

THE SYNTHESIS, CHARACTERIZATION, AND BINDING STUDIES OF
POLYCALIXCROWNS

THESIS

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DEDICATION

To everyone who helped me along the way.

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ABSTRACT

Two di-alkylated calix[4]arene-crown-6 and crown-5 monomers in the 1,3-alternate conformation have been synthesized and copolymerized with five silicon containing compounds via hydrosilation polymerization reactions. The ten polymers were characterized using Nuclear Magnetic Resonance (NMR) Spectroscopy, Infrared (IR) Spectroscopy, Thermal Gravimetric Analysis (TGA), and viscosity techniques. The number of repeating units and molecular weights of the polymers ranged from 5 to 10 repeating units and 7000 to 13500 g/mol. The inherent viscosities of the polymers ranged from 0.17 to 0.34 dL/g. The thermal stabilities of the polymers varied between 398 °C and 427 °C at 10% weight loss in air.

The cation binding properties of the two calixcrown monomers and a representative sampling of the polymers were determined using liquid/liquid extraction and Na, K, Rb, and Cs cations. The calixcrown monomers and the corresponding polycalixcrowns bound the cations similarly. The calixcrown-6 compounds exhibited a strong preference for cesium cations and a less significant preference for rubidium, potassium, and sodium cations. The calixcrown-5 compounds exhibited a strong preference for potassium cations followed by a less significant preference for rubidium, cesium, and sodium cations.

1.0 INTRODUCTION

1.1 Calixarenes

Calixarenes are metacyclophanes that have been studied for their ability to participate in host–guest complexation chemistry and act as enzyme mimics, sensors, and catalysts.¹

Calixarenes were first synthesized with limited success in 1941 by Zinke and Ziegler.² Forty years later, Dr. David Gutsche significantly improved the synthesis of these compounds and coined the name *calixarenes*.³ This name was chosen because the molecules resemble a type of Greek vase called a *calix crater* and because they contain aromatic rings.⁴

A calix[*n*]arene is a cyclic oligomer formed from the base-induced reaction of an *n* number of *p-tert*-butylphenol and formaldehyde molecules.³ The phenol residues are connected by methylene groups at the positions *ortho* to the hydroxyl groups (see Figure 1.1).

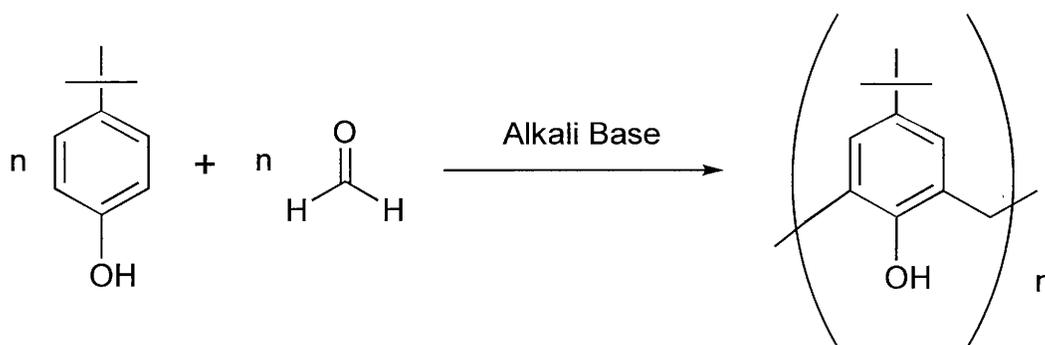


Figure 1.1. General Synthesis of Calix[*n*]arene.

Calix[n]arenes are generally depicted with the aryl carbons (usually with an oxygen function) between the methylene groups pointing downward and the aryl *para* carbons pointing upward.⁵ The face bearing the hydroxyl groups is labeled the lower rim and the face bearing the *para* substituents is labeled the upper rim (see Figure 1.2).⁵

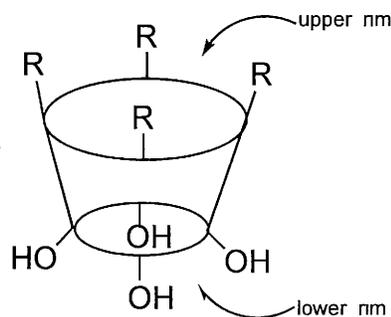


Figure 1.2. Representation of the Calix[4]arene and Designation of the Faces.

Depending on the specific reaction conditions, calix[n]arenes of various sizes can be synthesized where [n] represents the number of phenolic residues in the compound (see Figure 1.3).³ Calix[n]arenes with four, six, and eight phenolic residues can be synthesized in high yields by using specific amounts of certain bases. For example, from a three step process using *p-tert*-butylphenol, aqueous formaldehyde, and sodium hydroxide (0.045 molar equivalents of sodium hydroxide relative to *p-tert*-butylphenol), *p-tert*-butylcalix[4]arene can be synthesized.⁴ From a one step process using *p-tert*-butylphenol, paraformaldehyde, and rubidium hydroxide (0.34 molar equivalents) in refluxing xylene, *p-tert*-butylcalix[6]arene can be synthesized. *p-tert*-Butylcalix[8]arene is synthesized in the same manner as calix[6]arene except only a trace amount of rubidium hydroxide is used.⁵ Calix[n]arenes with

an odd number of phenolic residues or with residues in excess of eight, are difficult to synthesize and isolate.⁴

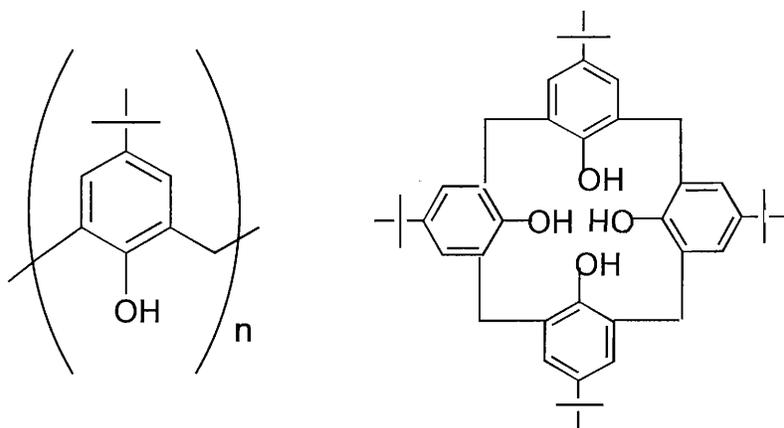


Figure 1.3. Calix[n]arene and Calix[4]arene.

1.2 Calix[4]arenes

1.2.1 Orientation of Calix[4]arenes

Calix[4]arenes are a widely researched group of calix[n]arenes due largely to their synthetic versatility and their ability to act as hosts to a variety of different guests. According to Chemical Abstracts calix[4]arenes are named based on the numbering scheme shown in Figure 1.4. For example, the calix[4]arene with *p-tert*-butyl groups at positions 5, 11, 17, and 23 and hydroxyl groups at positions 25, 26, 27, and 28 is called (5, 11, 17, 23-tetra-*tert*-butyl)-25, 26, 27, 28-tetrahydroxycalix[4]arene. A more general name for this compound is *p-tert*-butylcalix[4]arene.³

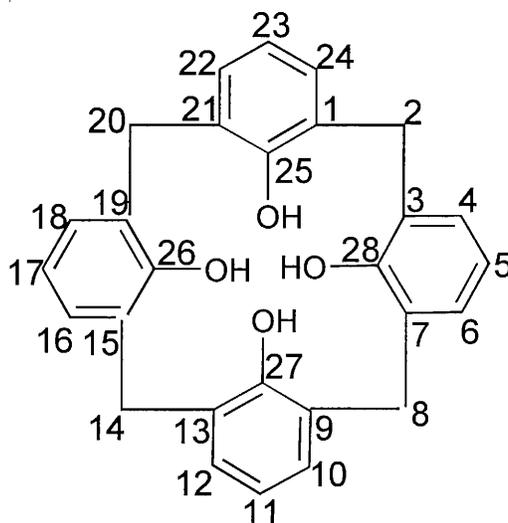


Figure 1.4. Numbering Pattern for Calix[4]arene.

Calix[4]arenes have four major conformations with varying numbers of the *para* positions of the aryl groups projecting either upward ('u') or downward ('d') relative to a plane defined by the bridging methylene groups: cone, partial cone, 1,2-alternate, and 1,3-alternate.⁶ The cone conformation (all syn orientation) exists when all R groups are oriented in the same plane and can be described as (u, u, u, u). Partial cone occurs when one R group is in a different orientation than the other three R groups (u, u, u, d). When two adjacent R groups are in an orientation different from the other two R groups, 1,2-alternate exists (u, u, d, d). 1,3-alternate (all anti orientation) exists when two opposing R groups are oriented differently from the other two R groups (u, d, u, d) (see Fig 1.5). These four conformations have been verified by X-ray crystallography.^{7,8}

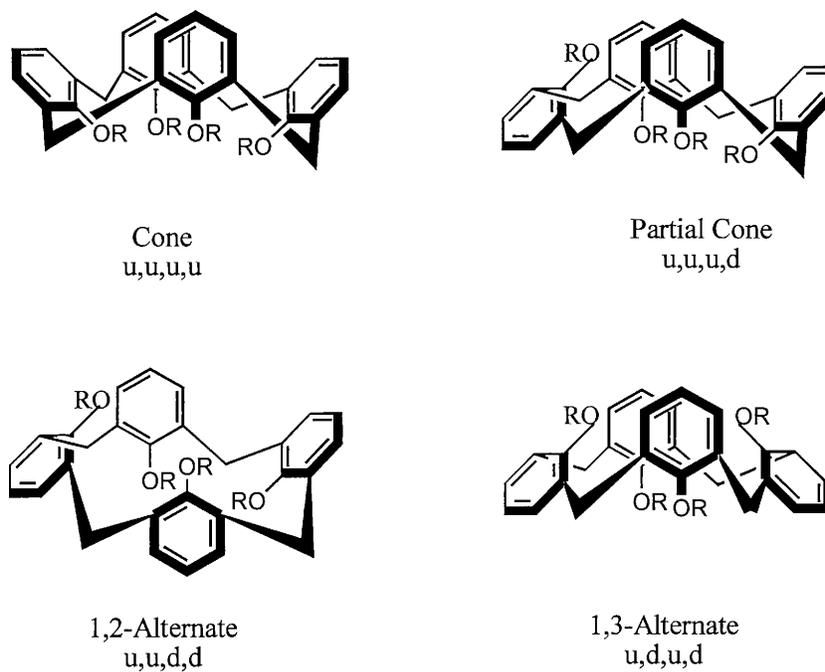


Figure 1.5. Conformations of Calix[4]arenes.

Syn orientation exists when the two aryl groups attached to a methylene carbon are both pointing upward or downward and anti orientation exists when one of the aryl groups is pointing upward and the other is pointing downward (see Figure 1.6).⁹

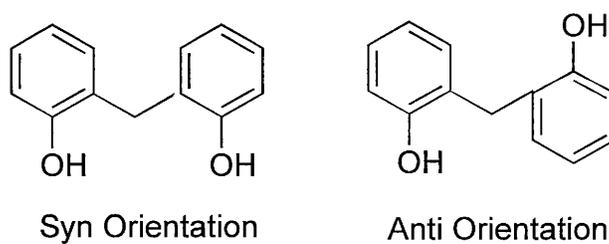


Figure 1.6. Syn and Anti Orientation.

There are general NMR patterns which distinguish between the four possible conformers (see Figure 1.7).⁴ In the ¹H-NMR spectrum, the cone conformation exhibits a pair of doublets (AB system) between 3 and 4.5 ppm for the pseudoaxial and pseudoequatorial methylene hydrogens linking the aromatic rings. In the ¹³C-NMR spectrum, the methylene carbons exhibit one signal at approximately 31 ppm indicating syn orientation of the adjacent aromatic rings. The 1,3–alternate conformation exhibits a singlet at 3.8 ppm for the methylene hydrogens and one signal at approximately 38 ppm for the methylene carbons indicating anti orientation of the adjacent aromatic rings. The methylene hydrogens in the partial cone and 1,2–alternate conformations exhibit a combination of a singlet and an AB quartet in the ¹H-NMR spectrum. The methylene carbons exhibit two signals of equal intensity at 31 and 38 ppm in the ¹³C-NMR spectrum indicating both syn and anti orientation of the adjacent aromatic rings.^{10,11}

At room temperature, unfunctionalized calix[4]arenes are conformationally mobile and can exist as conformational isomers in solution.⁴ Rotation can occur at the methylene groups connecting the phenolic residues. A phenolic residue will rotate so the hydroxyl group is brought up through the annulus of the calixarene (16-membered macrocyclic ring). In the solid state, *p-tert*-butylcalix[4]arene is primarily in a cone conformation due to intramolecular hydrogen bonding of the phenolic hydrogens.^{7,8} As a result of the cone conformation, this compound adopts a C_{4v} symmetry and has a π-basic cavity in the upper rim.⁸ Rigid conformations can be obtained by substituting bulky alkyl groups (larger than ethyl) for the phenolic hydroxyl hydrogens. These large groups hinder the free rotation of the aromatic rings around the bridged methylene groups and “lock” the calix[4]arene into a

specific conformation. The experimental factors that control which conformations are synthesized include the particular base and solvent used, the reaction stoichiometry, as well as the reaction temperature and time.

When the calix[4]arenes are partially substituted (i.e. mono-, di-, tri-substitution) or when they are substituted with different R groups, the $^1\text{H-NMR}$ spectra patterns for the methylene hydrogens are not as defined and depend on the specific substitution pattern. In the $^{13}\text{C-NMR}$ spectrum the methylene carbons exhibit patterns as stated above.¹⁰

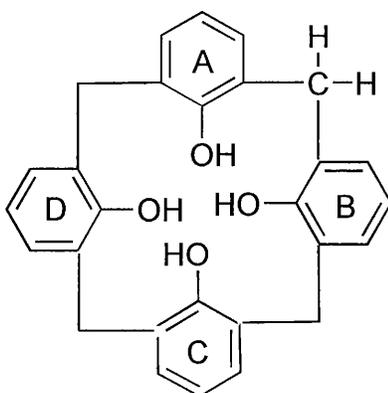


Figure 1.7. Bridging Methylene Carbon and Hydrogens of Calix[4]arene.

1.3 Functionalization of Calix[4]arenes

The conformational shape of calix[4]arenes and the functional groups attached to the molecules dictate the role of the calix[4]arene (i. e. molecular complexing agents, enzyme mimics, catalytic agents). The parent compound, *p-tert*-butylcalix[4]arene, contains two unique binding sites. On the lower rim the four hydroxyl groups exist in very close proximity and can be used for cation binding and transport.¹² The upper rim contains a hydrophobic cavity that can potentially form complexes with small, neutral substrates such as

toluene, benzene, and chloroform.¹³ Calix[4]arenes can be functionalized at both the upper and lower rims to optimize the binding capabilities of the compound. Selective functionalization of calix[4]arene molecules is possible and allows the molecules to be designed for a specific purpose.⁵

1.3.1 Upper Rim

After removal of the four *p-tert*-butyl groups from the upper rim of the calix[4]arene molecule via a reverse Friedel-Crafts alkylation, the upper rim can undergo additional functionalization (see Fig. 1.8).¹⁴

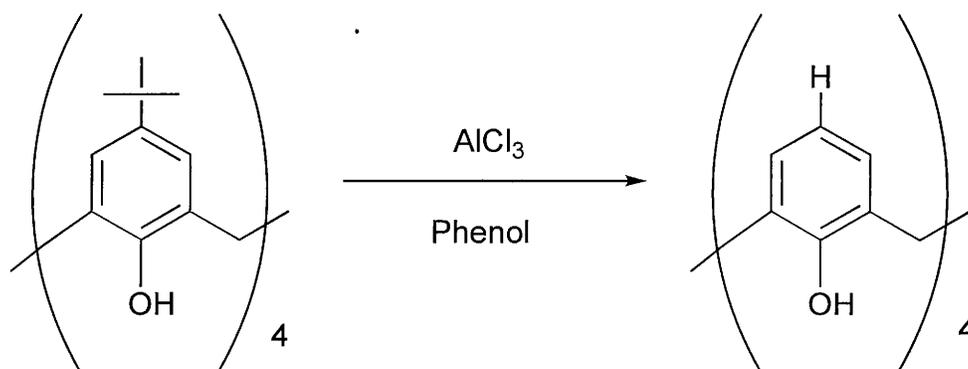


Figure 1.8. Dealkylation of *p-Tert*-Butylcalix[4]arene.

Functionalization processes include aromatic electrophilic substitution and Claisen rearrangements (pericyclic reactions involving sigmatropic rearrangements).^{15,16} Electrophilic substitutions can replace the *para*-hydrogen with a variety of substituents including halogens, NO_2 , SO_3H , SO_2Cl , CHO , COR , COAr , CH_2Cl , and ArN_2 . Mono-, di-, tri-, and tetra-substitution can be obtained.⁵

1.3.2 Lower Rim

The lower rim of the calix[4]arene can be modified using a number of techniques including esterification and alkylation. Both methods can result in mono-, di-, tri-, and tetra-substitution depending on the reaction conditions. Selective distally-alkylated (A, C-substitution) calix[4]arenes can be obtained by using 1.1 molar equivalents of potassium carbonate and 2 molar equivalents of an alkylating agent.^{9,13} This pattern of alkylation occurs due to hydrogen bond stabilization of the phenolate oxygens. Monodeprotection of the phenolic oxygen occurs easily due to the stabilization of the resulting anion by the two neighboring phenolic hydrogens. After monoalkylation, the distally-deprotonated oxygen is stabilized by the two neighboring phenolic hydrogens. If one of the other two phenolic oxygens is deprotonated, the resulting anion would be stabilized by only one hydrogen.¹⁷

1.4 Calix[4]arene crowns

The lower rim can also be bridged to create molecules that have a rigid, defined structure and contain a site for binding charged species. One of the first examples of a lower rim distally-bridged (A, C-ring bridged) calixarene is a calix[4]arene crown (see Figure 1.9).⁵

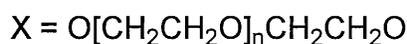
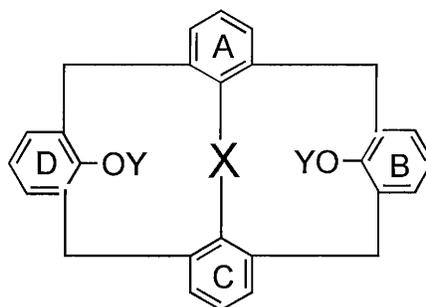


Figure 1.9. Calix[4]arene crown.

When the Y groups are small (methyl, ethyl), the calix[4]arene crown compounds retain conformational mobility and can exist in cone, partial cone, and 1,3-alternate conformations. As the Y group becomes larger and bulkier, the calix[4]arene crown conformation becomes fixed with the 1,3-alternate conformation predominating.⁵ Other crown ether-type bridges include a variety of spanners of the general structure Ar–Ar or X–Ar–Y–Ar–X (X = SO₂, CO, or CH₂; Y = CO, or SO₂) as well as calixsalophencrowns, calix–binaphthylcrown ethers, azacrowns, and bipyridyls.⁵

It is well known that the selectivity and efficiency of metal ion binding by calixarene ionophores depends on the conformation of the calixarene as well as the nature of the attached binding groups.^{18,19} Crown ethers are cyclic polyethers that are easily synthesized and structurally modified, and are capable of binding a variety of cations of different sizes and charges.²⁰ The combination of calix[4]arenes in the 1,3-alternate conformation and crown ethers results in the synthesis of molecules capable of highly efficient and selective metal cation binding.²¹

Calix[4]arene-crown molecules are a class of calix[4]arenes that exhibit ionophoric properties and demonstrate high binding affinity and selectivity toward different alkali metal cations (i.e. K^+ , Na^+ , Li^+ , Rb^+ , Cs^+)^{7,22} The calix[4]arene-crown molecules consist of calix[4]arenes in the 1,3-alternate conformation with crown ether loops of various sizes bridging two phenolic oxygens (see Figure 1.10).²¹

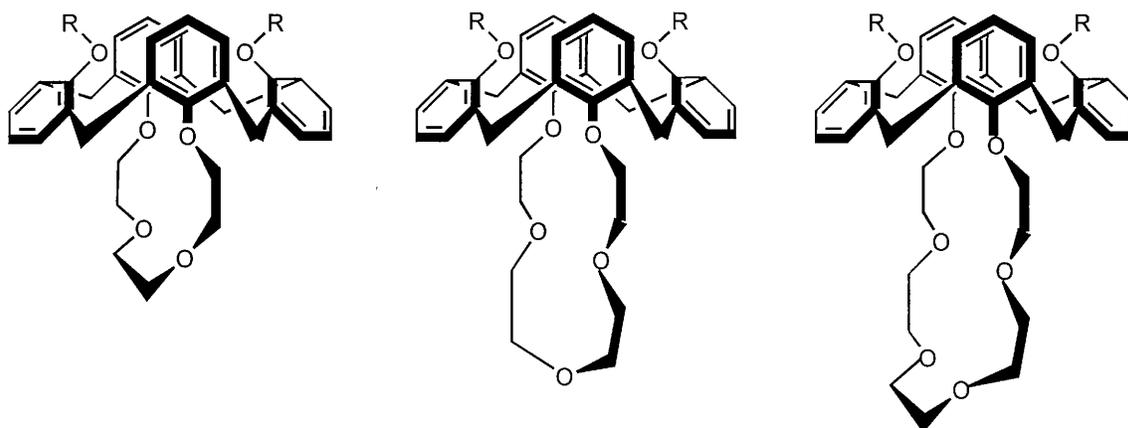


Figure 1.10. Calix[4]arene-crown-4, crown-5, and crown-6.

The crown ether loops comprise the binding site for the metal cations.⁸ The selectivity of the binding can be controlled by the size of the crown ether. Calix[4]arene-crown-4, crown-5, and crown-6 in 1,3-alternate conformation have demonstrated a high affinity and selectivity for Na, K, and Cs cations, respectively.¹⁸ It has been shown that the analogous monomers in the cone conformation do not bind cations nearly as well as the 1,3-alternate monomers because the 1,3-alternate conformation maximizes the cation- π interactions governing the cation binding.^{18,23}

As metal ion binders calix[4]arene-crown molecules are an improvement upon calix[4]arene molecules with non-macrocyclic ligands as binding sites as well as crown ethers which are structurally not preorganized.^{24,25} This improvement is due to the increased pre-organization and rigidity of the crown ether structure attached to the calixarene skeleton that does not exist with the other systems.⁵ The well defined cavity allows a metal cation bound in the crown ether loop to interact with the π -electron clouds of the aromatic rings.¹⁹

The study of calix[4]arene-crown molecules is of interest for many reasons. One reason focuses on the problem faced by the nuclear industry with respect to the disposal of medium level radioactive waste. This problem can potentially be resolved by the use of calix[4]arene-crown molecules. One method to selectively remove radioactive metal ions (i.e. $^{137}\text{Cs}^+$) from an aqueous solution would be to collect them in a molecular container. This results in a complex that can readily be removed from the solution safely and easily.^{26,27} To be able to selectively complex $^{137}\text{Cs}^+$, the molecular container must have a very high binding affinity for $^{137}\text{Cs}^+$ and must have a very high selectivity for cesium ions over other cations in the solution. Calix[4]arene-crown molecules are a family of container molecules that can be synthetically designed to meet these requirements.

1.5 Hydrosilation Polymerization Reactions of Calix[4]arene-crowns

Calixcrown molecules can be incorporated into electrodes or membranes where their binding capabilities can be utilized.²⁷ One way to do this is to blend the calixcrown monomers into polymer matrices and to then incorporate these blends into electrodes or membranes.²⁸ Problems with this technique include the leaching out of the calixcrown

moieties from the blends and the random orientation of the moieties within the polymer matrix. These problems can be solved by synthesizing copolymers that contain the calixcrown monomers as part of the polymer backbone. The copolymers can then be processed into membranes or electrodes.

Calixarenes have been incorporated into polymers in a variety of ways. Calixarenes can be appended to the polymer backbone with the site of polymerization on the lower or upper rim of the calixarene molecules.^{27,29} Calixarenes can also be incorporated directly into the polymer backbone by condensation polymerization reactions³⁰ and radical initiated reactions.²⁷

Hydrosilation is an addition reaction of Si-H compounds to π -unsaturated, vinyl or allyl groups.³¹ Hydrosilation reactions have been successfully used for room temperature vulcanization reactions and for Starburst dendrimers.³¹ Until recently, hydrosilation polymerization reactions have not been used successfully for the synthesis of high molecular weight polymers. Prior attempts resulted in low molecular weight and oligomeric products.³² These unsuccessful attempts used hexachloroplatinic acid (H_2PtCl_6), (CPA), in isopropyl alcohol as the reaction catalyst. CPA is the classic, most commonly used catalyst for hydrosilation polymerization reactions, yet not enough attention was given to the fact that after reduction CPA generates hydrochloric acid. Hydrochloric acid can attack growing polymer chains and result in desilylation at the silicon-carbon bonds causing low molecular weight polymers.³³

The platinum-1,3-divinyltetramethyldisiloxane complex [Pt-DVTMDS] is one complex that catalyzes hydrosilation polymerization reactions without producing

hydrochloric acid or any other ionic byproduct.^{31,34} The [Pt-DVTMDS] complex allows hydrosilation polymerization reactions to proceed without side reactions and allows these polymerizations to produce high molecular weight polymers (see Figure 1.11).

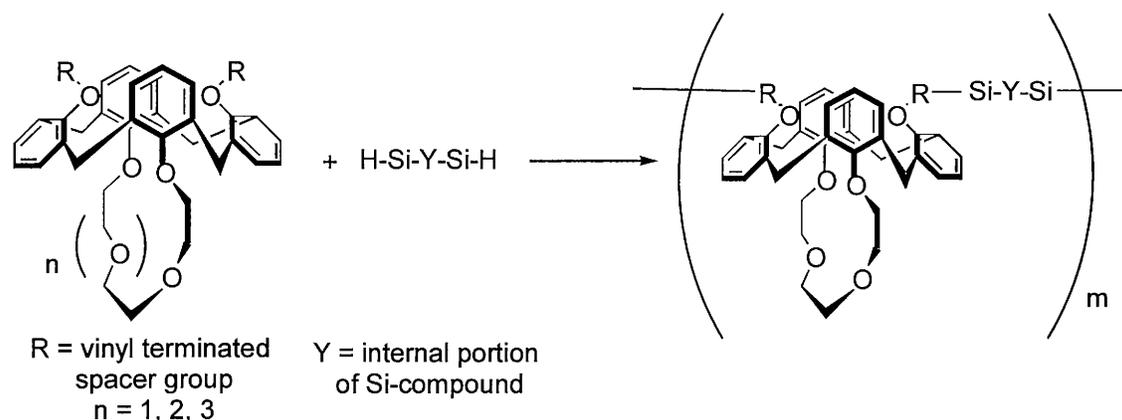


Figure 1.11. General Hydrosilation Polymerization Reaction with Calix[4]arene-crown.

1.6 Binding Studies

Calix[4]arenes have been studied extensively because of their ability to complex a variety of cationic species.^{7,22} The complexation studies are generally NMR titration experiments, X-ray crystallography of solid-state complexes, and liquid-liquid extraction studies.^{18,23} Calix[4]arene-crown-4, crown-5, and crown-6 compounds in the 1,3-alternate conformation have been shown by these methods to bind Na, K, and Cs cations, respectively.¹⁸

Liquid/liquid extraction experiments of aqueous picrate metal salts (Pic^-Na^+ , Pic^-K^+ , Pic^-Rb^+ , Pic^-Cs^+) with hosts (i.e. calixcrowns) in organic solvents have been developed by Pedersen to establish qualitatively and quantitatively the complexation and phase transfer

abilities of the hosts.³⁵ These studies provide information about the percentages of cation extracted per unit mass of host as well as provide information about the association constant, extraction constant, complex stoichiometry, thermodynamic parameters, and rates of complexation of the host compounds.³⁶

The picrate extraction experiments are a measure of the host's ability to complex cations from an aqueous phase.³⁵ These experiments are designed to be an initial screen for identifying the compounds that exhibit the strongest binding capabilities. These superior binding compounds can then be studied in more detail using a larger variety of metal cations as well as more complex methods.

1.7 Thesis Proposal

This research will address the synthesis and characterization of polycalixcrown compounds that are capable of selectively binding alkali metal cations.

Calix[4]arene-crown-4, crown-5, and crown-6 compounds in the 1,3-alternate conformation have been studied for their ability to selectively bind Na, K, Rb, and Cs cations. These compounds may potentially be used in the removal of $^{137}\text{Cs}^+$ from radioactive waste, and as electrodes and sensors.

Di-alkylated calix[4]arene-crown-6 and crown-5 monomers in the 1,3-alternate conformation were synthesized. The vinylic alkylating groups contained a double bond suitable for subsequent hydrosilylation polymerization reactions. The ionophoric crown ether groups comprised the sites for cation binding. Five different silane and siloxane monomers were polymerized with the two calix[4]arene-crown monomers resulting in a total of ten polymers.

The ten polymers were analyzed using $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, IR, viscosity, and TGA techniques. The cation binding properties of the two calixarene monomers and a representative group of the polymers were determined using liquid/liquid extractions and UV-Vis spectroscopy. The alkali metal cations used were Na^+ , K^+ , Rb^+ , and Cs^+ in the form of their picrate salts. These studies provided qualitative information about the complexation abilities of the calix[4]arene-crown monomers and their analogous polymers. From these studies it was determined whether cooperative binding by the supramolecular crown moieties in the copolymers existed as well as if the polymer backbone played a significant role in the metal binding.

2.0 EXPERIMENTAL

2.1 Materials

Toluene was dried over sodium spheres and freshly distilled prior to use in polymer syntheses. For the picrate extraction experiments, chloroform was distilled from calcium hydride. All other solvents were purchased from Aldrich and used as received. The silicon-containing compounds were purchased from Gelest, Inc. and used without further purification. All other reagents were purchased from Aldrich and were used without further purification. All reactions were carried out in a dry argon atmosphere. Analytical Thin Layer Chromatography (TLC) was performed on precoated silica gel plates (Silica Gel 1B2-F) and precoated aluminum oxide plates (Type WB-8: Basic). Column chromatography was performed using aluminum oxide (activated, basic, Brochmann I, 150 mesh). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ data were obtained on a 400 MHz Varian NMR using CDCl_3 as the solvent. Chemical shifts (δ) were expressed in ppm relative to the internal standard, tetramethylsilane (TMS), and the residual chloroform. IR data were obtained using a Perkin Elmer Spectrum One spectrophotometer and samples were prepared as thin films. All melting points were carried out in unsealed capillary tubes using a Mel-Temp II and are uncorrected. Inherent viscosities were obtained from chloroform solutions using an Ostwald viscometer at 23.0 °C. Ultraviolet-Visible (UV-Vis) readings were taken on a Beckman DU 7000 UV-Vis spectrophotometer. TGA data were obtained on a Rheometric

Scientific TGA. Elemental analyses were determined by Desert Analytics (Tucson, AZ).

2.2 Synthesis

See Appendix A for NMR spectra, Appendix B for IR spectra, and Appendix C for thermograms.

2.2.1 Synthesis of 5, 11, 17, 23–Tetra-*t*-Butylcalix[4]arene (1)

The starting materials, 4-*tert*-butylphenol (150 g, 0.99 mol) and 37% formaldehyde (93.35 mL, 3.367 mol), were added to a 3 L, three necked, round bottom flask equipped with a mechanical stirrer. The flask was placed in a 130° C oil bath and allowed to heat for 15 minutes in order to dissolve the phenol. Sodium hydroxide (1.795 g, 0.04489 mol) dissolved in 5 mL water was added to the stirring solution. The beaker used to dissolve the sodium hydroxide was rinsed with an additional 5 mL of water. The mixture was stirred at 130° C for 1-2 hours. When the mixture became a clear, orange solution that foamed, the “precursor” was complete and was removed from the oil bath. Diphenyl ether (1 L) was added to the precursor and the mixture was heated in a heating mantle with stirring until the temperature reached 252° C. During this heating a strong flow of argon was used to facilitate the removal of water from the mixture. At 252° C the flask was equipped with a reflux condenser and the solution was allowed to reflux for 2 hours. The solution was cooled and ethyl acetate (2 L) was added with stirring. The product precipitated from solution. After 2 hours of stirring the product was collected by vacuum filtration and washed two times with ethyl acetate

(2 x 200 mL), one time with glacial acetic acid (150 mL), and one more time with ethyl acetate (150 mL). The product was dried in a 90° C oven to give 107. g (66.%) of compound **1** as a white powder. mp 341-344 ° C (lit. 344-346 ° C).³

2.2.2 Synthesis of **25, 26, 27, 28-tetrahydrocalix[4]arene (2)**

In a flame-dried, 2 L round bottom flask equipped with a mechanical stirrer, compound **1** (40.0 g, 0.0617 mol) was dissolved in toluene (1 L). Aluminum chloride (65.85 g, 0.4938 mol) and phenol (34.86 g, 0.3704 mol) were added. The solution was stirred under argon at room temperature for 48 hours. Hydrochloric acid (1 M, 500 mL) was added to the round bottom flask to quench the reaction. The mixture was transferred to a 2 L separatory funnel and the layers were separated. The organic layer was washed three times with water (3 x 200 mL), one time with brine (200 mL), dried over magnesium sulfate, and filtered. The solvent was concentrated under reduced pressure to 30 mL. This solution was slowly poured into stirring, cold methanol (1 L). The product precipitated from solution and was collected by vacuum filtration to give 22.66 g (86.6%) of compound **2**. mp 313-315 ° C (lit. 315-318 ° C)¹⁴; ¹H-NMR (CDCl₃) δ 3.50-3.64 (br s, 4H), 4.20-4.38 (br s, 4H), 6.77 (t, 4H), 7.09 (d, 8H), 10.19 (s, 4H); ¹³C-NMR (CDCl₃) δ 31.68, 122.22, 128.22, 128.95, 148.74.

2.2.3 Synthesis of **9-Decene-1-ol Tosylate (3)**

9-Decene-1-ol (10.00 g, 0.06399 mol) was mixed with anhydrous pyridine (150 mL) in a 250 mL Erlenmeyer flask. *p*-Toluenesulfonyl chloride (13.42 g, 0.07039 mol) was added and stirred until dissolved. The flask was covered and placed

in a freezer for 24 hours. The pyridine hydrochloride crystals were removed by vacuum filtration and the mother liquor was slowly added to 750 g of stirring ice and water. The tosylate **3** precipitated out of solution. After the ice was completely melted, diethyl ether (200 mL) was added. The layers were separated and the aqueous layer was extracted two times with ether (2 x 100 mL). The organic layer was washed three times with cold hydrochloric acid (6 M, 3 x 150 mL), dried over magnesium sulfate, and filtered. The solvent was removed under reduced pressure to give 17.03 g (85.71%) of product **3** as a clear, colorless liquid that solidified to white crystals within 24 hours.

mp 31-32 ° C; ¹H-NMR (CDCl₃) δ 1.17-1.30 (m, 10H), 1.55-1.58 (m, 2H), 1.93-1.98 (m, 2H), 2.38 (s, 3H), 3.96 (t, 2H), 4.90 (q, 2H), 5.67-5.74 (m, 1H), 7.29 (d, 2H), 7.73 (d, 2H); ¹³C-NMR (CDCl₃) δ 21.48, 25.16, 28.65, 28.69, 28.71, 28.80, 29.00, 29.07, 33.61, 70.56, 114.07, 127.72, 129.68, 132.84, 138.91, 144.52. Anal. calcd. for C₁₇H₂₆O₃S: C, 65.77%; H, 8.44%; O, 15.46%; S, 10.33%. Found: C, 66.06%; H, 8.48%.

2.2.4 Synthesis of 25, 27-Bis(9-decenyloxy)calix[4]arene (**4**)

In a 1 L round bottom flask equipped with a stir bar and reflux condenser, dealkylated calix[4]arene **2** (10.00 g, 0.02358 mol) was suspended in acetonitrile (300 mL). Potassium carbonate (3.580 g, 0.02594 mol), and compound **3** (14.64 g, 0.04716 mol) were added. The reaction mixture was allowed to reflux under argon for 48 hours. The solvent was removed under reduced pressure and the residue was taken up in methylene chloride (400 mL). The organic layer was washed three times with hydrochloric acid (1 M, 3 x 150 mL), one time with brine (100 mL), dried over magnesium sulfate, and filtered. The solvent was concentrated to 100 mL under reduced

pressure, slowly poured into stirring methanol (600 mL), and allowed to stir for 48 hours. The solid was collected by vacuum filtration to give 11.42 g (69.09%) of compound **4**. mp 119-121° C; ¹H-NMR (CDCl₃) δ 1.43-1.56 (m, 18H), 1.76-1.80 (m, 4H), 2.10-2.17 (m, 6H), 3.44 (d, 4H), 4.06 (t, 4H), 4.39 (d, 4H), 5.05 (q, 4H), 5.86-5.93 (m, 2H), 6.73 (t, 2H), 6.74 (t, 2H), 6.95 (d, 4H), 7.12 (d, 4H), 8.31 (s, 2H); ¹³C-NMR (CDCl₃) δ 25.94, 28.92, 29.18, 29.45, 29.48, 29.98, 31.39, 33.78, 76.67, 114.14, 118.86, 125.18, 128.11, 128.36, 128.82, 133.32, 139.05, 151.91, 153.31. Anal. calcd. for C₄₈H₆₀O₄: C, 82.24%; H, 8.63%; O, 9.13%. Found: C, 82.51%; H, 8.96%.

2.2.5 Synthesis of 25, 27-Bis(9-decenyloxy)calix[4]arene-crown-6 (**5**)

In a 2 L round bottom flask equipped with a stir bar and reflux condenser, compound **4** (10.00 g, 0.01430 mol) was suspended in acetonitrile (1 L). Cesium carbonate (18.64 g, 0.05720 mol) and penta(ethylene glycol)di-*p*-toluene sulfonate (8.60 g, 0.0157 mol) were added. The reaction mixture was allowed to reflux under argon for 24 hours. The solvent was removed under reduced pressure and the residue was taken up in methylene chloride (500 mL). The organic layer was washed three times with hydrochloric acid (1 M, 3 x 200 mL), one time with brine (150 mL), dried over magnesium sulfate, and filtered. The solvent was removed under reduced pressure. The crude product **5** (13.6 g) was a viscous, brown oil and was purified by column chromatography (aluminum oxide, methylene chloride/ethylacetate, 95:5) to give 6.72 g (52.2%) of the solid, white product **5**. mp 58-59 ° C; ¹H-NMR (CDCl₃) δ 1.15-1.45 (m, 24H), 2.09 (q, 4H), 3.38-3.78 (m, 32H), 5.00 (q, 4H), 5.82-5.88 (m, 2H), 6.78

(t, 2H), 6.84 (t, 2H), 7.02 (d, 4h), 7.09 (d, 4H); ^{13}C -NMR (CDCl_3) δ 25.74, 28.95, 29.12, 29.25, 29.52, 29.61, 33.79, 37.84, 69.78, 69.81, 70.54, 70.90, 71.00, 71.12, 114.13, 122.03, 129.55, 129.69, 133.65, 133.95, 139.06, 156.41, 156.84. Anal. calcd. for $\text{C}_{58}\text{H}_{78}\text{O}_8$: C, 77.13%; H, 8.70%; O, 14.17%. Found: C, 77.16%; H, 8.91%.

2.2.6 Synthesis of 25, 27-Bis(9-decenyloxy)calix[4]arene-crown-5 (6)

In a 2 L round bottom flask equipped with a stir bar and reflux condenser, compound 4 (10.00 g, 0.01430 mol) was suspended in acetonitrile (1 L), Cesium carbonate (18.64 g, 0.05720 mol) and tetra(ethylene glycol)di-*p*-tosylate (7.91 g, 0.0157 mol) were added. The reaction mixture was allowed to reflux under argon for 24 hours. The solvent was removed under reduced pressure and the residue was taken up in methylene chloride (500 mL). The organic layer was washed three times with hydrochloric acid (1 M, 3 x 200 mL), one time with brine (150 mL), dried over magnesium sulfate, and filtered. The solvent was removed under reduced pressure. The crude product 6 (13.3 g) was a viscous, brown oil and was purified by column chromatography (aluminum oxide, methylene chloride/ethylacetate, 95:5) to give 6.02 g (49.0%) of the solid, white product 6. mp 53-55 ° C; ^1H -NMR (CDCl_3) δ 1.06-1.42 (m, 24H), 2.07 (q, 4H), 3.13 (t, 4H), 3.34-3.35 (m, 8H), 3.54-3.58 (m, 8H), 3.83 (s, 8H), 4.98 (q, 4H), 5.80-5.86 (m, 2h), 6.79 (t, 2H), 6.86 (t, 2H), 7.00 (d, 4H), 7.08 (d, 4H); ^{13}C -NMR (CDCl_3) δ 25.72, 28.98, 29.08, 29.16, 29.54, 29.63, 33.82, 38.15, 68.28, 69.90, 70.27, 70.52, 72.61, 114.14, 122.29, 129.14, 129.27, 133.99, 134.15, 139.09, 156.05, 156.92. Anal. calcd. for $\text{C}_{56}\text{H}_{74}\text{O}_7$: C, 78.29%; H, 8.68%; O, 13.04%. Found: C, 78.03%; H, 8.80%.

2.2.7 Synthesis of Polymer 1 (7)

In a 25 mL round bottom flask with stir bar and reflux condenser, compound **5** (2.00 g, 2.214 mmol) was dissolved in distilled toluene (3.0 mL). 1,4-Bis(dimethylsilyl)benzene (0.4304 g, 2.214 mmol) was added followed by platinum-1, 3-divinyltetramethyldisiloxane complex catalyst solution (Pt-DVTMDS) (0.024 mL, 0.024 g) to yield a solution of 0.1773 g atom Pt/mol alkene. The reaction mixture was allowed to reflux under argon for 48 hours. The solvent was removed under reduced pressure. The residue was taken up in methylene chloride (15 mL) and slowly poured into stirring methanol (150 mL). The product oiled out from the solution. The solvent was decanted off and the residue was taken up in methylene chloride (20 mL) and decolorized with activated charcoal. The solution was filtered and the solvent was removed under reduced pressure to give 1.39 g (57.2%) of compound **7** as a pale yellow, sticky solid. $^1\text{H-NMR}$ (CDCl_3) δ 0.10-0.36 (m, 16H), 1.17-1.36 (m, 32H), 3.39-3.79 (m, 32H), 6.78 (t, 2H), 6.85 (t, 2H), 7.03 (d, 4H), 7.10 (d, 4H), 7.53 (m, 4H); $^{13}\text{C-NMR}$ (CDCl_3) δ 0.90, 0.96, 15.64, 23.91, 25.79, 29.26, 29.40, 29.54, 29.60, 29.65, 29.75, 32.62, 33.72, 37.87, 69.84, 70.58, 70.94, 71.02, 71.15, 76.68, 122.04, 129.56, 129.72, 132.14, 132.75, 133.65, 133.99, 140.12, 156.43, 156.88. Anal. calcd. for $\text{C}_{68}\text{H}_{96}\text{O}_8\text{Si}_2$: C, 74.40%; H, 8.82%; O, 11.66%; Si, 5.12%. Found: C, 71.18%; H, 8.68%; Si, 5.98%.

2.2.8 Synthesis of Polymer 2 (8)

In a 25 mL round bottom flask with stir bar and reflux condenser, compound **6** (2.00 g, 2.328 mmol) was dissolved in distilled toluene (3.0 mL).

1,4-Bis(dimethylsilyl)benzene (0.4526 g, 2.328 mmol) was added followed by Pt-DVTMDS catalyst (0.031 mL, 0.030 g) to yield a solution of 0.1773 g atom Pt/mol alkene. Polymer 2 was obtained as described in section 2.2.7. 1.40 g (57.1%) of compound **8** (off-white, sticky solid) was obtained. $^1\text{H-NMR}$ (CDCl_3) δ 0.08 (s, 10H), 0.26 (s, 6H), 1.08-1.33 (m, 32H), 3.15 (s, 4H), 3.37 (s, 8H), 3.57 (s, 8H), 3.84 (s, 8H), 6.80 (t, 2H), 6.87 (t, 2H), 7.01 (d, 4H), 7.09 (d, 4H), 7.50 (s, 4H); $^{13}\text{C-NMR}$ (CDCl_3) δ 0.85, 15.59, 23.85, 25.67, 28.93, 29.04, 29.35, 29.58, 33.66, 33.74, 38.10, 68.23, 70.45, 70.64, 71.24, 72.36, 74.29, 114.13, 122.28, 123.06, 129.12, 129.26, 132.10, 132.13, 132.72, 133.67, 134.11, 139.01, 140.07, 155.99, 156.87. Anal. calcd. for $\text{C}_{66}\text{H}_{92}\text{O}_7\text{Si}_2$: C, 75.24%; H, 8.80%; O, 10.63%; Si, 5.33%. Found: C, 74.30%; H, 8.63%; Si, 5.30%.

2.2.9 Synthesis of Polymer 3 (9)

In a 25 mL round bottom flask with stir bar and reflux condenser, compound **5** (2.00 g, 2.214 mmol) was dissolved in distilled toluene (3.0 mL). 1, 1, 3, 3, 5, 5, 7, 7-Octamethyltetrasiloxane (0.6257 g, 2.214 mmol) was added followed by Pt-DVTMDS catalyst (0.024 mL, 0.024 g) to yield a solution of 0.1773 g atom Pt/mol alkene. Polymer 3 was obtained as described in section 2.2.7. 1.33 g (50.7%) of compound **9** (yellow, sticky solid) was obtained. $^1\text{H-NMR}$ (CDCl_3) δ 0.06 (s, 28H), 1.14-1.30 (m, 32H), 3.37-3.75 (m, 32H), 6.77 (t, 2H), 6.81 (t, 2H), 6.99 (d, 4H), 7.06 (d, 4H); $^{13}\text{C-NMR}$ (CDCl_3) δ 0.20, 0.99, 1.20, 18.30, 23.23, 25.83, 29.32, 29.52, 29.68, 29.81, 33.55, 37.87, 69.91, 70.38, 70.70, 70.83, 70.99, 71.05, 71.18, 76.68, 122.08, 129.64, 129.80, 133.68, 133.86, 134.01, 156.45, 156.9. Anal. calcd. for $\text{C}_{66}\text{H}_{104}\text{O}_{11}\text{Si}_4$: C, 66.85%; H, 8.84%; O, 14.84%; Si, 9.47%. Found: C, 65.13%; H, 8.88%; Si, 9.76%.

2.2.10 Synthesis of Polymer 4 (10)

In a 25 mL round bottom flask with stir bar and reflux condenser, compound **6** (2.00 g, 2.328 mmol) was dissolved in distilled toluene (3.0 mL). 1, 1, 3, 3, 5, 5, 7, 7-Octamethyltetrasiloxane (0.6580 g, 2.328 mmol) was added followed by Pt-DVTMDS catalyst (0.031 mL, 0.030 g) to yield a solution of 0.1773 g atom Pt/mol alkene.

Polymer 4 was obtained as described in section 2.2.7. 1.38 g (51.9%) of compound **10** (light yellow, sticky solid) was obtained. $^1\text{H-NMR}$ (CDCl_3) δ 0.08 (s, 10H), 0.26 (s, 6H), 1.08-1.33 (m, 32H), 3.15 (s, 4H), 3.37 (s, 8H), 3.57 (s, 8H), 3.84 (s, 8H), 6.80 (t, 2H), 6.87 (t, 2H), 7.01 (d, 4H), 7.09 (d, 4H), 7.50 (s, 4H); $^{13}\text{C-NMR}$ (CDCl_3) δ 0.19, 0.96, 1.17, 18.28, 18.36, 23.25, 25.75, 25.87, 29.07, 29.24, 29.51, 29.68, 29.76, 29.91, 29.95, 30.01, 33.53, 33.72, 38.17, 68.22, 68.31, 69.93, 70.16, 70.32, 70.53, 72.60, 122.30, 129.06, 129.16, 129.30, 133.98, 134.16, 156.05, 156.94. Anal. calcd. for $\text{C}_{64}\text{H}_{100}\text{O}_{10}\text{Si}_4$: C, 67.33%; H, 8.82%; O, 14.01%; Si, 9.84%. Found: C, 65.98%; H, 8.69%; Si, 10.26%.

2.2.11 Synthesis of Polymer 5 (11)

In a 25 mL round bottom flask with stir bar and reflux condenser, compound **5** (2.00 g, 2.214 mmol) was dissolved in distilled toluene (3.0 mL). 1, 1, 3, 3-Tetramethyldisiloxane (0.2974 g, 2.214 mmol) was added followed by Pt-DVTMDS catalyst (0.024 mL, 0.024 g) to yield a solution of 0.1773 g atom Pt/mol alkene.

Polymer 5 was obtained as described in section 2.2.7. 1.24 g (54.0%) of compound **11** (brown, sticky solid) was obtained. $^1\text{H-NMR}$ (CDCl_3) δ 0.06 (d, 16H), 1.30 (s, 32H), 3.38-3.77 (m, 32H), 6.77 (t, 2H), 6.82 (t, 2H), 7.01 (d, 4H), 7.16 (d, 4H); $^{13}\text{C-NMR}$

(CDCl₃) δ 0.37, 0.95, 18.41, 23.30, 25.78, 29.26, 29.48, 29.64, 29.69, 29.76, 33.50, 37.85, 69.82, 70.58, 70.92, 71.00, 71.13, 76.68, 122.02, 129.55, 129.70, 129.78, 133.64, 133.97, 156.41, 156.86. Anal. calcd. for C₆₂H₉₂O₉Si₂: C, 71.77%; H, 8.94%; O, 13.88%; Si, 5.41%. Found: C, 70.33%; H, 8.95%; Si, 5.67%.

2.2.12 Synthesis of Polymer 6 (12)

In a 25 mL round bottom flask with stir bar and reflux condenser, compound **6** (2.00 g, 2.328 mmol) was dissolved in distilled toluene (3.0 mL). 1, 1, 3, 3-Tetramethyldisiloxane (0.3127 g, 2.328 mmol) was added followed by Pt-DVTMDS catalyst (0.031 mL, 0.030 g) to yield a solution of 0.1773 g atom Pt/mol alkene. Polymer **6** was obtained as described in section 2.2.7. 1.63 g (70.5%) of compound **12** (light yellow, sticky solid) was obtained. ¹H-NMR (CDCl₃) δ 0.07-0.09 (d, 16H), 1.09-1.35 (m, 32H), 3.15 (s, 4H), 3.38 (s, 8H), 3.58 (s, 8H), 3.85 (s, 8H), 6.81 (t, 2H), 6.88 (t, 2H), 7.02 (d, 4H), 7.10 (d, 4H); ¹³C-NMR (CDCl₃) δ 0.19, 0.38, 0.95, 1.17, 18.26, 18.42, 23.25, 23.31, 25.74, 29.06, 29.49, 29.67, 29.76, 33.52, 38.15, 68.29, 69.90, 70.27, 70.51, 72.59, 122.28, 129.13, 129.20, 129.27, 133.69, 134.14, 156.04, 156.92. Anal. calcd. for C₆₀H₈₈O₈Si₂: C, 72.54%; H, 8.93%; O, 12.88%; Si, 5.65%. Found: C, 69.56%; H, 8.88%; Si, 7.44%.

2.2.13 Synthesis of Polymer 7 (13)

In a 25 mL round bottom flask with stir bar and reflux condenser, compound **5** (2.00 g, 2.214 mmol) was dissolved in distilled toluene (3.0 mL). 1, 1, 4, 4-Tetramethyldisilylethylene (0.3241 g, 2.214 mmol) was added followed by Pt-DVTMDS

catalyst (0.024 mL, 0.024 g) to yield a solution of 0.1773 g atom Pt/mol alkene.

Polymer 7 was obtained as described in section 2.2.7. 1.32 g (56.8%) of compound **13**

(brown, sticky solid) was obtained. $^1\text{H-NMR}$ (CDCl_3) δ 0.4 (d, 20H), 1.15-1.31

(m, 32H), 3.39-3.77 (m, 32H), 6.78 (t, 2H), 6.82 (t, 2H), 7.01 (d, 4H), 7.07 (d, 4H);

$^{13}\text{C-NMR}$ (CDCl_3) δ 0.95, 7.12, 14.74, 23.95, 25.80, 29.28, 29.48, 29.70, 29.78, 33.81,

37.86, 53.36, 69.85, 70.60, 70.95, 71.02, 71.15, 122.03, 129.58, 129.73, 133.66, 133.99,

156.43, 156.89. Anal. calcd. for $\text{C}_{64}\text{H}_{96}\text{O}_8\text{Si}_2$: C, 73.24%; H, 9.22%; O, 12.19%;

Si, 5.35%. Found: C, 71.11%; H, 9.47%; Si, 5.02%.

2.2.14 Synthesis of Polymer 8 (14)

In a 25 mL round bottom flask with stir bar and reflux condenser, compound **6** (2.00 g, 2.328 mmol) was dissolved in distilled toluene (3.0 mL). 1, 1, 4, 4-

Tetramethyldisilylene (0.3408 g, 2.328 mmol) was added followed by Pt-DVTMDS catalyst (0.031 mL, 0.030 g) to yield a solution of 0.1773 g atom Pt/mol alkene.

Polymer 8 was obtained as described in section 2.2.7. 1.66 g (70.9%) of compound **14**

(brown, sticky solid) was obtained. $^1\text{H-NMR}$ (CDCl_3) δ 0.04 (s, 9H), 0.08 (s, 9H), 0.37

(s, 4H), 1.07-1.31 (m, 30H), 3.14 (s, 4H), 3.37 (s, 8H), 3.57 (s, 8H), 3.84 (s, 8H), 6.80

(t, 2H), 6.87 (t, 2H), 7.01 (d, 4H), 7.09 (d, 4H); $^{13}\text{C-NMR}$ (CDCl_3) δ 0.97, 7.12, 14.76,

23.97, 25.76, 29.07, 29.51, 29.63, 29.70, 29.78, 33.84, 28.16, 68.30, 69.92, 70.26, 70.53,

72.62, 122.29, 129.14, 129.28, 133.99, 134.17, 156.05, 156.95. Anal. calcd. for

$\text{C}_{62}\text{H}_{92}\text{O}_7\text{Si}_2$: C, 74.05%; H, 9.22%; O, 11.14%; Si, 5.59%. Found: C, 70.57%;

H, 9.12%; Si, 7.73%.

2.2.15 Synthesis of Polymer 9 (15)

In a 25 mL round bottom flask with stir bar and reflux condenser, compound **5** (2.00 g, 2.214 mmol) was dissolved in distilled toluene (3.0 mL). 1,2-Bis(tetramethyldisiloxanyl)ethane (0.6520 g, 2.214 mmol) was added followed by Pt-DVTMDS catalyst (0.024 mL, 0.024 g) to yield a solution of 0.1773 g atom Pt/mol alkene. Polymer 9 was obtained as described in section 2.2.7. 1.92 g (72.5%) of compound **16** (beige, sticky solid) was obtained. $^1\text{H-NMR}$ (CDCl_3) δ 0.08 (s, 24H), 0.42 (s, 4H), 0.55 (s, 4H), 1.17-1.34 (m, 32H), 3.40-3.81 (m, 32H), 6.78 (t, 2H), 6.84 (t, 2H), 7.02 (d, 4H), 7.09 (d, 2H); $^{13}\text{C-NMR}$ (CDCl_3) δ 0.37, 0.90, 0.94, 9.62, 18.41, 18.46, 23.31, 25.70, 25.77, 29.18, 29.24, 29.48, 29.57, 29.68, 29.76, 29.88, 33.50, 37.83, 69.82, 70.54, 70.92, 70.98, 71.13, 122.00, 129.33, 129.53, 129.69, 133.61, 133.95, 156.40, 156.85. Anal. calcd. for $\text{C}_{68}\text{H}_{104}\text{O}_{10}\text{Si}_4$: C, 68.18%; H, 9.09%; O, 13.36%; Si, 9.38%. Found: C, 68.45%; H, 8.84%; Si, 9.26%.

2.2.16 Synthesis of Polymer 10 (16)

In a 25 mL round bottom flask with stir bar and reflux condenser, compound **6** (2.00 g, 2.328 mmol) was dissolved in distilled toluene (3.0 mL). 1,2-Bis(tetramethyldisiloxanyl)ethane (0.6860 g, 2.328 mmol) was added followed by Pt-DVTMDS catalyst (0.031 mL, 0.030 g) to yield a solution of 0.1773 g atom Pt/mol alkene. Polymer 10 was obtained as described in section 2.2.7. 1.55 g (57.7%) of compound **16** (dark brown, sticky solid) was obtained. $^1\text{H-NMR}$ (CDCl_3) δ 0.05 (s, 26H), 0.47 (d, 8H), 1.07-1.32 (m, 30H), 3.14 (s, 4H), 3.36 (s, 8H), 3.56 (s, 8H), 3.83 (s, 8H), 6.80 (t, 2H), 6.86 (t, 2H), 7.00 (d, 4H), 7.08 (d, 4H); $^{13}\text{C-NMR}$ (CDCl_3) δ 0.41,

0.99, 9.69, 18.48, 23.37, 25.78, 25.91, 29.10, 29.54, 29.71, 29.80, 29.95, 33.57, 38.20, 68.35, 69.96, 70.33, 70.56, 72.64, 121.85, 122.32, 129.18, 129.33, 134.01, 134.20, 156.09, 156.99. Anal. calcd. for $C_{66}H_{104}O_9Si_4$: C, 68.70%; H, 9.08%; O, 12.48%; Si, 9.74%. Found: C, 66.61%; H, 8.94%; Si, 10.01%.

2.3 Alkali Metal Picrate Extractions

2.3.1 Preparation of Solutions

Freshly distilled chloroform was washed with deionized water to avoid volume changes during the extraction experiments. The chloroform was used to prepare the host solutions and the water was used to prepare the picrate salt solutions.³⁷

Alkali metal picrate solutions (Na^+Pic^- , K^+Pic^- , Rb^+Pic^- , Cs^+Pic^-) were prepared with an approximate concentration of 1.0×10^{-3} M by neutralizing picric acid (1 wt. % solution in H_2O) with the appropriate metal hydroxide (NaOH, KOH, RbOH, CsOH). Host solutions of the calix[4]arene-crown-6 and crown-5 monomers (**5** and **6**) were prepared with concentrations of 5.093×10^{-4} M and 5.028×10^{-4} M (46 mg/100 mL and 43 mg/100 mL), respectively. Host solutions of copolymers **7**, **8**, **11**, **12**, **15**, and **16** were prepared with 51, 50, 45, 45, 50, and 56 mg per 100 mL chloroform, respectively.

2.3.2 Preparation of Extraction Experiments

In a glass vial, 2.00 mL of a host solution was placed via a glass syringe followed by 2.00 mL of a picrate salt solution via a micropipette. The vial was sealed, shaken for 5 minutes, and then allowed to sit overnight. This was repeated for all host and picrate salt solution combinations.

2.3.3 Determination of Percent Cation Extracted

The initial aqueous picrate salt concentrations, the host-picrate complex concentrations, and the percent cation extracted per gram of host were calculated using the following set of equations (1-3).³⁷

$$[Pic^-, M^+]_{aqi} = AD/\epsilon l \quad (1)$$

$$[Pic^-, H, M^+]_{org} = AD/\epsilon l \quad (2)$$

$$\% \text{ Cation extracted per mg host} = ([Pic^-, H, M^+]_{org} / [Pic^-, M^+]_{aqi}) * 100\% / \text{mg H} \quad (3)$$

Pic^- and M^+ are the picric and metal ions of the metal picrate solutions. H is the calixarene host. $[Pic^-, M^+]_{aqi}$ is the initial picrate salt concentration in the aqueous phase. $[Pic^-, H, M^+]_{org}$ is the host-picrate complex concentration in chloroform calculated at equilibrium from direct UV-Vis measurements. A is the measured absorbance (au), D is the factor by which the aliquots from the organic and aqueous layers were diluted, l is the light path length of the UV cell (1.0 cm), and ϵ is the extinction coefficient ($\epsilon_{354nm} = 14500 \text{ cm}^{-1} \text{ M}^{-1}$, $\epsilon_{380nm} = 18000 \text{ cm}^{-1} \text{ M}^{-1}$).³⁷

The exact concentrations of the picrate salt solutions were obtained by UV-Vis spectroscopy using the extinction coefficient for H_2O ($\epsilon_{354 \text{ nm}} = 14500 \text{ cm}^{-1} \text{ M}^{-1}$) and equation 1.^{35,36} The calculations were based on the Beer's law relationship, $a = \epsilon bc$, where a equals the absorbance, ϵ equals the extinction coefficient, b equals the path length of the cell, and c equals the concentration of the measured species. The aqueous picrate solutions were diluted with water (used in the chloroform washing) so the

absorbance readings ranged from 0.10 to 1.0 au. 100 μL of the picrate solutions were diluted with 2.00 mL of water (20:1 dilution).

The concentrations of the host-picrate complexes in the organic phases were analyzed by UV-Vis spectroscopy. The organic phases were diluted with acetonitrile prior to analysis to obtain absorbance readings in the range of 0.10 – 1.00 au (see Table 2.1 for dilution factors). The concentration of the picrate salt in the host phase was calculated using the extinction coefficient for acetonitrile ($\epsilon_{380\text{ nm}} = 18000\text{ cm}^{-1}\text{ M}^{-1}$) and equation 2.³⁷

Table 2.1. Dilution Factors of Complexed Picrate Salt Solutions.

Host Compound	Aqueous Picrate Solutions			
	Na	K	Rb	Cs
5	1:1 ^a	1:1	1:2 ^b	1:8 ^c
6	1:1	1:8	1:8	1:1
7	1:1	1:1	1:1	1:6 ^d
8	1:1	1:8	1:10 ^e	1:1
11	1:1	1:1	1:4 ^f	1:6
12	1:1	1:8	1:6	1:1
15	1:1	1:1	1:1	1:6
16	1:1	1:8	1:6	1:1

^a1:1=1 mL host : 1 mL CH₃CN

^b1:2 =1 mL host : 2 mL CH₃CN

^c1:8 = 0.25 mL host : 2 mL CH₃CN

^d1:6 = 0.25 mL host : 1.5 mL CH₃CN

^e1:10 = 0.25 mL host : 2.5 mL CH₃CN

^f1:4 = 0.51 mL host : 2 mL CH₃CN

3.0 RESULTS AND DISCUSSION

3.1 Synthesis

Tetra-*t*-butylcalix[4]arene was chosen as the starting material for two monomeric derivatives that were tailored to react in hydrosilation polymerization reactions with a series of silicon-containing monomers. The monomers were also structurally modified to function as compounds capable of binding alkali metal cations.

3.1.1 Synthesis of 5, 11, 17, 23-Tetra-*t*-Butylcalix[4]arene (1)

Procedures for the synthesis of compound **1** have been well established by Gutsche and co-workers.⁴ The principle starting material, tetra-*t*-butylcalix[4]arene, was synthesized from the base-induced condensation reaction of *p*-*t*-butylphenol and formaldehyde using 0.045 molar equivalents of sodium hydroxide relative to phenol (see Figure 3.1). The amount of sodium hydroxide used was very precise to ensure that only calix[4]arene **1** was formed and in relatively good yield (66%). It has been proposed that the sodium cation acts as a template for the formation of calix[4]arene.⁴ At room temperature tetra-*t*-butylcalix[4]arene was in the cone conformation in solution as indicated by the pair of doublets at 3.5 and 4.2 ppm for the methylene hydrogens in the ¹H-NMR spectrum.

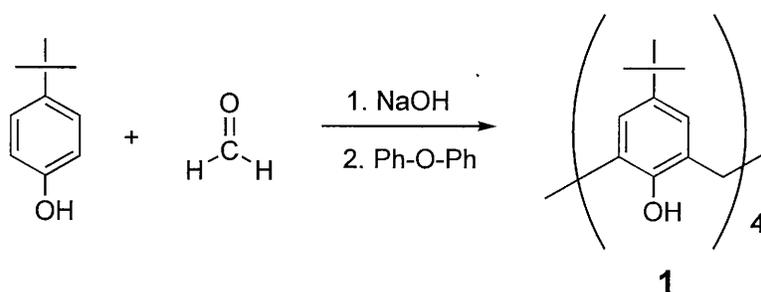


Figure 3.1. Synthesis of 5, 11, 17, 23-Tetra-*t*-Butylcalix[4]arene **1**.

3.1.2 Synthesis of 25, 26, 27, 28-Tetrahydroxycalix[4]arene (**2**)

Calix[4]arene **2** was obtained by a reverse Friedel Crafts alkylation reaction. The de-*tert*-butylation reaction was catalyzed by aluminum chloride and resulted in an 86% yield (see Figure 3.2).¹⁴

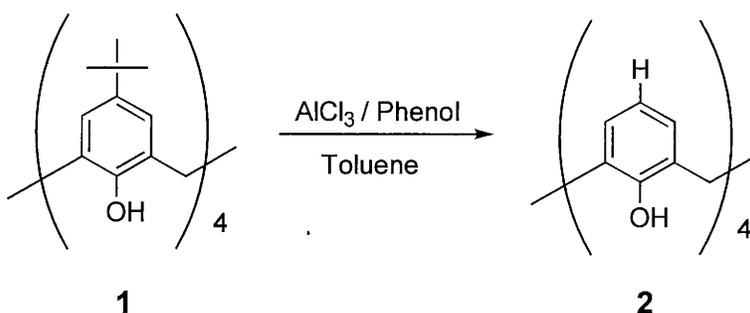


Figure 3.2. Synthesis of 25, 26, 27, 28-Tetrahydroxycalix[4]arene **2**.

With the four *t*-butyl groups clipped from the calix[4]arene structure, the dealkylated calix[4]arene **2** was conformationally mobile. The broad signals at 3.5 and 4.2 ppm in the ¹H-NMR spectrum and the signal at 32 ppm in the ¹³C-NMR spectrum for the bridging methylene hydrogens and carbons, respectively, indicated that compound **2**

was found mostly in the cone conformation but was conformational mobile. Compound **2** was an excellent starting material for lower rim functionalization.

3.1.3 Synthesis of 9-Decene-1-ol Tosylate (**3**)

Tosylates are well known for their excellent ability to act as leaving groups. The reaction of 9-decene-1-ol and *p*-toluenesulfonyl chloride in pyridine resulted in 86% of the vinylic, long chain tosylate **3** (see Figure 3.3).³⁸ This tosylate was used to functionalize the lower rim of the dealkylated calix[4]arene **2**.

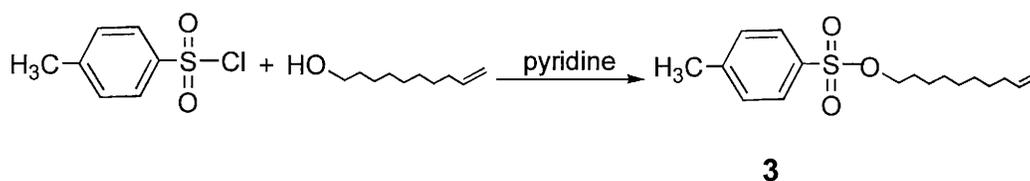


Figure 3.3. Synthesis of 9-Decene-1-ol Tosylate **3**.

A long alkyl group designed to attach to the calix[4]arene structure was synthesized to improve the polymerization reactions of the calixarene monomers. Polymerization reactions using calix[4]arene monomers with short ‘arms’ extending from the calixarene moiety have resulted in low molecular weight, oligomeric products.³⁰ The use of longer ‘arms’ has resulted in higher molecular weight polymers. The longer ‘arms’ moved the site of polymerization away from the large calixarene structure and decreased the steric interactions which may have interfered with the polymerization process.²⁷

3.1.4 Synthesis of 25, 27-Bis(9-decenyloxy)calix[4]arene (4)

The dealkylated calix[4]arene **2** was selectively distally-alkylated at the phenolic oxygens using 1.1 molar equivalents of potassium carbonate and 2.5 molar equivalents of alkylating agent **3** (see Figure 3.4).^{9,13} These reaction conditions optimized the stability of the phenolate oxygens that were formed during the course of the substitution reaction and resulted in the 25 and 27 carbons being selectively alkylated (see Figure 1.4). The crude di-alkylated material was purified by precipitation in stirring methanol, resulting in 69% of pure compound **4**.

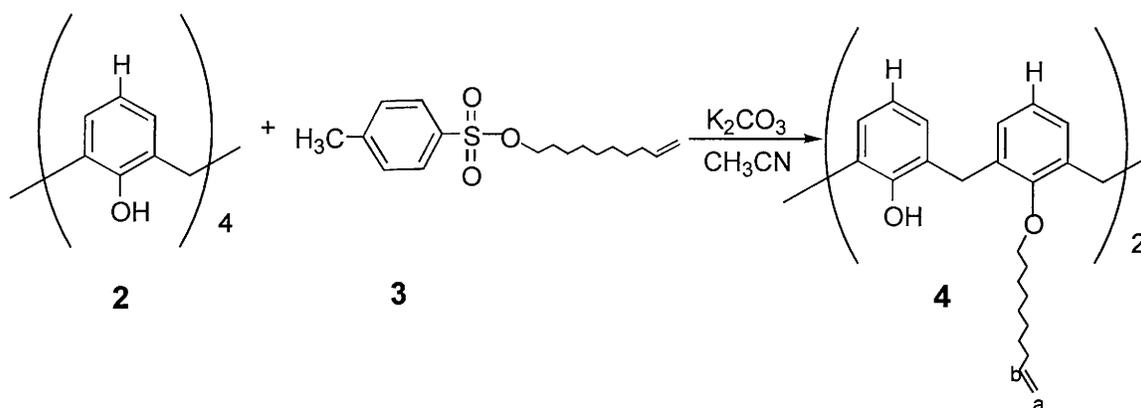


Figure 3.4. Synthesis of 25, 27-Bis(9-decenyloxy)calix[4]arene **4**.

Calix[4]arene **4** was in the cone conformation as indicated by the pair of doublets at 3.4 and 4.4 ppm in the ¹H-NMR spectrum and a signal at 31 ppm in the ¹³C-NMR spectrum for the bridging methylene hydrogens and carbons, respectively. The vinyl groups on the side chains exhibited characteristic NMR signals. The hydrogens on carbons *a* and *b* of the vinyl group were identified as multiplets at 5.0 ppm and 5.9 ppm, respectively in the ¹H-NMR spectrum. In the ¹³C-NMR spectrum, carbons *a* and *b* were

identified as signals at 114 and 139 ppm, respectively. This di-alkylated calix[4]arene **4** was now predisposed to be bridged at the two unfunctionalized phenolic oxygens.

3.1.5 Synthesis of 25, 27-Bis(9-decenyloxy)calix[4]arene-crown-6 (**5**) and crown-5 (**6**)

The bridged calix[4]arene compounds **5** and **6** were synthesized and purified using similar reaction conditions. The calix[4]arene-crown-6 and crown-5 compounds were synthesized by reacting the di-alkylated calix[4]arene **4** with 1.1 molar equivalents of penta(ethylene glycol)di-*p*-toluene sulfonate and tetra(ethylene glycol)di-*p*-tosylate, respectively, in the presence of excess cesium carbonate since it was proposed that the cesium ion acts as a template for the cyclization reaction (see Figure 3.5).^{18,19}

The reactions were carried out in dilute conditions in order to promote intramolecular bridging of the ether loop versus the intermolecular bridging of two calix[4]arene molecules.⁷ The crude calixcrown compounds were purified using column chromatography (aluminum oxide) and 52% and 40% of purified **5** and **6** were obtained.

Once bridging occurred, the calix[4]arene-crown compounds adopted a 1,3-alternate conformation. The ¹H-NMR spectrum contained a singlet at 3.7 ppm for the bridging methylene hydrogens and the ¹³C-NMR spectrum contained a signal at 38 ppm for the bridging methylene carbons. This step completed the synthesis of the two monomers **5** and **6**.

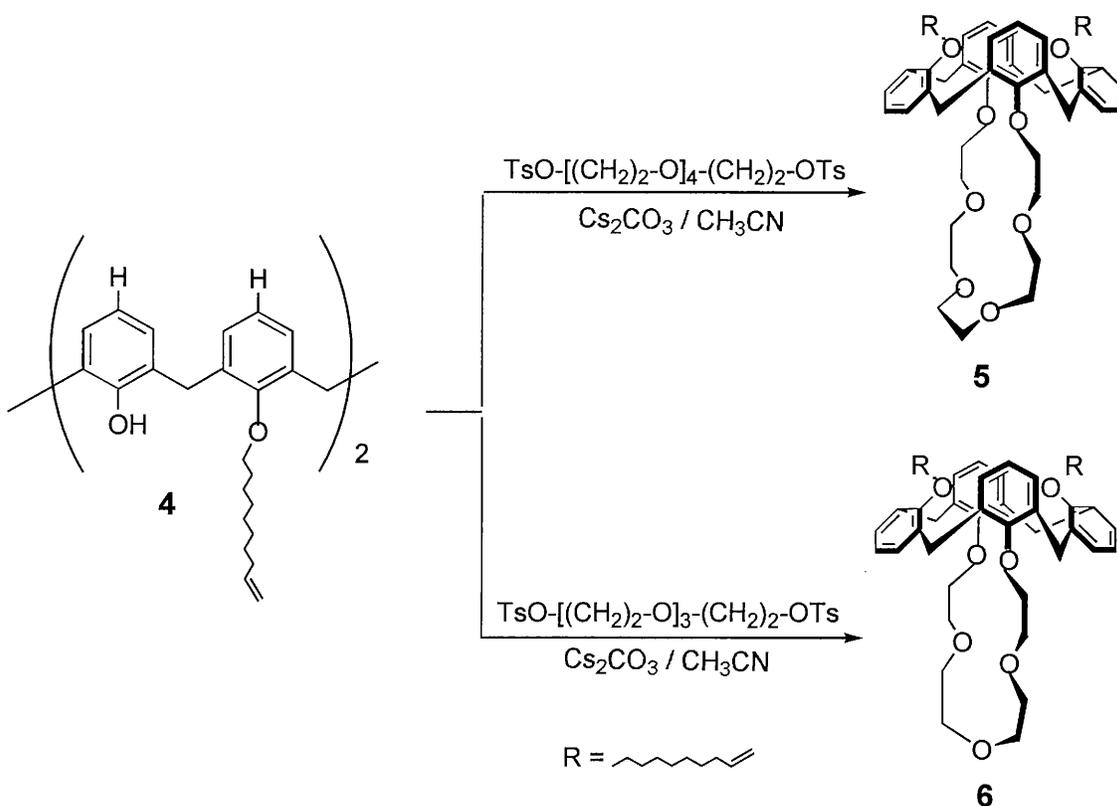


Figure 3.5. Synthesis of 25, 27-Bis(9-decenyloxy)calix[4]arene-crown-6 **5** and crown-5 **6**.

3.1.6 General Polymer Synthesis

Monomers **5** and **6** were structurally suited to undergo hydrosilylation polymerization reactions. The vinylic functional group on each 'arm' was able to react with H-terminated silane and siloxane compounds. The reactions were carried out in concentrated solutions (2 g monomer/ 3 mL solvent) in order to promote polymerization versus intramolecular reactions.^{33,34}

Five silicon-containing compounds were selected as co-monomers in the polymerization reactions (see Figure 3.6). The ten polymers (**7-16**) were synthesized by reacting equal molar amounts of calix[4]arene monomer **5** or **6** with a single silicon monomer in the presence of platinum-divinyltetramethyldisiloxane (Pt-DVTMDS)

complex catalyst (0.18 g atom Pt per mole of alkene) (see Figure 3.6).³³⁻³⁴ The Si-H groups added to the vinylic double bonds in the monomers with anti-Markovnikov-like regioselectivity.³⁹

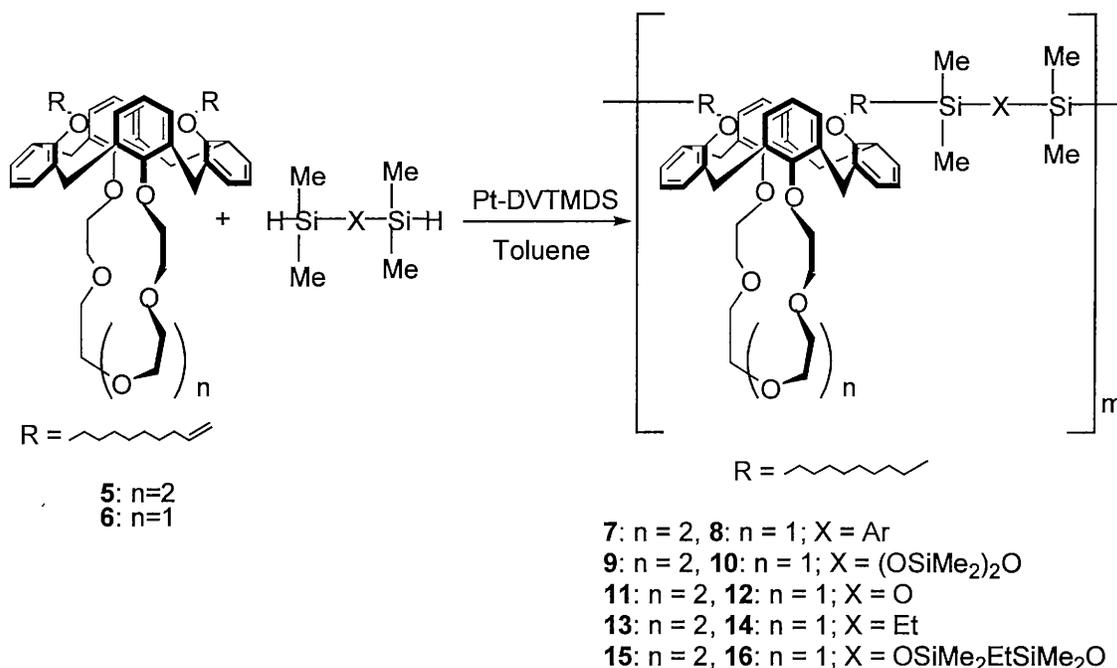


Figure 3.6. Synthesis of Polycalixcrowns 7-16.

The reaction was monitored by $^1\text{H-NMR}$ and IR spectroscopy. The almost complete loss of signals for the vinylic hydrogens at 5.9 and 5.0 ppm in the $^1\text{H-NMR}$ indicated that all the calix[4]arene monomer had reacted and the reaction was complete. The absence of the Si-H signal at approximately 2100 cm^{-1} in the IR spectra also indicated the reaction's completion. Each polymer was purified by precipitation in methanol followed by decolorization with activated charcoal. The percent yields of the polymers ranged from 51% to 72% (see Table 3.1).

3.2 Polymer Analysis

The number of repeating units and molecular weight for each polymer was approximated from the integration of signals in the compound's $^1\text{H-NMR}$ spectrum. The polymers were terminated with either vinyl calixcrown or silane moieties. The assumption was made that the polymers were terminated with only vinyl calixcrown moieties. This assumption was based on the absence of signals for H-Si in the $^1\text{H-NMR}$ (4.5 ppm) and in the IR (2100 cm^{-1}) and the presence of small signals for the vinyl hydrogens in the $^1\text{H-NMR}$ of the polymers.

Each polymer had a definite number of aromatic hydrogens specific to its calix[4]arene structure as well as one signal representing the *b* hydrogens of the two terminal vinyl moieties in the $^1\text{H-NMR}$ spectrum (see Figure 3.4). The ratio between the integration of the aromatic signals to the integration of the *b* hydrogen signal gave the ratio between the number of non-terminal calix[4]crown moieties relative to the two terminal moieties in the polymer. From this ratio the number of repeating units for each polymer was determined.

The number of repeating units ranged from 5 to 10 with molecular weights of 7000 g/mol to 13500 g/mol. All values are listed in Table 3.1. Based on the number of repeating units, the compounds were oligomeric rather than polymeric in nature. The physical appearances of the polymers were similar; the compounds were all sticky solids and ranged in color from an off-white to a dark brown. The inherent viscosities of the polymers ranged from 0.17 dL/g to 0.34 dL/g (see Table 3.1).

The calculated percent composition analysis of polymers **7**, **12**, and **14** differed significantly from the actual percent composition analyzed by Desert Analytics. The

three polymers were all consistently high in the percent silicon and oxygen and consistently low in the percent carbon and hydrogen. This may have been due to contamination of the compounds by silicon stopcock grease. The other seven polymers had observed elemental compositions within 0.3% of the calculated values (see 2.2.7-2.2.16).

The thermal stabilities (TGA data) of the ten polymers varied only slightly and ranged from 398 °C to 427 °C at 10% weight loss in air. The lack of variability indicated that the thermal stability of each polymer was due mainly to the calix[4]arene crown moiety and was unaffected by the variability in the silicon-containing compounds. If the stability was affected by this variability, the TGA values would vary with the different silicon monomers present in the polymers (see Table 3.1).

Table 3.1. Physical Data for Polycalixcrowns.

Polymer	Repeating Units	MW ^a (g/mol)	η_{inh} (dL/g)	TGA ^b (°C)
7	10	11000	0.29	401
8	7	7000	0.34	417
9	8	9500	0.33	413
10	8	9000	0.25	415
11	10	13500	0.25	406
12	10	10000	0.21	427
13	5	5000	0.26	397
14	8	8000	0.22	423
15	6	7000	0.17	414
16	8	9000	0.22	420

^aCalculated from NMR integration data

^b10% weight loss in air

3.3 Binding Studies

An estimation of the ionophoric properties of monomers **5** and **6** and polymers **7**, **8**, **11**, **12**, **15**, and **16** was determined using liquid/liquid extraction studies based on Pedersen's procedures.^{18,35} These polymers were selected based on the variation in the silicon monomer structure (i.e. aromatic, short, and long monomer). Based on calixcrown monomer studies and other systems, the assumption was made that each crown formed a one to one complex with the metal cation.¹⁸ The results are reported in Tables 3.2 and 3.3 and Figures 3.7 and 3.8. The data in Table 3.3 were normalized by reporting the values as percent extraction per milligram of host.

Table 3.2. Extraction Data for Calix[4]arene-crown Monomers and Polycalixcrowns.

Host	Weight (mg)	Percent Extraction of Cations ^a (%)			
		Na ^b	K ^b	Rb ^b	Cs ^b
Crown-6 Moiety					
5	46	<1	1.5	10	32
7	51	<1	<1	6.7	23
11	45	<1	<1	5.7	17
15	50	<1	<1	6.1	20
Crown-5 Moiety					
6	43	<1	40	35	3.7
8	50	<1	40	34	2.8
12	45	<1	27	24	2.8
16	56	<1	25	20	2.1

^a% Extraction = ($\frac{[Pic^-]_{org}}{[Pic^-]_{aq}}$) * 100%

^bMolar concentration picrate salt solutions = 1×10^{-3} M

Table 3.3. Normalized Extraction Data for Calix[4]arene-crown Monomers and Polycalixcrowns.

Host	Percent Extraction of Cations/mg Host ^a ([%/mg] x 10 ²)			
	Na ^b	K ^b	Rb ^b	Cs ^b
Crown-6 Moiety				
5	<1	3.3	22	70
7	<1	1.4	13	44
11	1.1	1.8	13	38
15	<1	1.9	12	40
Crown-5 Moiety				
6	1.6	94	82	8.6
8	1.4	81	68	5.6
12	1.6	60	54	6.2
16	1.4	45	36	3.8

^a% Extraction/mg host = ($\frac{[Pic^-]_{org}}{[Pic^-]_{aq}} \times 100\%$)/mg host

^bMolar concentration picrate salt solutions = 1×10^{-3} M

These results revealed a strong preference of all the compounds containing crown-6 moieties for Cs⁺ over Na⁺, K⁺, and Rb⁺. All of the compounds containing crown-5 moieties exhibited a strong preference for K⁺ and a weaker preference for Rb⁺, Na⁺, and Cs⁺. These cation selectivities for both the crown-6 and crown-5 monomers were similar to cation selectivities previously reported in the literature.^{7,18} Qualitatively, the cation selectivities observed in these experiments were valid and were based on the size of the crown moieties. However, the quantitative comparison of the percent extractions of one crown moiety over another (i.e. compound **7** vs. **11**) did not reflect the fact that one mg of a particular polymer may have contained more or less numbers of crown units relative to a comparative polymer and the crown-6 and crown-5 monomers.

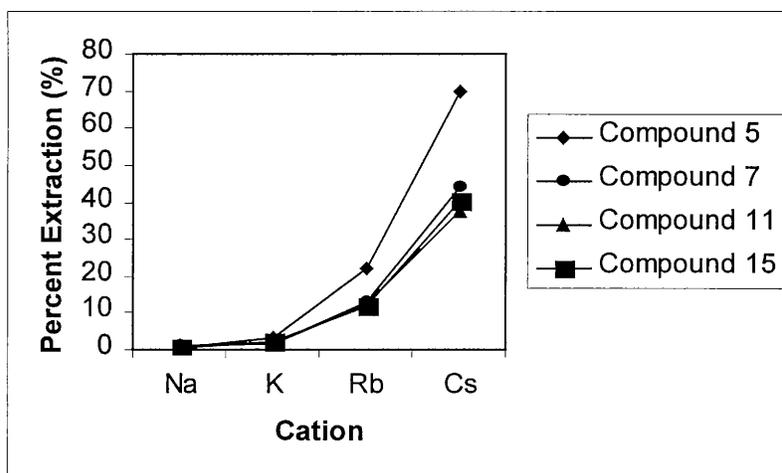


Figure 3.7. Normalized Percent Extraction of Alkali Metal Cations by Calix[4]arene-crown-6 Moieties.

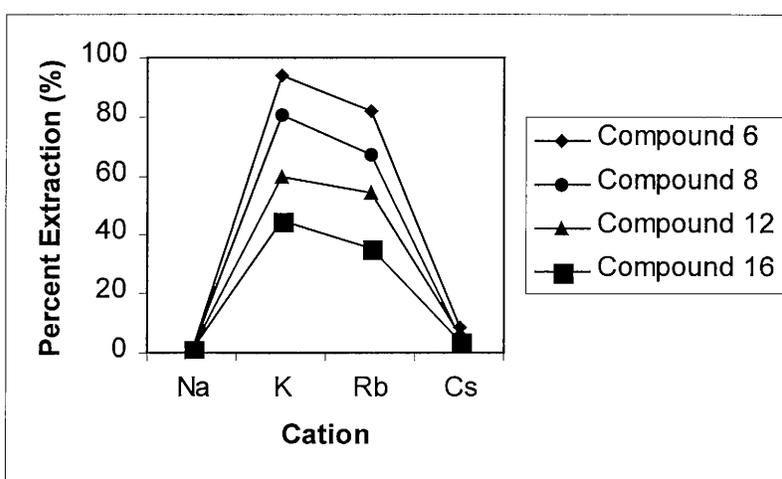


Figure 3.8. Normalized Percent Extraction of Alkali Metal Cations by Calix[4]arene-crown-5 Moieties.

Table 3.4 contains the relative selectivity ratios of host compounds **5-16** for the cations. These ratios were calculated using the normalized extraction data in Table 3.3

and are qualitative. The ratios involving the strongest bound cations (Cs^+ and Rb^+ for crown-6 moieties and K^+ and Rb^+ for crown-5 moieties) were calculated.

Table 3.4. Relative Cation Selectivities for Calix[4]arene Monomers and Polycalixcrowns Based on Normalized Extraction Data.

Host	Cation Pair				
	Cs^+/Rb^+	Cs^+/K^+	Cs^+/Na^+	Rb^+/K^+	Rb^+/Na^+
Crown-6 Moiety					
5	3.2	21	90	6.5	28
7	3.4	31	52	9.3	15
11	3.1	20	48	6.8	16
15	3.4	21	65	6.3	19
	K^+/Rb^+	K^+/Cs^+	K^+/Na^+	Rb^+/Cs^+	Rb^+/Na^+
Crown-5 Moiety					
6	1.1	11	59	9.5	51
8	1.2	14	58	12	49
12	1.1	9.7	38	8.8	34
16	1.3	12	32	9.5	26

All of the crown-6 compounds exhibited a relative Cs^+/Rb^+ selectivity of approximately 3. This indicated that the crown-6 moiety's preference for the cesium cation was three times greater than its preference for the rubidium cation. The crown-6 compounds' selectivities for Cs^+/K^+ , Cs^+/Na^+ , Rb^+/K^+ , and Rb^+/Na^+ were approximately 20, 50, 7, and 20, respectively. The crown-5 compounds exhibited relative selectivities for K^+/Rb^+ , K^+/Cs^+ , K^+/Na^+ , Rb^+/Cs^+ , and Rb^+/Na^+ approximately equal to 1, 12, 47, 10, and 40, respectively.

The binding of the cation by the crown moieties was due to the fit of the cation within the ether loop. If the cation was too small or too large, the crown ether loop was

unable to wrap around the cation due to the steric hindrance of the calix[4]arene skeleton.¹⁸ It was determined that the silicon monomers played no role in the cation binding by the use of the sodium cation. This cation was too small to be bound by either the crown-6 or crown-5 moieties. Therefore, if it was determined that this cation was being bound, it would have to be due to the silicon monomers in the polymer backbone. This was not the case and all of the cation binding was due to the crown moieties.

The difference in the percentages of cations bound by the monomers and the analogous polymers was small. The variation in the values may have been due to the inconsistency in the number of crown moieties in each monomer and polymer sample. The similarities in the data implied that the binding capabilities of the crown moieties were neither improved nor worsened by their incorporation into a polymer backbone. The binding function of the polycalixcrowns was dictated by the size of the crown in the calix[4]arene moiety and was not significantly affected by the polymeric arrangement of the calixcrown units.

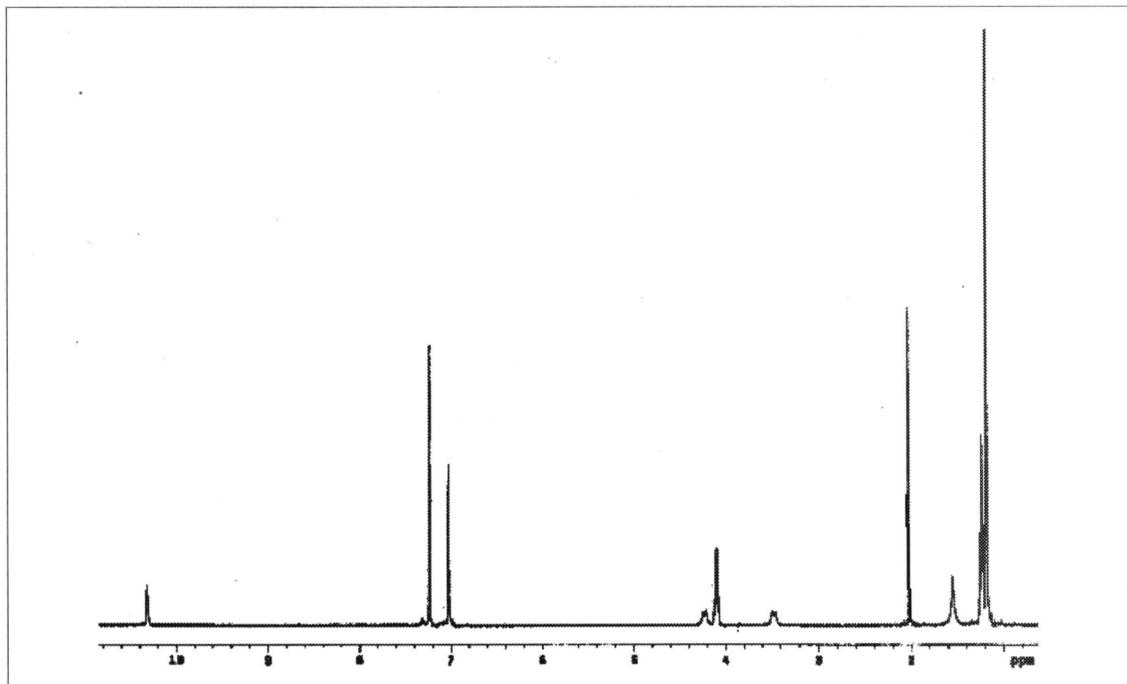
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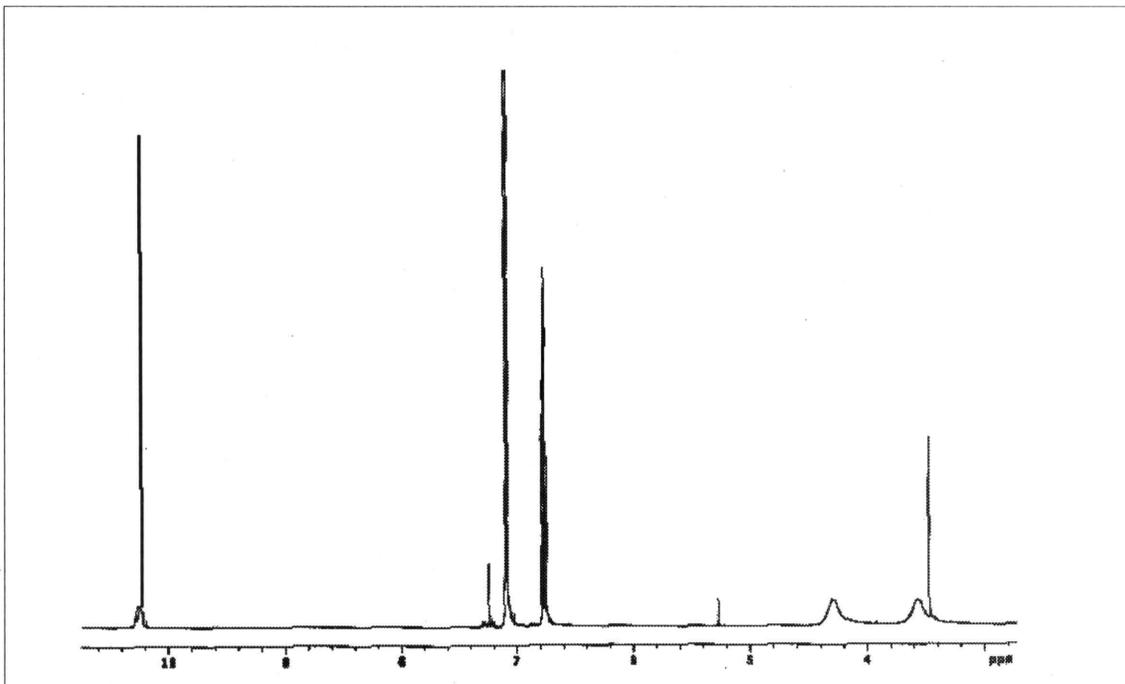
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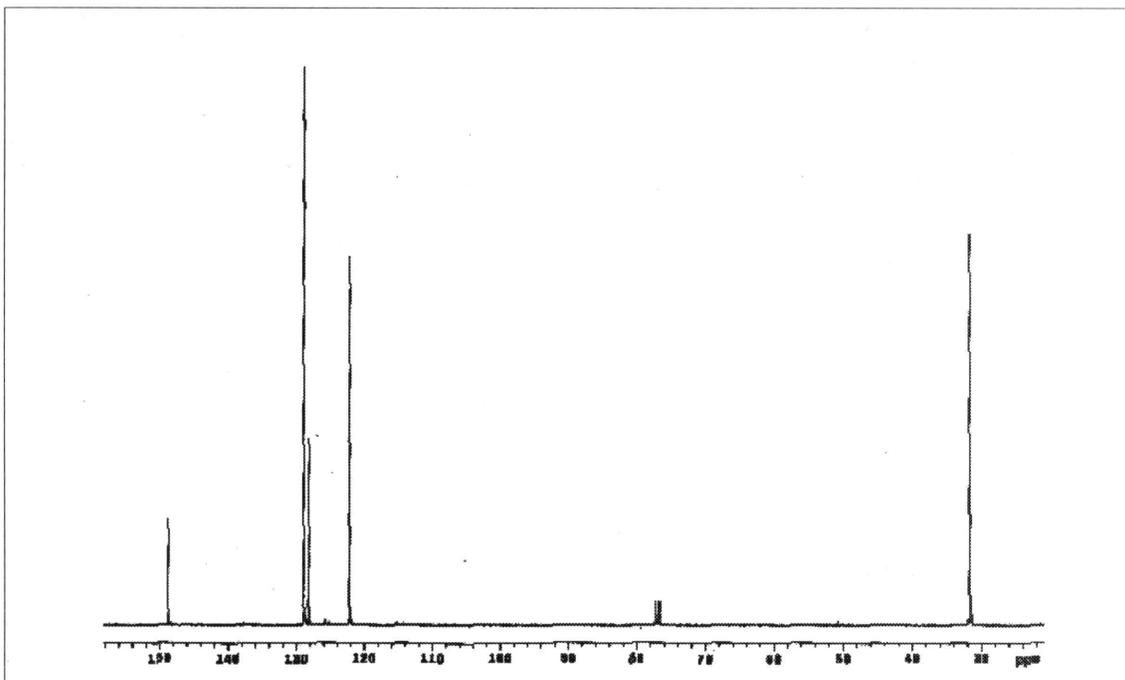
APPENDIX A. NMR SPECTRA



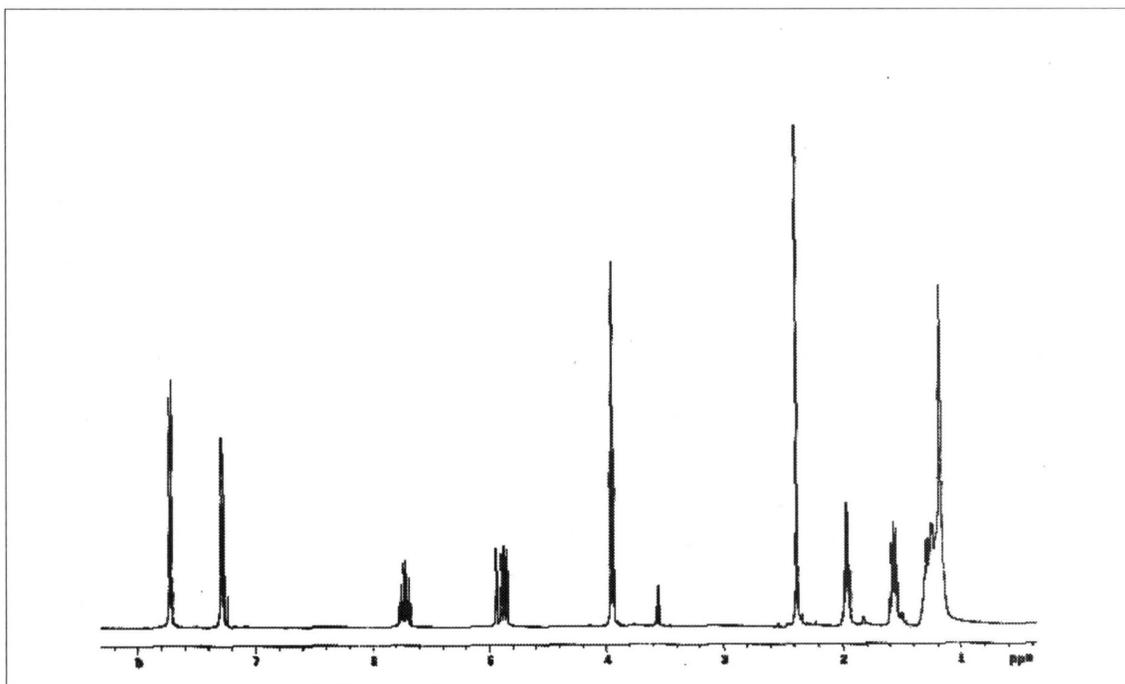
Spectrum 1: $^1\text{H-NMR}$ of 5, 11, 17, 23-Tetra-*t*-butylcalix[4]arene (**1**).



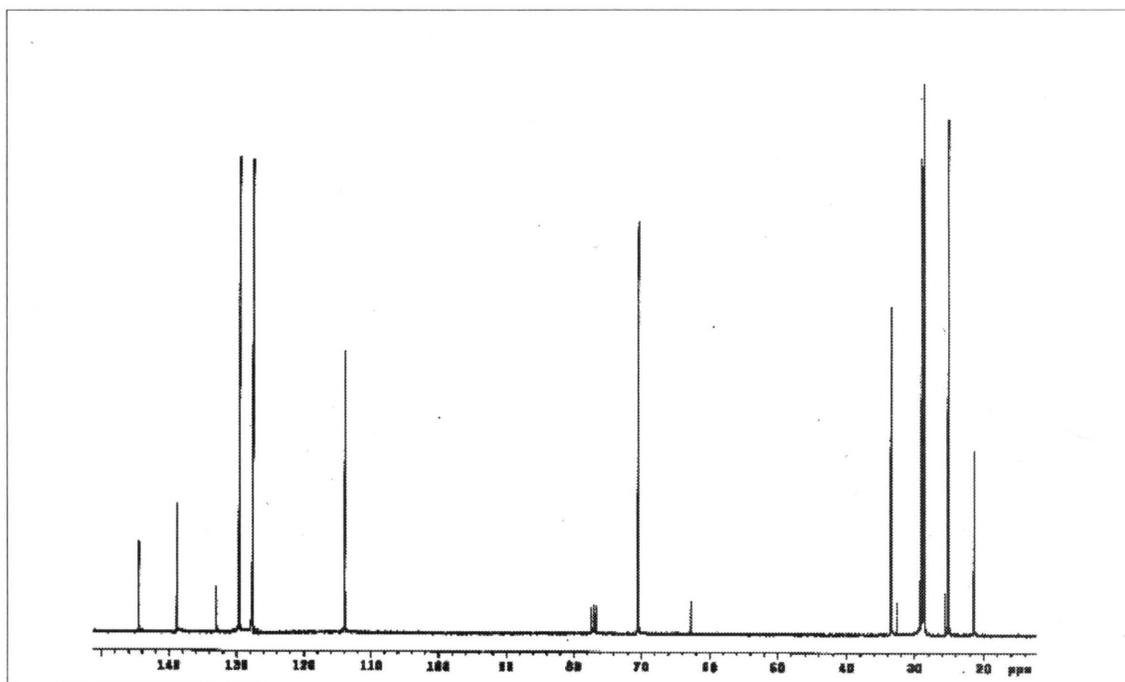
Spectrum 2: ¹H-NMR of 25, 26, 27, 28-Tetrahydrocalix[4]arene (**2**).



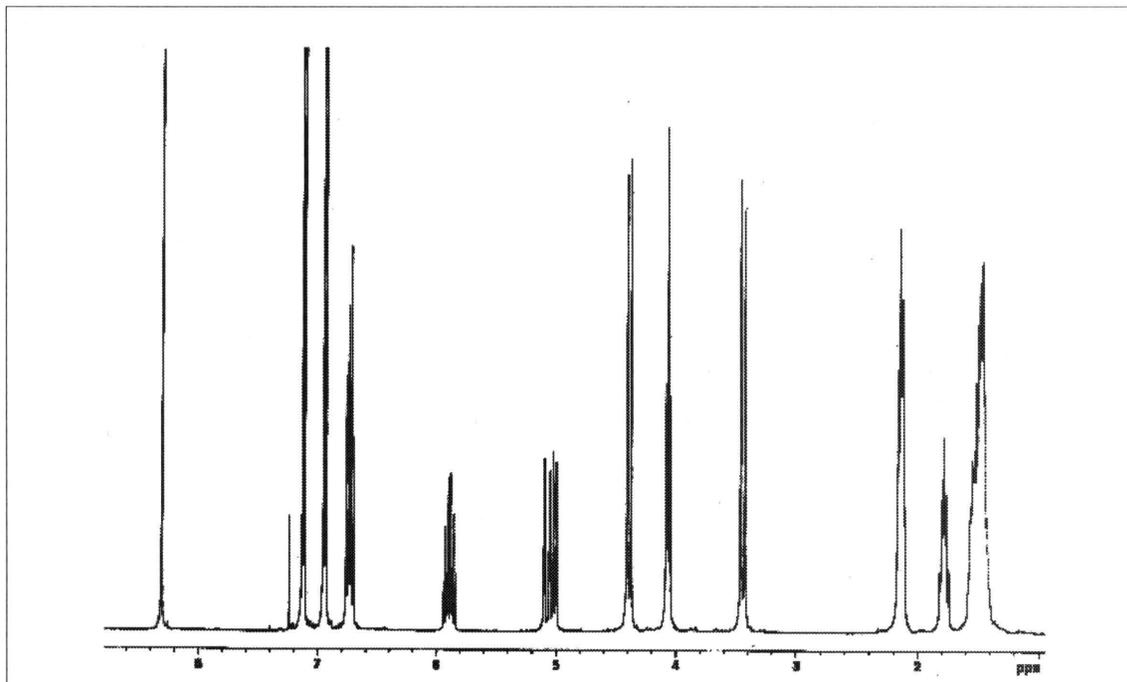
Spectrum 3: ¹³C-NMR of 25, 26, 27, 28-Tetrahydrocalix[4]arene (**2**).



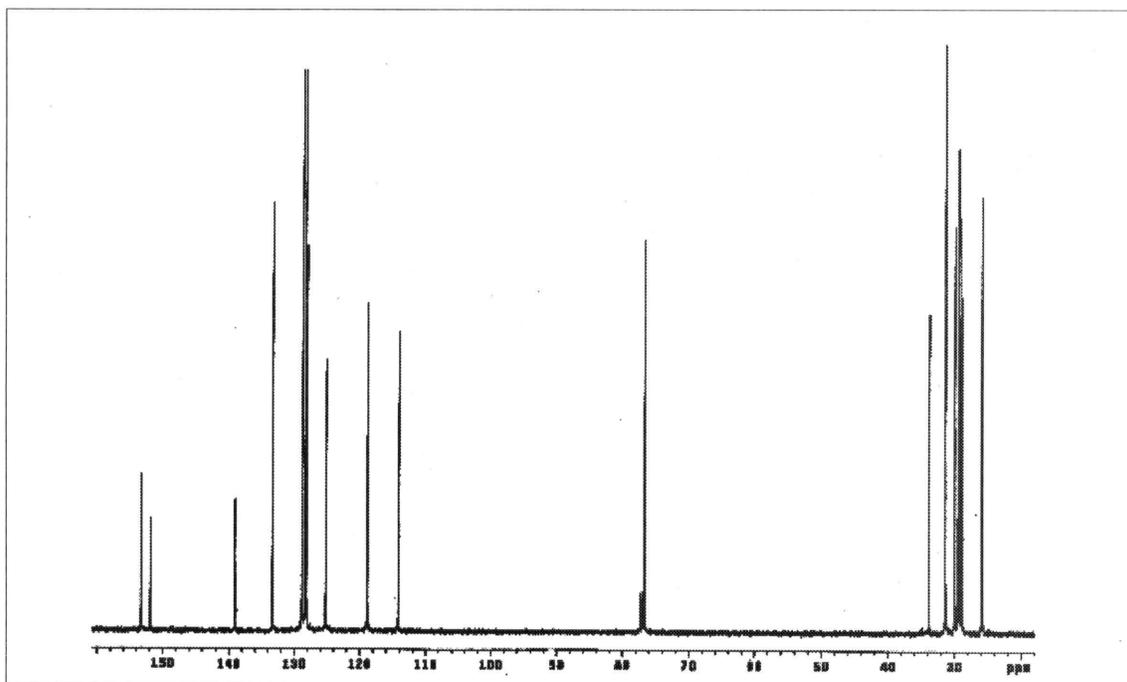
Spectrum 4: ^1H -NMR of 9-Decene-1-ol tosylate (**3**).



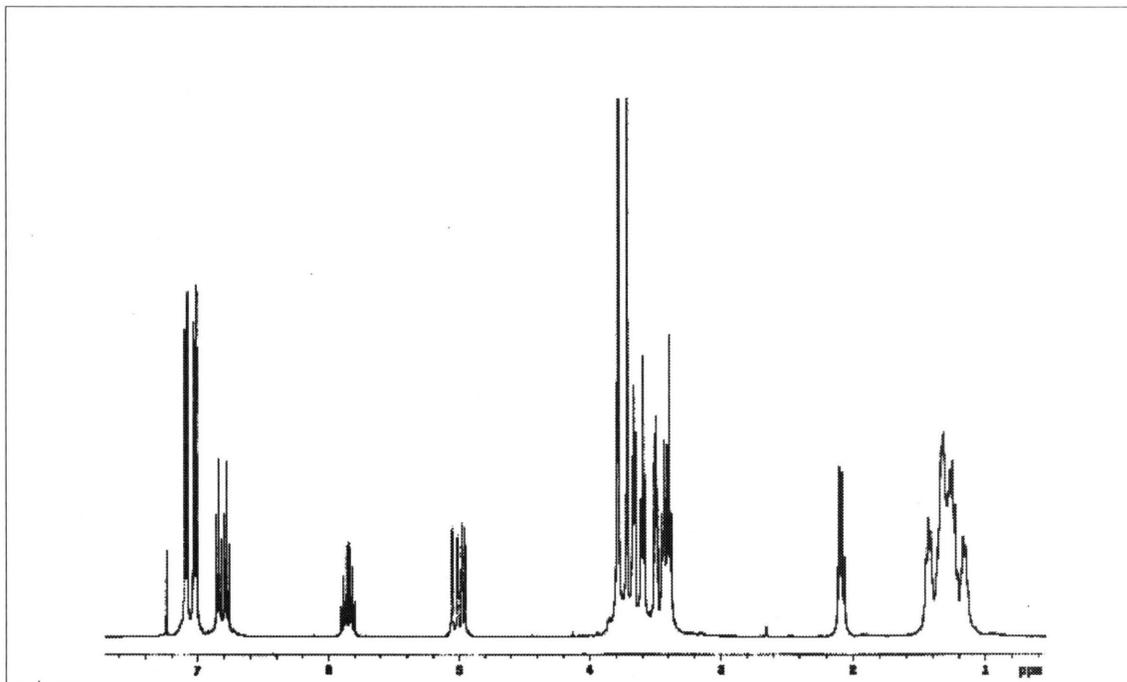
Spectrum 5: ^{13}C -NMR of 9-Decene-1-ol tosylate (**3**).



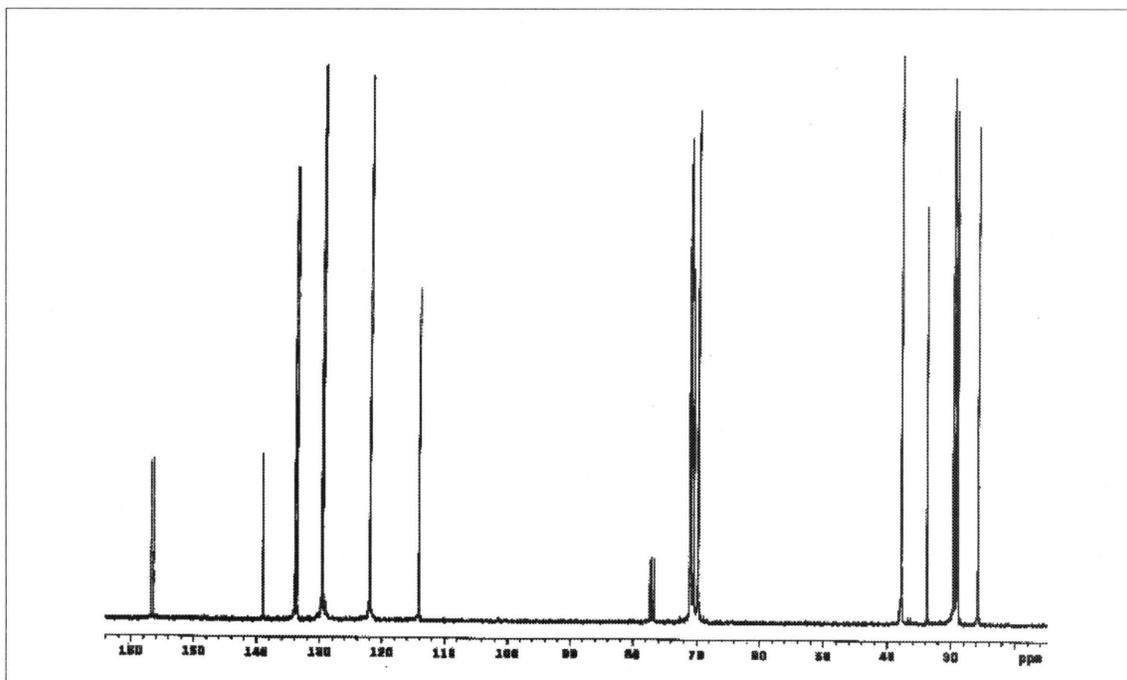
Spectrum 6: $^1\text{H-NMR}$ of 25, 27-Bis(9-decenyloxy)calix[4]arene (**4**).



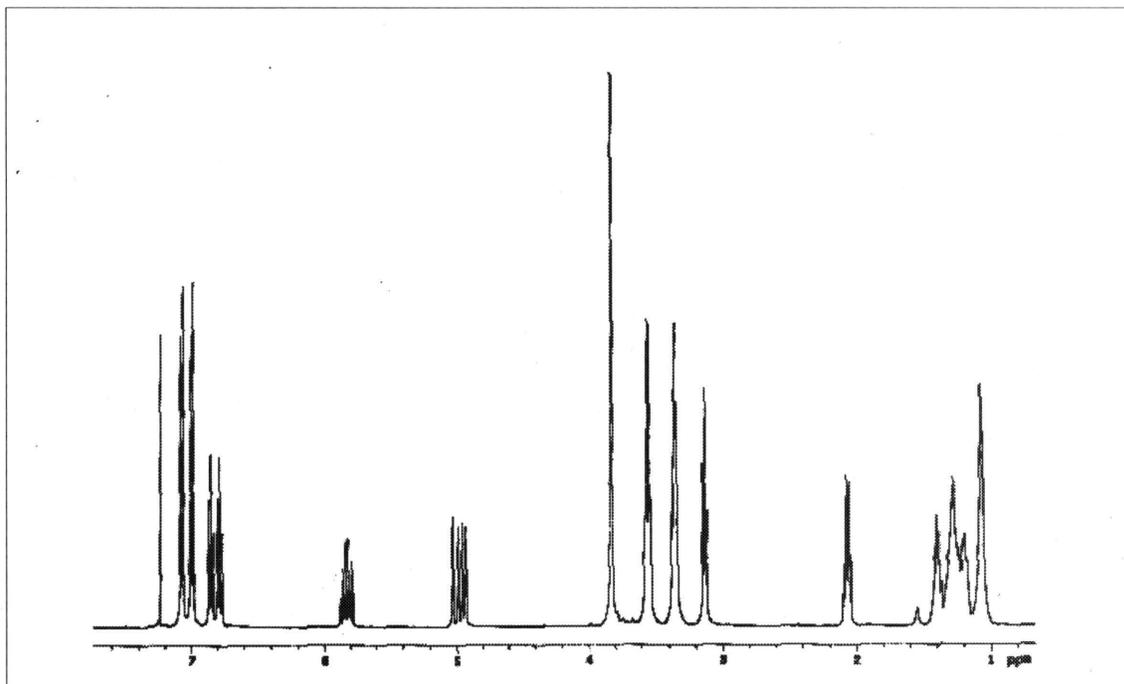
Spectrum 7: $^{13}\text{C-NMR}$ of 25, 27-Bis(9-decenyloxy)calix[4]arene (**4**).



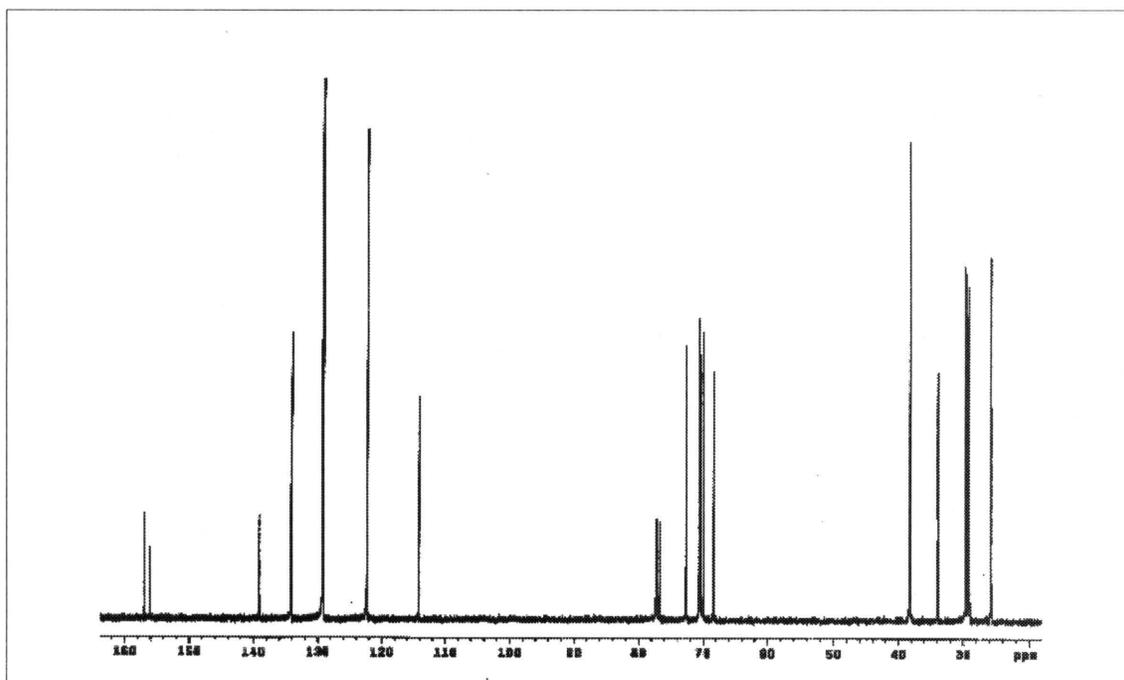
Spectrum 8: ¹H-NMR of 25, 27-Bis(9-decenyloxy)calix[4]arene (5).



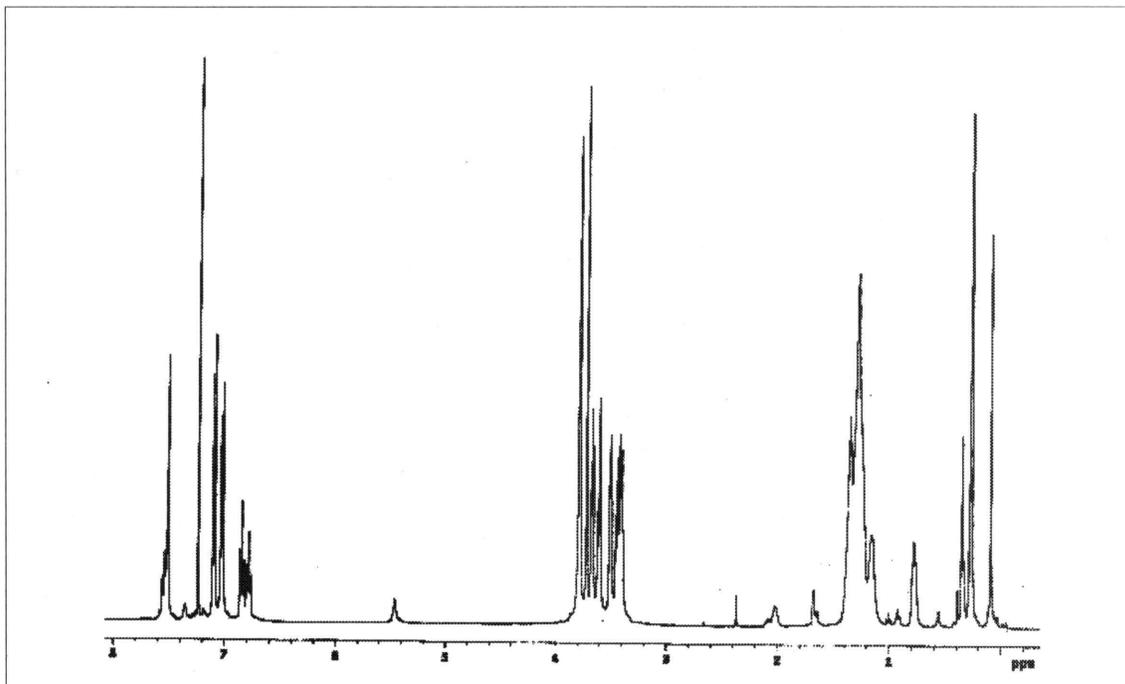
Spectrum 9: ¹³C-NMR of 25, 27-Bis(9-decenyloxy)calix[4]arene (5).



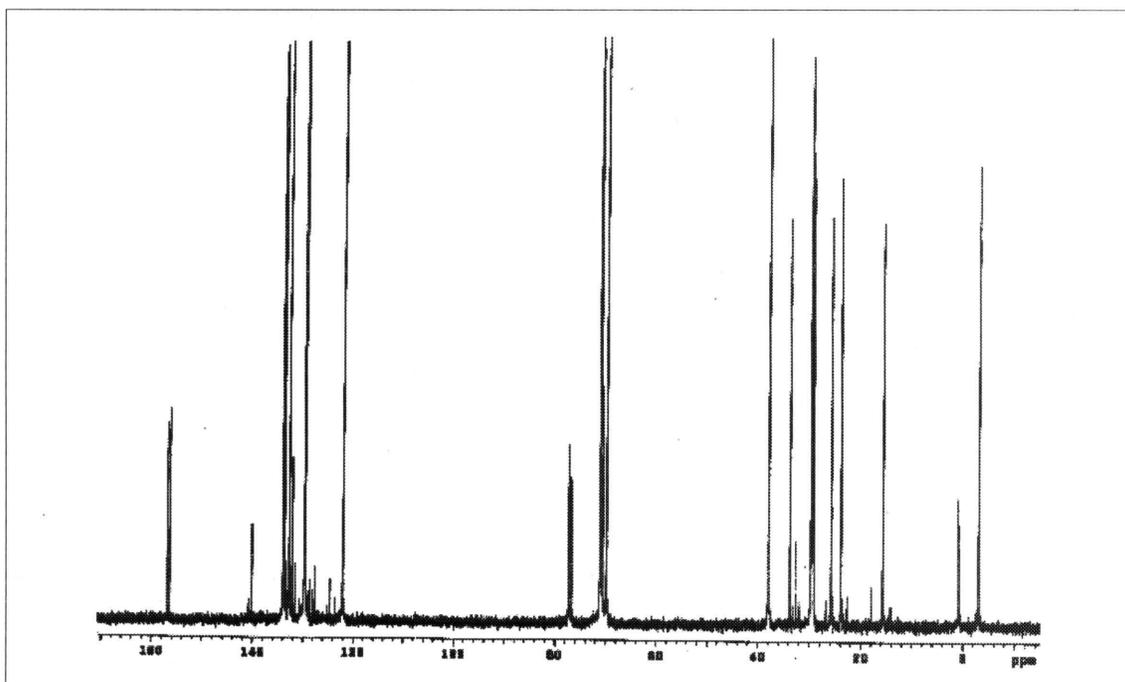
Spectrum 10: ^1H -NMR of 25, 27-Bis(9-decenyloxy)calix[4]arene (6).



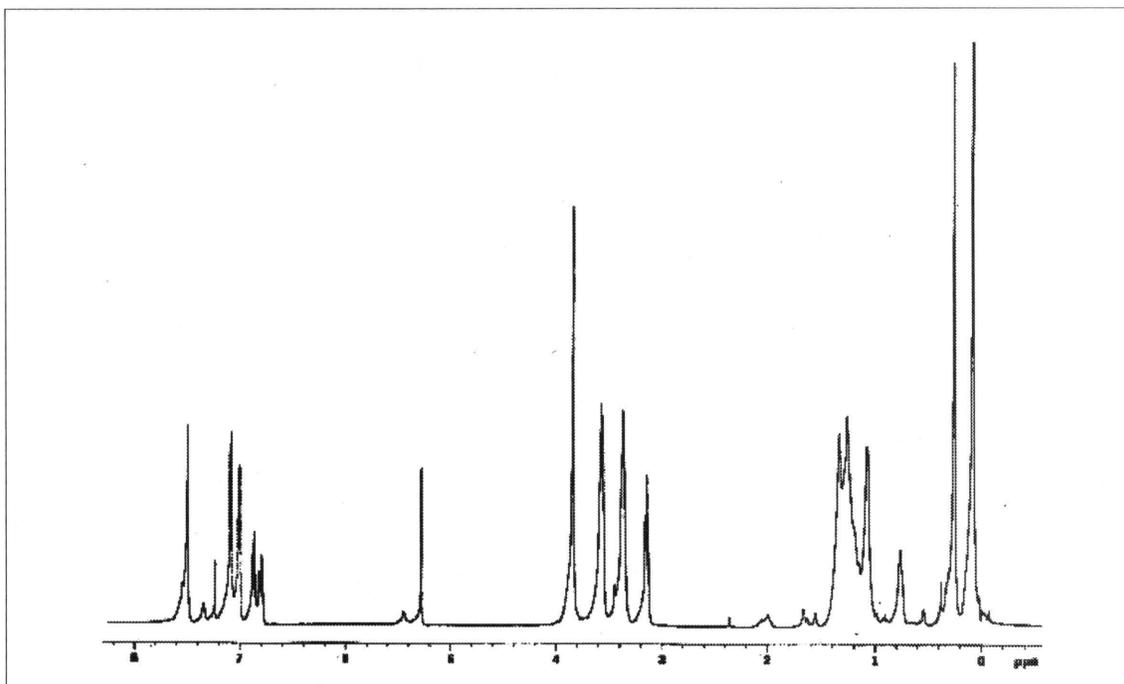
Spectrum 11: ^{13}C -NMR of 25, 27-Bis(9-decenyloxy)calix[4]arene (6).



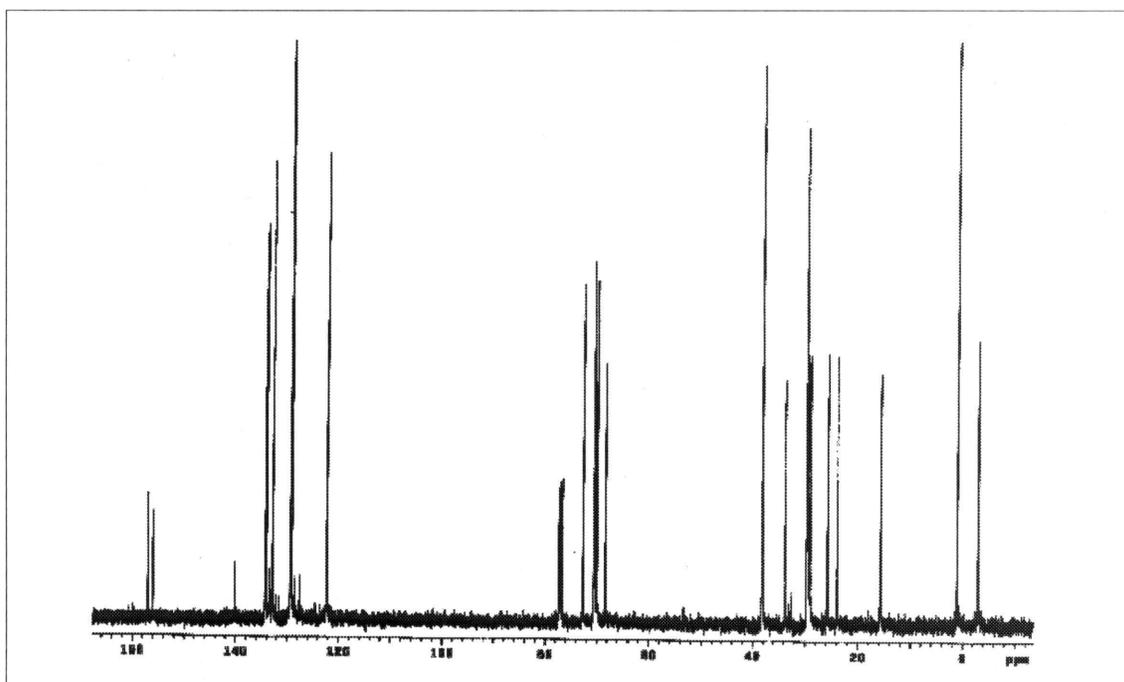
Spectrum 12: $^1\text{H-NMR}$ of Polymer 1 (7).



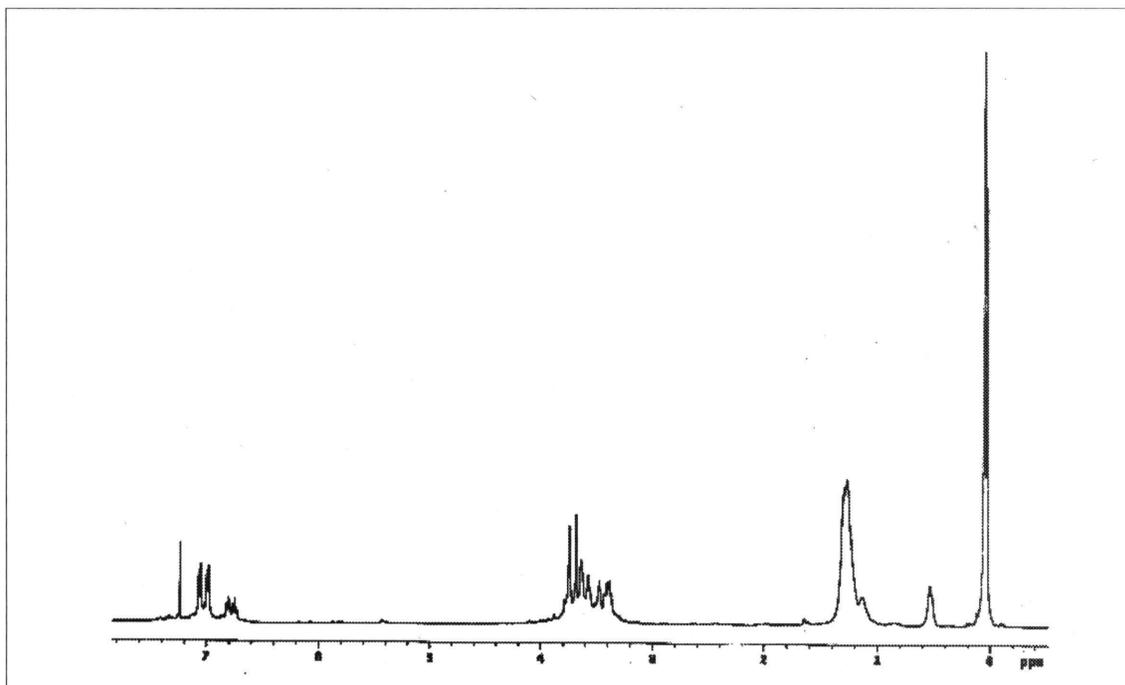
Spectrum 13: $^{13}\text{C-NMR}$ of Polymer 1 (7).



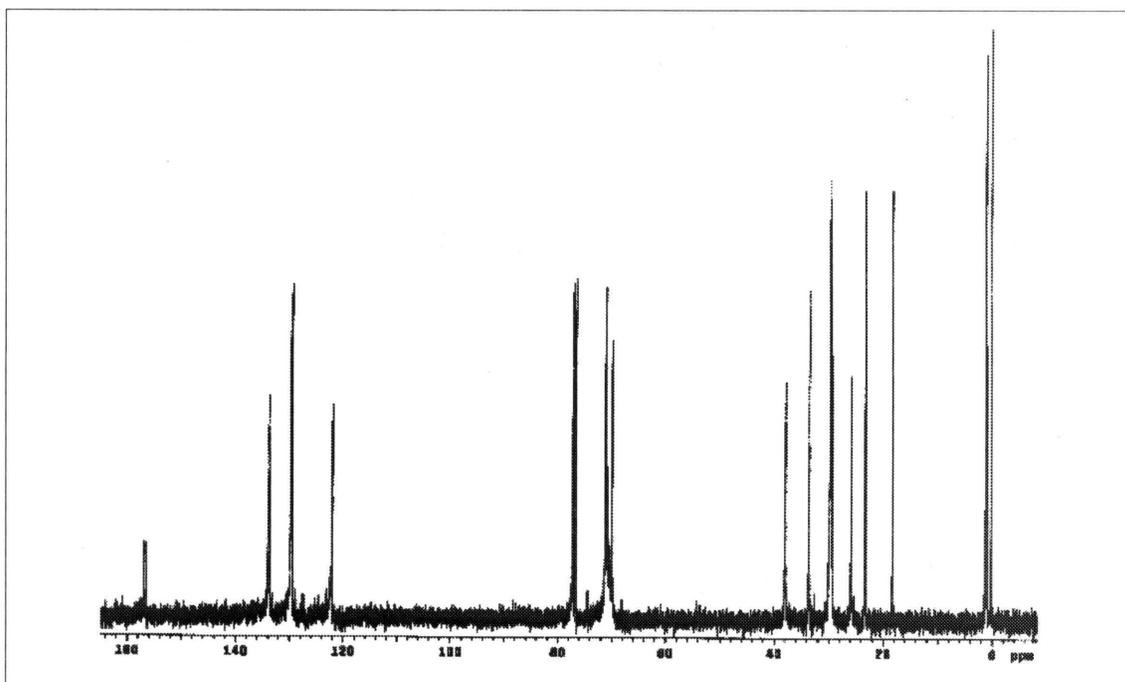
Spectrum 14: $^1\text{H-NMR}$ of Polymer 2 (8).



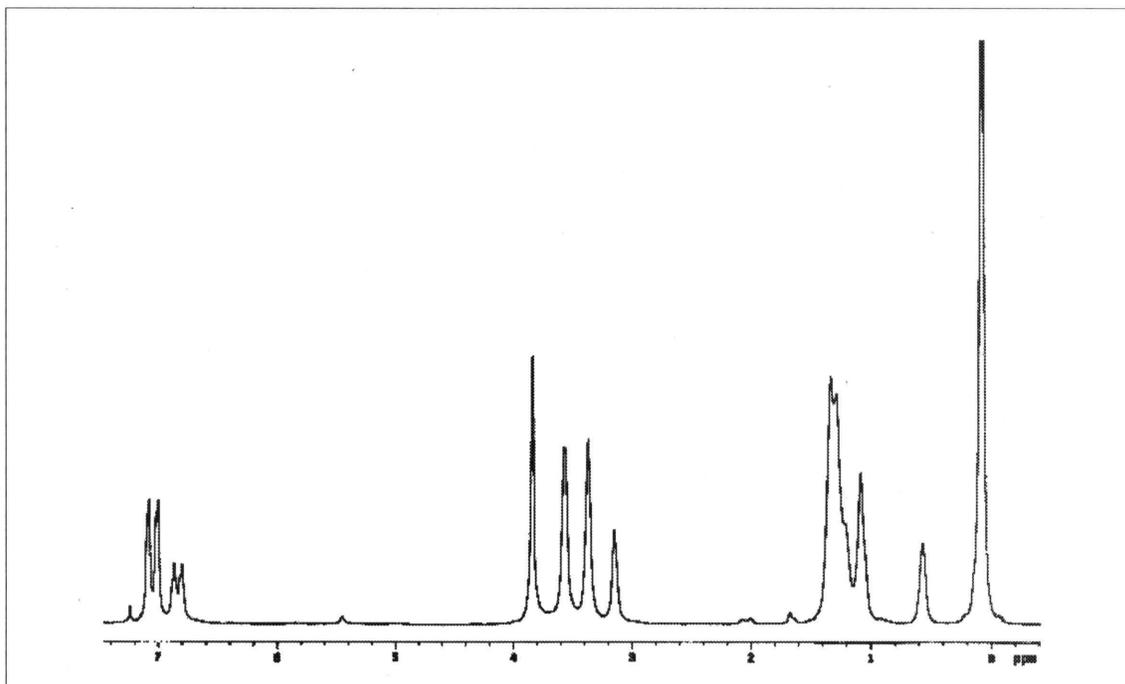
Spectrum 15: $^{13}\text{C-NMR}$ of Polymer 2 (8).



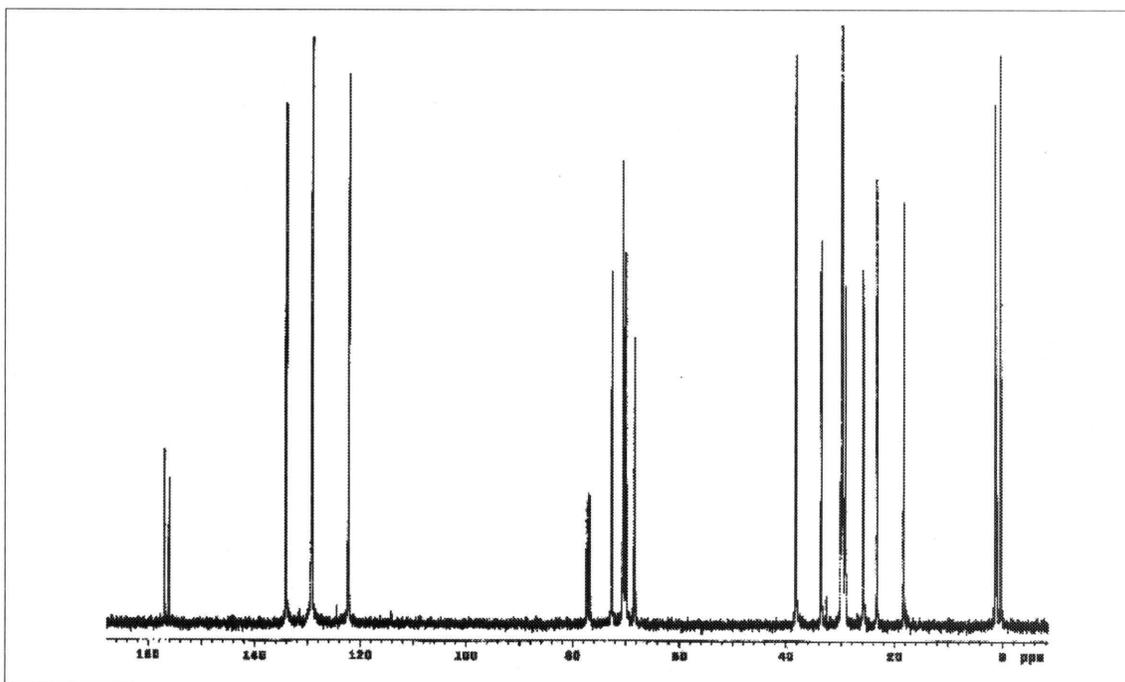
Spectrum 16: $^1\text{H-NMR}$ of Polymer 3 (9).



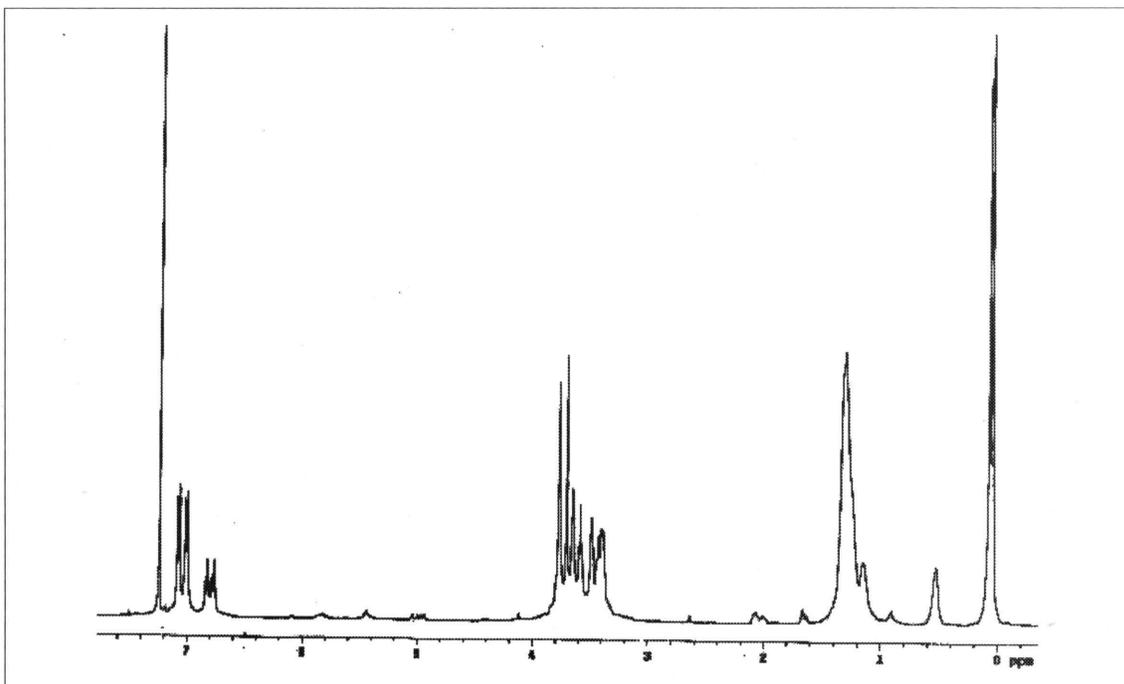
Spectrum 17: $^{13}\text{C-NMR}$ of Polymer 3 (9).



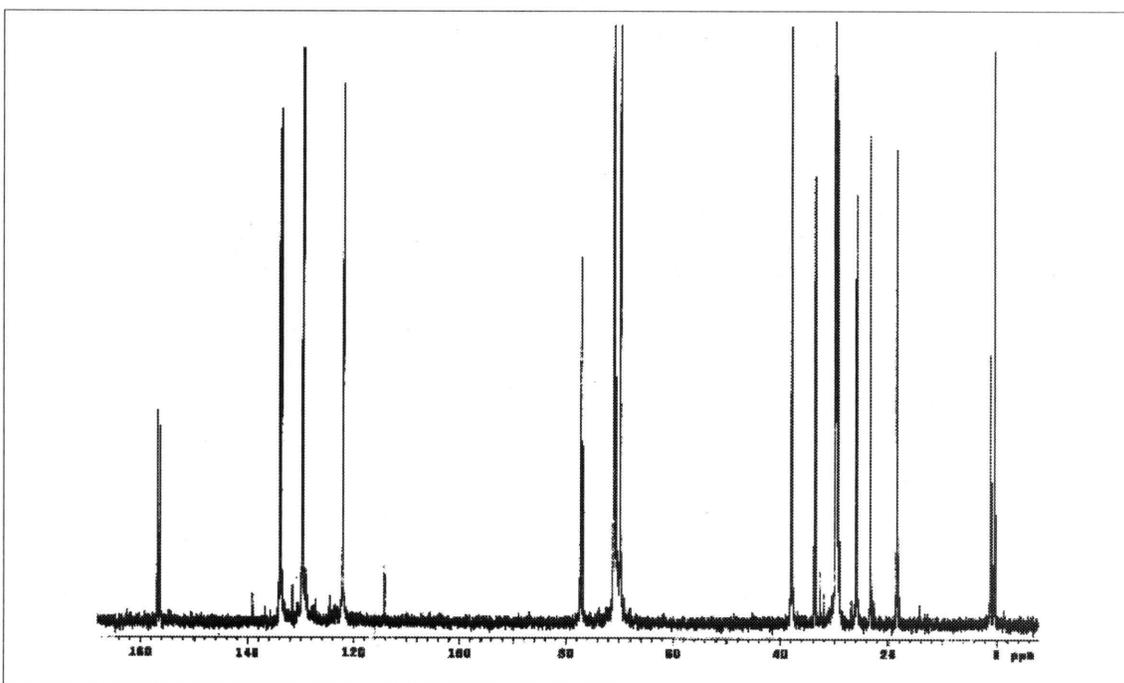
Spectrum 18: $^1\text{H-NMR}$ of Polymer 4 (10).



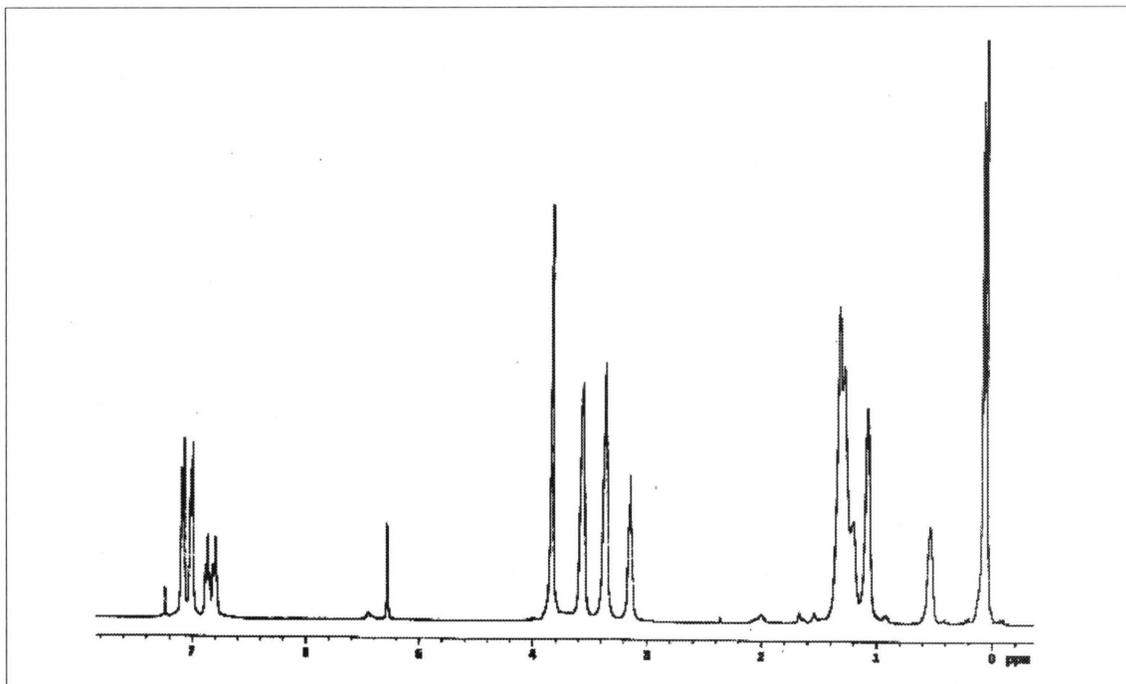
Spectrum 19: $^{13}\text{C-NMR}$ of Polymer 4 (10).



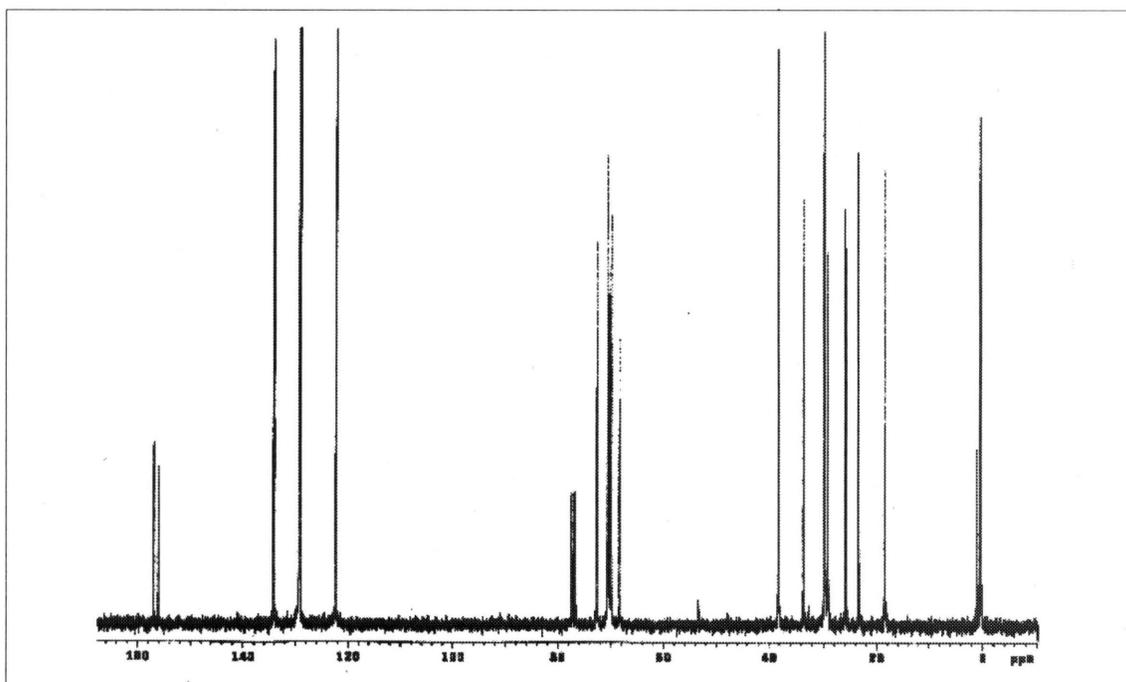
Spectrum 20: $^1\text{H-NMR}$ of Polymer 5 (11).



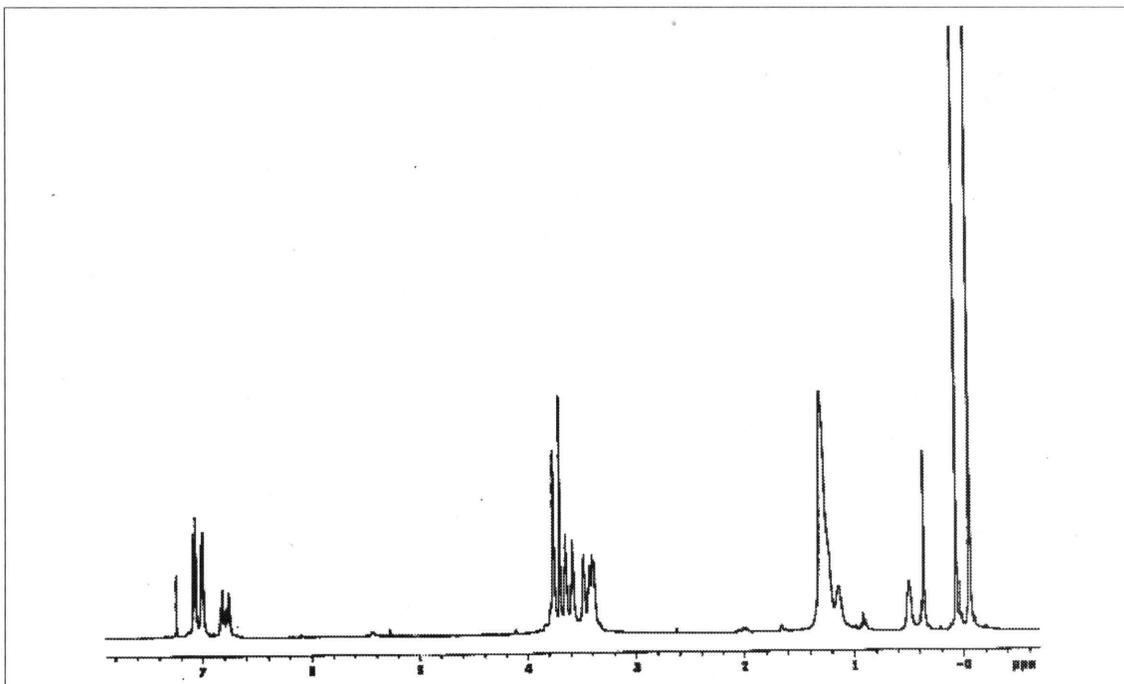
Spectrum 21: $^{13}\text{C-NMR}$ of Polymer 5 (11).



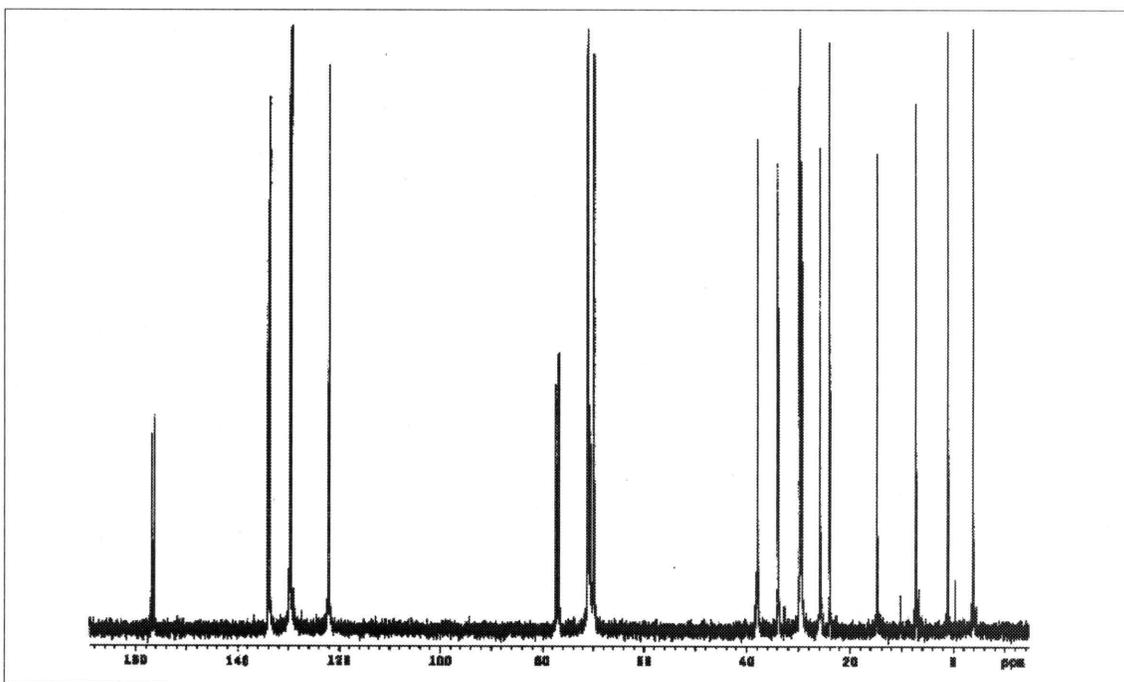
Spectrum 22: $^1\text{H-NMR}$ of Polymer 6 (12).



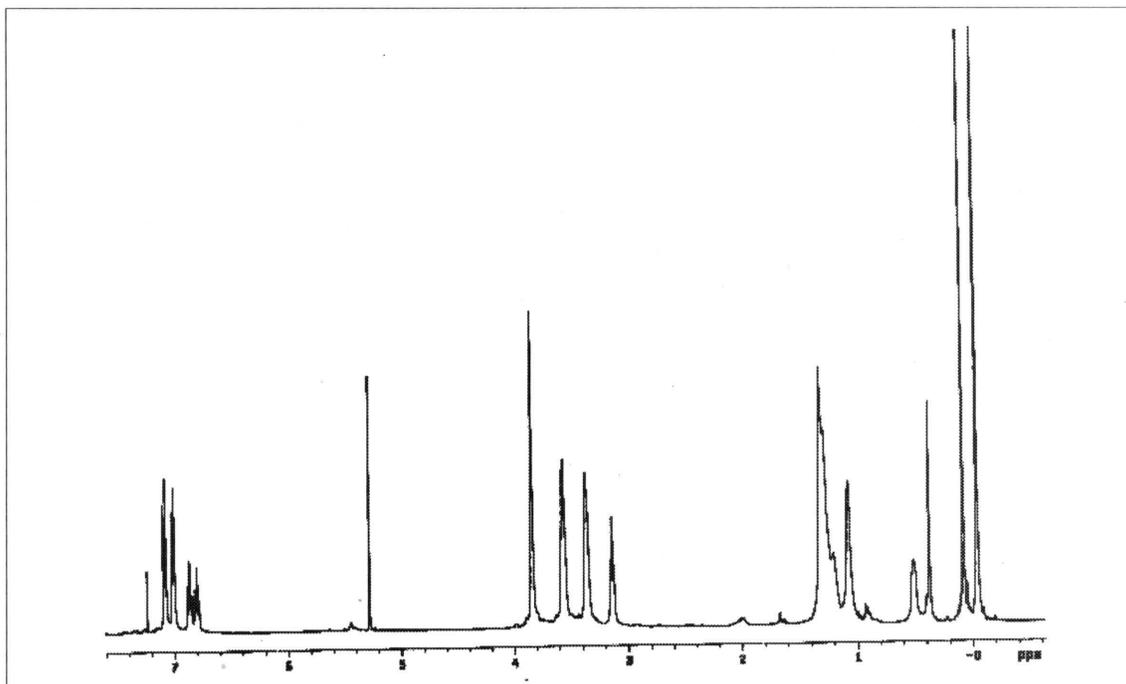
Spectrum 23: $^{13}\text{C-NMR}$ of Polymer 6 (12).



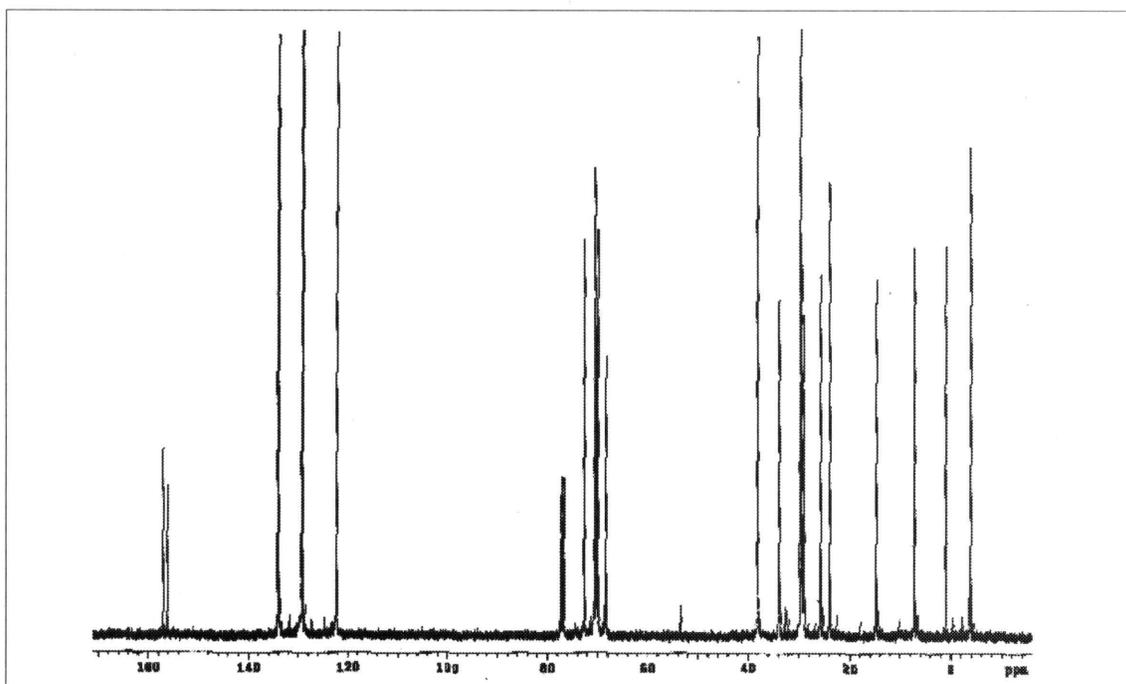
Spectrum 24: $^1\text{H-NMR}$ of Polymer 7 (13).



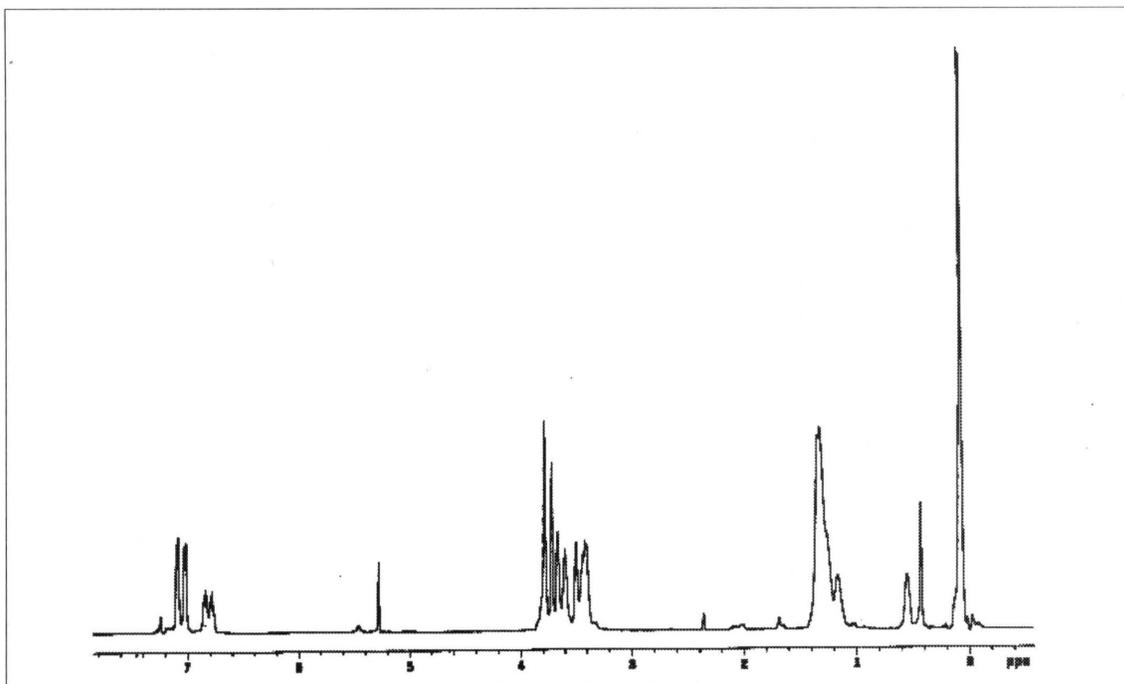
Spectrum 25: $^{13}\text{C-NMR}$ of Polymer 7 (13).



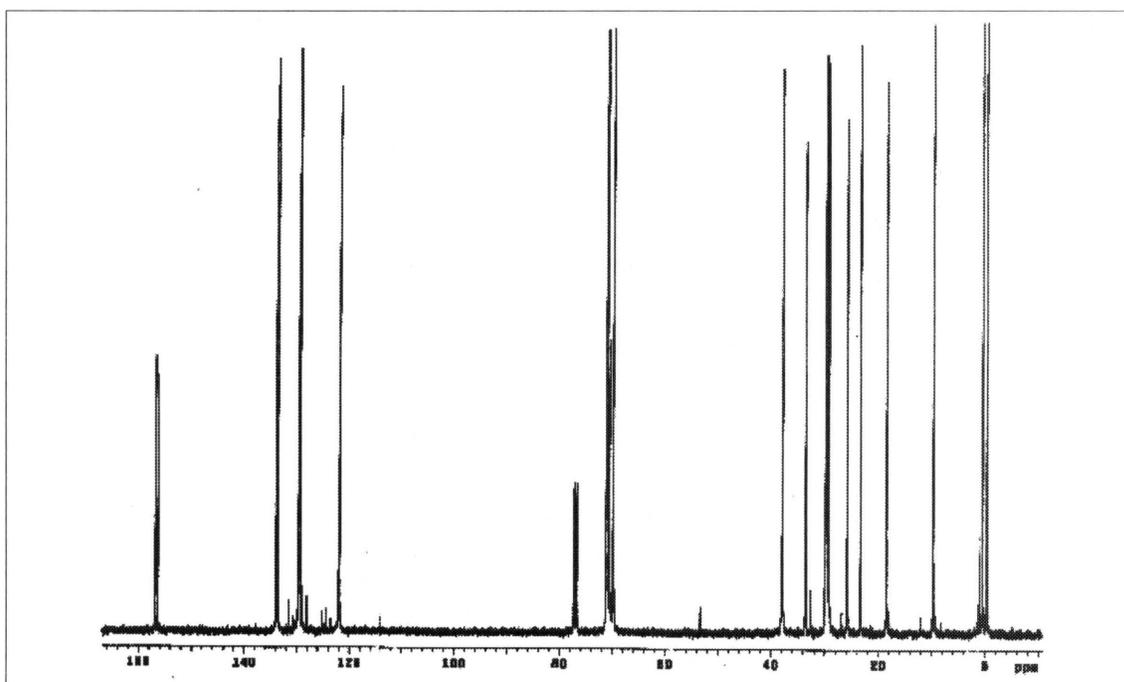
Spectrum 26: $^1\text{H-NMR}$ of Polymer 8 (14).



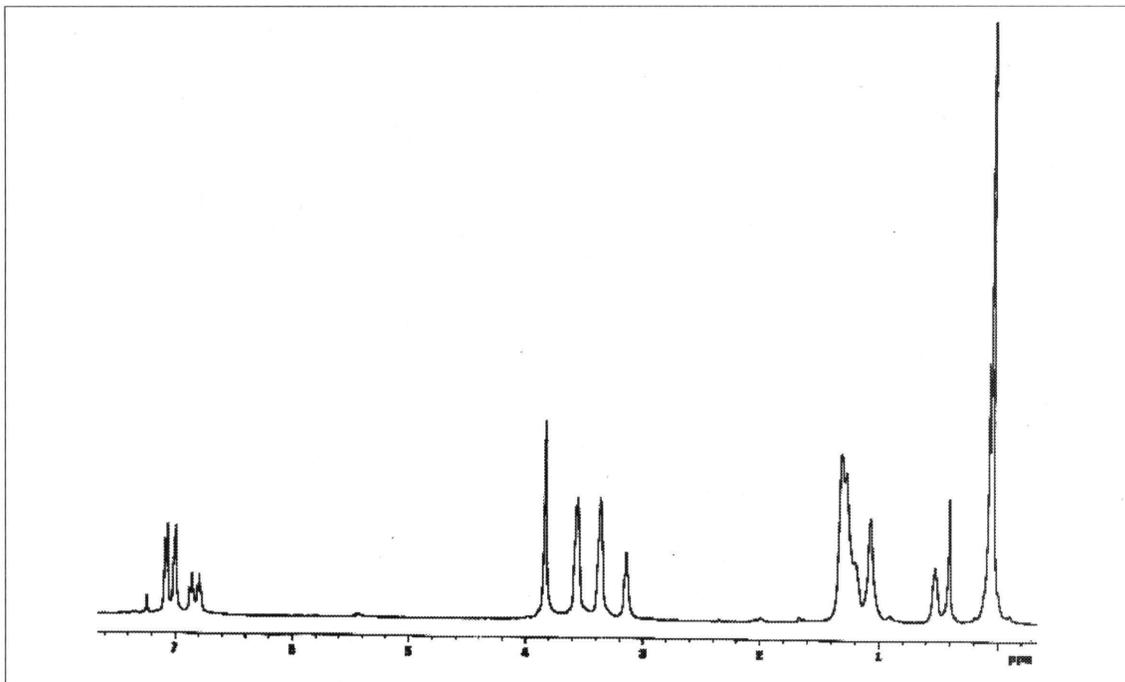
Spectrum 27: $^{13}\text{C-NMR}$ of Polymer 8 (14).



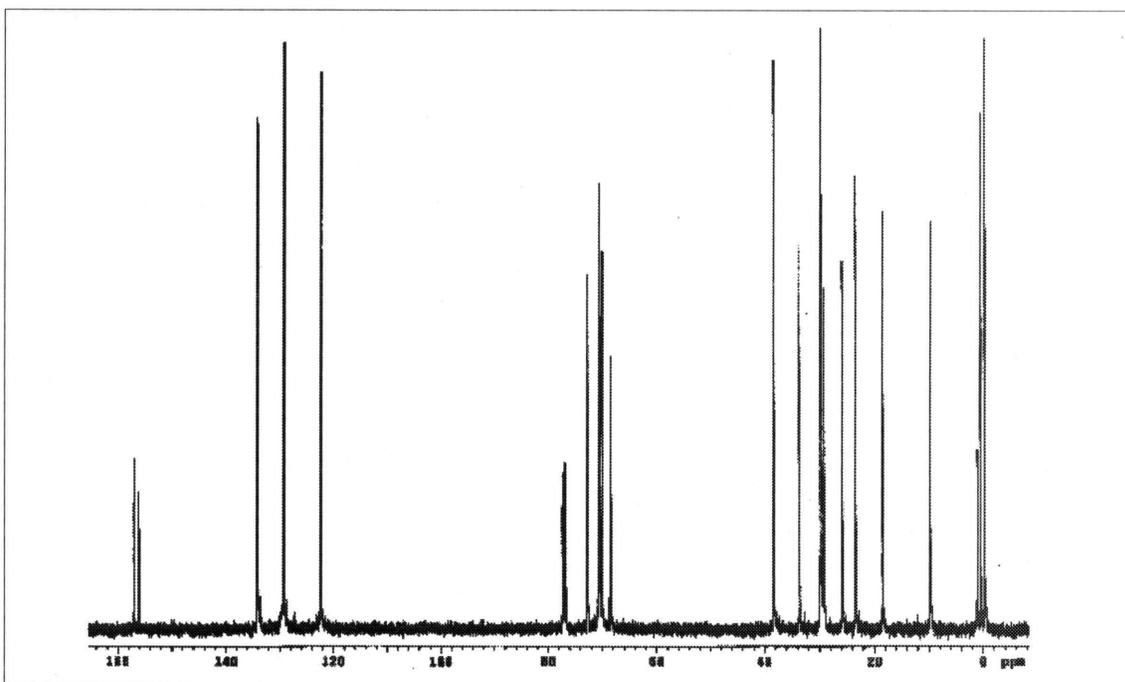
Spectrum 28: $^1\text{H-NMR}$ of Polymer 9 (15).



Spectrum 29: $^{13}\text{C-NMR}$ of Polymer 9 (15).

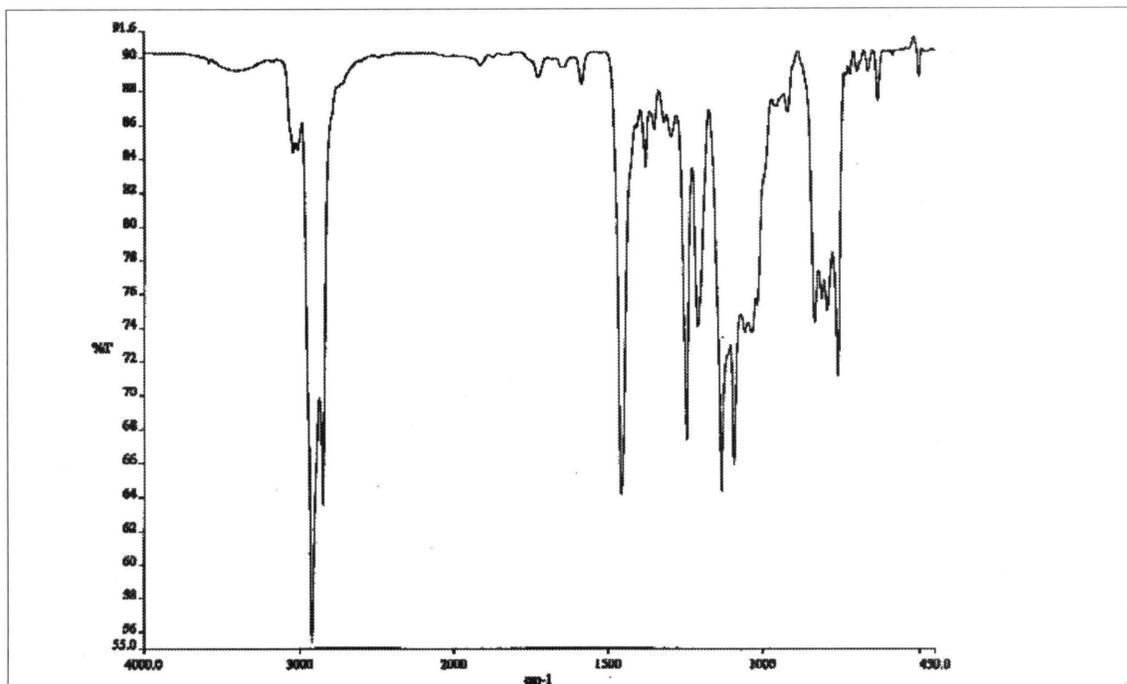


Spectrum 30: $^1\text{H-NMR}$ of Polymer 10 (16).

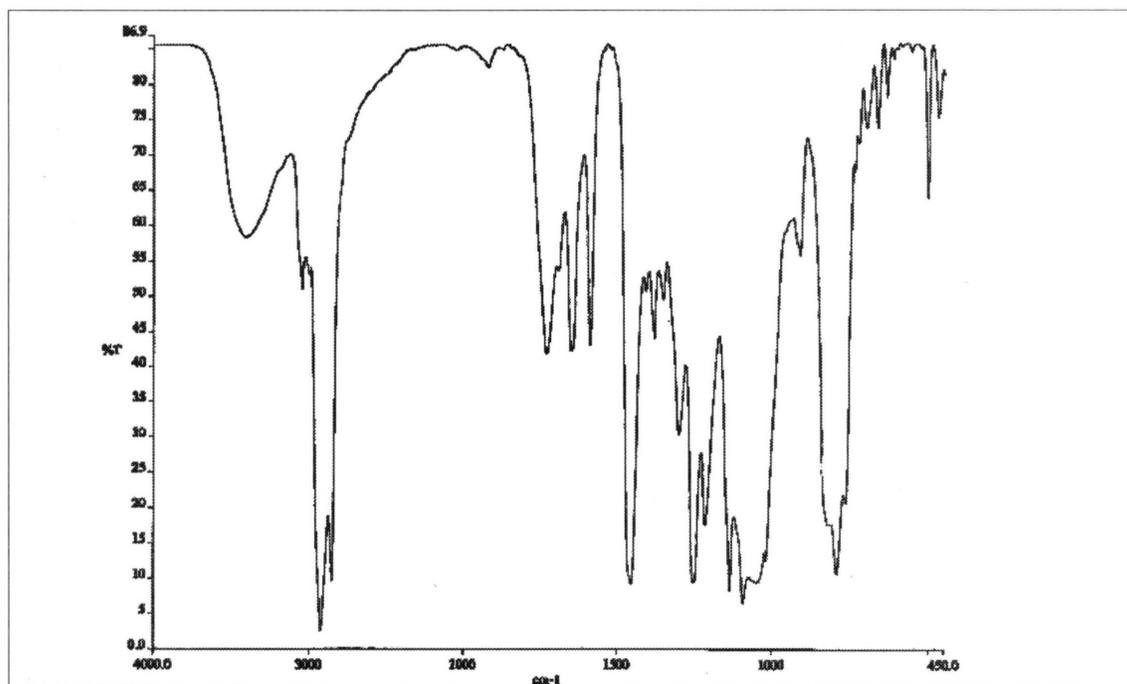


Spectrum 31: $^{13}\text{C-NMR}$ of Polymer 10 (16).

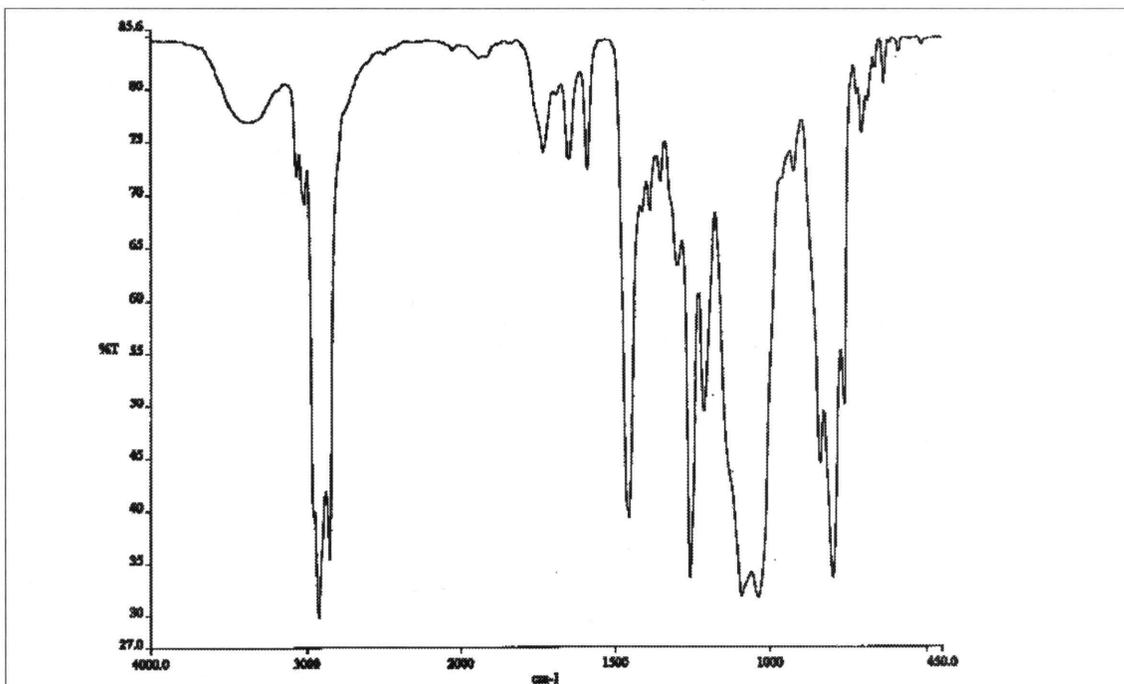
APPENDIX B. IR SPECTRA



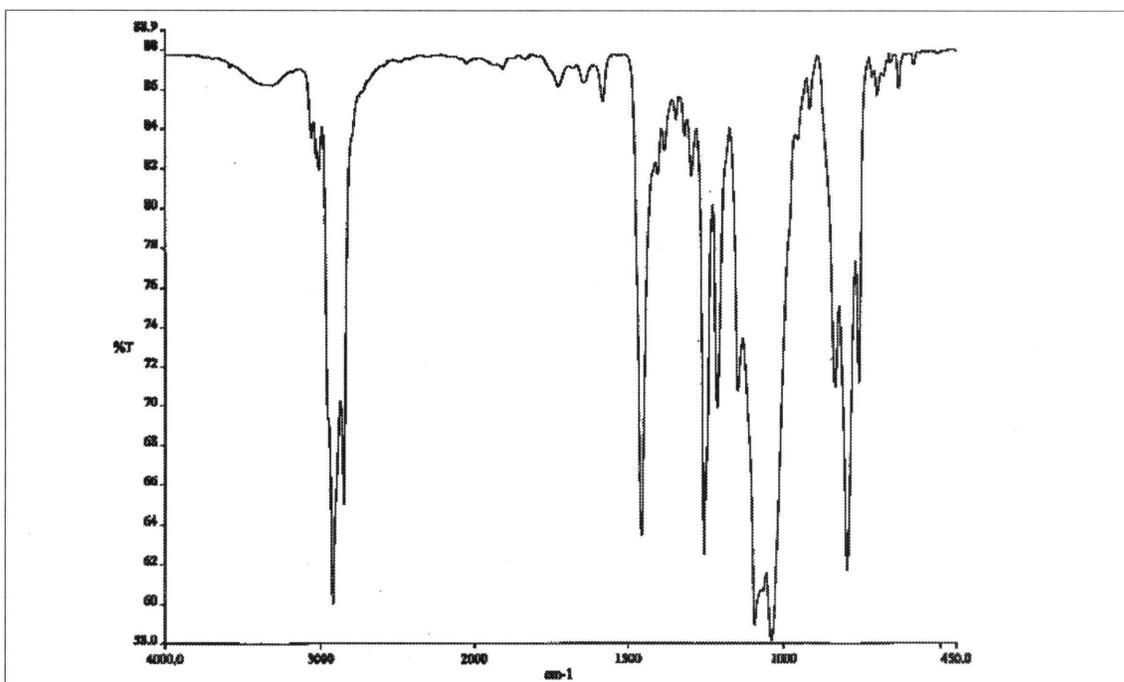
Spectrum 1: IR of Polymer 1 (7).



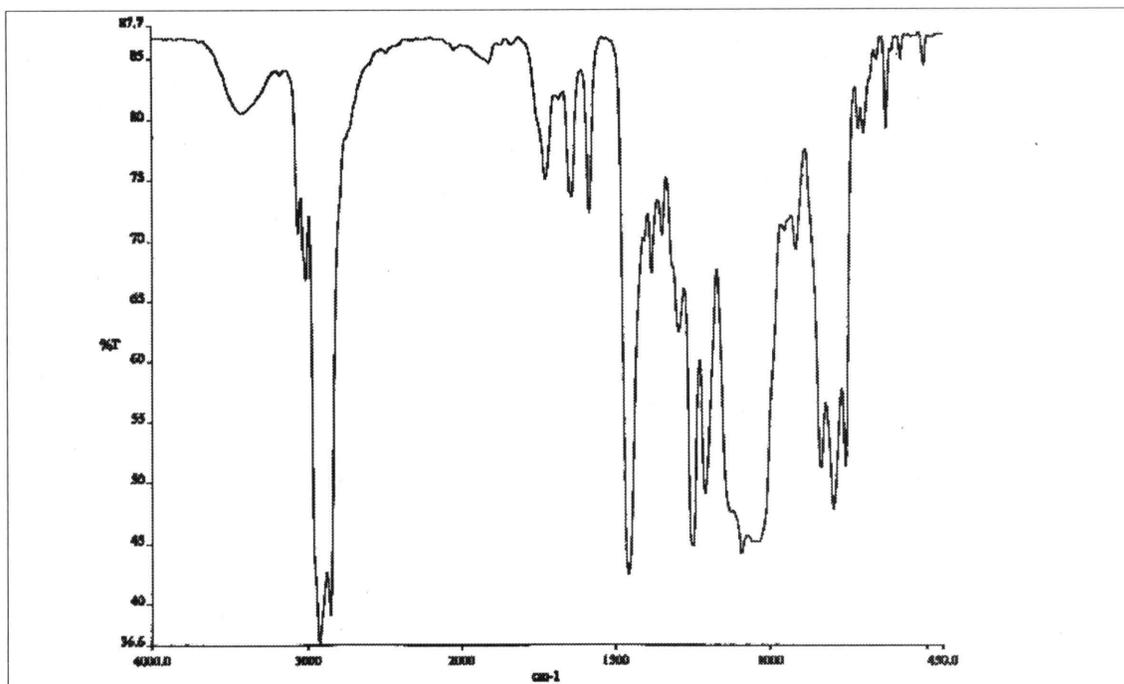
Spectrum 2: IR of Polymer 2 (8).



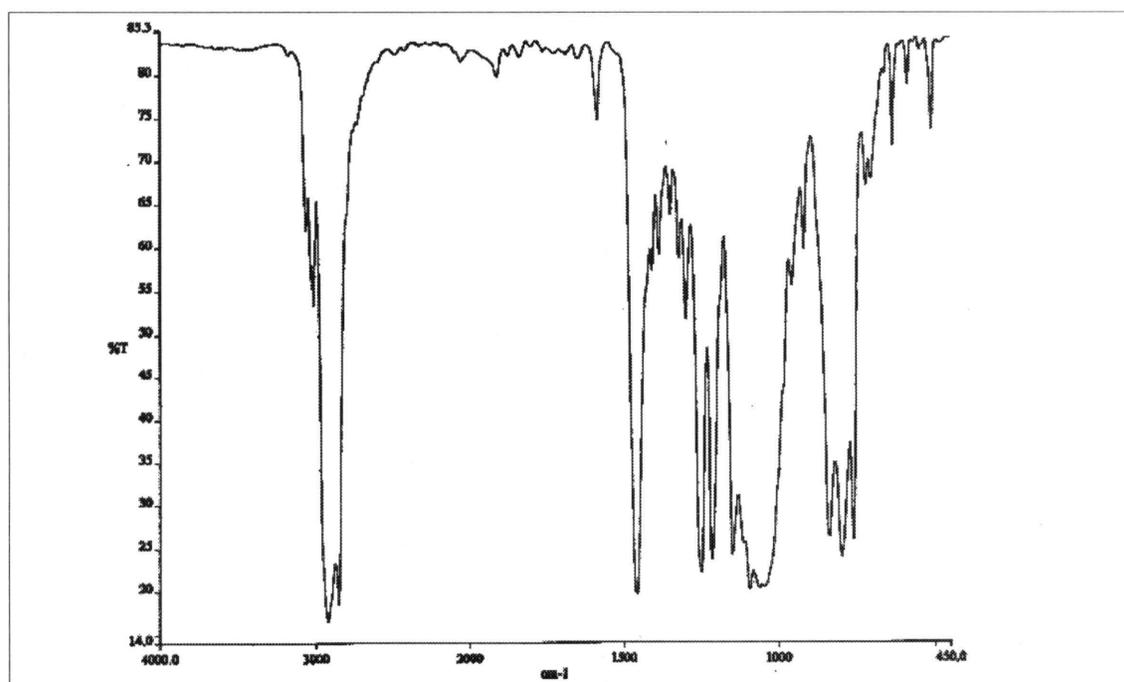
Spectrum 3: IR of Polymer 3 (9).



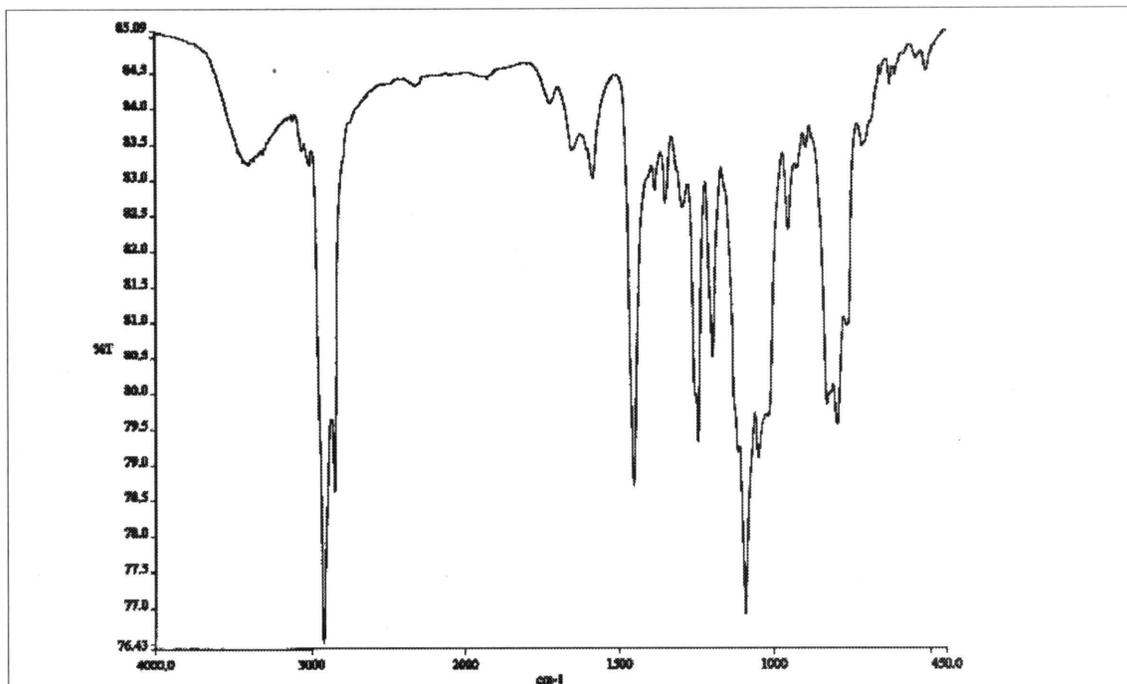
Spectrum 4: IR of Polymer 4 (10).



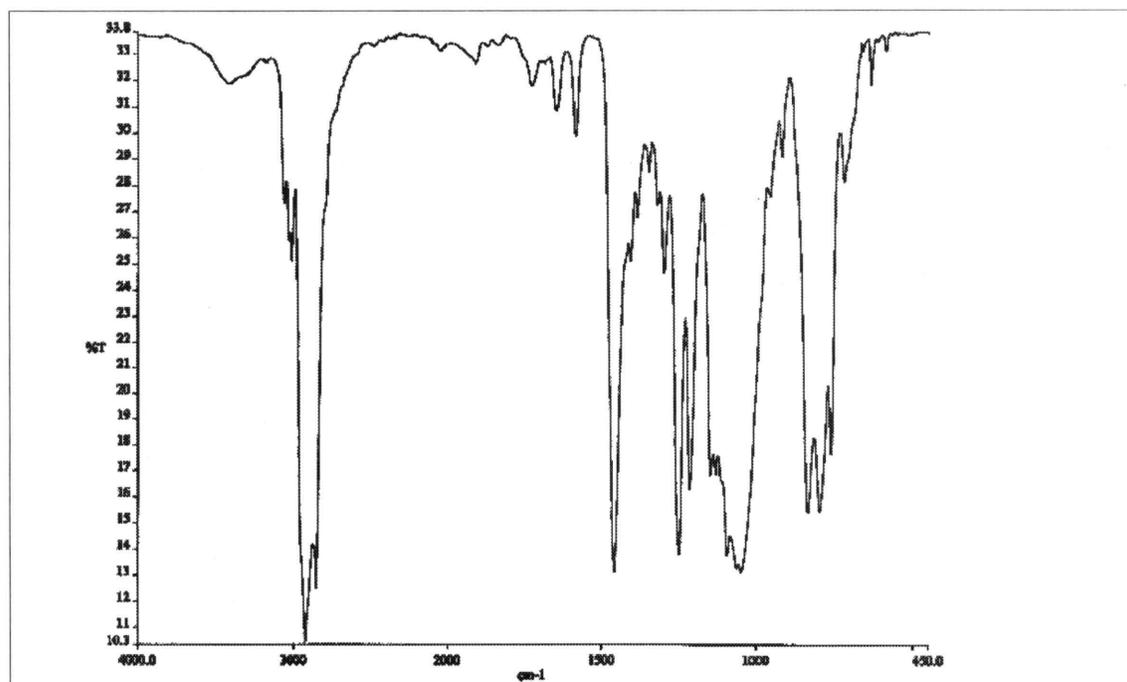
Spectrum 5: IR of Polymer 5 (11).



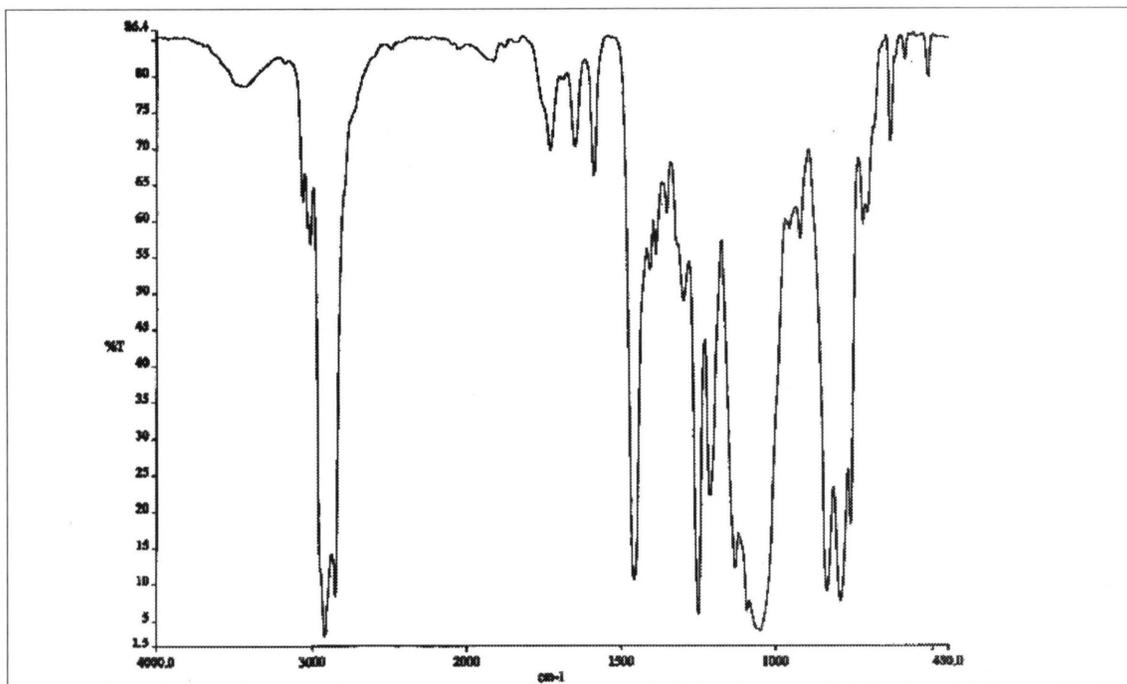
Spectrum 6: IR of Polymer 6 (12).



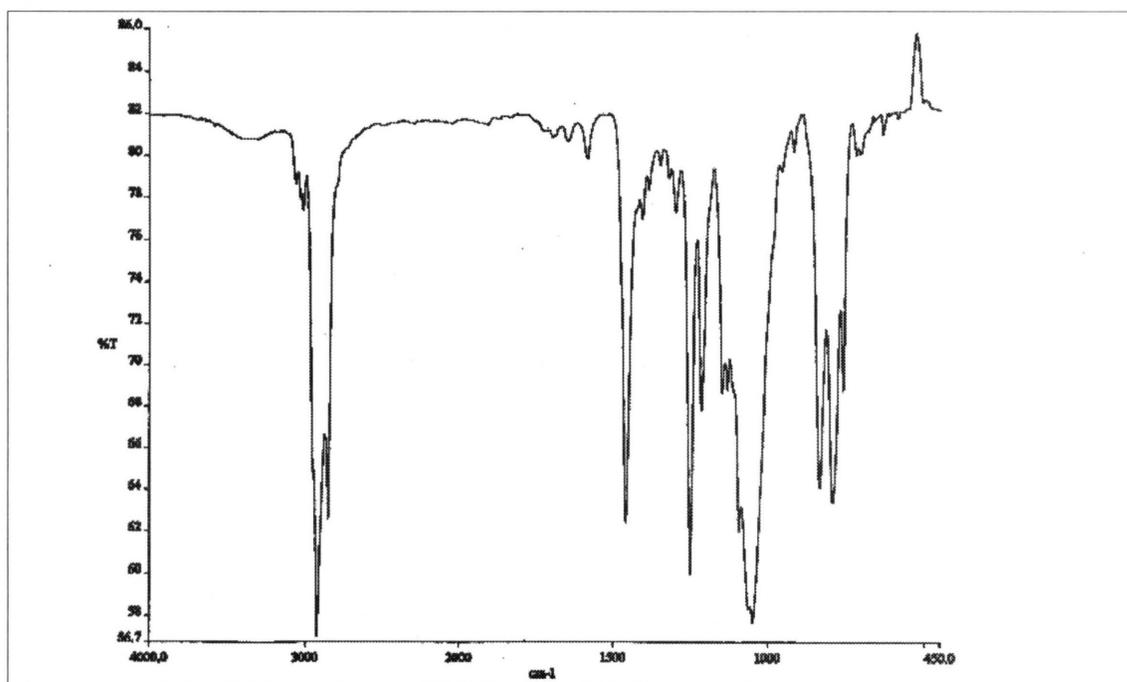
Spectrum 7: IR of Polymer 7 (13).



Spectrum 8: IR of Polymer 8 (14).

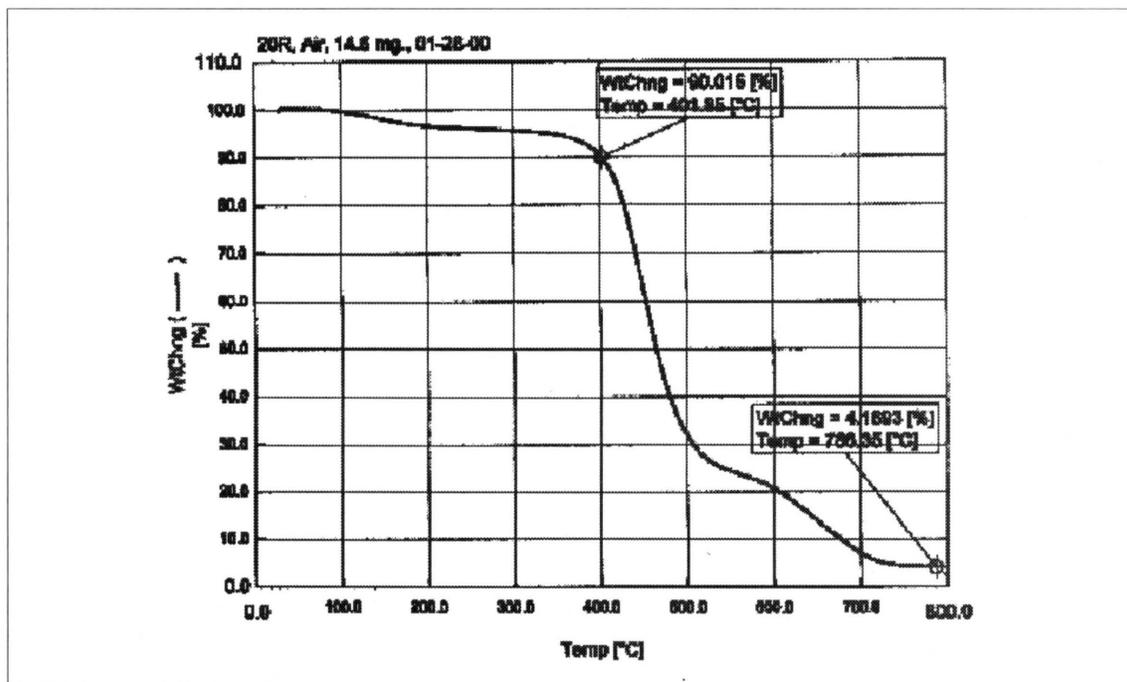


Spectrum 9: IR of Polymer 9 (15).

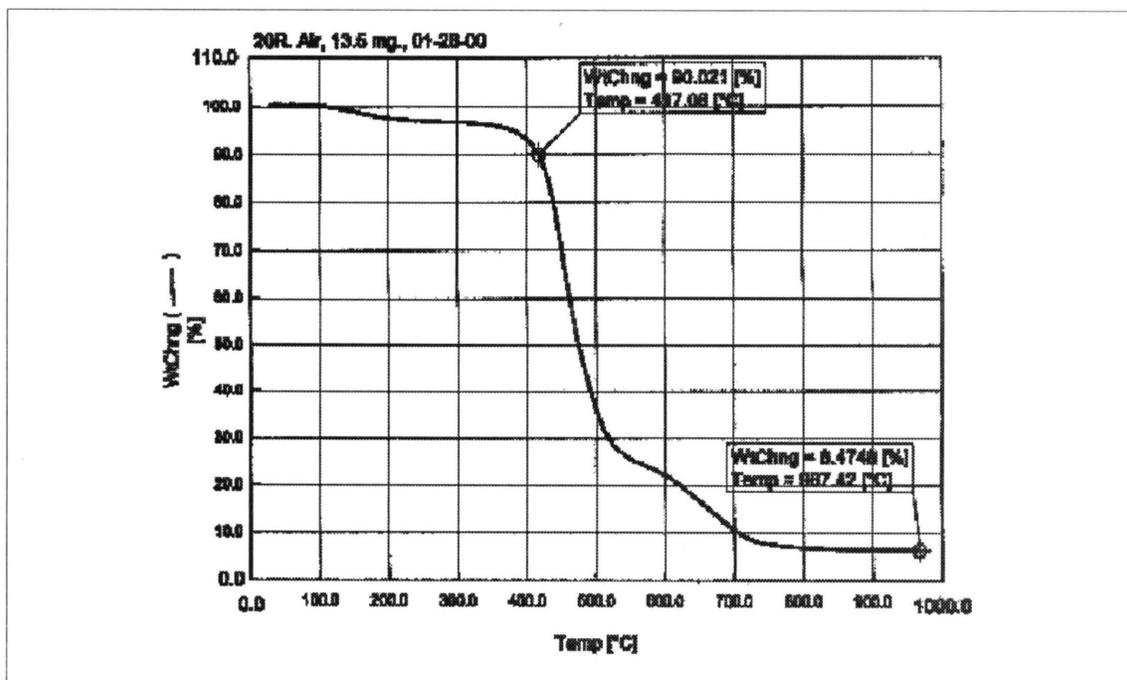


Spectrum 10: IR of Polymer 10 (16).

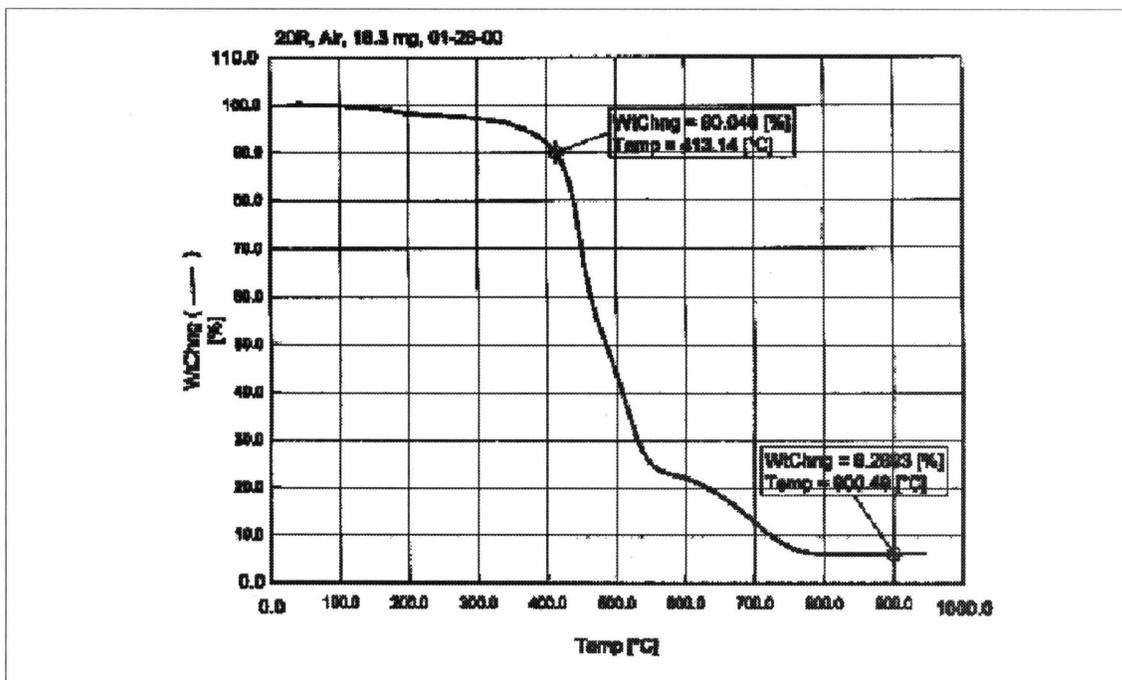
APPENDIX C. THERMOGRAMS



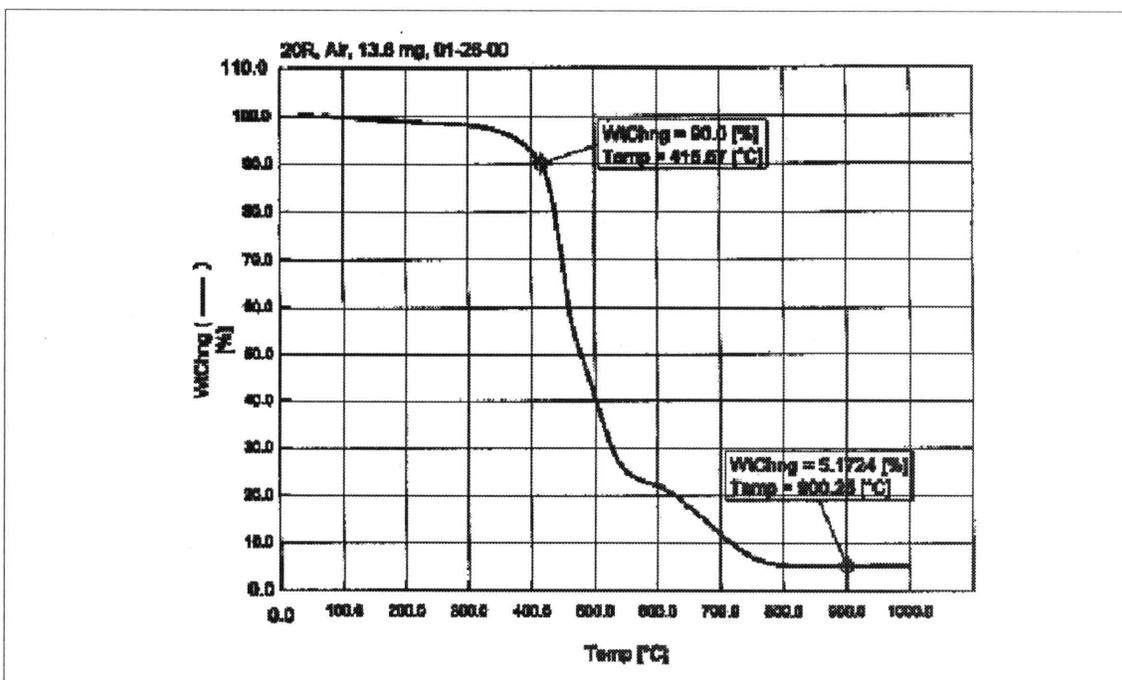
Spectrum 1: TGA of Polymer 1 (7).



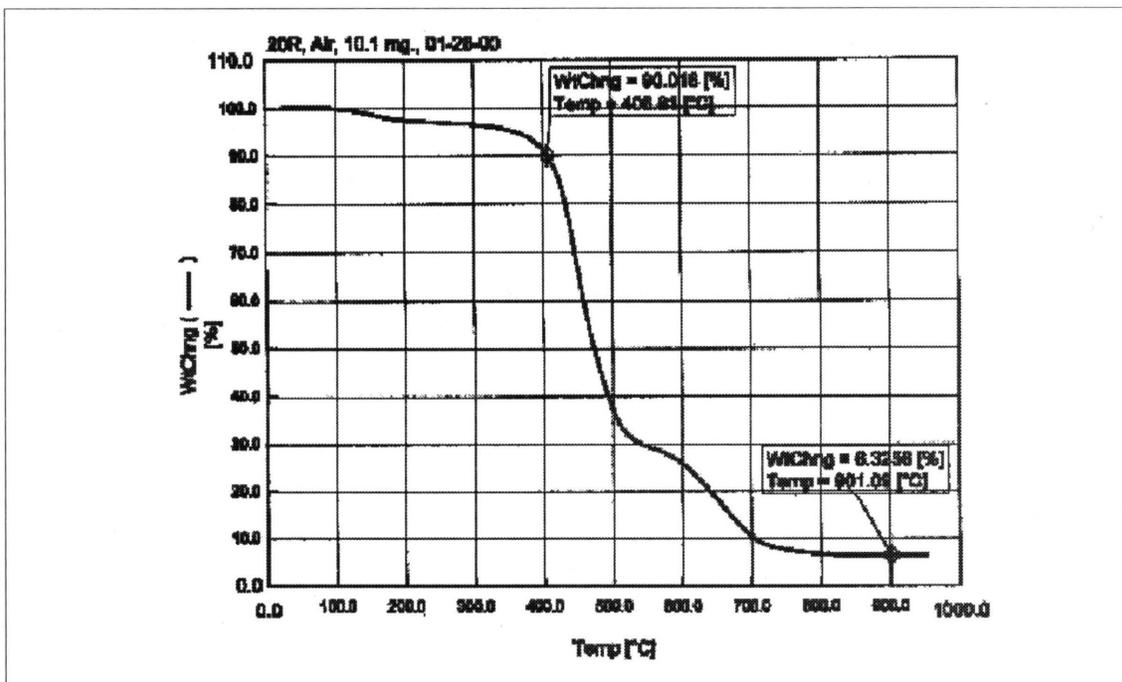
Spectrum 2: TGA of Polymer 2 (8).



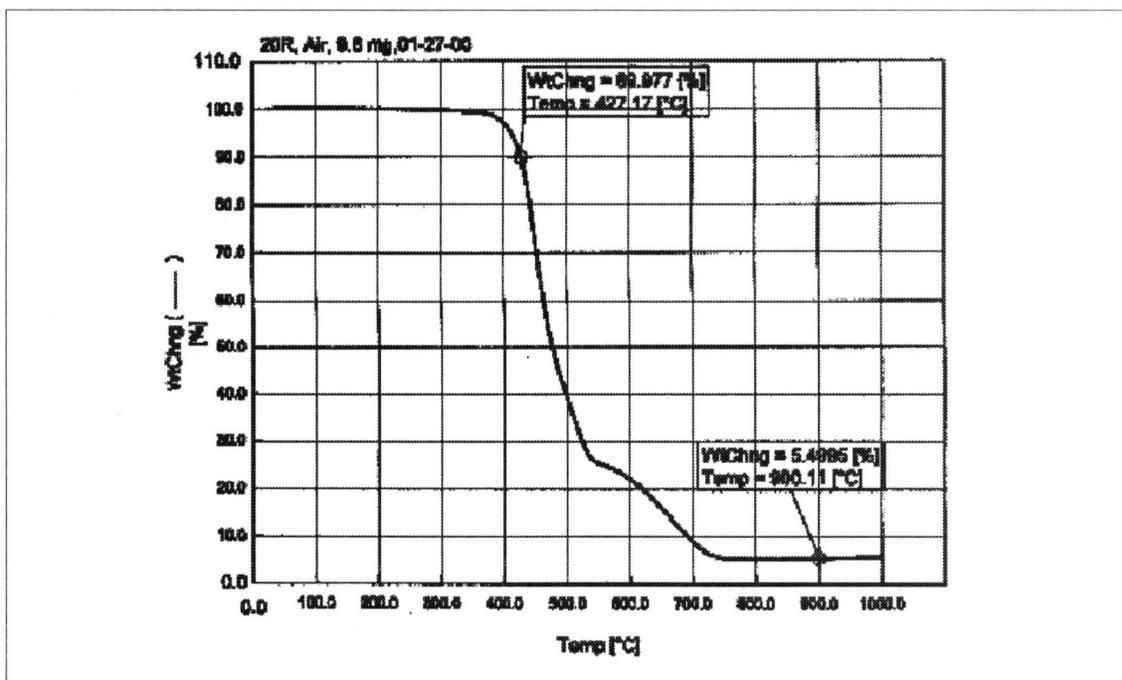
Spectrum 3: TGA of Polymer 3 (9).



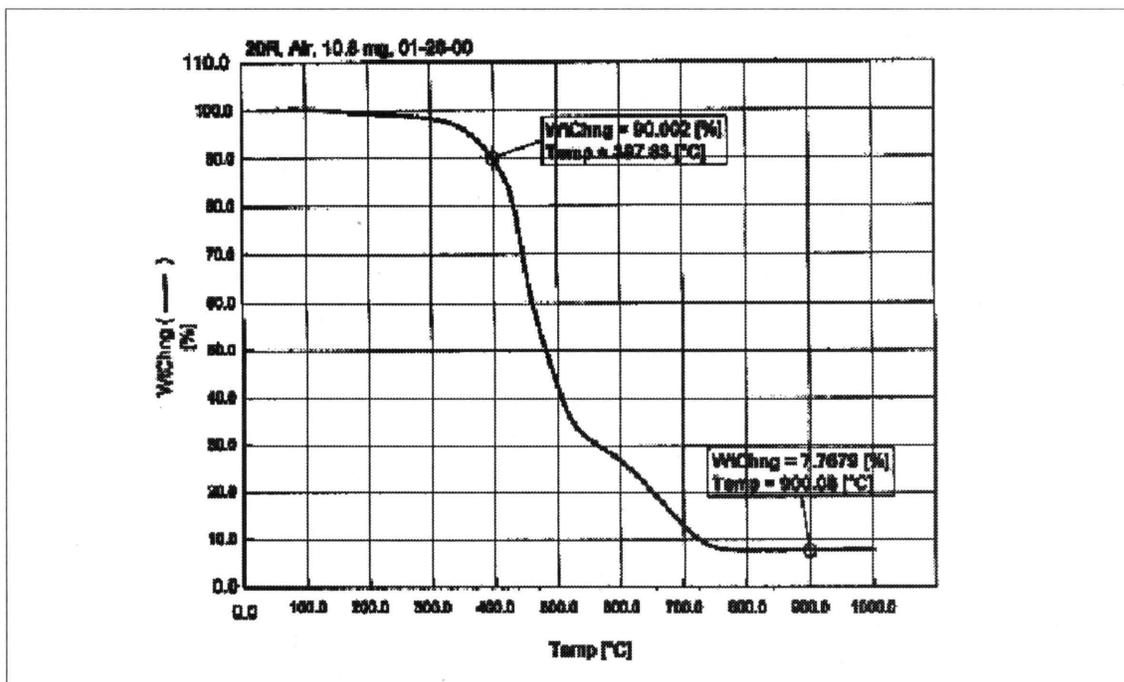
Spectrum 4: TGA of Polymer 4 (10).



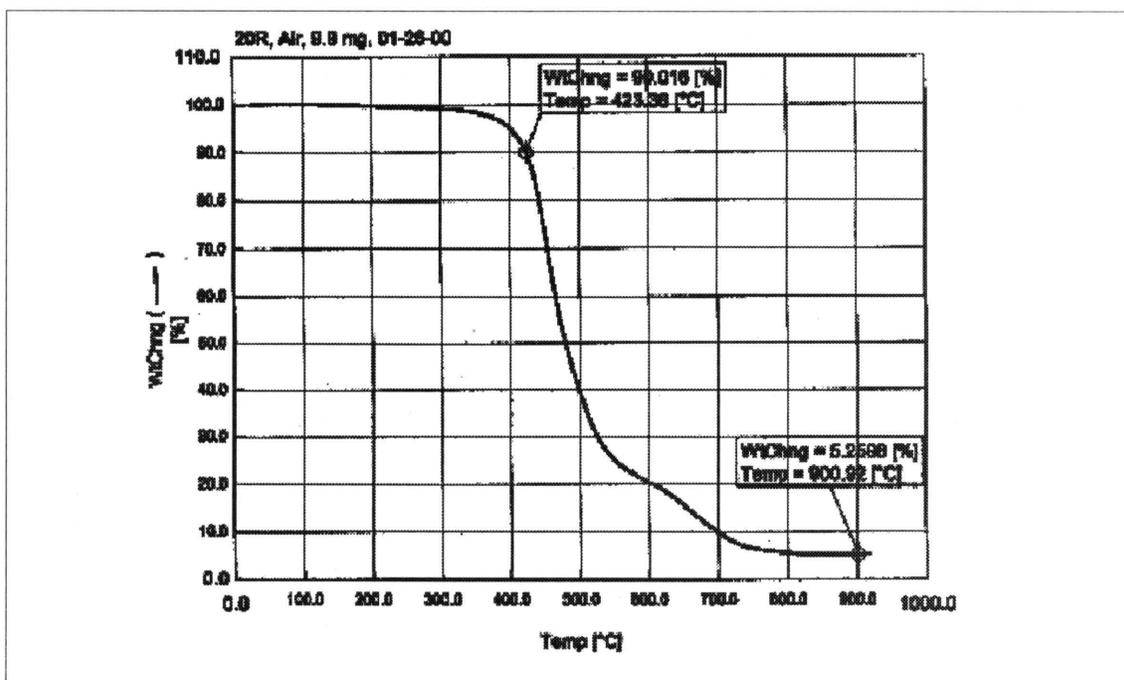
Spectrum 5: TGA of Polymer 5 (11).



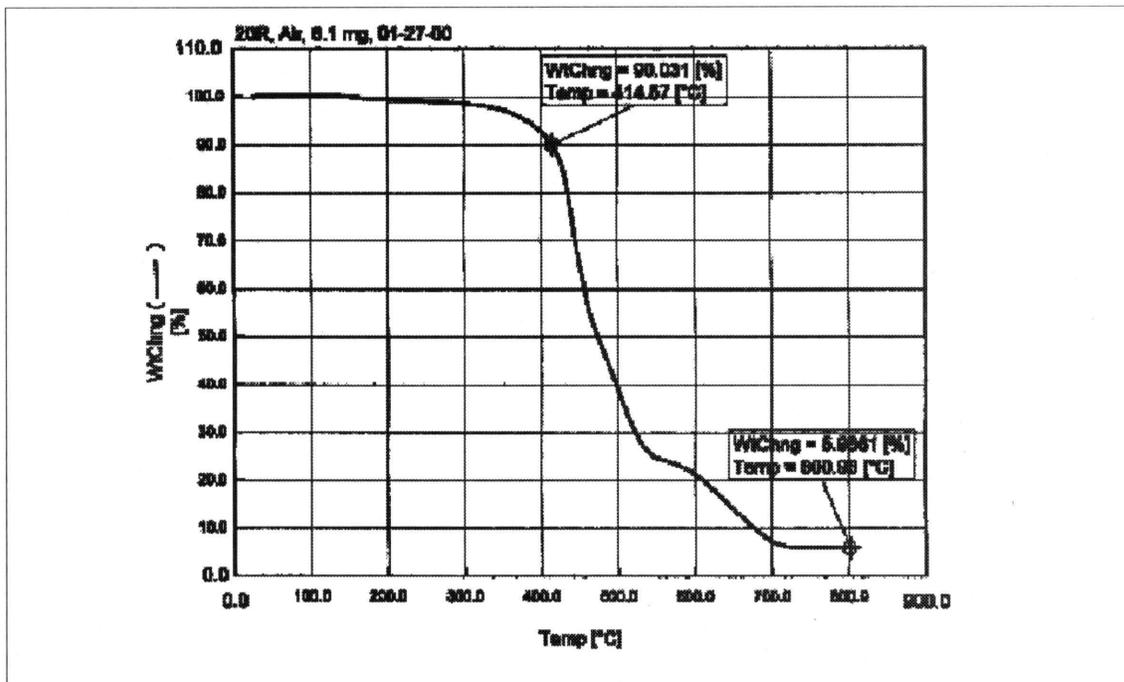
Spectrum 6: TGA of Polymer 6 (12).



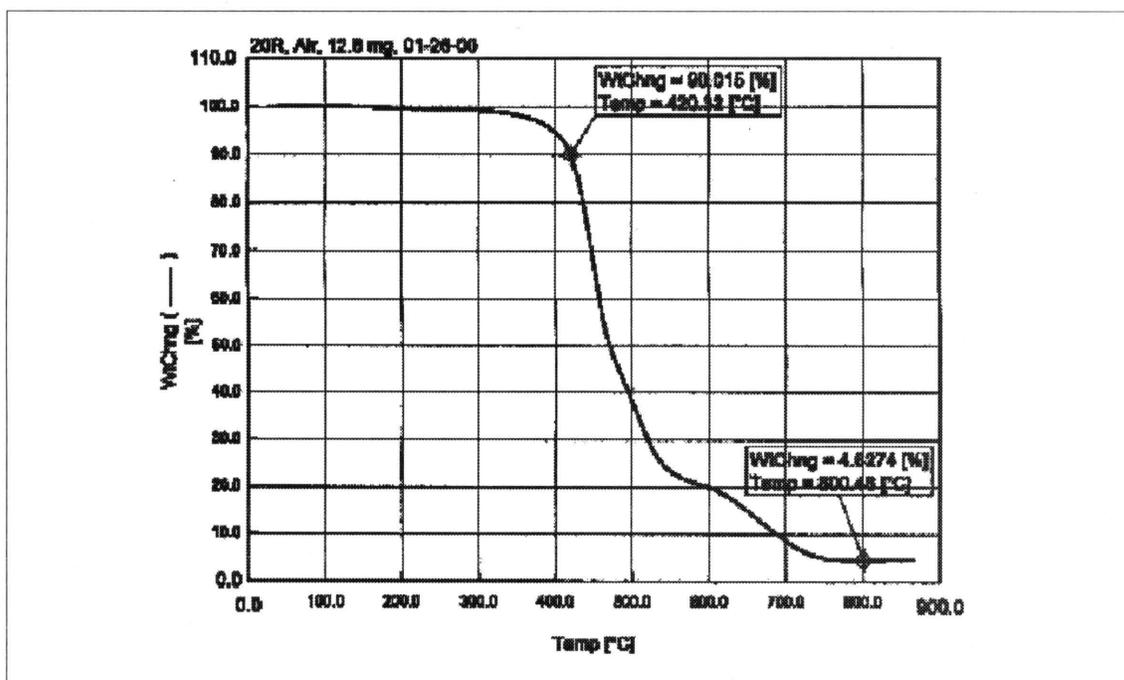
Spectrum 7: TGA of Polymer 7 (13).



Spectrum 8: TGA of Polymer 8 (14).



Spectrum 9: TGA of Polymer 9 (15).



Spectrum 10: TGA of Polymer 10 (16).