when iodine is added. CHCl₃ is also transparent in the 300-700 nm wavelength range, allowing good visualization of any changes in UV-Vis absorption and Cotton effects for these CT complexes. A quick dissolution of Poly-39, in an iodine doped CHCl₃ solution revealed an almost instantaneous color change from purple to orange (Figure 3.61A). As previously mentioned, dissolution of iodine in an aliphatic solvent such as cyclohexane results in very weak CT complexation and a retention of a deep purple color, therefore we expect no color change to occur from iodine interacting with the long aliphatic n-octadecyl chains of Poly-39. The culprit for such a drastic color change from purple to orange must be either the naphthalene units or the nitrogens on the polymer backbone or both. UV-Vis spectroscopy was performed on a Poly-39 solution (44 ppm in CHCl₃) and a separate I₂ solution (106 ppm in CHCl₃) as shown in Figure 3.61B. The Poly-39 spectrum has two peak maxima at 306 and 243 nm. The I₂ solution has a broad absorption at 509 nm which results in the purple solution color and a small CT band observed at 260 nm from CHCl₃. Both spectra were taken at room temperature. It can also be seen that the polymer has a much larger extinction coefficient than the iodine solution and because of this, using close to 1:1 molar ratios of polymer repeat unit to iodine would result in a solution too dilute to observe iodine or CT absorbance. To rectify this problem, a more concentrated solution of polymer had to be analyzed rendering any absorption below 350 nm useless. However, when adding molar equivalents of I₂ to a 1.09 mg/mL solution of Poly-39, a clear CT absorption band can be seen at 368 nm after subtracting the polymer absorbance as a baseline
The peak at 509 nm can be explained as a mixture of the new iodine adduct absorption (See Figure 3.58) and free iodine that is not complexed to the polymer.

**Figure 3.61** – (a) Picture of (from left to right) Poly-39 in CHCl₃ (2 mg/mL), CHCl₃ only, I₂ in CHCl₃ (0.1 mg/mL), Poly-39 (2 mg/mL) + I₂ (0.1 mg/mL) in CHCl₃. (b) UV-Vis spectrum of Poly-39 in CHCl₃ (44 ppm) and I₂ in CHCl₃ (106 ppm).

**Figure 3.62** – Overlay of UV-Vis spectra for (a) I₂ in CHCl₃ (106 ppm), and solutions of Poly-39 (1.09 mg/mL) with additive amounts of I₂ (b) 25:1, (c) 12:1, (d) 8:1, (e) 6:1, and (f) 5:1 ratio of moles of polymer repeat unit to iodine. For (b-f), the polymer absorption was subtracted from the spectrum revealing the charge transfer band at 368 nm.
Since CT complexes are a weak bonding interaction, we were curious to see if these complexes have an induced chirality by being non-covalently bound to a chiral macrostructure. ECD was performed on these solutions to determine if there is any “chiralization” of the I₂-CT complex. ECD reveals no change in observed Cotton Effects between pure Poly-39 in CHCl₃ and solutions with I₂ doped at various molar ratios with respect to moles of polymer repeat unit (Figure 3.63). Therefore, although the formation of a CT band is evident by UV-Vis spectroscopy, these complexes do not organize themselves in a chiral manner around the helical backbone of the polymer and are not observed by ECD.

**Figure 3.63** – Overlay of ECD spectra of (a) Poly-39 (101 ppm) in CHCl₃ and mixtures of 4:1, 2.3:1 and 1:1 moles polymer repeat unit to moles iodine added. (b) Same iodine solutions in (a) but with polymer absorbance subtracted. No Cotton effects in the 368 nm range are observed.

These studies show that thorough solvation of Poly-39 in CHCl₃, benzene, and toluene is occurring all the way to the aromatic corona of the polymer chain as evidenced by
the formation of CT complexes with iodine and a visual color change. Future studies can be performed on the effect of these CT complexes on the switching behavior for these systems.

3.12.2 Investigation of Solvation Using a Mixed Solvent System

If the difference in switching temperature is indeed influenced by different solvation capabilities within the arene and aliphatic coronas around the polymer, then one can expect Poly-39 dissolved into mixed solutions of two switching solvents such as CHCl$_3$ and toluene to behave in a non-linear fashion with respect to solvent composition and switching temperature. The basis behind this hypothesis is thought of as a quasi-osmotic effect, where the solvent of higher solvation capability, in this case CHCl$_3$, where switching occurs at lower temperature, will be able to penetrate the inner coronas of the polymer in mixtures lower than 100 % and therefore result in drastic lowering of the switching temperature. In other words, by increasing the concentration of CHCl$_3$ in toluene, the polymer switching profile should become similar to that of pure CHCl$_3$ even at lesser concentration. To test this theory, Poly-39 was dissolved in various mixtures of CHCl$_3$ and toluene and variable temperature polarimetry was performed on each sample to determine the effects on the switching temperature (Figure 3.64). The results prove our hypothesis false; the switching temperature behaves in an almost linear fashion as a function of solvent composition. This indicates that the polymer switches as a function of the overall properties of the mixed solvent system and not with a preferential solvation of one solvent over another. This study is good evidence that adequate solvation is being made by both of these solvents and that the
induced switching temperature lies with a collective property of the solvent mixture as a whole.

**Figure 3.64** – Variable temperature polarimetry of Poly-39 in (a) CHCl₃, ((b) 80%, (c) 60%, (d) 30% CHCl₃ in toluene), and (e) toluene. (c = 0.20 – 0.25 g/100mL, l = 0.5 dm)

### 3.12.3 Attempts at Synthesizing Switching Polycarbodiimides From Chiral Monomers

Although the effects of molecular weight and regioregularity on the switching behavior for these polymer systems has been studied, the excess helical sense of the polymer may be another large contributor to the switching amplitudes that are observed. Unfortunately, it is difficult to monitor and control the excess helical sense of these polymers when using achiral monomers since the excess helical sense relies completely on the catalyst. It was discussed in Chapter 2 that an excess helical sense can be thermodynamically obtained by annealing diastereomeric helices into the lower energy helical sense. Because of this potential way of inducing a large excess helical sense, a number of chiral carbodiimide
monomers containing a potentially switching polyarene group were designed (Figure 3.65). The ability to adopt excess helical sense through annealing allows the polymerizations of these monomers to be performed with the achiral, less bulky, and highly active trichlorotitanium(IV)-2,2,2-trifluoroethoxide catalyst (Cat-15). However, even with a sterically reduced catalyst system, Mono-55, Mono-57, and Mono-58 were still unable to be polymerized. These results reinforce the steric trends observed by Goodwin in Chapter 2. Attempts at copolymerizing Mono-57 with the less bulky di-n-hexyl carbodiimide (Mono-6) were also unsuccessful and only low yield of homo-Poly-6 was recovered. Using a 105:1 monomer to catalyst ratio, neat polymerization of Mono-56 with Cat-15 was somewhat successful and had gelled within a day. After 3 days, workup was performed on Poly-56 (26 % yield) which has only limited solubility in CHCl₃ and offers no solubility in a range of other common solvents. Poly-56 has a very hard granular texture unlike most of the

**Figure 3.65** – Newly synthesized chiral carbodiimide monomers containing a potentially switching pendant group.
previously discussed polymers containing a long aliphatic chain and a fluffy texture. The solubility of Poly-56 in CHCl₃ is so limited, it would not dissolve at typical ¹H-NMR concentrations. IR of a dispersed thin film reveals a very sharp single imine stretch at 1617 cm⁻¹. A dilute solution (c = 0.21 g/100mL) of virgin Poly-56 in CHCl₃ was tested on the polarimeter at room temperature, [α]²⁵⁴₃⁵ = 30°. Upon heating to 60 °C, the specific optical rotation changed slightly [α]⁶⁰⁴₃⁵ = -8°. Continued annealing was attempted but the increased solvent pressure at this temperature resulted in a cracking of the polarimetry cell. After this, it was decided that annealing will be performed outside the polarimetry cell in a sealed Schlenk flask. A 0.215 g/100mL solution of Poly-56 was dissolved in CHCl₃, sealed within the flask, and heated at 60 °C overnight. In the morning, the polymer solution had adopted a white, milky, opaque appearance. It was determined that the adoption of a highly ordered excess helical sense may have caused the polymer, with already limited solubility, to fully precipitate from the solvent. When filtering this solution and performing polarimetry, all optical rotation was lost, confirming that the filtered precipitates was indeed the polymer. Due to these collective issues with solubility, no further investigations were performed on this polymer.

It is possible that moving the chiral stereocenter from the α- to the β-carbon of the an aliphatic pendant group such as Mono-59 and Mono-60 could relieve steric interference and result in successful polymerization. A β-stereocenter was found to successfully polymerize when the other pendant group is phenyl (Mono-12, Chapter 2) but polymerizations were deemed unsuccessful when coupled with an anthracene group (see supporting information of
ref. 18) Therefore, the success of Mono-59 and Mono-60 could go either way. Although (S)-(−)-2-methylbutylamine is available for purchase to synthesize Mono-59, any polymer resulting from this monomer is expected to be insoluble due to the lack of aliphatic character. Therefore the (R)-(−)-2,6-dimethylheptyl pendant group was also synthesized from (R)-Pulegone shown in Scheme 3.2. Unfortunately, it was discovered that neither Mono-59 nor Mono-60 will polymerize using Cat-15. It is possible that using a γ-stereocenter will result in successful polymerization as was seen for Mono-23, but Poly-23 did not show any switching behavior and this has not yet been pursued.

Scheme 3.2 – Synthesis (R)-2,6-dimethylheptyl isocyanate from (R)-Pulegone

3.12.4 Induction of Excess Helical Sense on Poly-39 through Chiral Acid

It is common to perform an activity test on newly synthesized catalysts to ensure they will successfully polymerize reliable monomers prior to adding them to more expensive, and never before attempted monomers. After synthesizing Cat-15 for these studies, an activity
test of the catalyst was performed by adding a portion of a previously made batch of Mono-39 to the newly purified catalyst before storage. The polymerization was successful proving the catalyst to be active but to our surprise, the IR spectrum of the newly polymerized achiral Poly-39 revealed the polymer to be highly regioregular with a sharp imine stretch at 1639 cm$^{-1}$. Poly-39 possessing a high regioregularity in favor of the C=N-aryl isomer was sought after in Section 3.8 and it was found that higher polymerization temperatures could deliver a preference for this regioisomer but at the cost of helical racemization during polymerization. We have now stumbled upon Poly-39 that was polymerized at room temperature and highly favors this regioisomer, the problem now is that this polymer has no excess helical sense due to the use of achiral Cat-15. In an effort to induce an excess helical sense on this polymer, a molecular chaperone study using chiral camphorsulfonic acid (CSA) was attempted. Polarimetry of the virgin Poly-39 shows $[\alpha]_{24}^{2435} = -10^\circ$ in CHCl$_3$ ($c = 0.208$ g/100mL). The experiment was setup as shown in Table 3.5. Solutions 1 and 4 were made the same except solution 4 will be annealed within a sealed Schlenk flask at higher temperatures while solution 1 remains at room temperature. Solution 2 provides the optical rotation of (-) CSA without polymer and the specific optical rotation was calculated as $[\alpha]_{24}^{2435} = -44.7^\circ$ in CHCl$_3$. Solution 3 provides a baseline optical rotation from the polymer prior to addition of (-) CSA. By subtracting the $[\alpha]$ contribution of (-)CSA from solution 4, it was calculated that Poly-39 adopted an excess helical sense ($[\alpha]_{24}^{2435} = -254.3^\circ$) after being annealed at 65 °C in CHCl$_3$ for 120 hours. Therefore, we successfully induced an excess helical sense on Poly-39 resulting in a specific optical
Table 3.5 – Experimental setup for chiral acid (-)CSA molecular chaperone study on achiral Poly-39.

<table>
<thead>
<tr>
<th>Solution #</th>
<th>mass Poly-39 (mg)</th>
<th>mass (-)CSA (mg)</th>
<th>Vol. CHCl₃ (mL)</th>
<th>Mol acid: mol r.u.</th>
<th>$\alpha_{24,435}$ (l = 1.0 dm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22.4</td>
<td>68.1</td>
<td>10</td>
<td>5:1</td>
<td>-0.2829</td>
</tr>
<tr>
<td>2</td>
<td>None</td>
<td>61.2</td>
<td>10</td>
<td>-</td>
<td>-0.2735</td>
</tr>
<tr>
<td>3</td>
<td>22.4</td>
<td>None</td>
<td>10</td>
<td>-</td>
<td>-0.0069</td>
</tr>
<tr>
<td>4*</td>
<td>22.4</td>
<td>68.6</td>
<td>10</td>
<td>5:1</td>
<td>-0.8762</td>
</tr>
</tbody>
</table>

* - Solution 4 was annealed in a sealed flask at 65 °C for 120 hours

rotation increase of almost 250°. However, the acidified polymer exhibited no switching in CHCl₃ at lower temperatures (Solution 4, $\alpha_{24,435} = -0.444°$ (l = 0.5 dm), $\alpha_{10,435} = -0.520°$ (l = 0.5 dm)). The inability for this polymer to switch is possibly due to the increased helical pitch resulting from electrostatic repulsions of the cationic protonated polymer backbone. In addition, the increased polarity of the polymer backbone through protonation caused it to precipitate out of CHCl₃ at temperatures lower than 10 °C. Attempted neutralization of the polymer by washing with aqueous sodium carbonate solution resulted in negative side effects; the polymer solution turned brown in color possibly due to some decomposition pathway. Attempted polarimetry on this brown solution was unsuccessful due to the absorption of the polarimetry light. Although future research on successfully neutralizing polycarbodiimide backbones is necessary, this experiment shows that a highly regioregular polymer favoring the C=N-aryl isomer is obtained by polymerization of Mono-39 with
Cat-15 and the adoption of an excess helical sense is possible for Poly-39 through a chiral acid molecular chaperone. Also it is found that protonation of the Poly-39 backbone will lead to a loss of switching behavior.

3.12.5 Attempts at Synthesizing Fluorescent Carbodiimide Copolymers

Throughout this research, continued applications and new ways of being able to observe and study the switching behavior of these polycarbodiimides has been an area of interest. One idea was the potential design of a switching polycarbodiimide capable of fluorescence which would potentially allow visualization of any changes in absorption and emission of light during these conformational changes. Since some of the previous polymers designed contain large arene fluorophores, it is disappointing to discover that none of these polymers, especially the large 1-pyrenyl containing Poly-42, exhibited any fluorescence as a homopolymer in CHCl₃, THF, or toluene above and below the respective switching temperatures. Fluorescence can often be seen from the carbodiimide monomers when visualizing TLC plates under a UV lamp at 355 nm. The idea of why these polyarene pendant groups do not fluoresce once polymerized was distilled down to a few potential reasons; (1) the electronic effects of the attached nitrogen differs between the carbodiimide moiety and the polymer backbone moiety in such a way that fluorescence is dissipated by intersystem crossing (ISC) resulting from $n-\pi^*$ interconversion or (2) the polyarene pendant groups, which are held close to one another on the polymer scaffold, may prevent fluorescence through collisional quenching. If the polyarene pendant groups are undergoing
ISC with the polymer backbone then there is nothing much we can do, but if they are being quenched by bimolecular interactions with each other, then we may be able to see fluorescence if we separate the chromophores through copolymerization. A simplistic experiment was performed by co-polymerizing \( N\)-(1-pyrenyl)-\( N'\)-(n-octadecyl) carbodiimide (Mon-42) with the non-chromophore containing di-n-hexyl carbodiimide (Mon-6) (Figure 3.66). A 1:2.24 ratio of Mon-42:Mon-6 will hopefully allow adequate spacing between pyrene units with non-quenching hexyl chains in between them. After one day of polymerization using Cat-15, a bright yellow fluffy polymer was obtained after workup. Through \(^1\)H-NMR and IR analysis it was confirmed that Poly-42-co-6 contained both comonomer segments. Observation of fluorescence was performed using a 355 nm UV-lamp

**Figure 3.66** – Copolymerization of Mon-6 and Mon-42 for potential fluorescent polycarbodiimide studies.

of Poly-42-co-6 in CHCl\(_3\), pentane, THF, and in the solid film state. No fluorescence was observed for this copolymer when dissolved in these three solvents but a faint green glow.
was observed for the solid film. Through post experimental discussions, it may be possible that the ratio of Mono-42 needs to be decreased even further such as 100:1 Mono-6:Mono-42. As it stands, fluorescence has yet to be seen for these polyarene containing polycarbodiimides.

3.13 Conclusions

We have discovered 7 new polymers (Poly-39, 42, 49, 50, 52 53, and 54) that undergo reversible switching uniquely in a variety of solvents. Of these polymers, the 1-naphthyl pendant group, Poly-39, is found to be the most versatile while Poly-54 exhibits the most total change in optical rotation equaling up to 1850° in THF. We have determined that the size, spatial arrangement, connectivity, and aromaticity, on these polyarene pendant groups are crucial to observe the conformational switching process. In addition, polymer properties such as molecular weight and regioregularity have been probed. Switching amplitude has been shown to decrease when the polymer systems are too low in $M_w$ but variations in $M_w$ do not seem to affect the temperature at which these polymers switch in respective solvents. The C=N-aryl regioisomer seems to favor an amplification in the switching of Poly-39, but other polymers such as Poly-42, Poly-50, and Poly-54 have displayed switching capabilities even though their structures are highly regioregular favoring the C=N-alkyl regioisomer. The regioregularity of Poly-39 from Cat-4 can be manipulated by the polymerization temperature and leads to a preference in the C=N-aryl regioisomer at
temperatures 35 °C and above, however, polymerizations at higher temperature will result in racemization of the helix during the polymerization process. A wide variety of solvents have been tested and shown to each have their own switching temperature fingerprint but currently no global conclusions about the effect of solvent can be justified. A few specific conclusions about solvent can be made: (1) Non-polar solvents will not display any switching behavior within their respective temperature range. (2) Increasing an n-aliphatic chain size on toluene as a solvent (ethylbenzene, propylbenzene, etc.) will result in a lowering of the switching temperature and a decrease of the switching amplitude. (3) CHCl₃, toluene, and benzene have each been shown capable of thoroughly solvating Poly-39 chains and carrying I₂ molecules close enough to the polymer backbone to allow CT complexation with either the naphthalene rings or the backbone nitrogens. (4) Dissolving Poly-39 in a mixture of two solvents capable of switching will result in a new switching temperature directly and nearly linearly proportional to the composition of the solvent. Also, the incorporation of electron donating or electron withdrawing substituents on the naphthalene pendant group is shown to have profound behavior of the temperatures of switching in respective solvents and further enforces belief that switching is a behavior associated with the electronics and/or dipole moment associated with the arene pendant group.

Switching has been shown to behave identically, but in opposite rotatory directions when Poly-39 is synthesized into opposite handed helices. These polymer systems were discovered to be tunable and capable of maintaining a desired specific optical rotation anywhere within the switching profile when held isothermal. This gives these polymer
systems a new function as tunable polarizers in addition to their potential application in optical sensor and optical display technologies. The aliphatic pendant group on these polymer systems is not believed to play a role on the switching process as evidenced by nearly identical switching profiles of Poly-39 and Poly-40 in CHCl₃.

These polymer systems represent, to our knowledge, the only class of helical polymers comprised from achiral monomers that show a large reversible change in optical rotation without the influence of chiral perturbations and, most importantly, without inversion of the helical backbone. This discovery could warrant the redefinition of similar behavior seen by other helical polymer systems that are attributed to helical inversions and could provide breakthrough understanding of how complex helical macromolecular systems can behave intramolecularly on a chiral foundation.

3.14 Experimental Section

3.14.1 Materials

Unless otherwise noted reagents used were obtained from Aldrich (Sigma-Aldrich, Milwaukee, WI) and used without further purification. Common laboratory supplies and solvents were purchased from the NCSU Chemistry Stockroom via Fisher Scientific (Fair Lawn, NJ). Solvents used for polymerization or catalyst synthesis were dried, distilled, degassed, and stored over molecular sieves prior to use. ECD and UV-Vis experiments were performed in spectroscopy grade solvents also purchased from Aldrich.
Dibromotriphenylphosphorane salt was purchased from VWR (Suwanee, GA) and deuterated NMR solvents were purchased from Cambridge Isotope Labs (Andover, MA).

3.14.2 Instrumentation

Infrared spectroscopy was performed on a Jasco FT-IR 140 Fourier transform infrared spectrometer using potassium bromide crystal windows purchased from Aldrich. IR of polymers were performed on KBr plates by thin film deposition of a dissolved polymer solution, typically in CHCl₃, followed by evaporation of the solvent. UV-Vis spectroscopy was performed on a Jasco V-550 UV-Vis spectrometer using high clarity quartz cells. The instrument is baselined by filling the reference and sample cell with the appropriate solvents being tested. Polarimetry was performed on a Jasco P-1010 polarimeter with interchangeable wavelength filters and using a jacketed 0.5 dm cell. Cells are analyzed periodically with solvent only to ensure no chiral material has accumulated within the cell. The polarimeter performance is checked using standard solutions of sucrose in water according to the instrument manual. Cell temperature is adjusted by a Neslab RTE-140 circulation bath attached to the jacketed cell and the solution temperature within the cell is monitored by an Omega K-Type thermocouple attached to a Barnant digital thermocouple thermometer. ECD experiments were performed at the laboratory of Dr. Clay Clark (NCSU, Biochemistry) in high clarity quartz cells with a Jasco J-600 spectropolarimeter equipped with a variable temperature stage heated/cooled by a circulation bath. GPC analyses were performed using 2 sequential PL-Gel 5 µm Mixed-C columns 300 x 7.5 mm (Polymer Laboratories, Amherst, MD) that are kept isothermal in an Eppendorf CH-500 column heater. A mixture of 0.5%
dimethylaminoethylamine (DMAEA) in HPLC grade THF is used as a mobile phase and standards of poly-2-vinylpyridine (PSS-USA, Silver Spring, MD) or polystyrene are used for universal calibration. A Jasco PU-1580 intelligent HPLC pump and a Jasco RI-1530 refractive index detector are also used. Polarimetry and GPC solutions are pre-filtered before analysis using a 0.45 µm PTFE syringe filter. $^1$H and $^{13}$C-NMR analyses were performed on a Mercury 300 or 400 spectrometer using deuterated solvents with tetramethylsilane internal standard. Mass spectra were obtained at the NCSU Department of Chemistry Mass Spectrometry Facility using electrospray ionization (ESI) on an Agilent Technologies 6210 LC-TOF mass spectrometer.

3.14.3 General Preparation of Monomers

1:1 Molar equivalents of appropriate amine is added slowly to an isocyanate pre-diluted in DCM in a 250 mL round bottom flask cooled to 0 °C. The reaction mixture is allowed to warm to room temperature and then refluxed if necessary overnight. The resulting urea typically precipitates out of DCM once cooled and is removed by aspiration filtration. Urea is then recrystallized in mixtures of ethanol and methanol, filtered, and dried under vacuum. In a round bottom flask, X moles of PPh$_3$ is dissolved in minimal DCM in a 250 mL round bottom flask with an egg-shaped stir bar and the solution is cooled to 0 °C using an ice bath. The flask should be capped with an N$_2$ blanked between additions. X moles of Br$_2$ is slightly diluted in DCM and added to a pressure equalizing addition funnel. The bromine solution is added dropwise into the PPh$_3$ solution at 0 °C resulting in the formation
of a yellow-white slurry. (Note: If using the pre-made dibromotriphenylphosphorane salt, all that is needed is addition of X moles of this salt to minimal DCM and cooling) To the slurry, 2.2X moles of TEA are added all at once (Note: some smoking during this addition is normal) To the charged solution at 0 °C, the urea is added in 1/3 portions over about 30 minutes. Once all the urea is added the reaction is allowed to warm to room temperature and allowed to stir overnight. A urea that lacks solubility in DCM will digest effectively in this slurry over time resulting in a brown colored solution from the formation of reaction by-products. The dehydration of urea into carbodiimide can be monitored by infrared spectroscopy by formation of a strong N=C=N absorption band at ~2100 cm⁻¹. Once complete, the resulting monomer is purified by quenching the reaction solution with pentane and filtering away unwanted triphenylphosphine oxide and triethylammonium bromide salt. The filtrate, containing the dissolved monomer, is then reduced via rotary evaporation and the pentane quenching cycle repeated up to three times to remove as much unwanted byproducts as possible. Final purification of the monomer can be performed by column chromatography using neutral silica gel as the stationary phase and mixtures of DCM/hexanes as the mobile phase. Due to the large aliphatic chains on most monomers, the monomer typically elutes first and well ahead of other by-products. Therefore a short-bus column can typically be used for proper purification. Once collected, the mobile phase is reduced by rotary evaporation followed and full drying of the pure monomers by high vacuum and backfilling with dry nitrogen several times using Schlenk techniques is done
prior to polymerization and storage. Monomers are stored in an MBraun Unilab dry box freezer (-25 °C) under inert N2 atmosphere.

3.14.4 General Preparation of Catalysts

The BINOL based catalyst systems (Cat-4, 5, and 7) were all prepared in the same manner as reported in literature.31 Titanium tetraisopropoxide (or tetra-t-butoxide for Cat-7) is dried, distilled, and degassed prior to use. BINOL ligands are kept in an MBraun Unilab dry box under dry nitrogen atmosphere and used as received. In the dry box 1:1 molar equivalents of the appropriate titanium tetra-alkoxide and BINOL ligand are slightly diluted in dry, degassed toluene and added to a 50 mL top-sealing Schlenk flask. The flask is sealed, removed from the dry box, and stirred at room temperature for 3-5 hours. Using a Schlenk line equipped with high vacuum and dry nitrogen, toluene and liberated alcohol is removed from the flask by reduced pressure azeotropic distillation, resulting in a red-orange crude solid (yellow solid is observed for Cat-7) which is further dried to completion by reduced pressure. The crude catalyst is recrystallized in dry, degassed, diethyl ether (DEE). After cooling in an ice bath, the DEE is carefully removed from the crystals using a dry syringe. The crystals are then fully dried by reduced pressure and transferred back into the dry box for storage.

The trichloro-titanium(IV)-2,2,2-trifluoroethoxide catalyst (Cat-15) was prepared in a dry clean Schlenk flask under N2 atmosphere by cannulating in 1:1 molar equivalents of titanium tetrachloride and 2,2,2-trifluoroethanol in dry degassed DCM at 0 °C. (Note: TiCl4
will smoke when exposed to air resulting in deposition of TiO, which can later be removed from glassware by washing in an acid bath; minimize exposure of TiCl$_4$ to air if possible and always use in a hood.) The yellow solution was allowed to warm to room temperature overnight and then volatiles were removed from the Schlenk flask by reduced pressure yielding yellow-white solids. The solids were washed multiple times with dry hexanes which were removed via cannula. (Note: It is important to wash away the liberated HCl thoroughly due to the reactivity of carbodiimides with free acid) The resulting white solids were dried fully by reduced pressure and transferred to a dry box for storage.

3.14.5 General Preparation of Polymers

In a dry box, monomer is added to a clean vial and weighed (typically ~1 g of monomer is used for polymerizations). To the monomer is added the appropriate amount of catalyst pre-dissolved in dry, degassed CHCl$_3$ at a known concentration. The polymerization vial is capped tightly and stirred within the dry box for 3-5 days. The vials may also be wrapped in paraffin film and stirred outside the dry box during this time. Depending on the nature of the monomer and catalyst, solidification and seizing of the stir bar could occur within 3 days or up to 5 days. Once the stir bar is seized, the polymer gel is usually allowed to further diffuse for 1-3 days in the vial. The polymer is then purified by dissolving in wet CHCl$_3$ and precipitated by dropping the solution into stirring methanol, ethanol, or n-butanol. The choice of alcohol depends on the miscibility of the residual monomer within it. The
polymer is filtered, collected, and re-dissolved / re-precipitated up to three times for further purity. Polymers are then dried under vacuum.

3.14.6 Characterization of Catalysts

(R)-(+-)1,1’-Bi-2,2’-naphthoxy-titanium(IV) diisopropoxide (Cat-4): Titanium tetraisopropoxide was distilled prior to use. (R)-(+-)1,1’-Bi-2,2’-naphthol (BINOL) was purchased from TCI and kept dry by storage in a dry box under N\textsubscript{2} atmosphere. In the dry box, 0.5350 g (1.9 mmol) of (R)-BINOL was submerged in 4 mL of dry, degassed toluene in a 20 mL scintillation vial equipped with a stir bar. (Note: The BINOL ligand will not fully dissolve in the toluene until the titanium tetraisopropoxide is added) 0.5314 g (1.9 mmol) of titanium tetraisopropoxide was added to the toluene solution and the vial was capped and stirred until all the BINOL had dissolved. The reaction solution was transferred to a top-sealing Schlenk flask using a syringe; the stir bar was transferred also. The Schlenk flask was sealed tightly and removed from the dry box. The Schlenk flask was attached to a Schlenk manifold equipped with high vacuum and dry nitrogen gas. The reaction solution was allowed to stir at room temperature for 1 hour followed by azeotropic distillation of toluene and liberated isopropanol to yield a red-orange solid. After full drying, the solids were recrystallized from dry DEE. The DEE was decanted using a cannula and the crystals were dried fully by reduced pressure. The Schlenk flask was once again sealed and the dry catalyst crystals were moved back into the dry box where they were transferred to a clean vial for cold storage.
Yield: 0.52 g (62 %). $^1$H NMR (300 MHz, CDCl$_3$ stored over molecular sieves) $\delta$ (ppm): 1.06 (d, 12H), 4.49 (m, 2H), 6.75 (d, 2H), 7.15 (d, 2H), 7.34 (m, 4H), 7.46 (d, 2H), 7.86 (d, 2H). (NMR matches literature values) Activity test performed on di-n-hexyl carbodiimide successful, polymer solid achieved within 24 hrs.

(S)-(−)-1,1′-Bi-2,2′-naphthoxy-titanium(IV) diisopropoxide (Cat-5): The exact same procedure used for Cat-4 was used here. 0.999 g (3.52 mmol) titanium tetraisopropoxide and 1.005 (3.51 mmol) (S)-BINOL purchased from TCI.

Yield: 1.5101 g (96 %). $^1$H NMR (300 MHz, CDCl$_3$ stored over molecular sieves) $\delta$ (ppm): 1.06 (d, 12H), 4.49 (m, 2H), 6.75 (d, 2H), 7.15 (d, 2H), 7.34 (m, 4H), 7.46 (d, 2H), 7.86 (d, 2H). (NMR matches literature values) Activity test performed on di-n-hexyl carbodiimide successful, polymer solid achieved within 24 hrs.

(R)-(+)−3,3-dibromo-1,1′-bi-2,2′-naphthoxy-titanium(IV) di-tert-butoxide (Cat-7): The exact same procedure used for Cat-4 was used here. 0.779 g (2.3 mmol) titanium tetra-tert-butoxide and 1.009 g (2.3 mmol) (R)-(+)−3,3-dibromo-1,1′-bi-2,2′-naphthol (Br$_2$-BINOL) purchased from Aldrich.

Yield: 0.865 g (58 %). $^1$H NMR (300 MHz, CDCl$_3$ stored over molecular sieves) $\delta$ (ppm): 1.02 (s, 18H), 6.93 - 7.20 (m, 4H), 7.21 – 7.41 (d, 4H), 8.06 (s, 2H). Activity test performed on di-n-hexyl carbodiimide successful, polymer solid achieved within 24 hrs.

Trichloro-titanium(IV) 2,2,2-trifluoroethoxide (Cat-15): 3.768 g (20 mmol) of titanium tetrachloride was added to a top-sealing Schlenk flask in the dry box. The flask was sealed and removed from the dry box and attached to a Schlenk manifold. After cooling the
TiCl₄ to 0 °C, 10 mL of distilled, dry DCM was cannulated into the flask. The mixture was cooled again and 2.00 g (20 mmol) of pre-distilled 2,2,2-trifluoroethanol was cannulated into the flask resulting in a yellow coloration. Flask was sealed and stirred at r.t. overnight followed by removal of volatile by vacuum. The yellow-white solids were washed 3 times with dry hexanes which was removed via cannula. Final drying of the white solids was performed followed by transfer of the solids into the dry box for cold storage.

Yield: 1.460 g (29 %) (yield is low due to inability to remove a lot of catalyst from the flask because of static). Activity test performed on di-n-hexyl carbodiimide, solidification occurred within 1 hour.

3.14.7 Characterization of Monomers

Due to the insolubility of most ureas synthesized, proper characterization of them was limited. Therefore, successful urea synthesis is verified by obtainment and characterization of the resulting carbodiimides following dehydration. Most monomers obtained are oils at room temperature. Monomers that are a solid at room temperature can be identified by the reporting of a melting point.

\textit{N-}(3\text{-}\text{bromophenyl})\text{-}\textit{N'}-\text{(n-octadecyl)} \text{carbodiimide (Mono-36)}: \text{The procedure described in Section 3.14.3 was used and any changes noted below. 4.811 g (28 mmol) of 3-bromoaniline was combined with 8.883 g (30 mmol) of octadecyl isocyanate resulting in white needle crystals which precipitated from CHCl₃. The urea was obtained in two crops by aspiration filtration from CHCl₃ through recrystallization. Total mass urea} = 10.13 g (77 %).
4.083 g (16 mmol) of PPh₃, 0.8 mL (16 mmol) of Br₂, and 4.33 mL (33 mmol) of TEA diluted in approximately 30 mL of DCM was used to dehydrate 7.283 g (16 mmol) of the urea. After purification of the monomer through a short bus silica gel column using DCM as the mobile phase, pure waxy white solid monomer was obtained following full removal of volatiles. Yield: 58 %. m.p. 30 – 32 °C, ¹H NMR (300 MHz, CDCl₃) δ(ppm): 0.88 (t, 3H), 1.00 – 1.50 (br, 30H), 1.68 (m, 2H), 3.43 (t, 2H), 7.00 (d, 1H), 7.14 – 7.26 (m, 3H). IR(cm⁻¹): 3052 (m, C-H aryl), 2927 (vs, C-H alkyl), 2854 (s, C-H alkyl), 2141 (vs, N=C=N), 1588 (s, C=C aryl). HRMS-ESI: M_{theoretical} = 449.2526, M_{sample} = 449.2534, ∆M = -0.93 mmass units (-2.08 ppm), C₂₅H₄₁BrN₂.

**N-(3-cyanophenyl)-N'-(n-octadecyl) carbodiimide (Mono-37):** The procedure described in Section 3.14.3 was used and any changes noted below. 0.989 g (8 mmol) of 3-cyanoaniline was combined with 2.469 g (8 mmol) of octadecyl isocyanate resulting in white needle crystals which precipitated from CHCl₃. The urea was filtered from CHCl₃ and recrystallized from boiling toluene. Total mass urea = 2.709 g (78 %).

1.7179 g (6.5 mmol) of PPh₃, 0.37 mL (7.2 mmol) of Br₂, and 2.04 mL (14.7 mmol) of TEA diluted in approximately 30 mL of DCM was used to dehydrate 2.709 g (6.5 mmol) of the urea. After purification of the monomer through a short bus silica gel column using DCM as the mobile phase, a light yellow oil monomer was obtained following full removal of volatiles. Yield: 68 %. ¹H NMR (300 MHz, CDCl₃) δ(ppm): 0.87 (t, 3H), 1.00 – 1.50 (br, 30H), 1.68 (m, 2H), 3.45 (t, 2H), 7.29 – 7.41 (m, 2H), 7.51 - 7.75 (m, 2H). IR(cm⁻¹):
N-(3-nitrophenyl)-N’-(n-octadecyl) carbodiimide (Mono-38): The procedure described in Section 3.14.3 was used and any changes noted below. 1.731 g (13 mmol) of 3-nitroaniline was combined with 3.755 g (13 mmol) of octadecyl isocyanate resulting in white needle crystals which precipitated from CHCl₃. The urea was recrystallized from CHCl₃. Total mass urea = 3.079 g (57 %)

1.487 g (5.7 mmol) of PPh₃, 0.32 mL (6.2 mmol) of Br₂, and 1.77 mL (12.8 mmol) of TEA diluted in approximately 30 mL of DCM was used to dehydrate 2.461 g (5.7 mmol) of the urea. After purification of the monomer through a short bus silica gel column using DCM as the mobile phase, a light yellow solid monomer was obtained following full removal of volatiles. Yield: 52 %. m.p.: 36 – 38 °C. ¹H NMR (300 MHz, CDCl₃) δ(ppm): 0.88 (t, 3H), 1.00 – 1.50 (br, 30H), 1.71 (m, 2H), 3.49 (t, 2H), 7.37 – 7.44 (m, 2H), 7.91 – 7.95 (m, 2H). IR(cm⁻¹): 3054 (m, C-H aryl), 2926 (vs, C-H alkyl), 2854 (s, C-H alkyl), 2147 (vs, N=C=N), 1533 (vs, NO₂), 1353 (s, NO₂). HRMS-ESI: M_{theoretical} = 416.3272, M_{sample} = 416.3281, ΔM = -0.92 mmass units (-2.20 ppm), C_{25}H₄₁N₃O₂.

N-(1-naphthyl)-N’-(n-octadecyl) carbodiimide (Mono-39): This monomer was made many times throughout this research with continual procedural improvements, however, the procedure described in Section 3.14.3 presents the most used and most successful procedure which was applied to many other monomer synthesis techniques throughout. Any specifics to this reaction are listed here. 9.9286 g (69 mmol) of
1-aminonaphthalene was combined with 25 g (85 mmol) of octadecyl isocyanate (better yields result from a slight excess of isocyanate) in DCM. Due to the reduced nucleophilicity of the aminonaphthalene precursor, these reagents can be combined quickly at room temperature without any significant exothermic behavior. Formation of the urea can be achieved by stirring at room temperature or accelerated by refluxing. Upon completion, the DCM is removed by rotary evaporation yielding purple-white solids. Recrystallization of the solids is performed in boiling EtOH and the white needle crystals are filtered and dried by vacuum. Total mass urea = 28.05 g (92 %). Cleanest monomer results from using pre-made dibromotriphenylphosphorane salt for dehydration, although at the expense of a slight decrease in yield. Dehydration is performed in DCM at room temperature overnight and purification after repeated pentane quenching is best using a short bus silica gel column and DCM as the mobile phase resulting in a clear yellow hued oil after full drying. Yields typically range from 70 – 80 % and the monomer oil freezes at the storage temperature, improving shelf life.

m.p.: 6 – 8 °C. ¹H NMR (300 MHz, CDCl₃) δ(ppm): 0.86 (t, 3H), 1.24 (br, 28H), 1.43 (m, 2H), 1.71 (m, 2H), 3.45 (t, 2H), 7.28 (d, 1H), 7.38 (t, 1H), 7.48 (m, 2H), 7.59 (d, 1H), 7.79 (m, 1H), 8.26 (m, 1H). ¹³C-NMR (75 MHz, CDCl₃) δ(ppm): 14.4, 23.0, 27.0, 29.4, 29.6, 29.8 (overlapped), 29.9 (br, overlapped), 31.7, 32.1, 47.1, 119.8, 123.8, 124.6, 126.0 (overlapped), 126.6, 128.0, 129.1, 134.6, 135.8, 137.5. IR(cm⁻¹): 3052.3 (m, C-H aryl), 2926.5 (vs, C-H alkyl), 2853.7 (s, C-H alkyl) 2134.8 (vs, N=C=N). 1575 (s, C=C aryl).
HRMS-ESI: $M_{\text{theoretical}} = 420.35045$, $M_{\text{sample}} = 420.34974$, $\Delta M = 0.71$ mmass units (1.70 ppm), $C_{29}H_{44}N_2$.

$N$-(1-naphthyl)-$N'$-(n-dodecyl) carbodiimide (Mono-40): The exact same procedure used for Mono-39 is used here. Differences associated with using dodecyl isocyanate precursor are as follows: Urea recrystallization from a 50:50 mixture of MeOH and EtOH works more effectively. Resulting monomer is also clear oil with a tint of yellow but this monomer will not freeze at temperatures above -25 °C.

Yield: 83 %. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm): 0.88 (t, 3H), 1.25 (br, 16H), 1.44 (m, 2H), 1.73 (m, 2H), 3.47 (t, 2H), 7.28 (d, 1H), 7.40 (t, 1H), 7.46 -7.52 (m, 2H), 7.61 (d, 1H), 7.81 (m, 1H), 8.28 (m, 1H). IR(cm$^{-1}$): 3050.8 (m, C-H aryl), 2924.5 (vs, C-H alkyl), 2853.2 (s, C-H alkyl) 2131.9 (vs, N=C=N). 1574.6 (s, C=C aryl). HRMS-ESI: $M_{\text{theoretical}} = 336.25655$, $M_{\text{sample}} = 336.25660$, $\Delta M = -0.05$ mmass units (0.16 ppm), $C_{23}H_{32}N_2$.

$N$-(2-naphthyl)-$N'$-(n-octadecyl) carbodiimide (Mono-41): The exact same procedure used for Mono-39 is used here. Differences associated with using 2-naphthylamine precursor are as follows: Resulting monomer is a white solid at room temperature.

Yield: 62 %. m.p. 42 – 45 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm): 0.88 (t, 3H), 1.25 (br, 28H), 1.44 (m, 2H), 1.72 (m, 2H), 3.46 (t, 2H), 7.24 (d, 1H), 7.26 – 7.49 (m, 3H), 7.72 – 7.80 (m, 3H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$(ppm): 14.4, 23.0, 27.0, 29.4, 29.6, 29.8 (overlapped), 29.9 (br, overlapped), 31.6, 32.2, 47.2, 120.6, 123.4, 125.3, 126.7, 127.3, 127.9, 129.4, 131.2, 134.3, 136.2, 138.4. IR(cm$^{-1}$): 3053 (m, C-H aryl), 2916 (vs, C-H alkyl),
2850 (s, C-H alkyl) 2142 (vs, N=C=N), 1597 (s, C=C aryl). HRMS-ESI: $M_{\text{theoretical}} = 421.3577$, $M_{\text{sample}} = 421.3588$, $\Delta M = -1.12$ mmass units (-2.66 ppm), C$_{29}$H$_{44}$N$_2$.

**N-(1-pyrenyl)-N’-(n-octadecyl) carbodiimide (Mono-42):** The exact same procedure used for Mono-39 is used here. Differences associated with using 1-aminopyrene precursor are as follows: Urea formation requires refluxing in DCM to fully dissolve 1-aminopyrene properly. Resulting monomer is a yellow solid at room temperature.  

Yield: 74 %. m.p.: 44 – 46 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm): 0.88 (t, 3H), 1.25 (br, 28H), 1.49 (m, 2H), 1.78 (m, 2H), 3.54 (t, 2H), 7.84 (d, 1H), 7.96 – 8.00 (m, 3H), 8.06 – 8.16 (m, 4H), 8.49 (d, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$(ppm): 14.4, 23.0, 27.1, 29.4, 29.6, 29.8 (overlapped), 29.9 (br, overlapped), 31.7, 32.2, 47.3, 121.6, 123.0, 124.9, 125.0, 125.1, 125.5, 126.4, 126.6, 127.4 (overlapped), 128.4, 131.7, 131.7, 135.1, 135.8. IR(cm$^{-1}$): 3053 (s, C-H aryl), 2985 (m, C-H aryl/alkyl), 2927 (vs, C-H alkyl), 2854 (s, C-H alkyl) 2135 (vs, N=C=N), 1599 (s, C=C aryl). HRMS-ESI: $M_{\text{theoretical}} = 494.3734$, $M_{\text{sample}} = 494.3745$, $\Delta M = -1.15$ mmass units (-2.32 ppm), C$_{35}$H$_{46}$N$_2$.

**N-(2-methyl-1-naphthyl)-N’-(n-octadecyl) carbodiimide (Mono-43):** The exact same procedure used for Mono-39 is used here. No differences were observed by using 2-methyl-1-naphthylamine precursor instead. The resulting monomer is colorless oil.  

Yield: 86 %. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm): 0.88 (t, 3H), 1.26-1.49 (br, 30H), 1.70 (m, 2H), 2.54 (s, 3H), 3.43 (t, 2H), 7.29 (d, 1H), 7.37 – 7.59 (m, 3H), 7.78 (d, 1H), 8.23 (d, 1H). IR(cm$^{-1}$): 3051 (w, C-H aryl), 2925 (vs, C-H aryl/alkyl), 2854 (s, C-H alkyl), 2148 (vs, N=C=N), 1570 (m, C=C aryl).
**N-(4-indanyl)-N’-(n-dodecyl) carbodiimide (Mono-44):** The same procedure used for Mono-39 is used here. The differences to the procedure as a result of using 4-aminooindan and dodecyl isocyanate are described. Pink urea crystals were recrystallized from a 50:50 mixture of EtOH and H$_2$O (94 % Yield). Purification of monomer was performed using a 20:80 volumetric ratio of hexanes:DCM as the mobile phase. The resulting monomer after drying is colorless oil.

Yield: 73 %. $^1$H NMR (300 MHz, CDCl$_3$) δ(ppm): 0.88 (t, 3H), 1.25 – 1.43 (br, 28H), 1.67 (m, 2H), 2.08 (m, 2H), 2.93 (dd, 4H) 3.38 (t, 2H), 6.87 (d, 1H), 6.98 (d, 1H), 7.08 (t, 1H). $^{13}$C-NMR (75 MHz, CDCl$_3$) δ(ppm): 14.4, 23.0, 25.0, 27.1, 29.4, 29.6, 29.8 (overlapped), 29.9 (br, overlapped), 30.9, 31.5, 32.2, 33.4, 47.3, 120.9, 121.4, 127.5, 136.2 136.7, 138.7, 146.2. IR (cm$^{-1}$): 3059 (w, C-H aryl), 2925 (vs, C-H alkyl), 2852 (s, C-H alkyl) 2135 (vs, N=C=N), 1587 (s, C=C aryl). HRMS-ESI: M$_{theoretical}$ = 327.2795, M$_{sample}$ = 327.2797, ΔM = -0.25 mmass units (-0.77 ppm), C$_{22}$H$_{34}$N$_2$.

**N-(2-fluorenyl)-N’-(n-octadecyl) carbodiimide (Mono-45):** The same procedure used for Mono-39 is used here. The differences to the procedure as a result of using 2-aminofluorene are described. Urea was recrystallized from EtOH (98 % Yield). Column chromatography was performed using DCM as the mobile phase and resulting monomer is a yellow solid at room temperature.

Yield: 26 % (some lost, human error). m.p. 42 – 44 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ(ppm): 0.88 (t, 3H), 1.24 – 1.43 (br, 28H), 1.71 (m, 2H), 3.43 (t, 2H), 3.87 (s, 2H), 7.10 (d, 1H), 7.24 – 7.34 (m, 2H), 7.36 (t, 1H), 7.52 (d, 1H), 7.66 – 7.73 (m, 2H). IR (cm$^{-1}$): 3053
\((m, \text{C-H} \text{aryl}), 2927 \text{ (vs, C-H} \text{ alkyl}), 2854 \text{ (s, C-H} \text{ alkyl}) \) 2135 \text{ (vs, N=C=N), 1612} \& 1579 \text{ (w, C=C} \text{ aryl).}

\textit{N-(1-naphthylmethyl)-N'-(n-dodecyl) carbodiimide (Mono-46):} The same procedure used for Mono-39 is used here. The differences to the procedure as a result of using 1-naphthylmethylamine and dodecyl isocyanate are described. 1-naphthylmethylamine should be cooled to 0 °C in DCM before addition to isocyanate due to the increased reactivity of the amine nitrogen. Urea was recrystallized from MeOH (85 % Yield). Column chromatography was performed using DCM as the mobile phase and resulting monomer is light yellow oil at room temperature.

Yield: 82 %. \(^1\text{H NMR (300 MHz, CDCl}_3\text{) \(\delta\text{ (ppm): 0.89 (t, 3H), 1.05} \text{ – 1.40 (br, 20H), 2.95 (t, 2H), 4.78 (s, 2H), 7.42} \text{ – 7.59 (m, 4H), 7.81 (d, 1H), 7.88 (d, 1H), 8.06 (d, 1H). IR (cm}^{\text{-1}}\text{: 3047 (m, C-H aryl), 2924 (vs, C-H} \text{ alkyl), 2853 (s, C-H} \text{ alkyl) 2127 (vs, N=C=N), 1693 (m, NCN-CH}_2\text{-aryl). HRMS-ESI: M}_{\text{theoretical}}\text{ = 350.2722, M}_{\text{sample}}\text{ = 350.2725, \(\Delta M = -0.3 \text{ mmass units (-0.85 ppm), C}_{24}\text{H}_{34}\text{N}_2.}}\)

\textit{Di-(1-naphthyl) carbodiimide (Mono-47):} The same procedure used for Mono-39 is used here. The differences to the procedure as a result of using 1-isocyanatonaphthalene and 1-aminonaphthalene are described. White urea solids were recrystallized from MeOH (69 % Yield). Initial quenching of DCM dehydration solution with pentane was successful to remove most of the unwanted salt but after rotary evaporation of all solvent, pure pentane would not redissolve the solid monomer. Therefore the excessive pentanes washing cycle was by-passed and column chromatography was performed with DCM as the mobile phase.
The initial clear band eluent was collected and reduced to a white powder and dried fully by vacuum.

Yield: 52 %. m.p. 84 – 87 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ(ppm) 7.44 – 7.48 (m, 4H), 7.53 – 7.60 (m, 4H), 7.71 (d, 2H), 7.87 (d, 2H), 8.38 (d, 2H). $^{13}$C-NMR (75 MHz, CDCl$_3$) δ(ppm): 121.2, 123.7, 125.8, 126.1, 126.7, 126.9, 128.2, 129.0, 134.3, 134.7, 135.1. IR (cm$^{-1}$): 3053 (s, C-H aryl), 2141 (vs, N=C=N), 1591 (m, C=C), 1572 (s, C=C).

$N$-(5-quinolyl)-$N'$-(n-octadecyl) carbodiimide (Mono-48): The same procedure used for Mono-39 is used here. Differences associated with using the 5-aminoquinoline precursor are described. Urea was obtained by refluxing in DCM overnight followed by removal of DCM by rotary evaporation and recrystallization of solids from EtOH (95 % Yield). Dehydration of this urea was performed by making the dibromotriphenylphosphorane salt in-situ resulting in a dark brown monomer solid which did not polymerize. Column chromatography in DCM using 5% pyridine removed some of the brown coloration but most of it persisted. This dehydration procedure was later improved for the synthesis of Mono-49 but some characterization of this monomer is described below.

Yield: 95 % (crude). m.p. 35 – 40 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ(ppm): 0.88 (t, 3H), 1.25 – 1.55 (br, 30H), 1.73 (m, 2H), 3.49 (t, 2H), 7.29 – 7.46 (m, 2H), 7.63 (t, 1H), 7.87 (d, 1H), 8.61 (d, 1H), 8.91 (m, 1H). IR (cm$^{-1}$): 3053 (m, C-H aryl), 2924 (vs, C-H alkyl), 2854 (s, C-H alkyl) 2139 (vs, N=C=N), 1589 (m, C=C), 1572 (m, C=C).

$N$-(5-quinolyl)-$N'$-(n-dodecyl) carbodiimide (Mono-49): The same procedure used for Mono-39 is used here. Differences associated with using the 5-aminoquinoline and
dodecyl isocyanate precursors are described. Urea was obtained by refluxing in DCM overnight followed by removal of DCM by rotary evaporation and recrystallization of solids from MeOH (66 % Yield). Dehydration of this urea was performed using the pre-made dibromotriphenylphosphorane salt which eliminates the presence of free bromine in the reaction mixture. Following dehydration, the reaction was quenched with 200 mL of pentane and allowed to stir for 3 hours to allow as much salt as possible to crash out. After filtering, the filtrate was reduced and the pentane quenching cycle repeated. TLC on the crude yellow oil revealed DCM to not be an effective mobile phase for this monomer. After testing multiple mobile phases by TLC, column chromatography was performed using a 20:80 volumetric ratio of ethyl acetate:DCM. After full drying the monomer was obtained as a yellow oil.

Yield: 79 % ¹H NMR (300 MHz, CDCl₃) δ(ppm): 0.88 (t, 3H), 1.20 – 1.60 (br, 18H), 1.73 (m, 2H), 3.49 (t, 2H), 7.33 (d, 1H), 7.40 (m, 1H), 7.63 (t, 1H), 7.86 (d, 1H), 8.60 (d, 1H), 8.91 (m, 1H). ¹³C-NMR (75 MHz, CDCl₃) δ(ppm): 14.4, 22.9, 27.0, 29.3, 29.6, 29.7, 29.7-29.8 (overlapped), 29.9, 31.6, 32.1, 47.1, 120.0, 121.0, 124.4, 125.8, 129.4, 132.4, 135.0, 138.0, 149.2, 151.1. IR (cm⁻¹): 3062 & 3030 (w, C-H aryl), 2925 (vs, C-H alkyl), 2854 (s, C-H alkyl) 2133 (vs, N=C=N), 1589 (m, C=C), 1610 & 1570 (s, C=C and C=N ring stretch). HRMS-ESI: M_{theoretical} = 338.2591, M_{sample} = 338.2593, ∆M = -0.23 mmass units (-0.69 ppm), C₂₂H₃₁N₃.
**N-(4-methyl-1-naphthyl)-N’-(n-dodecyl) carbodiimide (Mono-50):** The same procedure used for Mono-39 is used here. 4-methyl-1-aminonaphthylamine was synthesized from 1-methylnaphthalene as described:

**4-Nitro-1-methylnaphthalene:**

42.54 (0.30 mol) of 1-methylnaphthalene was added to a 300 mL, 3-necked round bottom flask. 40 mL of acetic anhydride was added and the solution was cooled to 0 °C using an ice bath. 26.6 mL of >90% fuming nitric acid (36 – 40 grams total or 0.635 mol) was one drop at a time very slowly with an addition funnel not allowing the reaction temperature to exceed 15 °C which was carefully monitored by a thermometer. (CAUTION: this reaction is extremely exothermic and will get out of control if it gets too hot and the HNO₃ is added too quickly, each drop of HNO₃ was observed to raise the solution temperature about 2 °C even when stirring in an ice bath. Be patient when executing this step) After all the acid is added, the reaction mixture is allowed to warm to ambient and stirred for 1 hour. The nitrated 1-methylnaphthalene can be crystallized out of the reaction mixture by capping the reaction flask and placing it in a freezer. The resulting yellow needle crystals of 1-nitro-4-methylnaphthalene are filtered and washed with EtOH then MeOH, collected, and fully dried by vacuum.

Yield: 15.46g (27 %). m.p. 61-64 °C (lit. 68 °C). \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 2.79 (s, 3H), 7.39 (d, 1H), 7.60 – 7.75 (m, 2H), 8.09 – 8.17 (m, 2H), 8.61 (d, 1H). \(^{13}C\)-NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 20.5, 123.9, 124.1, 124.9, 125.2, 125.4, 127.4, 129.2, 133.4, 142.6, (ipso-NO\(_2\) carbon was not resolved due to extremely slow relaxation time). IR
(cm$^{-1}$): 3084 (m, C-H aryl), 3057 (m, C-H aryl), 3016 (m, C-H aryl), 2964 (m, C-H methyl),
1599 (m, C=C), 1576 (m, C=C), 1510 (vs, NO$_2$), 1334 (vs, NO$_2$ bend).

**4-methyl-1-aminonaphthalene:** 15.46 g (82.6 mmol) of 4-nitro-1-
methylnaphthalene was added to a jar and dissolved in 40 mL of toluene with a stir bar.
277.5 mg of Pd/C (10 %) was added to the solution. Jar was lowered into a Parr vessel with a
moat of toluene added around the jar to limit toluene from evaporating out of the jar. The
Parr reactor was sealed and pressurized with 60 psi of H$_2$ gas. The Parr reactor was partially
submerged in an oil bath on a stir plate and the reaction solution was heated at 100 °C for
24 hours with continual H$_2$ pressure. After cooling, the jar was removed from the vessel and
the purple-red solution was filtered through a plug of celite to remove catalyst. After drying
over Na$_2$SO$_4$ for 15 min, the filtrate was dried to a red oil.

Yield: 10.049 g (77 %). $^1$H NMR (300 MHz, CDCl$_3$) δ/ppm: 2.60 (s, 3H), 4.03
(s, br, 2H), 7.71 (d, 1H), 7.13 (d, 1H), 7.48 – 7.55 (m, 2H), 7.87 (d, 1H), 7.97 (d, 1H).
$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm): 19.2, 109.9, 121.6, 124.4, 124.9, 125.1, 125.2, 125.9,
127.0, 133.4, 140.7. IR (cm$^{-1}$): 3348, 3375 (br, N-H). HRMS-ESI: $M_{\text{theoretical}}$ = 157.0964,
$M_{\text{sample}}$ = 157.0963, $\Delta M$ = 0.13 mmass units (0.84 ppm), C$_{11}$H$_{11}$N.

Reaction with dodecyl isocyanate in DCM refluxed overnight yielded white solid
urea which was recrystallized from MeOH. Subsequent dehydration resulted in Mono-50
as a yellow oil after CC purification using DCM as the mobile phase.

Yield: 73 % $^1$H NMR (300 MHz, CDCl$_3$) δ/ppm: 0.88 (t, 3H), 1.20 – 1.50 (br, 18H),
1.70 (m, 2H), 2.65 (s, 3H), 3.46 (t, 2H), 7.18 – 7.25 (m, 2H), 7.51 – 7.56 (m, 2H), 7.94
(d, 1H), 8.31 (d, 1H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$(ppm): 14.4, 19.5, 22.9, 27.1, 29.4, 29.6, 29.8 (overlapped), 29.9 (overlapped), 31.7, 32.2, 47.2, 119.4, 124.3, 124.4, 125.7, 126.4, 126.7, 129.0, 131.0, 133.5, 135.6, 136.4. IR (cm$^{-1}$): 3066 (w, C-H aryl), 3033 (w, C-H aryl), 2925 (vs, C-H alkyl), 2854 (s, C-H alkyl) 2135 (vs, N=C=N), 1581 (m, C=C). HRMS-ESI: $M_{\text{theoretical}}$ = 351.2795, $M_{\text{sample}}$ = 351.2796, $\Delta M$ = -0.09 mmass units (-0.24 ppm), C$_{24}$H$_{34}$N$_2$.

$N$-(4-methyl-1-naphthyl)-$N'$-(n-hexyl) carbodiimide (Mono-51): 4-methyl-1-aminonaphthalene was synthesized as shown for Mono-50 and reacted with hexyl isocyanate. The resulting urea was recrystallized twice from MeOH (62 %). Dehydration was performed and after 3 pentane quenching cycles the yellow oil looked clean enough to bypass the column chromatography step. The yellow oil was fully dried and filtered through syringe filter to remove residual salts that crashed out upon drying.

Yield: 67% $^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm): 0.88 (t, 3H), 1.20 – 1.50 (br, 6H), 1.71 (m, 2H), 2.66 (s, 3H), 3.46 (t, 2H), 7.18 – 7.25 (m, 2H), 7.49 – 7.56 (m, 2H), 7.94 (d, 1H), 8.31 (d, 1H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$(ppm): 14.4, 19.5, 22.8, 26.7, 31.6, 31.7, 47.2, 119.4, 124.3, 124.4, 125.7, 126.4, 126.7, 129.0, 131.0, 133.5, 135.6, 136.3. IR (cm$^{-1}$): 3066 (m, C-H aryl), 3033 (m, C-H aryl), 2925 (vs, C-H alkyl), 2854 (s, C-H alkyl), 2135 (vs, N=C=N), 1581 (m, C=C).

$N$-(4-bromo-1-naphthyl)-$N'$-(n-dodecyl) carbodiimide (Mono-52): The same procedure used for Mono-39 is used here. The differences to the procedure as a result of using 4-bromo-1-aminonaphthalene and dodecyl isocyanate are described. Reagents were distilled together in DCM and resulting urea was recrystallized from 50:50 MeOH:EtOH
(60% Yield). Subsequent dehydration resulted in a brown hued oil which was purified by column using DCM as the mobile phase.

Yield: 77 % $^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm): 0.88 (t, 3H), 1.20 – 1.50 (br, 18H), 1.70 (m, 2H), 3.48 (t, 2H), 7.14 (d, 1H), 7.55 (t, 1H), 7.61 (t, 1H), 7.68 (d, 1H), 8.18 (d, 1H), 8.30 (d, 1H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$(ppm):14.4, 22.9, 27.0, 29.3, 29.6, 29.7, 29.8, 29.9 (overlapped), 31.6, 32.2, 47.1, 118.1, 120.0, 124.4, 126.8, 127.3, 128.0, 129.9, 130.2, 132.8, 134.9, 137.9. IR (cm$^{-1}$): 3068 & 3043 (w, C-H aryl), 2924 (vs, C-H alkyl), 2852 (s, C-H alkyl) 2139 (vs, N=C=N), 1583 (vs, C=C). HRMS-ESI: $M_{\text{theoretical}}$ = 415.1743, $M_{\text{sample}}$ = 415.1742, $\Delta M$ = -0.07 mmass units (-0.17 ppm), C$_{23}$H$_{31}$BrN$_2$.

$N$-(4-chloro-1-naphthyl)-$N'$(n-dodecyl) carbodiimide (Mono-53): The same procedure used for Mono-39 is used here. The differences to the procedure as a result of using 4-chloro-1-aminonaphthalene and dodecyl isocyanate are described. Reagents were distilled together in DCM and resulting urea was recrystallized from 50:50 MeOH:EtOH (84% Yield). Subsequent dehydration resulted in colorless oil which was purified by column using DCM as the mobile phase.

Yield: 82 % $^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm): 0.88 (t, 3H), 1.20 – 1.50 (br, 18H), 1.72 (m, 2H), 3.48 (t, 2H), 7.20 (d, 1H), 7.48 (d, 1H), 7.53 – 7.64 (m, 2H), 8.21 (d, 1H), 8.31 (d, 1H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$(ppm):14.4, 22.9, 27.0, 29.3, 29.6, 29.7, 29.8, 29.9 (overlapped), 31.6, 32.2, 47.1, 119.5, 124.3, 124.6, 126.2, 126.7, 127.7, 130.0, 131.6, 135.0, 137.1. IR (cm$^{-1}$): 3070 & 3047 (w, C-H aryl), 2925 (vs, C-H alkyl), 2854 (s, C-H alkyl),
2137 (vs, N=C=N), 1585 (s, C=C). HRMS-ESI: $M_{\text{theoretical}} = 371.2249$, $M_{\text{sample}} = 371.2248$, $\Delta M = 0.06$ mmass units (0.17 ppm), $C_{23}H_{31}ClN_2$.

$N$-(4-methoxy-1-naphthyl)-$N'$-(n-dodecyl) carbodiimide (Mono-54): The same procedure used for Mono-39 is used here. The differences to the procedure as a result of using 4-methoxy-1-aminonaphthalene and dodecyl isocyanate are described. 4-methoxy-1-aminonaphthalene was synthesized from purchased 4-methoxy-1-nitronaphthalene using the same procedure as described for the hydrogenation of 4-methyl-1-nitronaphthalene (See Mono-50).

4-methoxy-1-aminonaphthalene – 5.46 g (27 mmol) of 4-methoxy-1-nitronaphthalene was dissolved in 50 mL toluene and hydrogenated in a Parr reactor using a small amount of 10% Pd/C catalyst. After stirring under $H_2$ pressure at 50 psi and a temperature of 80 °C for 10 hours, the resulting pale yellow solution was removed from the reactor and filtered through Celite. (Note: Discoloration of this amine occurs very rapidly and protection of the amine from oxidation by reacting with isocyanate needs to be done directly following filtration) No yield or characterization done due to instability of the amine. Amine was protected by addition of dodecyl isocyanate to form white fluffy urea after recrystallization from 50:50 EtOH:n-BuOH. (85 % Yield overall from starting 4-methoxy-1-nitronaphthalene)

Subsequent dehydration resulted in yellow oil which was purified by column using DCM as the mobile phase.
Yield: 87% $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 0.88 (t, 3H), 1.20 – 1.50 (br, 18H), 1.71 (m, 2H), 3.44 (t, 2H), 3.99 (s, 3H), 6.74 (d, 1H), 7.20 (d, 1H), 7.48 – 7.55 (m, 2H), 8.22 (d, 2H). $^{13}$C-NMR (75 MHz, CDCl$_3$) δ (ppm): 14.4, 22.9, 27.0, 29.4, 29.6, 29.8 (overlapped), 29.9 (overlapped), 31.7, 32.2, 47.3, 55.9, 103.9, 119.5, 122.2, 123.5, 126.0, 126.2, 126.7, 129.6, 129.7, 137.0, 152.9. IR (cm$^{-1}$): 3070 & 3043 (w, C-H aryl), 3001 (w, C-H MeO), 2924 (vs, C-H alkyl), 2852 (s, C-H alkyl) 2129 (vs, N=C=N), 1589 (s, C=C), 1267 (s, Aryl C-O stretch), 1020 (m, alkyl C-O stretch). HRMS-ESI: $M_{\text{theoretical}} = 367.2744$, $M_{\text{sample}} = 367.2745$, $\Delta M = -0.13$ m mass units (-0.37 ppm), C$_{24}$H$_{34}$N$_2$O.

$N$-((S)-(+)-1,2,3,4-tetrahydro-1-naphthyl)-$N'$-(n-dodecyl) carbodiimide (Mono-55): The same procedure used for Mono-39 is used here. The differences to the procedure as a result of using (S)-(+)-1,2,3,4-tetrahydro-1-naphthylamine and dodecyl isocyanate are described. Reagents were distilled together in DCM and resulting urea was recrystallized from EtOH (60% Yield). Subsequent dehydration resulted in yellow oil which was purified by column using DCM as the mobile phase. Yield: 27%. Due to low yield all monomer was used for attempted polymerization and no characterization was performed except for confirmation of N=C=N absorption by IR. Due to unsuccessful polymerization, this monomer was never remade.

$N$-((S)-(+)-1,2,3,4-tetrahydro-1-naphthyl)-$N'$-(ethyl) carbodiimide (Mono-56): The same procedure used for Mono-39 is used here. The differences to the procedure as a result of using (S)-(+)-1,2,3,4-tetrahydro-1-naphthylamine and ethyl isocyanate are described. Due to the size and reactivity of ethyl isocyanate, a DCM diluted amine solutin
must be cooled to 0 °C using an ice bath prior to addition. Urea precipitation occurred almost immediately upon dropwise addition of ethyl isocyanate. Resulting urea was recrystallized from EtOH, although it is suspected MeOH would have worked also (70 % Yield). Subsequent dehydration resulted in yellow oil which was purified by column using DCM as the mobile phase. Yield 39 %. Due to low yield all monomer was used for attempted polymerization and no characterization was performed except for confirmation of N=C=N absorption. IR (cm⁻¹) 3054 (s, C-H aryl), 2980 (m, C-H alkyl), 2935 (s, C-H alkyl), 2118 (vs, N=C=N). This monomer was never remade.

N-((R)-(+)1-phenylethyl)-N’-(1-naphthyl) carbodiimide (Mono-57): The same procedure used for Mono-39 is used here. The differences to the procedure as a result of using (R)-(+)1-phenylethylamine and 1-naphthyl isocyanate are described. Resulting urea was washed with boiling EtOH but never fully dissolved. Solids were collected and dried (84 % Yield). Subsequent dehydration resulted in yellow oil product after purification using column chromatography and DCM as the mobile phase. Yield 77 %. IR (cm⁻¹) 3050 (s, C-H aryl), 2976 (s, C-H aryl), 2927 (m, C-H alkyl), 2127 (vs, N=C=N), 1574 (s, C=C). Full characterization was never performed due to unsuccessful polymerization.

N-((S)-(+)1-cyclohexylethyl)-N’-(1-naphthyl) carbodiimide (Mono-58): The same procedure used for Mono-39 is used here. The differences to the procedure as a result of using (S)-(+)1-cyclohexylethylamine and 1-naphthyl isocyanate are described. Resulting urea was washed with boiling EtOH but never fully dissolved. Solids were collected and dried (99 % Yield). Subsequent dehydration resulted in yellow oil product after purification
using column chromatography and DCM as the mobile phase. Yield 82 %. IR (cm\(^{-1}\)) 3049 (m, C-H aryl), 2976 (w, C-H aryl), 2927 (vs, C-H alkyl), 2852 (s, C-H alkyl), 2133 (vs, N=C=N), 1573 (s, C=C). Full characterization was never performed due to unsuccessful polymerization.

\textit{N-((S)-(\text{-}-2-methylbutyl)-N'-(1-naphthyl) carbodiimide (Mono-59):} The same procedure used for Mono-39 is used here. The differences to the procedure as a result of using (S)-(\text{-}-2-methylbutylamine and 1-naphthyl isocyanate are described. Resulting urea was recrystallized in EtOH and dried (75 % Yield). Subsequent dehydration resulted in yellow oil product after purification using column chromatography and DCM as the mobile phase. Yield 28 %. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 0.95 (t, 3H), 1.03 (d, 3H), 1.31 (m, 2H), 1.71 (m, 1H), 3.39 (m, 2H), 7.29 (d, 1H), 7.40 (t, 1H), 7.44 – 7.55 (m, 2H), 7.81 (d, 1H), 8.29 (d, 1H). IR (cm\(^{-1}\)) 3051 (m, C-H aryl), 2962 (s, C-H alkyl), 2929 (m, C-H alkyl), 2875 (m, C-H alkyl), 2137 (vs, N=C=N), 1574 (s, C=C).

\textit{N-((R)-(\text{+}-2,6-dimethylheptyl)-N'-(1-naphthyl) carbodiimide (Mono-60):} The synthesis of (R)-(\text{+}-2,6-dimethylheptyl isocyanate from (R)-Pulegone was previously performed by our group and my recommendation for the best synthesis description comes from Yujie Lu’s thesis.\(^{32}\) Each product was characterized by IR and \(^1\)H NMR and successfully compared to reported values.

\textit{(R)-(\text{+}-citronellic acid:} Yield: 41 %. b.p. 130 - 132 °C (3.8 mmHg).

\textit{(R)-(\text{+}-2,6-dimethylheptanoic acid:} Yield: 91 %. b.p. 100 – 102 °C (0.6 mmHg).

\textit{(R)-(\text{+}-2,6- dimethylheptanoic acid chloride:} Yield: 80 %. b.p. 67 - 69 °C (1.2 mm Hg).
(R)-(+-)2,6-dimethylheptyl isocyanate: Yield: 48 %. b.p. 47 – 50 °C (0.8 mmHg).

After reacting the resulting isocyanate with 1-naphthylamine, the resulting white urea was recrystallized in MeOH (Yield: 78 %). Subsequent dehydration and purification of the carbodiimide through a column using DCM as the mobile phase resulted in a faint yellow oil. Yield: 83 %.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm): 0.87 (d, 6H), 1.04 (d, 3H), 1.10 – 1.54 (m, 7H), 1.81 (m, 1H), 3.39 (m, 2H), 7.29 (d, 1H), 7.40 (t, 1H), 7.46 – 7.53 (m, 2H), 7.61 (d, 1H), 7.81 (m, 1H), 8.28 (m, 1H). IR (cm$^{-1}$): 3051 (m, C-H aryl), 2954 (vs, C-H alkyl), 2927 (vs, C-H alkyl), 2870 (s, C-H alkyl) 2129 (vs, N=C=N), 1574 (s, C=C).

3.14.8 Characterization of Polymers

Characterization and yields of polymers were reported in the main text body. Appendix (I) shows IR spectra for polymers. $^1$H-NMR was performed on most polymers and are shown in Appendix (II). Due to substantial broadening, little information is derived from NMR spectra at this time and due to the long delay times, long analysis times, and poor resolution of $^{13}$C NMR analyses, this was not performed on most polymers. GPC also results in substantial broadening of eluted peaks. This has been a continual observation of these polymer systems and early experiments performed by Goodwin using a low-angle light scattering detector proved that polymers of similar molecular weight were eluting over a very long range of elution times.$^{26}$ A brief GPC study was performed on some of these polymers and is detailed in Chapter 4. A comprehensive study on GPC characterization is needed but
unavailable at this time. X-ray diffraction (XRD) crystallography was attempted on Poly-39, but no ordered structural information was obtained.

3.15 References


Chapter 4: Regioregularity of Polycarbodiimides

4.1 Introduction to Polycarbodiimide Regioregularity

Differences in regioregularity or stereoregularity can result from inconsistencies when monomers with multiple addition pathways incorporate themselves on to the propagating polymer chain. The outcome of these structural possibilities can have profound effects on the properties of the resulting polymer systems. It was the pioneering discovery of the significance of these polymer properties that earned Ziegler and Natta a Nobel Prize in Chemistry in 1963. When considering commercially important monosubstituted vinyl monomers such as propylene, styrene and vinyl chloride, insertion can occur in a number of ways; head-to-head, head-to-tail, isotactic, syndiotactic, and atactic (Figure 4.1).  

Because the substituted vinylic carbon on these monomers becomes a stereocenter upon polymerization, these possible outcomes are usually referred to as the stereoregularity of the polymer. The stereoregularity can effect many properties of these commercial polymer systems such as crystallinity, thermal stability, processability, tensile strength, chain stiffness, and glass transition temperatures \( (T_g) \), to name a few. \(^{2-7}\) Importance of stereoregularity also translates into the chemistry of helical polymers systems exemplified by the previously discussed PMMA helical polymers in Chapter 1 which generally require highly isotactic polymer systems in order to achieve an excess helical sense. \(^8\)
Our polymer systems are no different, but instead of forming a stereocenter during polymerization, asymmetric carbodiimide monomers can result in polycarbodiimides containing different regioisomers dependant upon the resulting connectivity or positioning of the monomer pendant groups on the polymer chain (Figure 4.2). Therefore, instead of stereoregularity, we refer to these differences as the regioregularity or regioirregularity depending upon the resulting order. Regioregularity does not apply to symmetric polycarbodiimides which contain two identical pendant groups since there is no difference between the resulting regioisomers. By looking further into the mechanism of propagation for these polymer systems, we can deduce that the resulting regioregularity of polycarbodiimides is dictated by the mode of monomer insertion on the amidinate-titanium(IV) active chain end (Figure 4.3). Because of this, very similar pendant groups, such as n-heptyl versus n-hexyl, should not have a dominant mode of monomer insertion and therefore result in regioirregular polycarbodiimides. Oppositely, if the two pendant groups
are significantly different based on electronic, steric, or thermodynamic effects, the resulting regioregularity of the polycarbodiimide may be high and may favor one regioisomer over the
other. To accurately determine the polycarbodiimide regioregularity, two facts must be known; how much of a preferred regioisomer is present and which regioisomer it is (i.e. what pendant group lies on the imine or amine position). Ever since the discovery of polymerizing carbodiimide monomers in a living fashion by our research group, it has been with great interest to develop ways of controlling and analyzing the regioregularity of these polymer systems. Many of the pioneering experiments on polycarbodiimides discussed in Chapter 2 did not have sufficient characterization of the polymer regioregularity and therefore inconclusive results may be attributed to this polymer property. Even today, a definitive way to accurately quantify the regioregularity of polycarbodiimides eludes us, although some progress had been made. The purpose of this chapter will be to summarize and distill previously discussed research on this subject, discuss new trends in polycarbodiimide regioregularity and resulting polymer properties, and define old and new analytical attempts at determining polycarbodiimide regioregularity.

4.2 Early Attempts for Determination of Polycarbodiimide Regioregularity

Since the beginning, Goodwin and Novak were aware of the necessity for determination of polycarbodiimide regioregularity and, in unpublished research, made a few attempts at uncovering a means to do so by analyzing thermal decomposition products by gas chromatography in tandem with mass spectrometry (GC/MS). The decomposition of polycarbodiimides is a unique process that is believed to result from random homolytic
cleavage along the polymer backbone followed by a radical unzipping of the chain (Figure 4.4). The result is a clean return of the polymer to carbodiimide starting material.

![Chemical structure diagram](image)

**Figure 4.4** – Decomposition of symmetric polycarbodiimides results in a clean return to monomer through homolytic cleavage of the polymer chain followed by a radical unzipping process.

This mechanism was further enforced by the addition of butylated hydroxytoluene (BHT), a radical scavenger, and azobisisobutyronitrile (AIBN), a radical initiator, to the polymer decomposition process. Using differential scanning calorimetry (DSC), AIBN was observed to promote the decomposition of polycarbodiimides by lowering the observed temperature while BHT was discovered to improve their thermal stability. For symmetric carbodiimides,
Figure 4.5 – For regioregular asymmetric polycarbodiimides, the resulting decomposition product is the original asymmetric monomer regardless of where homolytic chain cleavage originates.

such as that shown in Figure 4.4, the resulting decomposition product is purely the original carbodiimide monomer, making these polymers a good candidates as recyclable or “green” polymers. For asymmetric carbodiimides, the decomposition products can take on new meaning if the polymer contains regioirregularity. To better understand this concept, we will first look at the decomposition of a regioregular asymmetric polycarbodiimide (Figure 4.5). For these polymers, the location of initial homolytic cleavage along the polymer chain is irrelevant because the resulting monomer products will always be the original asymmetric monomer. However, when looking at possible decomposition pathways of regioirregular polycarbodiimides, the location of initial chain cleavage becomes very relevant. As seen in
Figure 4.6, if chain scission occurs along an original monomer bond, such as pathway A, then the resulting decomposition products will be a mixture of the original asymmetric monomer and two new symmetric metathesis monomers. If scission occurs as seen in pathway B, which is a bond between monomers formed during the polymerization process, then the resulting decomposition products will only be the original asymmetric monomer. Similarly, an unzipping of the polymer chain that starts from the end of the chain will also result in only asymmetric monomer.

**Figure 4.6** – For regioirregular asymmetric polycarbodiimides, the resulting decomposition products depend on the location of homolytic chain cleavage and could result in two symmetric metathesis monomers in addition to the original asymmetric monomer.
With knowledge of the aforementioned decomposition products possible from regioirregular asymmetric polycarbodiimides, Goodwin proposed a method to determine the existence of regioirregularity within a small group of polymers by decomposing the asymmetric polymers and then injecting the decomposition products onto a GC/MS. The amount of metathesis monomers that resulted from the unzipping process could be used to identify relative amounts of regioirregularity in the polymer (Table 4.1). It was hypothesized that polymers composed of pendant groups that were sterically different to one another would display more affinity towards a preferred mode of monomer insertion and therefore result in higher regioregularity. Through this theory Poly-5 would be expected to contain a large amount of metathesis monomers while Poly-1 and Poly-61 would contain significantly less. As seen in Table 4.1 this hypothesis did not hold true. This table is not an exact replication of a table reported by Goodwin\textsuperscript{9} because the values reported for Poly-5 are backwards in the original table. Poly-5 resulted in 98.5\% asymmetric monomer and not di-n-hexyl monomer as originally reported and this is confirmed by the main body of the Goodwin’s thesis. Poly-2(rac) and Poly-2(R) were shown to decompose completely to original monomer. It was concluded that these polymers contained almost complete regioregularity and that regiocontrol is possible if the bulkiness of the pendant groups are sufficiently different. As mentioned, the metathesis monomers are a direct result of regioirregularity and therefore the amount of these monomers observed can be attributed to the overall amount of regioirregularity in the polymer system. In order for these conclusions to hold true, it must be accepted that homolytic cleavage initiates on the polymer backbone
randomly and is not influenced by the regiopositioning of the pendant groups. Although this study proves that metathesis monomers can be observed, there are a couple of flaws to the experiment. First, a majority of the polymers used will result in metathesis monomers that are highly volatile, such as diethylcarbodiimide, which may be lost during the decomposition process. Although Goodwin made effort to minimize this loss by sealing the polymers in a glass tube prior to depolymerization, the GC/MS only detected trace amounts of these volatile by-products and some may have been lost. Secondly, since decomposition was performed in a vessel prior to injection on the GC/MS, this lends the possibility of monomer metathesis following decomposition, as shown earlier in Figure 2.4, which may lead to
slightly skewed results. Finally, although this method identifies the existence of regioirregularity in these polycarbodiimides, it does not identify the location of the pendant groups along the polymer. Overall, this method shows promise for determination of regioregularity, but improvements to the method of decomposition, the instrumentation, and the polymers used are required.

Further study of regioregularity and regioposition of selected pendant groups of polycarbodiimides was reported by Lu.\textsuperscript{10} Through investigations using \textsuperscript{13}C NMR and IR on the imine C=N bond absorptions of model polymers, he provided preliminary conclusions of the preferred location (imine or amine) of phenyl versus alkyl based asymmetric polycarbodiimides as shown in Figure 4.7. Using \textsuperscript{13}C NMR, the di-n-hexyl Poly-6, was analyzed and it was concluded that two chemical shifts at 48.7 and 32.2 represented the methylene carbons in closest proximity to the nitrogens on the amine and imine location, with the higher chemical shift being attributed to the imine methylene carbon. However, this data might not be accurate. When observing typical \textsuperscript{13}C NMR of monomers containing alkyl substituents, carbon chemical shifts in the low 30s are seen and are attributed to methylene units further down the aliphatic chain and not directly attached to a nitrogen. Most of the monomers reported in Chapter 3.14 exemplify this. Therefore, it is unlikely that the chemical shift of 32.2 reported in Figure 4.7 can be conclusively attributed to the methylene directly attached to the amine nitrogen. Furthermore, due to extreme broadening and low resolution of carbon peaks for these polymer systems, it is possible that the absorption at 48.7 ppm is an unresolved mixture of both methylene carbons directly attached to the nitrogens. For this
Figure 4.7 – Previously reported IR and $^{13}$C data for asymmetric polycarbodiimides containing various aromatic and aliphatic substituents. **Poly-23** is reported incorrectly and should have the chiral stereocenter on the γ-position of the aliphatic pendant group.$^{10}$

reason, the $^{13}$C data should not be used to make any conclusions on the regioposition assigned for the polymers in Figure 4.7. Currently NMR spectroscopy, although a very powerful analytical technique for small molecules and some polymer systems, is still in need
of more development before any significant conclusions can be developed about the regioregularity of polycarbodiimides. Current research in our group being led by J.B. Clark, IV shows promise that NMR techniques may provide better information through the development of better analysis techniques but, for now, these analyses are generally too vague to present any definite conclusions.

A very interesting observation can be realized from the data in Figure 4.7 when observing the reported imine absorptions for Poly-6 versus Poly-16. Poly-6 represents a polymer on which all of the imine nitrogens have an alkyl group attached to it, and as a result, the imine vibrational absorption is 1644 cm\(^{-1}\). Oppositely, Poly-16 has only regioisomers where the imine is directly attached to an aryl substituent and the resulting imine absorption has increased to 1665 cm\(^{-1}\). When analyzing aryl-alkyl polycarbodiimides, such as Poly-39 in Chapter 3, two imine absorptions are often seen with one being around 1620 cm\(^{-1}\) and the other around 1640 cm\(^{-1}\). Based on the results from Poly-6 and Poly-16 it is concluded that the imine stretch of higher wavenumber (1640) is representative of the C=N-aryl regioisomer while the other (1620) is representative of the C=N-alkyl regioisomer. The basis for this conclusion is that electronic effects caused by the attachment of a phenyl group to the imine nitrogen will strengthen the imine bond through partial delocalization of the nitrogen lone pair and result in an absorbance at a higher wavenumber when compared to an alkyl group connected to the imine nitrogen. Although this conclusion was also made by Lu, misinterpretation of the \(^{13}\)C NMR may have led to improper regioisomer assignments for Poly-13 and Poly-23. Both of these polymers should have the aryl substituent attached to the
imine nitrogen as evidenced by their IR imine absorption at ~1640 cm$^{-1}$. Poly-14, we feel, is reported correctly having the alkyl substituent on the imine nitrogen and a resulting imine absorption of 1624 cm$^{-1}$. IR spectra were not included with the results of Figure 4.7 therefore conclusions on regioregularity by observing the presence of other imine absorptions are not possible. Previous publications should also be reexamined based on these conclusions to determine if the originally designated regiostructure of certain polymers are correct. An example of this is the previously reported Poly-23(R) and Poly-23(S) which were reported in literature of having an imine stretch solely at 1622 cm$^{-1}$ and the reported regioisomer of preference is the C=N-aryl.$^{11}$ This is inconsistent with Poly-21 which was reported to also have a regioregularity for the C=N-aryl regioisomer, except it had a reported imine absorption of 1642 cm$^{-1}$. Based on the previously stated conclusions with Poly-6 and Poly-16, the previously reported Poly-23(R) and (S) should have been designated the C=N-alkyl regioisomer. Since Poly-23 was reported to have incredibly stable helices, it may be worth investigating if this newly assigned regioregularity contributed to such properties. IR can give us an idea of the qualitative amounts of regioregularity and, unlike the GC/MS experiment, can also define the regiopositioning of aryl versus alkyl substituents. IR is limited to asymmetric polymers that contain pendant groups different enough to resolve individual imine absorptions and therefore does not provide much information for asymmetric dialkyl or asymmetric diaryl polycarbodiimides. Although we have seen some improvements for the determination of regioregularity, we still have a long way to go before definitive quantitative conclusions can be made.
4.3 An Interesting Case: GPC Analysis of Regioregular Polycarbodiimides

Throughout the synthetic investigations of this research, polymers of various aryl-alkyl pendant groups we made using various catalysts and under a variety of conditions. The end result has been polymers containing various levels of regioregularity as well as favoritism towards the C=N-aryl regioisomer or the C=N-alkyl regioisomer. For most of these polymers, quantitative information on the regioregularity is still unknown. Preliminary results indicate that the regioregularity of Poly-39 can have an effect on the switching intensities for this polymer. In addition, the observation of relative regioregularity dictated by the C=N vibrational absorbance has led to some other interesting comparisons between the regioisomer of preference and the resulting polymer properties.

In an effort to obtain molecular weight data for some of the switching polymer systems, preliminary analysis of a few select polymers was attempted through use of gel permeation chromatography (GPC). The GPC instrument was setup in THF with 0.5% dimethylaminoethylamine (DMAEA) as the mobile phase and calibration was performed using poly-2-vinylpyridine standards (Figure 4.8). We mentioned earlier that the large aliphatic pendant groups on these polymers were designed to dampen interchain interaction between polymers and allow better solubility. GPC analysis was performed on these polymers hoping that the aliphatic group would also dampen column affinitive interactions that have plagued our ability to analyze these polymers by GPC in the past. When observing the elution chromatograms of regioirregular Poly-39(80K) versus regioregular Poly-41 and
**Figure 4.8** – Calibration curve of poly-2-vinylpyridine $M_w$ standards and their elution by GPC in THF with 5 % DMAEA.

**Poly-42** (Figure 4.9), it can be seen that the regioregular polymers elute with significantly less broadening. The elution of low polydispersity poly-2-vinylpyridine (P2VP) standards has also been included in Figure 4.8 for comparison. Although **Poly-39(80K)** ($M_w = 78,000$, PDI = 4.2) was polymerized using the same catalyst and monomer to catalyst ratio as **Poly-41** ($M_w = 13,000$, PDI = 1.3) and **Poly-42** ($M_w = 12,600$, PDI = 1.7), the calculated $M_w$ based on the P2VP calibration for **Poly-39** was much higher and it had a much larger polydispersity (PDI). Coupling this with the fact that the polymers all had relatively good yields (80%, 73%, and 57% respectively), it is very interesting that **Poly-39** elutes so broadly when compared to **Poly-41** since these two polymers are constitutionally the same. Although we can not eliminate the possibility that **Poly-39** is polydisperse, we do not believe this to be the
Figure 4.9 – GPC elution overlay of regioirregular Poly-39 ($M_w = 78K$, PDI = 4.2) and regioregular Poly-41 ($M_w = 13K$, PDI = 1.3) and Poly-42 ($M_w = 12.6K$, PDI = 1.7).

case since the polymerization of carbodiimide monomers using titanium (IV) catalysts has previously been proven to be a living system. Although the living nature of polymerizations may be dependant upon catalyst ligands, we would also expect Poly-41 and Poly-42 to exhibit high polydispersity since they were polymerized using the same catalyst and polymerization parameters. When looking at these results from another angle, it may be possible that polycarbodiimides comprised of varying regioisomers could lead to alterations in the macroscopic properties of the polymer; more specifically, a rigid-rod like geometry versus random-coil. Due to the differences in the hydrodynamic volume associated with
these geometries, their elution through a GPC column would be different. For most polymer systems these differences are compensated by adjustment of the Mark-Houwink scalar coefficient used in the universal calibration for determination of $M_w$. However if separate polymer chains within a single GPC injection were comprised of varying amounts of rigid-rod and random-coil character, one can expect the size exclusion process to separate these chains based on these properties, and therefore lead to broadening of the elution. In order for these assumptions to hold water, differences in regioregularity would have to fluctuate between polymer chains and the placement of regioregular and regioirregular blocks would not be homogeneous. Although these results are very preliminary and lack any definite conclusions, it may be possible that broad elution of Poly-39 on the GPC is being caused by its regioirregularity which, in turn, translate into slight overall differences of the polymer geometry from chain to chain. This observation is worth revisiting once an improved and more reliable GPC analysis method has been determined and improved regiocontrol of polycarbodiimide systems is understood.

### 4.4 New Attempts at Determining Regioregularity

As discussed in Section 4.1, the possibility of gaining regioregularity information through the analysis of polymer decomposition monomers has promise but the initial experimental design requires a few improvements. We wanted to combine the discoveries of regioposition offered by IR and the decomposition by-products offered by GC into a new experiment where the two instruments combined could strengthen conclusions of their
individual results. The basic requirements for this new experiment are as follows: (1) The asymmetric polymer be comprised of an aryl and alkyl pendant group in order to allow visual differences of the qualitative imine absorptions for the two possible regioisomers by IR. (2) The asymmetric monomer and the resulting symmetric metathesis monomers be of sufficient size and have low volatility. (3) The asymmetric monomer and the metathesis monomers should be different enough to not co-elute from the GC column. (3) Polymer decomposition should occur within the heated injection chamber of the GC system to minimize any possible metathesis products that can result from a pre-decomposed pool of heated monomer. (4) By adjusting the polymerization conditions, such as catalyst and temperature, the asymmetric polymer will be given varying amounts of regioregularity, which can be confirmed by IR, in order to compare to the resulting metathesis monomers observed following decomposition.

The polymer system chosen for this analysis is shown in Figure 4.10. Previously reported Poly-6 and Poly-16 have shown to polymerize in good yield and the polymers have good solubility. Therefore we are confident that Poly-62 will also have these traits.

With the much appreciated assistance of undergraduate researcher Chris Kilgore, experimental procedures were began by setting up a proper method on the GC instrument followed by analysis and calibration of the three monomers. Gas Chromatography was performed on a Hewlett-Packard 6890 GC-FID using a Hewlett-Packard HP-5 (5%-diphenylpolysiloxane, 95%-dimethylpolysiloxane) 30 m X 0.32 mm X 0.25 μm capillary column. Method parameters for the GC are as follows; The injection port temperature is set to 290 °C, a temperature adequate for thermal decomposition of these polymer systems.
The temperature ramping settings of the oven are set to increase 10 °C every minute until a final temperature of 300 °C is reached. The oven is then held isothermal for 5 minutes. The injection port will use a split injection setup with a split ratio of 10:1, an inlet pressure of 9.53 psi, split flow if 21.0 mL/min, and total flow of 25.9 mL/min. Each monomer calibration solution and polymer sample solution will be spiked with an identical concentration of heptadecane internal standard to ensure that injections remain invariable. A preliminary injection of asymmetric Mono-62 in CHCl₃ revealed a clean elution of one monomer peak, confirming that no metathesis monomers were resulting from the conditions of the instrument. Calibration samples containing known concentrations of each monomer
were made in CHCl$_3$ and followed by 1 µL injections on the GC. Each injection was made in triplicate and peak area values were averaged. The error for each set of triplicate peak areas did not exceed 10%. Calibration curves were constructed comparing peak area as a function of concentration and linear fits were given to each plot (Figure 4.11). The slope of the linear fits represent the response factor (RF) for each monomer which is calculated to be 1.50 for Mono-6, 1.56 for Mono-16, and 1.57 for Mono-62. The retention times of each monomer were well separated and a sample injection is shown in Figure 4.12.

![Calibration Curves](image)

**Figure 4.11** – GC-FID calibration curves of Mono-6, Mono-16, and Mono-62 at known injection concentrations in CHCl$_3$. (Injection volume = 1 µL)
Now that we have calibration curves for each monomer, the next step will be to synthesize **Poly-62** with various amounts of regioregularity. Polymerizations were performed using approximately 1 g of **Mono-62**. **Cat-4**, pre-dissolved in a solution of CHCl₃ (< 3 mL), was added to obtain a 250:1 monomer to catalyst ratio and polymerizations were carried out at temperatures of 10, 25, 33, and 40 °C. Each polymerization had gelled after 24 hours of stirring and workup was performed after 1 day for the 33 and 40 °C polymers and 3 days for the 10 and 25 °C polymerizations. All polymers were purified by precipitation from EtOH yielding fluffy off-white polymers in very good yield (> 70%). When performing IR analysis on thin films of each of these polymers, we were shocked to find that every one of them was highly regioregular with a single imine absorption peak at 1624 cm⁻¹ (Figure 4.13).

**Figure 4.12** – Sample injection showing all three monomer elutions and internal standard (IS) heptadecane.
Another polymerization of Mono-62 was attempted with the achiral and highly active Cat-15 and also resulted in a highly regioregular polymer with the same preference for the C=N-alkyl regioisomer. Although this discovery thwarted our GC study, the most interesting question is why this monomer is polymerizing with such high regioregularity? Further discussion on this will be saved for the next section. Decision to inject these polymers was carried out anyway and the resulting monomer products after decomposition contained a majority of the original asymmetric monomer, which can be expected for a highly
regioregular polymer. However, some small peaks representative of the metathesis monomers were seen. The quantitative analysis is shown in Table 4.2. Poly-6 was also injected and since this polymer will result in clean decomposition to Mono-6, this gives us a benchmark for the polymer mass recovered as monomer, which was found to be approximately 50%. Injections of Poly-62 also resulted in approximately 50% of the initially injected mass recovered as monomer. This loss is likely caused by some of the decomposition products being blown out of the purge vent and split vent if slow

**Table 4.2 – GC-FID analysis of decomposition monomers from Poly-6 and Poly-62 solutions in CHCl3 (~1.5 mg/mL, 1 µL injections)**

<table>
<thead>
<tr>
<th>Polymer ID</th>
<th>Calc. Conc. Mono-6 (µg/mL)</th>
<th>Calc. Conc. Mono-62 (µg/mL)</th>
<th>Calc. Conc. Mono-16 (µg/mL)</th>
<th>% Mass of Mono-6</th>
<th>% Mass of Mono-62</th>
<th>% Mass of Mono-16</th>
<th>Total % Mass of Polymer Recovered as Monomer</th>
</tr>
</thead>
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<tr>
<td>Poly-6</td>
<td>716</td>
<td>None</td>
<td>None</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>48</td>
</tr>
<tr>
<td>Poly-62 (10°C)</td>
<td>41.4</td>
<td>743.0</td>
<td>54.7</td>
<td>5.0</td>
<td>88.5</td>
<td>6.5</td>
<td>56</td>
</tr>
<tr>
<td>Poly-62 (25°C)</td>
<td>68.2</td>
<td>663.1</td>
<td>91.5</td>
<td>8.3</td>
<td>80.6</td>
<td>11.1</td>
<td>52.4</td>
</tr>
<tr>
<td>Poly-62 (33°C)</td>
<td>52.2</td>
<td>602.7</td>
<td>67.9</td>
<td>7.2</td>
<td>83.4</td>
<td>9.4</td>
<td>47.2</td>
</tr>
<tr>
<td>Poly-62 (40°C)</td>
<td>40.1</td>
<td>665.9</td>
<td>52.0</td>
<td>5.3</td>
<td>87.8</td>
<td>6.9</td>
<td>49.5</td>
</tr>
</tbody>
</table>
decomposition is taking place. It is possible to rectify this issue in the future by switching to
a splitless injection system. The mass of each monomer recovered is consistent and 80-90% of the total monomer observed is the asymmetric monomer. Since Poly-62 was unable to be obtained with visual regioirregularity by IR, this study did not reach the full extent that we had initially hoped. However, we can conclude that Poly-62, in each case, does have some small degree of regioirregularity as evidenced by the presence of metathesis monomers. It is likely that the imine absorption by this small amount of regioirregularity is hidden underneath the dominant absorption at 1624 cm$^{-1}$. Therefore this technique could be useful for the determination of small quantities of regioirregularity that are unseen by IR. A reconstruction of the polymer design to obtain various quantities of regioirregularity will be needed. The reasoning for not using Poly-39 for this study is due to the high molecular weight of the monomer and its inability to elute easily from the GC column.

4.5 Influencing Regioregularity by Arene Pendant Group Substitution

After discovering that Mono-62 will consistently polymerize into a highly regioregular polymer favoring the C=N-alkyl regioisomer regardless of catalyst and polymerization temperature, which have been previously shown to greatly effect the regio-outcome of Poly-39, questions arose concerning this monomer and what might be causing such a regiopreference. Although first inclinations go towards steric and the fact that the phenyl group is much less sterically encumbered than a 1-naphthyl group, this idea is contradicted by the fact that Mono-42 which contains the largest arene group, 1-pyrenyl, also
Figure 4.14 – Newly synthesized polycarbodiimides designated with their preferred regioisomers.

polymerized into a highly regioregular polymer favoring the C=N-alkyl regioisomer. When feeding through all the regioregularity outcomes of the asymmetric aryl-alkyl polymers successfully synthesized and discussed in Chapter 3, an interesting trend was realized (Figure 4.14). When polymerized at room temperature using Cat-4, only two polymers exhibited a preferred C=N-aryl regioisomer, Poly-49 and Poly-53, while Poly-39 and Poly-52 both exhibited high regioirregularity and no distinct preference for a particular regioisomer. All of the other polymers showed a high favoritism for the C=N-alkyl regioisomer when polymerized under the same conditions. IR spectra for these polymers can be referenced in
Appendix I. When looking at the constitutional differences between these polymers it becomes apparent that aromatic substitution on the aryl pendant group may be dictating a preferred regioregularity. Poly-44, 45, 50, and 54 all have electron donating substituents (alkyl or methoxy) in either the para- or ortho-position relative the backbone nitrogen. Additionally, Poly-62 used in the GC study also had an alkyl group in the para-position and resulted in high regioregularity with the same regioisomer. Poly-39 and Poly-52 are both regioirregular and they contain indifferent substituents (hydrogen and bromine) on the ortho- or para-positioning of the ring. Poly-53 which has the much more electronegative chlorine atom in the para-position, resulted in a preference for the C=N-aryl regioisomer. Finally, Poly-49, although containing no substituents on the naphthalene ring, has a heterocyclic nitrogen placed on the 5 position which lies within resonance to have a withdrawing effect on the backbone nitrogen as well. Consequently, this polymer also exhibited a high preference for the C=N-aryl regioisomer. When observing these results collectively, it seems we may have uncovered a way to induce a preferred regioregularity of the polycarbodiimide systems through electron donating and electron withdrawing substituents placed selectively on the aryl pendant group. In an effort to explain why this behavior is occurring, we must focus on the amidinate-titanium propagation site. For an amidinate complex comprised from asymmetric aryl-alkyl monomers, one can expect some differences associated with an aryl versus an alkyl pendant group. It seems that under these polymerization conditions, these differences are not great enough to dictate a preferred mode of monomer insertion and the result is regioirregularity as seen for Poly-39 (Figure 4.15). However, when the aryl pendant
Figure 4.15 – Asymmetric aryl-alkyl monomers with no aryl substituents show no favored mode of monomer insertion as a result of no significant bias to amidinate nitrogen coordination on the titanium metal center.

Groups contain electron withdrawing or electron donating substituents placed within proper resonance of the amidinate nitrogen, this may translate into more favorable coordination to the titanium as a result of the availability of the nitrogen lone pair to donate to the electron deficient titanium(IV) metal center. Through the addition of an electron withdrawing effect on the amidinate nitrogen, the lone pair will be less favorable to coordinate when compared to an alkyl pendant group on the other nitrogen (Figure 4.16). Oppositely, if a substituent on the aryl pendant group donates to the nitrogen on the amidinate complex, this will activate this nitrogen to coordinate to the metal. When looking at the regioisomers that will result from this hypothesis, these results match perfectly with the preferred regioisomers seen from these polymer systems. To strengthen this hypothesis, a few more asymmetric aryl-alkyl monomers containing an electron withdrawing groups (such as –CN or –NO₂) will need to be
Figure 4.16 – Asymmetric aryl-alkyl monomers with electron withdrawing (EW) aryl substituents will show a favored mode of monomer insertion as a result reduced aryl-nitrogen coordination on the titanium metal center.

Figure 4.17 – Asymmetric aryl-alkyl monomers with electron donating (ED) aryl substituents will show a favored mode of monomer insertion as a result enhanced aryl-nitrogen coordination on the titanium metal center.
investigated. If indeed this discovery leads to a new way of synthesizing highly regioregular polycarbodiimides, then a cascade of new experiments to determine the effects of regioregularity on the properties of these polymer systems will be possible.

4.6 Conclusions

Although we are still in search of a definitive way to analytically determine regioregularity quantitatively for these polycarbodiimide systems, progress in this area has led us to a new remarkable discovery that polycarbodiimide regioregularity may be able to be controlled by the incorporation of electron donating and electron withdrawing substituents on the aryl pendant group of an asymmetric aryl-alkyl carbodiimide monomer. In our working hypothesis, electron withdrawing groups will lead to a favoritism of the C=N-aryl regioisomer while electron donating groups will lead to C=N-alkyl regiopreference. Additionally, we have determined that decomposition of polycarbodiimides within the injection system of a GC is a valid method for determination of resulting monomers with a high enough sensitivity to observe regioirregularity in polymer systems that are not observed by imine absorption overlap on the IR spectrum.

4.7 Experimental Section

4.7.1 GPC Analysis

GPC analyses were performed using 2 sequential PL-Gel 5 µm Mixed-C columns 300 x 7.5 mm (Polymer Laboratories, Amherst, MD) that are kept isothermal at 30 °C in an
Eppendorf CH-500 column heater. A mixture of 0.5% DMAEA in HPLC grade THF is used as a mobile phase and standards of poly-2-vinylpyridine (PSS-USA, Silver Spring, MD) are used for universal calibration. A Jasco PU-1580 intelligent HPLC pump and a Jasco RI-1530 refractive index detector are also used. Polymer injections were performed at a concentration close to 1 mg/mL and were pre-filtered through a 0.45 µm PTFE syringe filter prior to injection. The flow rate and column pressure were monitored extensively to ensure that polymer was eluting properly and not clogging the columns. Calibration check standards were injected periodically to ensure the calibration curve was still accurate. Data analysis was performed using BORWIN software for the GPC.

4.7.2 GC-FID Analysis

Most of the details pertaining to the GC Method used were previously described. A more detailed procedure is described here. Gas Chromatography was performed on a Hewlett-Packard 6890 GC-FID. The column used was a Hewlett-Packard HP-5 (5%-diphenylpolysiloxane, 95%-dimethylpolysiloxane) 30 m X 0.32 mm X 0.25 µm. The carrier gas is 5.0 grade purity helium and the FID flame was fueled by high purity helium and zero grade (0.1) air. The injection liner was a standard split/splitless liner with a glass wool plug. Prior to beginning the experiment the injection liner was removed, cleaned, and fresh glass wool replaced. The o-rings and injection septum were also replaced. The column was baked at 300 °C for 45 minutes prior to any injections to ensure that no residual material was
deposited in the injection liner or the capillary column. Following the bakeout, a blank injection of CHCl₃ was performed to ensure no ghost peaks were observed. The method parameters for the GC are as follows. The injection port temperature is set to 290 °C, the detector is set to 300 °C and the initial oven temperature is set to 100 °C. The temperature ramping settings of the oven are set to increase 10 °C every minute until a final temperature of 300 °C is reached. The oven is then held isothermal for 5 minutes. The injection port will use a split injection setup with a split ratio of 10:1, an inlet pressure of 9.53 psi, split flow if 21.0 mL/min, and total flow of 25.9 mL/min. The purge and split vent were both monitored using a Hewlett Packard soap bubble flow meter. Monomer calibration solutions were created by accurate dilutions of a pre-made master standard using an Eppendorf 100 – 300 µL micropipetter and volumetric flasks. In addition, a known concentration of heptadecane spike standard was also added to the calibration standards. Manual injections of 1 µL were performed for each sample and calibration standard in triplicate. The resulting peak areas were averaged and outliers (greater than 10 % error from resulting average) were removed and re-injections were made if necessary. HP-Chemstation Software was used for GC chromatogram analysis.

4.7.3 Preparation of Monomers

**Di-n-hexyl carbodiimide (Mono-6):** This monomer was made in accordance to previously reported procedures by our group but, for clarity, will be described here. 4.201 g (33 mmol) of hexyl isocyanate was diluted in 25 mL of DCM in a 250 mL round bottom
flask with a stir bar and cooled to 0 °C in an ice bath. 3.336 (33 mmol) of hexylamine was
diluted in 25 mL of DCM and added to a pressure equalizing addition funnel. The
hexylamine solution was added slowly to the cool isocyanate solution and once fully added
the solution was allowed to stir at 0 °C for 1 hour and then room temperature for another
hour. DCM was removed from the reaction solution by rotary evaporation leaving a crude
white residue which was purified by recrystallization in EtOH. Following aspiration filtration
and full drying by vacuum, the urea was recovered as a white solid (80 % Yield).

6.8756 g (26 mmol) of triphenylphosphine was dissolved in 10 mL of DCM and
cooled to 0 °C using an ice bath. 1.35 mL (26 mmol) of Br₂ was diluted in 15 mL of DCM
and added to a pressure equalizing addition funnel. The Br₂ solution was slowly added to the
PPh₃ solution resulting in a yellow-white slurry. 7.81 mL (56 mmol) of TEA was then added
to the slurry. Keeping the charged solution cool at 0 °C, 5.498 g (24 mmol) of urea was
dissolved in 15 mL of DCM and added to the charged solution dropwise by addition funnel.
The ice bath was allowed to slowly deplete overnight. A nitrogen blanket was applied
throughout this process to prevent water condensation within the reaction flask. The
following morning the reaction was quenched with ~200mL of hexanes and the precipitates
were filtered. The filtrate was reduced by rotary evaporation yielding a salty oil residue. The
hexanes quenching cycle was repeated and the resulting oil was vacuum distilled at 65 °C
(200 mtorr), to yield a colorless oil. Yield: 66 %. ¹H NMR (300 MHz, CDCl₃) δ(ppm): 0.89
(t, 6H), 1.25 – 1.40 (m, 12H), 1.57 (m, 4H), 3.19 (t, 4H). IR(cm⁻¹): 2930 (vs, C-H alkyl),
2859 (s, C-H alkyl), 2131 (vs, N=C=N). HRMS-ESI: \( \text{M}_{\text{theoretical}} = 211.2169, \text{M}_{\text{sample}} = 211.2169, \Delta M = -0.06 \text{ mmass units (-0.27 ppm)}, \text{C}_{13}\text{H}_{26}\text{N}_{2} \).

**Di-(4-butylphenyl) carbodiimide (Mono-16):** The procedure described in Section 3.14.3 was used and any changes noted below. 3.859 g (26 mmol) of 4-butylationine was combined with 4.749 g (27 mmol) of 4-butylphenyl isocyanate in DCM at 0 °C resulting in white solids after 2 hours. The urea was filtered after quenching the reaction in hexanes and then dried by vacuum. (Note: Recrystallization of this urea in MeOH failed due to high solubility) Total mass urea = 8.11g (97 %).

8.053 g (19 mmol) of dibromotriphenylphosphorane and 5.41 mL (39 mmol) of TEA diluted in approximately 30 mL of DCM was used to dehydrate 5.6273 g (17 mmol) of the urea. After purification of the monomer through a short bus silica gel column using DCM as the mobile phase, yellow monomer oil was obtained following full removal of volatiles. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta (\text{ppm}): 0.92 (\text{t, 6H}), 1.34 (\text{m, 4H}), 1.57 (\text{m, 4H}), 2.59 (\text{t, 4H}), 7.05 – 7.15 (\text{m, 8H}). \) IR(cm\(^{-1}\)) : 3024 (w, C-H aryl), 2956 (s, C-H alkyl), 2929 (vs, C-H alkyl), 2858 (s, C-H alkyl), 2136 (vs, N=C=N), 2109 (vs, N=C=N), 1604 (s, C=C). HRMS-ESI: \( \text{M}_{\text{theoretical}} = 306.2169, \text{M}_{\text{sample}} = 306.2173, \Delta M = -0.42 \text{ mmass units (-1.36 ppm)}, \text{C}_{21}\text{H}_{26}\text{N}_{2} \)

**N-(n-hexyl)-N'-(4-butylphenyl) carbodiimide (Mono-62):** The procedure described in Section 3.14.3 was used and any changes noted below. 3.234 g (32 mmol) of hexylamine was combined with 5.60 g (32 mmol) of 4-butylphenyl isocyanate in DCM at 0 °C resulting in white solids after 2 hours. The urea was filtered after quenching the reaction in hexane and then dried by vacuum. Total mass urea = 5.90 g (67 %).
Dehydration and purification was performed exactly the same as described for Mono-16 above. Yield: 71% \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 0.89 (m, 6H), 1.28 – 1.44 (m, 8H), 1.50 – 1.70 (m, 4H), 2.57 (t, 2H), 3.84 (t, 2H), 6.90 (d, 2H), 7.90 (d, 2H). IR (cm\(^{-1}\)): 3022 (w, C-H aryl), 2956 (s, C-H alkyl), 2929 (vs, C-H alkyl), 2858 (s, C-H alkyl), 2131 (vs, N=C=N), 1606 (m, C=C). HRMS-ESI: \(M_{\text{theoretical}} = 259.2169\), \(M_{\text{sample}} = 259.2175\), \(\Delta M = -0.61\) m/m mass units (-2.37 ppm), \(C_{17}H_{26}N_2\).

4.7.4 Preparation of Polymers

Synthesis procedures and IR spectra for Poly-62 were described in the main body of the text. A sample \(^1\)H NMR spectrum is provided in Appendix II.

4.8 References


APPENDIX
APPENDIX 1 – IR Spectra of Polymers

Note: IR spectra for many polymers are already included in the main text, this appendix will show the other polymers whose IR were not included.

Poly-36  \( N-(3\text{-bromophenyl})\)-\(N'\)-(n-octadecyl) polycarbodiimide
**Poly-37**  \(N\)-(3-nitrophenyl)-\(N'\)-(n-octadecyl) polycarbodiimide
Poly-40  \( N-(1\text{-naphthyl})-N'-(n\text{-dodecyl}) \) polycarbodiimide
Poly-44  *N*-(4-indanyl)-*N’*-(n-dodecyl) polycarbodiimide

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![Graph of wavenumbers vs %T]
Poly-45  *N*-\((2\text{-fluorenyl})\)-\(N'\)-(n-octadecyl) polycarbodiimide*
Poly-46  $N$-(1-naphthylmethyl)-$N'$-(n-dodecyl) polycarbodiimide
Poly-49  
*N*(5-quinolyl)-*N’*(n-dodecyl) polycarbodiimide

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[Graph showing IR spectra with labeled peaks]
**Poly-50**  \(N\)-(4-methyl-1-naphthyl)-N’-(n-dodecyl) polycarbodiimide

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![Graph](image-url)
Poly-52  \( N\)-(4-bromo-1-naphthyl)-\( N'\)-(n-dodecyl) polycarbodiimide

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Poly-53  \( N\)-(4-chloro-1-naphthyl)-\(N'\)-(n-dodecyl) polycarbodiimide

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![IR Spectrum](image)
Poly-54  \( N-(4\text{-methoxy-1-naphthyl})-N'-(n\text{-dodecyl})\) polycarbodiimide
**Poly-56**  
*N-((S)-1,2,3,4-tetrahydro-1-naphthyl)-N’-ethyl polycarbodiimide*

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![Graph](image)
Poly-42-co-6  $N$-(1-pyrenyl)-$N'$-(n-octadecyl) – co – di-n-hexyl polycarbodiimide
APPENDIX 2 – $^1$H-NMR Spectra of Polymers

**Poly-36**  $N$-(3-bromophenyl)-$N$-(n-octadecyl) polycarbodiimide
Poly-38  \( N-(3\text{-nitrophenyl})-N'-(n\text{-octadecyl}) \) polycarbodiimide
Poly-39(80K)  $N$-(1-naphthyl)-$N'$-(n-octadecyl) polycarbodiimide
**Poly-40**  \(N-(1\text{-naphthyl})-N'-(n\text{-dodecyl})\) polycarbodiimide
**Poly-41**  \(N\)-(2-naphthyl)-N'-(n-octadecyl) polycarbodiimide
Poly-42  \(N\-(1\text{-pyrenyl})-N'\-(n\text{-octadecyl})\) polycarbodiimide
**Poly-44**  
*N*(4-indanyl)-*N*′-(n-dodecyl) polycarbodiimide
Poly-45  \( N\)-(2-fluorenyl)-N'-(n-octadecyl)\) polycarbodiimide
Poly-46  \( N-(1\text{-naphthylmethyl})-N'-(n\text{-dodecyl}) \) polycarbodiimide
Poly-49  \(N-(5\text{-quinolyl})-N'-(n\text{-dodecyl})\) polycarbodiimide
Poly-50  \( \text{N-}(4\text{-methyl-1-naphthyl})\text{-N'}\text{-}(n\text{-dodecyl}) \text{ polycarbodiimide} \)
Poly-52  \( N-(4\text{-bromo-1-naphthyl})-N'-(n\text{-dodecyl}) \) polycarbodiimide
Poly-53  $N$-(4-chloro-1-naphthyl)$-N'$-(n-dodecyl) polycarbodiimide
Poly-54  N-(4-methoxy-1-naphthyl)-N’-(n-dodecyl) polycarbodiimide
Poly-42-co-6  $N$-(1-pyrenyl)-$N'$(n-octadecyl) – co – di-n-hexyl polycarbodiimide
Poly-62  \(N\)-(4-butylphenyl)-\(N\)'-(n-hexyl) polycarbodiimide