Synthesis and Characterization of Ring-Opening Metathesis Polymers with Pendant Carborane Groups

by

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Submitted to the Department of Materials Science and Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Polymers at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Abstract

A series of ring-opening metathesis (ROMP) polymers functionalized with pendant carborane (C₂B₁₀H₁₂) groups was synthesized. Norbornene-based polymers with the bulky, pseudoaromatic functionality were found to have glass transition temperatures (T_g's) between 29 °C and 290 °C. This variation in T_g can be attributed to structural differences in how the functional group is attached to the polymer backbone. Block copolymerization was used to improve the material processibility. The block copolymers microphase separate into boron-rich and boron-free microdomains.

Carborane-functionalized monomers and polymers were used as precursors and models for the synthesis of polyanions with pendant cobalt dicarbollide (Co(C₂B₉H₁₁)₂⁻) and carborane anion (CB₁₁H₁₂⁻) groups via ROMP. These polyelectrolytes were found to work as hydrophilic ion-exchangers in aqueous acidic solutions. Polymers functionalized with either cobalt dicarbollide or carborane anions demonstrated selective binding of cesium over sodium. Copolymerization and cross-linking were used to reduce the hydrophilicity and solubility of the materials in a stripping solution of strong (8M) nitric acid.

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This thesis is dedicated to all the people who hate nuclear waste but love icosahedrons.
Contents

1 Background .......................... 14

1.1 Carboranes .......................... 14
   1.1.1 General Properties ............... 14
   1.1.2 Applications .................. 16
   1.1.3 Synthesis of Carborane Polymers ....... 20

1.2 Cobalt Dicarbollide .................. 22
   1.2.1 Nuclear Weapons, Nuclear Power, Nuclear Waste ........ 23
   1.2.2 A Summary of Cesium Separation Techniques .......... 24
   1.2.3 Cobalt Dicarbollide in Solvent Extraction .......... 26
   1.2.4 Cobalt Dicarbollide in Polymeric Solid Phase Separation ... 27

1.3 Ring-Opening Metathesis Polymerization
   (ROMP) ............................ 27
   1.3.1 Catalyst Systems ............... 28
   1.3.2 Kinetic Effects ................ 30

2 Synthesis of Carborane Functionalized Norbornene Monomers 32

2.1 Nor-Si-Carb: A Silicon Bridged Carborane-Norbornene .... 34

2.2 Nor-C-Carb: A Carbon Bridged Carborane-Norbornene ...... 35
   2.2.1 Effect of Reagent Stoichiometry on Yield .......... 44
   2.2.2 Unusual Tosyl Carborane Reaction ............... 49

2.3 Nor-CC-Carb: A Monomer with Twice-Bound Carborane ....... 50
   2.3.1 The Proton Transfer Mechanism ............... 53
2.4 Nor-6-Carb: A Norbornene Monomer with Pendant Carborane Attached through a Spacer Chain ........................................... 57
2.5 Nor-Si-Anion: A Norbornene Monomer with a Carborane Anion Group ................................................................. 60
2.6 Experimental Details ................................................................. 60
  2.6.1 Materials ........................................................................... 60
  2.6.2 Equipment ........................................................................ 63
  2.6.3 Nor-Si-Carb .................................................................... 63
  2.6.4 Nor-C-Carb .................................................................... 64
  2.6.5 p-Toluenesulfonyl Carborane ........................................... 64
  2.6.6 Nor-CC-Carb .................................................................. 65
  2.6.7 Nor-6-Carb .................................................................... 66
  2.6.8 Nor-Si-Anion, Cesium Salt ............................................... 67

3 Synthesis and Characterization of α-Carborane Functionalized Polymers .......................................................... 68
  3.1 Polymerization ....................................................................... 68
    3.1.1 Solvent Systems ............................................................. 69
    3.1.2 Kinetics and Polydispersity ............................................. 70
    3.1.3 Spectroscopic Characterization ....................................... 72
  3.2 Block Copolymers .................................................................. 81
  3.3 Structure/Thermal Property Relationships .............................. 84
    3.3.1 Glass Transition Temperature ......................................... 84
    3.3.2 Thermal Gravimetric Analysis ......................................... 85
  3.4 Magnetic, Optical, and Dielectric Properties ............................ 87
    3.4.1 Index of Refraction ......................................................... 87
    3.4.2 Dielectric Constant ....................................................... 87
    3.4.3 Magnetic Response ....................................................... 88
  3.5 Experimental Details .............................................................. 91
    3.5.1 Equipment ..................................................................... 91
    3.5.2 Processing ..................................................................... 92
3.5.3 Films for UV/IR .............................................. 93
3.5.4 Polymerization .............................................. 93

4 Cobalt Dicarbollide and Carborane Anion Polymers: Materials Synthesis .................................................. 97
4.1 Poly-Nor-C-Carb-Co: Attachment, Polymerization, Sandwiching ......................................................... 99
4.2 Poly-Nor-C-CDC: Attachment, Sandwiching, Polymerization ............................................................. 102
4.2.1 Sandwiching .................................................. 102
4.2.2 Polymerizing .................................................. 107
4.3 Poly-Nor-11-CDC: Sandwiching, Attachment, Polymerization .................................................. 113
4.4 Poly-CDC-siloxane: Polymerization, Sandwiching, Attachment .................................................. 115
4.5 Poly-Nor-Si-Anion: Polymerizing the Carborane Anion Monomer .................................................. 117
4.6 Experimental Details ............................................ 118
4.6.1 Degrading o-Carborane .................................. 118
4.6.2 Poly-Nor-C-Carb-Co ........................................ 123
4.6.3 Poly-Nor-C-CDC .............................................. 128
4.6.4 Poly-Nor-11-CDC .............................................. 133
4.6.5 Poly-CDC-Siloxane .......................................... 143
4.6.6 Poly-Nor-Si-Anion ............................................ 147

5 Cobalt Dicarbollide and Carborane Anion Polymers: Potential Applications ................................................. 152
5.1 Cesium Ion-Exchange ............................................. 152
5.1.1 Cobalt Dicarbollide and Carborane Anion Polymers for Cesium Binding ............................................. 153
5.1.2 Solubility in Nitric Acid ........................................ 159
5.1.3 Cesium Stripping ............................................. 161
5.1.4 Cesium and Sodium Binding ................................... 163
5.1.5 Conclusions .................................................... 166
5.2 Solid Electrolytes .................................................. 167
5.2.1 Ionic Conductivity with the Small Molecule Lithium Salts .................................................. 168
5.2.2 A Polyelectrolyte Lithium Salt ........................................ 170
5.2.3 Potential Pathway to an Unusual Comb Copolymer ............. 170

5.3 Experimental Details .................................................. 172
  5.3.1 Copolymerization ................................................... 172
  5.3.2 Testing a Potential Crosslinking Agent .......................... 175
  5.3.3 Sodium and Cesium Analysis ....................................... 175
  5.3.4 Converting to Lithium Salts ....................................... 178
  5.3.5 Reaction of Propylene Oxide with Norbornene Carborane Carb-anions .................................................. 179
# List of Figures

1-1 Carborane Isomers ........................................ 15  
1-2 Partial Charges on the o-Carborane Molecule ............ 15  
1-3 The Carborane Anion ..................................... 16  
1-4 A DEXSIL Polymer for High Temperature Use ............ 17  
1-5 The Use of a Carborane Framework for the Attachment of a Catalyst 19  
1-6 Examples of Polymers with Carborane Groups ............ 20  
1-7 Cobalt Dicarbollide ...................................... 23  
1-8 Some Materials Used in Cesium Separations ............. 25  
1-9 ROMP of Norbornene-Based Monomers .................... 28  
1-10 Two Organometallic Catalysts for ROMP ................ 30  

2-1 Carborane Functionalized Norbornene-Based Monomers ...... 33  
2-2 Butyl Lithium Deprotonation of o-Carborane ............. 33  
2-3 Unsuccessful Route to a Dicarborane Monomer (1) .......... 34  
2-4 HNMR of 5-(Chlorodimethylsilyl)-Norbornene in D-Chloroform ... 36  
2-5 Synthesis of Nor-Si-Carb .................................. 37  
2-6 HNMR of Nor-Si-Carb in D-Acetone ....................... 38  
2-7 HNMR of o-Carborane in D-Chloroform .................... 39  
2-8 $^{13}$CNMR of Nor-Si-Carb in D-Acetone .................. 40  
2-9 $^{13}$CNMR of o-Carborane in D-Chloroform ............... 41  
2-10 $^{11}$BNMR of Nor-Si-Carb in D-Acetone .................. 42  
2-11 $^{11}$BNMR of o-Carborane in D-Chloroform ............... 43  
2-12 Synthesis of Nor-C-Carb ............................... 44
4-22 \(^{13}\text{CNMR of Degraded Poly-Nor-C-Carb in D-THF}\) ........................................ 125
4-23 \(^{14}\text{BNMR of Degraded Poly-Nor-C-Carb in D-THF}\) ........................................ 126
4-24 IR Spectra of Polynorborne, Poly-Nor-C-CDC-Co, and Cobalt Dicarbollide ............................................................ 129
4-25 HNMR of Poly-Nor-C-CDC in D-Acetone ........................................ 132
4-26 HNMR of Norbornene Butanol Ester in D-Acetone ................................. 134
4-27 HNMR of Bromobutyl Cobalt Dicarbollide, Cesium Salt, in D-Acetone .... 136
4-28 HNMR of Nor-11-CDC in D-Acetone .................................................. 139
4-29 HNMR of Nor-11-CDC after Treatment with a Schrock Catalyst in D-Acetone ............................................................ 140
4-30 HNMR of Poly-Nor-11-CDC in D-Acetone ........................................ 141
4-31 HNMR of Elimination (Butene Cobalt Dicarbollide) and Substitution (Methoxynorborne Cobalt Dicarbollide) Products in D-Acetone ........................................ 144
4-32 HNMR of Polydimethylsilane/Polymethylhydrosilane in D-Chloroform .... 146
4-33 HNMR of Mixed Elimination/Substitution Products Reacted with a Polyhydrosilane in D-Acetone .................................................. 148
4-34 HNMR of First Hydrosilation Reaction Products Reacted with More Polyhydrosilane in D-Acetone ........................................ 149
5-1 HNMR of Polynorbornene(90)/Poly-Nor-Si-Anion(30) Block Copolymer in D-THF ............................................................ 154
5-2 HNMR of Polynorbornene/Poly-Nor-C-CDC Block Copolymer in D-Toluene ............................................................ 156
5-3 HNMR of Polynorbornene in D-Toluene .................................................. 157
5-4 Conductivity as a Function of Temperature for the Lithium Salts of Cobalt Dicarbollide and the Carborane Anion in POEM ......................... 169
5-5 Proposed Synthesis of Poly-Nor-C-Carb/PEO Comb Copolymer ................ 171
5-6 HNMR of the Reaction of Deprotonated Nor-Si-Carb with Propylene Oxide in D-Acetone ............................................................ 173
5-7  HNMR of the Reaction of Deprotonated Poly-Nor-Si-Carb with Propylene Oxdie in D-Acetone .................................................. 174

5-8  HNMR of a Polymerization of Mixed Nor-C-CDC and Bis(Nor-C)-CDC in D-Acetone .............................................................. 176

5-9  HNMR of a Polymerization of Nor-C-CDC with Bis(Nor-C)-CDC Added Later in D-Acetone ....................................................... 177
List of Tables

3.1 Comparison of o-Carborane Functionalized Materials .............. 84
3.2 Refractive Indices of Carborane Polymers ............................ 87
4.1 Elemental Composition of Poly-Nor-C-Carb-Co ....................... 127
4.2 Viscometry Results .................................................... 151
5.1 Weight Loss After 40 wt% Nitric Acid Treatment ..................... 160
5.2 Cesium Removal by Strong Nitric Acid ............................... 162
5.3 Cesium and Sodium Binding by Carborane Anion and Cobalt Dicarbollide Functionalized Polymers ........................................ 164
5.4 Cesium Binding Efficiency of Carborane Anion and Cobalt Dicarbollide Functional Groups in Polymers ............................... 166
Chapter 1

Background

In this research, we have used ring-opening methathesis polymerization (ROMP) of norbornene based monomers to synthesize polymers with pendant carborane groups. Carborane functionalized polymers are interesting materials because the carborane group may be expected to result in unusual to physical properties. These polymers may also be synthetic precursors for cobalt dicarbollide materials with selective cesium ion binding properties. Because carborane and cobalt dicarbollide are somewhat obscure molecules, their properties, applications, and polymer history are reviewed in Chapter I. We also review the aspects of ROMP that make it especially suitable for the synthesis of these materials.

1.1 Carboranes

1.1.1 General Properties

“Carborane” is the generic term for a family of polyhedral cage molecules containing boron, carbon, and hydrogen. The boron and carbon atoms in these molecules are not connected by normal covalent bonds, although each is covalently bonded to a hydrogen atom. Instead, carboranes have a three-dimensional pseudo-aromatic structure in which the electrons are delocalized and each skeletal atom is hypercoordinated [37]. The most common carborane is the ortho carbon isomer of the icosahedral $C_2B_{10}H_{12}$
molecule, 1,2-dicarbadodecaborane (see Figure 1-1). Typically known as o-carborane
or just carborane, this compound exhibits the high chemical, thermal, and biological
stability typical of carbon-boron clusters. Thermally, o-carborane is stable up to to
400 °C. o-Carborane rearranges into the meta isomer at around 425 °C, and converts
to the para isomer at higher temperatures [38, 91]. The biological inertness of o-
carborane is demonstrated by its unusually high LD_{50} of 9 g/kg (compared to 1 g/kg
for calcium chloride) [54, 55]. Chemically, the skeleton of o-carborane is stable enough
to tolerate a range of reactions to attach or modify substituent groups [38]. Carborane
is not degraded by acids, but can react with some bases and reagents such as butyl
lithium [92].

Other interesting properties also result from o-carborane's unusual structure. The
molecule has a strong permanent dipole moment of 4.45 D [93] with a slight positive
charge between the carbons (see Figure 1-2). This makes the hydrogens bonded to
carbons more acidic than those bonded to borons [52], and also makes the borons
adjacent to both carbons removable [39]. Upon removal of one B-H group, the icosahedral cluster becomes an open-faced anion [49, 137] that can form organometallic sandwich complexes [43, 46, 134, 48].

Similar in structure to o-carborane is the carborane anion \(\text{CB}_{11}\text{H}_{12}^\text{-} \) (see Figure 1-3). Carborane anions are unusual because the negative charge is delocalized over the entire molecule [62, 61, 112, 18]. This anion has an extremely low charge density and a low nucleophilicity [112]. The conjugate acid of this anion is exceedingly strong [18]. Salts of this carborane anion completely dissociate in non-aqueous solvents [106]. Many of the anion properties of \(\text{CB}_{11}\text{H}_{12}^\text{-} \) are shared by carborane based organometallic sandwich complexes such as cobalt dicarbollide [106], described in Section 1.2.

Carboranes are a high boron density material, and thus have some characteristics due to elemental boron properties. The \(^{10}\text{B}\) isotope of boron, which has a 20% natural abundance, is the lightest element that reacts with slow neutrons [45]. Carboranes enriched in \(^{10}\text{B}\) can be synthesized, maximizing the material’s ability to capture neutrons.

1.1.2 Applications

High Energy Fuel

Boron cluster compounds were initially developed as high energy-density fuels for rockets and jets [45, 106, 30]. The high burning rate and very high heat of combustion
of these boranes make them an interesting alternative to traditional hydrocarbon fuels. However, the solid boron oxide combustion products add unacceptable amounts of wear and tear to turbines and engines [45]. Although polyhedral boranes have not found successful commercial application as fuels, the research effort in this field did show that these compounds can be synthesized on a large scale [45].

High Temperature Rubber

The most successful commercialization of carborane materials has been the DEXSIL polymers developed by Olin corp [40]. These siloxane polymers incorporate m-carborane units into their main chains (see Figure 1-4). The carborane units dramatically improve the high temperature performance of the polymer; gaskets and o-rings made from DEXSIL products (containing fillers, crosslinking, antioxidants) can be used up to 900 °F [118, 40]. This increased high temperature performance is due to a combination of steric and chemical mechanisms [40]. The steric bulk of the carborane functionality (about 4 Å) inhibits polymer crystalization and impedes molecular motion [118]. The carborane group withdraws electrons from adjacent atoms and it is hypothesized that they provide resonance stabilized energy sinks [118].

Cancer Therapy

Recently, $^{10}$B enriched carborane compounds have been investigated as agents in boron neutron capture therapy (BNCT) for the treatment of brain cancers. BNCT has also been considered for lung and prostate cancers [45, 22]. In BNCT, boron
compounds are injected into the blood stream and accumulate in tumors. When the area near the tumor is irradiated with slow neutrons, high energy byproducts of the boron capture reaction destroy nearby cells. Only cells with significant boron concentration are damaged by the neutrons.

Carborane compounds are good candidates for use in BNCT because they have low toxicity and are quickly excreted from the body. These compounds can be modified to selectively accumulate to the necessary concentrations in cancerous cells [45].

Ceramic Precursor

Polymers containing carboranes or boron cluster compounds have been considered as easily processed precursors to boron carbide or boron nitride ceramics [11, 122, 121]. Polymers can be drawn into fibers, coated onto surfaces, filled into pores, or used as binders for other ceramic precursors. Because these cluster compounds are much more expensive sources of boron than naturally occurring boron compounds, such polymers would only be practical as ceramic precursors for applications that demand specialized shapes not achievable through standard ceramic shaping methods.

Optics

The permanent dipole of o-carborane can be modified and strengthened by attaching electron withdrawing or donating groups at the appropriate sites [93]. Modified carboranes have been patented as optical switching and optical modulation materials [69, 68]. A number of modified carborane compounds have been studied as potential materials for second-harmonic generation [93, 94]. While some of these compounds did show some second-harmonic generation activity, the magnitude of the effect was small because these compounds crystallize in centro-symmetric space groups [93, 94]. It is possible that polymers incorporating such compounds might show more significant non-linear optical behavior after poling, since carborane polymers are usually non-crystalline.
Non-aqueous Electrolytes

Borane and carborane anion salts dissociate completely in many non-aqueous solvents [106]. This strong ionic dissociation, in addition thermal and chemical stability, low charge density, and non-nucleophilicity, makes polyhedral boron compounds potentially useful for non-aqueous electrolyte applications. Several borane cluster lithium salts were found to be promising electrolytes in lithium-titanium disulfide battery cells [63, 64]. More recently, there has been an attempt to incorporate pendant boron cluster anions into polymers to make polyelectrolytes [21]. Such polyelectrolytes might be useful as ion-conductive membranes or electrolytes for rechargeable lithium batteries.

Ligands for organometallic catalysis

One challenge in engineering catalytic materials is how to firmly attach catalytic small molecules onto solid substrates without an accompanying loss of activity. The open-faced carboranes formed by the removal of a single boron vertex from C_{2}B_{10}H_{12} isomers have been used to complex with organometallic rhodium, forming catalytically active C_{2}B_{9}H_{11}RhH(PPh_{3})_{2} species. These catalysts can isomerize and hydrogenate alkenes in solution [44]. Carboranes can be grafted onto chloromethylated polystyrene beads through skeletal carbon or boron before attaching the rhodium complex [15, 129] (see Figure 1-5). Alternatively, carborane containing monomers can be polymerized and then functionalized with the rhodium complex. In either case, the catalytic species remains attached to the substrate and catalytic activity is maintained through multiple turnovers [29, 129]. The uncrosslinked functional-
ized polymer was found to be more catalytically active than the material made from crosslinked polystyrene beads, possibly because of a difference in catalyst site accessibility [29].

1.1.3 Synthesis of Carborane Polymers

The most commercially promising carborane-based materials have been polymers [40]. Carboranes have been incorporated into polymers both as part of the main backbone and as pendant groups, despite some synthetic challenges. Figure 1-6 shows some examples of such polymers. Primarily, difficulties in polymerization reactions are caused by the large steric bulk and electron withdrawing nature of the carborane group [36, 34, 35]. Additionally, difunctional o-carborane monomers sometimes have a tendency to form small cyclic oligomers instead of linear polymers during condensations reactions [118, 104].

Main Chain Carborane Polymers

A series of inorganic main chain carborane polymers has been synthesized with repeat units consisting of single atoms of silicon, germanium, lead, tin, carbon, phosphorus,
sulfur or mercury bonded to the skeletal carbon atoms of m-carborane or p-carborane. In the case of silicon, germanium, lead, or tin, the condensation reaction is between \( \text{Li}_2(\text{C}_2\text{B}_{10}\text{H}_{10}) \) and \( \text{R}_2\text{MC}_2 \), where M is any of the listed elements [40]. The sulfur and mercury bridged carborane polymers are unusual in that there are no substituents other than carborane bonded to the bridge atoms [118]. In the case of phosphorus bridge atoms, each phosphorus is also bonded to a chlorine. Carbon bridged carborane polymers have been synthesized with carbonyl carbons used as bridging atoms [118]. The meta- or para- isomers of carborane can form single atom bridged carborne polymers, but the ortho-isomer has too much of a tendency to cyclize. Such polymers have fairly low molecular weights, with at most 30 or so repeat units [118]. In some cases, random copolymers can be made from mixtures of meta- and para-carborane or mixtures of tin and germanium [118].

Many of the typical condensation polymerization methods can be used to make main chain carborane polymers. \( \text{o-Carborane diols, diacids, and diesters can be reacted with each other or with other difunctional monomers to form polyesters with molecular weights from 2000-20,000 [40, 34]. Condensation reactions were found to be inhibited when the carborane group was close to the functional ends of the monomer; this effect was attributed to both steric and electronic factors [34]. Polyamides, polyurethanes [138] and polyformals [34] have also been synthesized.

The commercially successful series of m-carborane siloxane polymers is described earlier in the Applications section 1.1.2. These DEXSIL polymers were synthesized from the ferric chloride catalyzed condensation reaction of difunctional methoxysilyl m-carborane monomers and chlorosilanes. Molecular weights of up to 16,000 have been measured but higher molecular weight materials were too insoluble for analysis [104]. Hydrolysis of difunctional bis(chlorosilyl) carborane monomers did not result in polymers, possibly due to the electron withdrawing effect of the carborane. Monomers made from the ortho-isomer were found to form cyclic oligomers [104]. Carborane siloxanes with fewer molecules between the carborane groups along the main chain backbone are crystalline, while those with a greater number of (Si-O) groups separating the carboranes are amorphous [104].
Polymers with Pendant Carborane

A wide variety of synthetic strategies have been used to make siloxane and vinyl polymers with pendant carborane groups. Both condensation and addition polymerizations have been employed, as well as grafting reactions [40]. Generally, the presence of the carborane cage tends to increase the thermal transition temperature of the polymers [35] and inhibit thermal degradation [40], although to a lesser extent than with main chain carborane polymers. The pendant carborane groups are generally the ortho-isomer.

Vinyl carborane polymers with molecular weights up to 140,000 have been synthesized by phenyl lithium catalyzed free radical initiation [30]. Similarly, methyl vinyl carborane and methyl isopropenyl carborane have been used. These monomers have also been copolymerized with butadiene [138]. Acrylate and methacrylate carboranes have also been homopolymerized and copolymerized free radically [40, 35]. Copolymerization has sometimes been necessary for monomers such as isopropenylcarborane, which do not homopolymerize [35]. The lowered activity of carborane monomers towards radical polymerization is attributed to both steric inhibition and electron withdrawing effects [35, 29]. The inductive effect can be avoided by converting the carborane into the open-faced, anionic form before polymerization [29].

A series of polysiloxanes with pendant carborane groups was synthesized by both hydrolysis-condensation and ring-opening polymerization of cyclic carborane siloxanes [40]. The first method has been used to make polymers up to 14,000 molecular weight, with large amounts of cyclic side product. A grafting reaction to attach isopropyl carborane to poly(hydrosiloxanes) has also been reported [40].

1.2 Cobalt Dicarbollide

Cobalt dicarbollide is an organo-metallic compound analogous to ferrocene (see Figure 1-7). Described as “peanut shaped” [106], it is constructed from two modified o-carborane fragments and a cobalt center [46, 48]. With a -1 charge delocalized over both carborane fragments, cobalt dicarbollide has an extremely low charge density.
The conjugate acid is one of the strongest known acids because there are no free electrons to bind a proton [106, 80]. Cobalt dicarbollide has been shown to be an effective and selective phase transfer agent for the solvent extraction of cesium from aqueous solutions [119, 106]. A practical method for separating cesium from solution could be very useful because the United States (and other countries) have large amounts of aqueous nuclear waste containing the radioisotope $^{137}$Cs [7, 103].

1.2.1 Nuclear Weapons, Nuclear Power, Nuclear Waste

Typically, nuclear power plants are fueled by uranium rods containing 3.3% $^{235}$U and 96.7% $^{238}$U [95]. After a usable life of about 3 years, spent fuel rods contain 0.81% $^{235}$U, 94.3% $^{238}$U, small amounts of plutonium, and 3.5% other fission products [95]. Thus, "spent" fuel rods are still extremely radioactive. Such spent fuel rods can be processed to separate uranium and plutonium from fission products such as cesium-137 and strontium-90. Because purified plutonium can be used for nuclear weapons, the reprocessing of fuel rods is controversial in the United States [96]. However, reprocessing to recover uranium is commonly practiced in France and the United Kingdom [56, 57].

When fuel rods are reprocessed to remove uranium and plutonium, the remaining
substance is left dissolved in strong acid (> 0.5M nitric) [119]. In the course of building nuclear weapons, the U.S. produced a large amount of this radioactive waste solution [119, 97, 103]. Currently stored in tanks at the Hanford and Savannah River sites, this solution is unacceptable for permanent disposal because it is difficult to reliably contain a liquid [103, 4]. A number of tanks have already leaked radioactive waste into the environment. Cesium-137 and strontium-90 are the most plentiful and dangerous radioisotopes in this waste [103, 7, 19]. Cost estimates for remediating these wastes have been steadily increasing, one estimate is $100 billion [89].

Reprocessing waste may be directly vitrified for disposal, or it may be separated into a small volume of highly radioactive material and a large volume of low radioactivity [103, 7]. Currently, the location and design of a permanent storage facility for highly radioactive materials is still being debated. However, it is projected that if cesium and strontium were separated from reprocessing waste, the total disposal costs would be much lower because there would be a much smaller volume of highly radioactive material to store [119, 7].

Thus, a method of separating cesium from aqueous solution would be useful in dealing with existing reprocessing waste. If cesium and strontium were separated from the waste solutions, they might become a resource instead of a liability. Recovered $^{137}$Cs can be used to sterilize food or medical supplies [119, 98, 19]. With a growing demand for food irradiation in the U.S., there will be a growing market for $^{137}$Cs. Strontium-90 can be used for long life, no maintainance thermoelectric generators for remote locations [119, 98, 19].

### 1.2.2 A Summary of Cesium Separation Techniques

Although reprocessing wastes are acidic, they are often made alkaline for storage to minimize container corrosion [103]. Some of the past storage and treatment processes have also produced waste sludges which will have to be dissolved in acidic solutions for element separations [7]. As the mechanisms of most ion binding processes are pH dependant, different separation techniques are needed to treat acidic and alkaline wastes.
Alkaline Wastes

Tetraphenylborate (see Figure 1-8) and metal ferrocyanides or ferricyanides can be used to precipitate cesium from alkaline solutions [87, 86, 78, 42, 119, 20]. Such precipitation processes have the disadvantage of producing a radioactive sludge. Additionally, the tetraphenyl borate releases large amounts of benzene byproduct [65]. Solvent extraction processes using phase transfer agents such as dipicrylamine, tetraphenylborate, polyhalides, and specialized phenols in a variety of solvents have also been studied [119]. However, the currently favored separation processes use solid phase extractants such as phenolic or resorcinol based ion-exchange resins, or inorganic zeolites [73, 7].

Acidic Wastes

Techniques for removing cesium from acidic solutions are less well developed than the alkaline side treatments. Phosphotungstic acid has been used as a precipitating agent. Crown ethers [83], calixarenes [105, 3, 72, 84, 60] (see Figure 1-8), specialized phenols [13], organo-phosphoric or sulfonic acids, and cobalt dicarbollide (see Section 1.2.3) have been studied as phase transfer agents in solvent extraction processes. Solid, inorganic ion-exchange materials such as titanium phosphate or ferrocyanide molybdate have also been examined [126, 140, 6, 132, 123, 88, 85]. Additionally, these inorganic materials have been combined with various supports to develop a material
more suitable for use as a column packing [131, 51, 135, 136].

Modified crown ethers and the cobalt dicarbollide molecule demonstrate promising cesium binding functionality, but separation processes using these reagents have not been fully developed [119]. Questions remain about how to effectively strip cesium from crown ether solutions and whether an acceptable solvent can be found for the cobalt dicarbollide solvent extraction process. Various researchers have functionalized polymers or other support with crown ethers [142, 66, 50, 10] or cobalt dicarbollide (see Section 1.2.4) to try and combine the selective binding activity of the functional group with the process advantages of a solid material. We believe that this approach is promising. Since the mechanisms of binding, selectivity, and stripping are more straightforward for the cobalt dicarbollide molecule than the crown ethers, we are concentrating on using cobalt dicarbollide to functionalize polymers for cesium binding.

1.2.3 Cobalt Dicarbollide in Solvent Extraction

Although there has been some investigation of cobalt dicarbollide as a precipitating agent [24, 25], the majority of studies have examined its properties as a phase transfer catalyst for cesium in water/organic systems [5, 80, 110, 1, 74, 109]. Generally, the organic phase is a polar solvent like nitrobenzene or ether [106]. With the addition of polyethylene glycols, strontium and barium can also be extracted [106, 109, 75, 5, 80, 1]. Other additives can shift selectivity to trivalent metals like europium and americum [110]. Thus, a cobalt dicarbollide based process might be useful in separating other radionuclides as well as cesium from nuclear waste solutions.

Several partially chlorinated versions of cobalt dicarbollide, with two to six of the boron hydrogens replaced by chlorine, have been synthesized [53]. Halogenation improves the molecule's stability in strong acid without affecting its cesium binding properties [106, 53]. In Russia, chlorinated cobalt dicarbollide in nitrobenzene has been used in a pilot scale solvent extraction process to selectively recover cesium from high level nuclear waste [119].

Because nitrobenzene is a relatively dangerous solvent, efforts have been made
to find alternative solvents for the extraction process[5]. Unfortunately, many polar solvents such as t-butanol seem to stabilized H\(^+\) in the organic phase and inhibit Cs\(^+\) extraction while non-polar solvents do not sufficiently dissolve cobalt dicarbollide [90]. One promising approach is to modify the solubility of cobalt dicarbollide by alkyl substitution at the carbons so that non-polar solvents can be used [90].

1.2.4 Cobalt Dicarbollide in Polymeric Solid Phase Separation

Separations processes which use solid phase ion-exchange materials have several advantages over solvent extraction processes. The primary advantage is the elimination of organic solvents, which may be carcinogenic, toxic, volatile, or flammable. Solid phase materials are much less likely to be lost into the aqueous phase than the organic solvents and phase transfer catalysts used in solvent extraction processes. In the particular application of radioactive waste treatment, a solid phase material could also be used as a relatively safe form in which to transport radioisotopes. For example, a filter with cesium bound to it could be moved from the waste generation location to the waste storage area without the danger of spilling radioactive liquids.

Researchers at Los Alamos have grafted cobalt dicarbollide directly onto cross-linked resin beads [133]. They found that cobalt dicarbollide functionalized polystyrene beads did not remove cesium from aqueous solutions, and attributed this to the hydrophobic nature of the polystyrene. Partial sulfunation of the cobalt dicarbollide functionalized bead increased hydrophilicity and cesium uptake, but probably adversely affected selectivity since sulfenate groups non-selectively bind cations.

1.3 Ring-Opening Metathesis Polymerization (ROMP)

There are two routes to produce a functionalized polymer. Either a monomer containing the desired functional group can be polymerized, or the functional group can
be grafted onto an existing polymer. Generally, the first method can produce more well defined polymers. Unfortunately, some functional groups tend to interfere with many methods of polymerization. The carborane group is already known to inhibit various methods of polymerization and cobalt dicarbollide may have similar effects. One polymerization system which tolerates a variety of functional substituents is the ring-opening metathesis polymerization of norbornenes (see Figure 1-9). Thus, the ROMP system has been identified as a promising route to well-defined carborane and cobalt dicarbollide containing polymers. This system also has the advantage that polymerization tends to go to completion with good yield of polymer. Additionally, it can be used to make copolymers, combining the desirable properties of multiple homopolymers.

1.3.1 Catalyst Systems

Functionalized norbornene monomers can be polymerized by three varieties of commercially available catalysts. The first catalysts to be used were transition metal chlorides [102]. Norbornene-type monomers with carboxylic acid, ester, anhydride, ether, and methyl chloride substituents have been polymerized with RuCl₃, MoCl₅/EtcAl, WCl₆/Me₄Sn, ReCl₅, IrCl₃/cycloocta-1,5-diene [79, 59, 58]. These catalyst systems are easy to use because they work at temperatures between 20-70 °C and in solvents such as water/ethanol. The main drawback of these catalysts systems is that they sometimes need long induction times (hours or days) before the metal chlorides un-
dergo reaction to form the actual initiating species [102]. The resulting polymers have molecular weight polydispersities of about 2 [79].

The later varieties of catalysts are both capable of initiating "living" polymerization. Polymers made with these organometallic catalysts can have very narrow molecular weight distributions; well-defined block copolymers can also be produced. The Schrock catalysts, which contain molybdenum or tungsten, are extremely sensitive to deactivation from oxygen or acidic protons. These catalysts have been used to polymerize norbornene monomers containing anhydrides, esters, amides, ethers, thioethers, pyridine, tertiary amines, buckeyballs, and organometallic complexes [17, 116, 8, 82, 141, 2] but are deactivated by alcohols, carboxylic acids, or thiols. Generally, moderate temperatures are used, and polymerization takes minutes or hours. Monomers and solvents used must be rigorously dried and purified.

The Schrock ROMP system has even been used to make resin particles for study as ion exchange materials. These particles have a "fur-like" structure, with many linear arms attached to a crosslinked core. The arms are first polymerized from a solution of metal binding monomer. Then a crosslinking agent is added and the growing chain ends become part of the core [12, 125].

The Grubbs catalysts, containing ruthenium, are much easier to use because they can tolerate water or other protic chemicals and are only slowly deactivated by oxygen [102]. However, monomers with alcohol or carboxylic acid groups near the olefin bond will still deactivate these catalysts by intramolecular interaction with the propagating metal center. If these groups are attached to the monomer through a spacer chain, they do not poison the catalyst. Strongly donating groups such as nitriles or pyridines also prevent polymerization [12]. These catalysts are considered somewhat less active than the Schrock catalysts [12]. Norbornene monomers with ester, ether, anhydride, imide, and "distant" alcohol or nitro groups have been polymerized with these catalysts [67, 100, 101, 139, 28]. Our research primarily used a Grubbs catalyst because preliminary efforts with a Schrock system were unsuccessful, probably due to insufficient purification of monomers. Figure 1-10 shows the structures of the catalysts used in this work.
1.3.2 Kinetic Effects

Polymerization Solvent

The main considerations in choosing a polymerization solvent are the solubilities of the monomer, catalyst, and resulting polymer. Generally, ROMP reactions will not go to completion in a living manner unless all three components are completely dissolved. The catalysts are soluble in common solvents, such as methylene chloride, toluene, and THF. Most norbornene based monomers are also soluble in these solvents. However, many of the substituted polynorbornenes which were synthesized in this project were found to precipitate from toluene or methylene chloride.

A secondary consideration for polymerization solvent choice is the effect of the solvent on the catalyst. Although the Grubbs catalysts have been found to have comparable activity in solvents of varying polarity or coordinating ability, polymerization is faster in non-coordinating solvents such as methylene chloride [101].

Substituents

The functionalized monomers used in this research were all a mixture of endo and exo isomers. Due to a combination of steric and intramolecular coordinating effects,
the endo isomer is usually less reactive than the exo isomer [67]. However, unless the substituent actually poisons the catalyst, this reactivity difference will probably not be noticeable in the mixed isomer monomers.

Unsubstituted norbornene polymerizes more readily and more quickly than functionalized norbornene monomers. If propagation is slow, there is more time for side reactions like chain transfer or catalyst deactivation to occur. Thus, slower polymerizations tend to produce broader molecular weight distributions. As molecular weight can have some effect on polymer properties, more monodisperse samples are preferable for characterization. However, a narrow molecular weight distribution is not necessary for applications such as high temperature use materials or ion-exchange resins.
Chapter 2

Synthesis of Carborane Functionalized Norbornene Monomers

This chapter discusses the synthesis of four o-carborane functionalized norbornene monomers and a carborane anion norbornene monomer (see Figure 2-1). The synthetic routes described in this chapter demonstrate that norbornene can be readily functionalized with o-carborane through a range of precursor monomers. The resulting carborane monomers may be used as intermediates in the synthesis of cobalt dicarbollide functionalized monomers or polymers. Additionally, the variety of carborane monomers made it possible to synthesize a series of polymers all containing the same bulky, pseudo-aromatic group attached in different ways and to compare the effects of specific means of attachment on polymer properties.

These monomers all have the carborane groups attached through a carborane skeletal carbon (as opposed to boron). This type of bond is readily made by first deprotonating the carborane with butyl lithium to form a carborane carbanion, as illustrated in Figure 2-2. Since the carbon protons are more acidic than the boron protons, skeletal carbon is selectively deprotonated. The resulting carbanion can displace leaving groups, forming a Si-C or C-C bond [38, 52]. Purification can be achieved through solvent extraction, recrystallization, and column chromatography.
Figure 2-1: Carborane Functionalized Norbornene-Based Monomers

Figure 2-2: Butyl Lithium Deprotonation of o-Carborane
In this research, the structure of monomer compounds was verified mainly through proton nuclear magnetic resonance (HNNMR). Some carbon-13 NMR, boron-10 NMR, and elemental analysis results were also used. Elemental analysis of some boron cage compounds underreports the amount of boron because the molecules are unusually stable and may be incompletely digested [133].

2.1 Nor-Si-Carb: A Silicon Bridged Carborane-Norbornene

Carbanions generally react extremely readily with Si-Cl bonds. Carborane carbanions are no exception, and there is a long history of using this route to attach groups to carboranes [38, 52]. Because a C-Si bond is more flexible than a C-C bond, functional groups attached to a polymer backbone through a silicon bridge may also be relatively mobile.

Although two carborane groups are reported to have been attached to the single silicon center of dimethyldichlorosilane [52], our attempts to attach two carborane groups to the commercially available 5-(dichloromethylsilyl)-norborne were unsuccessful. Figure 2-3 shows the attempted synthesis scheme. The resulting product mixture was found through chromatography to have approximately one equivalent of unreacted carborane, but was not further characterized. Possibly the steric effect of the norbornene and first carborane group prevents reaction of the second Si-Cl
bond. Alternatively, a proton transfer of the type describe in Section 2.3.1 may have occurred.

A monofunctional norbornene chlorosilane is not commercially available, but can be synthesized by a Diels-Alder reaction between chlorodimethylvinylsilane and dicyclopentadiene [27]. The resulting 5-(chlorodimethylsilyl)-norbornene (see Figure 2-4) readily reacts with butyl lithium deprotonated o-carborane in ether to form 5-(dimethylsilylcarborane)-norbornene in good yield (see Figure 2-5). Nor-Si-carb is a crystalline monomer that melts at 85-87 °C.

NMR supports the structure of this compound shown in Figure 2-5. Proton NMR (see Figures 2-6, 2-7) confirms the ratio of one carborane carbon-hydrogen to two olefin hydrogens to six dimethylsilyl hydrogens. As with all boron cage compounds, the boron hydrogen peaks are broad and overlapping. This problem can be eliminated by using $^{11}$B decoupling, but this option was not available at our facility. $^{13}$CNMR (see Figure 2-8) confirms that the two carborane carbons are non-equivalent, one with the weaker signal typical of quaternary carbons, and shows that both peaks are shifted downfield compared to the single carbon peak of o-carborane (see Figure 2-9). Also visible are the olefin carbon peaks (4, due to endo/exo splitting), 5 carbon peaks corresponding to the non-olefin carbons of the norbornene group, and a group of methylsilyl carbons peaks. $^{11}$BNMR (see Figures 2-10, 2-11) shows six main peaks consistent with the expected 2:2:2:2:1:1 ratio for this compound, along with minor peaks resulting from the endo/exo isomerism of the dimethylchlorosilyl-norbornene starting material.

2.2 Nor-C-Carb: A Carbon Bridged Carborane-Norbornene

Since Si-C bonds in which the carbon is part of an aromatic group tend to be less robust than C-C bonds, a carbon bridged carborane norbornene was expected to be more stable than the silicon bridged version. One way to form a C-C bond is
Figure 2-4: HNMR of 5-(Chlorodimethylsilyl)-Norbornene in D-Chloroform
the reaction of a carbanion species with a compound containing the tosylate leaving group (see Figure 2-12). Although tosylate leaving groups have not been used widely in carborane compound synthesis [21], we have found that the carborane carbanion displaces tosylate to form a C-C bond.

Nor-C-carb was synthesized from 5-(methyltosylate)-norbornene (see Figure 2-13), which can be synthesized from the commercially available endo/exo norbornene methanol. The reaction between deprotonated o-carborane and the tosylate has a lower yield than the reaction with the chlorosilane, but is still reasonable. Nor-C-carb has a crystalline melting point of 82-87 °C.

HNMR confirms a 2:1 ratio between olefin hydrogens and carborane carbon hydrogens (see Figure 2-14). As with other boron cage compounds, the boron hydrogens give broad, overlapping peaks which do not have clear integration ratios. $^{13}$CNMR (see Figure 2-15) shows one carborane carbon to be shifted downfield compared to o-carborane, while the other carborane carbon peak is too weak to be visible. Additionally, the expected endo/exo split olefin carbon peaks and the other six aliphatic carbon peaks (five of which show endo/exo splitting) are present. $^{11}$BNMR shows the expected six boron peaks with 1:1:2:2:2:2 ratio (see Figure 2-16).
Figure 2-6: HNMR of Nor-Si-Carb in D-Acetone
Figure 2-7: HNMR of o-Carborane in D-Chloroform
Figure 2-8: $^{13}$CNMR of Nor-Si-Carb in D-Acetone
Figure 2-9: $^{13}$CNMR of o-Carborane in D-Chloroform
Figure 2-10: $^{11}$BNMR of Nor-Si-Carb in D-Acetone
Figure 2-11: $^{11}$BNMR of o-Carborane in D-Chloroform
2.2.1 Effect of Reagent Stoichiometry on Yield

Unreacted norbornene tosylate can be recovered from the nor-C-carb synthesis reaction crude product. Since the butyl lithium deprotonation of o-carborane is known to proceed to completion, this suggests that it is the reaction between the carborane carbanion and norbornene tosylate which is hindered. One possibility is that the equilibrium for this reaction might not strongly favor the products. Another possibility relates to the proton transfer mechanism explained in Section 2.3.1.

According to the proton transfer mechanism, a carborane carbanion can abstract a proton from the carbon of a carborane moiety which is already attached to a norbornene monomer framework. The resulting carborane is unreactive, since it is no longer deprotonated, and the carborane carbanion monomer is deactivated by steric hinderance from the norbornene group. This carbanion monomer later reacts with ambient water to revert to nor-C-carb.

Both of these explanations suggest that increasing the carborane to norbornene...
Figure 2-13: HNMR of Nor-Tosylate in D-Chloroform
Figure 2-14: HNMR of Nor-C-Carb in D-Chloroform
Figure 2-15: $^{13}$CNMR of Nor-C-Carb in D-Chloroform
Figure 2-16: $^{11}$BNMR of Nor-C-Carb in D-Chloroform
tosylate ratio would increase the percentage of norbornene tosylate reacting. However, experimental results from changing the reagent ratio do not support either hypothesis as an explanation of incomplete reaction. A batch of nor-C-carb synthesized using a 2:1 carborane to norbornene tosylate ratio actually had a significantly lower yield calculated based on norbornene tosylate starting material.

This unexpected result could be explained by some difficulties encountered during the column chromatography purification of the crude product. Alternatively, there might be an impurity or side reaction that increases with increasing amounts of o-carborane or butyl lithium. A more detailed analysis of the reaction by-products would be necessary to understand the mechanisms by which reagent stoichiometry affects yield.

2.2.2 Unusual Tosyl Carborane Reaction

During another batch reaction to test the effect of reagent stoichiometry on the yield of nor-C-carb, old diethyl ether was inadvertently used as the solvent. Although this ether had been stored in a nitrogen glove box, it may have developed peroxides or free radicals that catalyzed an unusual reaction to make the alternate product, p-toluenesulfonyl carborane (see Figure 2-17). It is unusual but not unknown for a nucleophile to react with a tosylate group in this manner [81].

p-Toluenesulfonyl carborane is a white, crystalline solid melting between 125 and 135 °C. HNMR of this compound (see Figure 2-18) is very similar to o-carborane, with the addition of two aromatic peaks and one aliphatic peak which can be assigned to the toluenyl protons. The aromatic peaks are the same size and each is twice the size of the carborane carbon proton peak.
2.3 Nor-CC-Carb: A Monomer with Twice-Bound Carborane

In this section we describe how an attempt to synthesize one interesting monomer led to an unexpected, also interesting, alternative monomer.

All these carborane functionalized monomers are potential intermediates to a cobalt dicarbollide functionalized polymer. Since cobalt dicarbollide is made from two carborane derivatives, it might be synthetically advantageous if two carborane groups could be attached to a monomer. If the two carborane groups were attached so that the distance between them was approximately equal to the distance between the two carboranes derivatives in a cobalt dicarbollide molecule, it might be possible to convert the monomer with two carboranes into a cobalt dicarbollide monomer without any additional carborane.

As described in Section 2.1, an attempt to react two carboranes with a dichlorosilane was unsuccessful, possibly due to steric hindrance around the single silicon center. Trans-5,6-bis(methyltosylate)norbornene has two reactive sites which are far...
Figure 2-18: HNMR of p-Toluenesulfonyl Carborane in D-Chloroform
enough apart that substitution at one site may not hinder reaction at the second site. These sites would also provide appropriate spacing for two carborane groups to become incorporated into the same cobalt dicarbollide molecule. This ditosylate can be made from the trans dicarboxylic acid norbornene which is synthesized from cyclopentadiene and fumaric acid.

Upon reaction with deprotonated o-carborane, the ditosylate did not convert into a dicarborane monomer (as pictured in Figure 2-19). Instead, the resulting monomer contained single carborane group attached through carbon at both the 5 and 6 sites (see Figure 2-20). Thus, nor-CC-carb is pseudo-tetracyclic; a tricyclic structure fused to the pseudocyclic carborane group. Nor-CC-carb was somewhat more difficult to purify than nor-C-carb, and was recovered in slightly lower yield. The monomer is a white crystal that melts between 150 and 170 °C and is soluble in THF, chlorform, and acetone. None of the originally expected dicarborane monomer was recovered.

Unlike most of the precursor monomers used in this study, trans-5,6-bis(methyltosylate)norbornene does not have different endo/exo isomers, since each molecule has
one endo and one exo substituent. This is reflected in the HNMR, where there is no endo/exo peak splitting (see Figure 2-21). Similarly, HNMR spectrum of nor-CC-carb has no endo/exo splitting (see Figure 2-22). The expected broad, overlapping boron hydrogen peaks are visible and there is no remaining carborane carbon hydrogen peak. The expected norbornene framework hydrogen peaks are also present.

2.3.1 The Proton Transfer Mechanism

In order for both carborane carbons to form bonds to the ditosylate norbornene monomer, both skeletal carbons would have to be deprotonated since the protonated carborane carbon is not nucleophilic. It has been reported that if two equivalents of butyl lithium are used so that both carborane carbons are deprotonated, then the dicarbanion can react at both carbons [38, 52]. However, only 1.2 equivalents of butyl lithium were used in our synthesis and the nominal excess of 20% was used to compensate for partial deactivation of the butyl lithium.

We propose that during the course of the reaction, first some 5-(methylcarborane),6-(methyltosylate)-norbornene is formed (see Figure 2-23). Then, the remaining carborane carbon proton of the monomer is removed by a deprotonated carborane in solution. This type of proton interchange between carboranes and carborane carbanions has been previously reported [38]. An intramolecular reaction between the tosylate arm and the deprotonated carborane arm of the monomer completes the synthesis.
Figure 2-21: HNMR of Trans-5,6-bis(methyltosylate)norbornene in D-Methylene Chloride
Figure 2-22: HNMR of Nor-CC-Carb in D-Chloroform
Possibly, the attachment of the first carborane group slightly deactivates the second tosylate due to steric hinderance, and then the intramolecular reaction occurs in preference to the addition of a second carborane group.

The proton transfer between deprotonated carborane and a carborane already bound to a norbornene group could be studied by combining nor-C-carb with deprotonated carborane in solution, and then adding an unhindered chlorosilane, tosylate, or halide. For example, if ethyl iodide was used, the product would be examined for the relative amounts of 5-(methylethylcarborane)-norbornene and ethyl carborane.

It would also be interesting to repeat the synthesis starting from the commercially available cis-dicarboxylic acid norbornene and going through the cis-ditosylate norbornene. Both the substituents of the commercially available cis monomer are in the endo position, so the distance between and relative orientation of the two reaction sites would be different than they were for the trans monomer. If this spatial arrangement favored intermolecular instead of intramolecular reaction, use of the cis-ditosylate might result in a dicarborane norbornene, which would be a good candidate for a cobalt dicarbollide norbornene precursor.
2.4 Nor-6-Carb: A Norbornene Monomer with Pendant Carborane Attached through a Spacer Chain

Polymers with pendant carborane may find applications as ion-exchange resins or polymer electrolytes. For both applications, the accessibility or mobility of the functional group is important. Thus, a molecular architecture which uses spacer chains to separate the functional groups from the polymer backbone might improve properties. Although these applications are envisioned for polymers with ether cobalt dicarbolllide or carborane anion groups and not for polymers functionalized with o-carborane, we have synthesized a carborane monomer with a spacer chain because carborane monomers can be precursors to cobalt dicarbolllide polymers. Additionally, the reaction chemistry of carborane and the carborane anion are quite similar, so the analogous carborane anion monomer synthesis should be possible.

A spacer chain length of six atoms was chosen because spacer effects usually start to appear when the chain length reaches 4-6 atoms. The scheme used here (see Figure 2-24) can be easily extended to make spacer chains of various lengths by using different dibromoalkanes.

The functionalized norbornene precursor monomer has a bromide leaving group, which is less reactive than the tosylate group. However, deprotonated carborane has been successfully reacted with alkyl bromides [52]. We found that the deprotonated carborane is able to displace bromide, but that the product is recovered in relatively low yield. Nor-6-carb is a clear oil at room temperature.

HNMR shows the characteristic carborane carbon proton peak in 1:2 ratio with the olefin hydrogen peaks (see Figure 2-25). The broad carborane boron hydrogen peaks and the peaks corresponding to the hydrogens nearest the oxygen can be identified. Other peaks corresponding to the other spacer chain protons and the norbornene framework are also visible.
Figure 2-24: Synthesis of Nor-6-Carb
Figure 2-25: HNMR of Nor-6-Carb in D-Chloroform
2.5 Nor-Si-Anion: A Norbornene Monomer with a Carborane Anion Group

The chemistry of the carborane anion, CB$_{11}$H$_{12}$, has not been as extensively studied as those of o-carborane or cobalt dicarbolide. However, this anion has been recognized as sharing some of the interesting properties of the cobalt dicarbolide ion which result from an extremely low charge density [106, 112, 62, 18]. A polymer functionalized with carborane anion groups might be useful as a flexible solid electrolyte for batteries or as a selective ion exchange material.

Since the chemistry of the carborane anion is generally considered to be similar to that of the o-carborane [70, 71, 62, 107, 61], we have used a synthesis analogous to the one described in section 2.1 to make a carborane anion norbornene monomer (see Figure 2-26). However, the anion’s different solubility properties [61] make it necessary to adjust some parts of the synthesis and purification procedure.

Because our experience making o-carborane norbornene monomers showed that the best yield was obtained using the 5-(chlorodimethylsilyl)-norbornene precursor, we used the same chlorosilane precursor. The reaction produced a white, solid product that melted at 200-210 °C. The HNMR of nor-Si-anion shows the broad boron hydrogen peaks and the expected olefin and methylsilyl hydrogen peaks in the correct ratio (see Figure 2-27).

2.6 Experimental Details

Although these types of reactions can be done in a chemical hood using air-free apparatus, we carried out all butyl lithium reactions in a nitrogen glove box.

2.6.1 Materials

Tosyl chloride was purchased from Aldrich and purified by dissolving in the minimum amount of chloriform, adding 5 times by volume petroleum ether, filtering, and evaporating the filtrate to recover crystals. n-Butyl lithium in hexanes (either 2.5M
Figure 2-26: Synthesis of Nor-Si-Anion
Figure 2-27: HNMR of Nor-Si-Anion in D-Methanol
or 10.0M), anhydrous solvents, and silica gel were purchased from Aldrich and used without purification. o-Carborane was purchased from Consumer Health Research Inc, which became E. Kantor Ent and is now out of business, and used without purification. The trimethylammonium salt of carborane anion was purchased from Katchem Ltd in the Czech Republic.

2.6.2 Equipment

All $^1$BNMR and some HNMR and $^{13}$CNMR were done at 3M by Dr. James Hill, with interpretation by Dr. Richard Newmark. A 500 MHz UNITY spectrometer was used. The rest of the $^{13}$CNMR and HNMR was taken on a Bruker 400 MHz FTNMR.

Melting points were determined visually using a Mettler FP82 hot stage and Nikon optical microscope with a heating rate of 20 °C/minute.

2.6.3 Nor-Si-Carb

An endo/exo mixture of chlorodimethylsilyl norbornene was synthesized by Dr. Randall Saunders according to the Finkelshtein procedure [27] and donated for our research. Nor-Si-carb was synthesized in batches ranging from 1 to 5 grams of starting o-carborane. In a typical reaction, 1 g of o-carborane was dissolved in 10 ml of anhydrous diethyl ether. A solution of 2.77 ml of 2.5 M n-butyl lithium in 10 ml ether (one equivalent) was slowly added to the stirred carborane solution. After 1 hour, 1.295 g (one equivalent) of the liquid chlorodimethylsilyl norbornene was added. The solution became cloudy with precipitate and boiled. After stirring overnight at room temperature, the solution was shaken with 20 ml distilled water and 20 ml ether in a separatory funnel. The ether phase was dried and the solid recrystallized from boiling methanol. Typically, first batch yields were 60-70%. The monomer is soluble in ethanol, methylene chloride, THF, and acetone. Elemental analysis by Galbraith gave mass percents: carbon 44% (calc. 45%), hydrogen 8% (calc. 9%), boron 37% (calc. 37%), silicon 10% (calc. 10%).
2.6.4 Nor-C-Carb

An endo/exo mixture of 5-(methyltosylate)-norbornene was synthesized by the literature procedure [17, 116]. Nor-C-carb was synthesized in batches ranging from 1 to 5 grams of starting o-carborane. In a typical reaction, 1 g of o-carborane was dissolved in 10 ml of anhydrous diethyl ether. A solution of 2.77 ml of 2.5 n-butyl lithium (one equivalent) in 10 ml ether was slowly added to the stirred carborane solution. After 30 minutes, a solution of 1.93 g of norbornene tosylate (one equivalent) in 3 ml ether was added to the stirred solution. After 2 hours, off-white precipitate was observed. The solution was stirred overnight at room temperature and then added to 20 ml ether and 40 ml water in a separatory funnel. The ether phase dried to an peach colored wax. The crude product was fractionated using column chromatography, with a 5:1 hexane:ethyl acetate eluent and silica gel adsorbant. The product is the first eluting compound. After chromatographic purification, the yield is typically 40-50%. Approximately 35% of the crude product mass never elutes from the column, even if a very polar solvent like acetone is used at the end. Nor-C-carb is soluble in acetone, THF, and chloroform.

In the batch of 5-(methylcarborane)-norbornene synthesized with a 2:1 ratio of carborane to norbornene tosylate starting material, the procedure was identical except that half as much norbornene tosylate was used. The yield after purification was 16% based on the amount of norbornene tosylate starting material.

2.6.5 p-Toluenesulfonyl Carborane

The anhydrous ether used as solvent had been stored in a nitrogen glove box at room temperature for at least a year. A solution of 3.736 g o-carborane in 40 ml ether was stirred. A solution of 3.118 ml of 10M n-butyl lithium in hexanes (1.2 equivalents) in 40 ml ether was slowly added. The butyl lithium solution had recently been titrated and determined to be partially deactivated so that a 20% nominal excess was needed. After 30 minutes, a solution of 3.616 g 5,6-bis(methyltosylate)-norbornene (0.5 equivalents) in 12 ml ether was dripped into the stirred carborane solution.
After stirring overnight, the solution was evaporated to a thick liquid and rinsed with 20 ml hexane. The liquid was diluted with 20 ml ether and shaken with 3 times 20 ml distilled water. Upon addition of the water, gas was evolved from the solution. The ether fraction dried to a white crystalline solid melting between 125 and 135 °C. The product could be purified by either recrystallization from ether allowed to evaporate, or column chromatography using silica gel and a 1:2 mixture of ethyl acetate/hexane. The product is the first eluting fraction.

2.6.6 Nor-CC-Carb

The trans-5,6-bis(methyltosylate)-norbornene was synthesized by Vishak Sankaran during his graduate research [116]. It was stored for approximately 5 years in a clear glass jar at room temperature and used without further purification. To 25 ml of anhydrous diethyl ether was added 2.5 g o-carborane. To 25 ml anhydrous ether was added 2.00 ml of 10M n-butyl lithium in hexanes (1.2 equivalents). The butyl lithium solution was slowly dripped into the stirred carborane solution. After 30 minutes, 4 g of ditosylate norbornene (0.5 equivalents) in 10 ml anhydrous tetrahydrofuran was dropped into the stirring solution. The solution boiled and became cloudy. Although the ditosylate norbornene is not soluble in ether, it will mostly stay in solution if first dissolved in THF.

The solution was stirred overnight and filtered. The filtrate was extracted twice with 100 ml distilled water. The ether phase was dried to an orange solid. This crude product was purified using column chromatography with chloroform eluent and silica gel adsorbant. The product is the first fraction eluted. After column chromatography, the product is a white crystal melting between 112 and 170 °C. The product was further purified by recrystallization from boiling ethanol to give a white crystal in 32% yield, calculated on a ditosylate norbornene basis. The recrystallized product melted at 150-170 °C.
2.6.7 Nor-6-Carb

The synthesis of this monomer was done in anhydrous THF solution instead of diethyl ether, for no particular reason. Generally, diethyl ether is used in these kind of reactions because the resulting lithium salts (lithium chloride, lithium tosylate, or lithium bromide) have a low solubility in ether and precipitate, thus keeping the concentration of these coproducts low.

5-(metosybutylbromide)-norbornene was synthesized by Dr. Jin Kyu Lee using a method analogous to that of the literature [77].

A solution of 0.56 grams o-carborane in 15 ml THF was stirred while a solution of 0.466 ml 10 M n-butyl lithium in hexanes (1.2 equivalents) in 5 ml THF was slowly added. After 15 minutes, this solution was dripped into a stirred solution of 1.0 g 5-(methoxybutylbromide)-norbornene (1 equivalent) in 20 ml THF. The solution turned yellow and was stirred overnight. There was no precipitate.

Because there was concern that carborane carbanion might not readily displace the bromide leaving group at room temperature, a 15 ml aliquot of the reaction solution was then removed and heated to 55-60 °C for 4.5 hours. Both the unheated and heated solutions were drid to a thick liquid, and then 50 ml ether was added to each. Each was then extracted with three times 50 ml distilled water. The ether phases were dried to yellowish liquids.

The crude product from the unheated portion was purified by column chromatography using silica gel and a 1:8 mixture of ethyl acetate and petroleum ether. This particular chromatography system tended to have a lot of column cracking.

The crude product from the heated portion was purified by column chromatography using silical gel and a 1:1 mixture of hexane and chloroform. TLC tests comparing the two different solvent mixtures suggest that the ethyl acetate/petroleum ether mixture eleutes the fractions with less tailing. However, the chloroform/hexane system is preferred to minimize column cracking. In either case, the product is the second fraction eleuted. Because of the different purification schemes, the yields for the heated and unheated reactions could not be directly compared. The product fractions from
each batch were combined. The total yield was 23%.

2.6.8 Nor-Si-Anion, Cesium Salt

Upon deprotonation with butyl lithium, the carborane anion becomes a dianionic species containing one carbanion. The solubility of this dianionic species depends on its counterions. Since deprotonation is accomplished with butyl lithium, one of the cations must be lithium. However, the choice of the original cation for the carborane anion is critical [61]. The preferred counterion is trimethylammonium, because this ion reacts with butyl lithium, evolving the gas trimethylamine and leaving behind lithium as a replacement counterion. The dilithium salt of the deprotonated dianion is sufficiently soluble in THF to permit further controlled reaction [61].

A solution of 0.5 g of the carborane anion trimethylamine salt in 15ml THF was stirred and a solution of 0.542 ml 10 M n-butyl lithium in hexanes (2.2 equivalents) in 5 ml THF was slowly added. About halfway through the addition, the stirred solution became light yellow. This color change is associated with the deprotonation of the carborane anion. After 45 minutes, a solution of 0.506 g 5-(dichloromethylsilyl)nornbornene (1.1 equivalents) in 5 ml THF was added. The solution was stirred overnight, then dried to a paste. The paste was dissolved in 10 ml distilled water and aqueous cesium chloride was added to precipitate an off white solid. The solid was rinsed with 3 times 10 ml water and 3 times 10 ml hexane. The solids were dissolved in an acetone/water mixture and the solution allowed to evaporate until solids precipitated. The first fraction collected gave a 33% yield. The remaining liquid was evaporated to collect a fraction of approximately 33% yield of less pure material. These fractions were rinsed with hexane. The cesium salt of nor-Si-anion is soluble in methanol, THF and acetone, and slightly soluble in toluene.
Chapter 3

Synthesis and Characterization of o-Carborane Functionalized Polymers

We have synthesized a series of four norbornene-based polymers with pendant o-carborane groups through ROMP of monomers described in Chapter 2. Additionally, block copolymers containing a glassy carborane functionalized block and a rubbery block were synthesized. In each case, a commercially available Grubbs ruthenium catalyst was used as the initiator.

Some thermal and optical properties of these polymers were measured. Comparison of the polymers demonstrates how changes in molecular structure affect macroscopic properties. The diblock copolymers synthesized are the first reported polymers showing microphase separation between a carborane containing block and a boron-free block. Characterization of these copolymers also demonstrates that copolymerization can improve the processibility of materials synthesized by ROMP.

3.1 Polymerization

The Grubbs ruthenium catalyst system was selected because of its ease of use and ability to tolerate functional groups. Although the o-carborane group is not acidic,
nucleophilic, or otherwise chemically reactive, its electron withdrawing effect and steric bulk have inhibited some types of polymerization reactions \([34, 35, 36]\). We found that the o-carborane groups do slow polymerization compared to unsubstituted norbornene, but that the rate of reaction is still reasonably high.

ROMP is commonly used to make polymers with up to 1000 repeat units. Since there was no need for high molecular weights, we chose polymer lengths of approximately 100 repeat units for our homopolymers. Both block of the diblock copolymers were also approximately 100 repeat units.

Although the Grubbs catalysts are not deactivated by water and are only slowly deactivated by oxygen \([102]\), all polymerizations were carried out in a nitrogen glove box because the catalysts were stored there. All polymerization was done at room temperature.

3.1.1 Solvent Systems

Initially, methylene chloride was used as the polymerization solvent for our syntheses. Non-coordinating solvents such as methylene chloride result in the highest rates of polymerization for the Grubbs catalyst \([101]\). Although all the monomers are quite soluble in methylene chloride, some of the polymers have limited solubility. These polymers do not precipitate out of methylene chloride, but do form a separate polymer rich liquid phase. Such phase separation is undesirable because it can result in incomplete polymerization of the monomer. Phase separation is more pronounced with the two carbon bridged carborane polymers than with the silicon bridged carborane polymer.

The carborane functionalized polymers are not soluble in toluene, but are very soluble in THF. Thus, later polymerizations of the carborane monomers were all carried out in THF. The reaction remains homogenous in THF and the rate of polymerization is still acceptably high. THF solutions also have the advantage of precipitating more cleanly in methanol that methylene chloride solutions do. Although these polymers are at least somewhat soluble in acetone and ethanol, the use of these polar solvents was not investigated because satisfactory result were obtained with THF.
3.1.2 Kinetics and Polydispersity

The Grubbs ruthenium catalysts can produce polymers with very narrow molecular weight distributions [67]. Although a narrow molecular weight distribution is not critical to most polymer applications, measurement of the polydispersity index (PDI) can provide information about the polymerization process. If a sample has a PDI only slightly over 1, it indicates that initiation is fast compared to propagation and that no chain transfer or termination occurs. Termination, chain transfer or coupling can be caused by impurities in the monomer or solvent. Although the Grubbs catalysts are not deactivated by protic solvents, they can be poisoned by monomers with protic substituents in some positions [102]. Also, oxygen causes slow deactivation of the catalyst.

In order to obtain the minimal PDI, polymerization should be terminated by the addition of an agent such as ethyl vinyl ether. This cleaves the ruthenium species from the end of the polymer. We have found that low polydispersity samples will undergo chain transfer or coupling with time if not deliberately terminated. Samples left overnight may go from a PDI of 1.1 to 1.2 and evidence a high molecular peak “shoulder” in GPC data. This type of shoulder is probably due to the same type of chain coupling that is observed with the Schrock molybdenum catalyst system.

We have not conducted a rigorous study of polymerization kinetics, but have made some preliminary investigations. It is important to know approximately how long polymerization takes in order to allow sufficient reaction time per block when making block copolymers. If the second monomer is added before the first monomer is depleted, a statistical or “random” copolymer may be produced. Block copolymers and random copolymers may have very different physical properties, so it is important to be able to control copolymerization.

Norbornene polymerizes so quickly in methylene chloride with the Grubbs catalyst that the heat of reaction can cause the solvent to boil. Functionalized monomers react more slowly, and coordinating solvents such as THF also slow the reaction. However, the polymerization of carborane functionalized norbornene monomers still reaches...
90% or higher conversion within hours.

Batch process living polymerizations are modeled by the equation

\[
\ln\left(\frac{[M_o]}{[M]}\right) = K_p[I]t
\]

where \([M_o]\) is the original monomer concentration, \([M]\) the instantaneous monomer concentration, \(K_p\) the polymerization rate constant, \([I]\) the initiator concentration, and \(t\) is time. To calculate rate constants from molecular weight data, we used the relationship

\[
[M_o]/[M] = M_n f / (M_n f - M_n)
\]

where \(M_n f\) is the final number average molecular weight of the polymer and \(M_n\) is the instantaneous number average molecular weight of the polymer. Technically, the true final weight is only reached at infinite time, but can be estimated from finite time data. Figure 3.1.2 demonstrates a plot used to calculate \(K_p\).

Our carborane monomers have polymerization rate constants of approximately
30 l/mol·minute. For the initiator concentrations typically used, this means that it takes from one to three hours for 90% or more of the monomer to be polymerized. This is comparable to the rate of other substituted norbornenes such as norbornene methoxy trimethylsilane, and consistent with other reported rates of metathesis by Grubbs catalysts in THF [100].

An upper limit on reagent concentration is imposed by the viscosity of the resulting polymer solution. It is undesirable to produce a very viscous solution, as such solutions are more difficult to keep well-stirred. We have generally used between 0.05 and 0.2 g of monomer in 5 ml of solvent.

### 3.1.3 Spectroscopic Characterization

**NMR**

In general, the NMR spectra of polymeric materials have broad peaks due to slight variations in the environments of repeat units at different points along the polymer backbone. This means that it is much easier to analyze monomer chemical structure than polymer structure with NMR. As the ruthenium catalyzed ROMP process produces polymer structures which are predictable from the structure of the monomers, we have primarily analyzed the monomers and only used NMR on the polymers to confirm the expected reaction.

As expected, the carborane functionalized polymers have HNMR spectra similar to those of the monomers but with broader peaks. The primary difference between monomer and polymer spectra is the shift in position of the olefin hydrogen peaks from approximately 6ppm in the monomers to approximately 5ppm in the polymers. This shift reflects the change from a strained cyclic structure to a linear polymer structure (see Figure 1-9). The carborane carbon hydrogen peak and the broad carborane boron hydrogen peaks are evident at much the same positions as in the monomer spectra. As expected, the peaks due to the backbone norbornene structure are broadened the most upon polymerization, while the peaks due to the pendant carborane functionality are less affected (see Figures 3-2, 3-3). Similarly, $^{13}$CNMR
of the polymers resembles that of the monomers, with significant broadening of the norbornene carbon peaks (see Figures 3-4, 3-5). $^{11}$BNMR peaks are also broadened (see Figure 3-6).

**UV/IR**

Carborane compounds have a very strong characteristic mid IR absorption band at about 2600 cm$^{-1}$ which is attributed to the carborane boron-hydrogen bonds [34, 117, 104, 26, 1, 108]. This peak can be seen in the spectra of our carborane functionalized polymers (see Figure 3-7). o-Carborane also absorbs strongly in a number of peaks between 2850 and 2950 cm$^{-1}$, but these peaks are less useful for identification because aliphatic hydrocarbons have similar absorptions. The carborane peak near 700 cm$^{-1}$ is also not useful for identification purposes.

Another characteristic adsorption peak for carborane compounds is near 3070 cm$^{-1}$ [108, 26]. This band is due to the pseudoaromatic carbon-hydrogen bonds. Thus, the band is absent in carborane main-chain polymers where both carborane carbons lack attached hydrogen [104]. This peak is absent in the spectrum of poly-nor-CC-carb because the pendant carborane groups are bonded through both carbons to the norbornene structure and thus lack carborane carbon-hydrogen bonds. However, this peak is visible in the spectrum of polynorSicarb, reflecting the presence of the carbon-hydrogen bond in each pendant carborane group.

Carborane compounds also have a weak near IR adsorption peak around 1920 nm, an overtone of the strong boron-hydrogen absorption at 2600 cm$^{-1}$ [1]. This characteristic peak is present in the spectra of our polymers (see Figure 3-8). The other near IR adsorption peaks in our polymer spectra can be attributed to bonds within the norbornene framework. Carborane does not have other visible, UV, or near-IR adsorption peaks.
Figure 3-2: HNMR of Poly-Nor-Si-Carb in D-Acetone
Figure 3-3: HNMR of Poly-Nor-C-Carb in D-Methylene Chloride
Figure 3-4: $^{13}$CNMR of Poly-Nor-Si-Carb in D-Acetone
Figure 3-5: $^{13}$C NMR of Poly-Nor-C-Carb in D-THF
Figure 3-6: $^{11}$BNMR of Poly-Nor-C-Carb in D-THF
Figure 3-7: IR Transmittance of Carborane Functionalized Polymers
Figure 3-8: Near IR Transmittance of Carborane Functionalize Polymers
3.2 Block Copolymers

Copolymerization is often used to produce materials which combine the desirable properties of each homopolymer. Solubility, thermal behavior, and mechanical properties can be tailored through copolymerization. Block copolymerization can produce materials with microphase separation of the two component polymers. Such nanoscale morphology (lamellae, cylinders, or spheres) may enhance physical properties and can provide a way to segregate functional groups into small domains.

As describe in the following section, most of the carborane functionalized norbornene-based homopolymers that we synthesized have high glass transition temperatures (Tg). Such polymers are difficult to process into thick films, which are used in mechanical testing, because thermal decomposition may occur before the material begins to flow. Additionally, the materials are too brittle for normal handling. The Tg of carborane functionalized polymers can be lowered by attaching the functional group to the norbornene backbone via a long spacer chain. Alternatively, high Tg carborane polymers can be incorporated into block copolymers with a companion low Tg norbornene-based polymer. We have used poly(trimethylsilylmethoxynorbornene). The resulting material can be thermally processed at lower temperatures.

While statistical copolymers generally have thermal transition temperatures intermediate between those of the two homopolymers, block copolymers usually demonstrate two distinct transitions. The temperatures of these two transitions are nearly identical to the the transition temperatures of the homopolymers. Thus, tests on block copolymers can be substituted for tests on the component homopolymers. Our block copolymer materials were used to measure the Tg of the homopolymers through dynamic mechanical analysis (DMA).

Transmission electron microscopy was used to image the microphase separation of these block copolymers. Both lamellar and cylindrical morphology were observed (see Figures 3-9, 3-10). These materials are unusual because they contain phases with high boron density (37-43 wt%) and phases with no boron content. Pyrolysis of such polymers might produce nanoscale boron ceramic particles.
Figure 3-9: TEM of Poly-Nor-CC-Carb/Poly-Nor-OTMS Block Copolymer
Figure 3-10: TEM of Poly-Nor-OTMS/Poly-Nor-Si-Carb Block Copolymer
Table 3.1: Comparison of o-Carborane Functionalized Materials

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Tm(°C)</th>
<th>Tg(°C)</th>
<th>wt%boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>nor-Si-carb</td>
<td>87</td>
<td>187</td>
<td>37</td>
</tr>
<tr>
<td>nor-C-carb</td>
<td>87</td>
<td>200</td>
<td>43</td>
</tr>
<tr>
<td>nor-CC-carb</td>
<td>170</td>
<td>291</td>
<td>41</td>
</tr>
<tr>
<td>nor-6-carb</td>
<td>&lt;20</td>
<td>29</td>
<td>34</td>
</tr>
<tr>
<td>norbornene</td>
<td>46</td>
<td>32</td>
<td>0</td>
</tr>
</tbody>
</table>

3.3 Structure/Thermal Property Relationships

3.3.1 Glass Transition Temperature

It was anticipated that structural differences in how the carborane functional group was attached to the polymer backbone would affect thermal properties. Generally, the addition of bulky side groups raises a polymer’s Tg because chain motion is sterically hindered. Tightly bound groups near the backbone raise Tg significantly, while more distant groups have less effect. These trends were observed in our series of carborane polymers. Table 3.1 lists the monomer Tm, polymer Tg, and wt%boron for these materials.

Polynorbornene has a fairly low Tg of 32 °C. The addition of a pendant carborane group via a silicon bridge dramatically increases the Tg to 187 °C, as measured by DMA. The dimethyl silicon, although more bulky than a carbon bridge, is also more flexible because the Si-C bond is longer than the C-C bond. This flexibility difference is reflected in the higher Tg of the carbon bridged nor-C-carb, 200 °C. The twice-bound pendant carborane has much less freedom of motion than the singly-bound carborane. The measured Tg for the polymer with the twice-bound pendant carborane is 291 °C, significantly higher than either of the singly-bound carborane polymers.

Thus, the presence of the carborane group near the polymer backbone raises the polymer Tg by 150-260 °C, depending on the bridging structure. Our last carborane polymer was synthesized with a six atom long flexible spacer chain between the norbornene structure and the pendant carborane. It was expected that this length
would weaken the effect of the carborane group. The Tg of the carborane polymer with spacer chain is 29 °C, essentially the same as that of unfunctionalized polynorbornene.

Since a spacer chain length of six atoms is enough for the backbone chain motion to be unrestricted by the presence of the carborane pendant group, we can hypothesize that any deactivation of functional group properties due to attachment to a polymer backbone would also be ameliorated by a short spacer chain. This is important because our carborane functionalized monomers and polymers have been synthesized with the goal of using them as intermediates to cobalt dicarbollide functionalized polymers, and the main application of such polymers would be as ion-binding materials. It is common for the effectiveness of binding groups attached to a polymer backbone to be hindered by their proximity to the backbone. If the binding properties of cobalt dicarbollide are adversely affected by the norbornene backbone, spacer chains could be used to decouple any interaction.

### 3.3.2 Thermal Gravimetric Analysis

The weight loss of poly-nor-C-carb and poly-nor-CC-carb samples during heating to 900 °C at 20°C/min was measured. Both samples lost most of their mass during pyrolysis. However, the poly-nor-CC-carb polymer was stable to a higher temperature and retained more mass after pyrolysis. Weight loss began after the polymer glass transition temperatures were reached, but the majority of the weight was lost between 400°C and 500°C. Figure 3-11 shows the polymers's weight loss curves.

These result demonstrate that pendant carborane groups which raise a polymer's Tg also raise its decomposition temperature. The more tightly bound the carborane is to the polymer backbone, the greater its effect. Although we did not measure the thermal decomposition behavior of the other carborane functionalized polymers, it is anticipated that the behavior of poly-nor-Si-carb would be similar to that of poly-nor-C-carb, while poly-nor-6-carb would show weight loss at much lower temperatures.
Figure 3-11: Weight Loss as a Function of Temperature for Poly-Nor-CC-Carb vs Poly-Nor-C-Carb
### Table 3.2: Refractive Indices of Carborane Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>nor-Si-carb</td>
<td>1.568</td>
</tr>
<tr>
<td>nor-C-carb</td>
<td>1.558</td>
</tr>
<tr>
<td>nor-CC-carb</td>
<td>1.556</td>
</tr>
</tbody>
</table>

### 3.4 Magnetic, Optical, and Dielectric Properties

Polymers with low dielectric constants are used in integrated circuits. High dielectric constant materials can be used in capacitors. Most polymers are relatively low dielectric constant materials. The o-carborane group has a high dipole moment and polarizable electrons. This may result in interesting dielectric or optical properties, particularly when modified with electron donating or withdrawing substituents [93, 94]. Although our polymers are functionalized with only the unmodified o-carborane group, we have made some basic dielectric and refractive measurements.

#### 3.4.1 Index of Refraction

The index of refraction for poly-nor-Si-carb, poly-nor-C-carb, and poly-nor-CC-carb were measured on thin films spin coated onto silicon wafers. The measurements were taken at a wavelength of 633 nm at room temperature using an ellipsometer. These polymer films are believed to be non-crystalline and unoriented.

Polymeric materials have refractive indices ranging from 1.3-1.7 [120]. The refractive indices of these norbornene-carborane polymers lies in the average range, between those of amorphous polyethylene and amorphous polystyrene (see Table 3.2) [120]. The indices of the two carbon-bridged carborane polymers are essentially identical while the refractive index of the silicon-bridged carborane polymer is slightly higher.

#### 3.4.2 Dielectric Constant

A non-magnetic, non-absorbing material’s dielectric constant and index of refraction are related at a given wavelength by the equation $n^2 = \epsilon'$; where $n$ is the index of refrac-
tion and $\epsilon'$ the dielectric constant. Often, a polymer with a high dielectric constant or index of refraction has polarizable electrons or polar groups which are able to be aligned by an electric field. As the frequency of measurement increases, the dielectric constant usually drops, indicating that the frequency of the measurement is faster than the molecular motion of polar groups. This drop in dielectric constant is analogous to the drop in mechanical storage modulus at the glass transition temperature.

Our dielectric measurements were taken at room temperature at frequencies ranging from 20 to $10^6$ hz. This is much slower than the frequency of light used for the index of refraction measurements. The corresponding dielectric constant at a wavelength of 633 nm is 2.4, a lower bound for our materials. Figure 3-12 shows the changes in dielectric constant with frequency for poly-nor-Si-carb. The variation between samples can be attributed to local variation in film thickness. A dielectric constant of approximately 3.4 in the 100-10$^5$ hz range is comparable to that of PVC [16] and a silver loaded norbornene polymer [127]. However, it is much lower than that of poly(vinylidene fluoride) [130]. The beginning of a drop in dielectric constant between $10^5$ and $10^6$ hz is probably an artifact of the aluminum electrodes.

### 3.4.3 Magnetic Response

Although there is no particular reason to believe that carborane polymers would have unusual magnetic properties, we checked the magnetic response of poly-nor-C-carb. This polymer shows a very weak paramagnetic response (see Figure 3-13). This might be due to the presence of impurities with some permanent magnetic dipole moment, or could indicate that the carborane group has some magnetic behavior. The most likely contaminant is the polymerization catalyst or spent catalyst byproducts. A control study of poly-norbornene synthesized by the same methods could indicate whether catalyst contamination was responsible for the observed magnetic behavior.
Figure 3-12: Dielectric Constant Measurement for Poly-Nor-Si-Carb
Figure 3-13: Magnetic Response of Poly-Nor-C-Carb
3.5 Experimental Details

3.5.1 Equipment

Molecular weight measurements were taken using a GPC equipped with three Waters Styragel HR4 columns and a Waters 410 differential refractometer. Polystyrene calibration standards were used. All measurements were taken at a flow rate of 1 ml/min.

DMA measurements were taken with a Seiko DMS200 with nitrogen purge. TG/DTA measurements were taken on a Seiko TG/DTA 320 with nitrogen purge. Optical observation of Tg and Tm was done with a Nikon optical microscope and Mettler FP82 hot-stage. TEM was done on a JOEL 200CX operating at 200 kV. Samples were microtomed with a MT5000 Ultra Microtome at room temperature using glass knives made on a Sorvall LKB type 7801A glass knife maker.

IR spectra were taken on a Nicolet Magna-IR 860. UV-vis spectra were taken with a Cary 5E UV-Uis-NIR spectrophotometer. HNMR spectra were taken with a Bruker 400 MHz FTNMR at MIT. Carbon and boron spectra were taken at 3M Corporation by Dr. James Hill and assistance with interpretation provided by Dr. Richard Newmark. A UNITY 500 MHz spectrometer was used, with proton decoupling using Waltz broad-band decoupling.

Dielectric measurements were taken by Dr. Amlan Pal from Professor Michael Rubner's group. The polymer films were spin-coated between aluminum electrodes which were vacuum evaporated onto a glass slide by Jason Gratt. Gold leads were attached to the device with silver paste. Magnetic measurements were taken by Douglas Twisselmann from Professor Caroline Ross's group. Index of refraction was measured with a Gaertner ellipsometer at 633 nm. A Tencor P-10 profilometer was used to measure the thickness of spincoated films.
3.5.2 Processing

Hot-Pressing

DMA samples were prepared by hot-pressing polymer in a channel die with a width of approximately 6 mm. Generally, sample lengths ranged from 10 to 20 mm, with thicknesses of less than 1 mm. Pressures of approximately 10 Kpsi were used. Temperature were kept under 150 °C, to prevent polymer degradation. Poly-nor-C-carb and poly-nor-CC-carb could not be processed as homopolymers because higher temperatures were needed to induce material flow. However, copolymers of these carborane polymers with poly-nor-OTMS could be hot-pressed at approximately 120 °C. A lower temperature (50 °C) was used to hot-press poly-nor-6-carb. For each polymer, a high enough temperature was used so that the sample became uniformly translucent, indicating complete softening.

It is important to dry polymers under vacuum before hot-pressing. Polymers which are allowed to dry in air may retain enough solvent to cause foaming in the hot-press.

Samples which were hot-pressed at temperatures above 150 °C showed yellowing and were no longer completely soluble in THF. These samples were probably cross-linked through reaction of the olefin backbone bonds. Such heat-altered sample were not used for further testing.

Spin Coating

Solutions were spin coated onto either silicon wafer or untreated glass slides. Poly-nor-Si-carb samples were dissolved at a concentration of 20 μl/ml in chlorobenzene or THF. Spin rates of 1000 and 2000 rpm were used. A profilometer was used to measure film thickness on coated glass slides. Generally, the chlorobenzene solutions resulted in smoother films (smoothness is important for ellipsometry). Spin coating from chlorobenzene solution at 1000 rpm gave approximately 1000 Å thick films. A spin speed of 2000 rpm resulted in films approximately 800 Å thick. THF solutions spin coated at 1000 rpm resulted in films approximately 1700 Å thick.
3.5.3 Films for UV/IR

Both homopolymer and copolymer films were cast from solution for spectroscopic analysis. Some films were cast directly onto KBr pellets for IR analysis. Other films were cast onto Teflon-coated aluminum foil or glass slides and then peeled off to become free-standing films. Much thinner films could be cast onto glass than Teflon-coated foil because the polymer solutions all wet glass.

THF was used as the casting solvent, and casting was done in solvent saturated, enclosed spaces. Films cast onto glass had to be peeled off while still plasticized with solvent; most films became brittle upon complete drying. Some of the hot-pressed samples were also used for UV analysis.

3.5.4 Polymerization

All polymerization solvents were Aldrich anhydrous grade. Unless otherwise specified, the polymerization solvent was also used in the catalyst solutions. Polymerization was carried out in a nitrogen glove box at room temperature.

Poly-Nor-Si-Carb

This monomer was polymerized many times using a Grubbs ruthenium catalyst (see Figure 1-10) in methylene chloride or THF, with batch sizes of 0.1 to 1.0 g monomer. Polymerization was sometimes terminated by the addition of ethyl vinyl ether; other batches were allowed to terminate slowly in air.

In a typical polymerization, 0.122 g of monomer was dissolved in 4 ml methylene chloride. To the stirred solution, 1.139 ml of a 15 mg in 5 ml solution of Grubbs catalyst was added for a target length of 100 repeat units. Upon addition of the purple catalyst solution, the colorless monomer solution turned peach colored. After 30 minutes, the solution was pinkish gold. After 24 hours, the solution was golden. The polymerization was terminated with 10 μl of ethyl vinyl ether and precipitated in 60 ml of methanol. The solids were filtered from methanol for a yield of 0.1 g (82%). The incomplete yield was caused by some polymer getting through the filter,
not incomplete polymerization. Precipitation is supposed to remove catalyst residue, but often the precipitated polymer retains a gray color indicative of catalyst residue.

**Poly-Nor-C-Carb**

Poly-nor-C-carb was synthesized in batches ranging from 0.1 to 1.5 g of monomer. Both methylene chloride and THF were used as polymerization solvents, though THF is preferred to eliminate phase separation of the polymer.

In one batch using methylene chloride, 1.5 g of nor-C-carb was dissolved in 40 ml methylene chloride and 49 mg Grubbs catalyst in 5 ml methylene chloride added for a target length of 100 repeat units. After 4 hours, the reaction was terminated with 50 μl ethyl vinyl ether. A viscous blob of polymer separated from the solution. The blob was removed, and the rest of the methylene chloride solution precipitated in 200 ml methanol. Solids were filtered from the methanol and combined with the phase separated solid. Approximately 1.2 g (80% yield) was recovered. Because of the phase separation during reaction, polymerization may have been incomplete and the molecular weight lower than target.

**Poly-Nor-CC-Carb**

In one batch, 0.5 g of monomer was dissolved in 8 ml methylene chloride. For a target length of 105 repeat units, 1.5 ml of a 20 mg in 2 ml solution of the Grubbs catalyst was added. Upon addition of the purple catalyst solution, the colorless monomer solution became rose colored and then yellow and cloudy. Purple blobs separated from solution. It is likely that this polymer did not achieve the target molecular weight due to phase separation. THF can be used as the polymerization solvent, eliminating the phase separation problem. After stirring overnight, the viscous solution was thinned out by the addition of 2 ml THF. The solution was precipitated in 100 ml methanol and the solids recovered by filtration.
**Poly-Nor-6-Carb**

A solution of 0.15 g nor-6-carb in 5 ml THF was stirred, and 0.464 ml of a 33 mg in 4 ml Grubbs catalyst solution added for a target length of 100 repeat units. The solution became peachy-yellow after minutes. The reaction was terminated after 3 hours with 10 μl of ethyl vinyl ether and precipitated in 20 ml methanol. The polymer was recovered as a sticky tar by decanting the methanol.

**Block Copolymers**

The carborane monomers were copolymerized with trimethylsilylmetoxynorbornene (nor-OTMS). Poly-nor-OTMS was chosen because it has a low Tg (13 °C) and is easily stained for TEM by diethyl zinc vapor. Additionally, the ether units cause poly-nor-OTMS to strongly microphase separate from the less polar carborane polymers. Nor-OTMS monomer was synthesized by Jason Gratt according to the literature procedure, stored in a nitrogen glove box, and used without further purification.

To make a nor-CC-carb/nor-OTMS block copolymer, a solution of 0.065 g nor-CC-carb monomer in 4.75 ml THF was polymerized to a target length of 100 repeat units with 0.25 ml of 33 mg in 4 ml Grubbs catalyst solution. At 15, 30, and 60 minutes, 0.05 ml aliquots were withdrawn and terminated with 0.5 μl ethyl vinyl ether. After 1 hour, a solution of 0.049 g nor-OTMS in 0.5 ml THF was added, for a target block length of 100 repeat units. At 15, 30, and 60 additional minutes, similar aliquots were taken. At the end of the second hour, the entire solution was terminated with 0.05 ml of ethyl vinyl ether. This polymerization was later repeated in reverse order and 3 hours allotted for the polymerization of each block. The solution was precipitated in 50 ml methanol and the solid recovered by filtration.

To make a nor-OTMS/nor-Si-carb block copolymer, 0.088 g of nor-OTMS was dissolved in 4.75 ml THF. For a target of 90 repeat units, 0.5 ml of a 33 mg in 4 ml solution of the Grubbs catalyst was added. Aliquots of 0.1 ml were taken at 1, 2, and 3 hours and terminated with 2 μl ethyl vinyl ether. After 3 hours, 0.126 g of nor-Si-carb in 0.6 ml THF was added for a target block length of 90 repeat units.
After 15, 45, 105, and 180 additional minutes, aliquots were similarly taken. After the second 3 hours, the entire solution was terminated with 40 μl of ethyl vinyl ether. The solution was precipitated in 50 ml methanol and the solid recovered by filtration.

To make a nor-OTMS/nor-C-carb block copolymer, 0.078 g of nor-OTMS was dissolved in 3 ml THF and 0.308 ml of a solution of 32 mg in 3 ml Grubbs catalyst added for a target block length of 100 repeat nits. After 2 hours and 40 minutes, 0.1 g of nor-C-carb in 0.7 ml THF was added for a target block length of 100 repeat units. After an additional 3 hours, the reaction was terminated with 40 μl of ethyl vinyl ether. The solution was precipitated in 20 ml methanol and the solid recovered by filtration.
Chapter 4

Cobalt Dicarbollide and Carborane Anion Polymers: Materials Synthesis

A cobalt dicarbollide or carborane anion polymer might have application as an ion-exchange resin for removing cesium from solution, or as a polymer electrolyte in lithium batteries. In this chapter, we describe and evaluate some synthetic routes to produce such materials.

Polymers functionalized with organometallic sandwich compounds such as cobalt dicarbollide are the result of three synthetic steps which will be referred to as sandwiching, attachment, and polymerization. Because these steps can be taken in any order, there are many possible approaches to the synthesis of a cobalt dicarbollide functionalized polymer.

I use the term “sandwiching” to describe the process of forming the organometallic complex. In the case of cobalt dicarbollide, carborane must first be degraded to the open-faced \( \text{C}_2\text{B}_9\text{H}_{10} \) dianion which then reacts with cobalt (see Figure 4-1). This degradation process requires basic conditions. Thus, if sandwiching happens after attachment, any group previously attached to the carborane moiety must be stable to base.

Since it is not practical to make a polymer which contains only cobalt and carbo-
Figure 4-1: "Sandwiching" to Synthesize Cobalt Dicarbollide

\[
\begin{align*}
C_2B_{10}H_{12} & \xrightarrow{\text{KOH, EtOH}} K\left[ C_2B_9H_{12} \right]^{-1} + B(OCH_2CH_3)_3 \\
\text{NH}(CH_3)_3^+ \left[ C_2B_9H_{12} \right]^{-1} & \xrightarrow{\text{NaH, THF}} 2Na^+ \left[ C_2B_9H_{11} \right]^{-2} + 2H_2 + N(CH_3)_3 \\
2Na^+ \left[ C_2B_9H_{11} \right]^{-2} & \xrightarrow{3/2 \text{CoCl}_2, \text{THF}} Na \left[ (C_2B_9H_{11})_2\text{Co} \right]^{-1} + 1/2 \text{Co} + 3 \text{NaCl}
\end{align*}
\]
rane fragments [43], "attachment" to some other compound is necessary. Carborane or cobalt dicarbollide may be attached to polymers or monomers. It may be easier to attach carborane, because the cobalt center of the sandwich compound can undergo side reactions.

Polymerization can take place after attachment, or before. We believe that ROMP is a good way to polymerize monomers functionalized with carborane or cobalt dicarbollide. Alternatively, a pre-made polymer can be functionalized by grafting on these groups onto the polymer backbone. While the use of a pre-made polymer can reduce the amount of chemical synthesis necessary, functionalization of such pre-made polymers may not go to completion. Additionally, there are few pre-made polymers to which cage compounds can be easily attached.

W. P. Steckle and others at Los Alamos National Laboratory have investigated attaching cobalt dicarbollide onto pre-made polymer resins in addition to attaching carborane onto resins and then sandwiching. Their studies have emphasized the need to control polymer hydrophobicity so that ions in solution can access the functional groups. Our approach has primarily been attachment before polymerization. This approach takes advantage of the synthetic flexibility of ROMP and norbornene-based monomers to produce deliberately tailored materials.

4.1 Poly-Nor-C-Carb-Co: Attachment, Polymerization, Sandwiching

This approach consists of attaching a carborane group to a norbornene monomer, polymerizing to form a polymer with pendant carborane groups, and then building the cobalt dicarbollide functionality from pendant carborane groups on the polymer and additional carborane and cobalt (see Figure 4-2). The advantage of this route is that the synthesis and polymerization of the carborane norbornene monomer is fairly straightforward. The disadvantage is that reactions on polymer functional groups are difficult to drive to completion, thus there may be incomplete conversion of pendant
carborane into cobalt dicarbollide. Additionally, pendant carborane groups from different polymer chains can sandwich the same cobalt center and create crosslinking. Although a crosslinked resin is actually the desired form for real world cesium clean-up applications, a strictly soluble model polymer would be much easier to characterize and study.

Nor-C-carb was used as the carborane polymer. A procedure modelled on the established methods for degrading carborane to the open-faced $\text{C}_2\text{B}_9\text{H}_{12}^-$ anion, deprotonating, and then reacting with cobalt chloride to form cobalt dicarbollide was applied to the polymer.

The degradation step was modified by using tetrahydrofuran with a small amount of ethanol instead of pure ethanol as solvent because the carborane polymer is not soluble in ethanol before degradation. The polymer salt was then left in potassium form, instead of converting to trimethylammonium form. Changing to the trimethylammonium form is helpful for recrystallization of the $\text{C}_2\text{B}_9\text{H}_{12}^-$ species, but the polymer form did not need to be recrystallized for recovery.

Once the polymer's pendant carborane groups were converted into the $\text{C}_2\text{B}_9\text{H}_{12}^-$

Figure 4-2: Synthesis of Poly-Nor-C-Carb-Co
form, they were deprotonated and combined with cobalt dicarbollide and additional $C_2B_9H_{12}^2$. During this reaction, the product precipitated out of THF solution as a greenish powder. The solid product is believed to be a crosslinked, anionic resin (see Figure 4-3) with sodium and potassium counterions. Elemental analysis confirms the presence of cobalt, but was inconclusive in determining the complete material composition with a large percentage of the total mass was unaccounted for by any element checked. Possibly this result may be explained by the unusual stability of cobalt dicarbollide compounds, which can result in underreporting of elemental composition, especially for boron. IR spectroscopy is not useful for distinguishing between various carborane and carborane organometallic sandwich species.

This product, poly-nor-C-carb-Co, is in the form of a fine powder. These particles might be too small in diameter for use as a solid column packing for water treatment. However, the degree of crosslinking and particle size could probably be controlled by
altering the reaction conditions. An attachment-polymerization-sandwiching route is promising for producing a cobalt dicarbollide functionalized resin, but other routes are favored for producing soluble materials which can be better characterized.

4.2 Poly-Nor-C-CDC: Attachment, Sandwiching, Polymerization

This approach uses a carborane functionalized norbornene monomer as an intermediate to a cobalt dicarbollide functionalized norbornene monomer, which is then polymerized. The advantage of this approach is that it produces a linear, soluble polymer that can be characterized. This product can then be crosslinked by reacting the unsaturated bonds in the polymer backbone to form an insoluble resin. Alternatively, the cobalt dicarbollide monomer can be copolymerized with a crosslinking agent. The disadvantage of this scheme is that the carborane functionalized monomer must be stable to the basic conditional necessary for sandwiching. This requirement imposes limits on the possible structure of the carborane monomer.

4.2.1 Sandwiching

Preliminary experiments showed that the bond between silicon and the carborane carbon in nor-Si-carb is susceptible to base cleavage. This was true both in KOH/ethanol and piperidine/toluene. Thus, further efforts to convert a carborane functionalized norbornene monomer into a cobalt dicarbollide monomer focused on nor-C-carb. The resulting synthetic scheme is shown in Figure 4-4. Nor-C-carb can be treated with KOH/ethanol to degrade the carborane group and purified as the trimethyl ammonium salt. Although the twice-bound carborane monomer, nor-CC-carb, was not used in these experiments, it is also expected to be stable to base.

The structure of this intermediate monomer was confirmed by H, $^{13}$C, and $^{11}$B NMR. Proton NMR shows the expected upfield shift in the position of the carborane carbon hydrogen. Also, the expected 2:9 ratio of olefin to trimethylammonium
hydrogens is found (see Figure 4-5). $^{13}\text{C}$ NMR shows that the carborane carbon peaks have shifted and the trimethylammonium carbon is visible (see Figure 4-6). The $^{11}\text{B}$ NMR spectrum shows the complicated splitting pattern expected, with nine major peaks of approximately the same area, some of which are split (see Figure 4-7). The $^{11}\text{B}$ spectrum is complicated because in addition to the endo/exo isomerism, the monomer now has additional isomerism relating to the orientation of the open face of the carborane. The carborane carbon bonded to the norbornene methyl carbon is now chiral, and the product contains both isomers.

The monomer functionalized with degraded carborane can then be deprotonated with sodium hydride and combined with additional degraded, deprotonated carborane plus cobalt chloride. A mixture of three products was expected: cobalt dicarbollide, norbornene methyl cobalt dicarbollide (nor-C-CDC), and bis (norbornene-methyl) cobalt dicarbollide. However, because the norbornene carborane is less reactive than the unhindered carborane, no measurable amount of the third product is formed. Both cobalt dicarbollide and norbornene methyl cobalt dicarbollide can
Figure 4-5: HNMR of Degraded Nor-C-Carb, Trimethylammonium Salt, in D-Acetone
Figure 4-6: $^{13}$CNMR of Degraded Nor-C- Carb, Trimethylammonium Salt, in D-Acetone
Figure 4-7: $^{11}$BNMR of Degraded Nor-C-Carb, Trimethylammonium Salt, in D-Acetone
be recovered from this reaction. Bis(norbornene methyl) cobalt dicarbollide can be formed if the degraded, deprotonated carborane methyl norbornene is mixed with cobalt chloride without additional carborane, but this reaction is slower than the others. (See Figure 4-8 for the HNMR spectrum of bis(nor-C)-CDC.)

Nor-C-CDC can be mostly separated from the cobalt dicarbollide side product based on solubility differences. Since the presence of cobalt dicarbollide does not affect the polymerization catalysts used, rigorous purification was unnecessary. The cesium salt of nor-C-CDC (mixed with some residual cobalt dicarbollide) was analyzed using HNMR (see Figure 4-9). Four distinctive cobalt dicarbollide carbon hydrogen peaks are visible. One corresponds to the residual cobalt dicarbollide, whose carbon hydrogens are all identical. The other three correspond to the three non-equivalent carbon hydrogens of the cobalt dicarbollide attached to norbornene. The broad boron hydrogen peaks are also visible. Integration ratios between the olefin hydrogens and the pendant cobalt dicarbollide carbon hydrogens are approximately correct. This monomer is a glassy, orange solid. (Figures 4-10, 4-11, 4-12 show the NMR spectra of cobalt dicarbollide for comparison.)

4.2.2 Polymerizing

Both Grubbs and Schrock type catalysts were investigated for use as initiators in the ROMP of the cobalt dicarbollide functionalized monomer. Both types of catalysts initiated polymerization, but the Grubbs system was chosen for further investigation because of ease of use. Homopolymers were analyzed by GPC. The polymers did not elute from the polystyragel GPC columns using THF, so a 50 mM solution of LiBr in THF was used as eluant. However, this did not enable the homopolymers to elute, even though a poly-C-CDC/poly-norbornene copolymer was eluted. These polymers are brittle, orange solids which are soluble in THF and acetone.
Figure 4-8: HNMR of Bis(Nor-C)-CDC in D-Acetone
Figure 4-9: HNMR of Nor-C-CDC in D-Acetone
Figure 4-10: HNMR of Cobalt Dicarbollide, Cesium Salt, in D-Acetone
Figure 4-11: $^{13}$CNMR of Cobalt Dicarbollide, Cesium Salt, in D-Acetone
Figure 4-12: $^{11}$BNMR of Cobalt Dicarbollide, Cesium Salt, in D-Acetone
4.3 Poly-Nor-11-CDC: Sandwiching, Attachment, Polymerization

This approach involves attaching a cobalt dicarbollide functionality to a norbornene-based monomer and then polymerizing. It has similar advantages to the previous approach, in that a soluble polymer product can be produced. Additionally, a broader range of monomer structure is possible, since the chemically harsh sandwiching step occurs before the norbornene group is attached. A disadvantage of this route is that cobalt dicarbollide is more difficult to attach to a norbornene-based monomer than carborane is, so the monomer synthesis yields are much lower.

Similar to carborane, cobalt dicarbollide can be deprotonated to undergo nucleophilic substitution [90, 14]. Unfortunately, deprotonated cobalt dicarbollide preferentially reacts with the olefin bond of norbornene-based monomers. Thus, it is not possible to use routes analogous to those described in Chapter 2 to produce a cobalt dicarbollide functionalized norbornene monomer.

We have taken the approach of first functionalizing cobalt dicarbollide with an alkyl bromide (see Figure 4-13), and then reacting that to a norbornene alcohol. Although norbornene methanol is a primary alcohol, the steric influence of the norbornene structure hinders the substitution reaction and leads to the formation of an elimination side product (see Figure 4-14). Since we were unable to separate the
Figure 4-14: Mixed Elimination and Substitution Products Resulting from the Reaction of Norbornene Methanol and Bromobutyl Cobalt Dicarbolide
cobalt dicarbollide functionalized norbornene product from the alkene cobalt dicarbollide side product, this mixture of synthetic products was used as described in the section below and a different norbornene alcohol was investigated.

The commercially available norbornene acid can be converted to an acid chloride and then reacted with a diol to produce an ester linked norbornene alcohol (see Figure 4-15). Since the alcohol functionality in this monomer is distant from the norbornene moiety, the alcohol should be react as a typical primary alcohol. The reaction of alkyl bromide cobalt dicarbollide with this alcohol produces a cobalt dicarbollide functionalized norbornene with a long spacer chain (see Figure 4-16). However, this reaction proceeds with very low yield and only minute amounts of the functionalized norbornene were recovered. The Grubbs catalyst seems to react with the norbornene olefins of this monomer based on HNMR (Figure 4-30), but the resulting amount of material was not enough to fully characterize. This synthetic route is impractical unless the product yield can be improved.

### 4.4 Poly-CDC-siloxane: Polymerization, Sandwiching, Attachment

This is the approach used by the Los Alamos group, in which cobalt dicarbollide is grafted onto a polymer. Their products were limited by the selection of commercially available resins which can react with deprotonated cobalt dicarbollide. In our research, we investigated a variation of this approach which extends the pool of commercially available polymers which can be functionalized. Instead of attaching cobalt
Figure 4-16: Synthesis of Nor-11-CDC
dicarbollide directly onto a polymer, we attached a cobalt dicarbollide derivative. First, cobalt dicarbollide was attached to a spacer chain with a reactive end. Then, the reactive end of the cobalt dicarbollide derivative was grafted onto a polymer. Although we were able to use hydrosiloxanes, an alternative variety of commercially available polymer, the resulting product proved to be unsatisfactorily liquid.

We had not planned to try this route, but some materials serendipitously synthesized during investigations of the previous approach (see Figure 4-14) were appropriate for grafting onto silane polymers. Additionally, there was the possibility that the alkene component might preferentially react, leaving purified cobalt dicarbollide functionalized norbornene monomer. We found that both components of the previously synthesized mixture of terminal olefins and norbornene olefins react with hydrosilanes in the presence of hexachloroplatinic acid. Unfortunately, the norbornenes reacted preferentially. The resulting polymer was a liquid. This route could have produced a solid product if a higher molecular weight hydrosilane polymer had been used.

4.5 Poly-Nor-Si-Anion: Polymerizing the Carborane Anion Monomer

The first batch of carborane anion monomer was less pure than the second batch. Attempts to polymerize the product from the first batch with a Schrock molybdenum catalyst in a THF/toluene mixture were unsuccessful. This monomer also did not react with the Grubbs ruthenium catalyst in methanol. However, the Grubbs catalyst did react with this monomer in THF, as shown by the disappearance of the strained olefin bonds of the monomer and the appearance of the olefin bonds typical of norbornene-based polymers. GPC analysis using THF eluent and polystyragel columns did not show any polymeric peaks. Viscometry measurements suggest an oligomeric product. Additionally, GPC analysis using THF with 50 mM LiBr as eluent suggests that the product was a mixture of oligomeric and low molecular weight material. It is not clear if some of the low molecular weight signal from the GPC
traces were artifacts of interactions between the polymer and the column packing materials.

Reaction of the second batch of purer carborane anion monomer with the Grubbs ruthenium initiator in THF produced polymer with a cleaner HNMR spectra than the first batch. The polymer spectra showed the expected broad peaks, the correct ratio of olefin hydrogens to methyl silyl hydrogens, and the characteristic broad, overlapping carborane boron hydrogen peaks. (see Figure 4-17). This material did not have a high enough solubility in THF with 50 mM LiBr to obtain GPC data. The polymer is somewhat soluble in THF and acetone, but very soluble in methanol.

4.6 Experimental Details

Reagent grade sodium hydride and potassium hydroxide were purchased commercially and used without further purification. Reagent grade THF and absolute ethanol were used as purchased. Cobalt dicarbollide was purchased as the cesium salt from Boron Biologicals and also synthesized according to the literature procedure (ref).

4.6.1 Degrading o-Carborane

Carborane must be degraded for to its open-faced form in order to make cobalt dicarbollide compounds. The degradation of o-carborane into the $\text{C}_2\text{B}_9\text{H}_{12}$ anion was carried out following the literature procedure [47] on a scale of 2 to 10 g o-carborane per batch. In a typical reaction, 10.0 g o-carborane was added to a solution of 7.78 g KOH (2 equivalents) in 120 ml ethanol. The solution was refluxed overnight. An additional 40 ml ethanol was added, and CO$_2$ from dry ice was bubbled thought the solution for 7 hours. The white precipitate was filtered off. The filtrate was dried and then dissolved in 70 ml water. The product was precipitated with a solution of 8.6 g trimethyl ammonium chloride in 50 ml water. The solid product was filtered off and recrystallized from 450 ml boiling water, with a 94% yield. The NMR spectra for degrade o-carborane, trimethylammonium salt, are shown in Figures 4-18, 4-19, 4-20.
Figure 4-17: HNMR of Poly-Si-Anion in D-Methanol
Figure 4-18: HNMR of Degraded o-Carborane, Trimethylammonium Salt, in D-Acetone
Figure 4.19: $^{13}$CNMR of Degraded o-Carborane, Trimethylammonium Salt, in D$_2$-Acetone.
Figure 4-20: $^{11}$BNMR of Degraded o-Carborane, Trimethylammonium Salt, in D-Acetone
4.6.2 Poly-Nor-C-Carb-Co

Nor-C-carb was polymerized to approximately 100 repeat units with the Grubbs catalyst. A solution of 0.6 g KOH (2.2 equivalents) in 2 ml ethanol (7.2 equivalents) was added to a solution of 1.2 g polymer in 40 ml THF and stirred overnight. The solution developed an orange/yellow color. The solution was dried to a brownish, brittle film and then crushed into small pieces and washed with 2 times 100 ml water. The water filtrate was yellow. The solids were then washed with 2 times 20 ml diethyl ether. The ether remained colorless and the solids swelled in the ether. The polymer solids were cast into a film and dried. (See Figures 4-21, 4-22, 4-23 for NMR spectra of the degraded polymer.)

The recovered polymer product (1.227 g) was dissolved in 50 ml THF and added to a stirred solution of 0.265 g NaH (2.5 equivalents) in 50 ml THF. A solution of 0.850 g trimethylammonium salt of $C_2B_9H_{12}$ (1 equivalent) in 10 ml THF was added to the stirred solution. This was an error, as at least 3 equivalents of NaH were required to do all three things: deprotonate the $C_2B_9H_{12}^-$ groups on the polymer, react with the trimethylammonium on the free $C_2B_9H_{12}$, and deprotonate the free $C_2B_9H_{12}^2$. As the trimethylammonium is probably most reactive, and the free $C_2B_9H_{12}^2$ next most reactive, this error means that half of the functional groups on the polymer may not have been deprotonated.

The solution was refluxed for 3 hours, cooled, and added to 1.427 g CoCl$_2$ (2.5 equivalents) in 90 ml THF and stirred under nitrogen. The solution was refluxed for 2 hr and spontaneously separated into two phases. The clear blue top phase and cloudy blue bottom phase were separated. The 50 ml of bottom phase was poured into 800 ml water and precipitated as a greenish solid. This solid swelled in THF and DMSO, but was insoluble in toluene, methylene chloride, ether, acetone, methanol, and dilute aqueous HCl. The solids were swelled in 25 ml THF for 3 days and reprecipitated in 350 ml methanol. The swelling and reprecipitation was repeated.

The top phase was concentrated from 150 ml to 50 ml and then poured into 300 ml water. Only a small amount of orange/black tacky solid precipitated. This was
Figure 4-21: HNMR of Degraded Poly-Nor-C-Carb in D-THF
Figure 4-22: $^{13}$CNMR of Degraded Poly-Nor-C-Carb in D-THF
Figure 4-23: $^{11}$BNMR of Degraded Poly-Nor-C-Carb in D-THF
dissolved in 10 ml THF and reprecipitated in 200 ml methanol. Then, the solids were dissolved in 5 ml THF and reprecipitated in 150 ml methanol.

Since cobalt dicarbollide is soluble in methanol, the repeated precipitations should remove any cobalt dicarbollide side product. We have found that polynorbornene mixed with cobalt dicarbollide in THF is adequately cleaned by 1 to 2 precipitations in methanol.

**Elemental Analysis**

Elemental analysis by Galbraith Laboratories confirmed that some kind of organometallic complex was formed in this reaction. However, the low amount of sodium or potassium is puzzling, as is the low amount of boron found. The elemental mass percents do not add up to 100, reflecting some kind of underreporting which may be caused by the unusual chemical and thermal stability of carborane compounds [133]. Table 4.1 shows the element content of the product compared to the content of the poly-C-carb starting material and the theoretical fully pendant and fully cross-linked models.

**Spectroscopy**

The insoluble powder was mixed with KBr powder and compacted into a pellet under pressure. IR spectra of cobalt dicarbollide and polynorbornene on KBR pellets were compared (see Figure 4-24). The characteristic difference between the IR spectra
of cobalt dicarbollide and carborane is that cobalt dicarbollide shows a broad peak around 3400 cm\(^{-1}\). This peak is often associated with organometallic compounds. Unfortunately, this peak is attributed to the presence of adsorbed water. Thus, the IR results cannot confirm the presence of pendant cobalt dicarbollide functionalities.

**Suggested Modifications**

I suggest that certain modifications be made to this synthesis if it is repeated.

1. The poly-nor-C-carb should be dissolved in a THF/ethanol mixture with as little THF as possible. Upon standing, THF/ethanol/KOH solutions develop a yellow color, presumably due to some reaction between the chemicals. However, solutions with more THF develop this color faster than solutions with less THF. The polymer should be dissolved in a minimal amount of pure THF, and then ethanol added. If the polymer begins to precipitate, more THF can be added.

2. If the ratio of free carborane to polymer bound carborane is kept at 1:1, at least 3 and preferably 4 equivalents of NaH should be used instead of 2.5.

3. It may be desirable to increase the ratio of free carborane to polymer bound carborane to reduce polymer crosslinking. A 2:1 or 3:1 ratio could be used. The amount of NaH should be increased proportionally, since the free carborane requires NaH for both trimethylammonium removal and carborane deprotonation.

**4.6.3 Poly-Nor-C-CDC**

**Degradation of Nor-C-Carb**

This reaction was carried out at scales of 1 to 3 g monomer. In a typical reaction, 1 g of nor-C-carb was added to a solution of 0.5 g KOH (2.2 equivalents) in 8 ml ethanol. The solution was refluxed 5 hours and then CO\(_2\) from dry ice was bubbled through the solution for 2 hours. The solid precipitates were filtered off, and the filtrate dried. The filtrate was dissolved in 4 ml water and the product precipitated with 0.52 g trimethyl ammonium chloride (1.4 equivalents) in 2 ml water. The solid
Figure 4-24: IR Spectra of Polynorborne, Poly-Nor-C-CDC-Co, and Cobalt Dicarbollide
product was filtered off and recrystallized by evaporation of either water/methanol or water/ethanol with yields of 70-75%. The product is soluble in methanol, ethanol, acetone, THF.

**Sandwiching**

The sandwiching reaction between the monomer and free carborane was carried out at scales between 0.2 and 2.0 g of the trimethylammonium norbornene carborane salt. The larger scale is easier to work with. For that batch, 2.0 g of the trimethylammonium salt of the degraded nor-C-carb was dissolved in 23 ml of anhydrous THF and 0.384 g NaH (2.4 equivalents) was added. At the same time, 2.3048 g of the trimethylammonium salt of degraded carborane (1.78 equivalents) was dissolved in 31 ml anhydrous THF and 0.686 g NaH (2.4 TMA-carborane equivalents) was added. Both solutions evolved gas and became slightly yellow. The solutions were refluxed under nitrogen for 3 hours, then cooled for 2 hours.

An slurry of 2.0 g CoCl₂ (2.3 equivalents) in 50 ml anhydrous THF was stirred. A 0.75 ml aliquot of the CoCl₂ slurry was mixed with a 0.5 ml aliquot of the degraded nor-C-carb solution. This mixture became rose colored, and then black within ten minutes. The rest of the degraded nor-C-carb and carborane solutions were mixed together and added to the CoCl₂ slurry. This mixture became orange and then black immediately. Both mixtures were stirred overnight.

The aliquot mixture was dried and dissolved in 1 ml water. It was then filtered, and the solids rinsed with 1 ml water. The aqueous filtrate was precipitated with a few drops of aqueous cesium chloride. A pinkish red solid product was filtered off.

Nitrogen was bubbled through the larger mixture for 30 minutes, and then it was dried to a tar. The material was dissolved in 100 ml water and filtered. The solids were rinsed 3 times with 15 ml water. The filtrate was precipitated with aqueous cesium chloride. The product first separated from solution as an oily tar, but solidified upon standing in the water solution over two days. The solid was broken up into a powder and filtered off. The solid was partially dissolved in 10 ml chloroform and filtered. The remaining solids were stirred and rinsed 3 times in 10 ml chloroform.
The chloroform filtrates were combined and dried to a reddish, glassy solid containing both the nor-C-CDC product and some cobalt dicarbollide. The chloroform insoluble solids were orange. Analysis of the insoluble fraction in a smaller batch reaction identified it as cobalt dicarbollide.

The bis(methylnorbornene) cobalt dicarbollide is soluble in acetone, THF, methanol, and methylene chloride. The nor-C-CDC monomer is soluble in acetone, THF, methanol, toluene, methylene chloride, and chloroform but insoluble in hexane.

**Polymerization**

Based on HNMR peak integration, the content of the nor-C-CDC reaction after purification was about 80% nor-C-CDC with the balance being cobalt dicarbollide. We assumed an 80 mol% nor-C-CDC content for polymerization calculations (see Figure 4-9).

We considered two polymerization systems: the Grubbs catalyst in THF and the Schrock catalyst in toluene. Both solutions contained 0.1 g of the nor-C-CDC mixture in 2 ml solvent, and catalyst solution was added for a target polymerization length of 50 repeat units. This translated to 0.285 ml of a 32 mg in 3 ml Grubbs solution and 0.312 ml of a 13 mg in 2 ml Schrock solution.

After a few minutes, the toluene solution had visible orange precipitate. Both solutions were stirred overnight. The toluene was decanted from the solids, and precipitated in 20 ml hexane. The THF solution was also precipitated in 20 ml hexane. All solids were dried under vacuum at 60 °C overnight. HNMR showed that the product of the Grubbs catalyst reaction did not contain monomer olefin hydrogen peaks, but instead had typical polymer olefin hydrogen peaks (see Figure 4-25). Similarly, the small amount of solid which had precipitated from the Schrock polymerization reaction was identified as polymer. However, the rest of the Schrock reaction mixture was remained nor-C-CDC monomer.
Figure 4-25: HNMR of Poly-Nor-C-CDC in D-Acetone
4.6.4 Poly-Nor-11-CDC

Norbornene butanol ester

Norbornene acid (Frinton Laboratories) and thionyl chloride (Fluka) were purchased and used without further purification. To convert the acid into an acid chloride, 5.0 g of the norbornene acid was dropped into 4.7 g neat thionyl chloride (1.1 equivalents) and stirred. After 1 hour, the solution was slightly yellow. After 3 hours, the solution was darker yellow. The mixture was put under vacuum overnight to remove unreacted thionyl chloride. The remaining liquid was dropped into a solution of 32.6 g butanediol (10 equivalents) and stirred for 3 hours over an ice bath. Upon addition of 3.66 g triethyl amine (1 equivalent) dripped into the solution, a white precipitate was formed and white gas was evolved. The solution was stirred overnight under nitrogen. The white solids were filtered off and the yellow filtrate evaporated to an oil. The yellow oil was dissolved in 100 ml chloroform and shaken with 3 times 100 ml water. The chloroform phase was evaporated to about 6 ml of dark yellow oil. The product was purified using column chromatography with silica gel as adsorbent and either a 1:2 mixture of diethyl ether/petroleum ether or a 1:2 mixture of ethyl acetate/petroleum ether as eluent. The eluent mixture can be gradually increased in the more polar solvent after the first two components are eluted in order to reduce tailing. The product fraction is the last fraction eluted, after any unreacted butanediol or norbornene acid. Use of ethyl acetate instead of diethyl ether reduces column cracking.

NMR of the clear oil product shows peaks for hydrogens of carbons adjacent to oxygen in approximately the correct ratio with the olefin hydrogen peaks (see Figure 4-26). Aliphatic hydrogen peaks corresponding to the middle carbon hydrogens from the spacer chain are also visible. Although this is not definitive proof of structure, it is adequate confirmation for our purposes, since this type of acid chloride/alcohol reaction is very common and generally proceeds as expected.
Figure 4-26: HNMR of Norbornene Butanol Ester in D-Acetone
bromobutylcobalt dicarbollide

A dibromoalkane can be reacted in large excess with deprotonated cobalt dicarbollide to make a bromoalkylcobalt dicarbollide. We chose dibromobutane, available from Aldrich and used either after distilling from CaH or without further purification. There was no noticeable difference in yield depending on purification of the dibromobutane.

Between 1 and 1.28 equivalents of n-butyl lithium solution were added to a solution containing 1.0 g of the cesium salt of cobalt dicarbollide in 20 ml anhydrous THF. The butyl lithium solution used was originally 10 M in hexanes but was later diluted by the addition of 5 ml THF. There was no noticeable difference in yield between the batches to which different amounts of butyl lithium had been added. Upon deprotonation, the cobalt dicarbollide solution changes from orange to dark purple/black. The black solution was then added to 4.75 g dibromobutane (10 equivalents) in 20 ml THF. The solution became orange again and was stirred for 3 hours. After the unreacted NaH was filtered off, the solution was dried to a thick tar. The orange tar was rinsed with 3 times 30 ml petroleum ether to remove unreacted dibromobutane and then dissolved in water and precipitated with aqueous cesium chloride.

HNMR shows that approximately 55 mol% of the cobalt dicarbollide reacted with the dibromobutane while the rest was unreacted (Figure 4-27). If the solid mixture is rinsed with chloroform, bromobutylcobalt dicarbollide is dissolved along with some cobalt dicarbollide. The chloroform solubles are approximately 80 mol% bromobutyl cobalt dicarbollide. HNMR of the product mixture shows the three non-equivalent carborane hydrogens from the bromobutyl cobalt dicarbollide in the correct ratio with the hydrogens on the bromide substituted carbon. Additionally, the other aliphatic hydrogen peaks can be seen superimposed on the broad boron hydrogen peaks. Unreacted cobalt dicarbollide can be identified by the single carborane carbon hydrogen peak.
Figure 4-27: HNMR of Bromobutyl Cobalt Dicarbollide, Cesium Salt, in D-Acetone
Butanol norbornene ester can be reacted with the bromobutyl cobalt dicarbollide to form a cobalt dicarbollide functionalized norbornene monomer with 11 atoms between the functional group and the norbornene structure. It was found that sodium hydride undergoes reaction with bromobutyl cobalt dicarbollide. Thus, the preferred reagent addition order is to mix the norbornene ester with sodium hydride before adding the bromobutyl cobalt dicarbollide. This reaction was done on a small scale, using 0.1 g of bromobutylcobalt dicarbollide. Since this starting material was never completely separated from byproduct cobalt dicarbollide, the 0.1 g refers to the calculated amount of bromobutyl cobalt dicarbollide reagent present in a larger amount of mixed product. For example, if the 55 mol% bromobutylcobalt dicarbollide mixture is used, a total of 1.8 g material must be added in order to achieve a calculated 0.1 g of reagent.

A ratio of 2:1 norbornene ester to bromobutyl cobalt dicarbollide was used. Accordingly, 0.071 g of norbornene butanol ester was dissolved in 3 ml anhydrous THF and treated with 8 mg sodium hydride (1 ester equivalent) under reflux for 2 hours. The bromobutyl cobalt dicarbollide mixture was dissolved in 4 ml anhydrous THF, added to the norbornene ester solution, and stirred overnight. The solution was dried to a solid, dissolved in 20 ml water, and then precipitated with aqueous cesium chloride.

The product was purified by column chromatography using silica gel adsorbent and a mixture of 3:1 ethyl acetate/hexane eluant. The product elutes as the second component. The first component is clear, but the product fraction is reddish. The third fraction is orange. Generally, we have found that cobalt dicarbollide functionalized compounds are difficult to purify with column chromatography because the influence of the anionic group tends to dominate, causing different cobalt dicarbollide containing compounds to elute together. Also, these compounds tend to tail extensively and require very polar eluents. However, in this case, the product could be purified and was recovered in about 20% yield.

HNMR of the product shows the expected olefin hydrogen peaks and three nonequiv
alent cobalt dicarbollide carbon hydrogen peaks, although the area of the cobalt dicarbollide carbon hydrogen peaks is lower than expected (see Figure 4-28). The product is soluble in acetone and THF. In contrast to the norbornene methanol based reaction (described in Section 4.6.5), there was no sign of elimination side product.

**Polymerization**

Upon treatment with the Schrock fluorinated catalyst, HNMR of the product still showed olefin hydrogen peaks but all of the cobalt dicarbollide carbon hydrogen peaks were gone (see Figure 4-29). The exact reaction is unknown, but it seems evident that the Schrock fluorinated catalyst is inappropriate for polymerizing this monomer. The polymerization attempt was carried out in 1 ml THF, using 27 mg nor-11-CDC mixture and 0.021 ml of a 55 mg in 2 ml THF solution of the Schrock fluorinated molybdenum catalyst (MW 765.5). This would nominally produce 50 repeat units. It is unknown by what mechanism a catalytic amount of the molybdenum compound could cleave or destroy all the cobalt dicarbollide groups.

Upon treatment with the Grubbs catalyst, HNMR shows that the product spectrum’s olefin hydrogen peaks are much reduced in comparison to the pendant cobalt dicarbollide carbon hydrogen peaks (see Figure 4-30). This suggests that the Grubbs catalyst polymerized this monomer. The polymerization attempt was done in 0.3 ml THF, using about 5 mg nor-11-CDC mixture and 0.007 ml of a solution of 33 mg catalyst in 4 ml THF. This would nominally produce 100 repeat units.

**Reaction of olefin bonds and deprotonated cobalt dicarbollide**

Reaction between deprotonated cobalt dicarbollide and carbon-carbon double bonds was first observed during attempts to synthesize allyl cobalt dicarbollide by reaction with allyl bromide. HNMR analysis of the product showed no remaining unsaturated hydrogen peaks.

Since the olefin bonds of norbornene are part of a strained cyclic structure, they sometimes demonstrate different reactivity than terminal olefins. Thus, it was not certain that deprotonated cobalt dicarbollide would react with norbornene olefin bonds.
Figure 4-28: HNMR of Nor-11-CDC in D-Acetone
Figure 4-29: HNMR of Nor-11-CDC after Treatment with a Schrock Catalyst in D-Acetone
Figure 4-30: HNMR of Poly-Nor-11-CDC in D-Acetone
Following a reaction scheme analogous to that of nor-6-carb, deprotonated cobalt dicarbollide was reacted with methylnorbornene bromobutyl ether.

The product was separated into fractions using column chromatography with a 1:3 mixture of acetone and ethyl acetate. None of the five orange colored fractions collected showed the typical norbornene olefin hydrogen peaks in their HNMR spectra. Cobalt dicarbollide itself showed no reactivity toward methylnorbornene bromobutyl ether, but the deprotonated cobalt dicarbollide species did. The chemical structure of the reaction product or product mixture was undetermined.

**Reaction Description**  A solution of 1.85 g cobalt dicarbollide (cesium salt) in 45 ml THF was treated with 0.386 ml of 10 M BuLi in 5 ml THF. The orange solution became black. After stirring 10 minutes, an equimolar amount of methylnorbornene bromobutyl ether (1.0 g) was added. The solution became orange immediately, and was stirred for 45 minutes. The solvent was then evaporated, and the residue extracted with 100 ml ether and 150 ml water. The ether phase dried to a tacky orange solid. This solid was dissolved in a heated solution of 100 ml of 1M NaCl and 50 ml acetone, and aqueous CsCl was added. As the solution cooled, a dark orange liquid separated out. This orange product mixture was dissolved in 5 ml methylene chloride, applied to a silica gel column, and rinsed with methylene chloride. Rinsing with methylene chloride did not remove any of the orange product, but did elute a small amount of clear oil. The orange product was eluted with methanol and then dried. The product was then separated into 5 fractions using column chromotography with a 1:3 mixture of acetone and ethyl acetate. These fractions did not represent distinct spots on TLC, but an arbitrary division of the components of one long smear into fractions of equal volume. The crude product showed one long smear on TLC; each fraction showed a shorter subsection of the long smear.
4.6.5 Poly-CDC-Siloxane

Mixed substitution and elimination product

This reaction was carried out at two temperatures, 0 °C and 50 °C, to determine if the reaction temperature affects the ratio of substitution to elimination product. Often, low temperatures favor formation of substitution products. In our case, the product mixtures of the two reactions were found to have the same composition.

The 0 °C reaction was carried out as follows. The 50 °C reaction was similar, except for the temperature of reaction. Norbornene methanol (0.3 g) was dissolved in 5 ml anhydrous THF and stirred with 0.06 g sodium hydride (1 equivalent) for 30 minutes at 65 °C. Slight orange discoloration was observed. The pot was cooled to 0 °C and a solution of 0.68 g of a mixture consisting of approximately 80% bromobutylcobalt dicarbollide (cesium salt) mixed with 20% cobalt dicarbollide (cesium salt) in 2 ml THF was added. This represents approximately 2 equivalents of the norbornene methanol per bromo reagent. The pot was stirred for 30 minutes at 0 °C.

The solution was poured into a mixture of 30 ml water and 30 ml diethyl ether. Aqueous cesium chloride was added to the water phase. The ether phase was dried to 5 ml and fractionated with column chromatography. Silica gel was used as an adsorbant. Diethyl ether was run through the column to elute unreacted norbornene methanol, then acetonitrile was used to elute the orange product.

HNMR of the product mixture showed norbornene olefin hydrogen peaks as well as the unsaturated hydrogen peaks of the elimination product (see Figure 4-31). Separate cobalt dicarbollide carbon hydrogen peaks were also visible for both products. Based on the integration areas of the norbornene vs alkene peaks, the 0 °C reaction was found to be 53% elimination product and the 50 °C reaction was 55% elimination product, a negligible difference.

Thin layer chromatography using silica gel plates and various solvent eluents was unable to separate the two products. It is likely that there is a method to separate these products, but we were not able to find one. Since alkenes poison the polymerization catalysts used for norbornene monomers [111, 41], this product
Figure 4-31: HNMR of Elimination (Butene Cobalt Dicarbollide) and Substitution (Methoxynorborne Cobalt Dicarbollide) Products in D-Acetone
mixture is not useful for ROMP.

Alternative methods of reaction, perhaps using a two phase system with phase transfer catalyst, might produce less elimination product. We did not investigate any alternative methods.

**hydrosiloxane coupling**

Unsaturated hydrocarbons are known to react with hydrosilane groups, sometimes with the addition of a catalyst such as hexachloroplatinic acid. Thus, both components of the reaction product mixture described above could be grafted onto a polymer with hydrosilane groups. We investigated this grafting reaction to see if it would either produce a useful cobalt dicarbollide functionalized material or serve as a way to purify the substitution product by removing the elimination product. The norbornene product was found to react more readily than the alkene product, thus reaction with hydrosilane polymer cannot be used to purify the norbornene monomer.

The hydrosilane polymer used was purchased from Geleste, and is a siloxane copolymer of molecular weight 1900-2000, consisting of 25-30% methylhydrosilane and the balance dimethylsilane. (See Figure 4-32 for the HNMR spectrum.) The mixed elimination and substitution product (0.48 g, estimated 39 mol% elimination and 36 mol% substitution with the balance cobalt dicarbollide) was dissolved in 20 ml anhydrous toluene and 0.13 g of the polymer added. This amount of polymer, assuming 25% hydrosilane, is 1.45 equivalents on a substitution product basis. A drop of 0.12 M hexachloroplatinic acid in THF was added, and the solution stirred at 65 °C for 3 days.

HNMR shows that the product no longer contains hydrosilane groups or norbornene olefin groups (Figure 4-33). Methyl silyl hydrogen peaks, alkene hydrogen peaks, and cobalt dicarbollide carbon hydrogen peaks are still visible. The siloxane copolymer remained liquid after the norbornene cobalt dicarbollide monomer was grafted onto it, and we were unable to chromatographically separate the grafted polymer from the remaining elimination product. Probably this difficulty would be avoided if a higher molecular weight, solid polymer starting material were used, but
Figure 4-32: HNMR of Polydimethylsilane/Polymethylhydrosilane in D-Chloroform
none was available.

The product mixture from the hydrosiloxane grafting reaction was mixed with 10 ml THF and 0.09 g more hydrosiloxane polymer. One drop of the 0.12 M chloroplatinic acid in THF was added, and the solution was heated to 65 °C overnight. HNMR showed disappearance of the alkene hydrogen peaks as well as the hydrosilane hydrogen peaks (see Figure 4-34) The hydrosilation reaction easily attaches unsaturated groups to the functional polymer, but because the polymer has low molecular weight, it remains liquid after grafting. This product might be useful as a polyelectrolyte, but we did not investigate possible applications.

4.6.6 Poly-Nor-Si-Anion

Two batches of this monomer were synthesized. The first batch had some impurity containing silylmethyl groups. Possibly, excess butyl lithium had reacted with the dimethylchlorosilylnorbornene. The second batch was more pure, as shown by melting point measurements and HNMR results.

Schrock Catalyst

The Schrock catalyst did not polymerize this monomer. A solution of 0.113 g of the cesium salt of the carborane anion monomer (batch 1) in 5 ml anhydrous THF was dried overnight stirring over 4 Åmolecular sieves. The solution was filtered and 1 ml THF added. To the monomer, 0.3 ml of a 13 mg/2ml in toluene solution of the Schrock molybdenum catalyst was added, for a target length of 75 repeat units. The solution was stirred overnight and terminated with an excess of bezaldahyde. HNMR showed the product to be identical to the monomer.

Grubbs Catalyst, Methanol

The norbornene anion monomer is soluble in polar solvents such as methanol, acetone, and THF. Since methanol was the superior solvent for the monomer, we wanted to try using it as the polymerization solvent.
Figure 4-33: HNMR of Mixed Elimination/Substitution Products Reacted with a Polyhydrosilane in D-Acetone
Figure 4-34: HNMR of First Hydrosilation Reaction Products Reacted with More Polyhydrosilane in D-Acetone
Mixtures of methanol and toluene (ratios from 1:4 to 4:1) were previously tested as polymerization solvents for a norbornene ether using the Grubbs ruthenium catalyst. Our results were consistent with the literature, confirming that protic solvents such as methanol can be used for polymerization. However, an attempt to use methanol as the polymerization solvent for this monomer was unsuccessful.

A solution of 0.2 g of the cesium salt of the carborane anion monomer (batch 1) in 5.0 ml of methanol was treated to remove dissolved oxygen. The solution was sealed under a rubber septum and nitrogen was introduced into the solution through a needle while another needle vented from the headspace. A toluene solution (0.483 ml) of the Grubbs ruthenium catalysts solution (32 mg/2ml) was injected for a target length of 50 repeat units. During the first 10 minutes, nitrogen degassing was continued. At the end of 10 minutes, the solution was green. After approximately 6 hours, the solutions was yellow. After stirring overnight, the solution was dried. HNMR showed the reaction product to be identical to the monomer.

**Grubbs Catalyst, THF**

The unreacted monomer from the methanol polymerization attempt was added to 5 ml of THF. Then 0.688 ml of a 32mg/3ml ruthenium catalyst solution was added for a target length of 50 repeat units. This calculation assumed that 0.19 g of material was left from the 0.2 g originally used for the methanol reaction above. Within minutes, the solution darkened. The reaction was stirred overnight and terminated with an excess of ethyl vinyl ether. HNMR confirmed that the olefin bonds of the norbornene moity had reacted, but impurities remained, as evidenced by the unexplained methylsilyl hydrogen peaks. Since this batch of monomer was not very pure to begin with, and since this particular sample of the monomer had been recycled from a previous polymerization attempt, the polymerization experiment was repeated using monomer of higher purity.

0.05 g of the monomer from the 2nd batch was dissolved in 1 ml THF and 0.439 ml of a 33mg/3ml ruthenium catalyst solution was added for a target length of 20 repeat units. The solution turned brown and became slightly cloudy. The reaction
was stirred overnight and spontaneously separated into two phases. The top phase was clear and light brown. A small amount of a second clear, blue/grean phase was on the bottom of the vial. The solution was shaken up and dropped into 10 ml hexane. A sticky tar precipitated and the hexane was decanted. HNMR shows a clean polymer spectrum with the characteristic polynorbornene olefin bond peaks in the correct ratio with the broadened methylsilyl hydrogen peaks.

**Viscometry**

Solutions of the carborane anion monomer and the product of the first polymerization attempt of this monomer using the Grubbs catalyst in THF were analyzed by capillary viscometry. Each solution was 10 mg/1 ml; THF and methanol were used as solvents. Measurements were taken in a room temperature water bath. These measurements were not fitted to viscosity equations, instead the monomer and potential polymer product flow times were simply compared. Results showed little increase in viscosity for the solution containing reaction product (see Table 4.2). Flow times were very reproducible in multiple measurements.

<table>
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<th>Solution</th>
<th>Flow Time, seconds</th>
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<tr>
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</tr>
<tr>
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<td>71</td>
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<tr>
<td>product, THF</td>
<td>73</td>
</tr>
<tr>
<td>methanol</td>
<td>91</td>
</tr>
<tr>
<td>monomer, methanol</td>
<td>94</td>
</tr>
<tr>
<td>product, methanol</td>
<td>97</td>
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Chapter 5

Cobalt Dicarbollide and Carborane Anion Polymers: Potential Applications

The cobalt dicarbollide and carborane anion groups have similar properties. As discussed in Chapter 1, both molecules are voluminous anions with good thermal and chemical stability. Due to these shared characteristics, polymers functionalized with either cobalt dicarbollide or the carborane anion may have applications for selectively binding cesium. Additionally, such polymers may be interesting polyelectrolytes for use in lithium batteries.

Chapter 4 discussed the synthesis of novel cobalt dicarbollide and carborane anion functionalized polymers. In this chapter, we discuss preliminary testing of these materials for application as solid ion-exchangers and polyelectrolytes.

5.1 Cesium Ion-Exchange

Several novel polymers were examined for suitability as solid-phase cesium separation materials. In waste treatment applications, these polymers might be formed into filters or small column packing beads. For our preliminary tests, the soluble materials were simply cast into films. The cross-linked powder that resulted from the attach-
polymerize-sandwich scheme (poly-nor-C-carb-Co) was sealed into a “tea-bag” made from a non-woven, porous polypropylene material chosen for its inertness to acid and metal ions.

5.1.1 Cobalt Dicarbollide and Carborane Anion Polymers for Cesium Binding

Poly-nor-C-CDC and poly-nor-Si-anion homopolymers were considered as potential cesium ion-exchange materials. Because these materials are soluble in polar solvents such as methanol, there was concern that they would also be partially soluble in water. Some hydrophilicity is desirable in ion-exchange materials, to ensure contact between the polymer functional groups and aqueous ions. However, material loss due to solubility in water would negate one of the advantages of using a solid extractant instead of a second solvent phase extractant.

One way to control polymer solubility characteristics is copolymerization. Both nor-C-CDC and nor-Si-anion were copolymerized with norbornene to produce less hydrophilic materials. Additionally, a sample of the poly-nor-C-CDC/poly-norbornene copolymer was cross-linked for further reduction in solubility.

Copolymerizing Nor-Si-Anion

The nor-Si-anion monomer was copolymerized with norbornene to form a polynorbornene(90)/poly-nor-Si-carb(30) polymer. This copolymer does not phase separate from THF during polymerization, as the homopolymer does. The copolymer is also less readily soluble in methanol than the homopolymer and somewhat less brittle. HNMR confirms that approximately 25% of the copolymer is poly-nor-Si-carb from comparison of the olefin hydrogen and methylsilyl hydrogen peaks (see Figure 5-1).

Copolymerizing Nor-C-CDC

Copolymerization of the cobalt dicarbollide monomer with norbornene was investigated. The resulting copolymers were also brittle, orange solids but are less brittle
Figure 5-1: HNMR of Polynorbornene(90)/Poly-Nor-Si-Anion(30) Block Copolymer in D-THF
than the homopolymer material. A 100:35 copolymer was soluble in toluene but only slightly soluble in acetone while a 100:45 copolymer was fully soluble in acetone and partially soluble in toluene. This demonstrates that copolymerization can be used to tailor solubility.

GPC in THF with 50mM LiBr showed a copolymer peak with narrow weight distribution. A broad, lower molecular weight peak also appeared. HNMR suggests that somewhat less than the expected amount of nor-C-CDC was incorporated into the material (15% instead of 26% for the nominally 35:100 copolymer). (See Figure 5-2 for the spectrum. Figure 5-3 shows the HNMR spectrum of polynorbornene for comparison.) Since the nor-C-CDC monomer had never been completely separated from cobalt dicarbollide coproduct and the ratio of the two products was only estimated with HNMR, it is possible that the actual amount of nor-C-CDC added to the polymerization was less than calculated, and that cobalt dicarbollide was responsible for the large low molecular weight peak.

**Crosslinking the Copolymer** The copolymer was found to undergo cross-linking to an insoluble resin when held at 65 °C for four hours, probably due to reaction of the unsaturated bonds in the polynorbornene blocks. Since polynorbornene has a low Tg, it will heat crosslink at fairly low temperatures. Temperature triggered cross-linking might be useful, as the material could be processed into the desired shape while soluble and then easily crosslinked.

**Copolymer Morphology** Polynorbornene(100)-polynor-C-CDC(35) block copolymers were examined by TEM for microphase separation. Both a thin film cast from toluene and microtomed samples from a thick film cast from THF showed no microphase separation. After annealing at 45-75 °C for three hours, the thin film sample still showed no microphase separation. This indicates that the cobalt dicarbollide functional group is not polar enough to significantly alter the polymer's Flory-Huggins interaction parameter ($\chi$). This is somewhat surprising, since the presence of the cobalt dicarbollide group does significantly impact polymer solubility.
Figure 5-2: HNMR of Polynorbornene/Poly-Nor-C-CDC Block Copolymer in D-Toluene
Figure 5-3: HNMR of Polynorbornene in D-Toluene
However, there have been other examples of copolymers with an organometallic block that does not phase separate from an organic block [115].

The carborane anion copolymer was not examined for microphase separation. It is expected that this block copolymer would be similar to the cobalt dicarbollide functionalized material.

It has been reported that aqueous ions are able to diffuse through microphase separated films containing one hydrophobic and one hydrophilic phase. Phase separation may result in better ion diffusion through the material since the hydrophilic phase can form channels or pathways. However, our copolymer materials probably have a high enough average hydrophilicity that such channels are unnecessary for the diffusion of aqueous ions.

A Potential Crosslinking Agent for Poly-Nor-C-CDC

When cobalt chloride is combined with a solution of degraded nor-C-carb monomer, an organometallic sandwich compound with norbornene groups attached to both carborane fragments is formed. This difunctional monomer is a potential crosslinking agent because both norbornene groups may be polymerized. Such crosslinking agents would be useful for producing insoluble resin particles suitable for use in ion-exchange columns. Because this monomer also contains the cobalt dicarbollide group, adding such a crosslinking agent would not dilute the binding site density or decrease the material’s binding capacity.

Other studies have shown that microstructure can be controlled by the order of polymerization. We tested both simultaneous polymerization of crosslinking agent and nor-C-CDC monomer as well as the “linear arm first” method which has been found to produce microporous particles [12, 125].

These preliminary experiments showed that the bisnorbornene monomer does not have good crosslinking activity. Polymerization of a 1:2 mixture of crosslinking monomer and nor-C-CDC results in soluble polymers with remaining unreacted norbornene olefin bonds. HNMR suggest that only one norbornene group from each difunctional monomer reacts. This is true when both monomers are mixed together.
initially and when the monofunctional monomer is polymerized first. If crosslinking is desired, either a different difunctional monomer should be used in combination with nor-C-CDC or the heat triggered method could be used with the a polynorbornene copolymer.

**Poly-Nor-C-Carb-Co**

The cross-linked powder was judged to be unsuitable for use in its synthesized form and could not be heat-processed into other forms. After 0.1 g of the powder was sealed into a bag and soaked in a 1 wt% nitric acid solution for 1 day, the solution became noticeably orange and foamed when shaken. The solution color change and foaminess indicates that the material partially dissolved in the dilute acid. Additionally, significant amounts of the fine powder escaped from the bag. Because this material was such a fine powder, it was difficult to separate from solution. This material was not investigated further.

### 5.1.2 Solubility in Nitric Acid

Strong nitric acid treatment is commonly used to remove cesium ions from cobalt dicarbollide so that the binding agent can be reused. Thus, it is desirable for a cobalt dicarbollide functionalized polymer to be stable in acid, except for undergoing cesium-hydrogen ion exchange.

Approximately 30 mg each of poly-nor-Si-anion, polynorbornene(90)/poly-nor-Si-anion(30), poly-nor-C-CDC, polynorbornene(100)/poly-nor-C-CDC(45), and heat cross-linked polynorbornene(100)/poly-nor-C-CDC(45) were tested. These materials were soaked in 10 ml of 40 wt% (7.9 M) nitric acid to test for solubility and reactivity. After 4 days, the films were rinsed, dried, and weighed to determine mass loss. All of these polymers were synthesized in the cesium salt form, and it was expected that this strong acid treatment would convert them into their acid form for future metal ion binding tests. Therefore, some weight loss due to cesium-hydrogen counterion exchange was expected. The acid solutions were sampled using ICP-MS to measure
the amount of cesium in solution.

It was anticipated that the acid form of the polymers would be more hydrophilic than the cesium form. While hydrophilicity is desirable because it facilitates ion-exchange, extreme hydrophobicity could result in solubility and loss of the polymer. Copolymerization with norbornene and heat cross-linking were tested as ways to reduce solubility. Table 5.1 lists the materials' original weight and percent remaining after soaking in acid. Additionally, the percent of polymer dissolved is listed. The amount of polymer dissolved was calculated based on the material weight change, the amount of cesium detected, and the assumption that any cesium bound to dissolved polymer would also be detected (see Section 5.1.3 for calculation details).

These results show that both homopolymers have significant solubility in strong acid. For poly-nor-Si-anion materials, copolymerization with norbornene essentially eliminates solubility. For poly-nor-CDC, copolymerization did not significantly lower solubility. However, cross-linking in addition to copolymerization did reduce material solubility.

These experiments do not indicate whether the measured solubility is due extraction of low molecular weight fractions in the material or to polymer dissolving. For the cross-linked material, it is likely that some soluble fraction of the material was extracted and that subsequent acid treatment would not result in further material loss. Experiments with sequential acid treatments would be needed to check for subsequent material loss.

Table 5.1: Weight Loss After 40 wt% Nitric Acid Treatment

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<thead>
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<th>Original Weight, mg</th>
<th>Post-Acid wt%</th>
<th>% Dissolved</th>
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<td>42.5</td>
<td>52.5</td>
<td>36</td>
</tr>
<tr>
<td>poly-nor-anion(30)/poly-norbornene(90)</td>
<td>29.6</td>
<td>78.4</td>
<td>1</td>
</tr>
<tr>
<td>poly-nor-CDC(50)</td>
<td>31.0</td>
<td>61.9</td>
<td>33</td>
</tr>
<tr>
<td>poly-nor-CDC(45)/poly-norbornene(100)</td>
<td>29.3</td>
<td>64.5</td>
<td>31</td>
</tr>
<tr>
<td>poly-nor-CDC(45)/poly-norbornene(100)</td>
<td>28.3</td>
<td>71.4</td>
<td>23</td>
</tr>
<tr>
<td>heat cross-linked</td>
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</table>
Material Color Change

After the acid treatments, all the materials evidenced some color change. The three cobalt dicarbollide functionalized materials darkened somewhat from their original orange color. The carborane anion materials were originally gray. Afterwards, the homopolymer material was orange and the copolymer light orange. The cause of these color changes was not determined.

Solution Color Change

The acid solutions also evidenced subtle color changes. The solutions in contact with the carborane anion materials were very slightly yellow. The solution in contact with the cobalt dicarbollide functionalized homopolymer was slightly pink, while the solutions in contact with the cobalt dicarbollide copolymers were slightly yellow. All the solutions had some small tendency to foam. Although bubbles formed when the solutions were shaken, they quickly subsided. This effect was not quantified, but the solution of the poly-nor-anion/poly-norbornene copolymer seemed to be less foamy than the others. These changes were probably the result of partial dissolution of the polymers in the acid.

5.1.3 Cesium Stripping

The acid solutions were analyzed for cesium content to measure the effectiveness of nitric acid stripping for regenerating these ion-exchange materials. A preliminary test of 2.7 mg of the poly-nor-CDC(35)/poly-norbornene(100) material in 40 wt% nitric acid indicated that approximately 80% of the cesium would be stripped from the polymer. This calculation was made on the basis of the HNMR estimate of the cobalt dicarbollide content (15 mol%), which was lower than the nominal content.

Table 5.2 shows the percent of cesium stripped from each material by the acid treatment. The percentage of cesium stripped was calculated based on the amount of cesium calculated to be originally present in the materials and the measured concentration in the acid solutions. In the case of the copolymers, the calculated amount
of cesium originally present was based on the nominal copolymer ratios of functional to non-functional monomer (45:100 for the cobalt dicarbollide copolymer and 30:90 for the carborane anion copolymer. The original cesium content is probably accurate for the homopolymers and the carborane anion copolymer, but is probably overestimated for the cobalt dicarbollide copolymer (since HNMR analysis of the 35:100 batch indicated a lower percent of functional groups than expected). Thus, the actual percentage stripped from the cobalt dicarbollide copolymers may be higher than the table shows.

These results show that cesium can be stripped from the carborane anion materials more easily than from the cobalt dicarbollide materials. Additionally, the decrease in hydrophilicity due to copolymerization does not adversely affect stripping. Actually, copolymerization increases stripping efficiency in the carborane anion material. Heat-induced crosslinking also increases stripping. The anomalous result for the carborane anion copolymer (over 100% cesium stripped) was probably caused by experimental error during material weighing or solution sampling.

It is surprising that stripping efficiency should be improved by copolymerization or cross-linking, since it might be expected that measures undertaken to reduce solubility might also reduce the access of aqueous cations to the polymer functional groups.

**Calculation**

Assuming that all cesium associated with dissolved polymer is detected by ICP-MS, and that the polymer dissolves uniformly (i.e., the copolymer composition of the

---

### Table 5.2: Cesium Removal by Strong Nitric Acid

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage of Cesium Stripped</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly-nor-anion(20)</td>
<td>60</td>
</tr>
<tr>
<td>poly-nor-anion(30)/poly-norbornene(90)</td>
<td>110</td>
</tr>
<tr>
<td>poly-nor-CDC(50)</td>
<td>35</td>
</tr>
<tr>
<td>poly-nor-CDC(45)/poly-norbornene(100)</td>
<td>36</td>
</tr>
<tr>
<td>poly-nor-CDC(45)/poly-norbornene(100) heat cross-linked</td>
<td>43</td>
</tr>
</tbody>
</table>
remaining solid is the same as that of the dissolved material), we have the following mass balance equations

\[
Md = Moc \times (1 - Pd) \times Ps + Moc \times Pd
\]

\[
Mr = Mo \times (1 - Pd) \times ((MWcs \times (1 - Ps) + MWh \times (Ps))/MWcs)
\]

where \(Md\) = amount cesium detected in solution, \(Moc\) = amount of cesium in the original material, \(Pd\) = fraction of material dissolved, \(Ps\) = fraction of cesium stripped from the undissolved material, \(Mr\) = remaining material mass, \(Mo\) = original material mass, \(MWcs\) = molecular weight of original material per cesium, \(MWh\) = molecular weight of theoretical material per hydrogen if all cesium were exchanged for hydrogen.

We can solve for \(Pd\) and \(Ps\). \(Md\), \(Mo\), and \(Mr\) are measured experimentally. \(Moc\) is calculated from \(Mo\) and \(MWcs\). \(MWcs\) and \(MWh\) are calculated from the molecular structure of the materials. The largest potential inaccuracy is that since the exact composition of the cobalt dicarbollide containing copolymers is unknown, \(MWcs\) and \(MWh\) must be based on the nominal composition. \(Mo\) and \(Mr\) are subject to experimental uncertainty stemming from the milligram quantities being weighed. \(Mr\) is subject to error mainly due to inaccuracies in sample preparation for ICP-MS analysis. Since the actual acid solutions are too concentrated for the instrument used, samples were diluted by \(4 \times 10^5\) times for analysis and some volumetric measurement uncertainty was introduced. The error in \(Mr\) could be reduced by making up multiple dilutions from each sample.

### 5.1.4 Cesium and Sodium Binding

After the materials were partially converted into the hydrogen form, they were exposed to solutions containing cesium and sodium ions. The solutions were \(5.57 \times 10^{-3}\)M in both ions, and a sufficient volume of solution was used so that each sample of material was exposed to an amount of each cation equal to the total number of binding sites present. The solution was approximately 0.4 wt% nitric acid, which is about
Table 5.3: Cesium and Sodium Binding by Carborane Anion and Cobalt Dicarbollide Functionalized Polymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Theoretical Capacity, meq/g</th>
<th>Kd Cs ml/g</th>
<th>Kd Na ml/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly-nor-anion(20)</td>
<td>3.4</td>
<td>209</td>
<td>&lt;42</td>
</tr>
<tr>
<td>poly-nor-anion(30)/poly-norbornene(90)</td>
<td>1.7</td>
<td>124</td>
<td>&lt;17</td>
</tr>
<tr>
<td>poly-nor-CDC(50)</td>
<td>2.3</td>
<td>183</td>
<td>&lt;27</td>
</tr>
<tr>
<td>poly-nor-CDC(45)/poly-norbornene(100)</td>
<td>1.6</td>
<td>77</td>
<td>&lt;19</td>
</tr>
<tr>
<td>poly-nor-CDC(45)/poly-norbornene(100) heat cross-linked</td>
<td>1.6</td>
<td>71</td>
<td>&lt;17</td>
</tr>
</tbody>
</table>

0.06M.

Usually the binding of a dissolved ion by a solid material is described by the distribution coefficient Kd, defined as the amount of bound ion per weight solid divided by the amount of dissolved ion per volume solution. Kd is often quoted in units of ml/g. The distribution coefficient is useful in comparisons between materials of unknown composition. The theoretical capacity of an ion-exchange material is often described in meq/g, the millimoles of binding site per gram material. Table 5.3 lists the theoretical capacities of the materials tested and their distribution coefficients for sodium and cesium as measured in 0.06M nitric acid.

The amount of sodium uptake by these materials was too small to be detected with our techniques. Thus, the distribution coefficients for sodium could not be calculated. Instead, we list the minimum detectable Kd, assuming that our technique could detect a 5% decrease in solution sodium content. The actual Kd for sodium is less than this minimum detectable level. Different experimental conditions would be needed to measure the sodium binding constants so that the cation selectivity of these materials could be quantified. However, our results show that these materials are all selective for cesium over sodium.

Much research has been done recently on resorcinol-formaldehyde or phenolic resins, as well as composite materials consisting of inorganic cesium binding materials in a polymer matrix [9, 89, 23, 114, 99, 113, 76, 124]. However, these resins are designed for alkaline wastes and are only effective at high pH. Often, cation bind-
ing decreases with increasing acid concentration. Kd for cesium is strongly affected by pH and sodium concentration. This makes it somewhat difficult to compare our results with most literature values. For organic resins in alkaline media, distribution coefficients ranging from 10 to $5 \times 10^4$ have been measured [9, 89, 114, 113, 76]. The cesium distribution coefficients for our materials are comparable to some resins in acid and better than others [133].

Cesium capacity for our materials is comparable to some organic resins [9] but lower than others [23, 114]. However, our resins are able to bind cesium at pH of 1-2, while phenol or resorcinol resins are only useful at pH greater than 10.

Functional Group Efficiency

In order to compare the cesium binding efficiency of the functional groups in each of our materials, Table 5.4 lists the actual capacity, ratio of Kd to theoretical capacity, ratio of Kd to actual capacity, and ratio of cesium stripped to cesium bound. The actual capacity for each material was calculated with the equation

$$Ps/(MWcs * (1 - Ps) + MWh * (Ps))$$

where $Ps$ = fraction of cesium stripped from the undissolved material, $MWcs$ = molecular weight of original material per cesium, and $MWh$ = molecular weight of theoretical material per hydrogen if all cesium were exchanged for hydrogen. Kd/Ct ($Ct =$ theoretical capacity) gives an indication of how well each material binds cesium given theoretical binding site density, while Kd/Ca ($Ca =$ actual capacity) gives a measurement of how well each material binds cesium given the actual available binding site density. The ratio of cesium stripped by nitric acid to cesium bound by the material indicates what percentage of available (hydrogen form) binding sites actually exchanged hydrogen for cesium under the experimental conditions.

From a comparison of Kd/Ct, the nor-Si-anion copolymer and the cobalt dicarbol- lide homopolymer materials show the best performance. However, considering Kd/Ca or amount bound/amount stripped, we can conclude that the cobalt dicarbolide func-
Table 5.4: Cesium Binding Efficiency of Carborane Anion and Cobalt Dicarbollide Functional Groups in Polymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Actual Capacity meq/g</th>
<th>Kd Cs/Ct ml/meq</th>
<th>Kd Cs/Ca ml/meq</th>
<th>bound/stripped</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly-nor-anion(20)</td>
<td>1.7</td>
<td>62</td>
<td>121</td>
<td>0.53</td>
</tr>
<tr>
<td>poly-nor-anion(30)/poly-norbornene(90)</td>
<td>2.0</td>
<td>72</td>
<td>64</td>
<td>0.26</td>
</tr>
<tr>
<td>poly-nor-CDC(50)</td>
<td>0.7</td>
<td>79</td>
<td>270</td>
<td>1.11</td>
</tr>
<tr>
<td>poly-nor-CDC(45)/poly-norborenene(100)</td>
<td>0.5</td>
<td>49</td>
<td>156</td>
<td>0.72</td>
</tr>
<tr>
<td>poly-norbornene(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>heat cross-linked</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Each functional group is better at binding cesium than the carborane anion group. Furthermore, each functional group is most effective in the homopolymer, with copolymerization significantly lowering the likelihood of an available functional group binding to dissolved cesium. Being in a cross-linked material also lowers the binding effectiveness of the cobalt dicarbollide functional group.

5.1.5 Conclusions

We have found that both carborane anion functionalize polymers and cobalt dicarbollide functionalized polymers remove cesium ions from acidic solution. Copolymerization and crosslinking can be used to control undesirable polymer solubility in strong nitric acid, but there is a trade-off in binding efficiency. Strong nitric acid can be used to strip cesium off the polymers. These materials are all selective for cesium over sodium.

Our polymers were all functionalized with metal-binding groups attached near the polymer backbone. It would be interesting to see whether the use of a spacer chain improves cesium binding efficiency and decouples binding efficiency from material solubility.
5.2 Solid Electrolytes

Solid-state batteries need a solid electrolyte separating anode and cathode. Polymeric materials have a number of advantages for use as solid electrolytes. Unlike inorganic crystals or glasses, polymers can maintain good physical contact with electrodes under the stresses caused by battery operation. They also have much lower minimum use temperatures than molten salt electrolytes. Although polymer electrolytes usually have significantly lower ionic conductivity than these other materials, they can be formed into thin films so that larger area compensates for lower conductivity. Polymer electrolytes have been studied particularly for rechargeable lithium battery applications [31].

Many polymer electrolytes contain a polymer doped with a lithium salt. Poly(ethylene oxide) polymers (or non-crystalline variations on PEO) are commonly used because the ether groups are able to coordinate lithium ions strongly enough for good dispersion yet weakly enough to allow mobility. The lithium salt used must be able to dissociate in the polymer to allow movement of the cation and anion [32].

Other polymer electrolytes are actually polyelectrolytes, with immobile charged groups attached to the polymer structure and mobile counterions. This single ion conductivity has the advantage that salt layers cannot build up at the electrolyte/electrode interfaces. Such layers can interfere with conductivity [32]. Since most polyelectrolytes are brittle polymers, they often need to be either plasticized or incorporated into a copolymer [31]. In addition to use in lithium batteries, polyelectrolytes may have applications in fuel cells or thin film electrochromatic devices [33].

We have synthesized polyelectrolytes functionalized with carborane anions or cobalt dicarbollide. Since cobalt dicarbollide and the carborane anion are unusually diffuse anions, they easily dissociate from their counterions. The combination of an polymer-bound anion with a dissociated cation makes the the lithium salts of these polymers good candidates for use in lithium batteries. These brittle polymers could be plasticized by blending with PEO or other rubbery, ionically conductive polymers.

Alternatively, our polymers could be modified to contain PEO-like blocks. There
are a number of norbornene-based, ether functionalize monomers (describe in the appendix) which could be copolymerized with our anionic monomers. Alternatively, our polymers might be used as the basis for an interesting comb copolymer with PEO side-chains.

5.2.1 Ionic Conductivity with the Small Molecule Lithium Salts

Before testing our polyelectrolyte materials, we considered both the carborane anion and cobalt dicarbollide lithium salts for use as electrolytes in a poly(oligo(oxyethylene) methacrylate) (POEM) matrix. These experiments were conducted in cooperation with Philip Soo in Professor Anne Mayes’s group. Typically, polymer electrolyte candidate for use in a lithium battery would have a salt such as LiCF$_3$SO$_3$ mixed into a PEO-type polymer matrix. LiCF$_3$SO$_3$ dissociates well in PEO, but is known to undergo decomposition reactions with the lithium anode. Carborane salts may be more stable.

The carborane anion was obtained as the trimethylammonium salt, while cobalt dicarbollide was synthesized as the cesium salt. We converted these compounds into their lithium forms before testing so that our results could be compared to other lithium conductivity data. Lithium is a cation of interest for battery applications, because lithium batteries have a much higher theoretical energy density than nickel-cadmium or lead-acid batteries [33].

The lithium salt of the carborane anion was found to be very hygroscopic. Both salts were dried under vacuum at elevated temperatures before testing. The cobalt dicarbollide salt was tested at a lithium to ethylene oxide ratio of 1:20. The carborane anion salt was tested at ratios of 1:10, 1:21, and 1:30. Figure 5-4 shows the plots of conductivity versus temperature for POEM doped with these salts.

These results indicate that the lithium salts of cobalt dicarbollide and the carborane anion work as dopants for ionically conductive polymers. Measured conductivity for these samples was somewhat lower than for samples using LiCF$_3$SO$_3$ [128], but
Figure 5-4: Conductivity as a Function of Temperature for the Lithium Salts of Cobalt Dicarbolide and the Carborane Anion in POEM

169
may have been adversely affected by water contamination (in the case of the carborane anion). We anticipate that a polymer functionalized with either moiety would also work as a lithium dopant in a POEM matrix.

5.2.2 A Polyelectrolyte Lithium Salt

The carborane anion polymer was selected for testing as a polyelectrolyte lithium salt. Since cobalt dicarbollide is known to react with alkali metals, it would not be appropriate for use with a lithium anode. Poly-nor-Si-anion is glassy, so it would not be a good ion conductor on its own but might make a suitable dopant for a PEO-type polymer. We were unable to test blended samples, as a solution of the lithium salt of poly-nor-Si-anion and POEM in methanol demonstrated gross phase separation upon drying.

5.2.3 Potential Pathway to an Unusual Comb Copolymer

A variety of norbornene-based ether functionalized monomer are available for copolymerization with nor-Si-anion or nor-C-CDC to produce a polyelectrolyte with ether groups for lithium ion conductivity. This approach is similar to that of Douglass, combining the lithium ion conductivity of PEO, the low charge density of a carborane-based anion, and the synthetic flexibility of ROMP [21]. Douglass et al. encountered difficulties with monomer purification. Additionally, they used the $B_{12}H_{11}SMeR^-$ anion, which may have its negative charge localized at the S atom instead of being distributed over the boron cage [106]. Although it is not yet clear whether this approach will work, it seems promising.

We propose a route to an unusual comb copolymer containing PEO blocks for lithium ion transport and the lithium salt of the carborane anion. This copolymer would be similar to a poly-nor-C-carb/PEO comb copolymer (see Figure 5-5) except it would also contain nor-Si-Anion units in the backbone. Such a copolymer could be synthesized by a combination of ROMP and anionic polymerization. First, a carborane functionalized monomer could be deprotonated at the carborane carbon
Figure 5-5: Proposed Synthesis of Poly-Nor-C-Carb/PEO Comb Copolymer

and used to oligomerize a short chain of ethylene oxide units. Then, this monomer could be copolymerized with nor-Si-anion. Alternatively, a poly-nor-Si-anion/poly-nor-Si-carb copolymer could be synthesized, and then the carborane carbons could be deprotonated with butyl lithium and ethylene oxide chains grown from the carbanion sites. Either block or random copolymers could be made.

These schemes have the advantage that the PEO side chain length could be systematically varied to achieve the optimal ether/lithium salt ratio for conductivity. Probably the PEO segments would be prevented from crystallizing, as they would be relatively short and interspersed with the other components. (Crystallinity is undesirable, as it raises the minimum use temperature.) These polyelectrolytes would be single ion conductions, since the anionic groups are attached to the polymer backbone.

We conducted a preliminary investigation into this synthetic route. Because ethylene oxide is a gas, it is more difficult to handle than a liquid like propylene oxide. Thus, we substituted propylene oxide in these experiments. The reaction of propylene oxide with carborane carbanion has been reported before.
Our results showed that nor-Si-carb can be deprotonated at the carborane carbon with butyl lithium. This carbanion can react to add propylene oxide. Similarly, the pendant carboranes of poly-nor-Si-carb can be deprotonated with butyl lithium to create carbanions which add propylene oxide. Apparently, attachment to a nor-bornene framework or polymer backbone does not prevent carborane carbanions from reacting with propylene oxide. However, HNMR spectra of these products suggest that only one propylene oxide attached at each carbanion (see Figures 5-6 and 5-7).

We hypothesize that water or other impurities in the propylene oxide prevented anionic polymerization. If these experiments are repeated, the propylene oxide starting material should be more rigorously purified.

5.3 Experimental Details

5.3.1 Copolymerization

Polynorbornene(100)/Poly-Nor-C-CDC(45)

A solution of 0.031 g norbornene in 1 ml anhydrous THF was polymerized to a target length of 100 repeat units with 0.271 ml of 30 mg/3 ml Grubbs catalyst. After 1 hr, 0.1 g of nor-C-CDC product (approximately 80 mol% nor-C-CDC and 20 mol% cobalt dicarbollide) was added for a target length of 45 repeat units. After stirring overnight, the polymer solution was precipitated in 20 ml hexane. The hexane was decanted off and the solids dried under vacuum. Approximately 64% of the mass was recovered.

Polynorbornene(90)/Poly-Nor-Si-Anion(30)

A solution of 0.033 g norbornene in 1 ml anhydrous THF was polymerized to a target length of 90 repeat units with 0.322 ml of a 30mg/3ml Grubbs solution. After 4 hours, 0.05 g nor-Si-anion (cesium salt) was added for a target length of 30 repeat units. After stirring overnight, the solution was noticeably viscous. The polymer was diluted with 1 ml THF and precipitated in 20 ml hexane. The fluffy solid was recovered by
Figure 5-6: HNMR of the Reaction of Deprotonated Nor-Si-Carb with Propylene Oxide in D-Acetone
Figure 5-7: HNMR of the Reaction of Deprotonated Poly-Nor-Si-Carb with Propylene Oxdie in D-Acetone
5.3.2 Testing a Potential Crosslinking Agent

Bis(nor-C)-CDC was considered as a potential crosslinking agent for poly-nor-C-CDC. In one experiment, 0.05 g of the nor-C-CDC product was mixed with 0.0266 g bis(nor-C)-CDC in 1 ml anhydrous THF. 0.146 ml of 30 mg/3 ml Grubbs catalyst solutions was added. In another experiment, 0.05 g of the nor-C-CDC product in 0.5 ml THF was first polymerized with 0.146 ml of 30 mg/3 ml Grubbs solution and 0.0266 g bis(nor-C)-CDC added after 3.5 hours. In each case, there was an approximately 1:2 ratio between bis(nor-C)-CDC and nor-C-CDC and a 1:50 ratio between catalyst and nor-C-CDC. Each polymerization solution was stirred overnight and then precipitated in 17 ml hexane. The solids were let settle, and the hexane decanted. Figures 5-8 and 5-9 show the HNMR spectra for these reactions.

5.3.3 Sodium and Cesium Analysis

Cesium analysis was done by Barry Grant from the Department of Earth, Atmospheric, and Planetary Science. A quadrapole ICP-MS with microconcentric nebulizer, the VG Elemental Fison PQ2 Plus, was used. Samples were diluted $1/4 \times 10^5$ because the ICP-MS was set up to do ppb analysis. A 1% nitric acid solution was used as the the sample matrix. Although MilliQ water was used for these experiments, some cesium was detected in the blank 1% nitric acid in water sample. Thus, sample concentrations were calculated by correcting for the blank cesium content and then calibrating with a 1.02 ppb cesium standard. The standard was run every 2 or 3 samples so that machine sensitivity drift could be measured and corrected for.

Sodium analysis was done with an ICP-AES. This machine could not be used for cesium analysis because the cesium emission is very weak. Samples were diluted 1/2 and concentrations were calculated based on standard solutions.
Figure 5-8: HNMR of a Polymerization of Mixed Nor-C-CDC and Bis(Nor-C)-CDC in D-Acetone
Figure 5-9: HNMR of a Polymerization of Nor-C-CDC with Bis(Nor-C)-CDC Added Later in D-Acetone
5.3.4 Converting to Lithium Salts

Cobalt Dicarbollide

A solution of 0.1 g trimethylammonium chloride was dissolved in 1 ml methanol and added to a solution of 0.238 g cobalt dicarbollide (cesium salt) in 1 ml methanol. Some solids began to precipitate. Water was added until the solution was colorless, with orange precipitates. The solids were filtered off and rinsed with 10 ml water.

The cobalt dicarbollide (trimethylammonium salt) was dissolved in 6 ml anhydrous THF and treated with a solution of 0.051 ml 10M butyl lithium in 1 ml THF. The butyl lithium solution was dripped into the stirred cobalt dicarbollide solution until a persistent color change was observed. With each drop, the solution became black and then orange again. The black color signals deprotonation of cobalt dicarbollide. Butyl lithium is more reactive towards the trimethylammonium cation than cobalt dicarbollide, so all the trimethylammonium reacts first, leaving the cobalt dicarbollide in its lithium salt form.

After 1 day, the solution was dried and dissolved in 2 ml water. The product was extracted with 3x3 ml diethyl ether. The ether phases were collected and dried under vacuum.

Carborane Anion

The carborane anion was purchase in its trimethylammonium salt form. A solution of 0.2 g carborane anion (trimethylammonium salt) in 5 ml anhydrous THF was treated with 0.128 ml 10M BuLi in 1 ml THF (1.3 equivalents). The solution started to show some color change to yellow at the end of the addition.

The lithium salt is insoluble in ether, so it could not be purified by water/ether extraction. Instead, the solution was dried and redissolved in acetone. Insolubles were filtered off, and the filtrate dried under vacuum.

178
5.3.5 Reaction of Propylene Oxide with Norbornene Carborane Carbanions

Reaction with Poly-Nor-Si-Carb

A solution of 0.1 g of poly-nor-Si-carb(100) in 5 ml anhydrous THF was deprotonated with a solution of 0.034 ml 10M butyl lithium in 2 ml THF. Upon addition of the BuLi, the polymer precipitated in large pieces from solution. It is likely that the poly-carbanion is insoluble in THF. To the stirred solution, 0.98 g of propylene oxide in 3 ml THF were added. After 90 minutes, the polymer had redissolved but the solution was cloudy. A solution of 0.34 ml 1N HCl in 3 ml THF was added to the polymer solution. The polymer solution cloudiness mostly disappeared. The solution was dried to about 2 ml and precipitated in 100 ml methanol. Polymer precipitated as a rubbery tar. This material was dried overnight in a vacuum oven.

Reaction with Nor-Si-Carb Monomer

Propylene oxide was stirred with NaH and filtered. 0.1 g nor-Si-carb was dissolved in 5 ml anhydrous THF and deprotonated with a solution of 0.034 ml 10M BuLi in 2 ml THF. After 15 min, 1.0 g of the treated propylene oxide was added. After 30 minutes, the solution was yellow. After stirring overnight, a solution of 0.34 ml 1 N HCl in 2 ml THF was added to the monomer solution. Upon addition of the acid, the monomer solution became cloudy and some white precipitate was formed. The solution was dried in a vacuum oven overnight, then dissolved in acetone and filtered. The filtrate contained the product.


[71] W. H. Knoth. B_{10}H_{12}CNH_{2}, B_{9}H_{9}CH^{-}, B_{11}H_{11}CH^{-}, and Metallomonocarbonaranes. Inorganic Chemistry, 10(3):598–605, 1971.


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