

HYDROSILATION POLYMERIZATION IN SUPERCRITICAL CARBON DIOXIDE

THESIS

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Partial Fulfillment of
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Master Of Science

By

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SUMMARY

Supercritical carbon dioxide (ScCO₂) has a number of unique and beneficial properties that have been utilized in several polymerization reactions. This thesis comprises the novel approach of the formation of polysilanes and siloxanes via the hydrosilation reaction in ScCO₂. The research involved the synthesis of two new, fluorine-containing, vinyl-functionalized monomers: 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene and 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene. These monomers were chosen as coreactants with a series of commercially available dihydride-silanes/siloxanes, because polysiloxanes and fluoropolymers have been shown to be particularly soluble in ScCO₂. The polymerization was carried out in two solvents: ScCO₂ and the traditional organic solvent, benzene. The polymers were characterized by standard characterization techniques: solubility, nuclear magnetic resonance spectroscopy (NMR, proton and carbon), infrared spectroscopy (IR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), gel permeation chromatography (GPC), water contact angle, and inherent viscosity.

The polymers showed good solubility in organic solvents. The polymers formed in ScCO₂ have as high or higher molecular weights than those obtained in organic solvent. Inherent viscosities were low, ranging from .02 to .05 dL/g. The decyl polymers have lower glass transition temperatures, and are more thermally stable than propyl polymer. Water contact angles ranged from 60 to 90°.

2.0 INTRODUCTION

2.1 Supercritical Fluids

2.1.1 Background

Significant progress has been made in recent years in the utilization of supercritical fluids (SCFs) as media for various polymer applications, which have a number unique properties that are beneficial to the chemical industry. SCFs are used for polymer synthesis, purification, extraction, and processing, and there is a high potential for the use of SCFs as solvents for various chemical transformations.

2.1.2 Properties

A SCF may be defined as the state at which a substance occurs when heated beyond its critical temperature and pressurized above its critical pressure (Figure 1). [1] Table 1 lists a number of SCFs and their critical parameters [2]. In general SCFs display properties that are intermediate between those of a liquid and a gas [3]. In addition, they are highly compressible and the density (and therefore the solvent properties such as dielectric constant, solubility parameter, and transport properties) can be tuned over a wide range by varying the temperatures and pressures (see Figure 2) [2]. This variable solvent strength has been used in extraction methods as well as in the precipitation of polymers from solution [1]. The variable solvent strength has also been used to facilitate the impregnation of polymers with various additives such as plasticizers and other modifiers. Ultimately, the unique properties of SCFs have been beneficial in the development of new polymer applications.

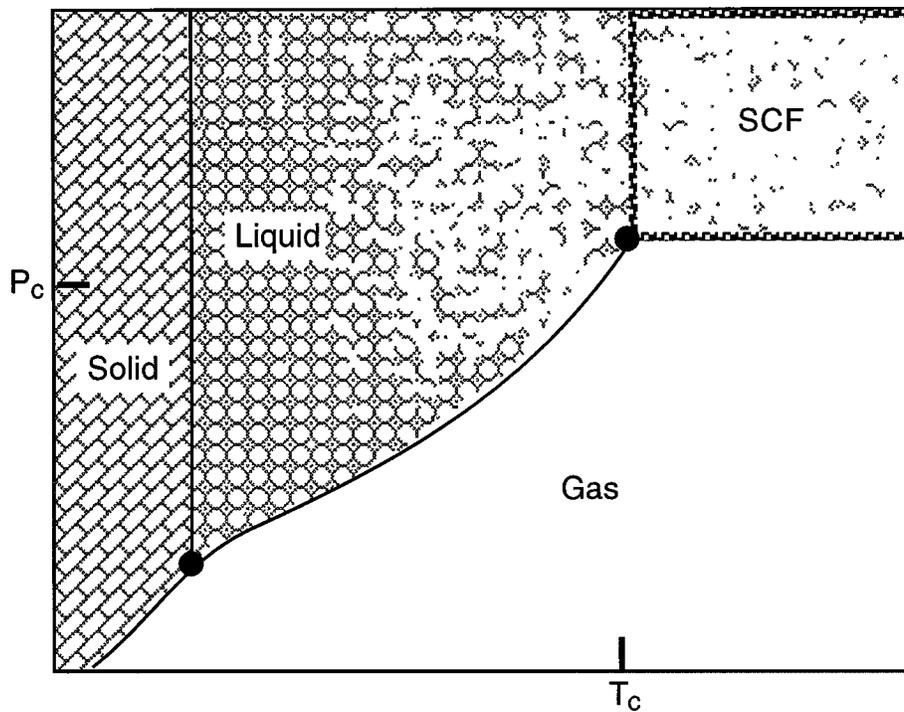


Figure 1. Schematic Pressure-temperature Phase Diagram for a Pure Substance Showing the Supercritical Region.

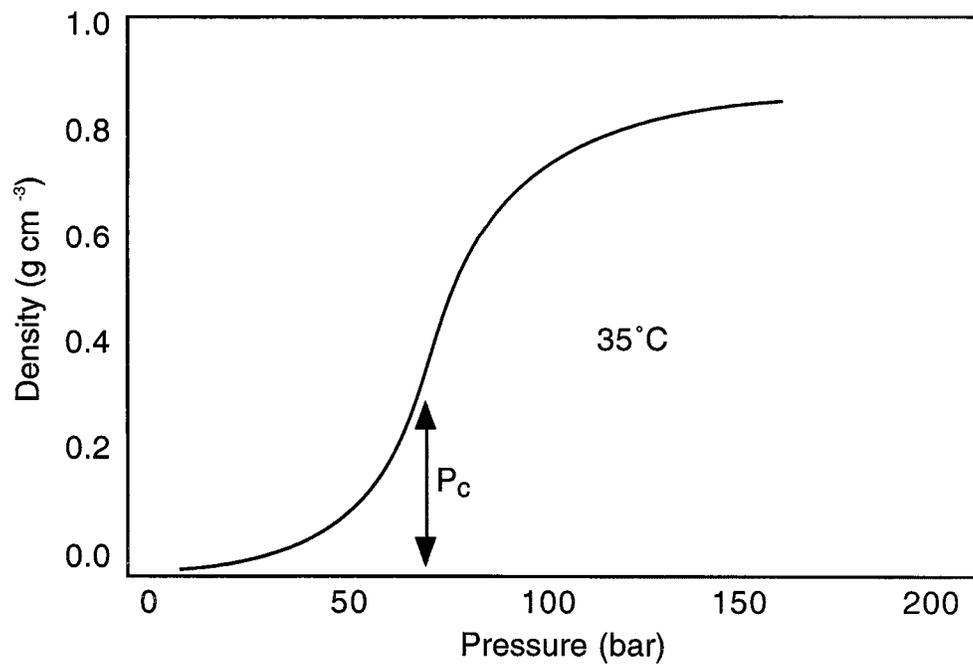


Figure 2. Pressure-density Dependence for Pure CO₂ at 35°C.

Table 1. Critical Parameters for Selected Substances

Substance	$T_c / ^\circ\text{C}$	P_c / bar^*	$\rho_c / \text{g cm}^{-3}$
CH ₄	-82.5	46.4	0.16
C ₂ H ₄	10.0	-51.2	0.22
C ₂ F ₆	19.9	30.6	0.62
CHF ₃	26.2	48.5	0.62
CClF ₃	28.9	38.6	0.58
CO ₂	31.1	73.8	0.47
C ₂ H ₆	32.4	48.8	0.20
SF ₆	45.6	37.2	0.73
Propylene	92.9	46.1	0.24
Propane	97.2	42.5	0.22
Pentane	187.1	33.7	0.23
iPrOH	235.4	47.6	0.27
MeOH	240.6	79.9	0.27
EtOH	243.5	63.8	0.28
iBuOH	275.1	43.0	0.27
Benzene	289.1	48.9	0.30
Pyridine	347.1	56.3	0.31
H ₂ O	374.2	220.5	0.32

* 0.06895 bar = 1 PSI

2.1.3 Supercritical Carbon Dioxide

Among the different SCFs, supercritical carbon dioxide (ScCO₂) is an attractive solvent, for polymer synthesis and processing. ScCO₂ offers a number of chemical, economical and environmental advantages with few disadvantages.

2.1.3.1 Chemical Advantages

CO₂ has easily accessible critical points ($T_c = 31.1^\circ\text{C}$ and $P_c = 73.8$ bar or 1070 PSI). CO₂ is also relatively inert and can be used as a solvent for a number of polymerization processes. It has been used for free radical chain growth, oxidative coupling, transition metal catalyzed, ring-opening-metathesis,

and melt phase condensation polymerizations. Carbon dioxide has a low dielectric constant (1.01-1.67), and its polarizability ($27.6 \times 10^{-25} \text{ cm}^3$) are similar to other gases such as methane, perfluoromethane, and fluoroform [2]. Under moderate conditions ($< 100^\circ\text{C}$, $< 5000 \text{ psi}$), ScCO_2 is a good solvent for many low molecular weight, non-polar molecules, and a poor solvent for most polar molecules [2]. ScCO_2 is a non-solvent for the many high molecular weight polymeric materials. However, certain amorphous fluoropolymers and silicones have shown good solubility in ScCO_2 . The increased solubility of fluoropolymers, is caused by a local density augmentation (solvent-solute clusters), which shields hydrocarbon main chains from interacting with the solvent. These clusters form as a result of CO_2 's structural symmetry. CO_2 does not have a dipole moment, it does however have an effective quadrupole moment that interacts over short distances. These local solvent clusters then form where the quadrupolar interactions dominate, such that CO_2 preferentially clusters near the C-F bonds, which are more polar than the C-H bonds (see Figure 3). The solubility of silicones is due to the flexible nature, and larger free volume of these polymers [4].

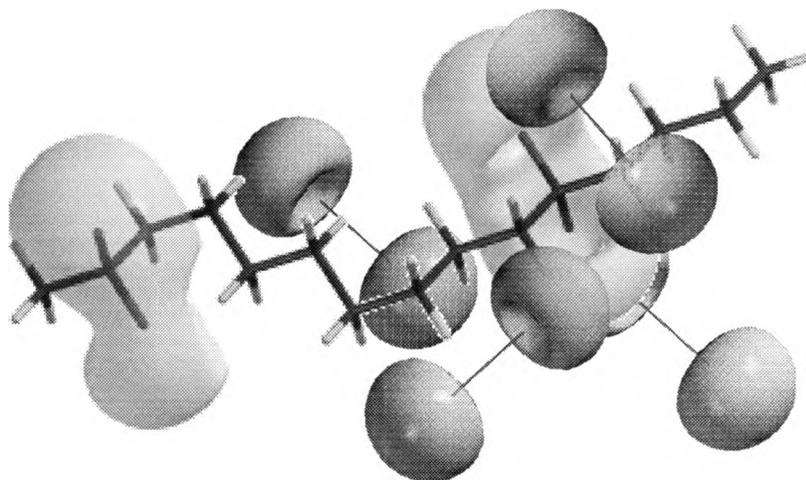


Figure 3. Preferential Clustering of CO_2 at the Fluorine Atom of the C-F Bond.

For nonpolar polymers ScCO_2 acts as a nonsolvent. However, this lack of solubility in common polymers does have its advantages. [ScCO_2 is an excellent solvent for heterogeneous polymerization techniques, (*suspension, emulsion, dispersion*) where it is necessary that the polymer be insoluble in the continuous phase]. ScCO_2 's poor solvent strength can also be employed to purify polymers by selectively removing low molecular weight species. ScCO_2 has also been used in the formation of polymer particles by antisolvent precipitation [52]. The advantages here is that, selective particle sizes can be achieved, by selectively tuning ScCO_2 's solubility parameters to hold a particle in solvent until the desired size is achieved. The lack of solubility of common polymers in ScCO_2 has other unique advantages as well. Many common commodity polymers will swell in ScCO_2 [52]. They can then be infused with various additives such as plasticizers and other modifiers, and polymer blends can be formed by infusing monomers and initiators into the swollen polymeric host [52]. For instance, unique polymer compositions can be achieved by infusing commodity polymers with higher performance-fluorinated materials. These heterogeneous materials have unique physical properties, that often resemble those of the higher cost high performance polymers at the price of common commodity plastics. The lack of solubility of common polymers in ScCO_2 can be overcome through the use of custom-synthesized fluorinated or silicon surfactants, and other reagents [5]. The use of these CO_2 -philic materials has been very successful; but, one must also consider the cost of developing these new CO_2 -philic materials, and whether the economic and environmental advantages of using ScCO_2 can counter the cost.

2.1.3 .2 Economical Advantages

There are a number of economical advantages to using ScCO_2 as a solvent. CO_2 is inexpensive, nontoxic, non-flammable and readily available

from a number of sources [6]. In addition, CO₂ is inert towards free radicals and cations under common polymerization conditions [2]. For an industrial process this is an important advantage because it eliminates chain transfer to the solvent, and therefore, cuts the cost of reinitiating the polymerization. Industrial scale condensation polymerizations can also benefit by using ScCO₂. In these systems the reaction is carried out in the melt phase and is driven by the removal of a small molecule-condensate, which are usually removed by costly high-vacuum systems. Furthermore, as the polymerization proceeds, the higher molecular weight polymer will trap the smaller condensate molecules in the growing polymer matrix. ScCO₂ can be used to solve both of these problems, in that it has some ability to plasticize and reduce the viscosity of the polymer matrix, while at the same time solvate and thus selectively remove the small condensate molecules, thereby driving the reaction to completion. Other organic solvents could do this as well, but it is costly to remove them from the polymer matrix. The advantage of CO₂, is that it can be easily separated from the polymer matrix by reducing the pressure and allowing it to revert to the gaseous state. The CO₂ can then be recovered, recycled and the polymer removed from the vessel as a dry-solvent-free product. By using ScCO₂ there is also a reduction/elimination of toxic organic solvents [2].

2.1.3.3 Environmental Advantages

ScCO₂ is an excellent candidate for replacing the environmentally (or otherwise harmful) and/or flammable organic solvents. ScCO₂ which has been used in food, fragrance, and petroleum processes for years in the extraction of many common compounds has proved to be an environmental and economical viable solvent. Recently, there has been interest in using ScCO₂ in other industrial processes as well. This has been brought on by the necessity to

replace chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) solvents. There have been a number of strict limitations imposed on the use of these solvents, because they have been correlated to the depletion of the earth's ozone layer. In 1987, representatives of industrialized countries from around the world, drafted the Montreal Protocol, an agreement which sets forth a global commitment to ban the use of all chlorinated fluorocarbons (CFCs) by the new millennium which are to be phased out completely by the year 2025 [7]. Both CFCs and HCFCs are widely used in the manufacture of polymer foams. Consequently, manufacturers that are looking for replacements for CFC are investigating carbon dioxide-based processes. In the traditional method foams are formed by dissolving the polymer in the required organic solvent followed by heating, and then inducing a phase separation through a thermal quench, followed by solvent removal. The alternative ScCO_2 process is carried out at moderate temperatures followed by rapid depressurization, (a pressure quench vs. temperature quench) [8].

Many industrial facilities which currently use CFCs for cleaning a variety of items are facing a difficult situation because of the banned use of CFCs. These companies must implement environmental and economical replacement technologies for cleaning applications. ScCO_2 is an alternative technology that uses a solvent that is both easily recycled and environment friendly. Large-scale bulk (dry-cleaned clothes) and precision (printed circuit boards, plastics, metals, rubbers, composites, and glasses) cleaning operations have been developed. ScCO_2 has shown to be an excellent cleaning solvent for many organic contaminants. However, many substances requiring removal of inorganic or ionic contaminants, so current research focuses on $\text{ScCO}_2/\text{ScH}_2\text{O}$ solutions [7]. ScCO_2 is also rapidly replacing CFCs traditionally employed in polymer processing and synthesis. CFCs are regularly used in the synthesis and

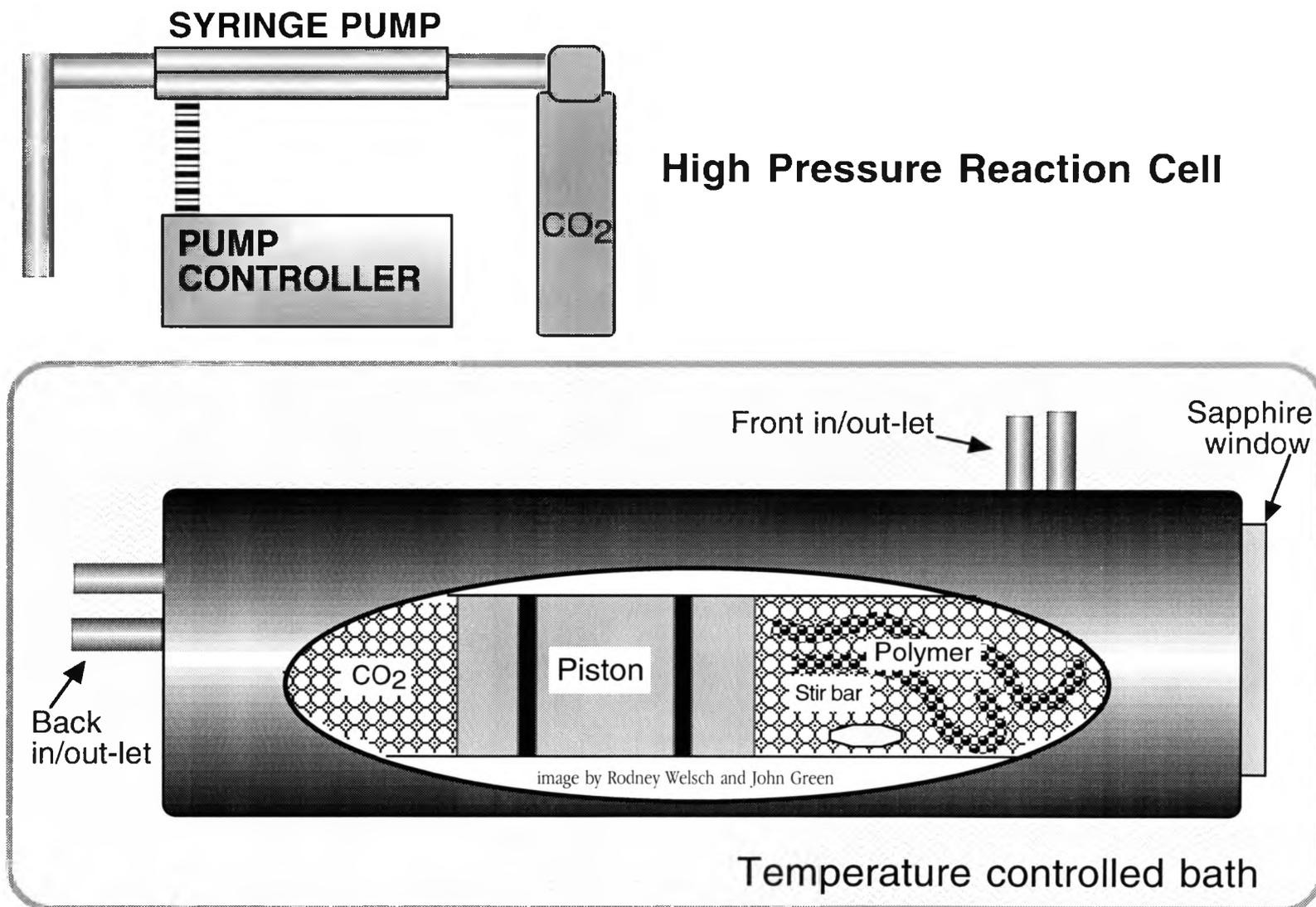
processing of fluoropolymers. As mentioned, ScCO_2 is an excellent solvent for fluoropolymers, with the added benefits of being nontoxic, non-flammable and inexpensive.

2.1.3.4 ScCO_2 Disadvantages

The major disadvantage to using ScCO_2 is the higher pressure necessary to bring about supercritical conditions. High pressure syringe pumps are needed to maintain the supercritical conditions and therefore, a small-scale reactor must be constructed of materials to withstand the high pressures. [9] In addition, they must be inert to other reagents. For high-temperature polymerizations, consideration of construction materials is especially important. Since most high-temperature sealing materials are fluorinated, they will exhibit some solubility in ScCO_2 swell and possibly fail. Also, during polymerization reactions as larger molecular weight polymers form, the solution becomes more viscous and difficult to stir. The reaction cell must be designed to allow for good mixing while still maintaining the high pressures. The cell must also be constructed so that it allows for the addition or removal of reagents during the reaction process. Current small-scale reactors are constructed of stainless steel, (see Figure 4). Short-term, low-temperature sealing materials that have been used include (Acetal®, Teflon® and Buna®); longer duration, higher temperature materials include (gold and copper rings, and graphite infused polyimides). More basic engineering will be needed to minimize or eliminate these obstacles.

For the chemist a more significant problem is at hand: the lack of solubility of common surfactants, reagents and catalysts. This problem will have to be addressed by designing new CO_2 -philic analogues of these materials. The most promising will be the development of custom-synthesized fluorinated or silicon analogues. These CO_2 -philic analogues will be the key to acquiring the economic and environmental advantages that can be gained by using ScCO_2 .

Figure 4. Viewable Variable-volume SCF Reactor Cell.



2.2 Silicon Chemistry

2.2.1 Background

Silicon is the second most abundant element on Earth. [11] However, silicon is never found in nature as the free element, but rather in combination with oxygen, the most abundant element. Silicon plays a vast role in materials today. In its relatively natural state it is in the form of silicon dioxide, SiO_2 , termed "silica". In its various amorphous forms, it is found in materials like granite, sand, and clay. In this state it is used in large quantities as a constituent of building materials, ceramics, concretes and glasses. At the performance end of the spectrum, wafers of silicon are used in the construction of electronic circuits found in virtually every computer built. Silica is also the sole source of elemental silicon which is used to synthesize organosilicon compounds, as none exist naturally. [11] Silicon-containing compounds and their polymer derivatives are generically known as silicones. Silicones are classified by their polymer backbone, and have the general formula $(\text{R}_n\text{SiX}_{(4-n)/2})_m$ where $n = 1-3$, $m =$ number of repeating units, R is an organic functional, or hydrogen or chlorine group, X can be oxygen, nitrogen, fluorine, an organic molecule or nothing at all. Organosilicon polymers share a number of useful traits: thermal stability, resistance to age, sunlight, moisture, temperature extremes, and exposure to many chemicals. Variation of the organic substituents, the number and type of repeat units in the chain, and the degree of cross-linking, afford the use of silicones in a wide range of commercial applications. Today 475,000 metric tons, worth \$3,500,000,000, of silicon-containing materials are produced worldwide, mainly as fluids, resins, and elastomers. [10]

2.2.2 Physical Properties of Silicon

Silicon, as mentioned, is the second most abundant element on Earth. It

exist as three isotopes (^{28}Si , 92.21 %), (^{29}Si , 4.70 %), (^{30}Si , 3.09 %) with respective spins of 0, 1/2, 0. Silicon is found in the same element group on the periodic chart as carbon, and their respective physical properties are often compared. Silicon's atomic radius and covalent radii are larger than carbon's (106 vs 66 Å and 117 vs 77 Å respectively). The first ionization potential is 187.9 k cal mole⁻¹ for silicon and 259.0 k cal mole⁻¹ for carbon. Silicon's electronegativity is 1.8 compared to carbon's 2.5 and hydrogen's 2.1. This is an important feature to point out, since silicon is more electropositive than hydrogen; the Si-H bond is polarized with Si⁺ and H⁻. Table 2 summarizes some average bond energies for silicon and carbon compounds. [14]

Table 2. Silicon Bond Energies

Bond	\bar{D} (Si-X)	Bond	\bar{D} (Si-X)
Si-Si	226	C-C	346
Si-C	317	C-H	413
Si-H	351	C-Cl	338
Si-Cl	397	C-N	305
Si-N	455	C-O	358
Si-O	464	C-F	485
Si-F	698		

kJ mol⁻¹

The bond dissociation energy for the Si-H bond lies in the range 351 - 435 kJ mol⁻¹. They are generally slightly weaker than the analogous C-H bonds which average 413 kJ mol⁻¹ in organic compounds. The Si-C bond is as strong as and in some cases stronger than, the analogous C-C bonds. For instance, the Si-C bond is 317 kJ mol⁻¹; with Me substituents it increases to 374 kJ mol⁻¹. This can be explained by the partial positive charge on silicon which acts as an electron drain polarizing the methyl group and rendering it less susceptible to attack, compared when at carbon the Me substituents weakens the C-C bond strength.[10] The Si-Si bond energy, 226 kJ mol⁻¹, however, is much weaker

than the analogous C-C bond at 346 kJ mol⁻¹. At the extreme are Si-halogen bonds which show extraordinarily high strengths. The Si-F bond at 698 kJ mol⁻¹, is the strongest single bond known. The analogous C-F bond is 485 kJ mol⁻¹. Si-O 464 kJ mol⁻¹ and Si-N 418 kJ mol⁻¹ bonds are also much stronger than their carbon counterparts.

2.2.3 Silicon-containing Polymers

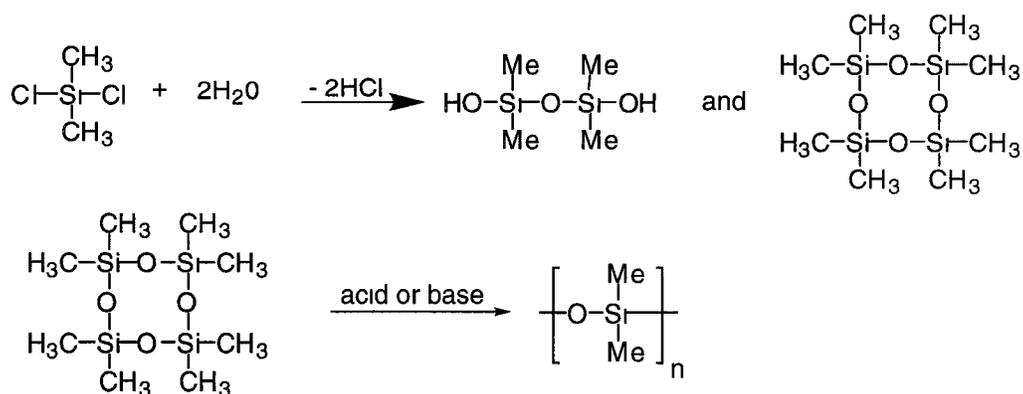
2.2.3.1 Classification

Silicon-containing polymers are classified by their polymer backbone, and have the general formula $(R_nSiX_{(4-n)/2})_m$ where $n = 1-3$, $m =$ number of repeating units, R is an organic functional, or hydrogen or chlorine group, X can be oxygen, nitrogen, fluorine, an organic molecule or nothing at all. Polysilanes which have a continuous backbone of silicon atoms; show lower solubility, higher glass transitions temperatures and perhaps most important unique optical properties. Polycarbosilanes which have the elements silicon and carbon alternating in the molecular skeleton forming Si-C-Si linkages, often serve as precursors which are converted to silicon carbon fiber *via* two stage pyrolysis. [15] Polysilazanes which have a backbone consisting of silicon and nitrogen; are used to produce silicon nitride for dielectric coatings for microelectronics. [12] Polysemiinorganics are silicones where inorganic elements constitute at least part of the polymer backbone. This has been an highly active area of research resulting from attempts to improve the high thermal stability of the organic polymers. This class includes silicone-polycarbonates, silicone-urethanes and silicone-acrylates. [16] Polysiloxanes are polymers with a backbone composed of alternating atoms of silicon and oxygen. These were the first silicones synthesized, and they have the largest commercial use.

2.2.3.2 Synthesis

2.2.3.2.1 Poly-condensation Synthesis

The most common siloxane polymer, polydimethylsiloxane, (PDMS), is formed when the chlorine atoms of the monomer, dichlorodimethylsilane ($\text{Si}(\text{CH}_3)_2\text{Cl}_2$), are replaced by hydroxyl groups by hydrolysis, forming a silanol ($\text{Si}(\text{CH}_3)_2(\text{OH})_2$). The silanol subsequently condenses under acidic or mild basic conditions in a step-growth fashion to form the polymer with concomitant loss of water. [17] Some cyclic products are also formed, which can be polymerized by ring opening polymerization as shown in Scheme 1. In the presence of a base catalyst the cyclic compound reacts faster than the growing polymer. As the cyclic species are consumed and the concentration of polymer increases, the system proceeds through a maximum molecular weight. In the presence of acid-catalyzed polymerizations, the polymer backbone is more reactive than the cyclic monomers. The reaction is characterized as a redistribution reaction in which no maximum molecular weight is observed. [10]



Scheme 1. Polysiloxane Ring Opening Polymerization.

2.2.3.2.2 Hydrosilation Synthesis

2.2.3.2.2.1 Hydrosilation Mechanism

Hydrosilation is another excellent method for preparing silicone polymers. The hydrosilation reaction, namely the addition of a silicon hydride (Si-H) bond to a multiple bond, was first reported in 1947 by Sommer, Pietrusza and Whitmore [19]. While the addition may be to a C=O, C=N, N=N, N=O, or C≡C bonds, the most common and the one which is of most use in the preparation silicon compound is to the C=C double bond. [The driving force for the reaction is the exothermic enthalpy change of turning the C=C π-bond into σ-bonds]. [14]

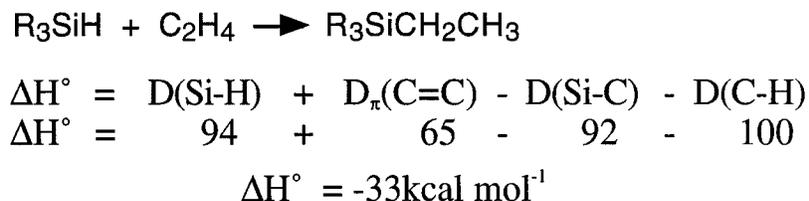
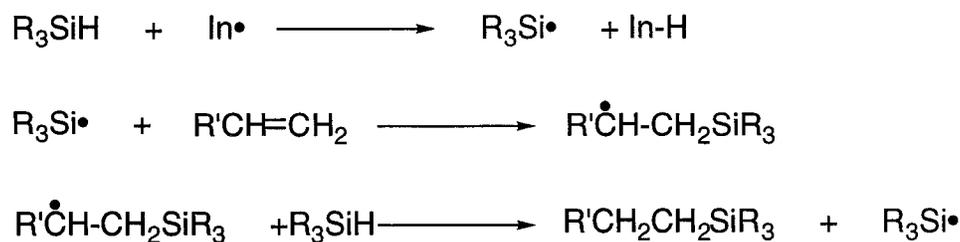


Figure 5. Enthalpy Change of Hydrosilation of Ethene.

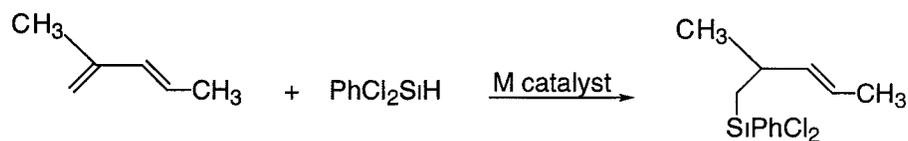
The hydrosilation reaction is generated in a variety of ways, including heat, peroxide, light, amines, and transition metal complexes. It proceeds with regioselectivity with anti-Markovnikov addition, with electronegative groups on silicon accelerating the reaction with a reactivity sequence of $\text{Cl}_3\text{SiH} > \text{Cl}_2\text{MeSiH} > \text{Et}_2\text{SiH}_2 > \text{Et}_3\text{SiH}$. [12]

The free radical reaction pathway, brought about by heat, peroxides or irradiation proceeds via the $\text{R}_3\text{Si}^\bullet$ radical, which then adds to the double bond.

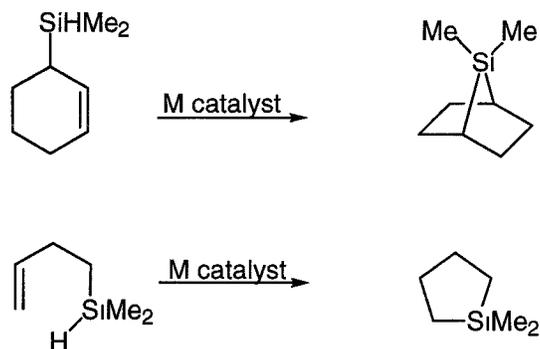


Scheme 2. Free Radical-initiated Hydrosilation. [12]

The transition metal complex pathway proceeds with a number of homogeneous and heterogeneous catalysts derived from palladium, platinum, and rhodium. As with the free radical-initiated hydrosilation, anti-Markownikoff addition is observed. Terminal double bonds react preferentially over internal double bonds as evidenced from the reaction in Scheme 3 [12]. The reaction can also be intramolecular, as shown in Scheme 4.

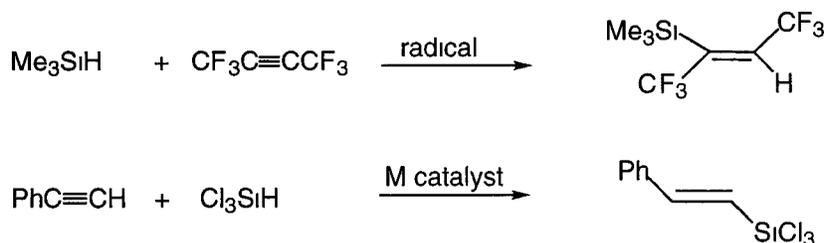


Scheme 3. Metal-catalyzed Hydrosilation.



Scheme 4. Intramolecular Metal-catalyzed Hydrosilation.

The hydrosilation of alkynes proceeds to produce a trans product with free radical catalysts and cis with metal catalyst.

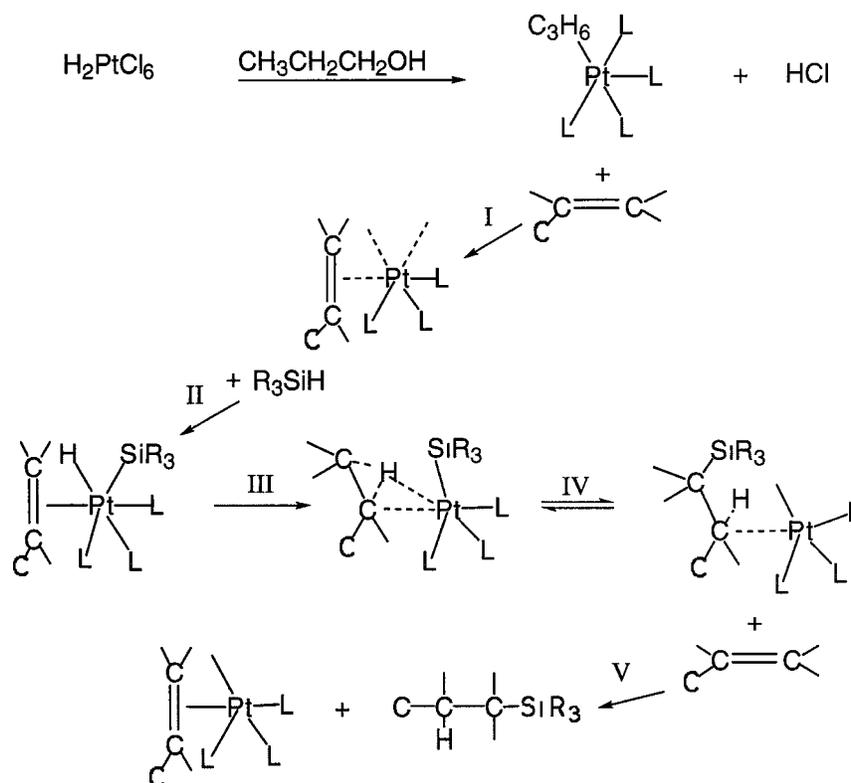


Scheme 5. Hydrosilation of Alkynes.

In 1957, J. L. Speier discovered the activity of hexachloroplatinic acid (CPA) as a hydrosilation catalyst. This material had such a high efficiency that it soon became the most highly used method for forming Si-C bonds. CPA has the advantage of being effective at very low concentrations (10^{-5} M), and the ability to carry out the reaction with or without solvent at room temperatures [18]. The catalyst is also very tolerant of a range of organic functional groups, including cyano, ester, amino, sulfonic esters, borate esters, and phosphine oxides, among others.

Following the discovery of Speier that chloroplatinic acid in isopropanol would catalyze the hydrosilation reaction many chemists have investigated the mechanism. Benkeser and Kang [24] reported that the isopropanol is oxidized to propanone, and that the Pt(IV) is converted to Pt(II). They performed spectroscopic studies on the orange solid obtained by evaporating the isopropanol, and concluded that the active catalyst species is the $\text{H}[(\text{C}_3\text{H}_6)\text{PtCl}_3]$ complex. Chalk and Harrod [21] proposed that the mechanism, shown in Scheme 6, involves the formation of a complex between the double bond of the olefin and the platinum (I), followed by the reaction with the hydrosilane (II). The third step involves a transfer of hydride to the olefin, the rearrangement from pi to a sigma complex giving rise to a carbanion (III). The carbanion is capable of tautomerization, the most stable form being terminal. This step accounts for the observed anti-Markovnikov addition, and the possible

isomerization. The next step (IV) is nucleophilic attack of the carbanion upon a silane, forming the new compound which is finally displaced by another olefin (V).



Scheme 6. Chalk and Harold Mechanism for Pt-catalyzed Hydrosilation.

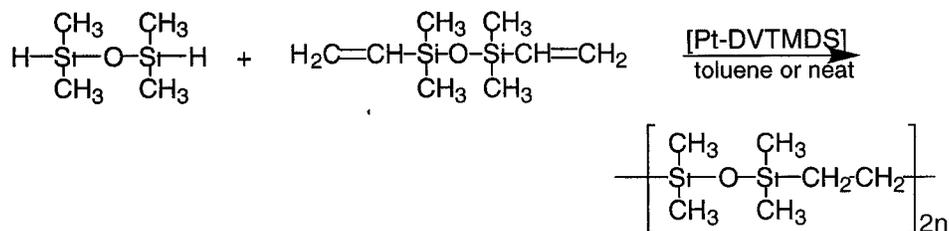
As shown in Scheme 5, HCl is generated during the formation of the initial active Pt complex. HCl generated during the course of a polymerization may attack the growing polymer chain and cause desilylation at the $\text{Si}-\text{C}$ bonds, and a reduction in molecular weight, as shown in Scheme 7 [22] [23]. Because of this, a number of new platinum catalysts were developed and are commercially available (see Table 3) [12]. One of them, platinum(0)-divinyltetramethyldisiloxane (Pt-DVTMDS or Karstedt's catalyst), can easily be derived from hexachloroplatinic acid [25]. It has the same advantages as CPA, without producing HCl .

The steps include the formation of a colloid, which is stabilized with oxygen which is adsorbed on the catalyst surface. Oxygen functions as a co-catalyst and activates the complex by withdrawing electrons. The platinum-oxygen complex coordinates a silane, but the Si-H bond is not broken during this addition. The newly formed complex has an electrophilic character, and the olefin, therefore, can now attack the transition complex nucleophilically, and the new organosilane is formed [26].

Oxygen stability is a very important feature in the catalyst's performance in this procedure since it makes the application of expensive inert gas atmospheres unnecessary. However, the requirement of oxygen leads to problems of a different kind in melt-phase reactions. At normal processing temperatures, about 200°C, oxygen reacts with the polymer chain, leading to degradation and formation of undesired oxidation products. Therefore, the oxygen necessary to activate the catalyst has to be introduced chemically, as a peroxide [26].

2.2.3.2.2 Optimizing Hydrosilation Polymerization

Though the use of platinum catalysts for vinyl-cured-crosslinked systems is well established, recent efforts have focused on the synthesis of high molecular weight linear polymers. Dvornic [18] and others recently described the first successful synthesis of a truly high molecular weight carbosiloxane, poly[1,1,3,3-tetramethyldisiloxanyl]ethylene], by a hydrosilation polymerization of 1,3-dihydroxytetramethyldisiloxane and 1,3-divinyldisiloxane in the presence of Karstedt's catalyst as shown in Scheme 9.



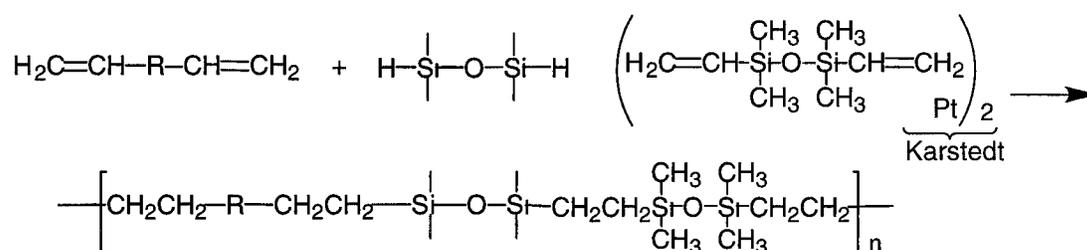
Scheme 9. Hydrosilation Polymerization *via* Karstedt's Catalysis.

The polymerization was carried out neat and in toluene *via* the one monomer deficient method [18]. This method consists of incremental additions of the dihydride siloxane to the divinyl compound and platinum mixture until stoichiometric balance is achieved. The paper also reported the effects of reactant concentrations, catalyst concentration, and reaction temperatures on the molecular weight of the polymer. The result of the paper showed that the most favorable synthetic procedures seem to be neat polymerizations, catalyst concentrations of about 2×10^{-6} mole of Pt per mole of $\text{CH}=\text{CH}_2$, and reaction temperatures between 40 to 50°C. The molecular weight of the polymer was 30,000 a.m.u., a value significantly higher than other values reported earlier in literature (the molecular weights of which normally ranged from about 1000 to about 2000 a.m.u.) [18].

2.2.3.2.2.3 Hydrosilation Disadvantages

A number of problems are encountered using platinum catalysts. The hydrosilation reactions seldom proceed quantitatively and can give rise to many by-products due to isomerization or elimination of the alkene, disubstitution of the silicon hydride, or metal-catalyzed Si-C bond cleavage. J. R. Sargent and others recently reported the non-terminal addition and isomerization of terminal alkenes to internal alkenes, which are less reactive. [29] Platinum catalyst can also be poisoned deactivated by sulfur compounds (mercaptans, sulfates, sulfides, sulfate, thiols and even rubbers vulcanized with sulfur) [12].

Nitrogenous compounds, such as, amides, amines, imides, nitriles and tin compounds also have been shown to deactivate the catalyst. As mentioned, the production of HCl from Speier's catalyst is also problematic. Though this can be avoided by using Karstedt's catalyst, this catalyst also creates a unique problem. As with other step-growth polymerization reactions, stoichiometric balance is extremely important. The Karstedt's catalyst contains two divinyl-functionalized moieties, which can also serve as reactants in the polymerization (see Scheme 10). At large catalyst concentrations these moieties result in stoichiometric imbalance, (excess vinyl functions), and limit the degree of polymerization.



Scheme 10. Karstedt's Catalyst as a Reactant in Hydrosilation Polymerization.

The expense of platinum coupled with the concentrations usually employed (10^{-5} - 10^{-8} mol platinum per mol of hydrosilane) [10] required to achieve desirable hydrosilation rates, often render these methods economically unattractive [26]. Contamination of the polymer with colloidal platinum is a common problem in the preparation of polymers by hydrosilation. In solution, the presence of the platinum can usually be seen as a brown coloration. In solutions where the amount of platinum contamination is comparatively high, the polymer appears gray, or sometimes black. In silanes and other low molar mass materials, complete removal of the colloidal platinum is achieved in the purification by distillation. In other materials it is achieved either by purification

procedures which involve conditions which destabilize the colloidal platinum or by filtration through an appropriate medium, usually activated carbon or dicalcite. In high molecular weight polymers where a distillation step is not possible, the use of absorption techniques have been described. The use of mercury to remove the platinum has also been reported [10].

In less-reactive alkenes, despite long reaction times and the addition of more catalyst, a small amount of the Si-H groups still remains. This is particularly true when the alkene chain is short, (e.g., vinyl) and in some cases bulky or contains deactivating cyano groups [10]. The residual Si-H groups are a problem because they may undergo other reactions such as hydrolytic or oxidative cross-linking. In instances where it has not been possible to fully react the Si-H groups during polymerization, a number of authors have reported the reaction of the residual groups with a more reactive alkene such as octene [30] [31] [32].

2.2.3.3 Polymer Characterization

The polymers formed by hydrosilation can be characterized in a number of ways: ^1H NMR, ^{29}Si NMR, IR, osmometry, titration, and GPC. The polymer is first isolated by standard procedures, normally three precipitations in methanol, which should remove both residual platinum catalyst and low molecular weight species. However, depending on the scale, and solvent properties of the precipitating system for the polymer and alkene, it is possible for the alkene to remain entrapped in the polymer even after several precipitations [33] [34] [35].

The molecular weights and weight distributions are usually determined by gel permeation chromatography. Often, an independent method for the determination of the number average molecular weight (M_n) is often reported. For, a degree of polymerization (DP) up to 50, this may be done by end-group

analysis using ^1H NMR [36] [37].

Alternative techniques include osmometry and ^{29}Si NMR. ^{29}Si NMR is useful for copolymers because it allows determination of the block lengths and composition [53]. It also allows for the identification of branching points introduced through impurities or side reactions.

The Si-H content of the polymers may be determined by ^1H NMR, IR spectroscopy, titration with mercury acetate, or by hydrogen evolution. While ^1H NMR spectroscopy is a useful technique for the characterization of the final polymer, its use in monitoring the reaction progress is limited by the inherent sensitivity of the ratio of the Si-H to other functional groups and the presence of a tailing peak from the large excess of solvent usually employed [38].

Infrared spectroscopy is the preferred monitoring method. The technique is more convenient for use in the periodic monitoring of the reaction system and is more sensitive to lower levels of Si-H groups, particularly if FT-IR is used [36]. In early work, where solutions were used, it was difficult to detect the Si-H group at 2160 cm^{-1} even at low extents of reaction. However by preparing evaporated films of the reactants the Si-H can still be seen at levels of reaction of greater than 99% [36].

2.2.3.4 Silicon Polymer Applications

Most silicon polymer research has been focused on polysiloxanes and a review of their properties and commercial applications is beneficial in understanding the basic chemistry that silicon can impart to a polymer. For instance, siloxanes have a number of useful properties that are defined by the variation of the organic substituents, and by the degree of cross linking. The simplest siloxane is poly-dimethylsiloxane (shown in Figure 6).

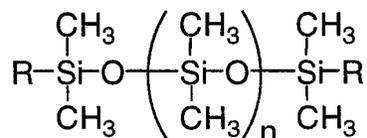


Figure 6. Structure of a Polysiloxane.

2.2.3.4.1 Silicone Fluids

The Si-O bond is highly resistant to heat and oxygen and is extremely flexible. Siloxanes are especially useful as lubricants in applications where there are extreme variations in temperature, because their viscosity changes very little with temperature. They also exhibit thermal stability, low flammability, shear stability, dielectric stability, low compressibility, chemical inertness, and low toxicity.

Siloxane polymers, when not cross-linked, are mostly liquids, which are used for a wide range of commercial applications. Siloxanes have the lowest glass transition temperatures of any polymer [10]. For example PDMS has a T_g of 150 K. The low T_g is a result of minimal amount of energy needed for rotation around the skeletal bonds. There are two factors that contribute to the ease of rotation: (see Figure 7), the long bond length and the wide bond angle of Si-O bond. The Si-O bond length is 1.63Å compared to 1.54Å for the C-C bond length and 1.43Å for the even shorter C-O bond. The bond angle of Si-O-Si is $\sim 143^\circ$ which is more open than the C-O-C bond angle of 118° . Both of these factors reduce the intramolecular steric interferences.

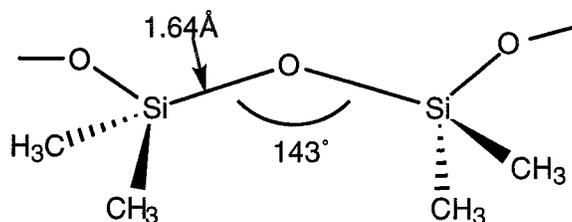


Figure 7. A Segment of PDMS.

Table 3 shows the glass transition temperatures (T_g) of selected siloxanes and how the group bulkiness affects the Si-O-Si bond angle and, thus, the flexibility of the polymer chain. For example, polymethylhydrogensiloxane has a lower T_g (-138°C) than polymethylethylsiloxane at -135°C . The stiffness and the bulk of the aromatic substituents hinders rotation even further given polyphenylsiloxane a higher T_g of 49°C . Symmetrically substituted chains like those in PDMS, T_g (150 K) pack closer together causing a greater interaction between chains and higher T_g than unsymmetrically substituted chains like polyethylmethylsiloxane T_g (-138°C) [10].

Table 4. Glass Transition Temperatures of Polysiloxanes

R_1^*	R_2^*	T_g (K)	Si-O-Si [39] Bond angle
CH ₃	CH ₃	150	144°
C ₂ H ₅	C ₂ H ₅	134	159°
C ₃ H ₇	C ₃ H ₇	164	158°
C ₄ H ₉	C ₄ H ₉	157	157°
C ₆ H ₅	C ₆ H ₅	322	139°
CH ₃	H	135	146°
CH ₃	C ₂ H ₅	138	145°
CH ₃	C ₃ H ₅	153	149°
CH ₃	C ₈ H ₁₇	181	141°
CH ₃	(CH ₂) ₂ CF ₃	203	146°
CH ₃	C ₆ H ₅	240	143°

*Polymer $-\text{[R}_1\text{R}_2\text{SiO]}_n-$

Another factor that affects the T_g is the polymer chain length. A number of theoretical models have been proposed to explain the behavior of linear siloxanes and predict T_g . The Di Marzio and Guttman theory successfully predicts that the glass transition of cyclic molecules increases as the molar mass decreases, while the T_g of linear polymers decreases with decreasing molar mass, as is observed for polysiloxanes [10].

The highly flexible siloxane chain also allows for a high degree of free volume. The large free volume permits diffusion of gases into the polymer matrix. Oxygen, nitrogen and carbon dioxide have high permeabilities in polysiloxanes, about one-thousand times those of polyethylene. For polysiloxane elastomers the permeability to oxygen is 10 times that of natural rubber and 100 times greater than butly rubber and nylon. [40]

While polysiloxanes exhibit low reactivity under many conditions certain environments are destructive. The Si-O bond is susceptible to hydrolysis and to attack by acids and bases. Siloxane elastomers are relatively weak and readily swollen by hydrocarbon oils. This is apparent to anyone who has mistakenly placed powersteering fluid (a hydrocarbon) into the brake master cylinder reservoir, which is designed to hold brake fluids (a siloxane). The flexibility of the Si-O bond can be problematic also. At room temperature; polysiloxanes are non-crystalline and exhibit low surface energy and low cohesive energy. As a result, the polymers have low modulus, tensile strength, and tear strength. To counter these properties, the polymers are often filled with particulate silica, which also adds abrasion resistance. [12] At higher temperatures the Si-O bond is susceptible to thermal degradation causing rearrangement and the formation of volatile by-products. [10]

Siloxanes can also be used to modify the critical surface tension of a substrate. Siloxanes show low critical surface tensions (22 to 25) compared to other polymers: PTFE 18.5, polypropylene 31, polyethylene 33, polystyrene 34. [17] The critical surface tension is associated with the watability or release qualities of the material. The critical surface tension is measured by determining the contact angle, the angle at which a liquid's surface meets the material. If this angle is zero, the liquid surface is parallel to the solid surface and is said to wet the surface completely. The low surface tension allows

siloxanes to be utilized in a number of applications, including mold release agents, fiber lubricants, softeners for textiles, water repellents, corrosion inhibitors and other surfaces modifiers.

The unique properties of siloxanes can be tuned further by variation of the attached organic substituents. At concentrations above about 5 mol % of functional groups, the character of the polymer begins to change and entirely new properties emerge [10]. Table 5 shows substituents vs. property relationships for silicone polymers. For instance; replacement of methyl groups with longer aliphatic moieties, produces silicones with properties that more closely resemble hydrocarbons. These polymers have lower compressibility, and improved lubricity, which is optimized when the alkyl unit is at least eight carbons long. The trade off is that there is a decrease in oxidative stability. This can, however, be overcome by incorporating stabilizers or by copolymerizing with aromatic siloxanes [41].

Table 5. Substituents and Properties Correlation

Substituent	Properties
Methyl	Good lubricity, low surface tension, high permeability for O ₂ and N ₂
Aliphatic	Increased solubility in hydrocarbons, lubricity, and melting point
Alkyleneoxy	Increased hydrophilicity
Aromatic	Increased: rigidity and thermal and hydrolytic stability
Trifluoropropyl	Increased chemical resistance, excellent lubricity, and lowered acoustic velocities

The hydrophilic silicones can be prepared by incorporating ethylene oxide substituents. Silicones with ethylene oxide contents of 75% and higher are freely soluble in water; as well as other common organic solvents such as methanol, isopropanol acetone and methylene chloride. These polymers are

used to facilitate wetting, and as surfactants [12].

As phenyl groups replace methyl groups, several properties change; lubricity, oxidation resistance, radiation resistance, thermal stability, hydrolytic stability and shear resistance are enhanced. These siloxanes are most commonly used as high temperature hydraulic or heat transfer fluids, having service temperatures from -55 to 290 ° C. The phenyl group is incorporated in two ways. It is introduced as a phenyl methyl siloxane or as a diphenylsiloxane. The phenyl groups also introduce rigidity, when substitution exceeds 75 mole percent the polymers are solids. At 15 to 20 mole percent, the refractive index matches that of amorphous silica and the compounds are transparent.

By incorporating fluoro substituents, a number of unique properties are achieved. These polymers are thermally stable and are used in aggressive service environments operating from -40 to 285°C [41]. Fluorosilicones are used as defoamers and as lubricants for electrical contacts. Fluorosilicones are not miscible with fuels or oils and have excellent lubricity under extreme pressure. The combination of these characteristics has led to many automotive and aerospace lubrication applications, since they are not easily leached by fuels from the mechanical joints. Fluorosilicones also have excellent acoustic velocities, which allows for sonar lens development and ultrasonic sensors [41]. Because of the electropositive nature of silicon, fluorine is incorporated into polysiloxanes as trifluoropropyl substituents at the gamma position [12]. Fluorination at the α and β positions usually results in poor thermal stability [41].

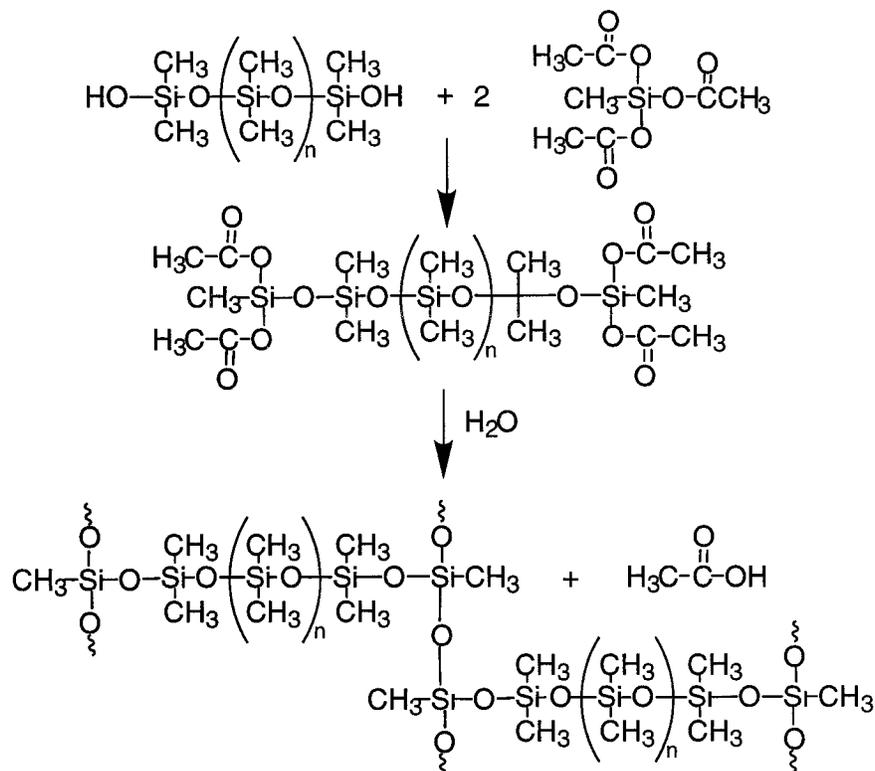
2.2.3.4.2. Reactive Silicones

Other groups, such as silanol, vinyl, and hydride, are incorporated to form what is termed "reactive silicones" [12]. The attached groups can be pendant and/or terminal position, and or used to form branched units, which introduce

rigidity into structure. These polymers form base stocks for most traditional vulcanized silicone elastomers. Silicone elastomers are used mainly in O-rings, heat-resistant seals, caulks, gaskets, and as electrical insulators. These polymers are converted from a highly viscous state, into a predominantly elastic state by cross-linking.

2.2.3.4.2.1 Silanol-functionalized

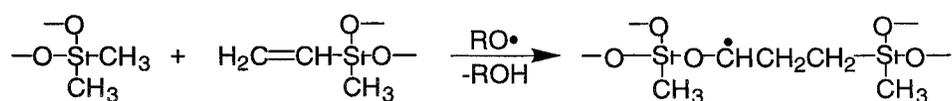
Silanol groups are susceptible to condensation under both mild acid and base conditions and can be cured by this process. However, silanol-functionalized silicones are more widely cured by using a two-stage process. This process is used in RTV (room temperature vulcanizing) silicone systems. The silanol-containing polymers, with typical molecular weights ranging from 15,000 to 150,000, are reacted with multi-functional alkoxy silanes, which produce four positions which are extremely susceptible to hydrolysis. The silicones is stored in this form, and protected from moisture. Upon use, the second stage occurs. The end groups are exposed to moisture, forming rapid cross linking and the acetic acid byproduct [12] (see scheme 11).



Scheme 11. Cross-linking Cure Process for Silanol RTV Silicones.

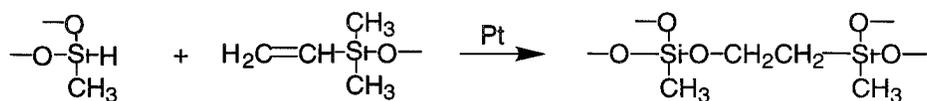
2.2.3.4.2.2 Vinyl-functionalized

Vinyl-functionalized polymers are cross-linked by peroxide-activated cure systems, which involve peroxide-induced free radical coupling between vinyl and methyl groups. The initial cross-linking reaction is shown in Scheme 12. For high consistency rubber applications a frequent requirement is that no curing takes place as the part is being extruded or molded, but once the shape is made, the curing happens quickly. The reaction typically occurs using vinylmethylsiloxane-dimethylsiloxane copolymers, with molecular weights ranging from 500,000 to 900,000 and initiated by benzoyl-peroxides at temperatures of 140 to 160°C. Following this initial cure, a post-cure at 25 to 30°C higher removes peroxide decomposition products and stabilizes the polymer properties. The elastomers formed by this process are referred to as HTV silicones (high temperature vulcanizing) [12].



Scheme 12. Cross-linking Peroxide Cure Process for Vinyl Silicones.

Vinyl-functionalized polymers can also be cross-linked by platinum-catalyzed hydrosilation reactions. The mechanism, Scheme 13, involves the addition of the silicon hydrogen bond to the vinyl carbon-carbon double bond. These reactive polymers form base stocks for 2-part RTV, and LTV (low temperature vulcanizing) silicones. An important feature of this cure system is that no by products are formed, allowing for fabrication of parts with good dimensional stability. Typical formulations would be based on a mixture of the platinum catalyst with equal molar amounts of vinyl-functional polysiloxane, and at least a three-site hydride functionalized polysiloxane cross-linker. This would ensure the formation of a three-dimensional network. The mixture also contains fillers, most notably hexamethyldisilazane treated fused silica, to enhance the mechanical properties. Typically, both base polymer's molecular weights range from 6,000 to 60,000 and cure temperatures are below 50°C for RTVs, and 50 to 130° for LTVs [12].

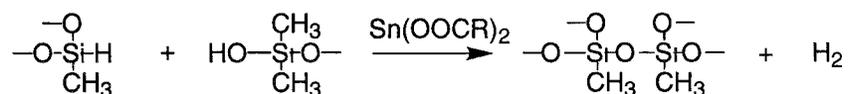


Scheme 13. Cross-linking Platinum Cure Process for Vinyl Silicones.

2.2.3.4.2.3 Hydride-functionalized

As mentioned, hydride-functionalized silicones serve as cross linkers in addition cure systems. They are also employed in dehydrogenative coupling reactions, as shown in Scheme 14. The reaction is employed to produce

foamed silicone materials by the evolution of hydrogen gas. The reaction is also used to impart water repellency to glass, water, paper, and fabrics, by bonding with the material's hydroxy surface groups.



Scheme 14. Dehydrogenative Reaction for Hydride Silicones.

2.2.3.4.2.4 Other-functionalized Silicones

A number of other reactive organic functions can be substituents in silicone polymers, such as acrylates, amines, carboxyl, and phenols [10]. The organic groups are attached to the silicon through propyl linkages. The three carbon spacer confers thermal and hydrolytic stability and acts as a transition group. This allows the organic group to behave independently and unperturbed by silicon. [10] These organo-functionalized polymers are most often copolymerized with other organic monomers. Silicone methacrylates, namely tris(trimethylsiloxy- γ -methacryloxypropylsilane), Figure 8, is copolymerized with methacrylate monomers. The resulting material is used in the formation of contact lenses. The siloxane imparts the necessary oxygen permeability and the methacrylate imparts the necessary optical and mechanical properties [42].

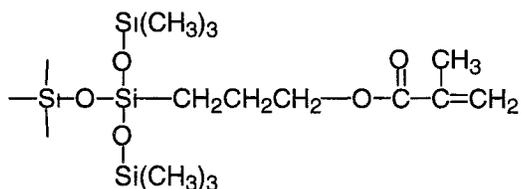
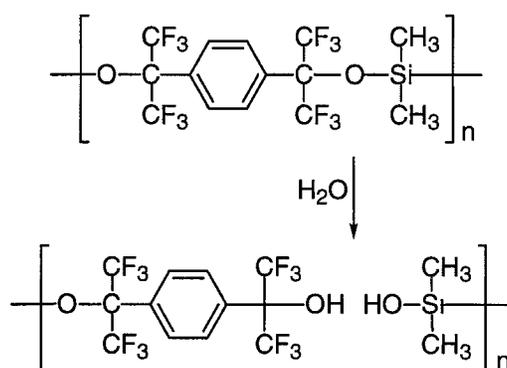


Figure 8. Silicon-methacrylate Monomer with Propyl Spacer.

Aminopropyl-terminated silicones are used to form a variety of block copolymers, including polyamides, polyurethane and polycarbonates.

Other copolymers can be formed using silicon carbinols, Si-C-OH. Carbinol siloxanes contain primary hydroxyl groups, which are linked to silicon by non-hydrolyzable transition groups. These groups are usually a block of ethylene or propylene.

Polymers without the non-hydrolyzable transition groups haven't met with such success. Recently, T.L. Lewis reported the synthesis of a polymer derived from the reaction of 1,4-bis(hexafluoro-2-propyl)benzene (1,4-Bis HFAB) and bis(N,N-dimethylamino) dimethylsilane (see Scheme 15). The hydrolytic stability of the polymer and other model compounds were investigated. Lewis reported the ease of hydrolysis at the Si-O-C bond of these compounds, and the depolymerization upon contact with water [43].



Scheme 15. Hydrolysis at the Si-O-C Bond of a Silicone Polymer without a Transition Group.

2.3 Fluorine Chemistry

2.3.1 Background

In the past seventy years, a considerable amount of research and development has been directed towards the synthesis of fluorocarbons. Fluorine is a yellowish, poisonous, highly corrosive halogen gas, which upon cooling forms a yellowish liquid. Elemental fluorine, makes up about 0.065 percent of the Earth's crust, mainly in the form of the minerals fluorite, cryolite, and fluorapatite and in small amounts in seawater. By treating fluorite with sulfuric acid hydrogen fluoride (HF) is obtained. By electrolysis of anhydrous hydrogen fluoride elemental fluorine, was first isolated in 1886 by the French chemist Henri Moissan. This process is still used today because it is impossible to free it by chemical means; no other element is powerful enough, as an oxidizing agent, to replace it [11]. Only one isotope occurs, ^{19}F with a spin of $1/2$.

Elemental fluorine, often diluted with nitrogen, reacts with hydrocarbons to form corresponding fluorocarbons, and with inorganics to prepare fluorides such as boron trifluoride (BF_3) and antimony trifluoride (SbF_3), which, like hydrogen fluoride, are important catalysts for organic reactions; cobalt trifluoride (CoF_3) and chlorine trifluoride (ClF_3) which are useful as catalysts and as fluorinating agents for organic compounds. The resulting fluorocarbons are usually characterized by great stability, chemical inertness, high electrical resistance, and other valuable physical and chemical properties.

A chief industrial use of fluorocarbons is as coolants for household refrigerators and air conditioners. And, it was research in this area which led to fluorocarbons success as industrial chemicals. In the 1930's, in a search for a new fluorine-containing refrigerant, serendipity played a role in R.J. Plunkett's accidental discovery of poly(tetrafluorethylene), PTFE. While cleaning up a

supposedly empty storage cylinder of tetrafluoroethylene, TFE, he found PTFE which had been formed by the spontaneous polymerization of TFE. This accidentally discovered material provided the plastic industry with a fluoropolymer possessing outstanding thermal stability, flame and chemical resistance, lubricity, low dielectric constant, weatherability and moisture impermeability [44]. Another pioneer in fluorine chemistry, Joe Simon, using arguments hinging on the outstanding high thermal stability and chemical inertness of saturated fluorocarbons, campaigned vigorously for the funding of fluoropolymer research. Taking into account the unique physical properties of fluoropolymers; he described an imaginary airplane in which hazards were minimized through the use of fluorine-containing plastics, elastomers, paints, and lubricants, in which the C-F content had been maximized to fit each application. Seventy years later, fluorinated polymers touch our everyday lives in numerous ways, in linings for non stick cookware, in cars as engine gaskets and drive train seals, and even in our bodies as artificial blood and body-parts.

2.3.2 Fluorine Properties

Today, driven by the aerospace and microelectronic industries, new fluoropolymers play key roles as electrical insulators, and as protective coatings for wide range of applications. Their use in these high-performance areas is a factor of the unique physical properties associated with fluorine. The small size of the fluorine atom, 0.64 Å, exerts but modest spatial demands when compared with the other halogens. Therefore, only in the case of fluorine can complete conversion of a hydrocarbon to fluorocarbon with the same carbon skeleton be conceived. Fluorine forms the strongest known single bond to carbon with a bond dissociation energy of 485 kJ mole⁻¹. The strength of the C-F bond imparts a number of characteristics to organic compounds, specifically higher thermal

stability when compared to its hydrocarbon derivative where the C-H bond is 413 kJ mole⁻¹ [44]. The strong C-F bond strength attributes not only thermal stability but also chemical inertness.

2.3.3 Fluoropolymers

These properties are most defined in perfluoro-polymers such as PTFE. The presence of only C-C and C-F bonds imparts a high degree of oxidative and hydrolytic stability, and, therefore, excellent resistance to nearly all chemicals and solvents. These excellent properties are attributed to a combination of the strong C-F and C-C bond and the shielding of the polymer backbone from attack by the sheath of the highly electronegative fluorine atoms [45]. The strength of the C-F bond also prevents chain transfer processes during polymerization, so that this class of polymers possesses a strictly linear chain. The strict linear chain imparts high degree of crystallinity which leads to relatively low gas permeability, making perfluoroplastics excellent barrier resins. Of greater significance to their applications are the outstanding electrical properties, and low surface energy of the perfluoroplastics. They are excellent insulators with high dielectric strengths and with dielectric constants of (2.0 to 2.1) the lowest known for solid materials [45], and they retain this properties over a wide temperature range. They also exhibit low moisture absorption which results in electrical properties that are little affected by humidity. The low surface energy of perfluoroplastics like PTFE, which has a critical surface tension of 18.5, make it ideal for coating applications.

Although the remarkable properties of perfluoroplastics are immediately apparent, so are the difficulties of converting these polymers into shaped objects since these polymers can neither be solution-processed or melt-processed by traditional techniques. The poor solubility and high melt viscosity

of perfluoroplastics make processing difficult, and other structures are often incorporated into the polymer to increase their processability.

2.3.4. Processability

To improve solubility and to reduce the glass transition temperature for easier processability, flexible spacer groups are introduced in the polymer backbone. Oxygen is added to form perfluoropolyethers the ether linkage acts as a hinge storing vibrational energy. The C-O bond (358 kJ mole^{-1}) is stronger than the C-C bond (346 kJ mole^{-1}), [44] which also enhances the thermal stability. A number of these polymers have been formed by direct fluorination of hydrocarbon using elemental fluorine and are commercially available. Another approach to improving processability is to incorporate bulky substituents into the polymer which deform the backbone and increase of the distance between adjacent polymers. This increase of free volume allows the polymers to move more freely, lowering their glass transition T_g and the melt viscosity of the polymer. For example fluorinated ethylenepropylene (FEP) and perfluoralkoxy (PFA) in Figure 9 can be processed by conventional methods such as extrusion or injection molding,

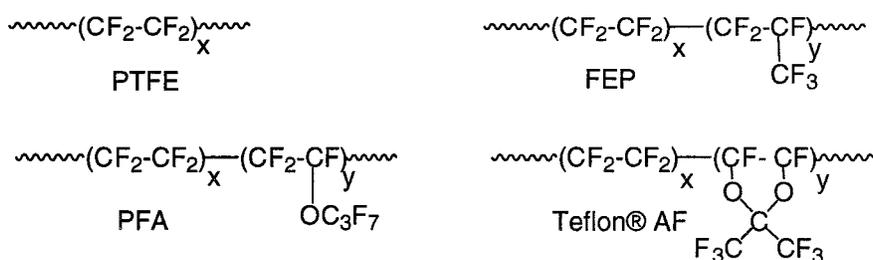


Figure 9. Perfluorinated Polymers.

where as spacer free PTFE cannot be normally melt processed, and requires more difficult (fine powder) paste extrusions [46] [44]. The increased free volume also has the added benefit of the lowering the dielectric constant for the

polymer. This low dielectric effect can be seen in Teflon AF[®], where the free volume imparted by the bulky fluorinated dioxolane ring gives the polymer the lowest dielectric constant of any known polymer [47].

The incorporation of the bulky aryl-6F group, Figure 10 into the polymer imparts a number of desirable properties. The kinky hexafluoroisopropylidene

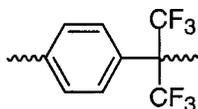


Figure 10. Bulky Aryl 6F Group.

(6F) moiety improves solubility by favorable interactions of the 6F fluorine atoms with organic solvents. Secondly the bulky aryl-6F group increases free volume improving the electrical insulating properties of the polymer and it lowers the T_g , improving the processability, while maintaining thermal stability.[48] Some of the more common aryl-6F-monomers are listed in Table 5 [49]. These compounds can easily be adopted for polymer synthesis.

Table 6. Commercially Available Aryl-6F-Monomers

Structure	Name {acronym*}
	2,2-bis(4-hydroxyphenyl)-hexafluoro-propane {Bis-AF}
	2,2-bis(4-carboxyphenyl)-hexafluoro-propane {Bis-B-AF}
	2,2-bis[4-(4-aminophenoxy)phenyl]-hexafluoro-propane {Bis-AF-A}
	1,4-bis(2-hydroxyhexafluoro-2-propyl) benzene {1,4-HFAB}
	1,3-bis(2-hydroxyhexafluoro-2-propyl) benzene {1,3-HFAB}

* acronyms are those adopted by Central Glass Co., Ltd. Tokyo, Japan

2.4 Thesis Proposal

Recent efforts have shown that certain fluoropolymers and silicones have good solubility in ScCO_2 . The purpose of this research will be to synthesize divinyl-functionalized, fluorine-containing monomers, which will then be polymerized with a series of commercially available dihydrosilanes/siloxanes, *via* platinum-catalyzed hydrosilation. The polymerization will be carried out in two media: organic liquid solvent and, ScCO_2 . The use of ScCO_2 as a solvent for hydrosilation polymerization is a novel approach, proposed for the purpose of eliminating volatile organic solvent waste. The resulting polymers will be characterized and the effect of solvent studied. It is proposed that the fluorine-containing and silicone-containing monomers and catalyst will be soluble in ScCO_2 . This combination should facilitate the polymerization of high molecular weight species.

3.0 EXPERIMENTAL

3.1 General

Melting Points Melting points were determined using a MEL-TEMP II hot-block melting point apparatus and are uncorrected.

Carbon and Hydrogen Analysis All elemental analyses were performed by Desert Analytics, Tuscon, Arizona, and are reported to within $\pm 0.2\%$.

Infrared Analysis Infrared spectra were obtained with a Perkin Elmer Model 1600 Fourier Transform IR. Liquid samples were analyzed neat, and polymeric materials were dissolved in chloroform and cast applied, on NaCl disk.

Proton and Carbon 13 Nuclear Magnetic Resonance ^1H and ^{13}C NMR FID were obtained at 400 MHz with an Varian Fourier Transform NMR Spectrometer. CDCl_3 was used as the solvent, the lock signal and the internal reference at 7.25 ppm for the ^1H and 77.0 ppm for the ^{13}C NMR. The ^{13}C NMR spectra were obtained with broad-band proton decoupling. The FIDs were transformed and the spectra analyzed using SwaNMR [50] [51].

Thermal Analysis Thermal analysis was performed using a Rheometric Scientific TGA 1000M3 Thermal Analyzer. Thermogravimetric data are reported as 10% weight loss in air and argon. Differential scanning calorimeter and thermogravimetric analysis data were obtained at a heating rate of $20^\circ\text{C}/\text{min}$.

Viscosity Measurements Inherent viscosities of polymer solutions were measured at a concentration of 0.010 to 0.020 g/10 dL in chloroform, using a 25 bore viscometer. Temperature was held constant using a Julabo 31A

constant temperature water bath.

Gel Permeation Chromatography Molecular weights and distributions, (M_n , M_w , and DP), of the polymers were performed on a Waters Millennium 32 GPC System. This was comprised of a Dual U injector, a Waters 600 series controller and pump, Waters 2410 refractive index detector, a Waters 2487 Dual λ absorbance detector, and three Styrgel packed divinylbenzene cross-linked polystyrene columns, (2 X HR4E packed with and 1 X HR5E), in series. HPLC-grade THF at a flow rate of 3.0 mL/min. was used as the solvent in the analysis. The retention times were measured against known monodispersed polystyrene standards with a molecular weight range of 1,320 to 1,080,000 a.m.u.

Water Contact Angle Contact angles were performed on a Tan Tec Contact Angle Meter, model Cam-Micro.

Supercritical Chemistry A 50 mL, stainless steel, viewable, variable - volume view cell was used as a reactor vessel. The vessel was sealed using Teflon, Buna, and Delrin gaskets. Supercritical pressure was maintained using an Isco 100DM model syringe pump, equipped with an Isco Series-D controller. A water bath was used to achieve critical temperature and was maintained by a Love Controls series 2600 portable controller.

Sources of Starting Materials The following compounds were obtained and used without further purification, unless otherwise noted: from Aldrich Chemical Company: allylbromide, benzene, hexachlorplatinic acid, 9-decen-1-ol, N,N-dimethylformamide, (DMF), p-toluenesulfonyl chloride, pyridine, and sodium anhydride; from Gelest Chemical Company: catalyst, platinum divinyltetramethyldisiloxane complex in xylene, (3 to 3.5% Pt), 1,4-bis(dimethyl silyl)benzene, diphenylsilane, 1,2-bis(tetramethyldisiloxaneyl)ethane, 1,1,3,3,5,5,7,7-octamethyltetrasiloxane,

1,1,4,4-tetramethyldisilylethylene-silane, 1,1,3,3-tetramethyldisiloxane; from Central Glass Company, LTD.: 2,2,2,2',2',2'-hexafluorocumyl alcohol (HFAB), 1,3-bis(hexafluoro-2-propyl)benzene (1,3-Bis HFAB), 1,4-bis(hexafluoro-2-propyl)benzene (1,4-Bis HFAB); from United Chemical Technologies; phenyl dimethyl silane; and from Praxair: supercritical fluid classification grade CO₂, (99.995%).

3.2 Allyl HFAB Synthesis

3.2.1 Preparation of Hexafluoro-2-Allyloxy-2-propyl Benzene (Model Monomer) (Compound IV). An oven-dried, 100 mL, airless flask was equipped with a condenser, flow control adapter, and magnetic stir bar, and was evacuated and filled with argon. Sodium hydride (60% in mineral oil) (1.6 g, 25.5 mmol) was placed in the flask and washed in with 10 mL of N,N-Dimethylformamide, (DMF) at 23°C. Hexafluoro-2-propyl benzene, (5.0 g 20.4 mmol), dissolved in 10 mL of DMF, was slowly added to the flask. The solution was heated to 40°C and stirred for one hour. Allylbromide (3.08 g 25.5 mmol), dissolved in 5 mL of DMF was added, dropwise, over a 30 minute period to the sodium-HFAB-alkoxide solution and stirred overnight, forming a yellow-colored solution. The DMF was removed under vacuum, leaving a brown, viscous solution. The solution was quenched with H₂O (100 mL) and stirred for 10 minutes, then transferred to a separatory funnel and extracted with 200 mL, (4 X 50 mL), of diethyl ether. The aqueous layers were removed and the ether layers were combined, dried over MgSO₄, and evaporated until a viscous, tan-yellow oil remained. The yield was 3.6 g (12.64 mmol, 62%). A ¹H NMR spectrum (Appendix I, Number 12) shows the following shifts, (ppm): 7.75, 7.47 (aromatic protons, 5 H), 5.97, 5.47, 5.27, (CH=CH₂, 3H), 4.09 (O-CH₂, 2H).

(aromatic protons, 5 H), 5.97, 5.47, 5.27, (CH=CH₂, 3H), 4.09 (O-CH₂, 2H).

3.2.2 Purification of 1,3-Bis(hexafluoro-2-propyl) Benzene (1,3-Bis HFAB) (Compound V). A mixture of 1,3 and 1,4-Bis HFAB (57.50 g, 140 mmol) and H₂O (2.52 g, 140 mmol) were placed in a 250 mL Erlenmyer flask. The solution was placed in the freezer over night; resulting in the formation of a white crystalline solid of 1,4-Bis HFAB which was removed by filtration. Toluene (5.0 mL) was added to the 1,3-Bis HFAB solution and then removed by vacuumed distillation along with the residual H₂O. The remaining 1,3-Bis HFAB was a colorless liquid. A ¹H NMR spectrum (Appendix I, Number 13) of the 1,3-Bis HFAB was obtained and used to calculate the isomeric purity reveals the following shifts, (ppm): 8.13, 7.81, 7.56 (aromatic protons, 4H), 1.82 broad, (OH, 1H). The ¹³C NMR spectrum of V is shown in Appendix II, Number 2. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons).

3.2.3 Preparation of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene (Propenyl Monomer) (Compound VII). An oven-dried, 250 mL, three-necked, round-bottom flask was equipped with a condenser, flow control adapter, and magnetic stir bar, and was evacuated and filled with argon. Sodium hydride (1.22 g - 60% in mineral oil) was obtained, and the mineral oil was removed with pentane to yield pure NaH (0.7317 g, 30 mmol). The NaH was then placed in the flask and washed in with 10 mL of DMF. The gray solution that formed, was chilled to 0°C with an ice bath and 1,3-bis(hexafluoro-2-propyl) benzene, (1,3-Bis HFAB), (5.0 g 12.2 mmol) diluted with 10 mL of DMF was added to the reaction mixture, dropwise, through an

addition funnel. The ice bath was removed and the solution was allowed to warm to room temperature. The reaction was continued for 2 hours at this temperature. Allylbromide (4.47 g, 36.2 mmol), dissolved in 10 mL of DMF, was added dropwise over a 30 minute period to the sodium-1,3-Bis HFAB-alkoxide solution. The solution was heated to 45°C and held there for 8 hours. The DMF was removed under vacuum, leaving a brown, viscous solution, which was quenched with H₂O (15 mL), stirred for 10 minutes, and then transferred to a separatory funnel. The solution was extracted with 200 mL (4 X 50 mL), of diethyl ether and the aqueous layers were removed; the ether layers were combined and dried over MgSO₄. The yellow solution was rotary evaporated until a viscous, tan-yellow, oily product remained which was eluted through a silica gel-packed column using pentane, and the product collected. The pentane was removed under vacuum, leaving the desired clear liquid product, 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene. The yield was (5.88 g, 12.0 mmol, 98%). The ¹H spectrum shown in Appendix I, Number 15 reveals the following shifts, (ppm): 7.82, 7.75, 7.47 (aromatic protons, 4 H), 5.97, 5.47, 5.27 (CH=CH₂, 6H), 4.09 (O-CH₂, 4H). The ¹³C NMR spectrum of VII is shown in Appendix II, Number 3. The significant peaks are as follows (ppm): 140 (the CH carbon in the CH=CH₂ group), 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 115 (the vinylic CH₂ carbon), 67.9 (O-CH₂ carbon). Calculated for C₁₈H₁₄F₁₂O₂, 44.10 %C, and 2.88 %H; found 44.32 %C, and 2.83 %H.

3.3 Propyl HFAB Silicone

3.3.1 Compound Derived from Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and Dimethylphenylsilane (Propenyl Model

Hydrosilation in Benzene) (Compound **XIII-b**). An oven-dried, 100 mL, airless flask equipped with an air cooled condenser and magnetic stir bar was evacuated and filled with argon. 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (1.00 g, 2.04 mmol), 4 drops of catalyst, (hexachloroplatinic acid), phenyldimethylsilane (0.56 g, 4.08 mmol), and 10 mL of benzene were placed in the flask. The reaction was heated to 40°C and stirred for 100 h, forming a tea-colored solution. The benzene was removed under vacuum and the resulting brown, oily product was transferred to a separatory funnel and washed with 100 mL of H₂O and extracted with 100 mL of chloroform. The chloroform was removed under vacuum. The remaining light-yellow, viscous oil was eluted through a silica gel cake using chloroform and the product was collected and the chloroform removed with rotary evaporation. The desired product, was a colorless liquid. The yield was (0.95 g, 1.24 mmol, 61%). The ¹H spectrum of **XIII-b** is shown in Appendix I, Number 19 reveals the following shifts, (ppm): 7.84, 7.67, 7.55 (aromatic protons, 4 H), 3.51 m (O-CH₂, 4 H), 1.75 m (CH₂, 4H), 0.77 m (Si-CH₂, 4 H), 7.55, 7.37 (Si- aromatic protons, 10H), 1.0 (Si-CH₃, 6H). The ¹³C NMR spectrum of **XIII-b** was not obtained.

3.3.2 Compound derived from reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and Dimethylphenylsilane (Propenyl Model Hydrosilation in ScCO₂), (Compound **XIII-s**). A 50 mL, stainless steel reactor cell was purged with argon. Then 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (1.0 g, 2.0 mmol), 4 drops of catalyst, (hexachloroplatinic acid), phenyl dimethyl silane (0.55 g, 4.0 mmol), and 10 mL of ScCO₂ were added to the cell. The reactor was pressurized to 5000 psi (345 bar), heated to 40°C and reacted for 100 h, forming a tea-colored solution. The ScCO₂ was vented and the resulting light

yellow oily product was transferred to a separatory funnel, and washed with 100 mL of H₂O and extracted with 100 mL of chloroform. Activated charcoal was added to the solution and stirred overnight and then filtered. The chloroform was removed under vacuum, leaving the desired colorless liquid product. The yield was (1.22 g, 1.95 mmol, 79%). The ¹H spectrum shown in (Appendix I, Number 20) reveals the following shifts, (ppm): 7.84, 7.67, 7.55 (aromatic protons, 4 H), 3.51 m (O-CH₂, 4 H), 1.75 m (CH₂, 4H), 0.77 m (Si-CH₂, 4 H), 7.55, 7.37 (Si- carbons 10H). The ¹³C NMR spectrum of **XIII-s** is shown in Appendix II, Number 4. The significant peaks are as follows (ppm): 137 (Si-) , 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 70.6, 24.6, 9.5, (three methylenes), -2.21 (Si-CH₃). Calculated for C₃₄H₃₈F₁₂O₂Si, 53.53 %C, and 5.02 %H; found 53.82 %C and 5.21 %H.

3.4 Propyl Polymers

3.4.1 Polymer Derived from the Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,4,4-Tetramethyldisilylethylene-silane (Compound **XXIp-b**). An oven-dried, 100 mL, airless flask equipped with an air-cooled condenser and magnetic stir bar was evacuated and filled with argon. Then 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (2.00 g, 4.08 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,1,4,4-tetramethyldisilylethylene; (0.59 g, 4.08 mmol), and 10 mL of benzene were placed in the flask. The reaction was heated to 40°C and stirred for 100 h, forming a tea-colored solution. The reaction was stopped and the benzene was removed under vacuum, leaving a viscous, brown material. Methanol (100 mL) was added and the solution stirred over night. The solution was transferred to a separatory funnel, and the viscous material was separated,

filtered, placed into a 50 mL flask, and vacuum-dried at room temperature. The desired product, **XXIp-b**, was a colorless, viscous material, and the yield was (1.65 g, 2.59 mmol, 64%). The ^1H spectrum shown in (Appendix I, Number 23) reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.47, 1.68, 0.49 m (methylene protons 4 H each), 0.35 (Si-CH₂-Si, 4H), 0.05 (Si-CH₃, 12H). The ^{13}C NMR spectrum of **XXIp-b** is shown in Appendix II, Number 5. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 69, 25, 18 (three methylenes), 3 (Si-CH₃), 7.0 (Si-CH₂-Si).

3.4.2 Polymer Derived from the Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,4,4-Tetramethyldisilylethylene-silane (Compound **XXIp-s**). A 50 mL, stainless steel reactor cell was purged with argon, and charged with 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (2.00 g, 4.08 mmol), 4 drops of catalyst (platinum divinyltetramethyldisiloxane complex in xylene), 1,1,4,4-tetramethyldisilylethylene; (0.59 g, 4.08 mmol), and 10 mL of ScCO₂ were added to the cell. The reactor was pressurized to 5000 psi (345 bar), heated to 40°C and reacted for 100 h, forming a tea-colored solution. The ScCO₂ was vented, and the resulting viscous material was dissolved in THF and transferred to a 250 mL beaker. The THF was evaporated, 100 mL of methanol was added, and the solution was stirred overnight. The product was transferred to a separatory funnel, and the viscous material was separated, filtered, placed into a 50 mL flask, and vacuum-dried at room temperature. The desired product, **XXIp-s**, was a colorless, viscous material, and the yield was (1.88 g, 2.95 mmol, 73%). The ^1H spectrum shown in Appendix I, Number 24 reveals the following shifts, (ppm): 7.84, 7.67, 7.53

(aromatic protons, 4 H), and 3.47, 1.68, 0.49 m (methylene protons 4 H each), 0.35 (Si-CH₂-Si 4H), 0.05 (Si-CH₃, 12 H). The ¹³C NMR spectrum of **XXIp-s** is shown in Appendix II, Number 6. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 69, 25, 18, (three methylenes), 3 (Si-CH₃), and 7.0 (Si-CH₂-Si). Calculated for C₂₄H₃₂F₁₂O₂Si₂: 45.28 %C, and 5.07 %H; found: 45.32 %C, and 5.11 %H.

3.4.3 Polymer Derived from the Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,4-Bis(dimethylsilyl) Benzene (Compound **XXIIP-b**). The preparation and work-up procedure generally followed that described for Compound **XXIp-b**, using the following reactants: 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (2.00 g, 4.08 mmol) 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,4-bis (dimethylsilyl) benzene (0.80 g, 4.08 mmol), and 10 mL of benzene. The desired product, **XXIIP-b**, was a colorless, viscous material and the yield was (2.03 g, 2.96 mmol, 73%). The ¹H spectrum shown in Appendix I, Number 25, and reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.51, 1.74, 0.76 m (methylene protons 4 H each), 7.50 (Si--Si) 4H), and 0.05 (Si-CH₃ 12H). The ¹³C NMR spectrum of **XXIIP-b** is shown in Appendix II, Number 7. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 69, 23, 10, (three methylenes), -3 (Si-CH₃), and 134 (Si--Si).

3.4.4 Polymer Derived from the Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,4-Bis(dimethylsilyl) Benzene,

(Compound **XXIIp-s**). The preparation and work-up procedure generally followed that described for Compound **XXIp-s**, using the following reactants: 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (2.00 g, 4.08 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,4-bis-(dimethylsilyl) benzene, (0.80 g, 4.08 mmol), and 10 mL of ScCO₂. The desired product, **XXIIp-s**, was a colorless, viscous material, and the yield was (2.59 g, 3.78 mmol, 92%). The ¹H spectrum shown in Appendix I, Number 26 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.51 m 1.74, 0.76 m (methylene protons, 4 H each), 7.50 (Si--Si), 4H), and 0.30 (Si-CH₃, 12H). The ¹³C NMR spectrum of **XXIIp-s** is shown in Appendix II, Number 8. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 69, 23, 10, (three methylenes), -3 (Si-CH₃), and 134 (Si--Si). Calculated for C₂₈H₃₂F₁₂O₂Si₂, 49.12 %C, and 4.71 %H; found 50.19 %C, and 5.19 %H.

3.4.5 Polymer Derived from the Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and Diphenylsilane (Compound **XXIIIp-b**)
 The preparation and work-up procedure generally followed that described for Compound **XXIp-b**, using the following reactants: 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (2.00 g, 4.08 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), diphenylsilane (0.75 g, 4.08 mmol), and 10 mL of benzene. The desired product, **XXIIIp-b**, was a colorless, viscous material, and the yield was (1.53 g, 2.27 mmol, 56%). The ¹H spectrum shown in Appendix I, Number 27 showed the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.55, 1.78, 1.18 (methylene protons, 4

H each), and 7.53, 7.42 (Si-()₂, 10 H). The ¹³C NMR spectrum of **XXIIIp-s** is shown in Appendix II, Number 10. The significant peaks are as follows (ppm): 129 (CF₃ group carbon), 128 (tertiary carbon), 131, 125, 124, 121 (aromatic carbons), 69, 23, 10 (three methylenes), and 135, 136, 137 (Si-()₂).

3.4.6 Polymer Derived from the Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and Diphenylsilane (Compound **XXIIIp-s**).
The preparation and work-up procedure generally followed that described for Compound **XXIp-s**, using the following reactants: 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (2.00 g, 4.08 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), diphenylsilane; (0.75 g, 4.08 mmol), and 10 mL of ScCO₂. The desired product, **XXIIIp-s**, was a colorless, tacky, solid like, material. Yield was (2.33 g, 2.27 mmol, 84%). The ¹H spectrum shown in Appendix I, Number 28, and reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.55, 1.78, 1.18 m (methylene protons 4 H each), 7.53, 7.42 (Si-()₂, 10 H). The ¹³C NMR spectrum of **XXIIIp-s** is shown in Appendix II, Number 10. The significant peaks are as follows (ppm): 129 (CF₃ group carbon), 128 (tertiary carbon), 131, 125, 124, 121 (aromatic carbons), 69, 23, 10, (three methylenes), and 135, 136, 137, (Si-()₂). Calculated for C₃₀H₂₆F₁₂O₂Si, 53.91 %C, and 3.88 %H; found 52.73 %C, and 4.42 %H.

3.4.7 Polymer Derived from the Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3-Tetramethyldisiloxane (Compound **.XXIVp-b**). The preparation and work-up procedure generally followed that

described for Compound XXI_p-b, using the following reactants: 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (2.00 g, 4.08 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,1,3,3-tetramethyldisiloxane (0.51 g, 4.08 mmol), and 10 mL of benzene. The yield was (1.77 g, 2.29 mmol, 70 %). The ¹H spectrum shown in Appendix I, Number 29 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.48, 1.71, 0.50 (methylene protons, 4 H each), and 0.06 m (Si-CH₃) total 12H). The ¹³C NMR spectrum of XXI_p-b is shown in Appendix II, Number 11. The significant peaks are as follows (ppm): 129 (CF₃ group carbon), 128 (tertiary carbon), 131, 125, 124, 121 (aromatic carbons), 69, 23, 13, (three methylenes), and -1 (Si-CH₃).

3.4.8 Polymer Derived from the Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3-Tetramethyldisiloxane (Compound XXI_p-s). The preparation and work-up procedure generally followed that described for Compound XXI_p-s, using the following reactants: 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (2.00 g, 4.08 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,1,3,3-Tetramethyldisiloxane; (0.51 g, 4.08 mmol), and 10 mL of ScCO₂. The desired product, XXI_p-s, was a yellow-tinted liquid, and the yield was (2.02 g, 3.29 mmol, 80%). The ¹H spectrum shown in Appendix I, Number 30 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.48, 1.71, 0.50 (methylene protons, 4 H each), 0.06 (Si-CH₃, total 12H). The ¹³C NMR spectrum of XXI_p-s is shown in Appendix II, Number 12. The significant peaks are as follows (ppm): 129 (CF₃ group carbon), 128 (tertiary carbon), 131, 125, 124, 121 (aromatic carbons), 69, 23, 13 (three methylenes), and -1 (Si-

CH₃). Calculated for C₂₂H₂₈F₁₂O₃Si₂, 42.30 %C, and 4.52 %H; found 44.18 %C, and 4.98 %H.

3.4.9 Polymer Derived from the Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane (Compound XXVp-b). The preparation and work-up procedure generally followed that described for Compound XXI_p-b, using the following reactants: 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (2.00 g, 4.08 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (1.15 g, 4.08 mmol), and 10 mL of benzene. The desired product, **XXVp-b**, was a yellow-tinted liquid material, and the yield was (2.43 g, 3.14 mmol, 77 %). The ¹H spectrum shown in Appendix I, Number 31 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.53 m 1.77, 0.54 m (methylene protons 4 H each), 0.07 m (Si-CH₃) total 24H). The ¹³C NMR spectrum of **XXVp-b** is shown in Appendix II, Number 13. The significant peaks are as follows (ppm): 129 (CF₃ group carbon), 128 (tertiary carbon), 131, 125, 124, 121 (aromatic carbons), 69, 23, 13 (three methylenes), and -1 (Si-CH₃).

3.4.10 Polymer Derived from the Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane (Compound XXVp-s). The preparation and work-up procedure generally followed that described for Compound XXI_p-s, using the following reactants: 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (2.00 g, 4.08 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,1,3,3,5,5,7,7-octamethyltetrasiloxane ; (1.15 g, 4.08 mmol), and 10 mL of

ScCO₂. The desired product, **XXVp-s**, was a colorless liquid material . Yield was (2.84 g, 3.67 mmol, 90%). The ¹H spectrum shown in Appendix I, Number 32 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.53 m 1.77, 0.54 m (methylene protons 4 H each), 0.07 m (Si-CH₃) total 24 H). The ¹³C NMR spectrum of **XXVp-s** is shown in Appendix II, Number 14. The significant peaks are as follows (ppm): 129 (CF₃ group carbon), 128 (tertiary carbon), 131, 125, 124, 121 (aromatic carbons), 69, 23, 13 (three methylenes), and -1 (Si-CH₃). Calculated for C₂₆H₄₀F₁₂O₅Si₄, 40.40 %C, and 5.22 %H; found 40.46 %C, and 5.24 %H.

3.4.11 Polymer Derived from the Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,2-Bis(tetramethyldisiloxaneyl)ethane (Compound **XXVIp-b**) The preparation and work-up procedure generally followed that described for Compound **XXIp-b**, using the following reactants: 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (2.00 g, 4.08 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,2-bis(tetramethyldisiloxaneyl)ethane (1.20 g, 4.08 mmol), and 10 mL of benzene. The desired product, **XXVIp-b**, was a colorless liquid material, and the yield was (2.73 g, 3.48 mmol, 85 %). The ¹H spectrum shown in Appendix I, Number 33 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.48 m 1.74, 0.50 m (methylene protons 4 H each), 0.07 m (Si-CH₃ total 24 H), and 0.38 m (Si-(CH₂)₂-Si,.4H). The ¹³C NMR spectrum of **XXVIp-b** is shown in Appendix II, Number 15. The significant peaks are as follows (ppm): 129 (CF₃ group carbon), 128 (tertiary carbon), 131, 125, 124, 121 (aromatic carbons), 69, 23, 13, (three methylenes), 0, (Si-CH₃), and 7, (Si-(CH₂)₂-Si).

3.4.12 Polymer Derived from the Reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,2-Bis(tetramethyldisiloxaneyl)ethane (Compound **XXVI**s). The preparation and work-up procedure generally followed that described for Compound **XXI**_{p-s}, using the following reactants: 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (2.00 g, 4.08 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,2-bis(tetramethyldisiloxaneyl)ethane; (1.20 g, 4.08 mmol), and 10 mL of ScCO₂. The desired product, **XXVI**s, was a colorless liquid, and the yield was (2.79 g, 3.55 mmol, 87%). The ¹H spectrum shown in Appendix I, Number 34 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.48, 1.74, 0.50, (methylene protons 4 H each), 0.07 m (Si-CH₃ total 24 H), and 0.38 m (Si-(CH₂)₂-Si, 4H). The ¹³C NMR spectrum of **XXVI**_{p-s} is shown in Appendix II, Number 16. The significant peaks are as follows (ppm): 129 (CF₃ group carbon), 128 (tertiary carbon), 131, 125, 124, 121 (aromatic carbons), 69, 23, 13, (three methylenes), 0, (Si-CH₃), 7, (Si-(CH₂)₂-Si). Calculated for C₂₈H₄₄F₁₂O₄Si₄, 42.84 %C, and 5.65 %H; found 43.08 %C, and 5.66 %H.

3.5 Decenyl HFAB Synthesis

3.5.1 Preparation of 1-decene1-ol Sulfonate (Tosylate) (Compound **IX**). 9-decene-1-ol (10 g, 64 mmol) was placed into a 1000 mL Erlenmyer flask, along with 450 mL of pyridine at 0°C. The solution was stirred for 5 minutes; then *p*-toluensulfonyl chloride (4.6 g, 77 mmol) was added and the solution was stirred for 10 minutes. The flask was then covered and placed into the freezer for 5 days. White, needle like, pyridium chloride crystals formed and were removed by filtration. Diethyl ether (200 mL) was added to the solution, and stirred for 10 minutes at 0°C. The solution was transferred to a separatory

funnel and washed with H₂O (4 times 100 mL each time) at 0°C. The aqueous layers were removed and the ether layers were combined and dried over MgSO₄. The colorless liquid was evaporated at room temperature, forming a white solid 1-decene10-sulfonate (Compound IX). The ¹H spectrum shown in Appendix I, Number 17 reveals the following shifts, (ppm): 7.74, 7.33, (aromatic protons, 4 H) 5.76, 4.98, 4.91, 3.99 (CH=CH₂, 3H) 2.42 (methyl group, 3H), 2.01, 1.59, 1.29, 1.20, and (methylenes 16 H total).

3.5.2 Preparation of 1,3-Bis [hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene (Decenyl Monomer) (Compound XI). A oven-dried, 500 mL, 3-necked round-bottom flask was equipped with a condenser, flow control adapter, and magnetic stir bar. The flask was evacuated and filled with argon. Sodium hydride (1.22 g - 60% in mineral oil) was obtained. The mineral oil was removed with pentane, to give (0.7317 g, 30 mmol) of NaH. The NaH pentane solution was placed into the flask. The pentane was then removed by vacuum. DMF (10 mL) was added to the gray solid. The solution was chilled to 0°C with an ice bath, then 1,3-bis(hexafluoro-2-propyl) benzene, (1,3-Bis HFAB), (5.0 g 12 mmol), diluted with 10 mL of DMF, was added to the reaction mixture, dropwise, through an addition funnel. The ice bath was removed and the solution was allowed to warm to room temperature and stirred for 30 minutes. 1-decene1-ol sulfonate, (8.3 g 26.8 mmol), dissolved in (10 mL) of DMF, was added dropwise, over a 30 minute period to the sodium-1,3-Bis HFAB-alkoxide solution. The solution was heated to 50°C and stirred for 6 hours. The DMF was removed under vacuum, leaving a yellow viscous solution. The solution was quenched with H₂O (15 mL). The mixture was stirred for 10 minutes and then dissolved in (200 mL) of diethyl ether and stirred for another 10 minutes.

The solution was transferred to a separatory funnel and washed with 0.1 M HCl (150 mL). The aqueous layer was removed and the ether layer was dried over MgSO₄. The product was dried under vacuum. The yellow-tinted-viscous-oil was eluted through a silica gel packed column using hexane, and the product was collected. The hexane was removed under vacuum, leaving the desired clear liquid product of 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene, (Compound XI). The yield was (5.34 g, 77 mmol, 65%). The ¹H spectrum shown in Appendix I, Number 18 reveals the following shifts, (ppm): 7.74, 7.33, (aromatic protons, 4 H), 5.76, 4.98, 4.91, 3.99, (CH=CH₂, 6H), 2.01, 1.59, 1.29, and 1.20, (methylenes 32 H total). The ¹³C NMR spectrum of XI is shown in Appendix II, Number 17. The significant peaks are as follows: 139 ppm (the CH carbon in the CH=CH₂ group), 129 ppm (CF₃ group carbon), 126 ppm (tertiary carbon), 125, 124, 121 ppm (aromatic carbons), 114 ppm (the CH₂ carbon in the CH=CH₂ group), 67 ppm (O-CH₂ carbon), 33, 29, 25 ppm (the CH₂-(CH₂)₄-CH₂ methylenes). Calculated for C₃₂H₄₂F₁₂O₂, 55.97 %C, and 6.17 %H; found 55.97 %C, and 6.50 %H

3.6 Decenyl Model

3.6.1 Compound Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and Dimethylphenylsilane (Decenyl Model Hydrosilation in Benzene) (Compound XIV-s). The preparation and work-up procedure generally followed that described for Compound XXI**p-b**, using the following reactants: 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (1.00 g, 1.40 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), dimethyl phenyl silane (0.4459 g, 3.27 mmol), and 10 mL of

benzene. The desired product, **XIV-b**, was a colorless liquid. The yield was (1.02 g, 1.06 mmol, 74 %). The ^1H spectrum shown in Appendix I, Number 21. reveals the following shifts, (ppm): 7.87, 7.71, 7.58 (aromatic protons, 4 H), 3.56 m (O-CH₂, 4 H), 1.73 m (CH₂, 4H), 0.77 m (Si-CH₂, 4 H), 1.31 broad (bulk middle methylenes, 28 H), (Si- carbons 10H), and 1.5, (Si-CH₃, 6H). The ^{13}C NMR spectrum of **XIV-b** was not performed.

3.6.2 Compound Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and Dimethylphenylsilane, (Decenyl Model Hydrosilation in ScCO₂) (Compound XIV-s). A 50 mL stainless steel reactor cell was purged with argon. Then 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (1.41 g, 2.05 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), phenyl dimethyl silane (0.62 g, 4.51 mmol), and and 10 mL of ScCO₂ were added to the cell. The reactor was pressurized to 5000 psi (345 bar) and heated to 40°C. The reaction turned green and later formed a dark black colored solution. After 100 h the reaction was stopped, and the ScCO₂ vented. A yellow oily solution remained, which was transferred to a separatory funnel, washed with 0.1M HCl (50 mL), extracted with chloroform (100 mL), and filtered. The resulting black tinted viscous oil was eluded through a short silica gel column, using chloroform. The chloroform was removed by rotary evaporation, leaving the desired colorless liquid product, **XIV-s**. The yield was (1.06 g, 1.10 mmol, 54 %). The ^1H spectrum shown in Appendix I, Number 22 reveals the following shifts, (ppm): 7.87, 7.71, 7.58 (aromatic protons, 4 H), 3.56 m (O-CH₂, 4 H), 1.73 (CH₂, 4H), 0.77 (Si-CH₂, 4 H), 1.31 broad (bulk middle methylenes, 28 H), (Si- carbons

10H), and 1.5 (Si-CH₃, 6H). The ¹³C NMR spectrum of **XIV-s** is shown in Appendix II, Number 18. The significant peaks are as follows (ppm): 137 (Si-) , 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 68, 34, 29, 26, 25, 16 (ten methylenes), and -2.4 (Si-CH₃). Calculated for C₄₈H₆₆F₁₂O₂Si, 60.10 %C, and 6.94 %H; found 60.66 %C, and 7.50 %H.

3.7 Decyl Polymers

3.7.1 Polymer Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,4,4-Tetramethyldisilylethylene
(Compound **XXId-b**). The preparation and work-up procedure generally followed that described for Compound **XXIp-b**, using the following reactants: 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (1.9972 g, 2.90 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,1,4,4-tetramethyldisilylethylene, (0.42 g, 2.90 mmol), and 10 mL of benzene. The desired product, **XXId-b**, was a colorless, viscous material, and the yield was (1.88 g, 2.25 mmol, 78%). The ¹H spectrum shown in Appendix I, Number 35 reveals the following shifts, (ppm): 7.84 s, 7.67, 7.53 (aromatic protons, 4 H), 3.53, 1.69, 1.30, 1.28, 0.49, broad (bulk methylenes, 40H), (Si-(CH₂)₂-Si) 4 H), and 1.5 (Si-CH₃, 12H). The ¹³C NMR spectrum of **XXId-b** is shown in Appendix II, Number 19. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 66, 34, 29, 25, 23, 14 (ten methylenes), -5 (CH₂)₂-Si), and 7 (Si-CH₃).

3.7.2 Polymer Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,4,4-Tetramethyldisiethylene (Compound **XXId-s**). The preparation and work-up procedure generally followed that described for Compound XXI_{p-s}, using the following reactants: 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (1.99 g, 2.90 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,1,4,4-tetramethyldisiethylene, (0.4252 g, 2.90 mmol), and 10 mL of ScCO₂. The desired product, **XXId-s**, was a colorless, viscous material, and the yield was (2.01 g, 2.27 mmol, 83%). The ¹H spectrum shown in Appendix I, Number 36 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.53, 1.69, 1.30, 1.28, 0.49, broad (bulk methylenes, 40H), 0.34 (Si-(CH₂)₂-Si) 4 H), and 1.5 (Si-CH₃, 12H). The ¹³C NMR spectrum of **XXId-s** is shown in Appendix II, Number 20. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 66, 34, 29, 25, 23, 14 (ten methylenes), and 7 (Si-CH₃). Calculated for C₃₈H₆₀F₁₂O₂Si₂, 54.79 %C, and 7.26 %H; found 55.45 %C, and 7.20 %H.

3.7.3 Polymer Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,4-Bis(dimethylsilyl)benzene (Compound **XXIId-b**). The preparation and work-up procedure generally followed that described for Compound XXI_{p-b}, using the following reactants: 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (1.89 g, 2.75 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,4-bis(dimethylsilyl)benzene (0.53 g, 2.75 mmol), and 10 mL of benzene. The desired product, **XXIId-b**, was a colorless, viscous material, and the yield was (2.23 g, 2.53 mmol, 92%). The ¹H spectrum shown in Appendix I, Number 37

reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.53, 1.72, 1.30, 1.29, 0.49, broad (bulk methylenes, 40 H), 7.50 m (Si--Si) 4 H), 0.25, (Si-CH₃, 12H). The ¹³C NMR spectrum of **XXIId-b** is shown in Appendix II, Number 21. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 66, 34, 29, 25, 23, 13 (ten methylenes), -2 (CH₂)₂-Si), 141, 134 (Si--Si).

3.7.4 Polymer Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,4-bis dimethylsilyl benzene-silane (Compound **XXIId-s**). The preparation and work-up procedure generally followed that described for Compound XXIId-p, using the following reactants. 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (1.89 g, 2.75 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,4-bis dimethyl silyl benzene, (0.53 g, 2.75 mmol), and 10 mL of ScCO₂. The desired product, **XXIId-s**, was a colorless, viscous material, and the yield was (2.09 g, 2.36 mmol, 86%). The ¹H spectrum shown in Appendix I, Number 38 reveals the following shifts, (ppm): 7.84 s, 7.67, 7.53 (aromatic protons, 4 H), 3.53, 1.72, 1.30, 1.29, 0.49, broad (bulk methylenes, 40H), 7.50 m (Si--Si) 4 H), 0.25 (Si-CH₃, 12H). The ¹³C NMR spectrum of **XXIId-s** is shown in Appendix II, Number 22. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 66, 34, 29, 25, 23, 13 (ten methylenes), 141, 134 (Si--Si). Calculated for C₄₂H₆₀F₁₂O₂Si₂, 57.27 %C, and 6.86 %H; found 57.10 %C, and 6.76 %H.

3.7.5 Polymer Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and Diphenyl-silane (Compound **XXIII-d-b**).

The preparation and work-up procedure generally followed that described for Compound XXI-p-b, using the following reactants: 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (2.00 g, 2.91 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), diphenyl-silane (0.75 g, 2.91 mmol), and 10 mL of benzene. The desired product, **XXIII-d-b**, was a colorless, viscous material, and the yield was (1.53 g, 1.75 mmol, 60%). The ¹H spectrum shown in Appendix I, Number 39 reveals the following shifts, (ppm): 7.84 s, 7.67, 7.53 (aromatic protons, 4 H), 3.54, 1.73, 1.34, 1.39, 1.58, broad (bulk methylenes, 40H), 7.56, 7.37 m (Si-()₂, 10 H). The ¹³C NMR spectrum of **XXIII-d-b** is shown in Appendix II, Number 23. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 66, 34, 29, 25, 24, 16 (ten methylenes), 137, 136, 135, 130 (Si-()₂).

3.7.6 Polymer Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and Diphenyl-silane (Compound **XXIII-d-s**)

The preparation and work-up procedure generally followed that described for Compound XXI-p-s, using the following reactants: 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (2.00 g, 2.91 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), diphenyl-silane; (0.54 g, 2.91 mmol), and 10 mL of ScCO₂. The desired product, **XXIII-d-s**, was a yellow tacky solid like material. Yield was (2.33 g, 2.67 mmol, 92%). The ¹H spectrum shown in Appendix I, Number 40 reveals the following shifts, (ppm): 7.84 s, 7.67, 7.53 (aromatic protons, 4 H), 3.54, 1.73, 1.34, 1.39, 1.58, broad

(bulk methylenes, 40H), and 7.56, 7.37 (Si-(C_6H_5)₂, 10 H). The ¹³C NMR spectrum of **XXIII-d-s** is shown in Appendix II, Number 24. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 66, 34, 29, 25, 24, 16 (ten methylenes), and 137, 136, 135, 130 (Si-(C_6H_5)₂). Calculated for C₄₄H₅₄F₁₂O₂Si₂, 60.68 %C, and 6.25 %H; found 59.97 %C, and 6.50 %H.

3.7.7 Polymer Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,3,3-Tetramethyldisiloxanediphenylsilane, (Compound **XXIV-d-b**). The preparation and work-up procedure generally followed that described for Compound **XXI-p-b**, using the following reactants: 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (1.6533 g, 2.40 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,1,3,3-tetramethyldisiloxane (0.29 g, 2.40 mmol), and 10 mL of benzene. The desired product, **XXIV-d-b**, was a brown free flowing liquid. The yield was (1.01 g, 1.24 mmol, 52 %). The ¹H spectrum shown in Appendix I, Number 41 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.51, 1.70, 1.28, 1.28, 0.50 m (bulk methylenes, 40H), and 0.34 (Si-CH₃), 12 H). The ¹³C NMR spectrum of **XXIV-d-b** is shown in Appendix II, Number 25. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 66, 33, 29, 23, 21, 17 (ten methylenes), and 0 (Si-CH₃).

3.7.8 Polymer Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-

decenyloxy-2-propyl)] Benzene and 1,1,3,3-Tetramethyldisiloxane (Compound **XXIVd-s**). The preparation and work-up procedure generally followed that described for Compound **XXIp-s**, using the following reactants: 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (1.6533 g, 2.40 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,1,3,3-tetramethyldisiloxane, (0.29 g, 2.40 mmol), and 10 mL of ScCO₂. The desired product, **XXIVd-s**, was a colorless liquid material . Yield was (1.56 g, 1.92 mmol, 80%). The ¹H spectrum shown in Appendix I, Number 42 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.51, 1.70, 1.28, 1.28, 0.50, (bulk methylenes, 40H), 0.34 (Si-CH₃), 12 H). The ¹³C NMR spectrum of **XXIVd-s** is shown in Appendix II, Number 26. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 66, 33, 29, 23, 21, 17 (ten methylenes), 0 (Si-CH₃). Calculated for C₃₆H₅₆F₁₂O₂Si₂, 52.67 %C, and 6.88 %H; found 54.42 %C, and 7.20 %H.

3.7.9 Polymer Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane (Compound **XXVd-b**). The preparation and work-up procedure generally followed that described for Compound **XXIp-b**, using the following reactants: 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (1.89 g, 2.76 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (0.78 g, 2.76 mmol), and 10 mL of benzene. The product was a yellow-tinted liquid material, and the yield of the desired product, **XXVd-b** was (2.30 g, 2.37 mmol, 86 %). The ¹H spectrum shown in Appendix I, Number 43 reveals the following shifts, (ppm): 7.84

s, 7.67, 7.53 (aromatic protons, 4 H), 3.51, 1.70, 1.28, 1.28, 0.50, broad (bulk methylenes, 40H), and 0.34 (Si-CH₃), 24 H). The ¹³C NMR spectrum of **XXVd-b** is shown in Appendix II, Number 27. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 66, 33, 29, 23, 21, 17 (ten methylenes), and 0 (Si-CH₃).

3.7.10 Polymer Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane (Compound XXVd-s). The preparation and work-up procedure generally followed that described for Compound XXI_p-b, using the following reactants: 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (1.89 g, 2.76 mmol), 4 drops of catalyst, (platinum divinyltetrasiloxane complex in xylene), 1,1,3,3,5,5,7,7-octamethyltetrasiloxane, (0.78 g, 2.76 mmol), and 10 mL of ScCO₂. The desired product, **XXVd-s**, was a colorless liquid material. The yield was (2.16 g, 2.22 mmol, 81%). The ¹H spectrum shown in Appendix I, Number 44 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.51, 1.70, 1.28, 1.28, 0.50, broad (bulk methylenes, 40H), 0.34 (Si-CH₃), 24 H). The ¹³C NMR spectrum of **XXVd-s** is shown in Appendix II, Number 28. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 66, 33, 29, 23, 21, 17 (ten methylenes), 0 (Si-CH₃). Calculated for C₄₀H₆₆F₁₂O₂Si₂, 49.57 %C, and 7.07 %H; found 50.39 %C, and 7.06 %H.

3.7.11 Polymer Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-

decenyloxy-2-propyl)] Benzene and 1,2-Bis(tetramethyldisiloxaneyl)ethane (Compound **XXVIId-b**). The preparation and work-up procedure generally followed that described for Compound XXI**p**-b, using the following reactants: 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (2.00 g, 2.91 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,2-bis(tetramethyldisiloxaneyl)ethane (0.425 g, 2.91 mmol), and 10 mL of benzene. The desired product, Decyl Polymer, was a yellow-tinted liquid material, and the yield was (2.73 g, 3.48 mmol, 85 %). The ¹H spectrum shown in Appendix I, Number 45 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.52, 1.69, 1.28, 1.27, 0.49, broad (bulk methylenes, 40H), 0.39 (Si(CH₂)₂, 4 H), 0.02 (Si-CH₃), 24 H). The ¹³C NMR spectrum of **XXVIId-b** is shown in Appendix II, Number 29. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 66, 33, 29, 23, 21, 17 (ten methylenes), 10 (Si(CH₂)₂), 0 (Si-CH₃).

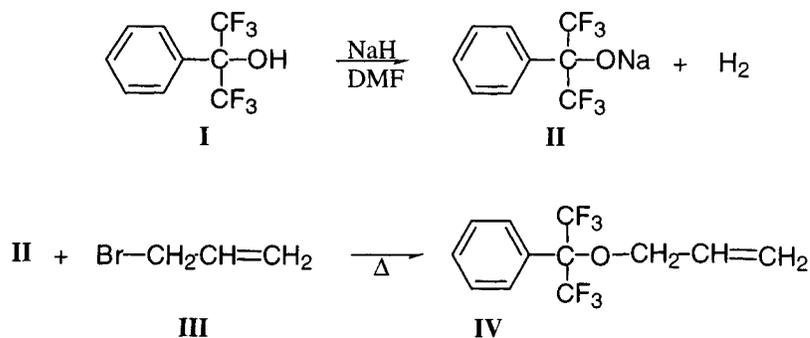
3.7.12 Polymer Derived from the Reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,2-Bis(tetramethyldisiloxaneyl)ethane (Compound **XXVIId-s**). The preparation and work-up procedure generally followed that described for Compound XXI**p**-s, using the following reactants: 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (2.00 g, 2.91 mmol), 4 drops of catalyst, (platinum divinyltetramethyldisiloxane complex in xylene), 1,2-bis(tetramethyldisiloxaneyl)ethane, (0.425 g, 2.91 mmol), and 10 mL of ScCO₂. A colorless liquid, **XXVIId-s**, was obtained. The yield was (1.83 g, 1.86 mmol, 76 %). The ¹H spectrum shown in Appendix I, Number 46 reveals the following shifts, (ppm): 7.84, 7.67, 7.53 (aromatic protons, 4 H), 3.52, 1.69, 1.28, 1.27,

0.49, broad (bulk methylenes, 40H), 0.39 (Si(CH₂)₂, 4 H), and 0.02 (Si-CH₃), 24 H). The ¹³C NMR spectrum of **XXVI**d-s is shown in Appendix II, Number 30. The significant peaks are as follows (ppm): 130 (CF₃ group carbon), 128 (tertiary carbon), 131, 126, 125, 122 (aromatic carbons), 66, 33, 29, 23, 21, 17 (ten methylenes), 10 (Si(CH₂)₂), and 0 (Si-CH₃). Calculated for C₄₂H₇₂F₁₂O₂Si₂, 51.40 %C, and 7.40 %H; found 51.63 %C, and 7.54 %H.

4.0 RESULTS AND DISCUSSION

4.1 Synthesis of Allyl HFAB

The synthesis of the model monomer compound, hexafluoro-2-propenyloxy-2-propyl benzene, was performed as shown in Scheme 16. Hexafluoro-2-propyl benzene, (HFAB), (I) was converted to the alkoxide (II), using the strong base, NaH. The reaction is evident by the out-gassing of the H₂ by-product. Allylbromide (III) was added in excess and reacted *in situ* to yield hexafluoro-2-propenyloxy-2-propyl benzene Allyl HFAB, (IV), which was purified by dissolution in hexane and elution through a silica gel cake. Compound IV was analyzed by ¹H NMR to prove the allylation, and the spectrum is shown in Appendix I, Number 12. The allylation was evident by the disappearance of the OH peak at 3.92 ppm of I, the disappearance of the Br-CH₂ peak at 3.90 ppm of III, and the appearance of the O-CH₂ peak at 4.07 ppm of IV (see Figure 11). The model compound was not analyzed further, and the syntheses of the divinyl-containing monomers were begun.



Scheme 16. Synthesis of Allyl Hexafluoro-2-propyl Benzene.

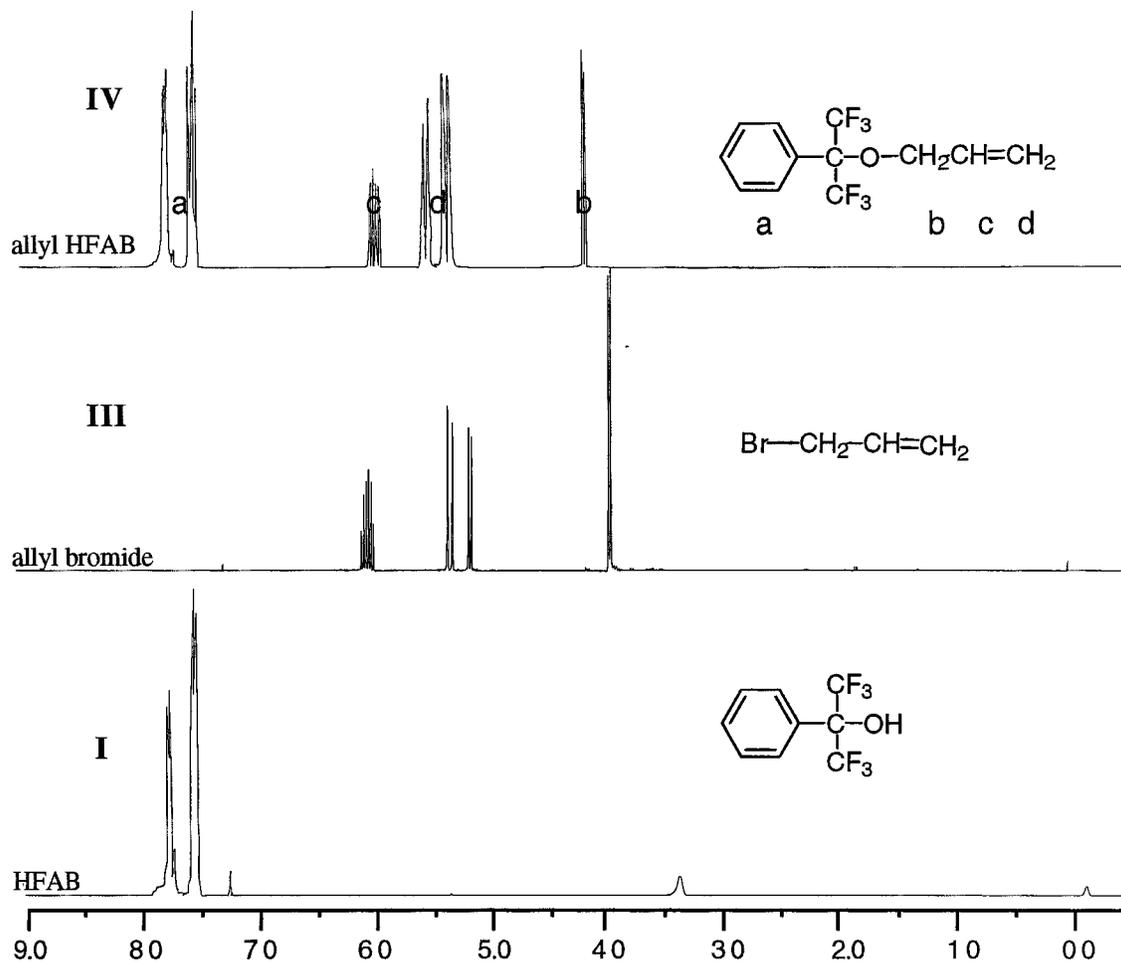


Figure 11. ^1H NMR Spectra Showing the Synthesis of the Model Monomer, IV.

4.2 Synthesis of Propenyl Monomer.

The Bis-HFAB was obtained as a mixture of the 1,3 and 1,4 isomers; so it was necessary to isolate the 1,3 compound, as described in the experimental section. The isomeric purity of 1,3-Bis HFAB was calculated by data obtained from the ^1H NMR spectrum, shown in Figure 12. The calculation for determining the purity is shown in Equation 1.

The synthesis of the monomer, 1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene, was performed as shown in Scheme 17. 1,3-bis(hexafluoro-2-propyl) benzene, (1,3-Bis HFAB), (V) was converted to the alkoxide (VI) using NaH. The alkoxide was reacted *in situ* with excess allylbromide (III) to yield

1,3-bis(hexafluoro-2-propenyloxy-2-propyl) benzene (VII).

Equation 1. Isomeric Purity Calculation for 1,3 & 1, 4 HFAB

Formula	Calculations for figure 12
i. For pure 1,3 $a + c = 2b$	$1.00 + 1.03 = 2.03$
ii. For 1,3 & 1,4 $2b + 4b' = \text{mixture}$	$\text{mixture} = 2.20$
iii. For pure 1,4 $4b' = \text{mixture} - 2b$	
sub {i} in {iii} $4b' = \text{mixture} - (a + c)$	$2.20 - 2.03 = 0.17$
so $b' = [\text{mixture} - (a + c)] / 4$	$0.17 / 4 = 0.04$
and percent 1,4 = $b' / [(a + c) / 2] \times 100$	$0.04 / 1.01 = 3.9\%$

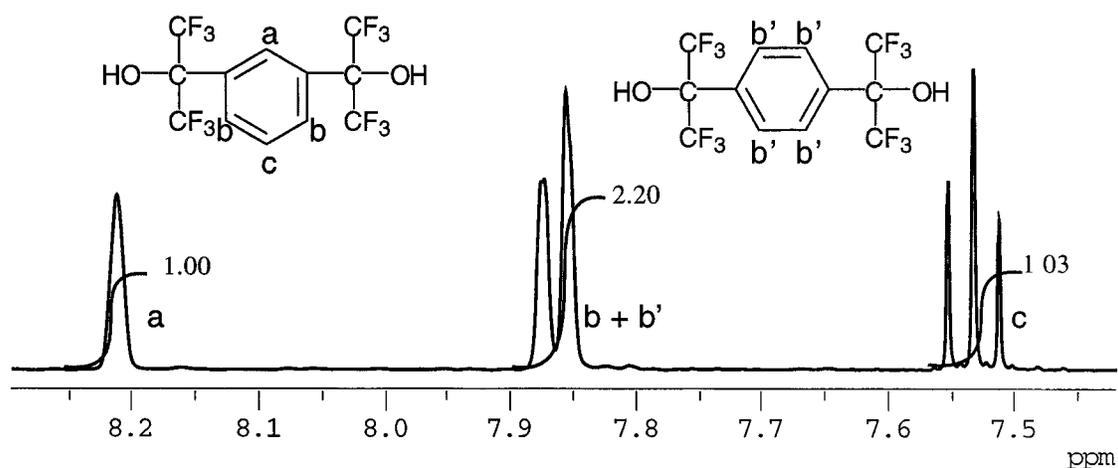
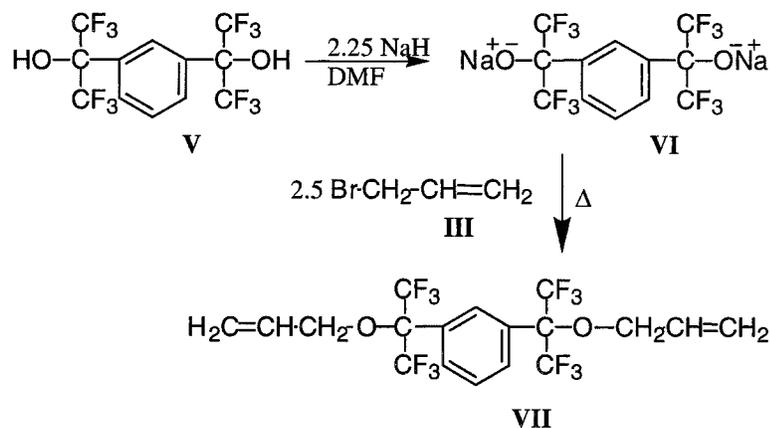


Figure 12. ¹H NMR Spectrum of 1,3-Bis HFAB.



**Scheme 17. Synthesis of Propenyl Momomer
1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene.**

A number of modifications were performed to achieve the desired yield of **VII**. Initially, the sodium anhydride (60% in mineral oil) and allyl bromide were added at room temperature, which caused an increased yellow color in both steps. In addition, the color and the mineral oil had to be removed by column chromatography, which proved to be difficult. A modified procedure, for larger scale reactions, involved removing the mineral oil prior to adding NaH to the reaction. This was accomplished by extraction the mineral oil from the NaH with pentane. Since NaH is extremely moisture sensitive, it was transferred to the reaction flask in a solution of pentane under argon, and the pentane was subsequently removed under vacuum. The increased yellow color was avoided by adding the 1,3-Bis HFAB at 0°C and then gently warming it to 70°C. A spot test on a TLC plate (using a 70:30 chloroform:hexane eluent) revealed that the reaction mixture contained three species. The desired product, **VII**, moved with the solvent front, followed by allylbromide and the last product, which was assumed to be the mono-substituted compound. TLC did not show any unreacted 1,3-Bis HFAB, which was non-mobile with this eluent. The reaction mixture had a slight yellow tint, which was removed when the reaction was passed through a silica gel-packed column with the 70:30 chloroform:hexane eluent. The desired product, **VII**, was collected as a clear, free-flowing liquid.

The ^1H NMR spectrum of **VII** is shown in Appendix I, Number 15, and with the corresponding peaks labeled in Figure 13. The ^{13}C NMR spectrum of **VII** is shown in Appendix II, Number 3. The significant peaks are as follows: 132 ppm (the CH carbon in the $\text{CH}=\text{CH}_2$ group), 130 ppm (CF_3 group carbon), 126, 125, 122 ppm (aromatic carbons), 115 ppm (the CH_2 carbon in the $\text{CH}=\text{CH}_2$ group), and 67.9 ppm (O- CH_2 carbon). The IR spectrum in Appendix III Number 9 shows a strong sharp band at 1650 cm^{-1} indicative of the C=C stretch, and the aliphatic C-H stretch at 2949 cm^{-1} . Thermal analysis plot of **VII** is shown in

Appendix IV Number 1 and Number 2. The initial thermal decomposition, (10% weight loss), was essentially the same in air and argon at 105°C and 102°C respectively, indicating that the decomposition was not caused by oxidation, but by thermally induced bond cleavage. Elemental analysis was performed by Dessert Analytical Inc and the calculated vs. found was within experimental error.

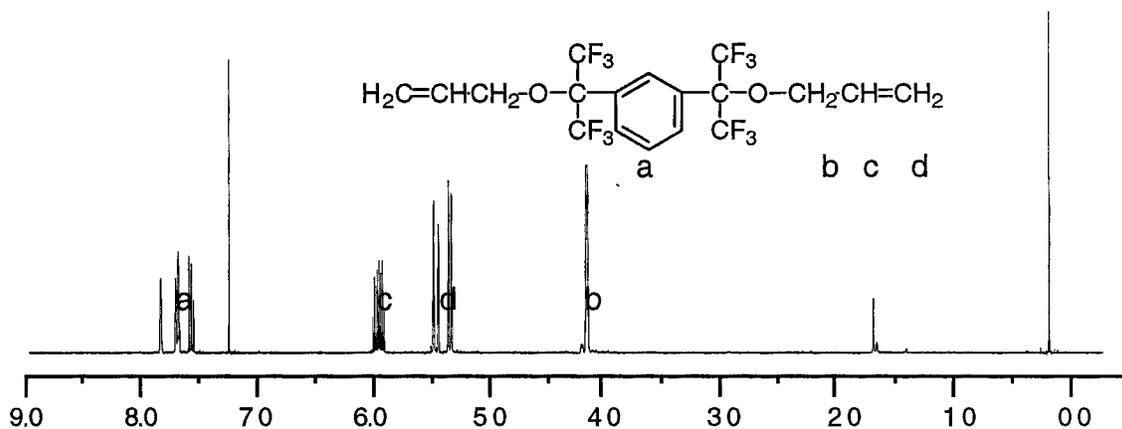
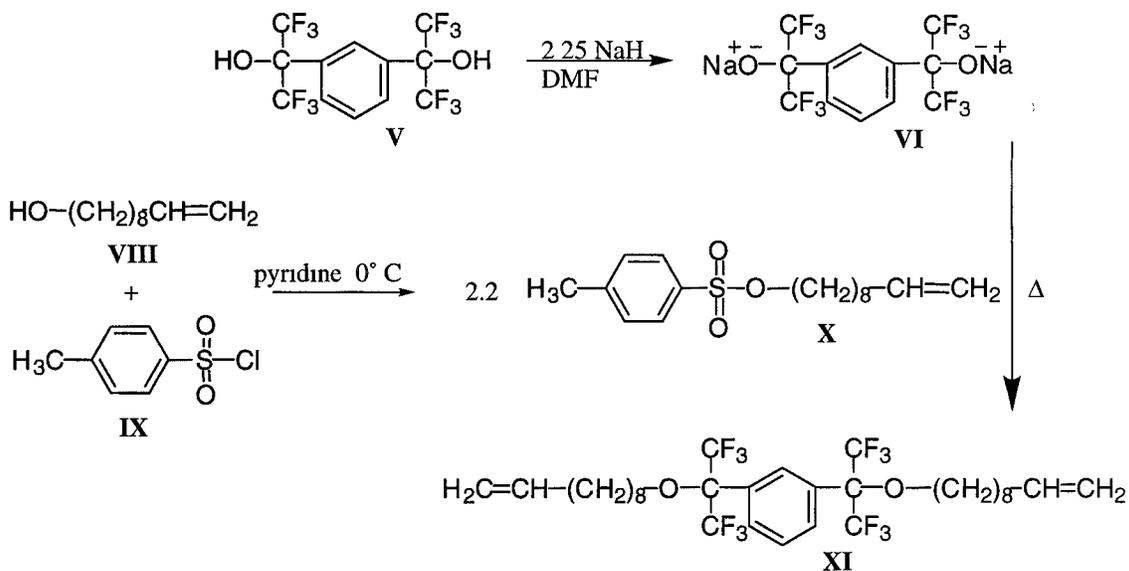


Figure 13 ^1H NMR Spectrum of (VII),
1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene.

4.3 Synthesis of Decenyl Monomer

The synthesis of the monomer, 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene, was performed as shown in Scheme 18. 1,3-bis(hexafluoro-2-propyl) benzene, (HFAB), (V) was converted to the alkoxide (VI) using NaH. VI was then reacted *in situ* with excess 1-decene-1-ol sulfonate (IX), which was previously prepared from 9-decene-1-ol (VII), to yield 1,3-bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (XI).



**Scheme 18. Synthesis of Decenyl Monomer
1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene.**

The success of this tosylate-forming reaction was very dependent on the temperature during both extractions in the work-up. The reversion back to the alcohol was evident by 9-decene-1-ol's sweet smell. Initial work-ups of this reaction involved removing the white, needle-like pyridinium hydrochloride crystals by filtration, followed by removing the excess pyridine by room-temperature vacuum distillation. The solution was then washed with water and extracted with ether. It was suspected that the tosylate could easily convert back to the alcohol; thus, the ether was removed at room temperature by vacuum, rather than by heated rotary evaporation. The yields for this procedure were 32 to 40 %; however, a more successful work-up, involved the same filtration process, followed by the addition of ice to the filtrate. The filtrate was then extracted at 0°C and the ether was removed by vacuum, leaving a white, crystalline solid, melting point 28°C, 66% yield.

The procedure for the synthesis of **XI** followed those optimized in the synthesis of the Propenyl monomer. After initial workup the monomer was isolated from other reactants by passing the mixture through a silica gel-packed

column using 100 % pentane as the eluent. The product, **XI** eluted first followed by the excess alcohol. Other products including the yellow color, were stationary. Figure 14, shows the ^1H NMR spectra sequence of modifying the reactants to achieve the desired product, **XI**. The formation of the tosylate **IX** from the alcohol **VIII** is evident by the disappearance of the O-H peak at 1.75, and the shift of the O-CH₂ from 3.55 to 3.96, because of the more electronegative attached sulfonate. The ^{13}C NMR spectrum of **XI** is shown in Appendix II, Number 17. The signal at 139 ppm for (the CH carbon in the CH=CH₂ group), was shifted from that of the propyl monomer, which has a signal at 132 ppm for the (CH₂ carbon in the CH=CH₂ group).

The IR spectrum of **XI** is shown in Appendix III, Number 10. The spectrum shows the strong sharp band at 1641.0 cm⁻¹ indicative of the C=C stretch. Also evident is the aliphatic C-H stretch at 29.28 cm⁻¹ and the methylenes peak at 727.9 cm⁻¹.

Thermal analysis (TGA) of **XI**, is shown in Appendix III Number 31, (in air) and Number 32, (in argon). The initial thermal decomposition, (10% weight loss), was essentially the same in both air and argon at 222°C and 213°C respectively. This indicates that the decomposition was not caused by oxidation, but by thermally induced bond cleavage. The plot in air also shows an inflection at 300°C to 410°C, which is possibly the final oxidation of the aromatic moiety. The Decenyl monomer also shows a higher degree of thermal stability when compared to the Propenyl monomer.

Elemental analysis was performed by Dessert Analytical Inc. The theoretical percent carbon and hydrogen were within experimental error.

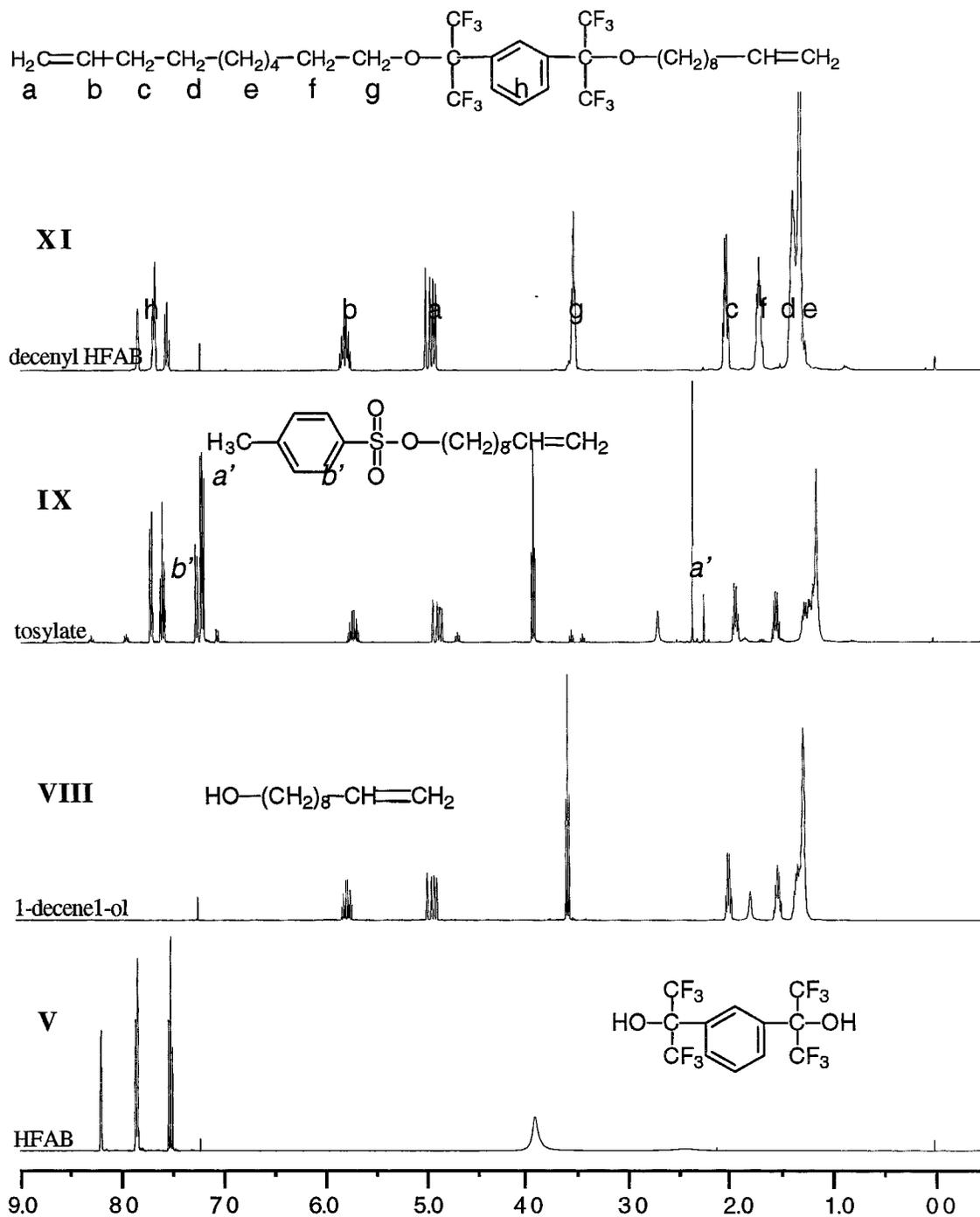


Figure 14. ¹H NMR of 1,3-Bis HFAB, 9-Decene-1-ol, the Tosylate, and 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene.

1.72 and 0.76 ppm of **XIII-b** (see Figure 15). The reaction was quenched at 30 h, when there was no further change in the spectra. The final spectrum of the propenyl model compound, even at the long reaction times, showed unreacted **VII** evident by the allylic proton peaks in the ^1H NMR spectrum shown in Appendix I Number 19.

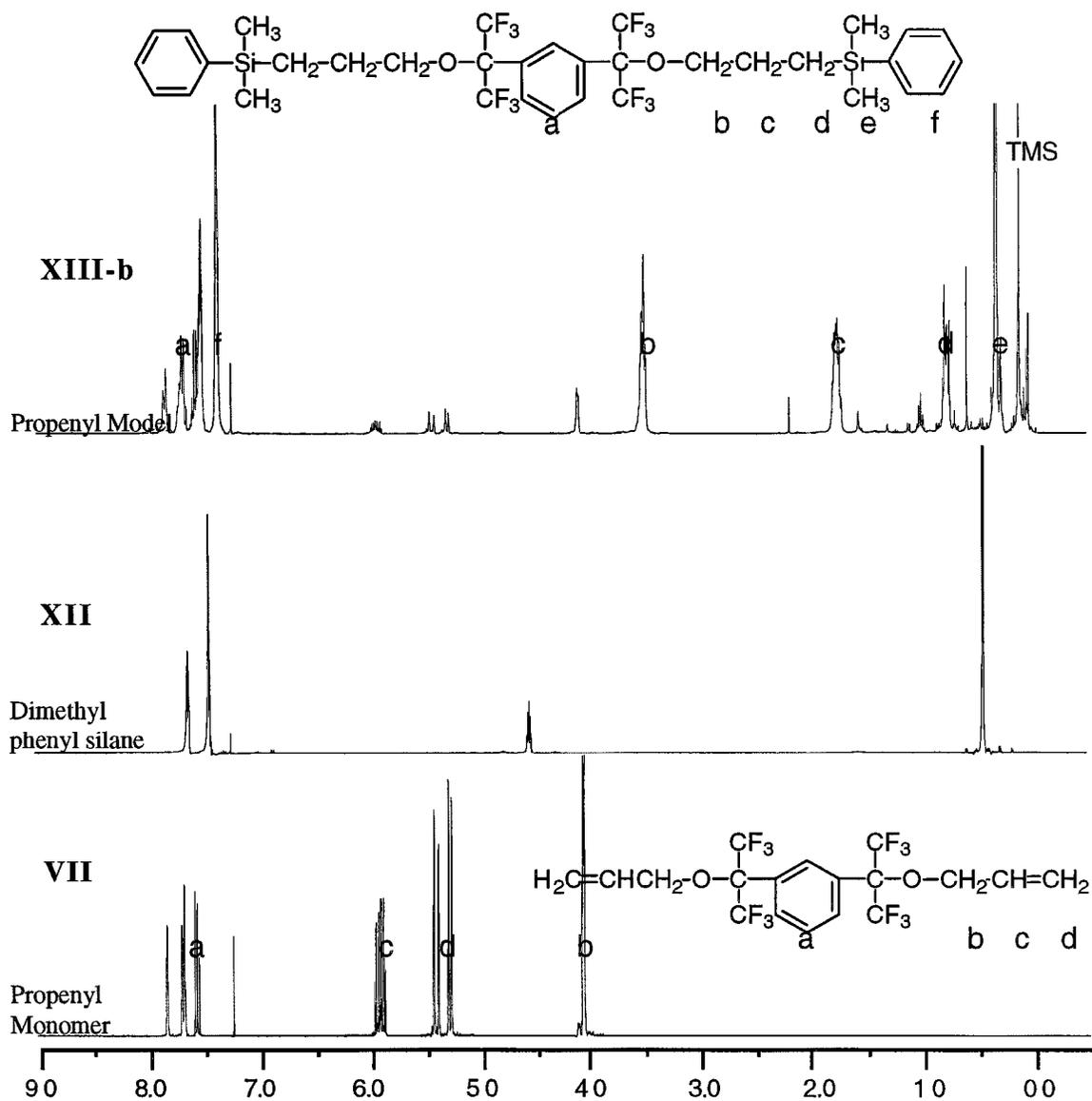


Figure 15. ^1H NMR Spectra Showing the Product, (XIII-b), of the Hydrosilation Reaction of the Propenyl Monomer (VII) and Phenyl dimethylsilane (XII).

The reaction in ScCO₂, was performed in a high-pressure stainless steel vessel and was observed through a sapphire viewing window. The reactants and catalyst were charged into the vessel and 10 mL of ScCO₂ were added. The reaction immediately turned tea-colored. No phase separation was evident, indicating that the Propenyl monomer and silane were soluble in the ScCO₂. The reaction time was only 14 h, compared to the 30 h for benzene, because it was believed that the seals in the high pressure reaction cell would fail at extended periods. The crude ¹H NMR spectrum of the hydrosilylation in ScCO₂ also showed the presence of unreacted VII (see Appendix I Number 20). The unreacted allylic moieties are believed to be due to stoichiometric imbalance, since the phenyl dimethyl silane (XII) is highly air sensitive.

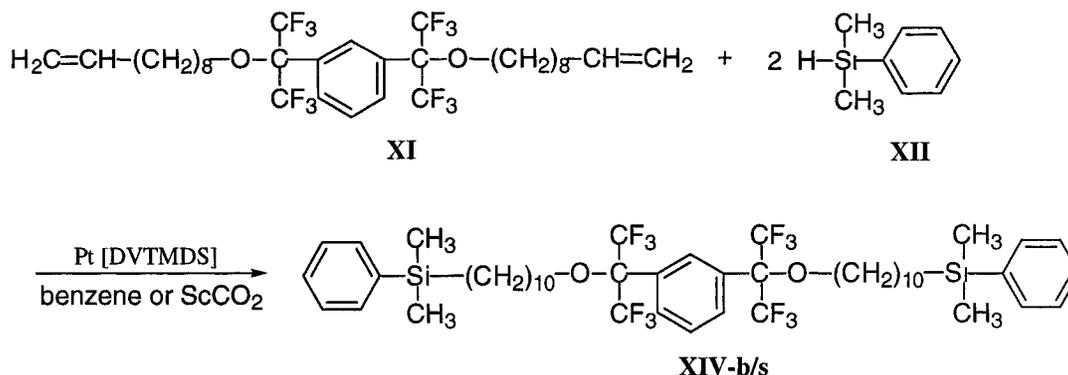
The ¹³C NMR spectrum of XIII_s is shown in Appendix II, Number 4. The spectrum also showed the signals at 139 ppm (the CH carbon in the CH=CH₂ group), 114 ppm (the CH₂ carbon in the CH=CH₂ group) indicating the presence of some mono-substituted product.

The percent carbon and hydrogen were only determined for the product obtained from ScCO₂, (XIII-s); the data confirmed the composition.

4.5 Decenyl Model Hydrosilation

Formation of the decenyl model compound XIV-b/s, derived from the hydrosilylation reaction of 1,3-bis [hexafluoro-2-(9-decenyloxy-2-propyl)] benzene (XI) and phenyl dimethyl silane (XII), was performed as shown in Scheme 20. The reaction procedure followed that of the short chain model with the exception of longer run-times 100 h, and the use of Karstedt's catalyst *divinyltetramethyl siloxane* (Pt [DVTMDS]) in xylene (3 to 3.5% Pt), instead of hexachloroplatinic acid. Karstedt's catalyst was chosen because it does not produce HCl, and it was believed that the siloxane platinum complex would

show enhanced solubility in ScCO_2 .



Scheme 20. Decenyl Model Hydrosilation.

The ^1H NMR spectra of the reaction sequence in ScCO_2 are shown in Figure 15. Success of the hydrosilation was evident by the disappearance of the allylic protons of **XI** at 5.80, 4.99, and 4.92 ppm and the disappearance of the Si-H of **XII** at 4.53 ppm. Also observed were the shift of the allylic methylene from 2.04 of **XI** to the signal at 1.35 ppm, and the appearance of the new Si- CH_2 methylene signal at 0.77 ppm. The ^1H NMR spectrum of **XIV-b** in benzene and **XIV-s** in ScCO_2 are shown in Appendix I Number 21 and 22 respectively.

The ^{13}C NMR spectrum of **XIII-s** is shown in Appendix II, Number 18. The spectrum showed signals at 139 and 114 ppm (the CH and the CH_2 carbon, respectively, for the $\text{CH}=\text{CH}_2$ group), indicating the presence of some mono-substituted product.

The percent carbon and hydrogen were only determined for the product obtained from ScCO_2 , (**XIV-s**); the data confirmed the composition.

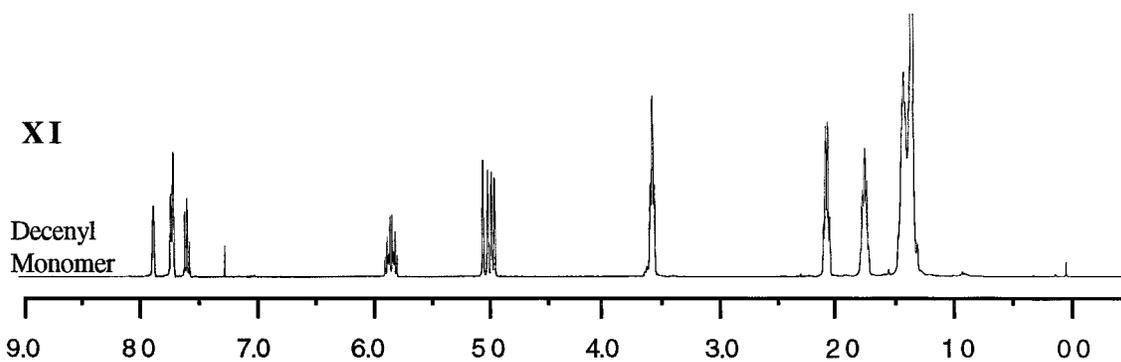
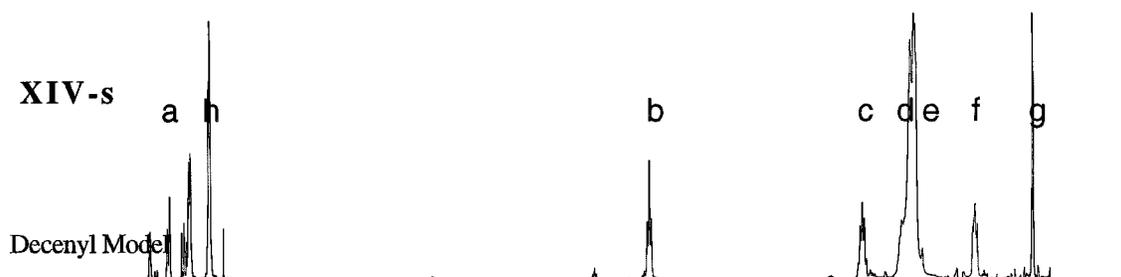
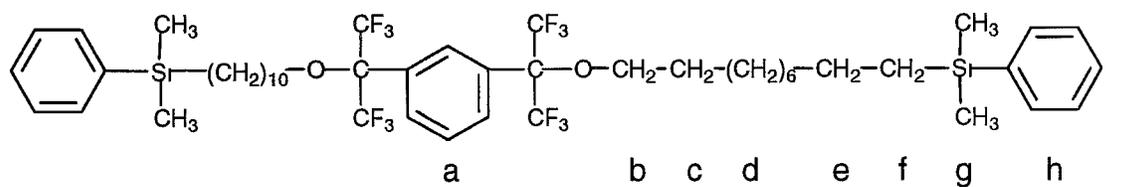


Figure 16. ^1H NMR Spectra for Compounds XI, XII, and XIV-s.

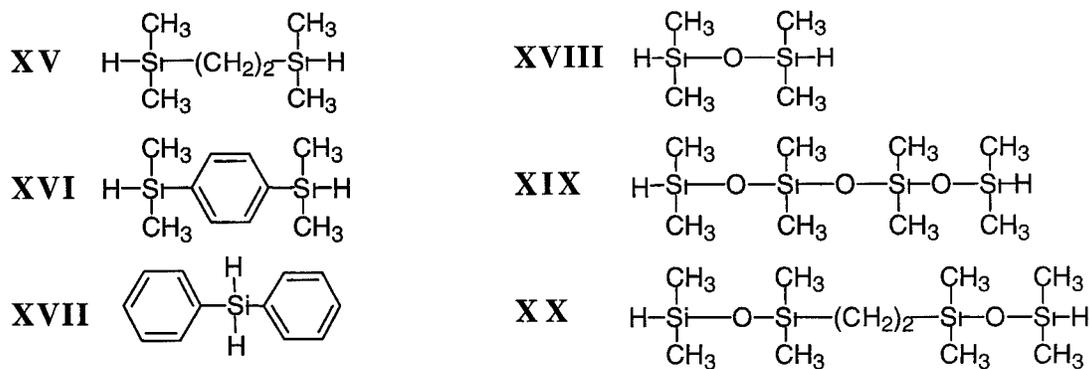


Figure 17. Commercial Dihydride Silanes and Siloxanes.

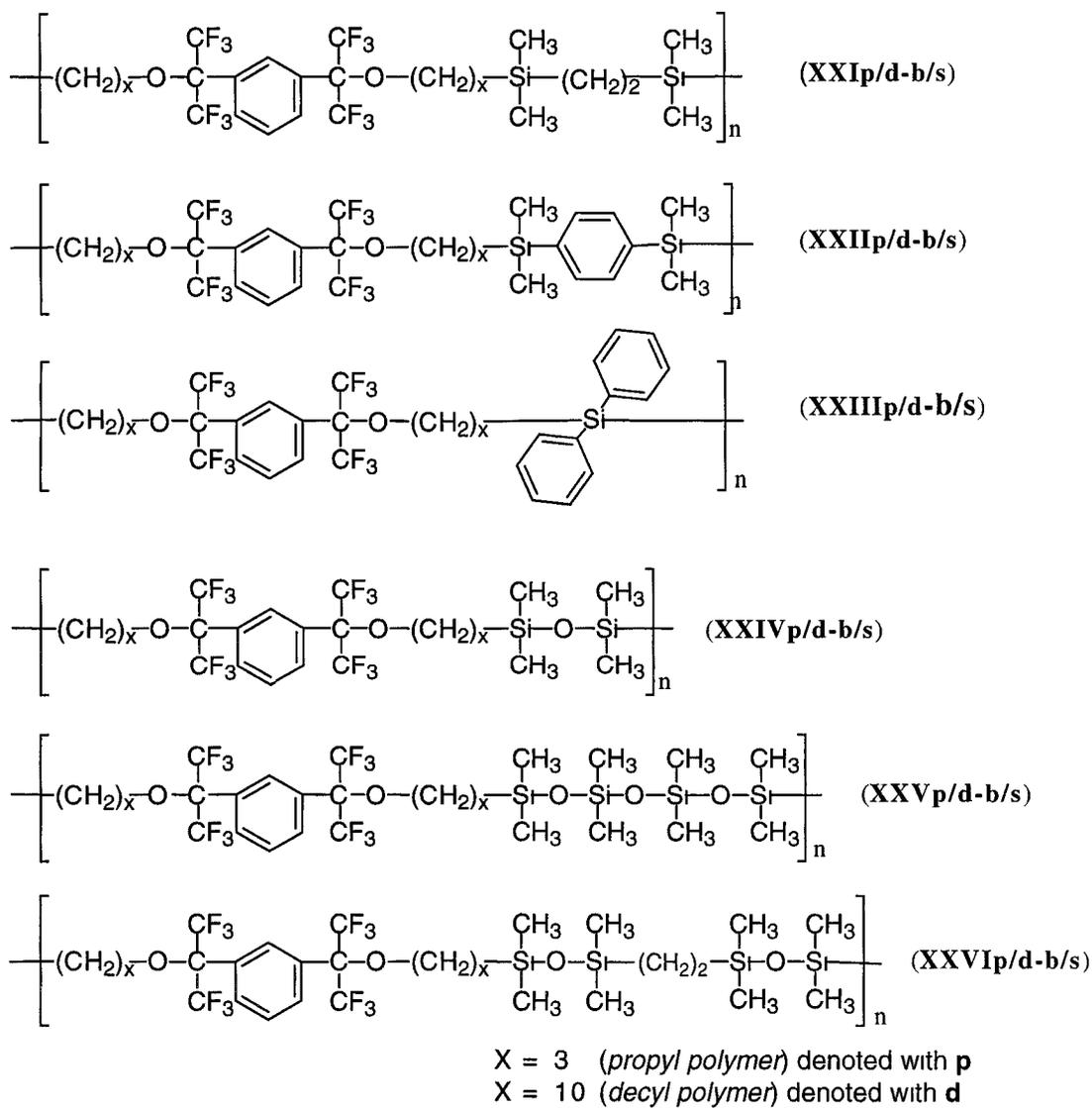


Figure 18. Polymers Formed by Hydrosilation Polymerization in Benzene and ScCO₂ Solvents.

The preparation and reaction conditions for the polymerizations generally followed that described by Dvornic. [18]. Dvornic reported the most favorable synthetic procedures for hydrosilation polymerizations seem to be catalyst concentrations of about 2×10^{-6} mole of Pt per mole of $\text{CH}=\text{CH}_2$, reaction temperatures between 40 to 50°C reaction times to 30 h. and neat polymerizations. Taking this data into consideration, a procedure was developed in which the polymerizations were performed. The mole concentration of catalyst was not considered, instead four drops of the (Pt [DVTMDS]) in xylene (3 to 3.5% Pt) catalyst were consistently delivered for each polymerization. The reactants as well as polymers showed good solubility in both solvents used. At the end of the polymerizations, the benzene solvent was removed by vacuum, and the ScCO_2 solvent was simply removed by venting the reaction cell. The crude polymers were dark brown to black viscous materials. Polymerizations performed in ScCO_2 appeared darker black, as a result of the Buna[®] o-rings bleeding into the reaction solution. Those performed in benzene were a dark brown. The polymers were isolated and purified by filtration, precipitation into methanol, separation of the viscous material, elution through a silica gel cake using chloroform eluent, and heating with activated charcoal in chloroform. The resulting polymers were clear to slightly yellow viscous materials. Polymer **XXIIIp-s** was the most solid-like, and the polymers containing siloxane moieties (**XXIVp/d-b/s**), (**XXVp/d-b/s**), (**XXVIp/d-b/s**), were more liquid-like. The polymer yields and color are shown in Table 7.

Table 7. Polymer Yield and Color.

Polymer	% Yield		Color	
	Benzene	ScCO ₂	Benzene	ScCO ₂
(XIII)	61	79	colorless	colorless
(XXIp)	64	73	colorless	colorless
(XXIIp)	73	92	colorless	colorless
(XXIIIp)	56	84	colorless	colorless
(XXIVp)	70	80	colorless	yellow
(XXVp)	77	90	yellow	colorless
(XXVIp)	85	87	colorless	colorless
(XIV)	74	52	colorless	colorless
(XXId)	78	84	colorless	colorless
(XXIIId)	92	86	colorless	colorless
(XXIIIId)	60	92	colorless	yellow
(XXIVd)	52	80	colorless	colorless
(XXVd)	86	96	yellow	colorless
(XXVIId)	85	76	yellow	colorless

4.7 Polymer Characterization

4.7.1 Elemental Analysis

Elemental analyses were obtained for both vinyl monomers and for the polymers formed in ScCO₂, and the theoretical and experimental data are shown in Table 8. Generally, the percent carbon and hydrogen found varied from calculated values. There are two explanations for the variation: first, since the polymers have a low number of repeat units the end groups will effect the observed percentages of C and H; and second, the Karstedt's catalyst can be incorporated into the polymer chain, altering the percent composition of the polymer.

Table 8. Elemental Analyses

Compound	Theoretical		Found	
	% carbon	% hydrogen	% carbon	% hydrogen
(VII)	44.10	2.88	44.32	2.83
(XIVs)	53.53	5.02	53.82	5.21
(XXIp-s)	45.28	5.07	45.32	5.11
(XXIIp-s)	49.12	4.71	50.19	5.19
(XXIIIp-s)	53.91	3.88	52.73	4.42
(XXIVp-s)	42.30	4.52	44.18	4.98
(XXVp-s)	40.40	5.22	40.46	5.24
(XXVIp-s)	42.84	5.65	43.08	5.66
(XI)	55.97	6.17	55.97	6.50
(XXIs)	60.10	6.94	60.66	7.50
(XXIId-s)	54.79	7.26	55.45	7.20
(XXIIIId-s)	57.27	6.86	57.10	6.76
(XXIVd-s)	60.68	6.25	59.97	6.50
(XXVd-s)	52.67	6.88	54.42	7.20
(XXVIId-s)	49.57	7.07	50.39	7.06
(XXVID-s)	51.40	7.40	51.63	7.54

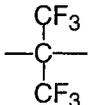
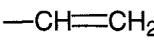
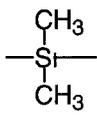
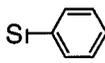
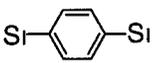
4.7.2 Solubility of Monomers and Polymers

The polymers and reactants showed good solubility in both the benzene and the ScCO₂ polymerization solvents. The polymers were also soluble in a number of common organic solvents, (DMF, CHCl₃, THF, diethylether, hexane, benzene, CH₂Cl₂, and acetone). The polymers were less soluble in methanol and ethanol. This solubility was expected since the hexafluoroisopropylidene moieties in the polymer are known to enhance the solubility of polymers [48] in organic solvents. The lack of solubility in methanol was also expected since this a non-solvent for most polymeric materials.

4.7.3 IR Spectroscopy

Table 9 summarizes the important IR frequencies for each compound. It should be noted that evidence of polymer formation cannot be proved directly by IR analysis alone. Direct evidence of the polymerization would be the presence of the Si-CH₂(CH₂)_x- bands from 1220 to 1170 cm⁻¹. Unfortunately the 6F moiety in the polymers exhibit a strong broad band from 1100 to 1300 cm⁻¹ making it difficult to resolve the Si-CH₂ bands. Evidence of the polymerizations can be proved indirectly. The two vinyl-functionalized monomers show the sharp band for the C=C at 1650 cm⁻¹ and 1641 cm⁻¹ for **VII** and **XI** respectively. The commercial dihydride-silanes and-siloxanes **XV**, **XVI**, **XVII**, **XVIII**, **XIX**, and **XX** showed the characteristically sharp Si-H band at approximately 2120 cm⁻¹. Assuming that the polymerization occurred, there should be no evidence of vinyl bands or the Si-H band in the polymer spectrum. Even though, the Si-H group can readily convert to the Si-OH group, if this conversion were to take place there would be evidence of the broad Si-OH band in the range 3400 to 3200 cm⁻¹ or a broad band in the range of 950 to 810 cm⁻¹. These Si-OH bands are only present in one spectrum, that of polymer **XXIII-d-b**. The spectra of the other polymers and models do not show the vinyl band or the Si-H band, nor is there evidence of conversion to Si-OH. Thus, these vinyl and Si-H groups reacted to form the desired polymers.

Table 9. Infrared Frequencies for Reactants and Polymers

Compound	Group	Frequency (cm ⁻¹)	
		727	s
Propenyl monomer (VII) & Decenyl monomer (XI)	 C—O—C 	1300 to 1100 1100 to 1070 1650 to 1640	b b v
	Si—H	2120	vs
		1250	vs
Dihydride-Silanes & -Siloxanes	 Si—CH ₂ CH ₂ —Si  Si—O—Si	1428 1300 to 1100 1135 1070	vs vs vs b
Polymers	Si—CH ₂ (CH ₂) _x CH ₂	1180 to 1120	s

v = variable, b = broad, s = sharp vs = very sharp band reference [41]

4.7.4 NMR Analysis.

The ¹H NMR spectra of the polymers and the dihydride-silanes and-siloxanes, as well as the ¹³C NMR spectra of the poly-silicones were obtained in CDCl₃ solutions, and are shown in Appendices I and II. Table 10 lists the ¹H NMR signals for the propyl polymers and Table 11 list those for the decyl polymers. The spectra also showed the end-group vinylic protons at 5.80, 4.99, 4.92, the methylene alpha to the vinyl group at 4.07 ppm and at 2.04 ppm for the propyl and decyl polymers, respectively.

Table 10. ¹H NMR Signals for Propyl Polymers

Polymer (XXI _p -b/s)	Signal (ppm)	Polymer (XXII _p -b/s)	Signal (ppm)	Polymer (XXIII _p -b/s)	Signal (ppm)
	7.84 7.67 7.53 3.47 1.68 0.49 0.05 0.35		7.84 7.67 7.53 3.51 1.74 0.76 0.30 7.50		7.84 7.67 7.53 3.55 1.78 1.18 7.53 7.42
Polymer (XXIV _p -b/s)	Signal (ppm)	Polymer (XXV _p -b/s)	Signal (ppm)	Polymer (XVI _p -b/s)	Signal (ppm)
	7.84 7.67 7.53 3.48 1.71 0.50 0.06		7.84 7.67 7.53 3.53 1.77 0.54 0.07 0.07		7.84 7.67 7.53 3.48 1.74 0.50 0.07 0.38

Table 11. ¹H NMR Signals for Decyl Polymers

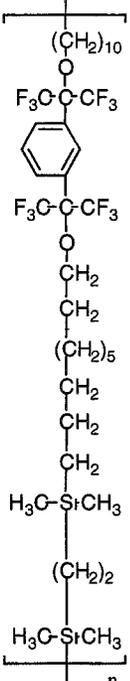
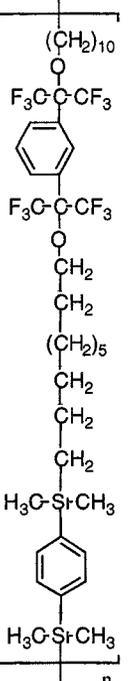
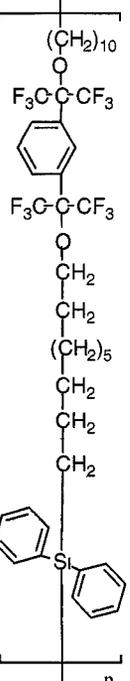
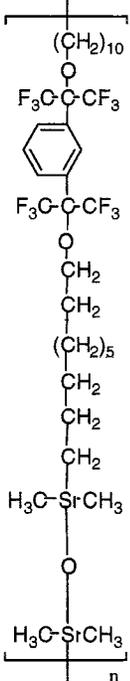
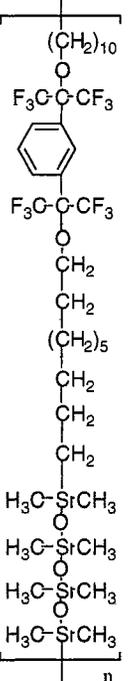
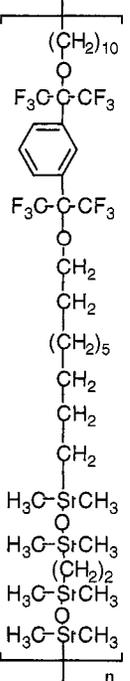
Polymer (XXId-b/s)	Signal (ppm)	Polymer (XXIId-b/s)	Signal (ppm)	Polymer (XXIIId-b/s)	Signal (ppm)
	7.84 7.67 7.53 3.53 1.69 1.28 1.30 0.49 -0.09 0.34		7.84 7.67 7.53 3.53 1.72 1.30 1.30 0.49 0.25 7.50		7.84 7.67 7.53 3.54 1.73 1.34 1.39 1.58 7.56 7.37
Polymer (XXIVd-b/s)	Signal (ppm)	Polymer (XXVd-b/s)	Signal (ppm)	Polymer (XVIId-b/s)	Signal (ppm)
	7.84 7.67 7.53 3.51 1.70 1.28 1.28 0.50 0.06		7.84 7.67 7.53 3.50 1.67 1.28 1.28 0.52 0.03		7.84 7.67 7.53 3.52 1.69 1.28 1.28 0.49 0.02 0.39

The ^{13}C NMR spectra of the polymers are shown in Appendix II, and the relevant signals for the polymers are listed in Table 12 and Table 13. The spectra also show signals at 139 and 114 ppm (the CH and the CH_2 carbon, respectively of the $\text{CH}=\text{CH}_2$ terminal end group).

Table 12. ^{13}C NMR Signals for Propyl Polymers

Polymer (XXIp-b/s)	Signal (ppm)	Polymer (XXIIp-b/s)	Signal (ppm)	Polymer (XXIIIp-b/s)	Signal (ppm)
	129 ^{C-F} 131, 125 124,121 128 ^{tertiary carbon} 69 25 9 -3 7		129 ^{C-F} 131, 125 124,121 128 ^{tertiary carbon} 69 23 11 -2 134		129 ^{C-F} 131, 125 124,121 128 ^{tertiary carbon} 69 23 10 134,135 136, 137
Polymer (XXIVp-b/s)	Signal (ppm)	Polymer (XXVp-b/s)	Signal (ppm)	Polymer (XVIp-b/s)	Signal (ppm)
	129 ^{C-F} 131, 125 124,121 128 ^{tertiary carbon} 69 23 13 -1		129 ^{C-F} 131, 125 124,121 128 ^{tertiary carbon} 69 23 13 -1 0		129 ^{C-F} 131, 125 124,121 128 ^{tertiary carbon} 69 23 13 0 8

Table 13. ^{13}C NMR Signals for Decyl Polymers.

Polymer (XXId-b/s)	Signal (ppm)	Polymer (XXIId-b/s)	Signal (ppm)	Polymer (XXIIId-b/s)	Signal (ppm)
	129 ^{C-F} 131, 125 124, 121 128 ^{tertiary carbon} 66 34 29 25 23 14 -5 7		129 ^{C-F} 131, 125 124, 121 128 ^{tertiary carbon} 66 32 29 25 23 14 1 134		129 ^{C-F} 131, 125 124, 121 128 ^{tertiary carbon} 66 34 29 25 24 16 128, 135 136, 137
Polymer (XXIVd-b/s)	Signal (ppm)	Polymer (XXVd-b/s)	Signal (ppm)	Polymer (XVIId-b/s)	Signal (ppm)
	129 ^{C-F} 131, 125 124, 121 128 ^{tertiary carbon} 66 33 29 23 22 18 0		129 ^{C-F} 131, 125 124, 121 128 ^{tertiary carbon} 66 33 29 23 22 18 0		129 ^{C-F} 131, 125 124, 121 128 ^{tertiary carbon} 66 33 29 23 21 18 0 10

4.7.5 Molecular Weight by ^1H NMR End-Group Analysis.

For this series of polymers there are two possible terminal units that can be used for the analysis: the Si-H and the $\text{CH}_2\text{-CH}=\text{CH}_2$ end groups. There were a number of difficulties encountered in determining integral values for these end groups, as discussed below.

The Si-H signal of the dihydride-silanes and -siloxanes was analyzed to determine its position in the spectrum (Table 14). The polymer spectra were then analyzed for the presence of this signal. However, the evidence of the Si-H signal was difficult to detect in the polymer spectra, and was evident only in polymers (XXIII**d-b**) and (XXIII**d-s**), which also only formed small oligomers *via* hydrosilation. Further, it is believed that the Si-H end-group band is converted to Si-OH band during the polymer clean-up making the Si-H bond more difficult to detect.

Table 14. Si-H Chemical Shifts of Silanes and Siloxanes

Dihydride -silanes	Si-H Signal (ppm)	Dihydride -siloxanes	Si-H Signal (ppm)
XV	3.76	XVIII	4.68
XVI	4.50	XIX	4.70
XVII	4.65	XX	4.68

The other possible end group ($\text{O-CH}_2\text{-CH}=\text{CH}_2$) provides three possible signals for detection. The signal at 5.80 ppm from the CH, the signal at 4.99 and 4.92 ppm from the terminal CH_2 , and the signal from the allylic CH_2 at 4.07 ppm for the propyl polymers and at 2.04 ppm for the decyl polymers. Because the Pt[DVTMDS] catalyst (Figure 19) used in the polymerization also contains the viny groups, which would introduce error in to the calculation, the signal from the allylic CH_2 was used to count end groups. This signal was well resolved and easily distinguishable.

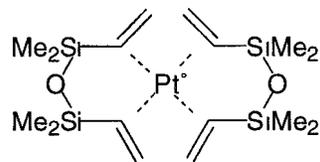


Figure 19. Pt[DVTMDS] Karstedt's Catalyst

The signal from the allylic CH₂ was also used to calculate the internal chain repeat unit for the propyl polymers. This signal shifts from 4.09 ppm to 3.51 ppm as vinyl groups are converted to methylene groups. The internal chain repeat unit for the decyl polymers was calculated from the polymer's Si-CH₂ group signal. As vinyl groups are converted to methylene groups, the signal at 2.04 ppm from the CH₂ next to the vinyl groups diminishes, and the polymer's Si-CH₂ signal at 0.49 ppm increases.

Even though the dihydride-silane, **XV**, and dihydride-siloxane, **XX**, contain a Si-CH₂ group in their monomeric units, the group's signals, 0.34 and 0.39 ppm, respectively, are shifted see Figure 20 from that of the **XXId-b/s** and **XXVIId-b/s** polymer's Si-CH₂ signal at 0.49 ppm, and do not interfere with the analysis.

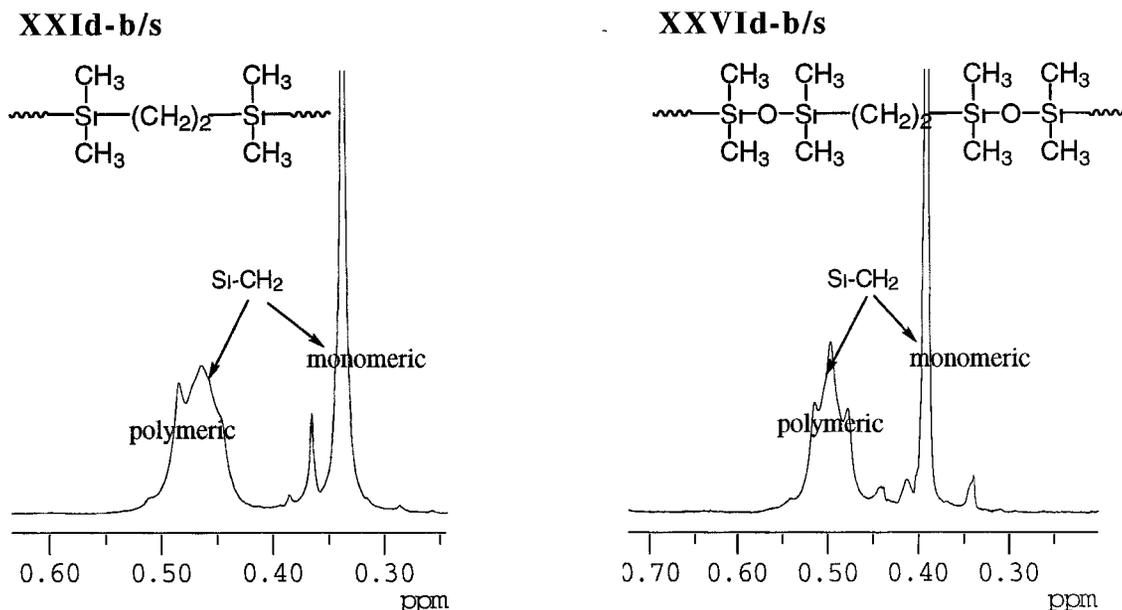


Figure 20. ¹H NMR Spectra Showing the Polymeric and Monomeric Si-CH₂ Signals

On the basis of end-group analysis the number-average molecular weights (M_n) of the polymers were calculated. Assuming that only Si-H and the CH₂-CH=CH₂ end groups are present, integration of the signal at 4.07 for the propyl polymers and at 2.04 ppm for the decyl polymers from the allylic CH₂ group were used to evaluate the number of end groups. The integrated areas of these peaks were then compared to the areas of the shifted methylene units at 3.51 ppm for the propyl polymers, and the signal at 0.49 ppm of the Si-CH₂ for the decyl polymers. From these values the extent of reaction $\{ \textit{extent} = \textit{internal unit of polymer} / (\textit{internal unit of polymer} + \textit{terminal unit}) \}$ was calculated, and from the extent of reaction [29] the degree of polymerization $\{ D_p = 1 / (1 - \textit{extent}) \}$ was determined. The molecular weights of the polymers were then calculated by multiplying the repeat-unit formula weight by the D_p . The integral values for the propyl polymers Si-CH₂ units, with terminal units normalized to 1 unit, and the molecular weight (M_n) are shown in Table 15 and in Table 16 for the decyl polymers.

Table 15. Integral Values for the Si-CH₂ Units of the Propyl Polymers and Determined Molecular Weights.

Polymers	Integral value*		Molecular weight**	
	Benzene	ScCO ₂	Benzene	ScCO ₂
(XXIp-b/s)	3.6	9.3	2900	6600
(XXIIp-b/s)	5.6	7.9	4500	6100
(XXIIIp-b/s)	4.0	5.1	3400	4100
(XXIVp-b/s)	3.7	7.0	2900	4900
(XXVp-b/s)	10.0	56.0	8900	43900
(XXVIp-b/s)	1.6	5.8	2000	5300

* ¹H NMR signal at 3.51 ppm. ** Number average molecular weight in a.m.u.

Table 16. Integral Values for the Si-CH₂ Units of the Decyl Polymers and Determined Molecular Weights.

Polymers	Integral value*		Molecular weight**	
	Benzene	ScCO ₂	Benzene	ScCO ₂
(XXId-b/s)	5	11.6	5100	10500
(XXIIId-b/s)	1.8	4.7	2500	5100
(XXIIIId-b/s)	1.0	1.0	1600	1600
(XXIVd-b/s)	4.4	4.6	4375	4520
(XXVd-b/s)	5.8	14.8	6600	14400
(XXVID-b/s)	3.1	27.5	4045	28000

* ¹H NMR signal at 3.51 ppm. ** Number average molecular weight in a.m.u.

Figure 21 shows a representative integral of the polymers formed in benzene and ScCO₂. Shown are propyl polymers XXVp-b/s and decyl polymers XXVd-b/s, which showed a large increase of molecular weight in the ScCO₂ solvent. The end group analysis showed that the polymers formed in ScCO₂ generally have higher molecular weight than those formed in benzene. The higher molecular weight in the ScCO₂ is possibly due to less hindered active sites on the catalyst when using the CO₂ vs benzene solvent. Assuming that each solvent will complex to the catalyst; then, when using ScCO₂ the small linear shape of the CO₂ molecules will block less of the active site on the catalyst,

the polymeric reactants can then more easily complex to these active sites than, when compared to that when the larger bulky benzene molecules are complexed, which would hinder the complexing of the polymeric reactants.

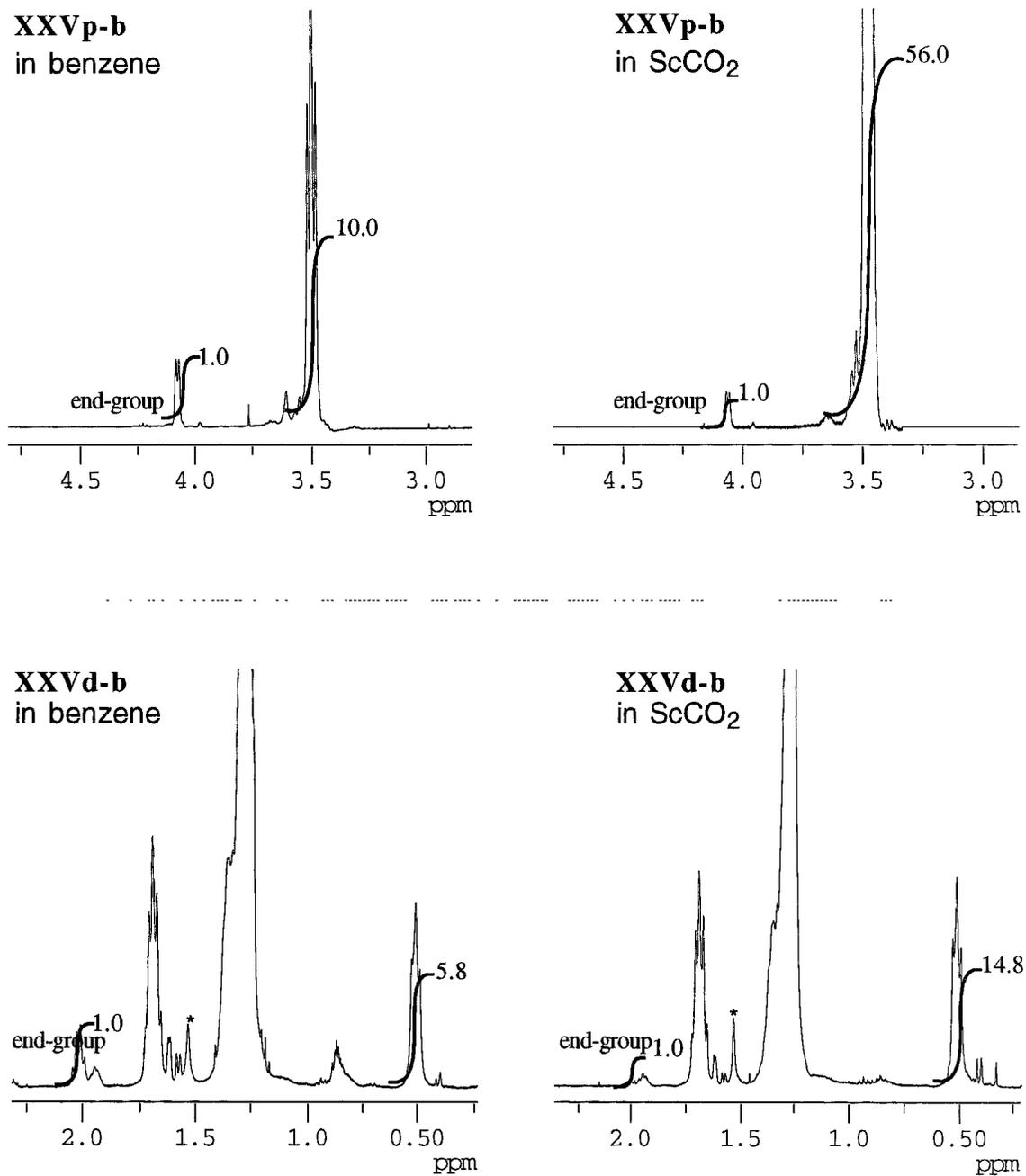


Figure 21. End-group Analysis *via* ¹H NMR Integrals Obtained from Polymers Formed in Benzene and ScCO₂ Solvents.

4.7.6 Isomerization of Vinyl End-groups

Sargent and Weber [29] have reported that Karstedt's catalyst can cause isomerization of terminal $C=C$ to internal $C=C$ bonds. They confirmed this process by the presence of a signal at 1.54 ppm in 1H NMR spectra due to terminal allylic methyl groups and the presence of a multiplet at 5.54 ppm due to the vinyl hydrogens of the internal double bond.

Evidence of this conversion was also seen in all decyl polymers where the signals at 5.54 ppm and 1.57 ppm are evident. The propyl polymers **XXIIp-b/s**, **XXIIIp-b/s**, and **XXVIp-s** showed evidence of the conversion by the pair of doublets centered at 5.34 ppm for internal and 5.31 ppm for terminal $=CH_2$ group and the unresolved multiplet of both types of $-CH=CH-$ at 5.9 ppm. Figure 22 shows the 1H NMR signals for the terminal vinyl end-groups of the Propenyl monomer (**VII**) and the signals of the conversion to internal vinyl end-groups during polymerization. Figure 23 shows the same for that of the Decenyl monomer (**XI**). The signal at 1.57 ppm due to terminal allylic methyl groups can be seen in Figure 21 on the previous page denoted with (*).

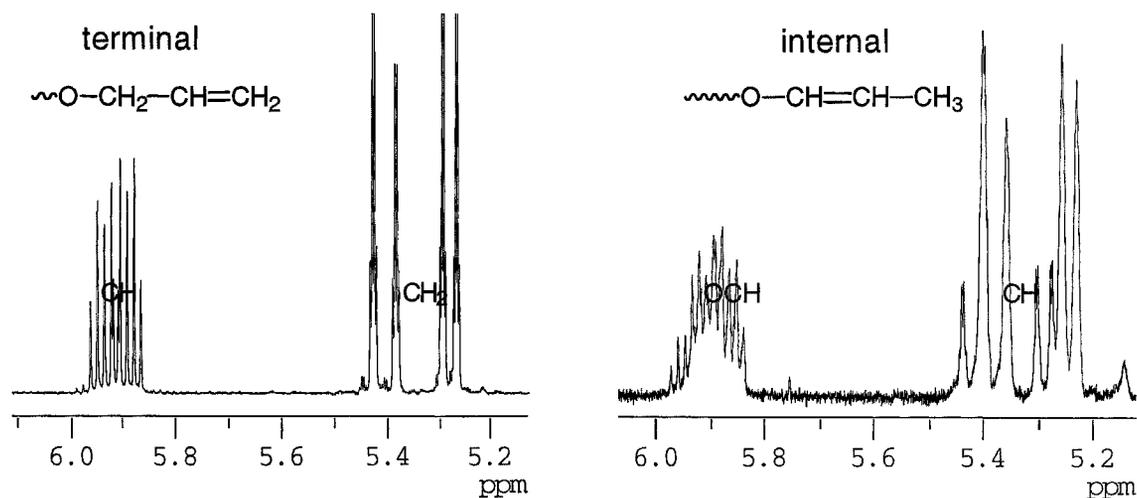


Figure 22. Terminal and Catalyst-generated Internal Vinyl End-groups for Propyl Compounds.

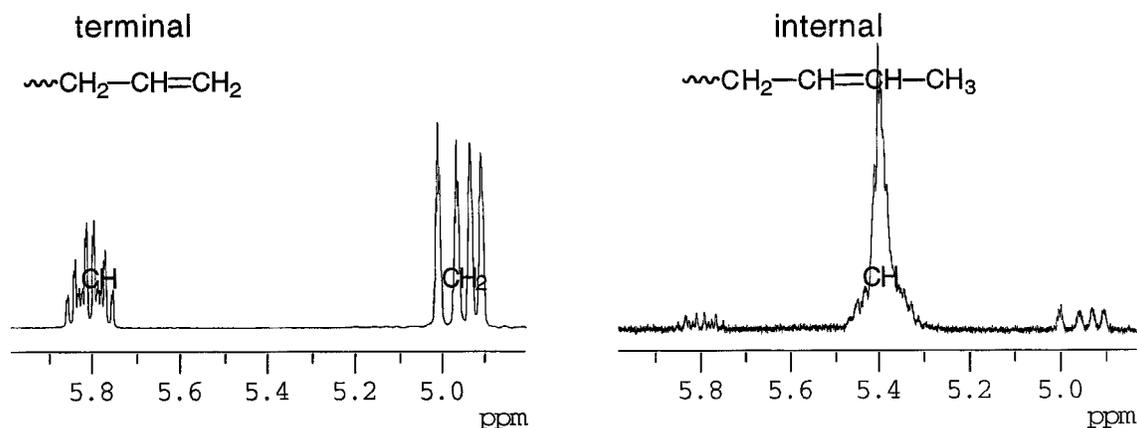


Figure 23. Terminal and Catalyst-generated Internal Vinyl End-Groups for Decyl Compounds.

4.7.7 Molecular Weights by Gel Permeation Chromatography

The molecular weights of the polymers were determined by gel permeation chromatography. The data for the propyl polymers are listed in Table 17 and those for the decyl polymers in Table 18. The data are consistent with the molecular weight calculated by end-group analysis, in that low-molecular-weight polymers were achieved. Comparing the data shows that the polymers formed in the ScCO₂ had as high or higher molecular weights than those formed in benzene. The average polydispersity (PD) for propyl polymers and decyl polymers formed in benzene were 1.33 and 1.91 respectively, and the average for those formed in ScCO₂ solvent were both 1.61.

Table 17. GPC Data for Propyl Polymers

Polymer	Mn*		Mw*		Dispersity**	
	Benzene	ScCO ₂	Benzene	ScCO ₂	Benzene	ScCO ₂
(XXIp-b/s)	5,200	8,000	6,600	10,900	1.29	1.35
(XXIIp-b/s)	3,500	5,300	5,100	8,600	1.45	1.60
(XXIIIp-b/s)	2,400	1,100	3,200	2,900	1.36	2.57
(XXIVp-b/s)	2,700	3,600	3,500	4,800	1.34	1.28
(XXVp-b/s)	4,900	10,000	6,300	15,000	1.28	1.50
(XXVIp-b/s)	2,400	4,000	3,000	5,600	1.24	1.38

* molecular weight in a.m.u.

** Mw/Mn

Table 18. GPC Data for Decyl Polymers

Polymer	Mn*		Mw*		Dispersity	
	Benzene	ScCO ₂	Benzene	ScCO ₂	Benzene	ScCO ₂
(XXId-b/s)	7600	10700	13000	13300	1.70	1.24
(XXIId-b/s)	6400	24600	10000	41700	1.53	1.69
(XXIIIId-b/s)	2500	2000	6800	3600	2.75	1.86
(XXIVd-b/s)	5900	10000	12400	18700	2.10	2.05
(XXVd-b/s)	4800	5100	9700	16700	2.01	1.60
(XXVIId-s)	9400	10600	13300	24900	1.40	2.34

* molecular weight in a.m.u. ** Mw/Mn

4.7.8 Inherent viscosity

Inherent viscosities of polymer solutions were measured at a concentration of 0.010 to 0.020 g/10 dL in chloroform. The data (see Table 19), again showed that low-molecular-weights polymers were achieved.

Table 19. Inherent Viscosities of Propyl and Decyl Polymers

Polymer	Propyl		Decyl	
	Benzene	ScCO ₂	Benzene	ScCO ₂
(XXIp/d-b/s)	0.02	0.02	0.02	0.03
(XXIIp/d-b/s)	0.03	0.02	0.02	0.02
(XXIIIp/d-b/s)	0.03	0.03	0.02	0.03
(XXIVp/d-b/s)	0.02	0.02	0.03	0.03
(XXVp/d-b/s)	0.01	0.04	0.03	0.03
(XXVIp/d-s)	0.02	0.02	0.03	0.03

values in (dL/g)

4.7.9 Thermogravimetric Analysis (TGA)

Thermogravimetric Analyses were performed on all of the polymers, and the plots are shown in Appendix IV. The data for 10 % weight loss, and the char yield at 600 °C in air and argon are shown in Table 20 for the propyl and decyl polymers. Further, Figure 24 shows the chart comparing the average 10 % weight loss of the polymers.

The data indicate that incorporation of phenyl-containing silane and siloxane moieties enhanced the thermal stability over methylene silane moieties. The initial decomposition (10% weight loss) was essentially the same in air and argon for all of the propyl polymers. Thus the initial weight loss was not caused by oxidation of the polymer. The decyl polymers showed an increased stability in argon, indicating that the initial decomposition in air was caused by oxidation. The decyl polymers also showed higher thermal stability than propyl polymers. This occurrence was not expected since the decyl polymer contain more methylene groups which are known to lessen thermal stability.

One explanation for this result is that since the propyl polymers are not decomposing by oxidation, they are decomposing through a thermally induced radical mechanism. Further, the weakest link in the polymers is Si-C bond (with a bond dissociation of 317 kJ mol^{-1}). It is possible that the initial break in the polymer chain would occur at the Si-C bond, by the initial formation of a radical. Free radicals start the chain scission which leads to degradation. The two polymer series differ in the amount of methylene groups. Methylene groups have an electron releasing effect that can stabilize the radical. In both polymer series the methylene groups inductive effects gets distributed between the $\text{C}_3\text{F}_6\text{-O}$ group and the silicon. In the propyl polymers there is a lesser amount of inductive effect to stabilize the radical. In the decyl polymers which have more methylene groups there is an enhanced stabilization of the initially formed radical and thus the decyl polymers have higher thermal stability.

The char yields for the polymers were low, this occurrence is a result of the low molecular weight of the polymers, and of the the rearrangement of the silicon-oxygen bonds to produce volatile byproducts.

4.7.10 Differential Scanning Calorimetry (DSC)

DSC thermograms of all the polymers formed were obtained and are shown in Appendix V. The result of the analysis are listed in Table 21. The polymers containing siloxane moieties (XXVp/d-b/s, XXIVp/d-b/s, XXVIp/d-s) had lowest glass transition temperatures. This result was expected since siloxanes are known to lower glass transition temperatures due to the flexibility of the Si-O bond. The polymers containing aromatic silanes had the highest glass transition temperatures, as expected, since aromatic groups are known to increase crystallinity. The decyl polymers except polymers XXIIId-b/s, had lower glass transition temperatures than propyl polymers. The longer methylene spacer in the decyl polymers result in a more flexible chain and lower glass transition temperature. Most of the polymers formed in benzene when compared to those formed in ScCO₂ had similar DSC values; except for XXIIIp-b and XXIIIp-s. It is possible that XXIIIp-s formed a cross-linked matrix *via* hydride-hydroxy condensation during clean up. The GPC data for XXIIIp-s showed a large dispersity, and the material was the most solid-like of the polymers synthesized, indicating the possibility of cross-linking. The cross linked-matrix would be less flexible than the linear polymer and therefore, would exhibit a higher glass transition temperature.

Table 21. DSC Data for Propyl and Decyl Polymers

Polymer	Propyl		Decyl	
	Benzene	ScCO ₂	Benzene	ScCO ₂
(XXIp/d-b/s)	-26	-13	-38	-39
(XXIIp/d-b/s)	-41	-40	-32	-36
(XXIIIp/d-b/s)	-37	2	-38	-38
(XXIVp/d-b/s)	-53	-39	-67	-65
(XXVp/d-b/s)	-48	-46	-59	-59
(XXVIp/d-s)	-50	-51	-59	-5

values in (dL/g)

4.7.11 Water Contact Angle

Water contact angles were determined by dissolving the polymers in chloroform, placing the solutions onto glass plates, and allowing the chloroform to evaporate, leaving a viscous film. The water contact angle measurements were performed, and the data are listed in Table 22. The data are consistent with other polymers containing the hexafluoroisopropylidene group, such as 12-FPEK with a contact angle of 100° [48]. The propyl and decyl polymers also contain the silicon moieties, which are known to have low contact angles (20–25°) [17]. This combination of functionality in the propyl and decyl polymers results in contact angles from 61 to 90°.

Table 22. Water Contact Angles for Propyl and Decyl Polymers

Polymer	Propyl		Decyl	
	Benzene	ScCO ₂	Benzene	ScCO ₂
(XXIp/d-b/s)	90°	89°	85°	83°
(XXIIp/d-b/s)	87°	88°	84°	80°
(XXIIIp/d-b/s)	85°	84°	89°	84°
(XXIVp/d-b/s)	61°	62°	69°	69°
(XXVp/d-b/s)	66°	66°	82°	82°
(XXVIp/d-s)	77°	79°	85°	82°

SUGGESTIONS FOR FUTURE RESEARCH

The research into this novel technique *Hydrosilation Polymerization in Supercritical Carbon Dioxide* has been successful; the polymers formed in ScCO_2 minimized the use of organic solvents. Although these polymers had low molecular weights, the molecular weights were as high or higher than those formed in benzene. The fault for the low molecular weight seems to be inherent with the platinum catalyst used in this project. The next step would be to initiate the hydrosilation by some other means. For example the hydrosilation reaction can be generated by heat, peroxides or irradiation. These free radical reaction pathways proceed *via* the $\text{R}_3\text{Si}^\bullet$ radical, which then adds to the double bond.

This project also showed that the propenyl monomer and propyl Polymers were less thermally stable than the decenyl monomer and decyl polymers. It is believed that this was caused by hexafluoroisopropylidene group delocalizing electrons away from Si-C bond in the propyl compounds. The next step would be to conduct a model study by synthesizing the non-fluorinated version of the propenyl monomer. This compound could then be reacted *via* hydrosilation with phenyldimethylsilane. The thermal stability of this model compound could then be compared to the two previously synthesized fluorine-containing model compounds.

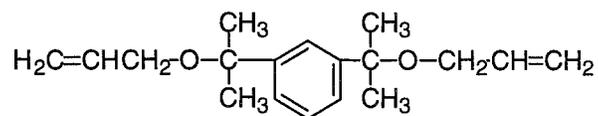


Figure 25. Non-fluorinated Version of the Propenyl Monomer.

APPENDIX I
 ^1H NMR

Index for Appendix I

Compound	¹ H NMR Number
Diphenylchlorosillane	1
1,1,4,4-Tetramethyldisiethylene; (Compound XV)	2
1,4 Bis(dimethylsilyl)benzene; (Compound XVI)	3
Diphenylsilane; (Compound XVII)	4
1,1,3,3 Tetramethyl disiloxane; (Compound XVIII)	5
1,1,3,3,5,5,7,7 Octamethyltetrasiloxane; (Compound XIX)	6
1-2-Bistetramethyldisiloxaneylethane; (Compound XX)	7
Dimethylphenylsilane; (Compound XII)	8
Platinum divinyltetramethyldisiloxane complex in xylene (catalyst)	9
Hexafluoro-2-propyl benzene; (Compound I)	10
Allyl bromide; (Compound III)	11
Hexafluoro-2-propenyloxy-2-propyl benzene Model monomer; (Compound IV)	12
1,3-Bis(hexafluoro-2-propyl) benzene (1,3-Bis HFAB); (Compound V)	13
1,4-Bis(hexafluoro-2-propyl) benzene (1,4-Bis HFAB)	14

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(continued)

Compound	¹ H NMR Number
1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene Propenyl monomer, (Compound VII)	15
9-Decen-1-ol; (Compound VIII)	16
9-Decen-1-o tosylate; (Compound IX)	17
1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene Decenyl monomer, (Compound XI)	18
Compound derived from reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and dimethyl phenyl silane;	
Propenyl Model Hydrosilation in Benzene, (Compound XIII-b)	19
Propenyl Model Hydrosilation in ScCO ₂ , (Compound XIII-s)	20
Compound derived from reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and Dimethylphenylsilane;	
Decenyl Model Hydrosilation in Benzene, (Compound XIV-b)	21
Decenyl Model Hydrosilation in ScCO ₂ , (Compound XIV-s)	22
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,4,4-Tetramethyldisilene-silane;	
in Benzene, (Compound XXI p -b)	23
in ScCO ₂ , (Compound XXI p -s)	24

Index for Appendix I

(continued)

Compound	¹ H NMR Number
<hr/>	
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,4-Bis(dimethyl silyl)benzene; in Benzene, (Compound XXIIp-b)	25
in ScCO ₂ , (Compound XXIIp-s)	26
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and Diphenylsilane; in Benzene, (Compound XXIIIp-b)	27
in ScCO ₂ , (Compound XXIIIp-s)	28
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3-Tetramethyldisiloxane; in Benzene, (Compound XXIVp-b)	29
in ScCO ₂ , (Compound XXIVp-s)	30
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane; in Benzene, (Compound XXVp-b)	31
in ScCO ₂ , (Compound XXVp-s)	32
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Index for Appendix I

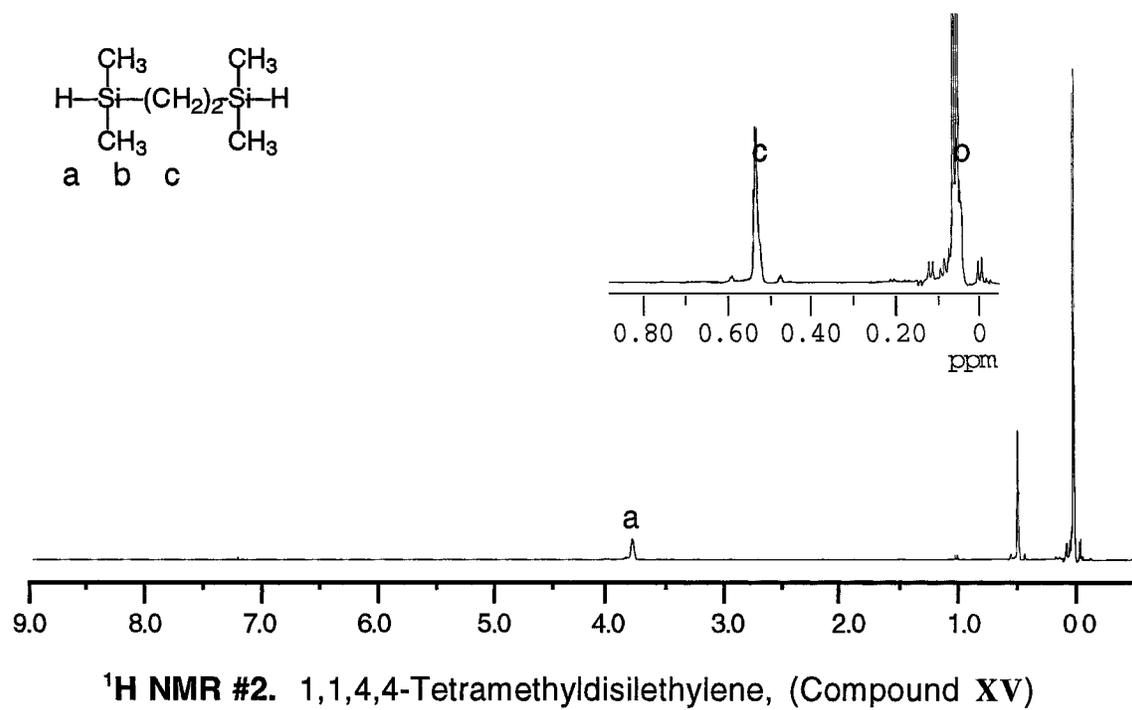
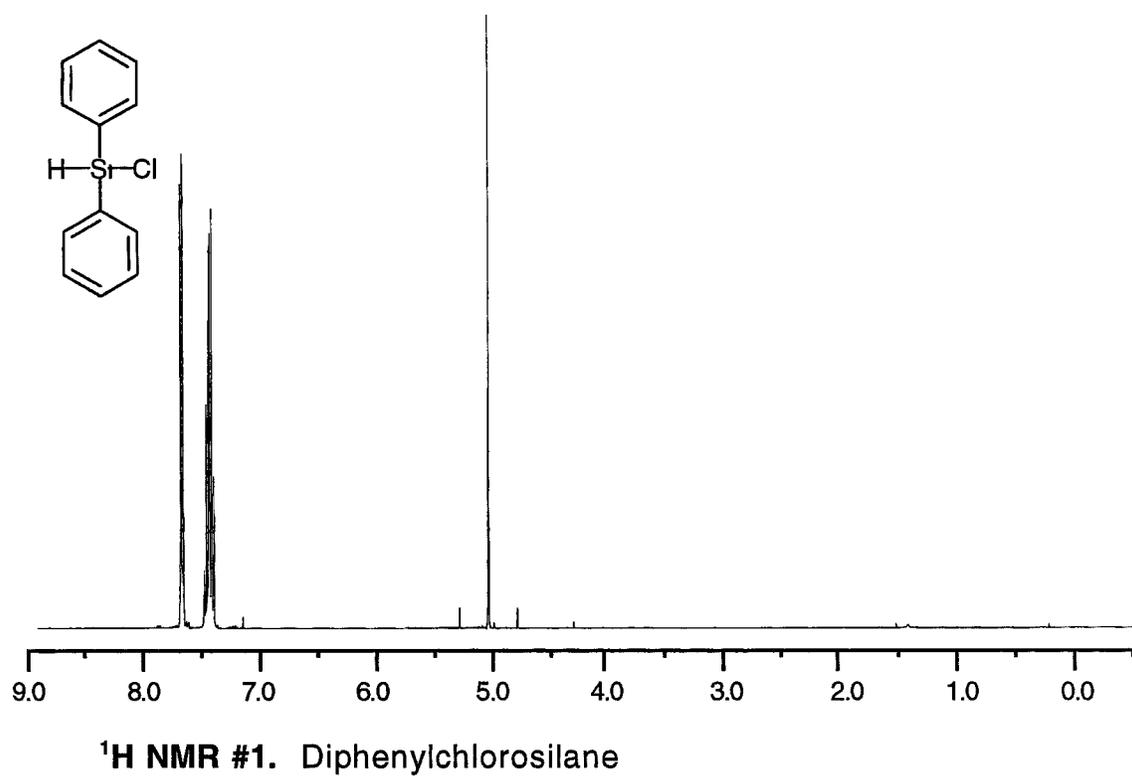
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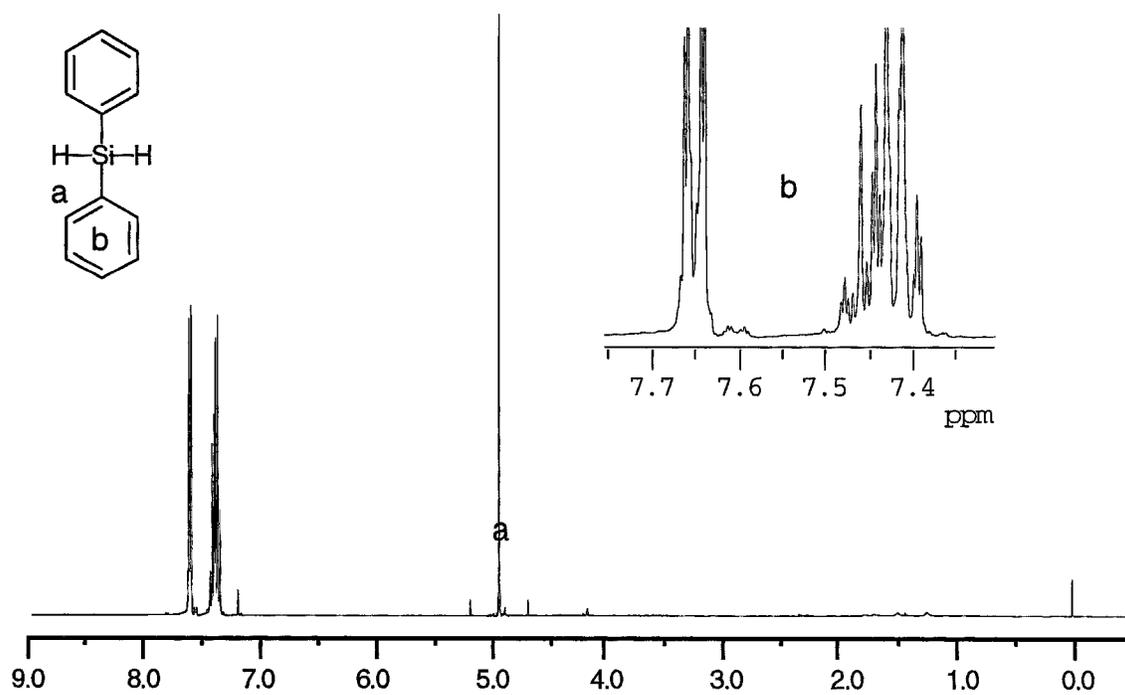
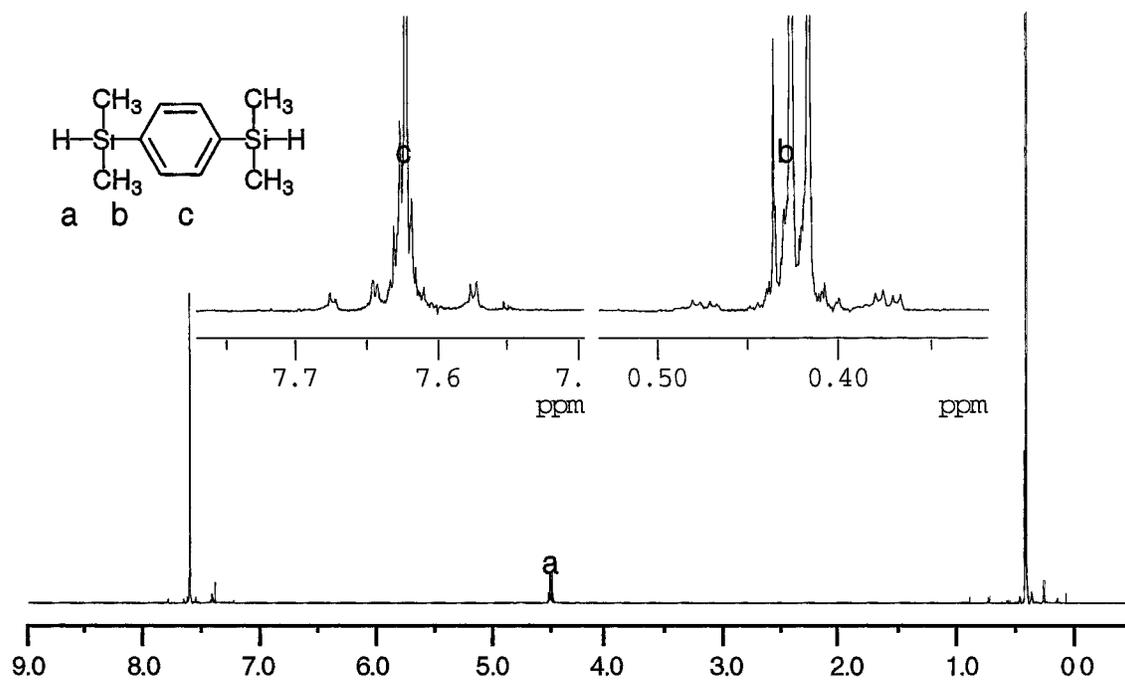
Compound	¹ H NMR Number
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Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,2-Bis(tetramethyldisiloxaneyl)ethane; in Benzene, (Compound XXVIp-b)	33
in ScCO ₂ , (Compound XXVIp-s)	34
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene and 1,1,4,4-Tetramethyldiethylene-silane; in Benzene, (Compound XXId-b)	35
in ScCO ₂ , (Compound XXId-s)	36
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene and 1,4-Bis(dimethyl silyl)benzene; in Benzene, (Compound XXIId-b)	37
in ScCO ₂ , (Compound XXIId-s)	38
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene and Diphenylsilane in Benzene, (Compound XXIIIId-b)	39
in ScCO ₂ , (Compound XXIIIId-s)	40
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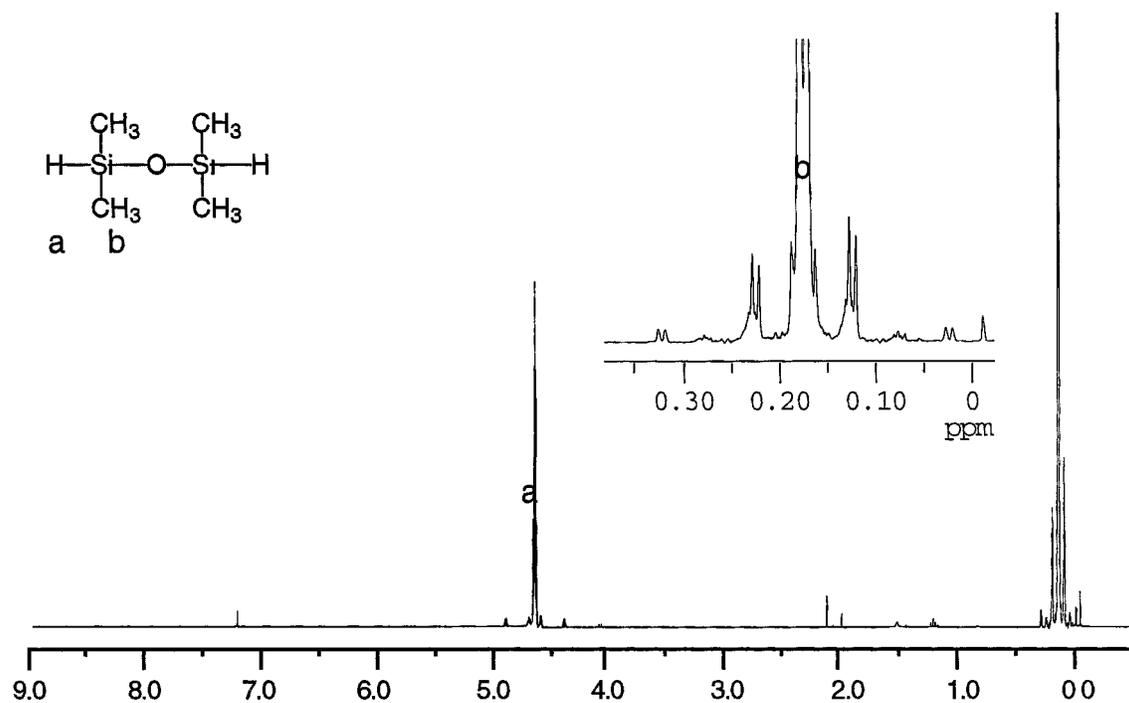
Index for Appendix I

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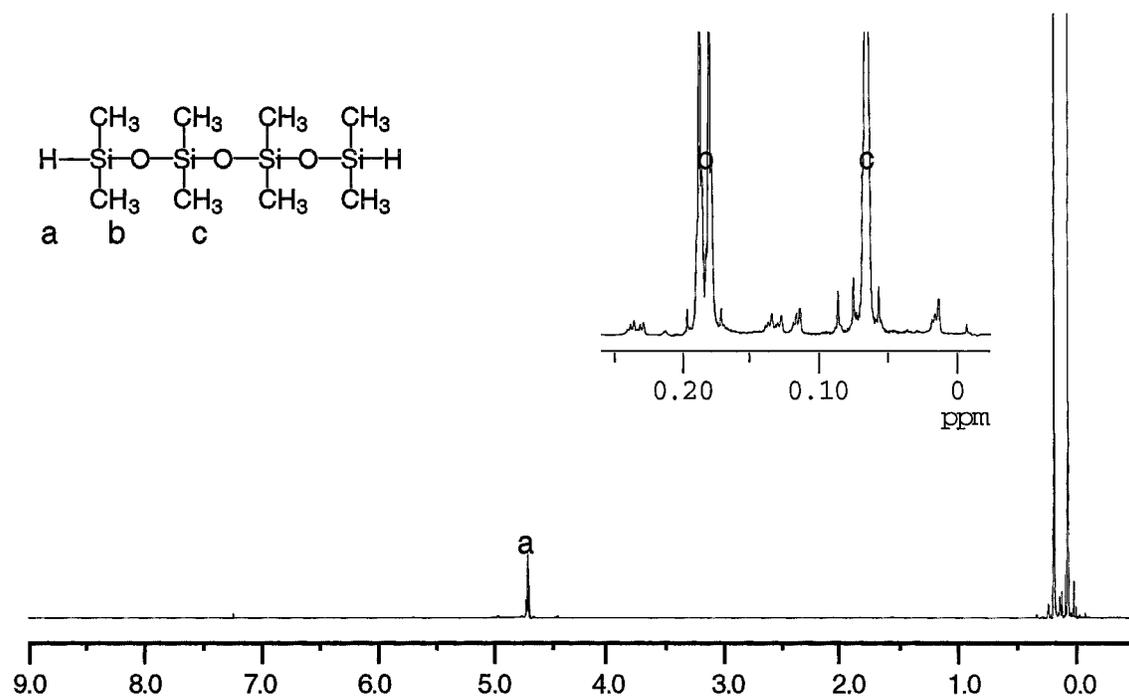
Compound	¹ H NMR Number
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Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene and 1,1,3,3-Tetramethyldisiloxane;	
in Benzene, (Compound XXIVd-b)	41
in ScCO ₂ , (Compound XXIVd-s)	42
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene and 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane;	
in Benzene, (Compound XXVd-b)	43
in ScCO ₂ , (Compound XXVd-s)	44
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] benzene and 1,2-Bis(tetramethyldisiloxaneyl)ethane;	
in Benzene, (Compound XXVIId-b)	45
in ScCO ₂ , (Compound XXVIId-s)	46
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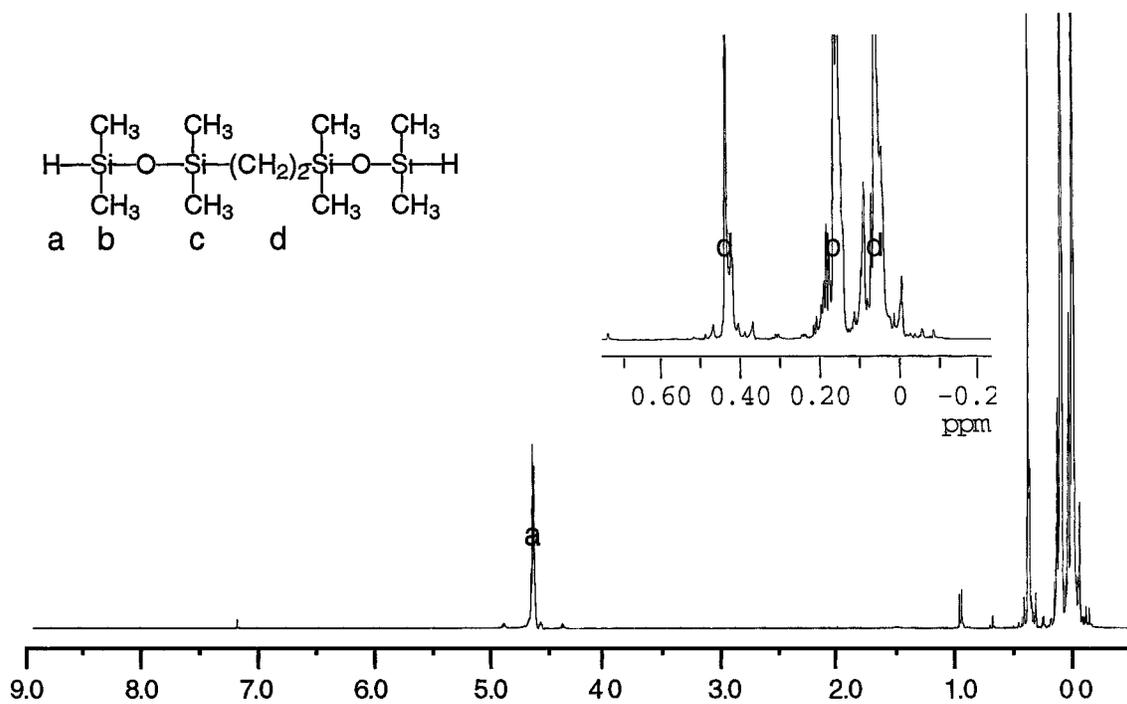




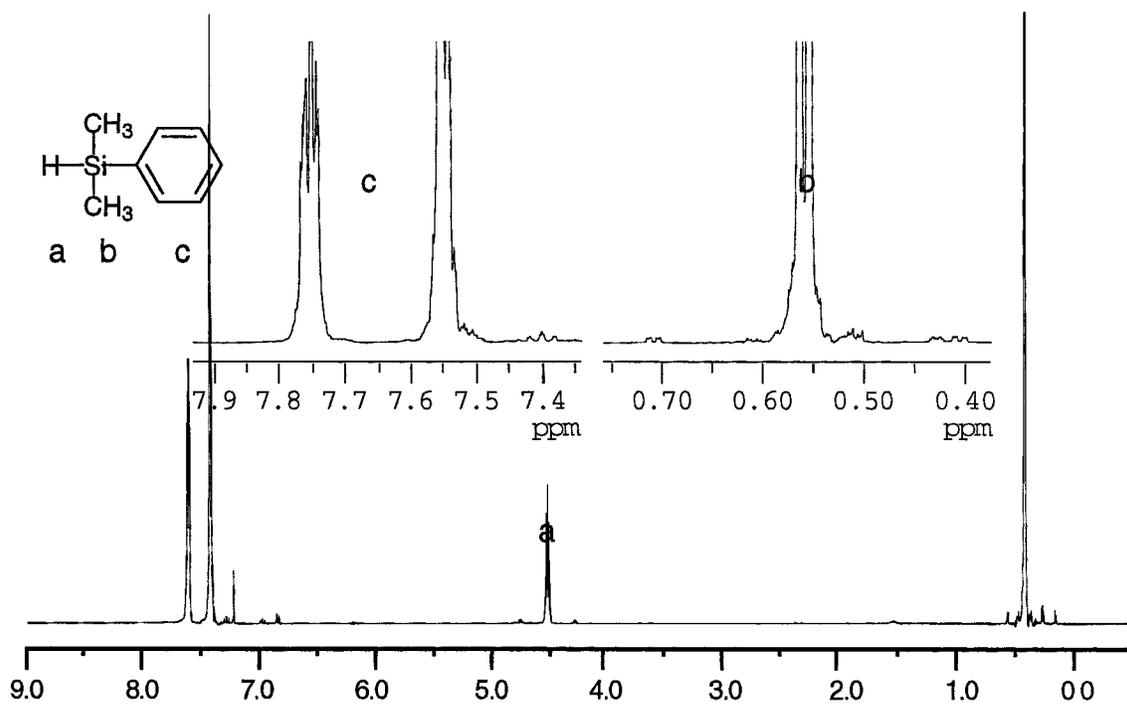
^1H NMR #5. 1,1,3,3-Tetramethyldisiloxane, (Compound XVIII)



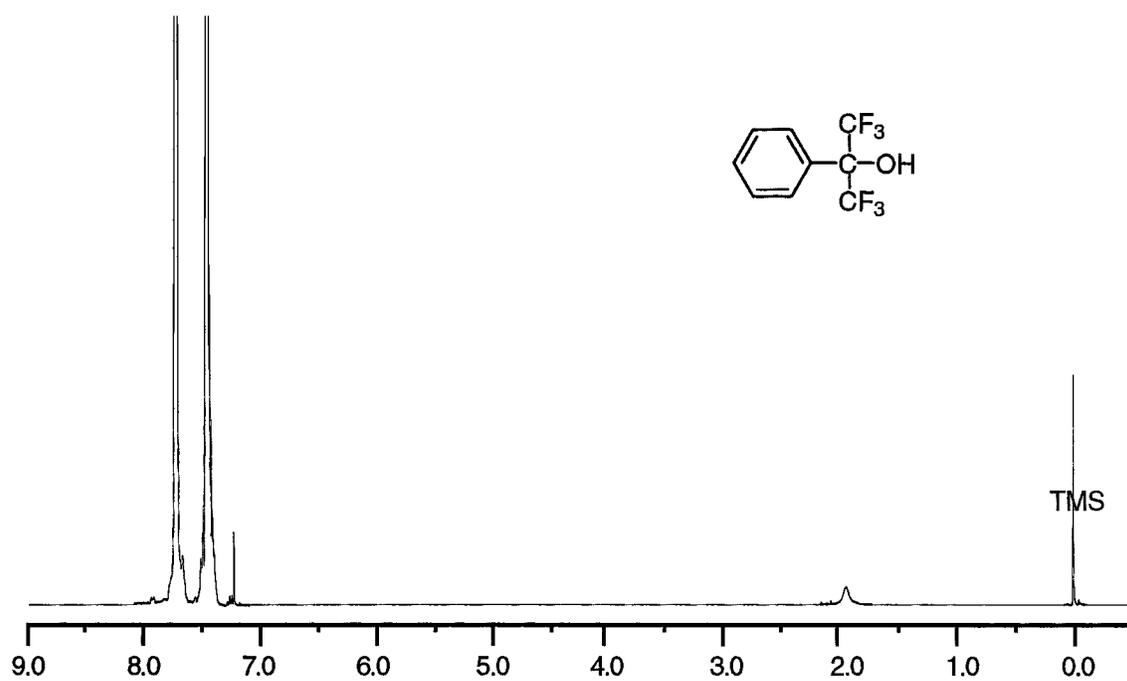
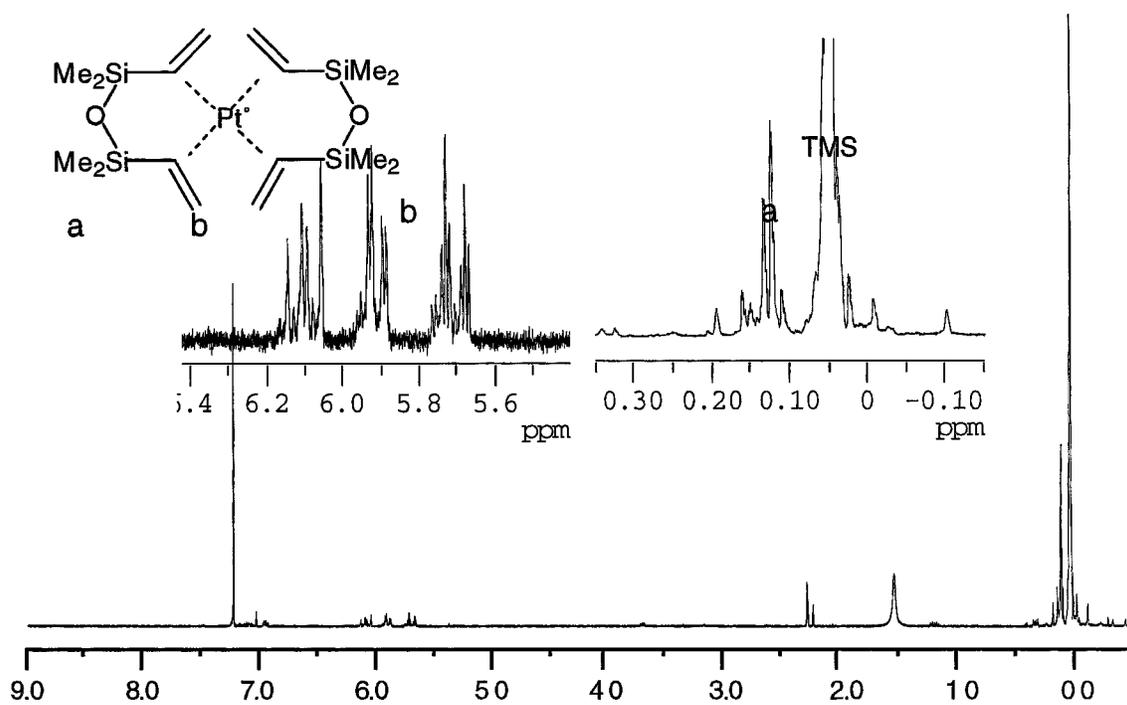
^1H NMR #6. 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane, (Compound XIX)

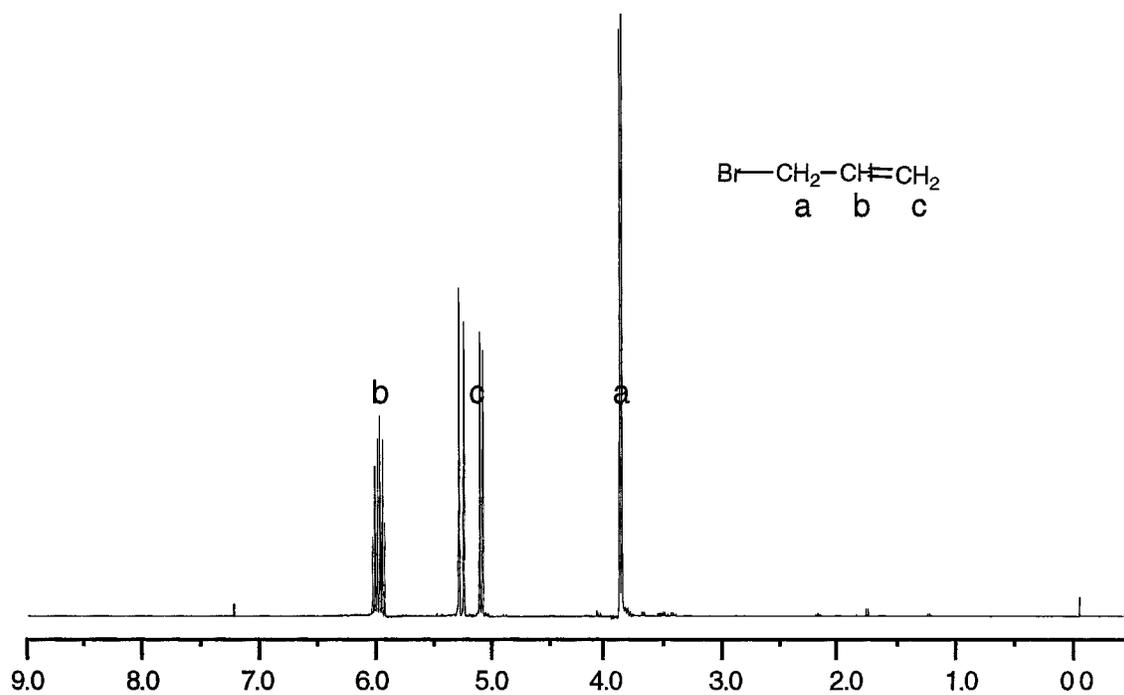


¹H NMR #7. 1-2-Bis(tetramethyldisiloxanyl)ethane,
(Compound XX)

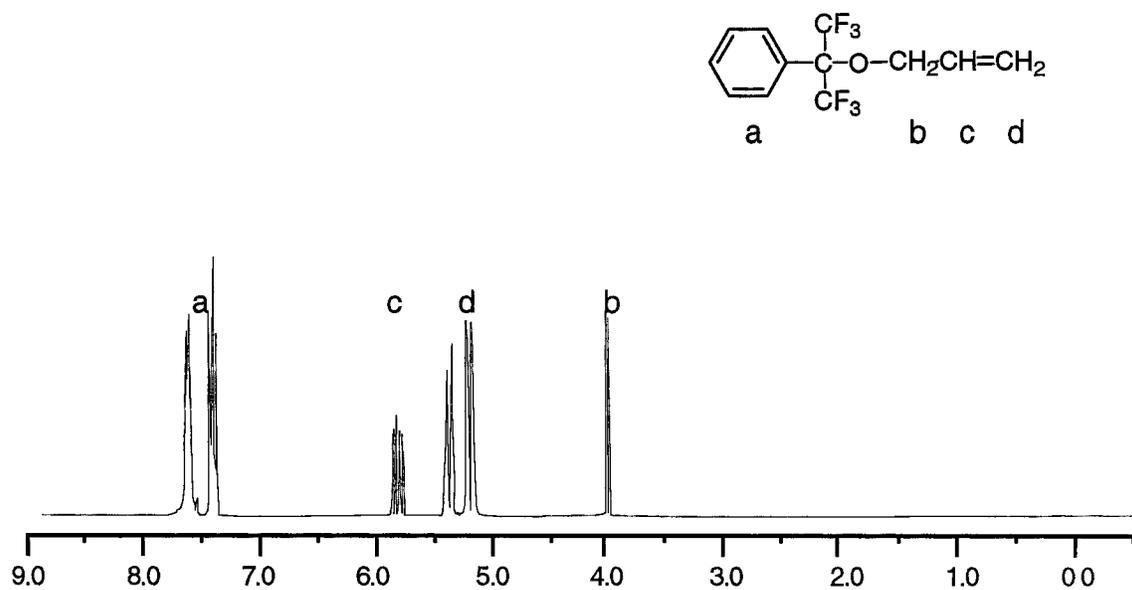


¹H NMR #8. Dimethylphenylsilane, (Compound XII)

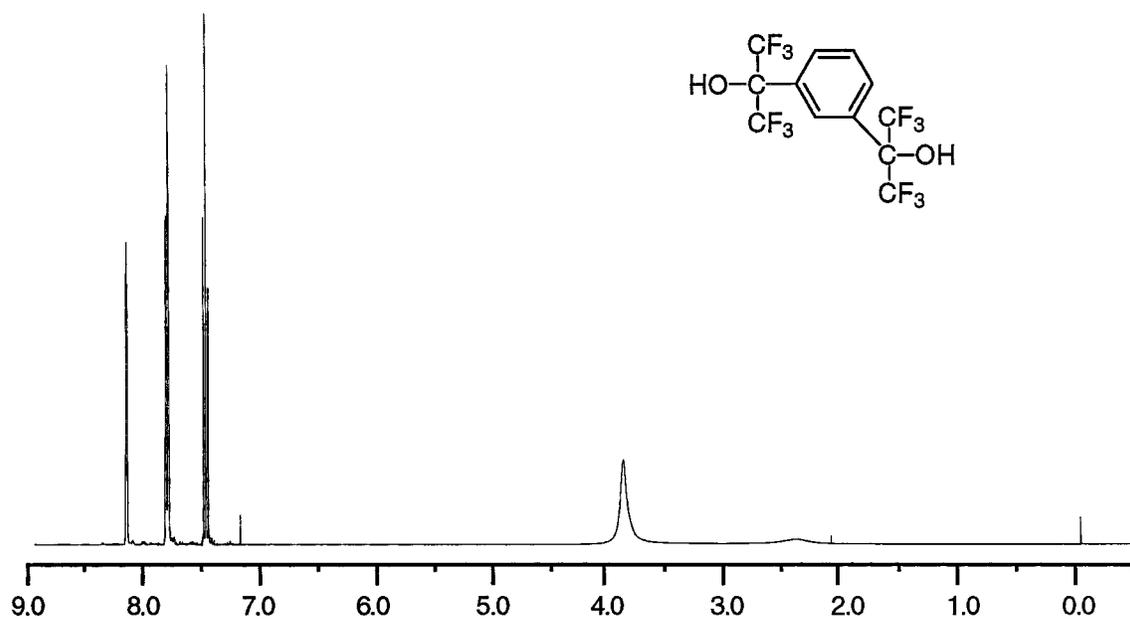




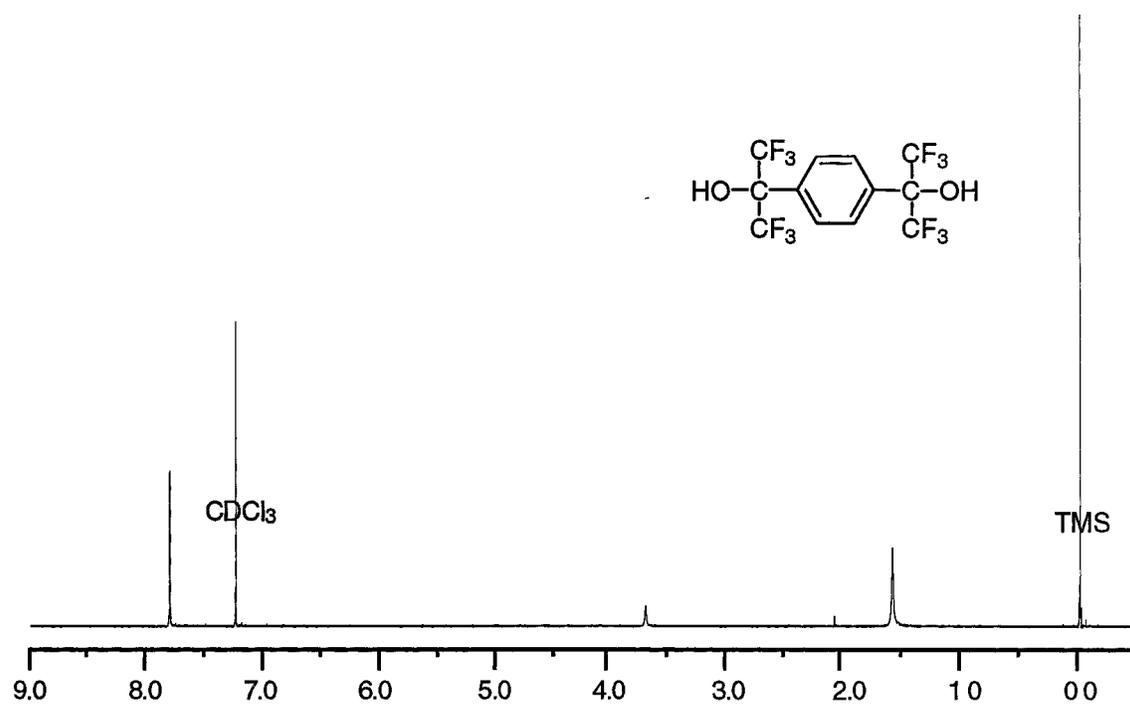
¹H NMR #11. Allyl bromide, (Compound III)



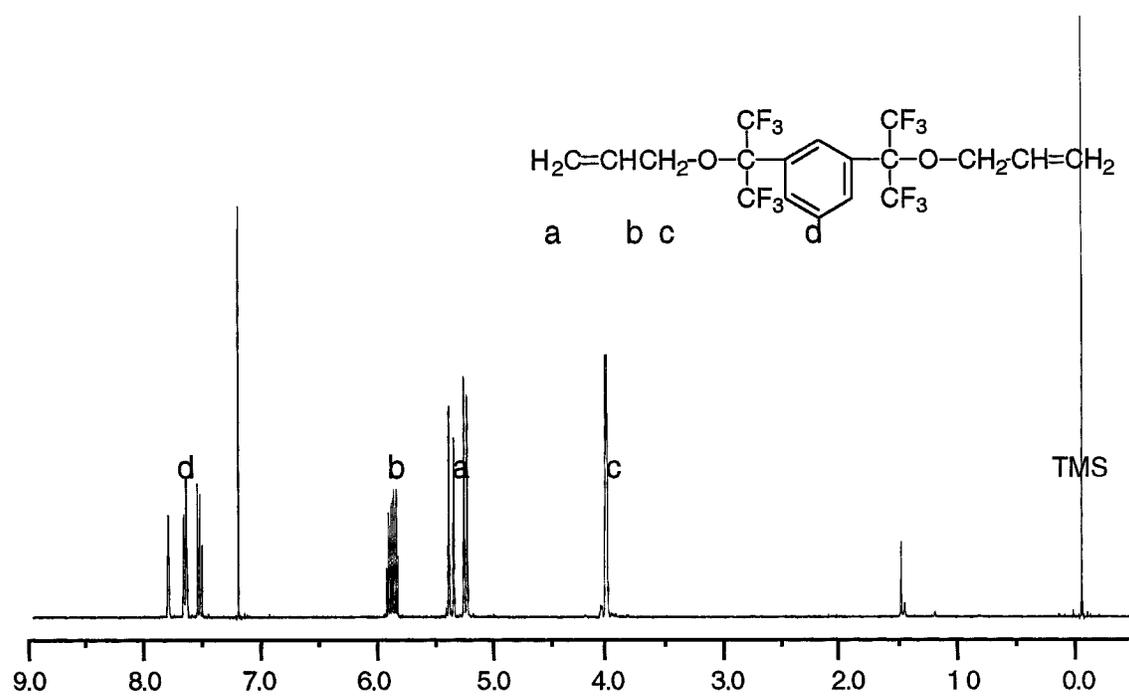
¹H NMR #12. Allyl (2-oxyhexafluoroisopropyl) benzene;
Model monomer, (Compound IV)



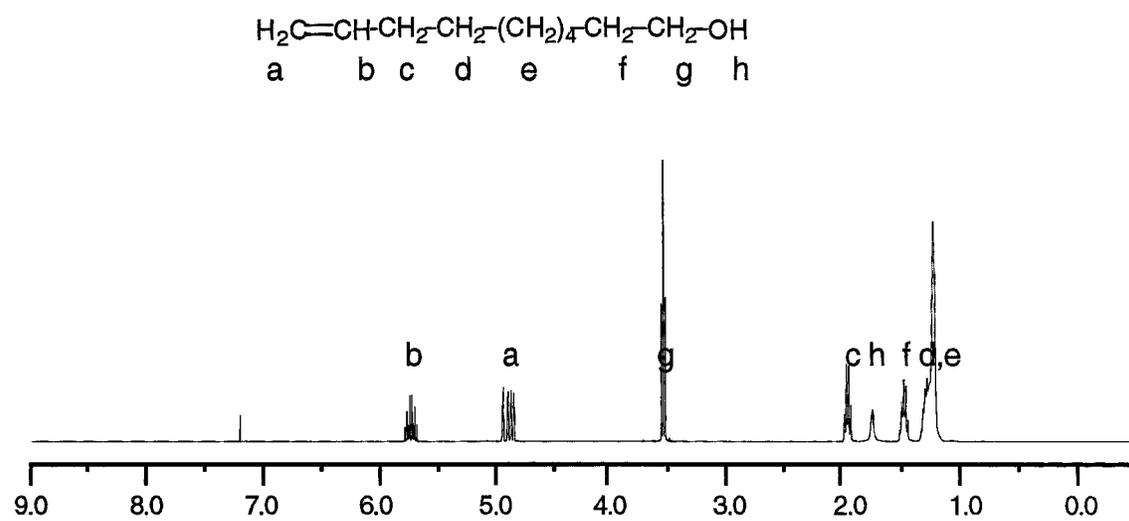
^1H NMR #13. 1,3-Bis(hexafluoro-2-propyl) benzene (1,3-HFAB),
(Compound V)



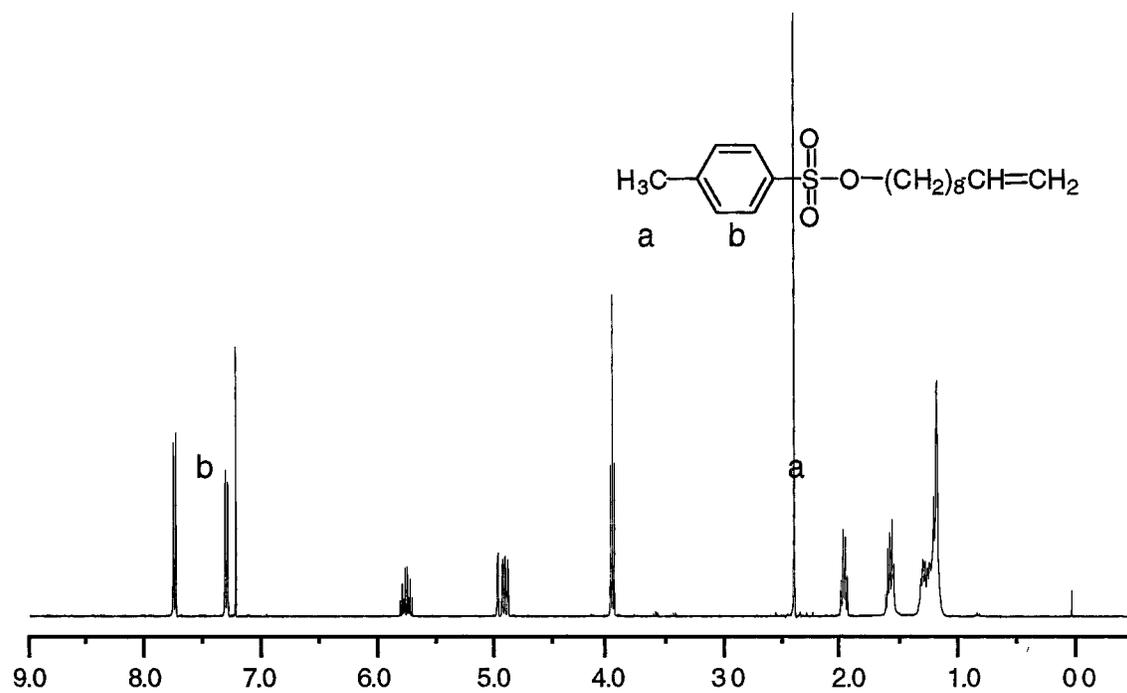
^1H NMR #14. 1,4-Bis(hexafluoro-2-propyl) benzene (1,4-HFAB)



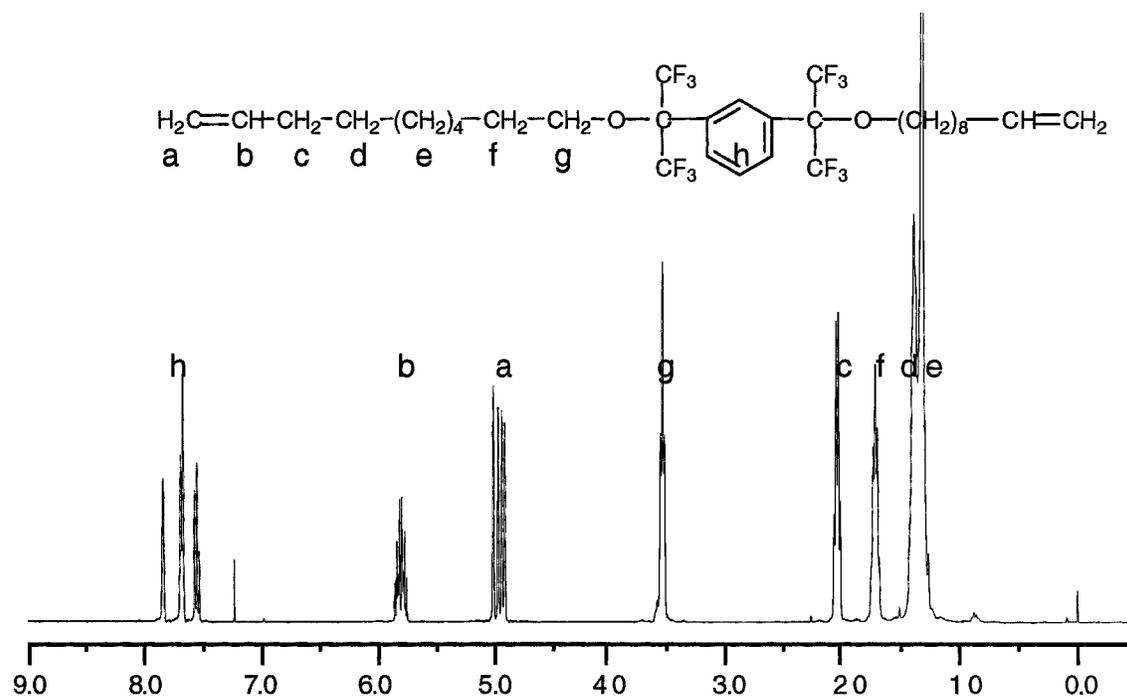
¹H NMR #15. 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) benzene
Propenyl monomer, (Compound VII)



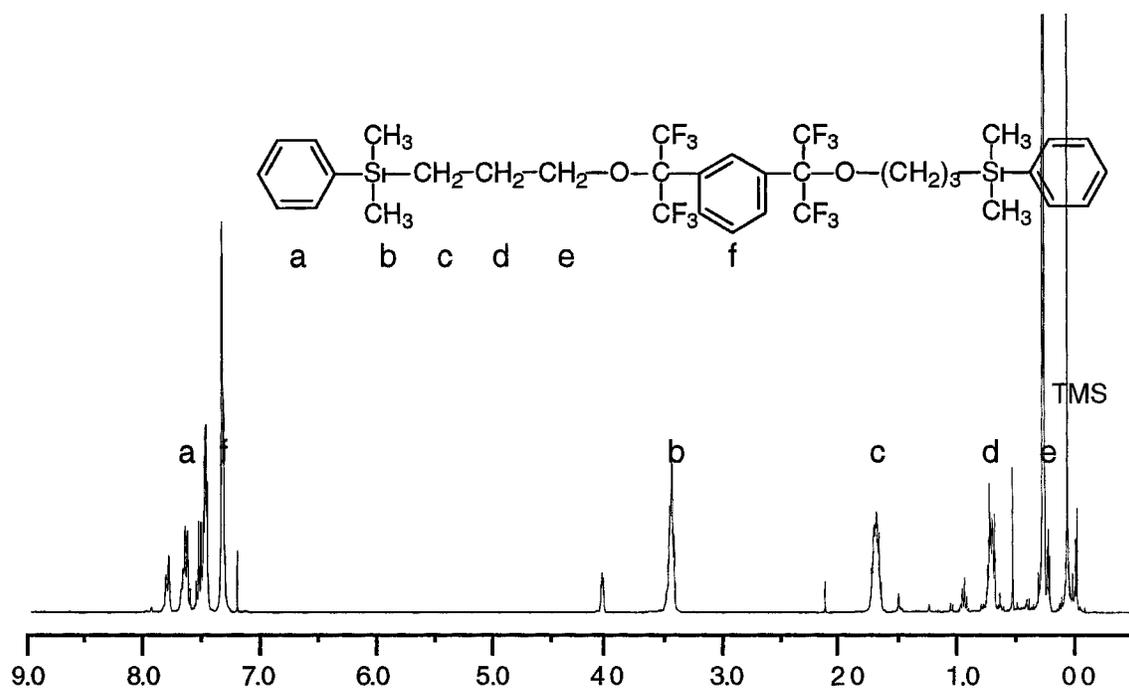
¹H NMR #16. 9-Decen-1-ol, (Compound VIII)



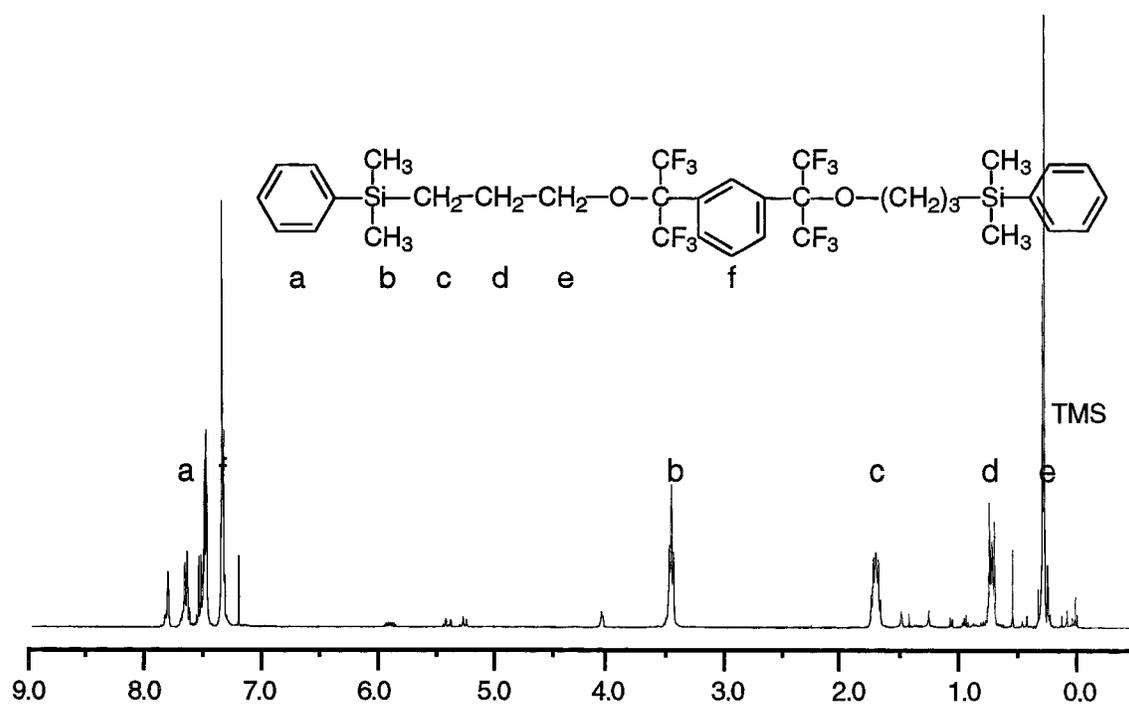
$^1\text{H NMR}$ #17. 9-Decen-1-ol tosylate, (Compound IX)



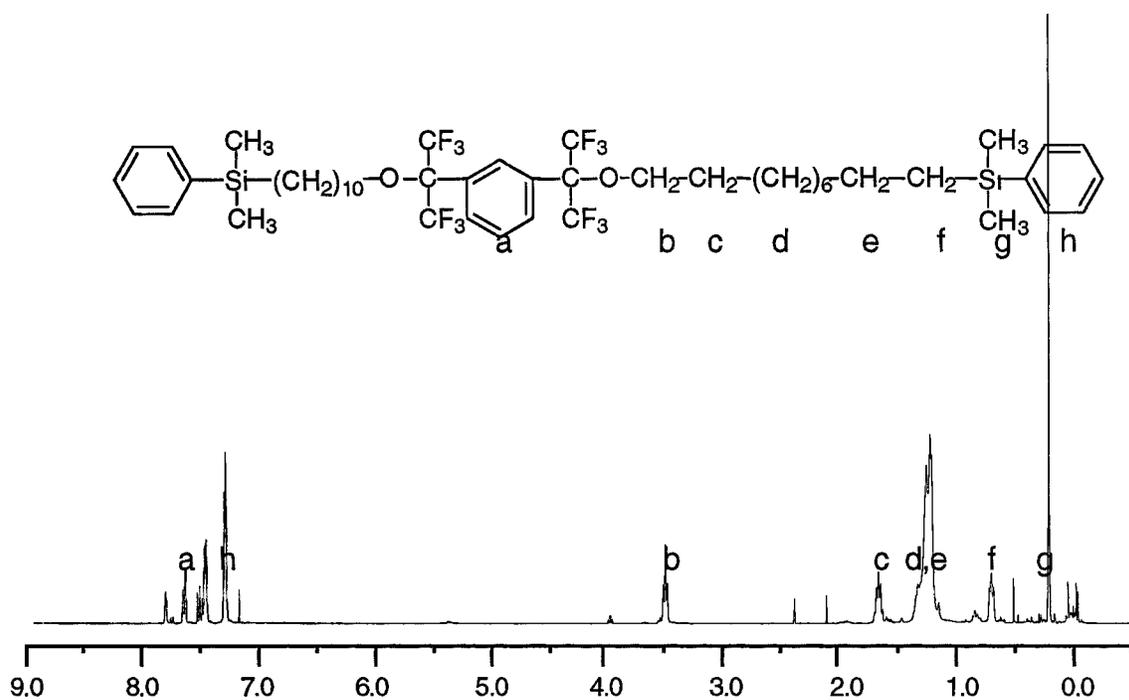
$^1\text{H NMR}$ #18. 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene, (Decenyl Monomer), (Compound XI)



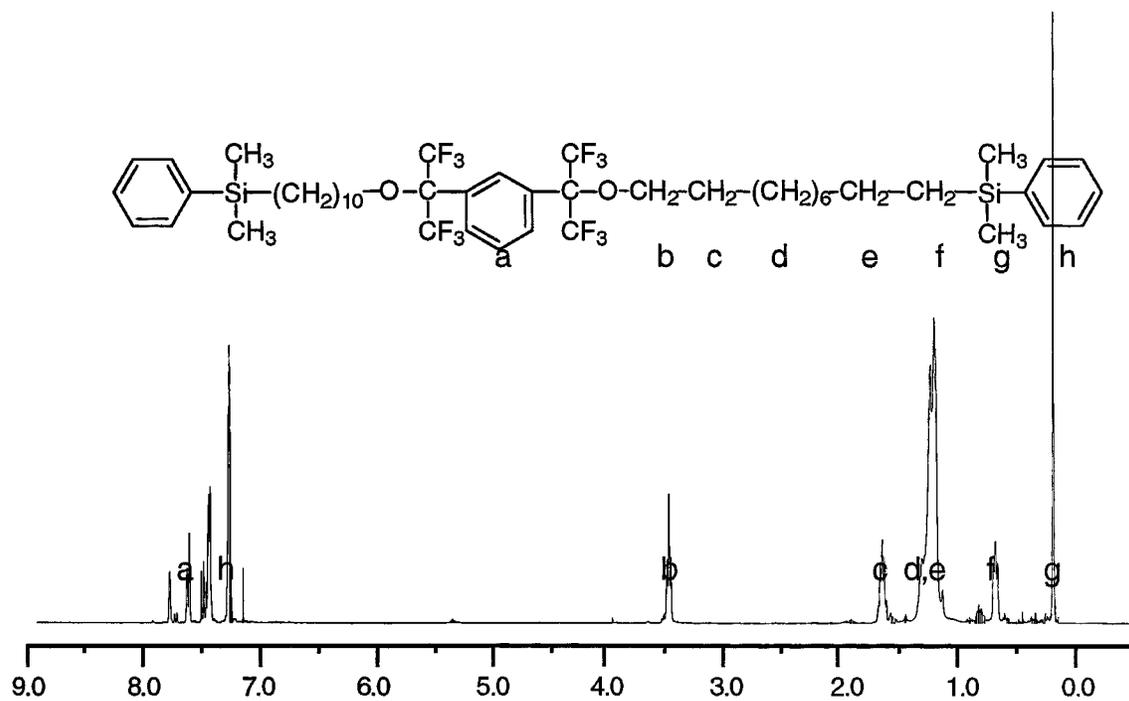
¹H NMR #19. Propenyl Model Hydrosilation in Benzene,
(Compound XIII-b)



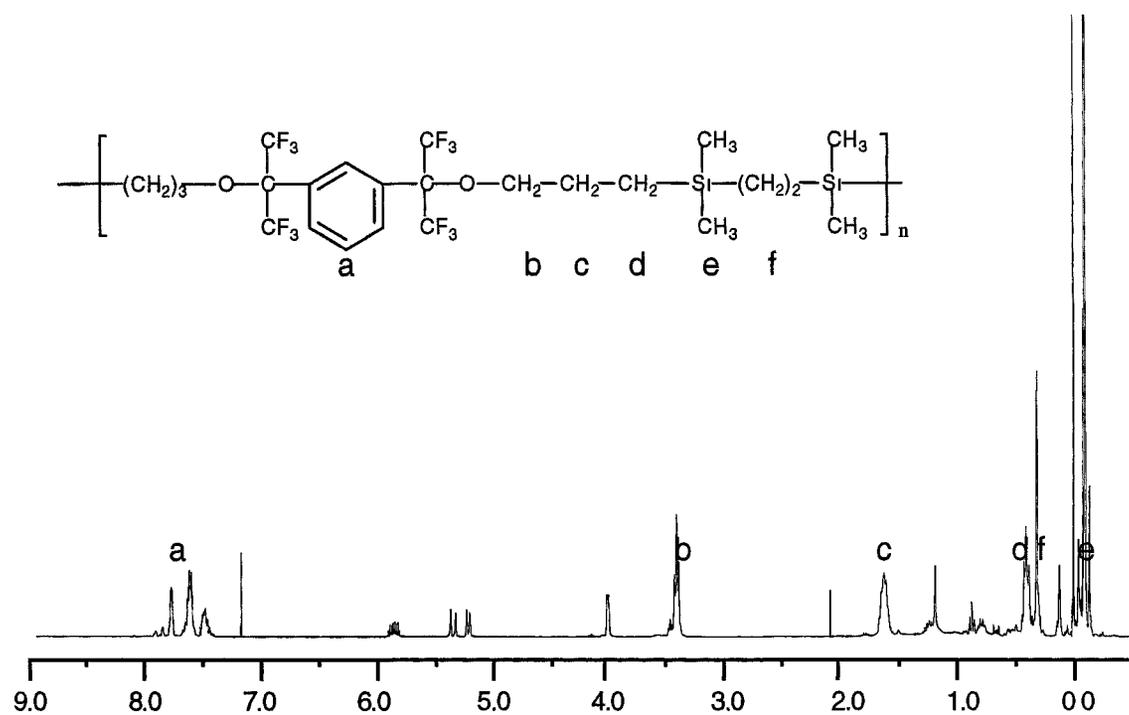
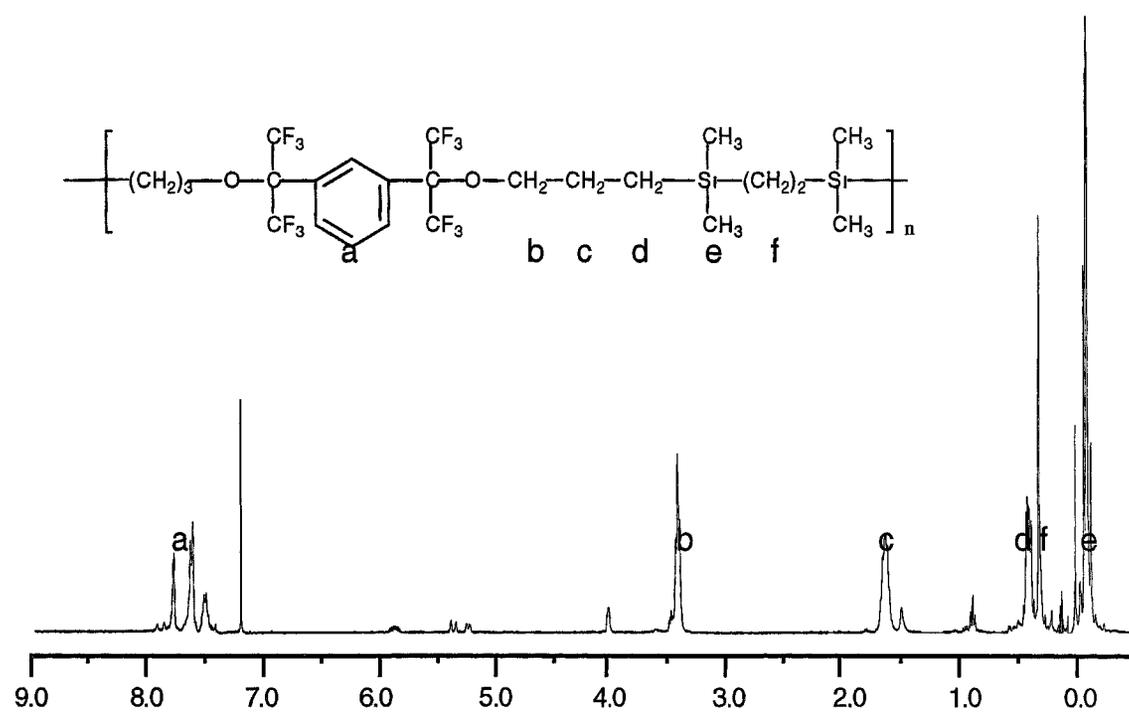
¹H NMR #20. Propenyl Model Hydrosilation in ScCO₂,
(Compound XIII-s)

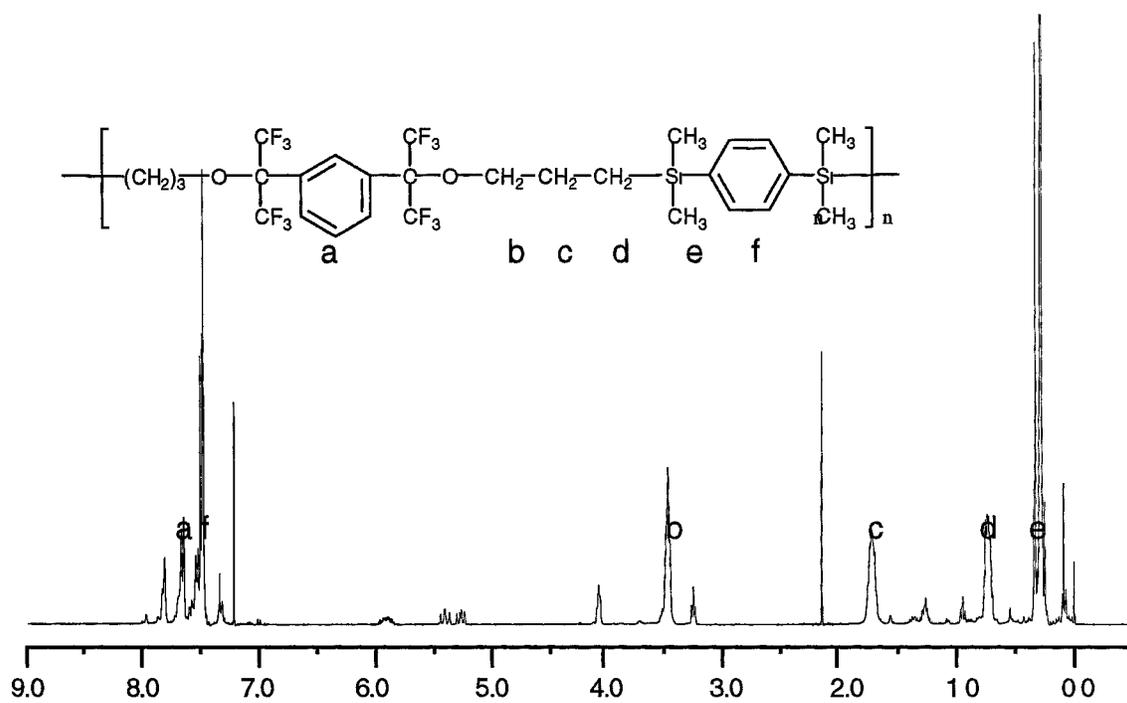


¹H NMR #21. Decenyl Model Hydrosilation in Benzene,
(Compound XIV-b)

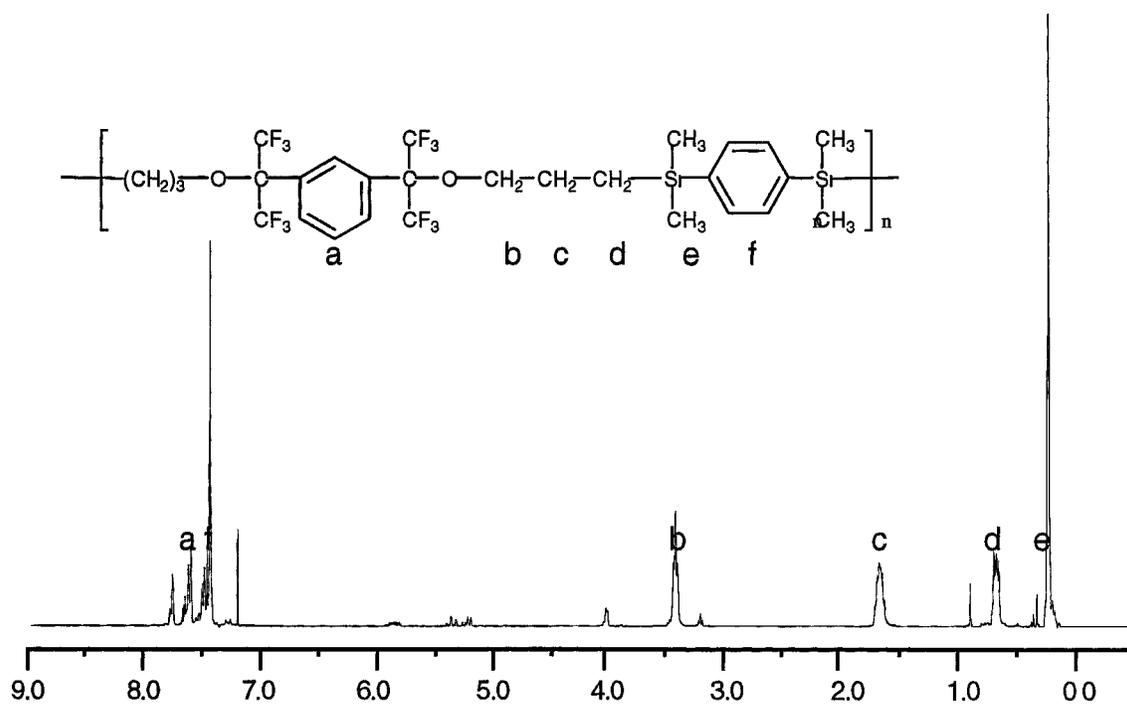


¹H NMR #22. Decenyl Model Hydrosilation in ScCO₂,
(Compound XIV-s)

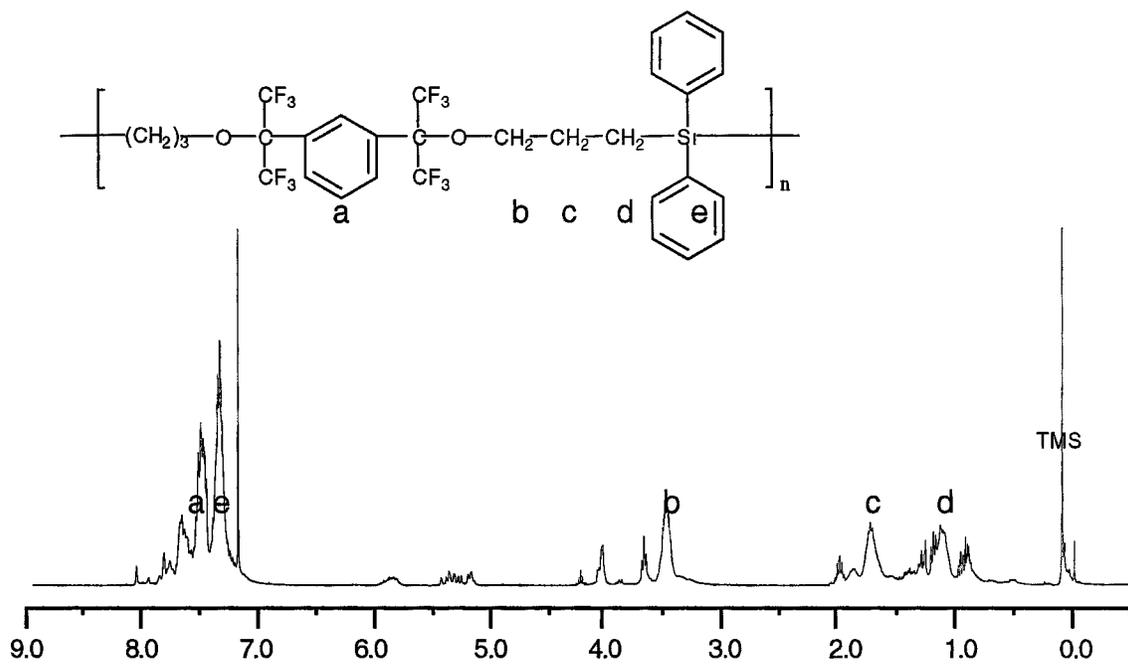
**¹H NMR #23. (Compound XXI-p-b)****¹H NMR #24. (Compound XXI-p-s)**



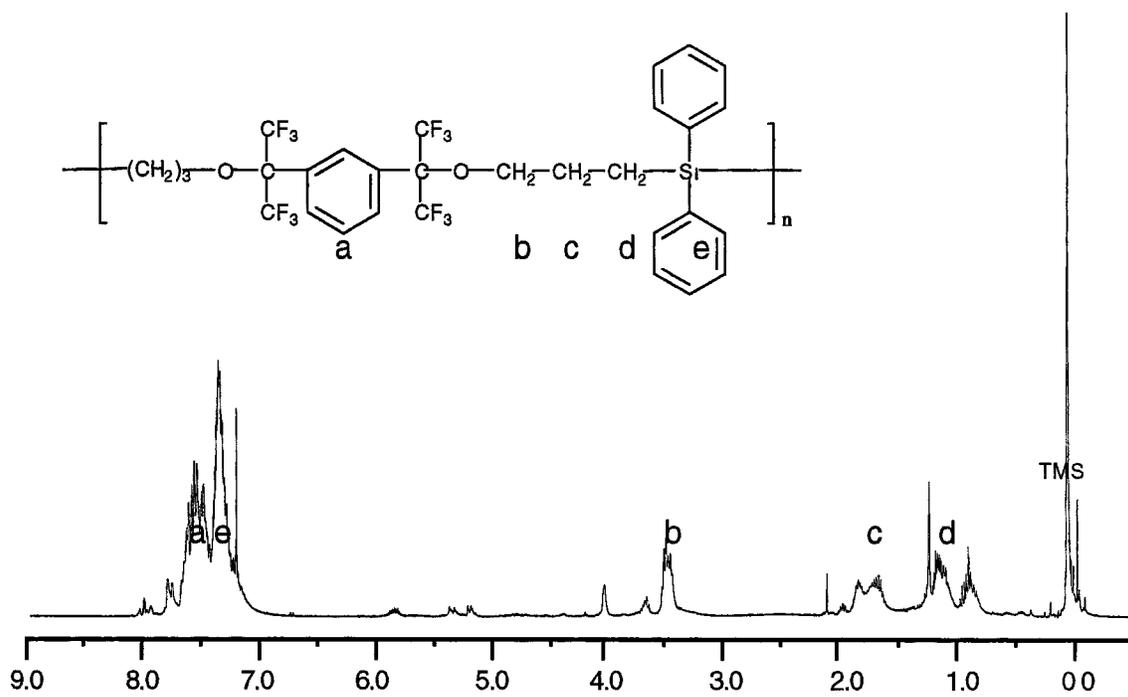
^1H NMR #25. (Compound XXIIp-b)



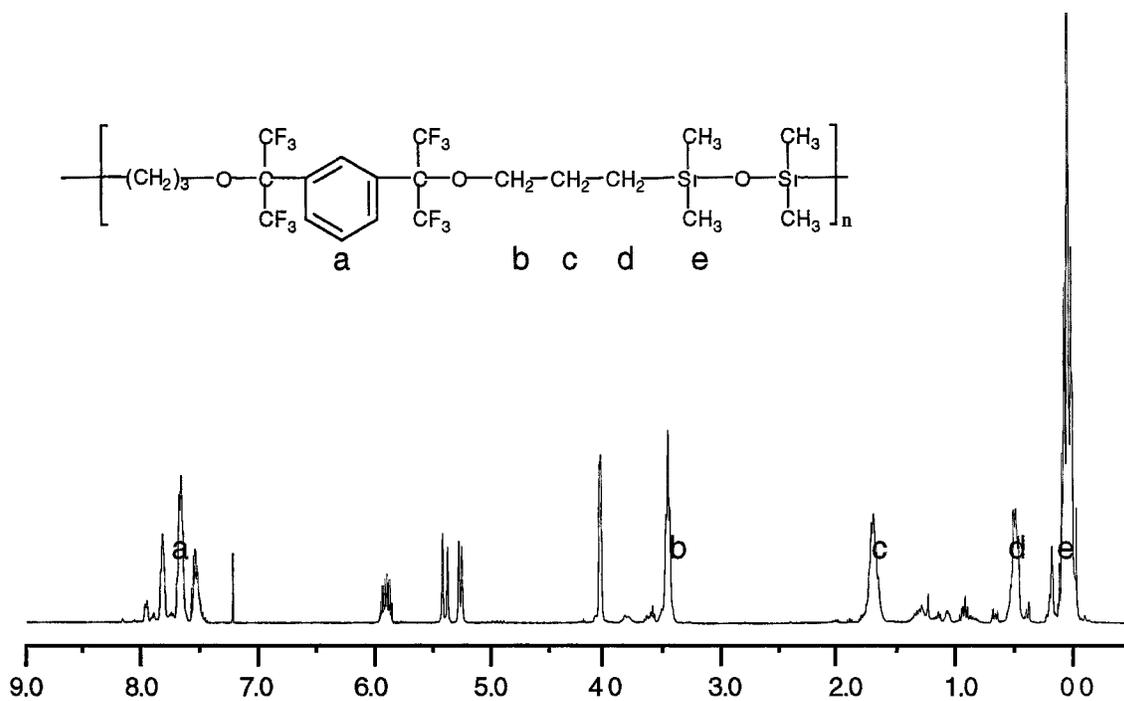
^1H NMR #26. (Compound XXIIp-s)



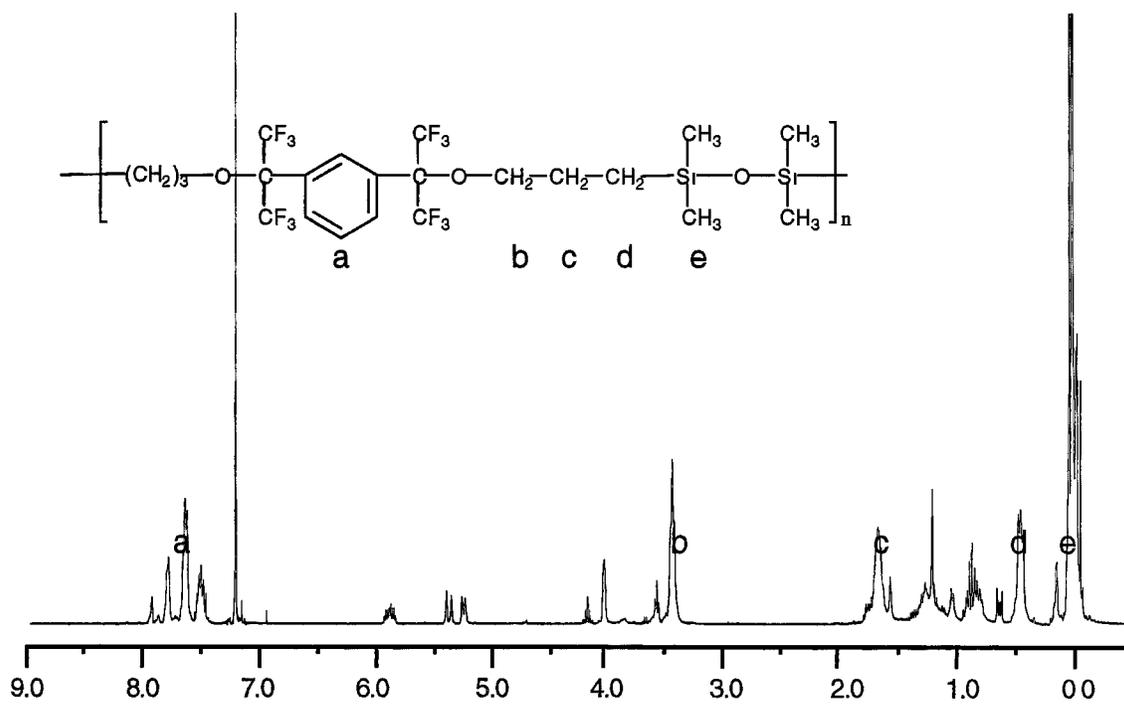
¹H NMR #27. (Compound XXIIIp-b)



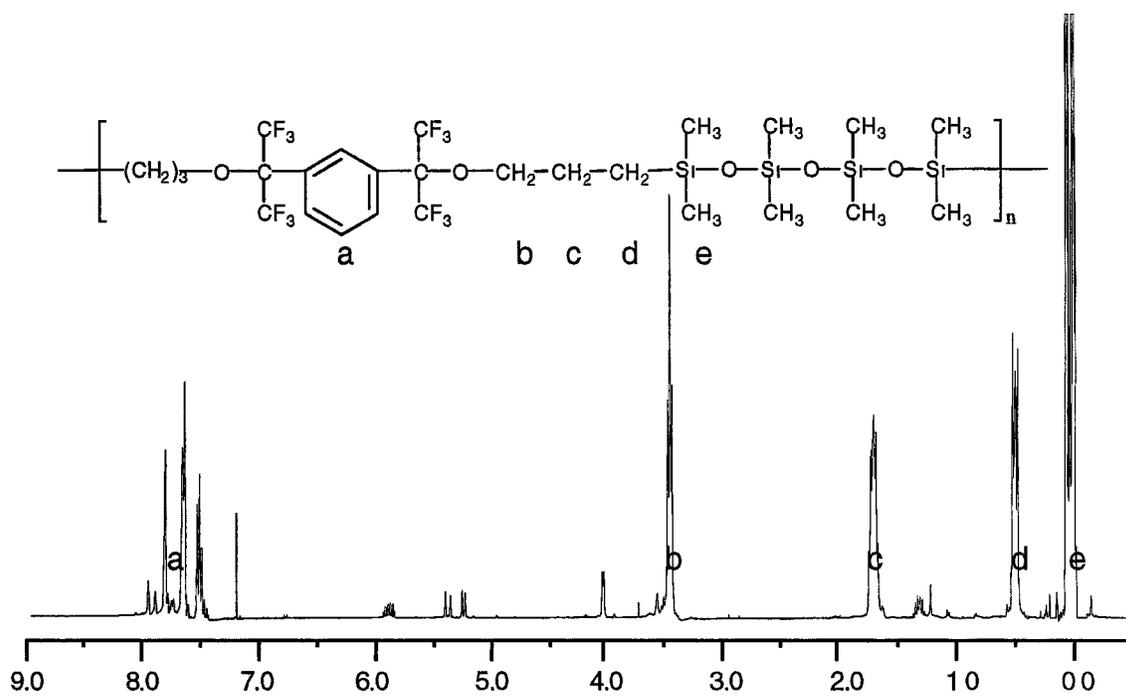
¹H NMR #28. (Compound XXIIIp-s)



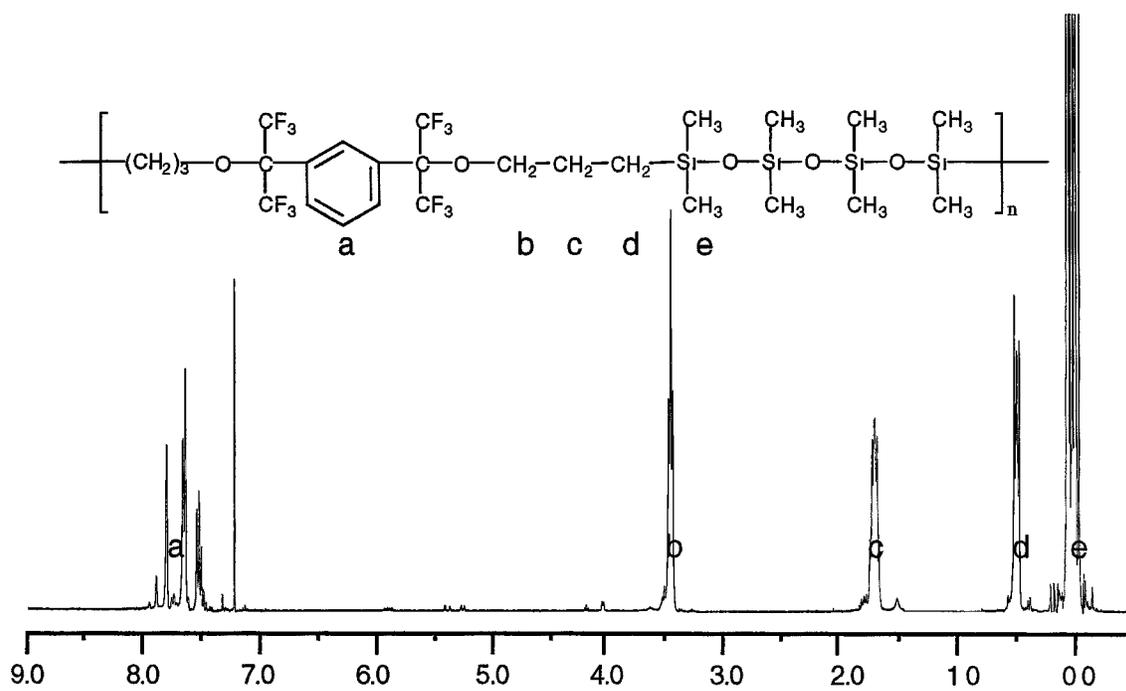
^1H NMR #29. (Compound XXIVp-b)



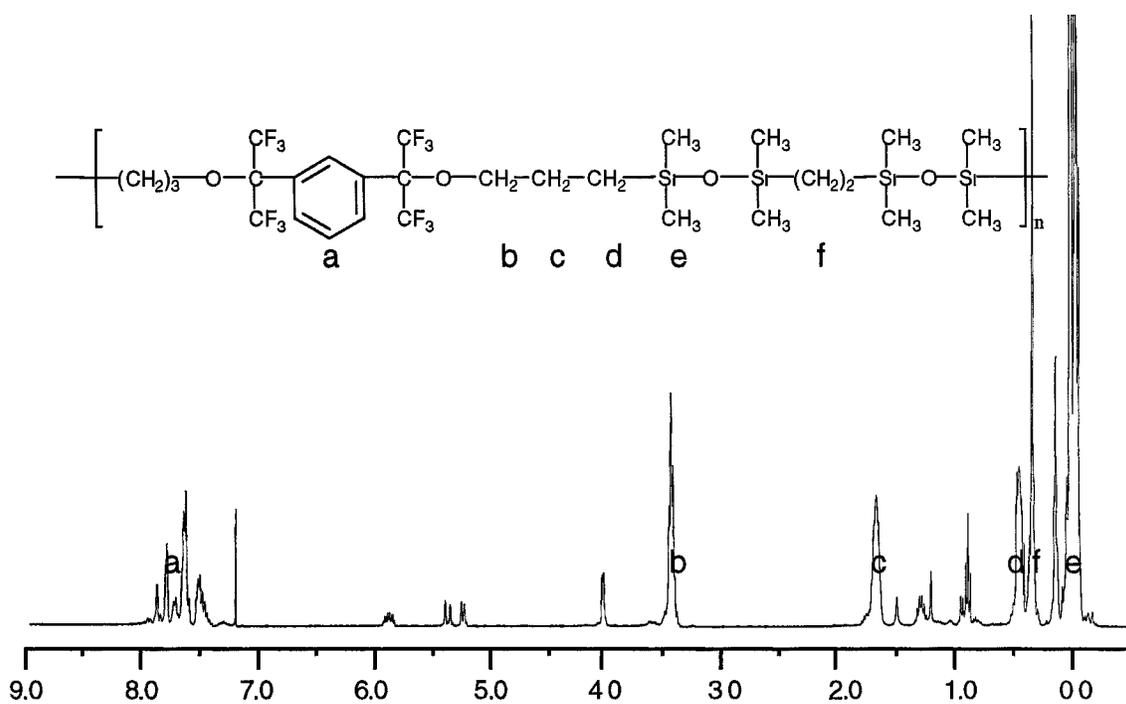
^1H NMR #30. (Compound XXIVp-s)



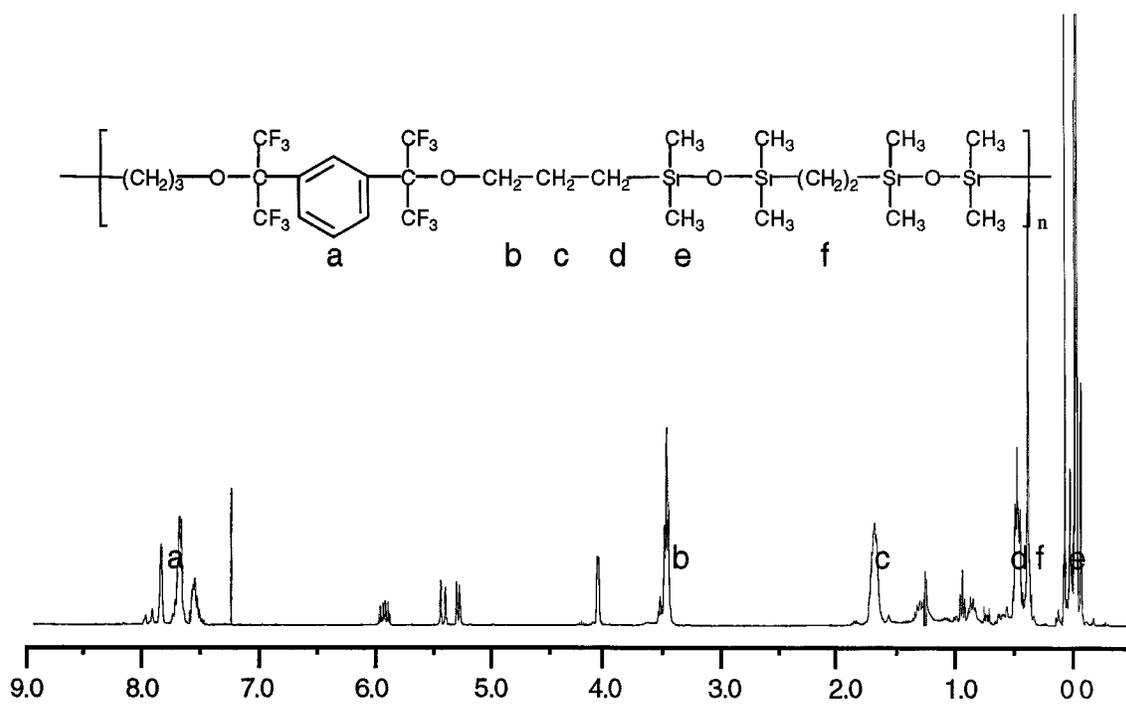
^1H NMR #31. (Compound XXVp-b)



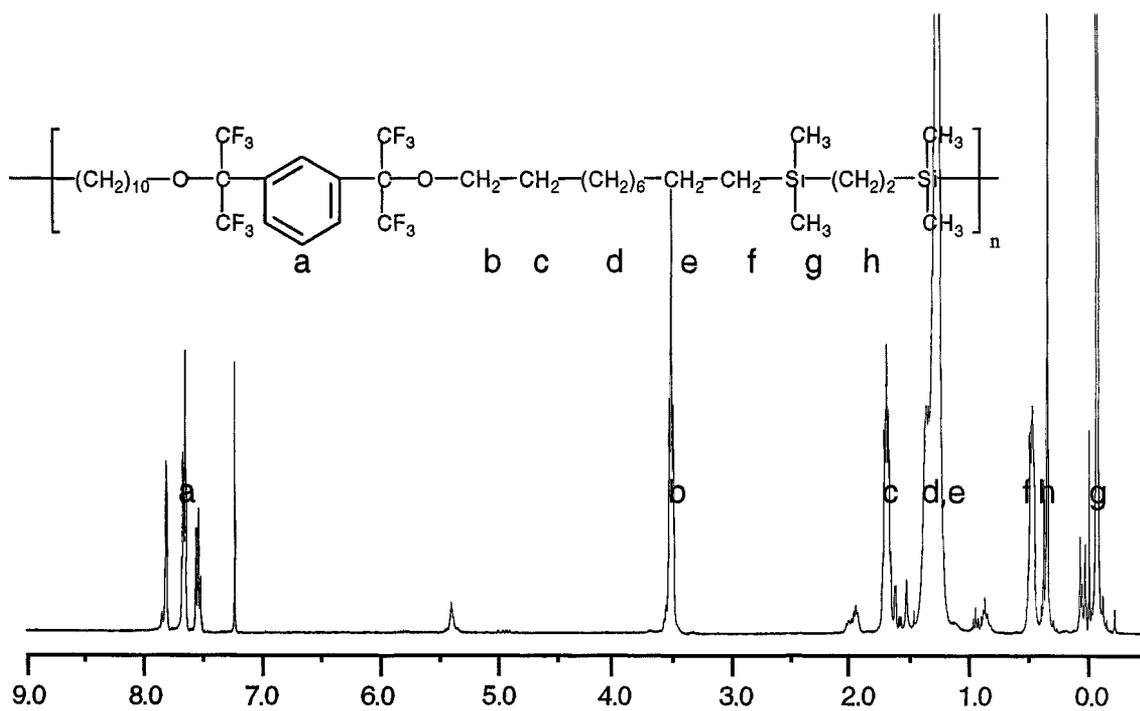
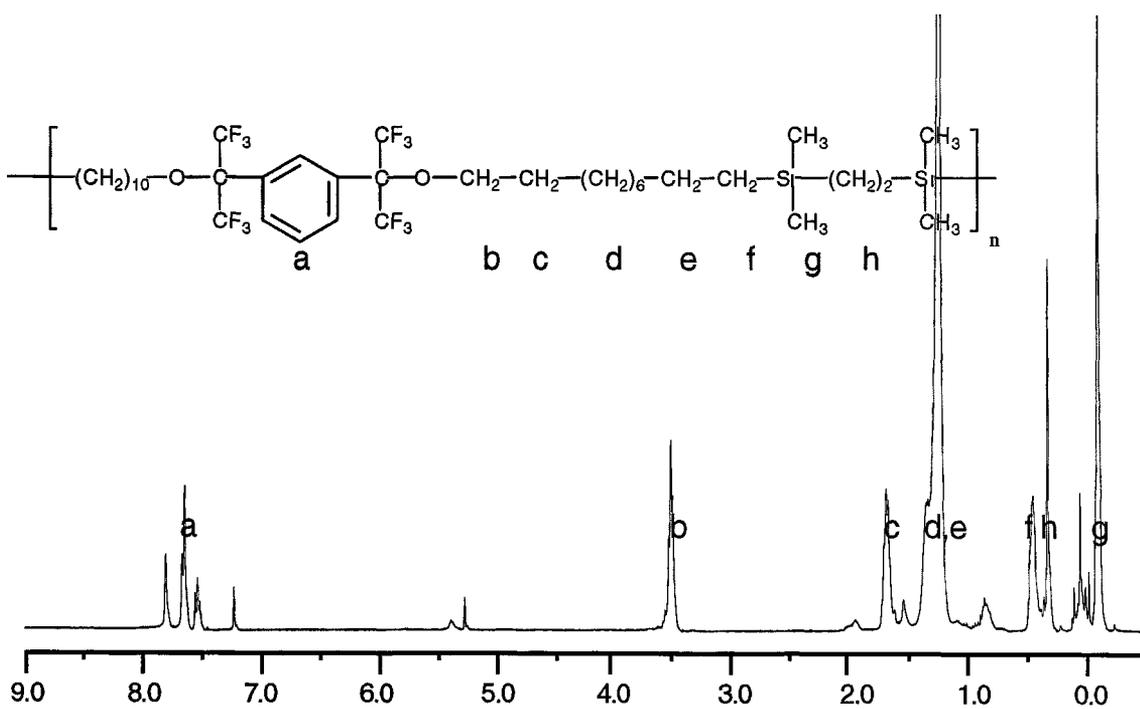
^1H NMR #32. (Compound XXVp-s)

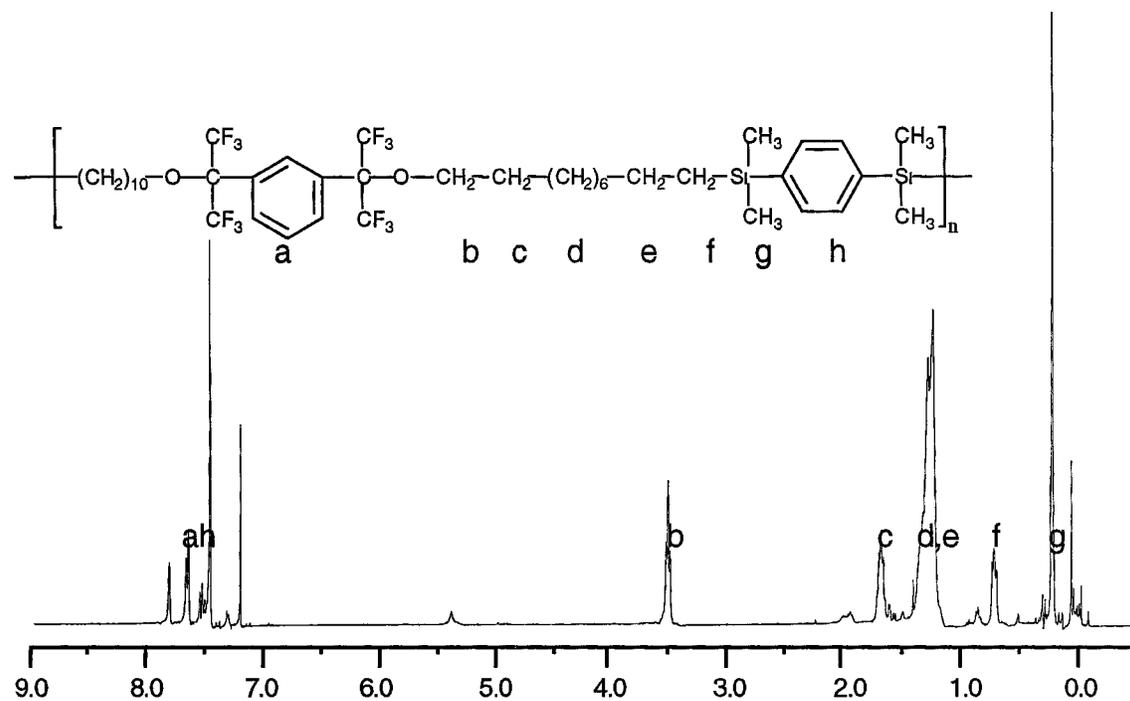
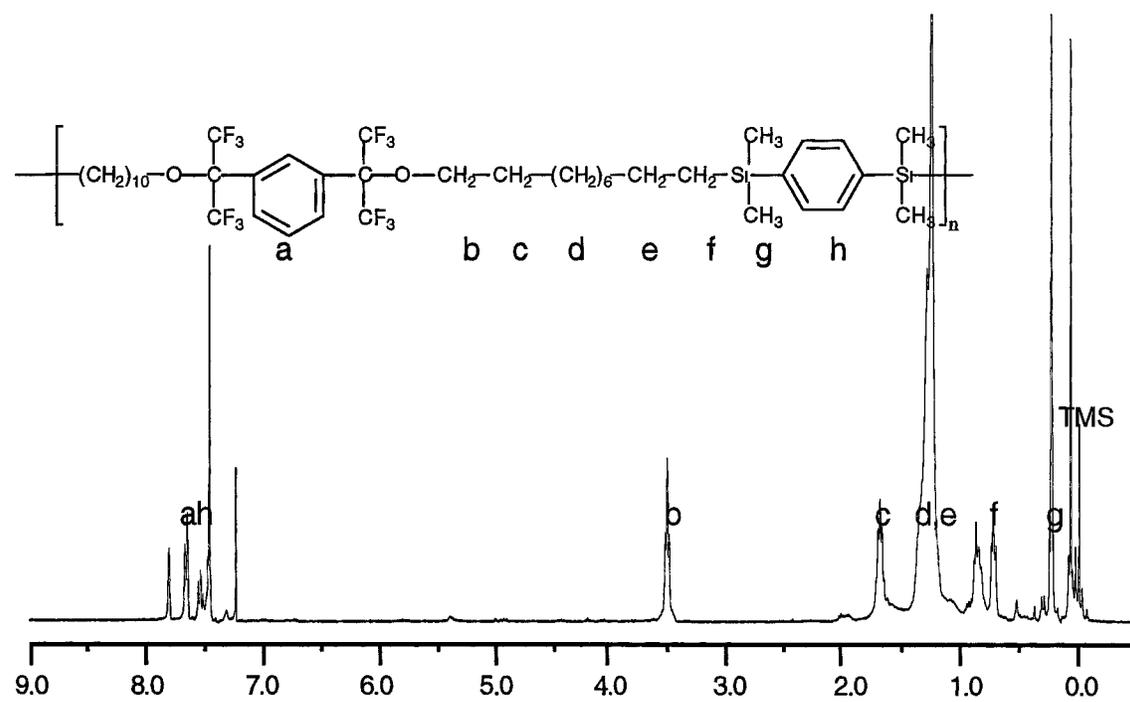


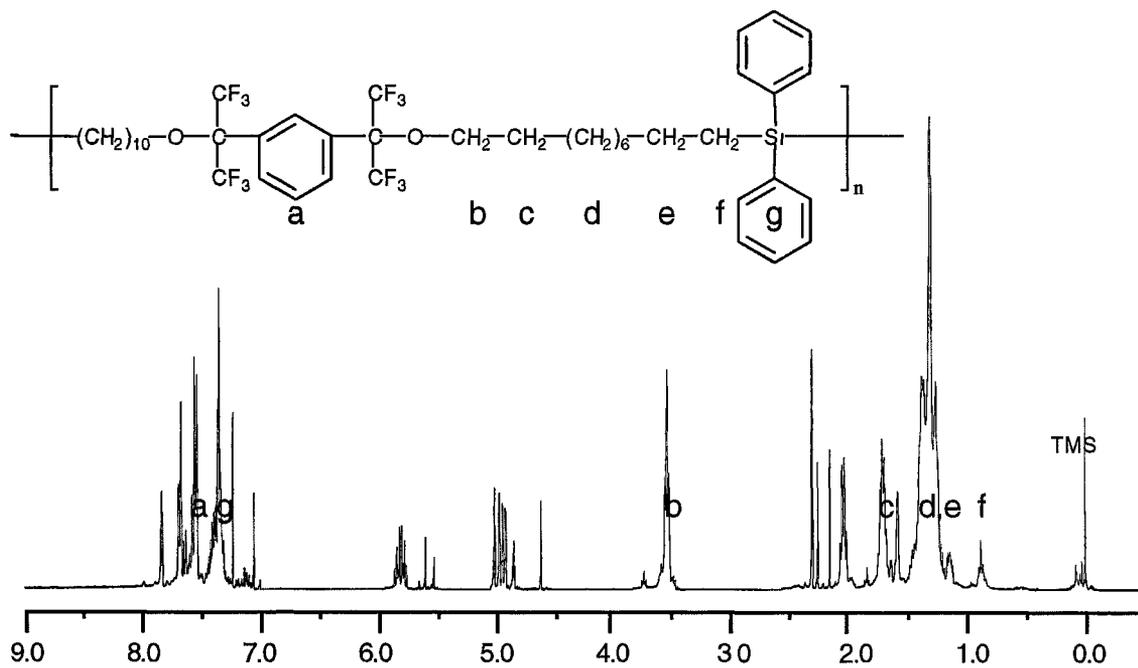
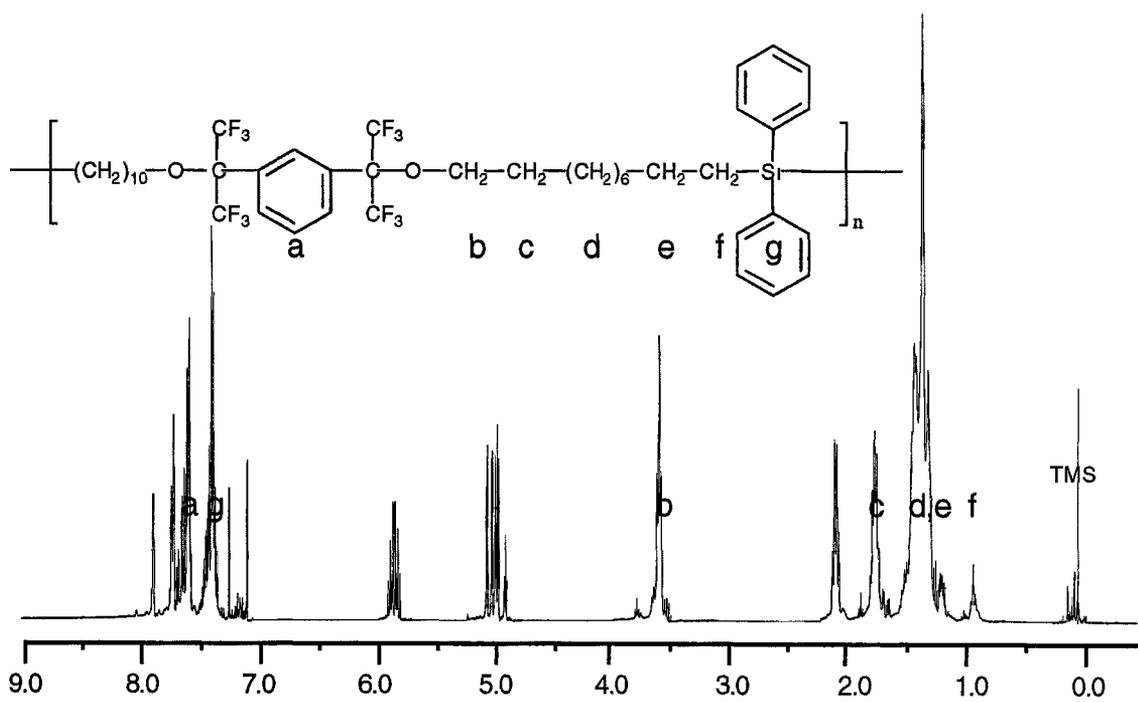
^1H NMR #33. (Compound XXVIp-b)

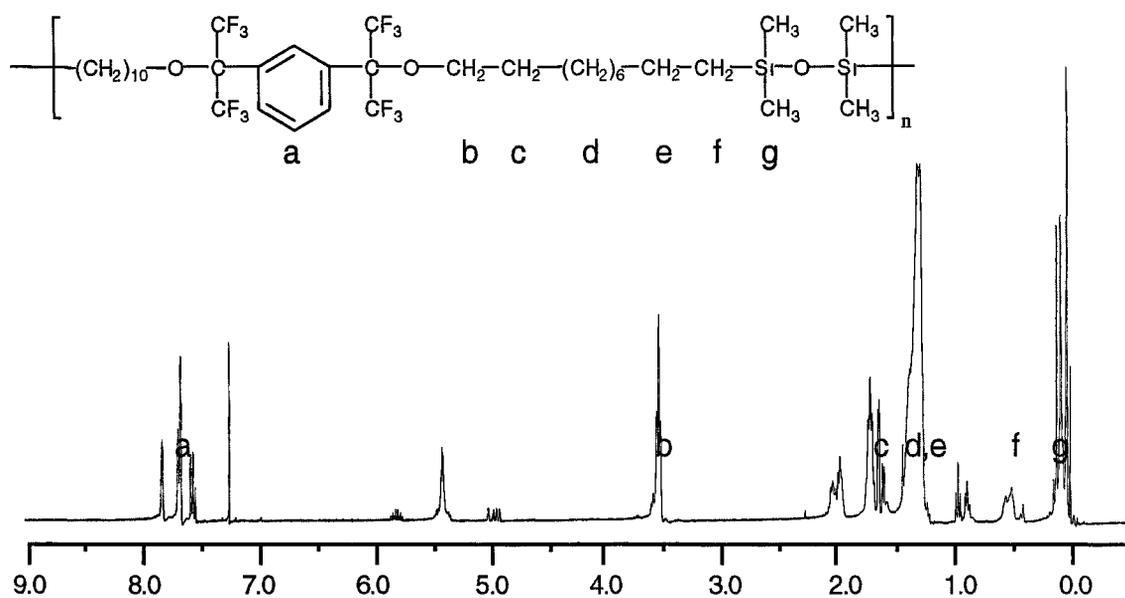
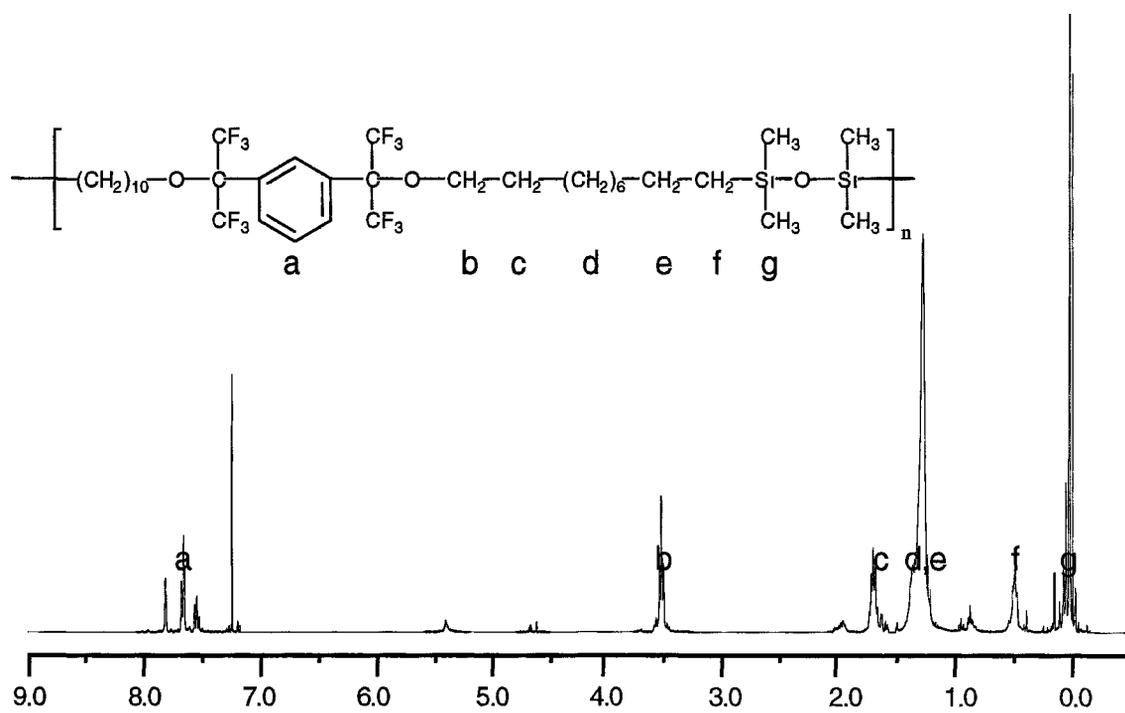


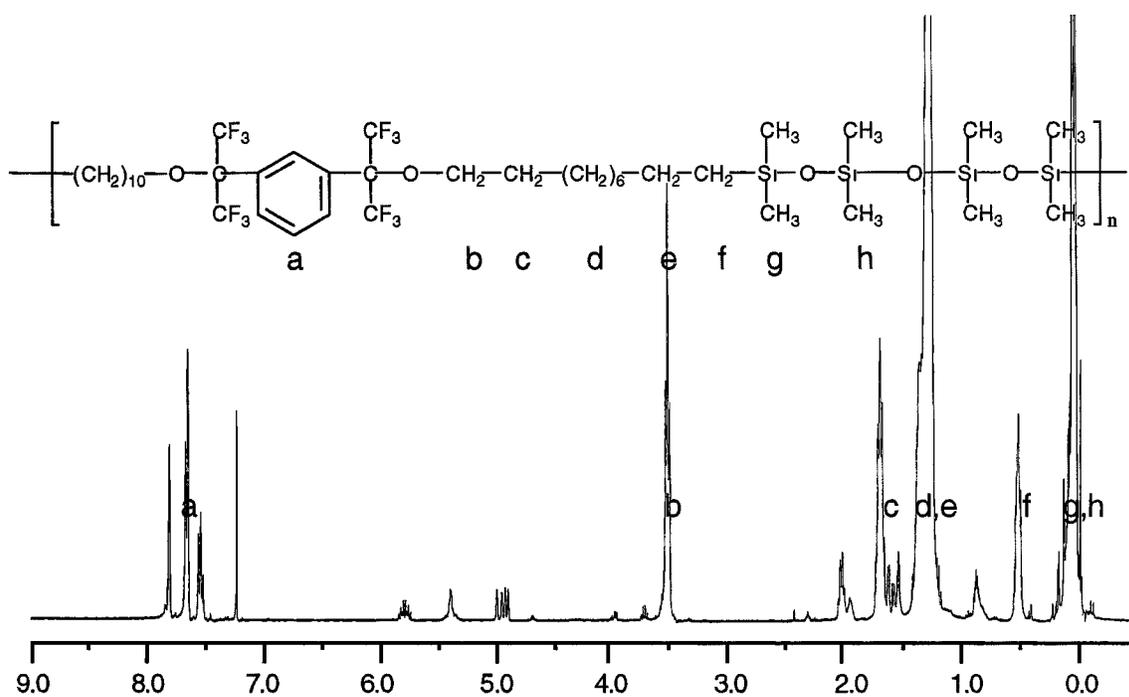
^1H NMR #34. (Compound XXVIp-s)

 **$^1\text{H NMR}$ #35. (Compound XXIId-b)** **$^1\text{H NMR}$ #36. (Compound XXIId-s)**

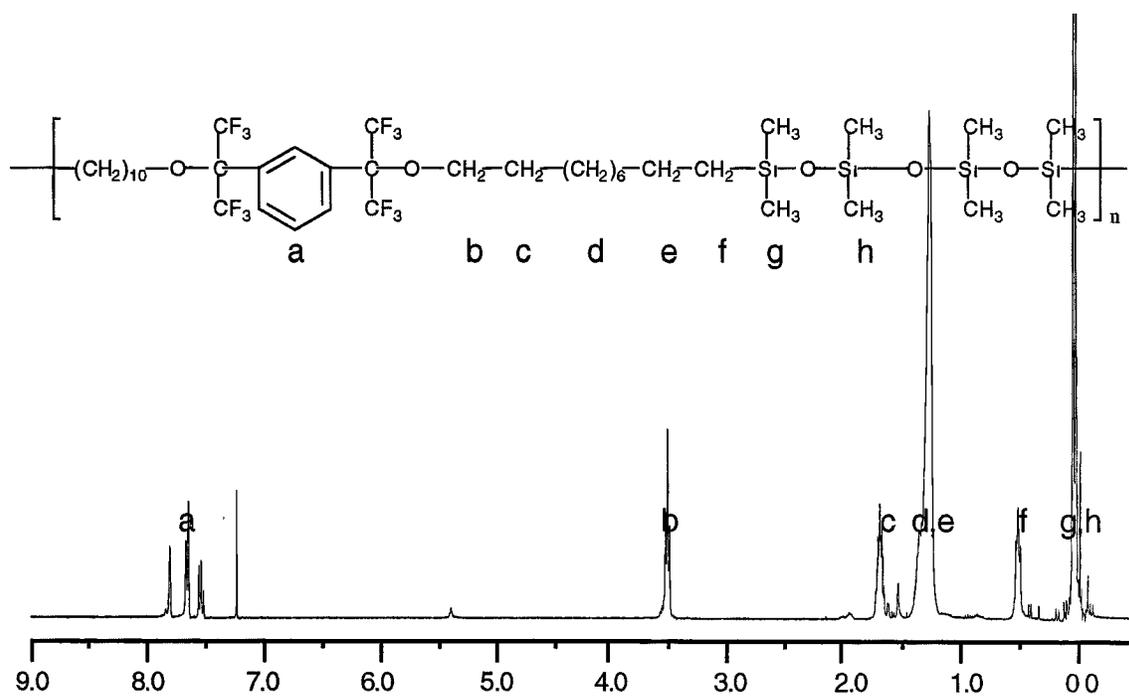
**¹H NMR #37. (Compound XXII-d-b)****¹H NMR #38. (Compound XXII-d-s)**

 **1H NMR #39.** (Compound XXIII d-b) **1H NMR #40.** (Compound XXIII d-s)

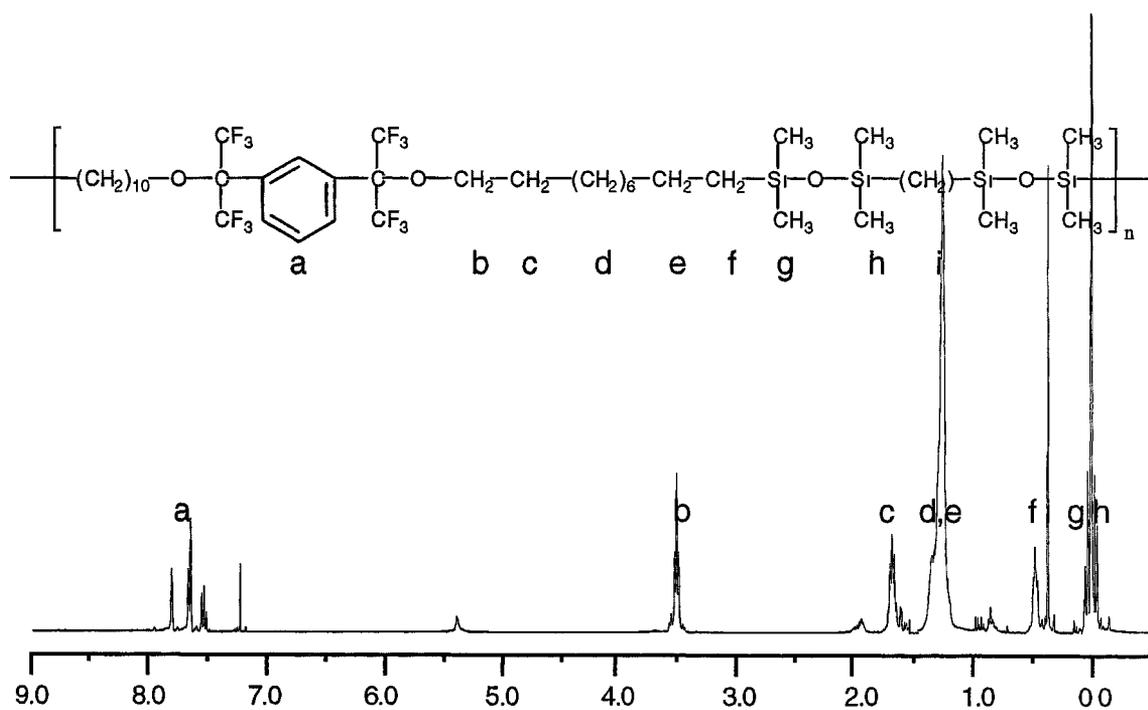
**¹H NMR #41. (Compound XXIVd-b)****¹H NMR #42. (Compound XXIVd-s)**



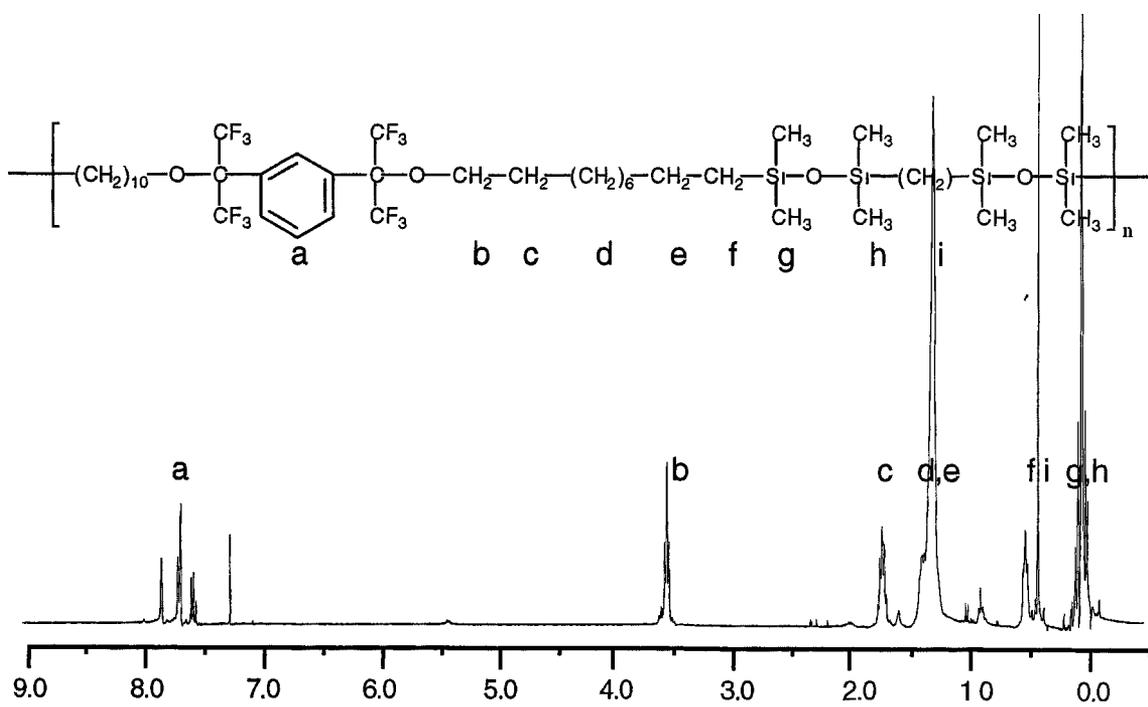
¹H NMR #43. (Compound XXVd-b)



¹H NMR #44. (Compound XXVd-s)



^1H NMR #45. "Decyl Polymer" (compound XXVIId-b)



^1H NMR #46. "Decyl Polymer," (compound XXVIId-s)

APPENDIX II
 ^{13}C NMR

Index for Appendix II

Compound	¹³ C NMR Number
Allyl bromide; (Compound III)	1
1,3-Bis(hexafluoro-2-propyl) Benzene (1,3-Bis HFAB); (Compound V)	2
1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene (Propenyl monomer), (Compound VII)	3
Compound derived from reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and Dimethyl phenyl silane; (Propenyl Model Hydrosilation in ScCO ₂), (Compound XIII-s)	4
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,4,4-Tetramethyldiethylene; in Benzene, (Compound XXIp-b)	5
in ScCO ₂ , (Compound XXIp-s)	6
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,4-Bis(dimethylsilyl)benzene; in Benzene, (Compound XXIIP-b)	7
in ScCO ₂ , (Compound XXIIP-s)	8

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(continued)

Compound	¹³ C NMR Number
Polymer derived from the reaction of	
1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and Diphenylsilane;	
in Benzene, (Compound XXIIIp-b)	9
in ScCO ₂ , (Compound XXIIIp-s)	10
Polymer derived from the reaction of	
1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3 tetramethyl disiloxane;	
in Benzene, (Compound XXIVp-b)	11
in ScCO ₂ , (Compound XXIVp-s)	12
Polymer derived from the reaction of	
1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3,5,5,7,7-Octamethyltetramethylsiloxane;	
in Benzene, (Compound XXVp-b)	13
in ScCO ₂ , (Compound XXVp-s)	14
Polymer derived from the reaction of	
1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1-2-Bis(tetramethyldisiloxaneyl)ethane;	
in Benzene, (Compound XXVIp-b)	15
in ScCO ₂ , (Compound XXVIp-s)	16
1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene (Decenyl monomer), (Compound XI)	17

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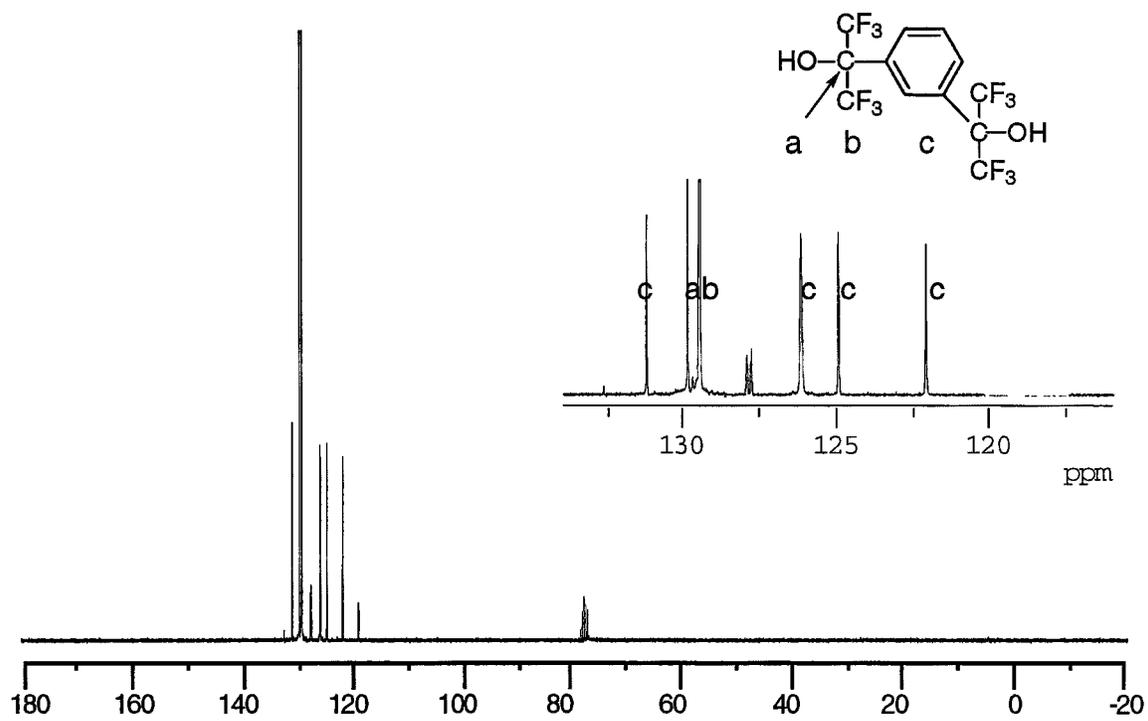
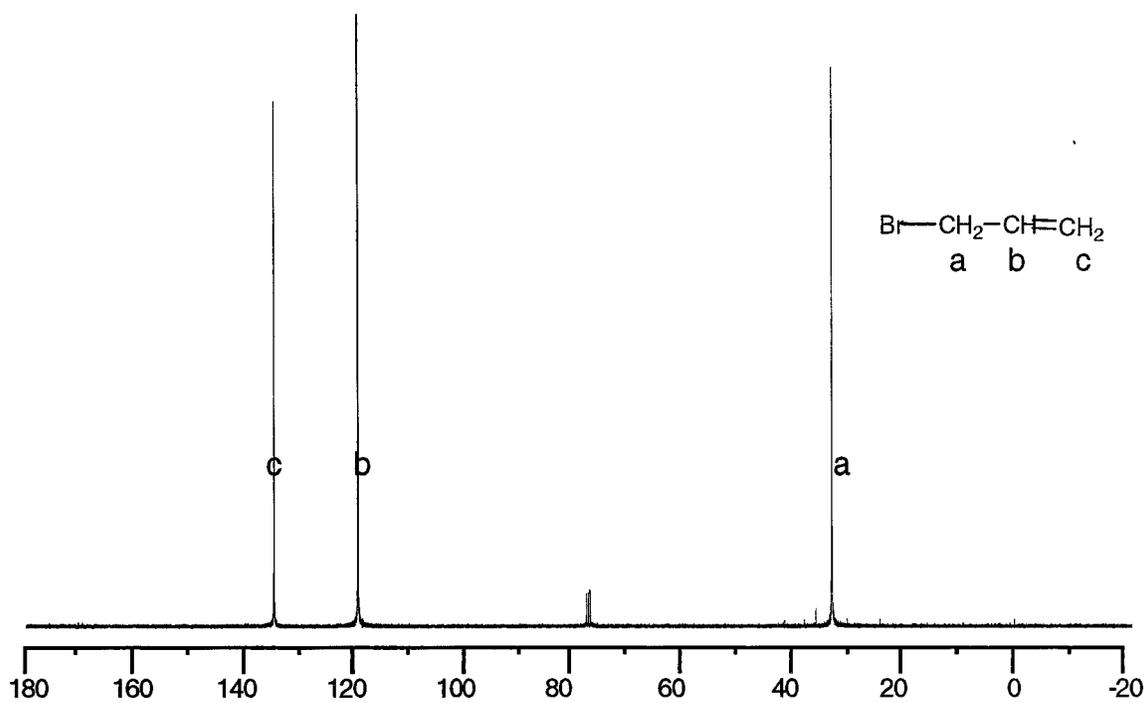
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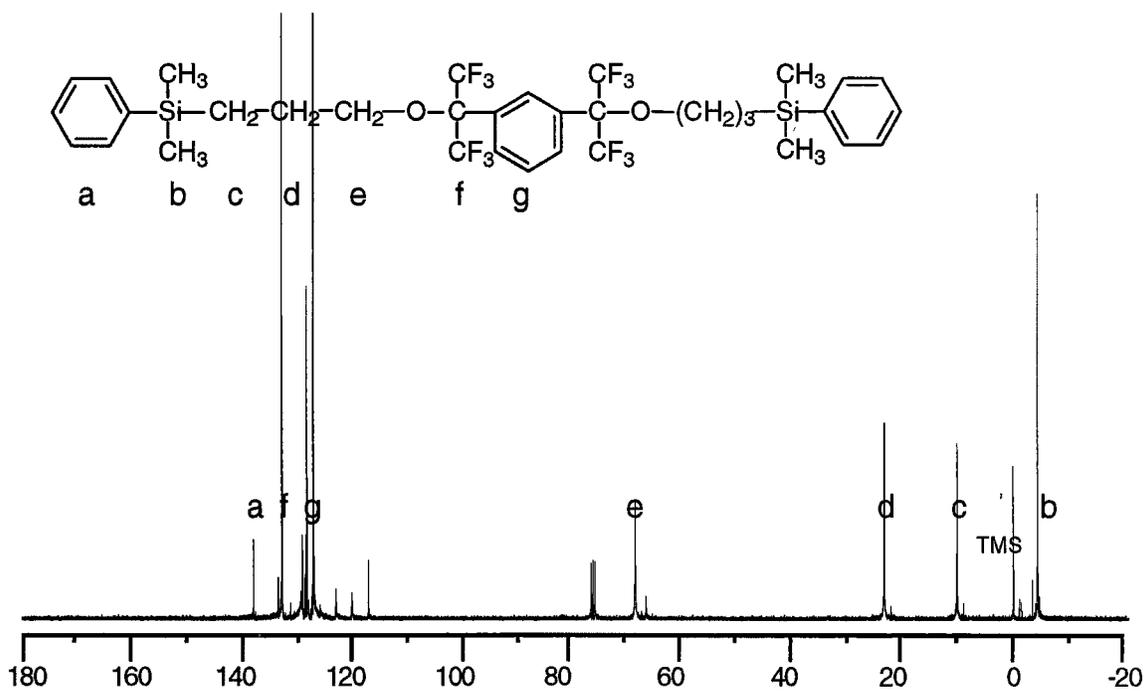
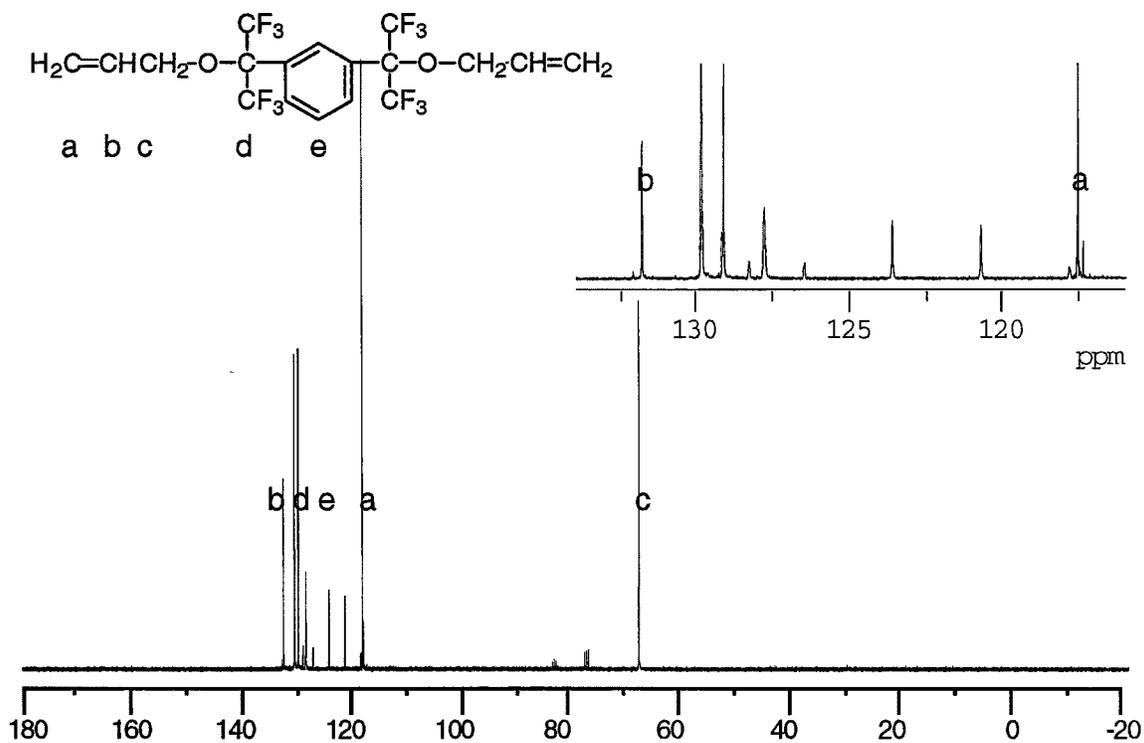
Compound	¹³ C NMR Number
Compound derived from reaction of 1,3-bis decyl (10-oxyhexafluoroisopropylidene) Benzene dimethyl phenyl silane; (Decenyl Model Hydrosilation in ScCO ₂), (Compound XIV-s)	18
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,4,4-Tetramethyldisethylene; in Benzene, (Compound XXId-b)	19
in ScCO ₂ , (Compound XXId-s)	20
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,4-Bis(dimethylsilyl)benzene; in Benzene, (Compound XXIId-b)	21
in ScCO ₂ , (Compound XXVIIId-s)	22
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and Diphenylsilane; in Benzene, (Compound XXIIIId-b)	23
in ScCO ₂ , (Compound XXIIIId-s)	24

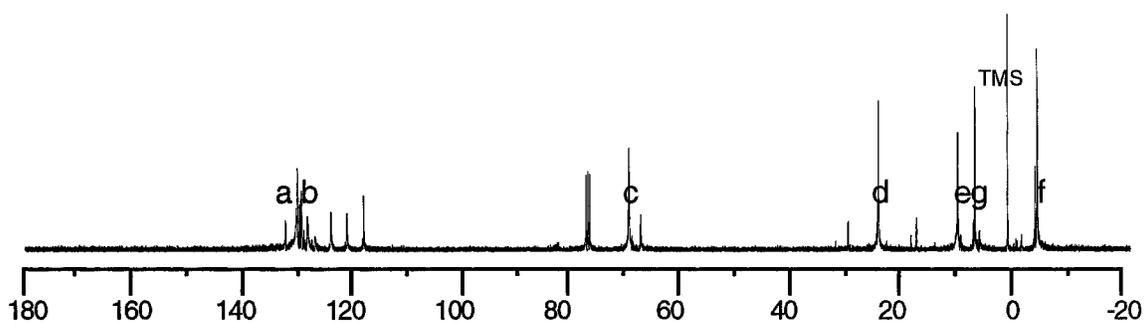
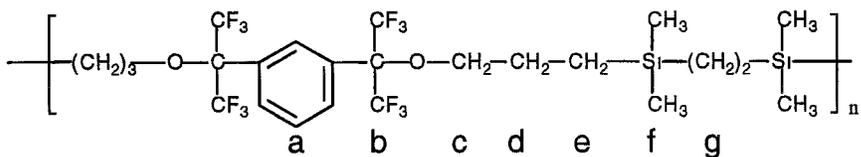
Index for Appendix II

(continued)

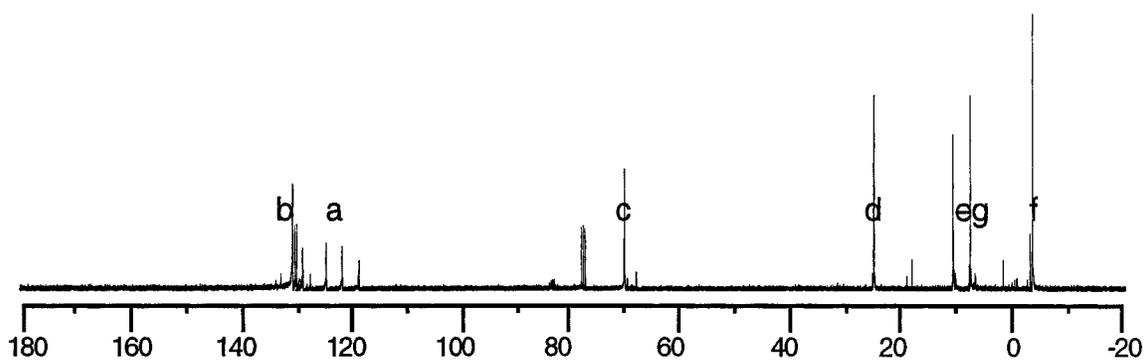
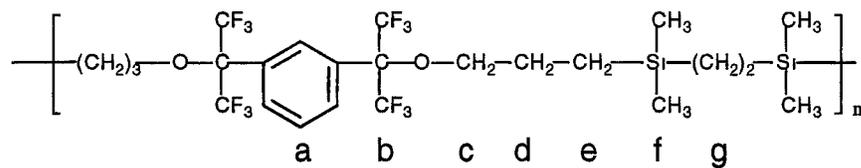
Compound	¹³ C NMR Number
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,3,3-Tetramethyldisiloxane; in Benzene, (Compound XXIVd-b)	25
in ScCO ₂ , (Compound XXIVd-s)	26
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,3,3,5,5,7,7 Octamethyltetrasiloxane; in Benzene, (Compound XXVd-b)	27
in ScCO ₂ , (Compound XXVd-s)	28
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1-2-Bis(tetramethyldisiloxaneyl)ethane; in Benzene, (Compound XXVIId-b)	29
in ScCO ₂ , (Compound XXVIId-s)	30



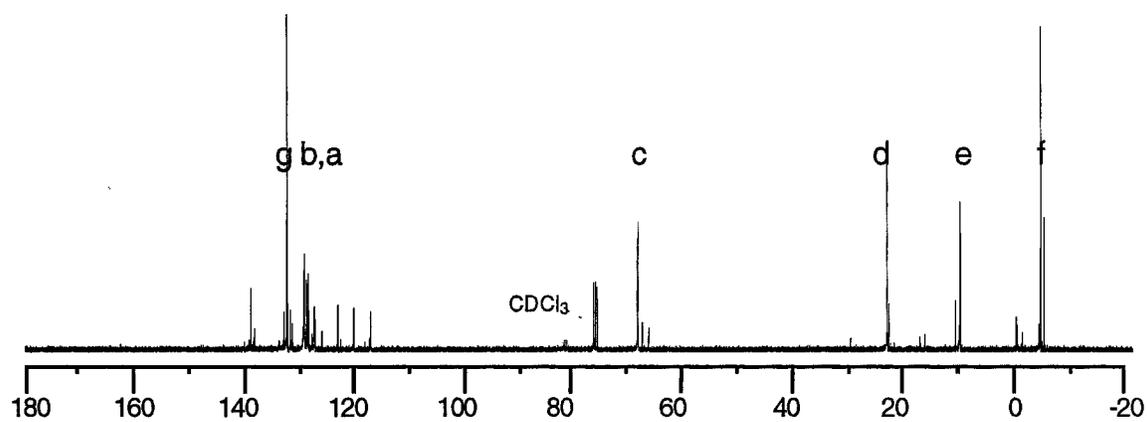
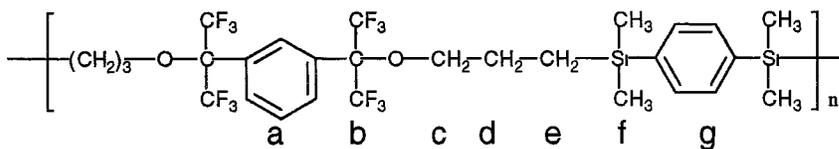




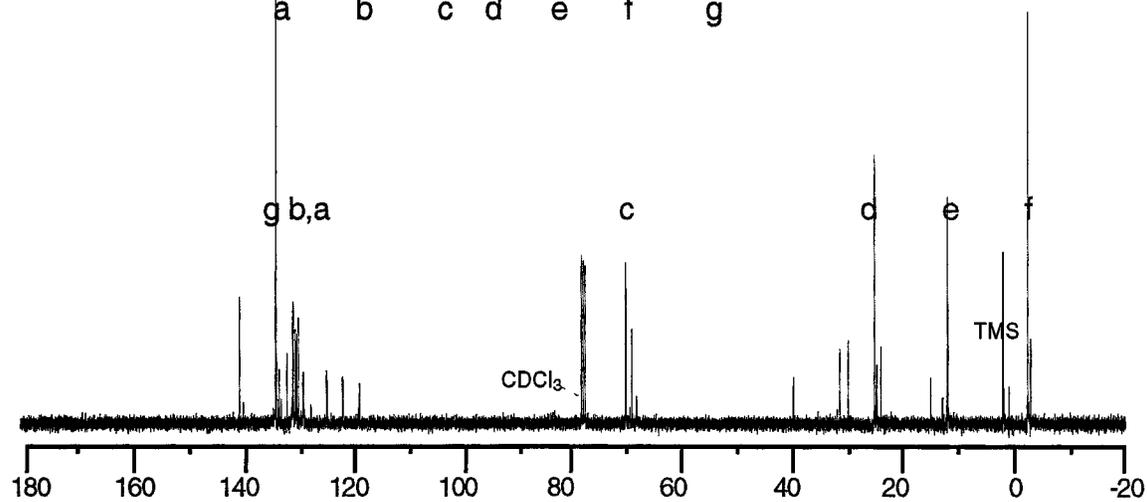
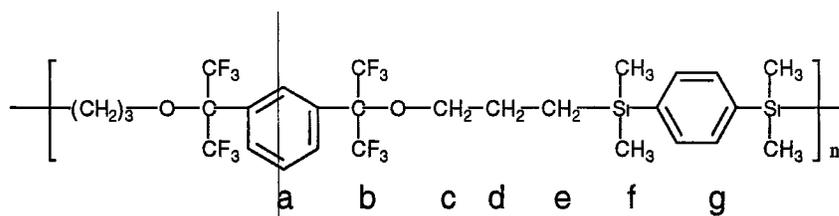
¹³C NMR #5. (Compound XXI p-b)



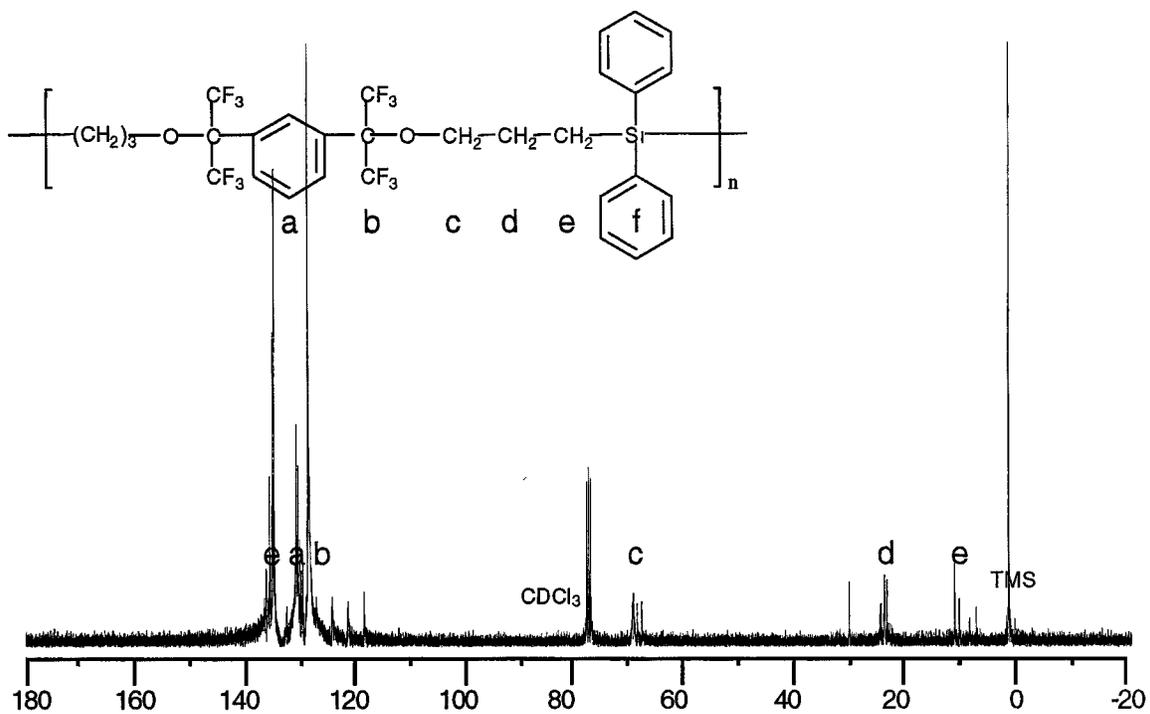
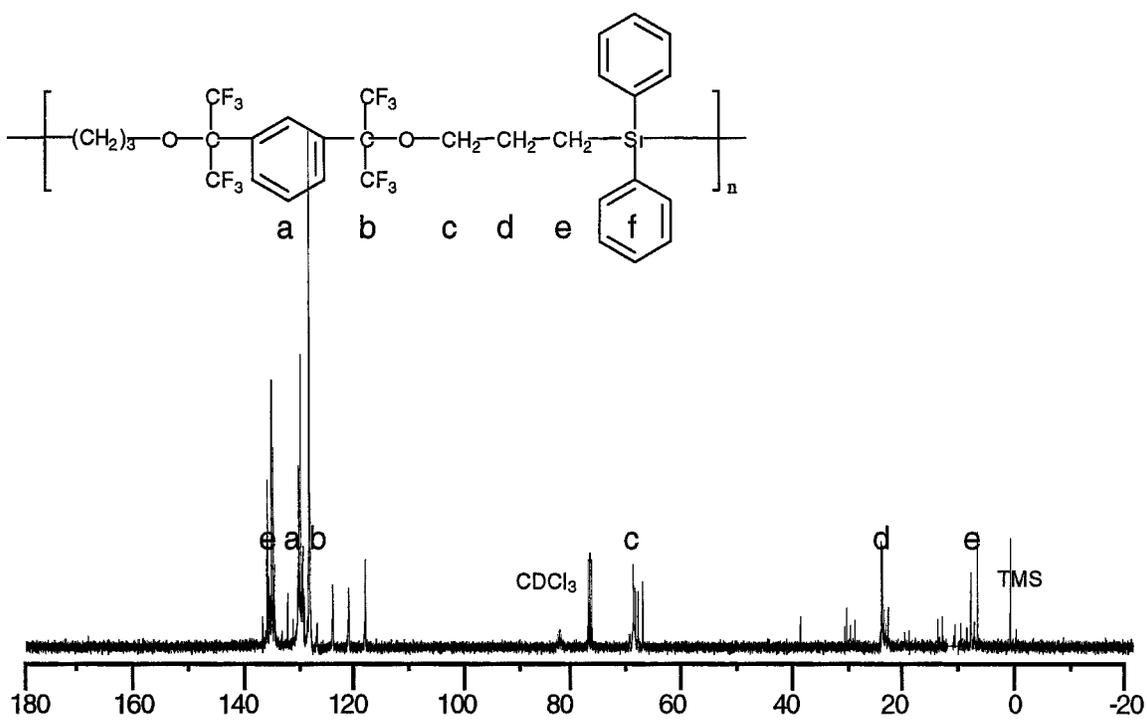
¹³C NMR #6. (Compound XXI p-s)

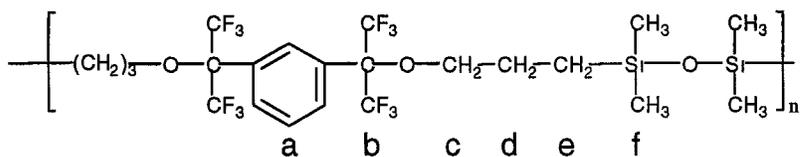


^{13}C NMR #7. (Compound XXIIp-b)

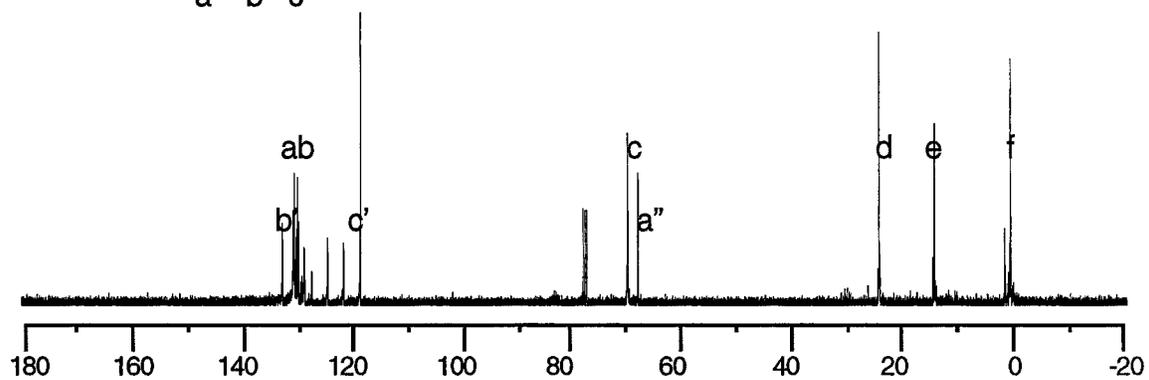


^{13}C NMR #8. (Compound XXIIp-s)

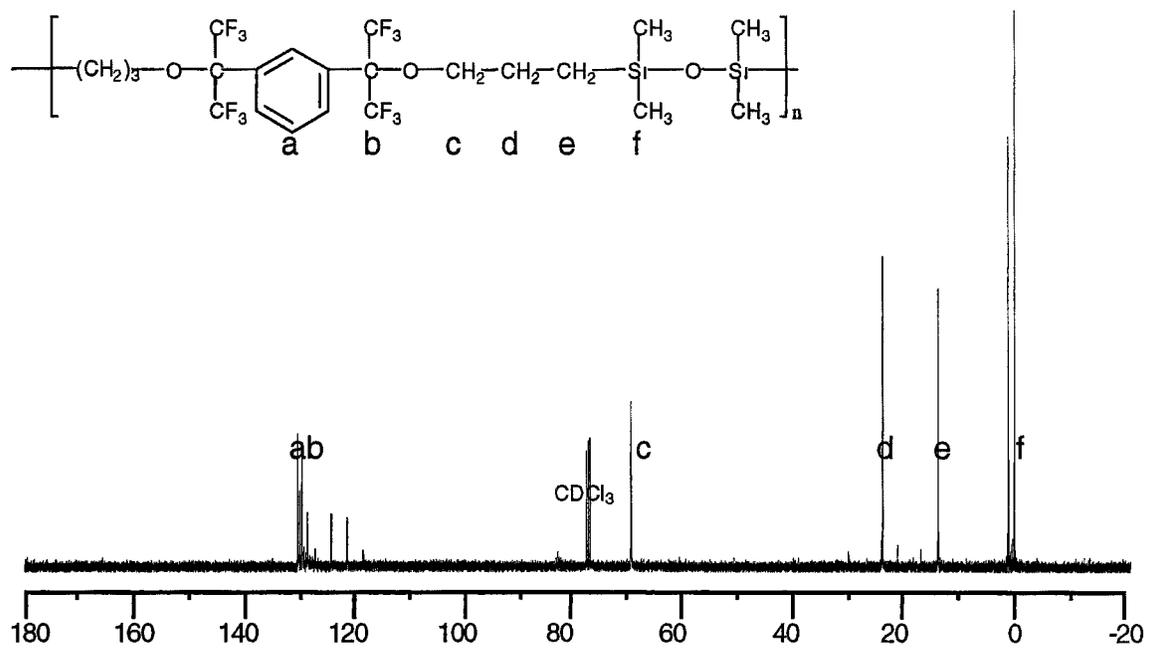
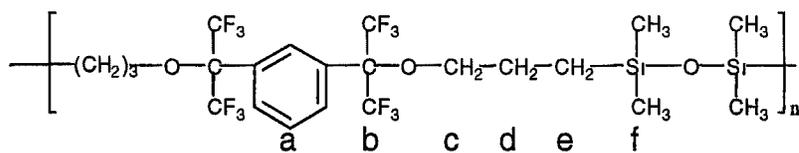
 **^{13}C NMR #9. (Compound XXIIIp-b)** **^{13}C NMR #10. (Compound XXIIIp-s)**



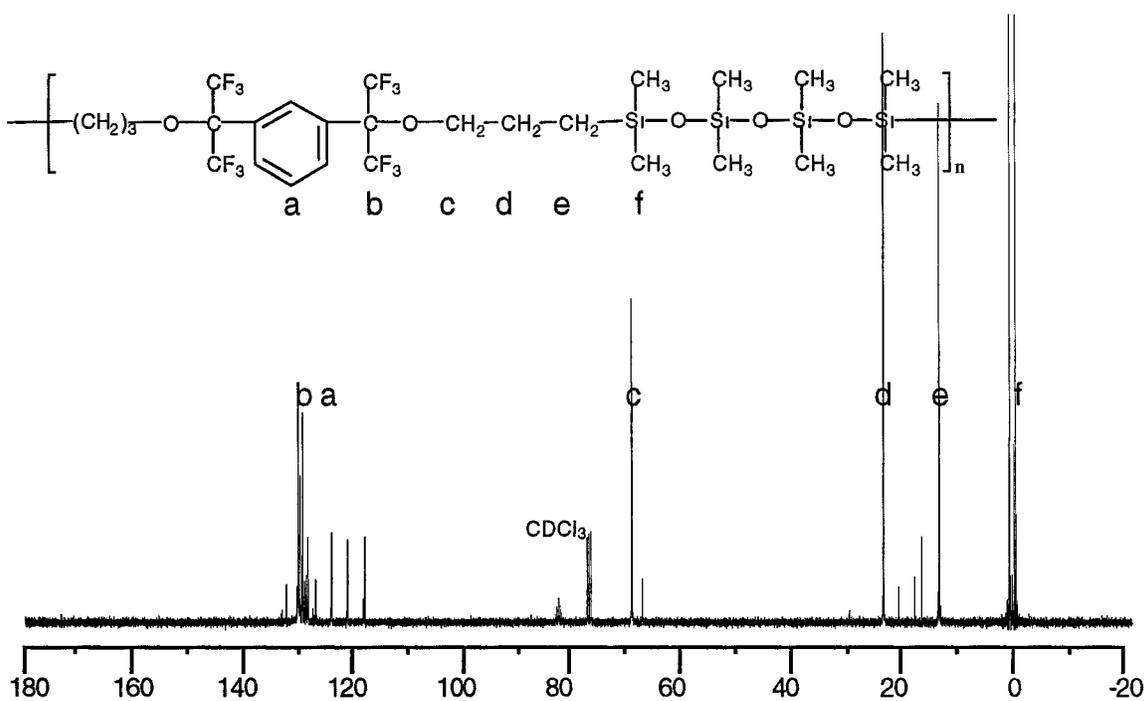
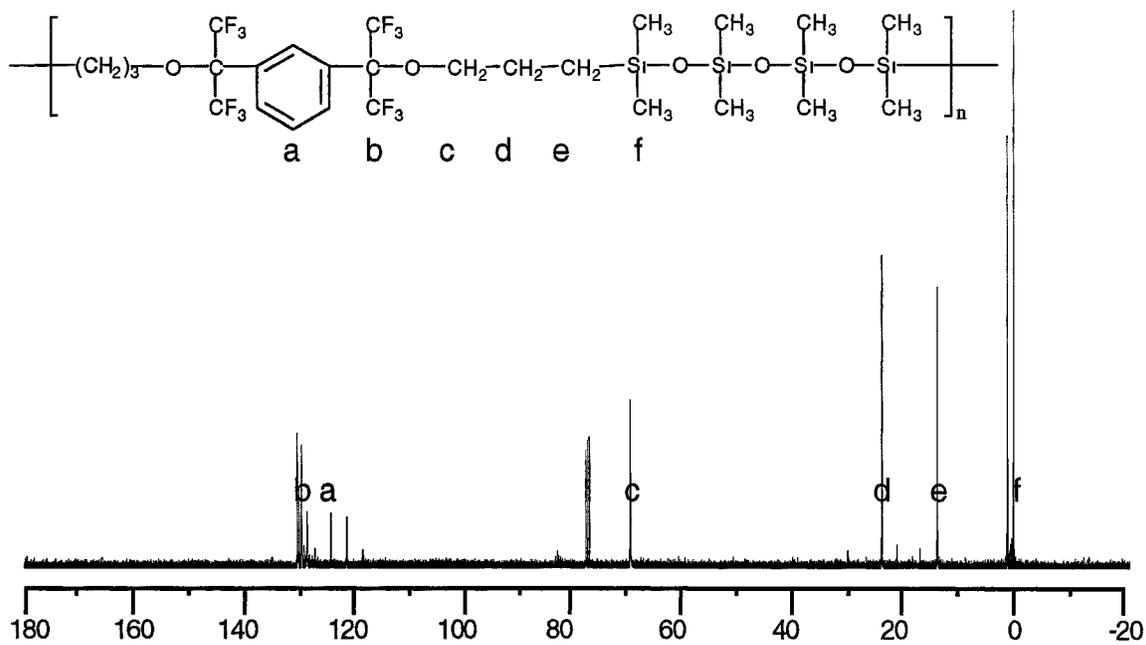
unreacted O-CH₂-CH=CH₂
a' b' c''

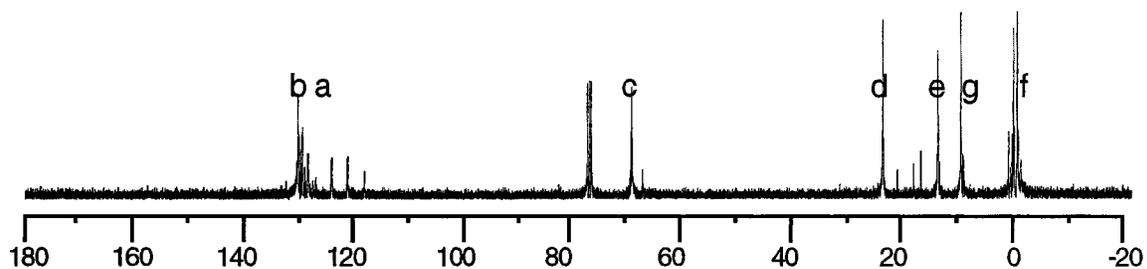
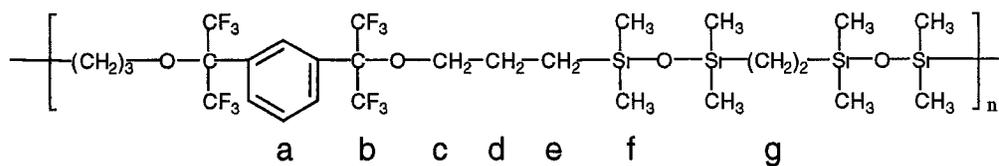


¹³C NMR #11. (Compound XXIVp-b)

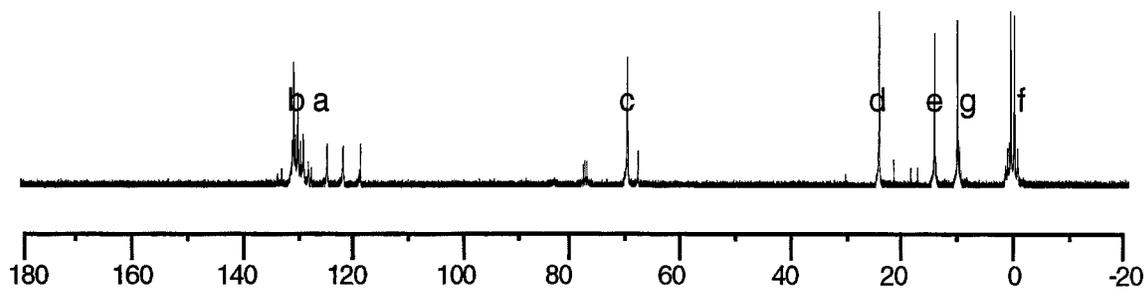
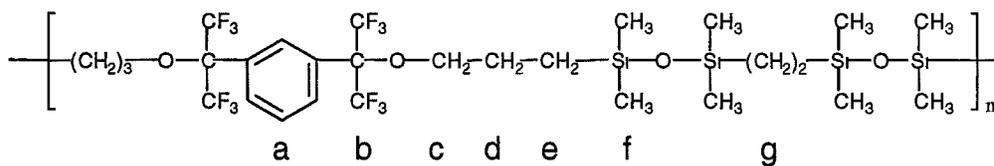


¹³C NMR #12. (Compound XXIVp-s)

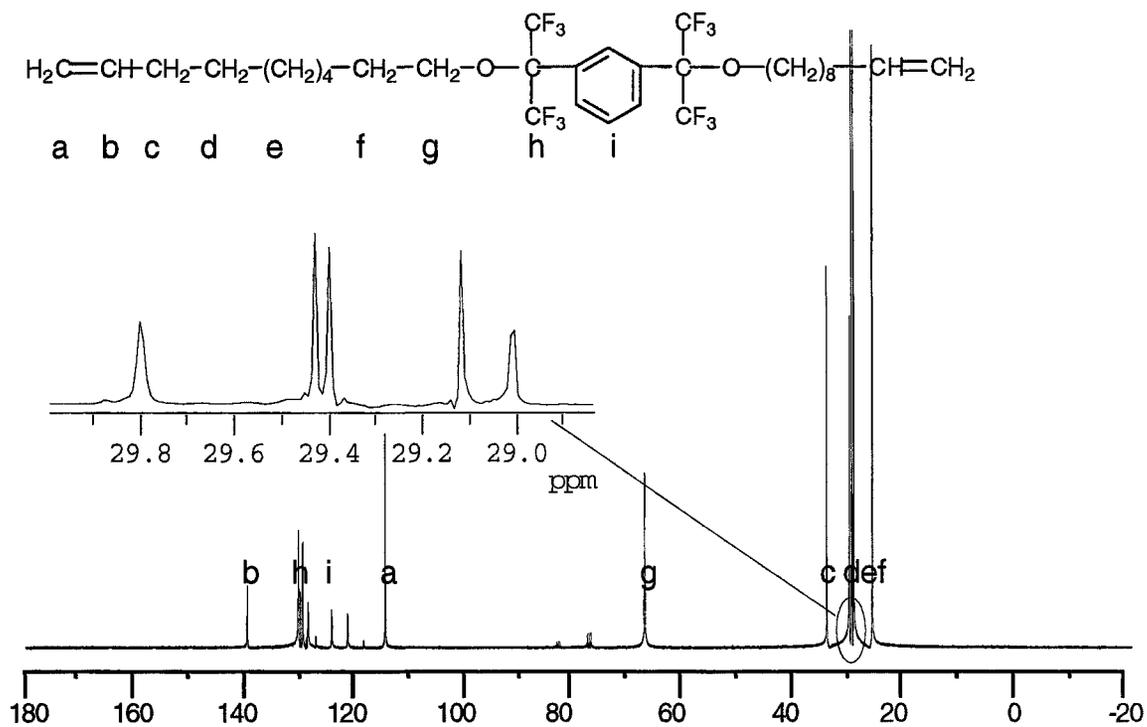
 **^{13}C NMR #13. (Compound XXVp-b)** **^{13}C NMR #14. (Compound XXVp-s)**



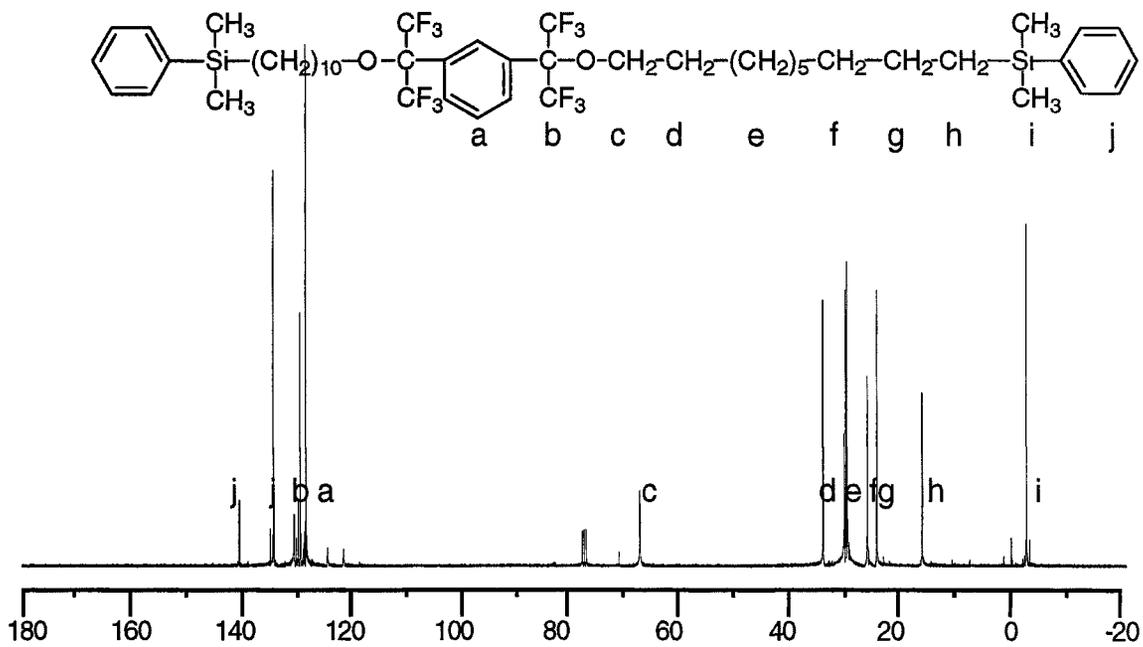
^{13}C NMR #15. (Compound XXVIp-b)



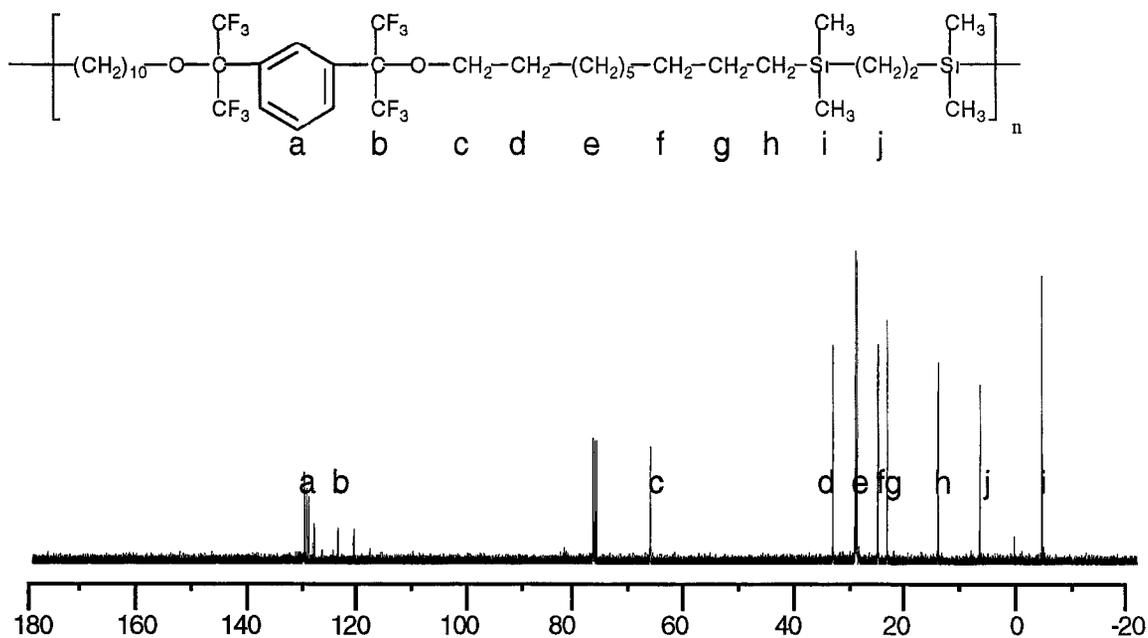
^{13}C NMR #16. (Compound XXVIp-s)



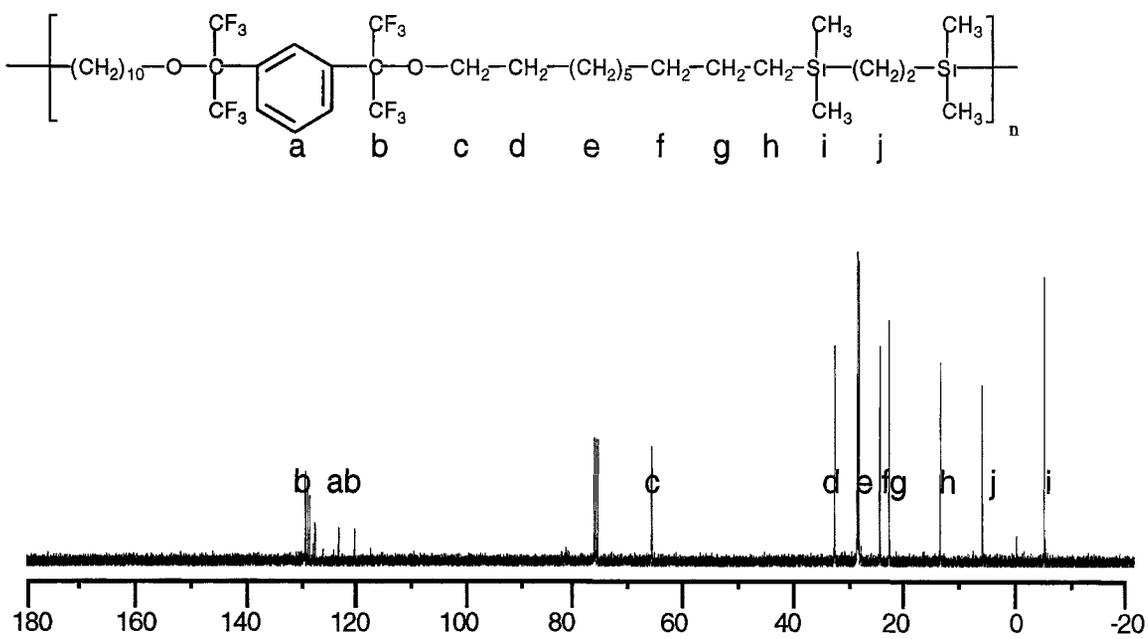
¹³C NMR #17. 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene (Decenyl monomer), (Compound XI)



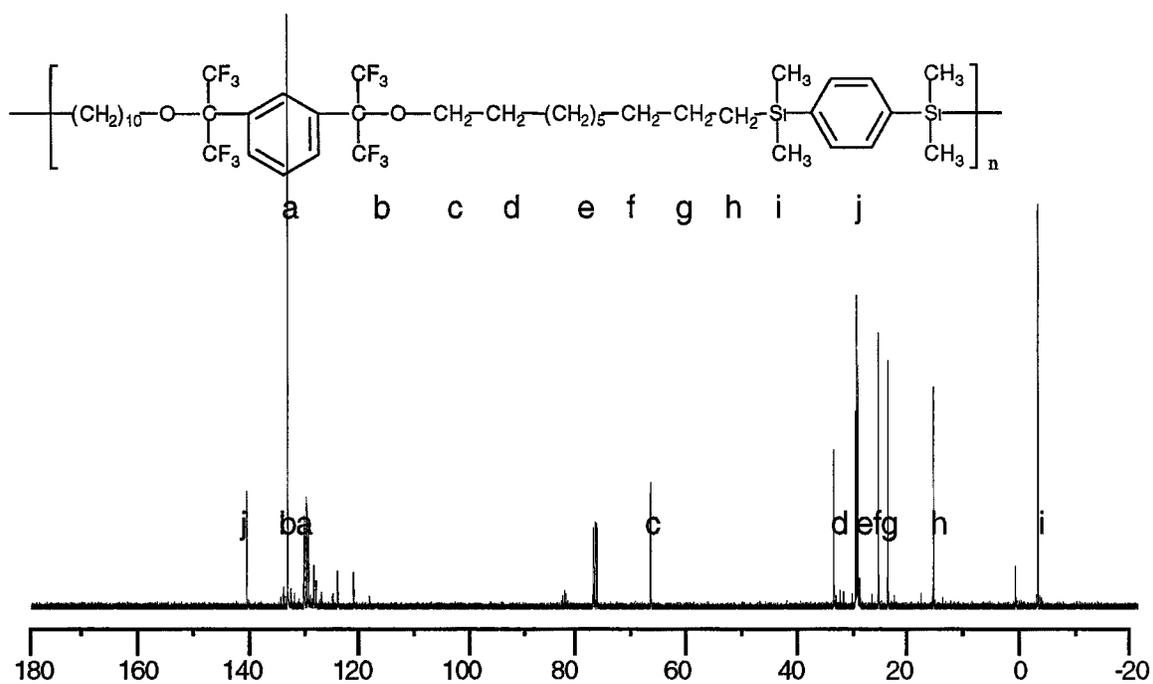
¹³C NMR #18. (Decenyl Model Hydrosilation in ScCO₂), (Compound XIV-s)



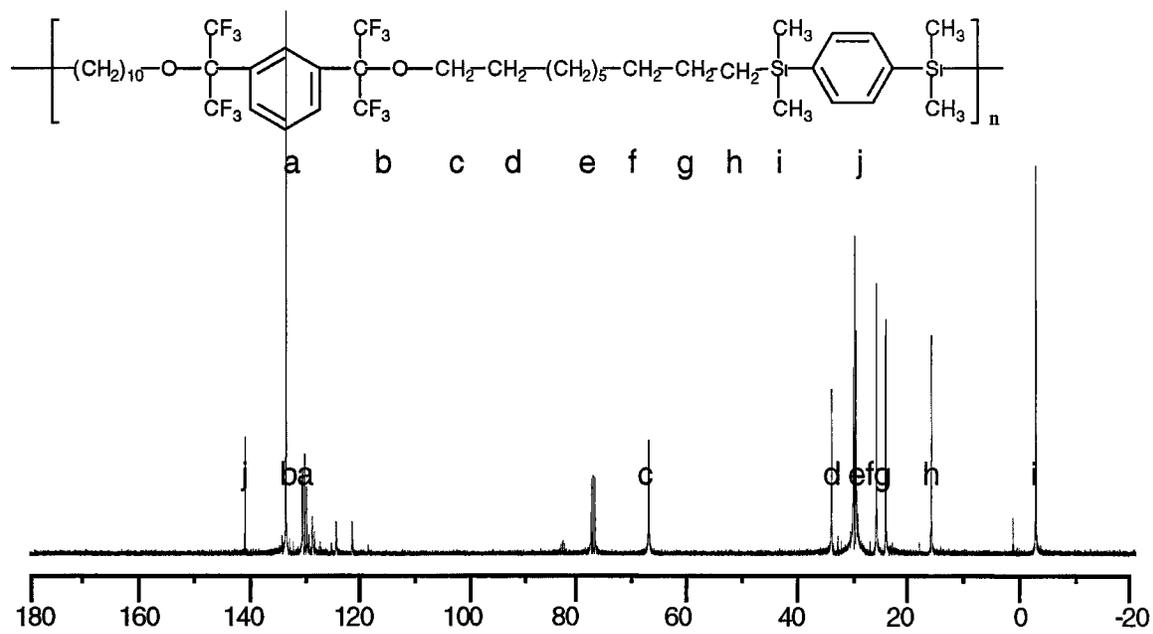
¹³C NMR #19. (Compound XXIId-b)



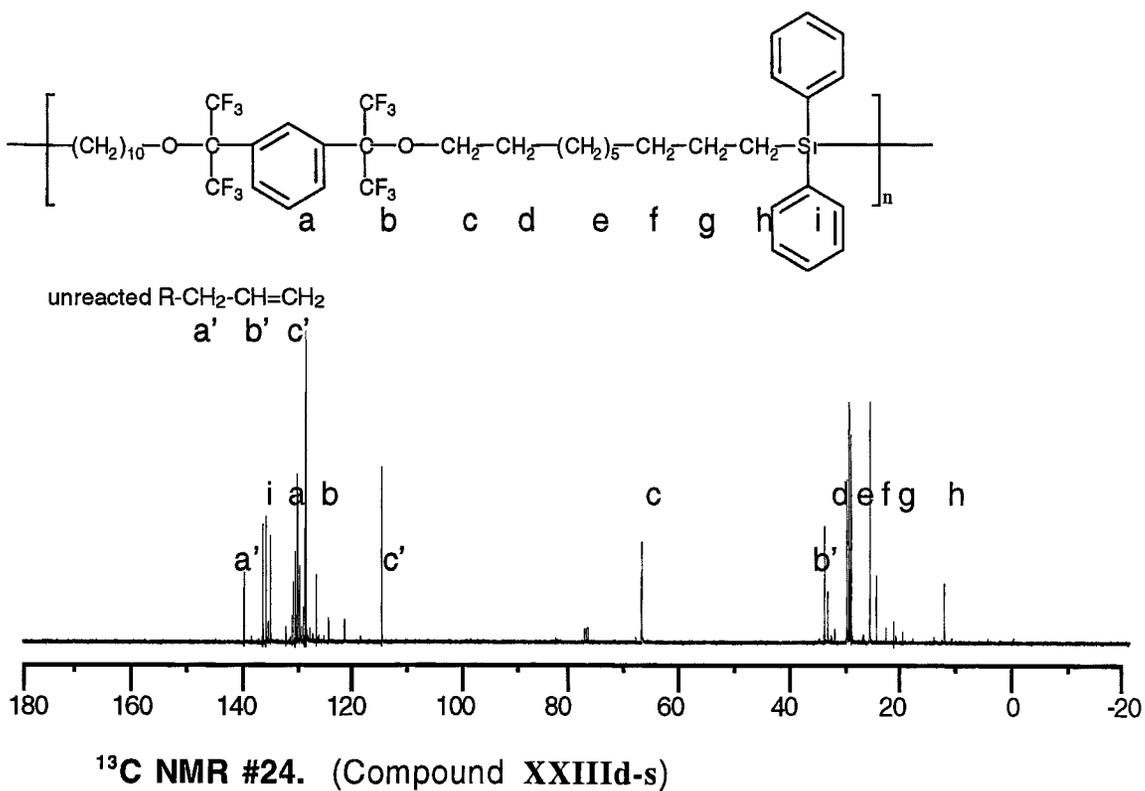
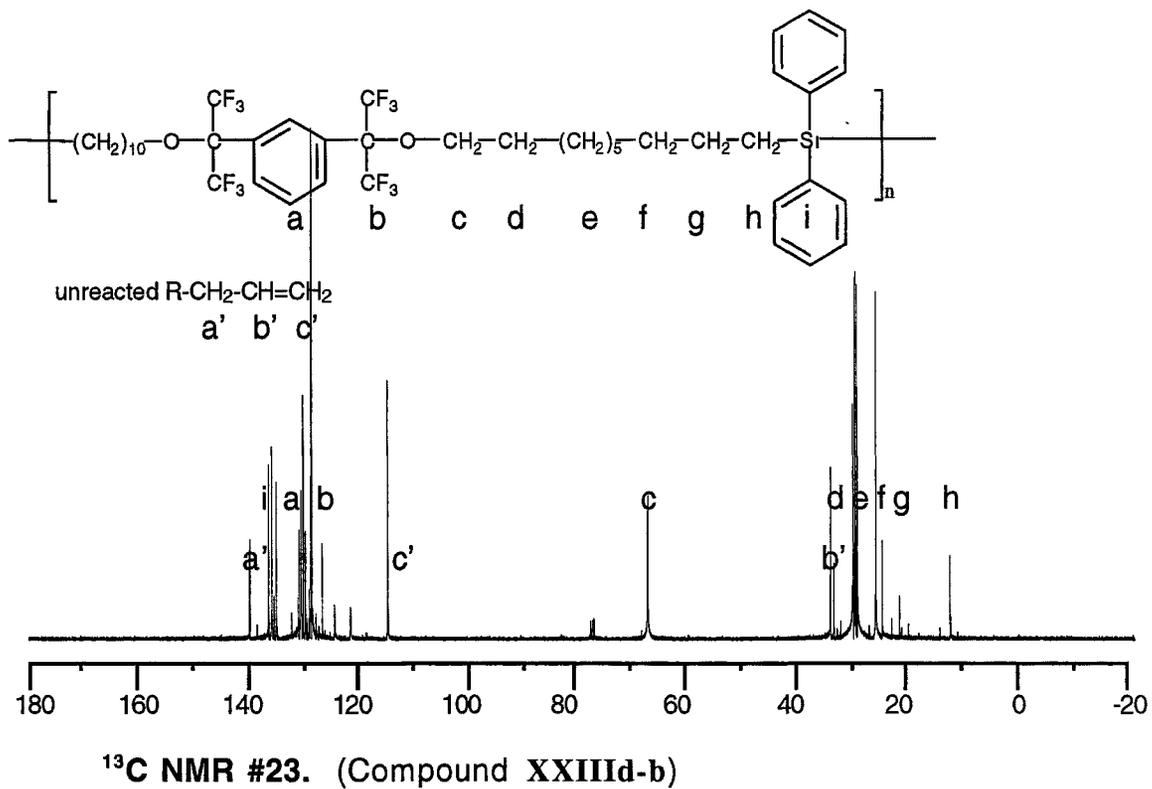
¹³C NMR #20. (Compound XXIId-s)

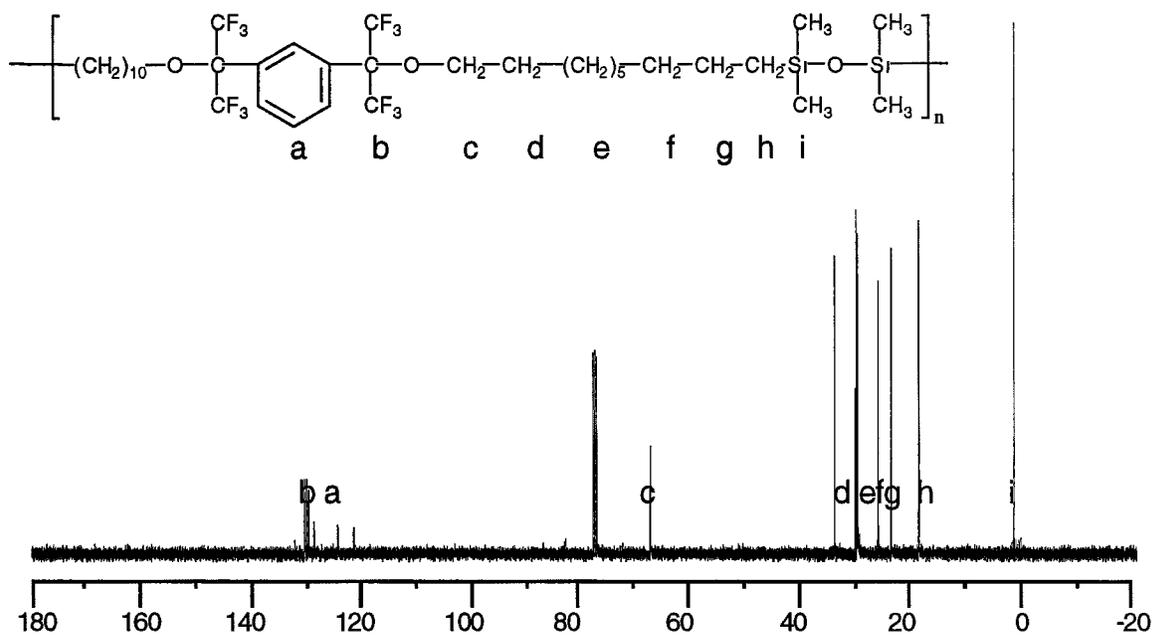
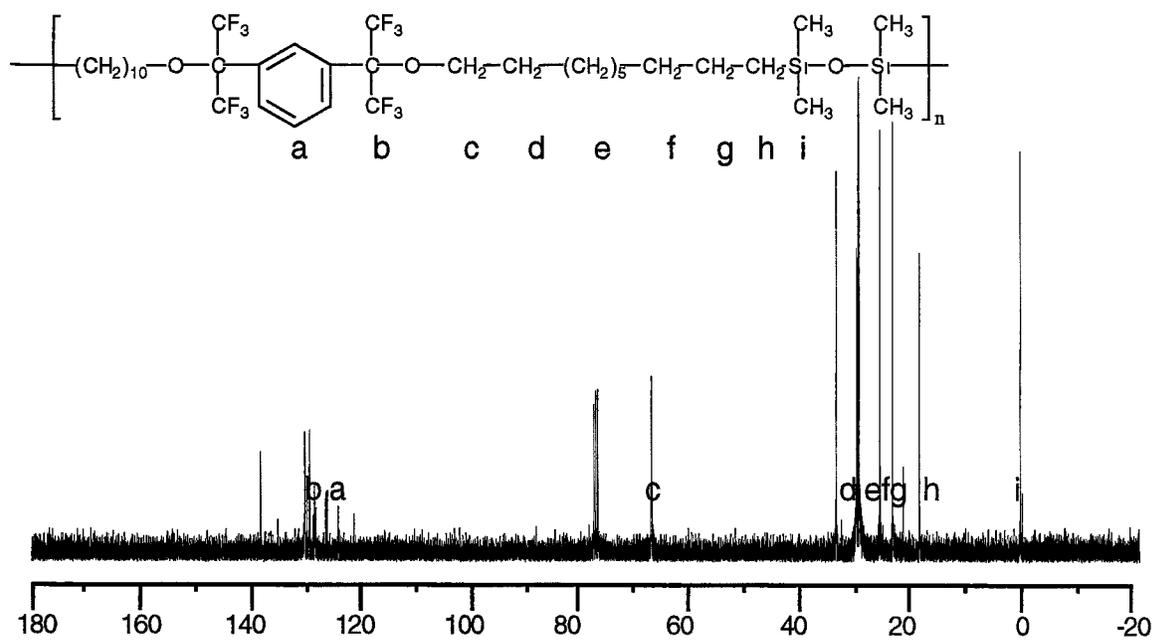


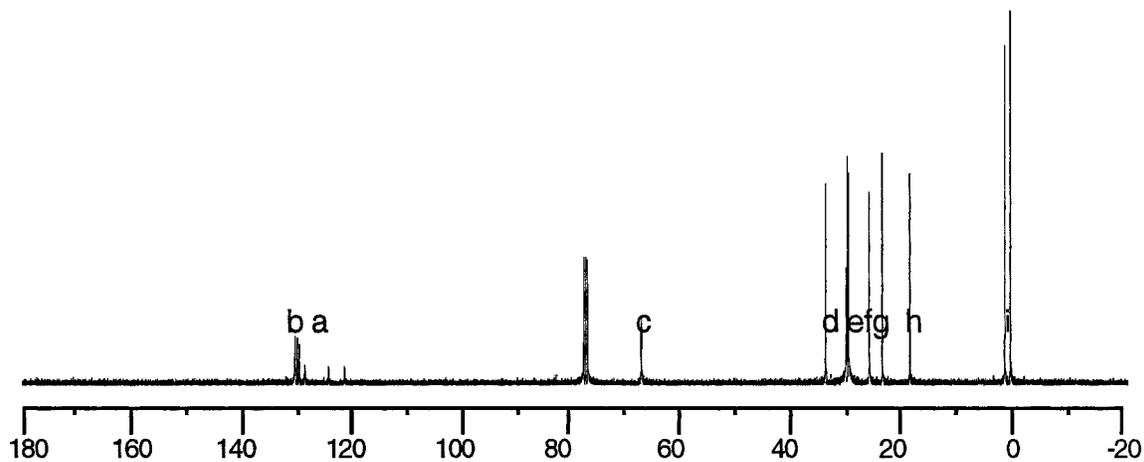
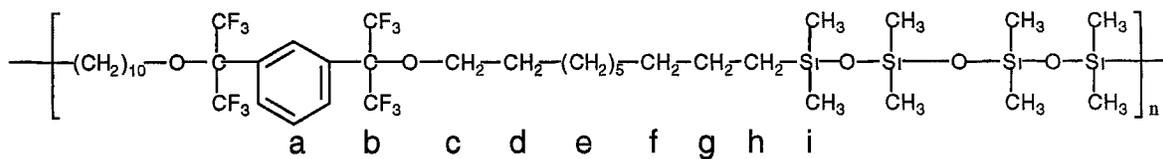
^{13}C NMR #21. (Compound XXII d-b)



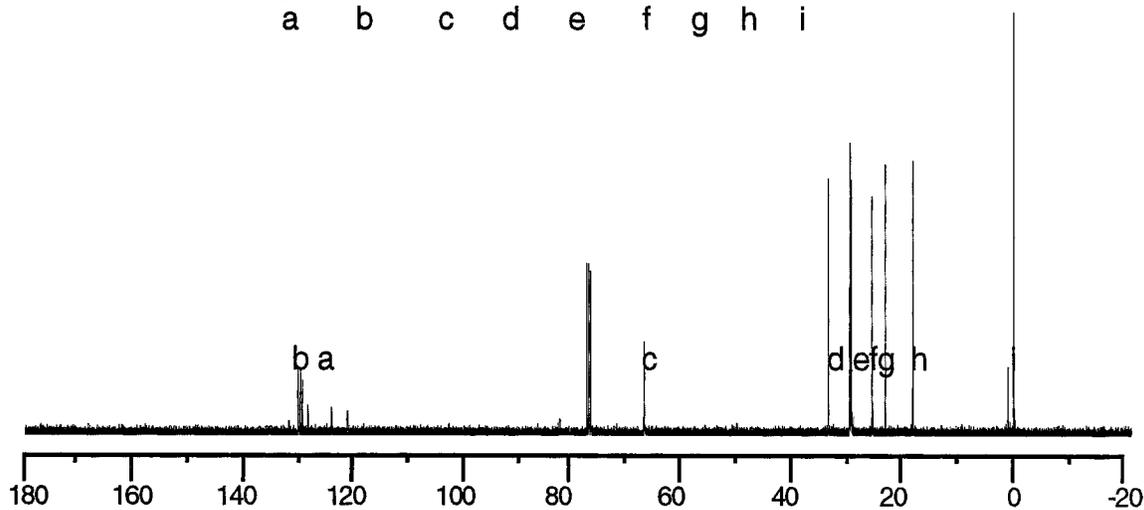
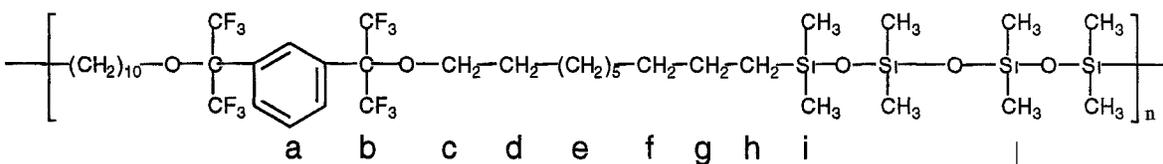
^{13}C NMR #22. (Compound XXII d-s)



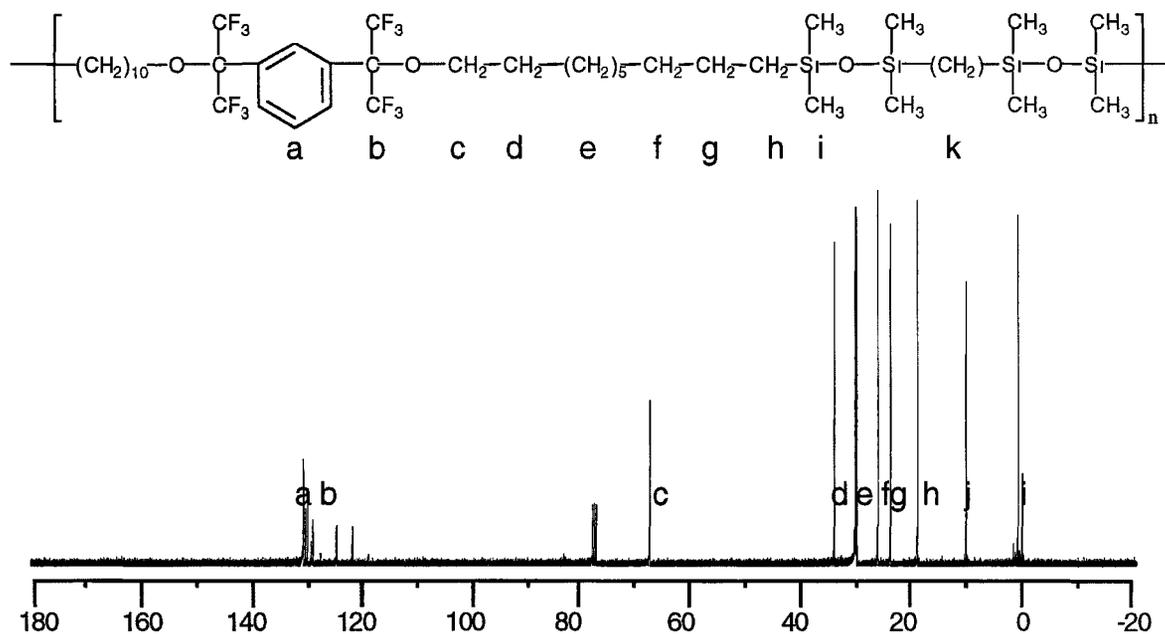
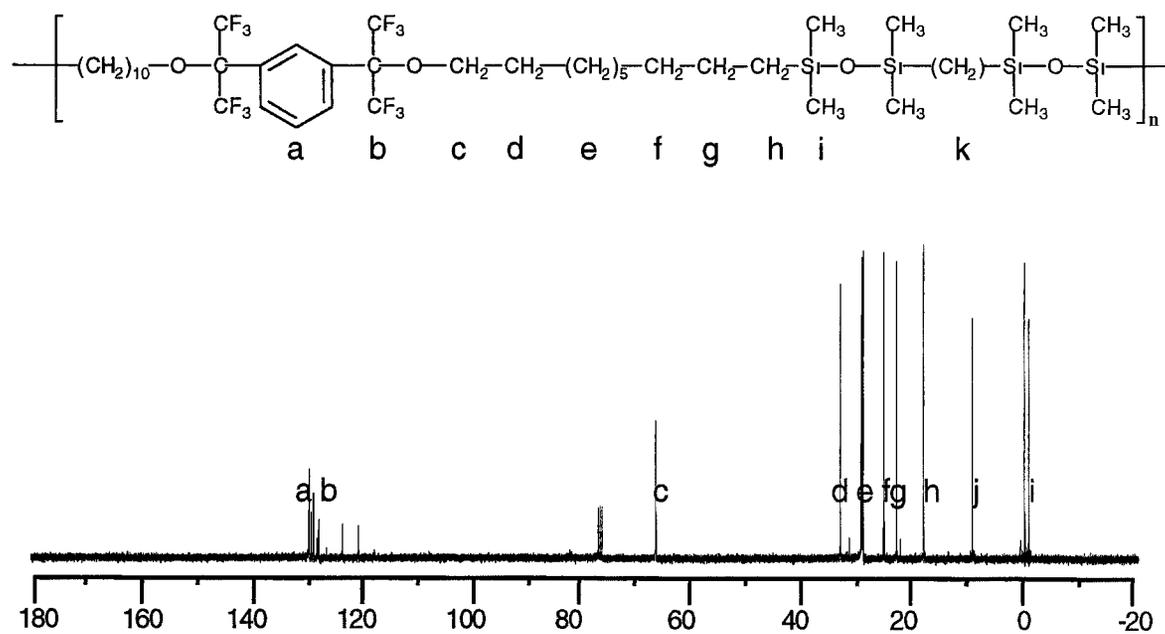
 **^{13}C NMR #25. (Compound XXIVd-b)** **^{13}C NMR #26. (Compound XXIVd-s)**



^{13}C NMR #27. (Compound XXVd-b)



^{13}C NMR #28. (Compound XXVd-s)

 ^{13}C NMR #29. (Compound XXVIId-b) ^{13}C NMR #30. (Compound XXVIId-s)

APPENDIX III

IR

Index for Appendix III

Compound	IR Number
1,1,4,4-Tetramethyldiethylene; (Compound XV)	1
1,4-Bis(dimethyl silyl)benzene; (Compound XVI)	2
Diphenylsilane; (Compound XVII)	3
1,1,3,3-Tetramethyldisiloxane; (Compound XVIII)	4
1,1,3,3,5,5,7,7-Octamethyltetrasiloxane; (Compound XIX)	5
1,2-Bis(tetramethyldisiloxaneyl)ethane; (Compound XX)	6
Dimethyl Phenyl Silane; (Compound XII)	7
Platinum divinyltetramethyldisiloxane complex in xylene (catalyst)	8
1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) benzene (Propenyl monomer), (Compound VII)	9
1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene (Decenyl monomer), (Compound XI)	10
Compound derived from reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) benzene and dimethyl phenyl silane; (Propenyl Model Hydrosilation in Benzene), (Compound XIII-b)	11

Index for Appendix III

(continued)

Compound	IR Number
Compound derived from reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) benzene and dimethyl phenyl silane; (Propenyl Model Hydrosilation in ScCO ₂), (Compound XIII-s)	12
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) benzene and 1,1,4,4-Tetramethyldisilethylene; in Benzene, (Compound XXIp-b)	13
in ScCO ₂ , (Compound XXIp-s)	14
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) benzene and 1,4-Bis(dimethylsilyl)benzene; in Benzene, (Compound XXIIP-b)	15
in ScCO ₂ , (Compound XXIIP-s)	16
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) benzene and Diphenyl silane; in Benzene, (Compound XXIIIp-b)	17
in ScCO ₂ , (Compound XXIIIp-s)	18
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) benzene and 1,1,3,3-Tetramethyldisiloxane;	

Index for Appendix III

(continued)

Compound	IR Number
in Benzene, (Compound XXIVp-b)	19
in ScCO ₂ , (Compound XXIVp-s)	20
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) benzene and 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane;	
in Benzene, (Compound XXVp-b)	21
in ScCO ₂ , (Compound XXVp-s)	22
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) benzene and 1-2-Bis(tetramethyldisiloxaneyl)ethane;	
in Benzene, (Compound XXVIp-b)	23
in ScCO ₂ , (Compound XXVIp-s)	24
Compound derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and Dimethyl Phenyl Silane;	
(Decenyl Model Hydrosilation in Benzene), (Compound XIV-b)	25
Compound derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and Dimethyl Phenyl Silane;	
(Decenyl Model Hydrosilation in ScCO ₂), (Compound XIV-s)	26

Index for Appendix III

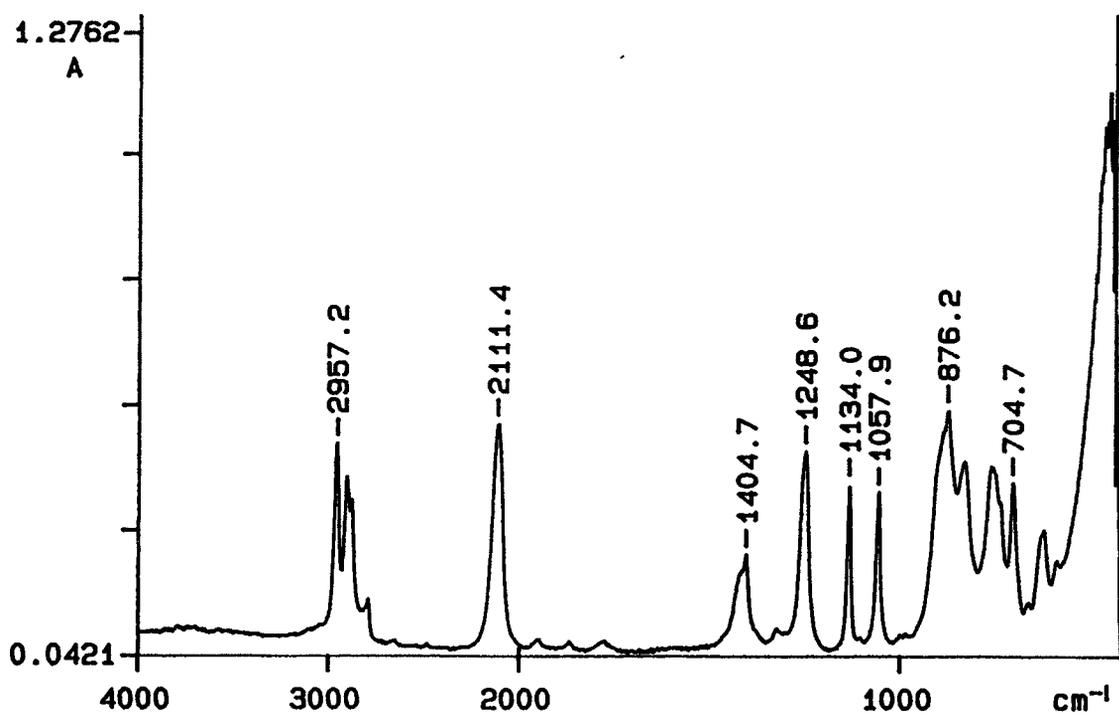
(continued)

Compound	IR Number
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,4,4-Tetramethyldisilethylene; in Benzene, (Compound XXId-b)	27
in ScCO ₂ , (Compound XXVIId-s)	28
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,4-Bis(dimethylsilyl)benzene; in Benzene, (Compound XXIIId-b)	29
in ScCO ₂ , (Compound XXVIIId-s)	30
"Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and Diphenyl Silane; in Benzene, (Compound XXIIIId-b)	31
in ScCO ₂ , (Compound XXIIIId-s)	32
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,3,3-Tetramethyldisiloxane; in Benzene, (Compound XXIVd-b)	33
in ScCO ₂ , (Compound XXIVd-s)	34
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene	

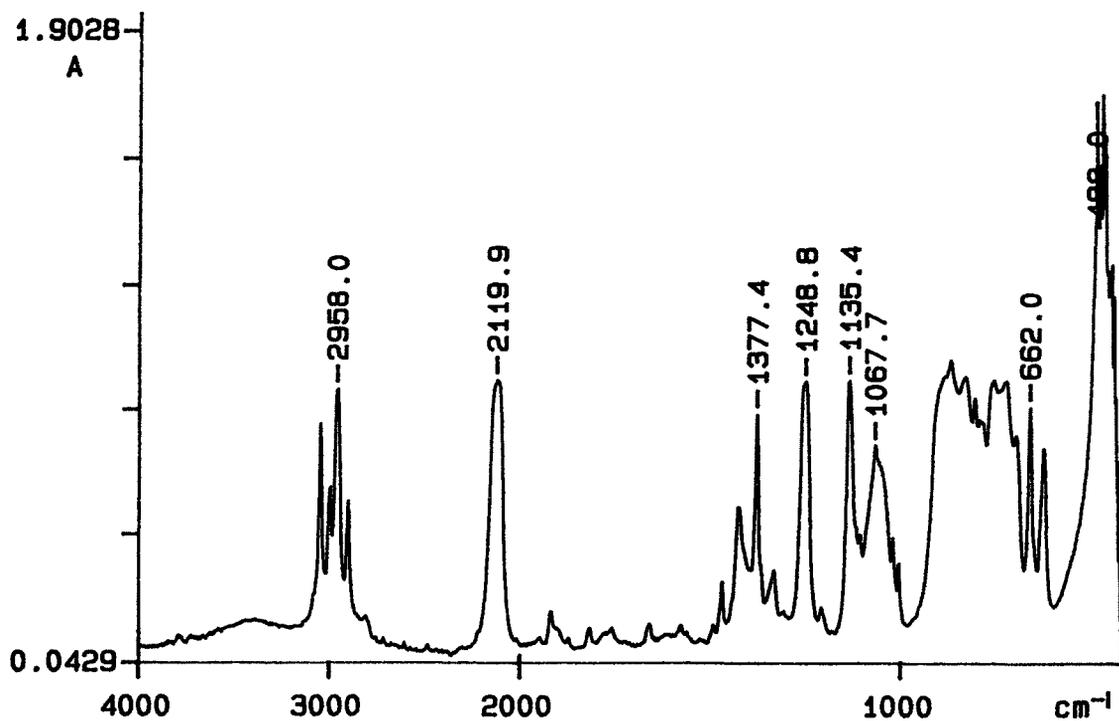
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(continued)

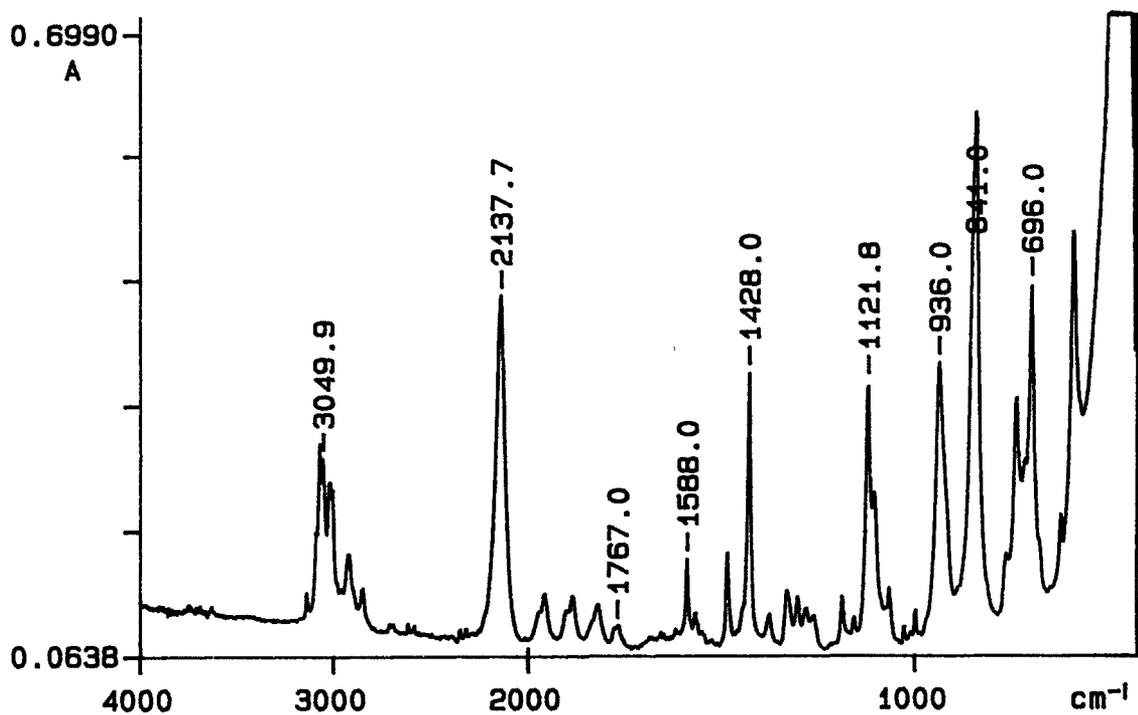
Compound	IR Number
and 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane;	
in Benzene, (Compound XXVd-b)	35
in ScCO ₂ , (Compound XXVd-s)	36
 Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1-2-Bis(tetramethyldisiloxaneyl)ethane;	
in Benzene, (Compound XXVIId-b)	37
in ScCO ₂ , (Compound XXVIId-s)	38



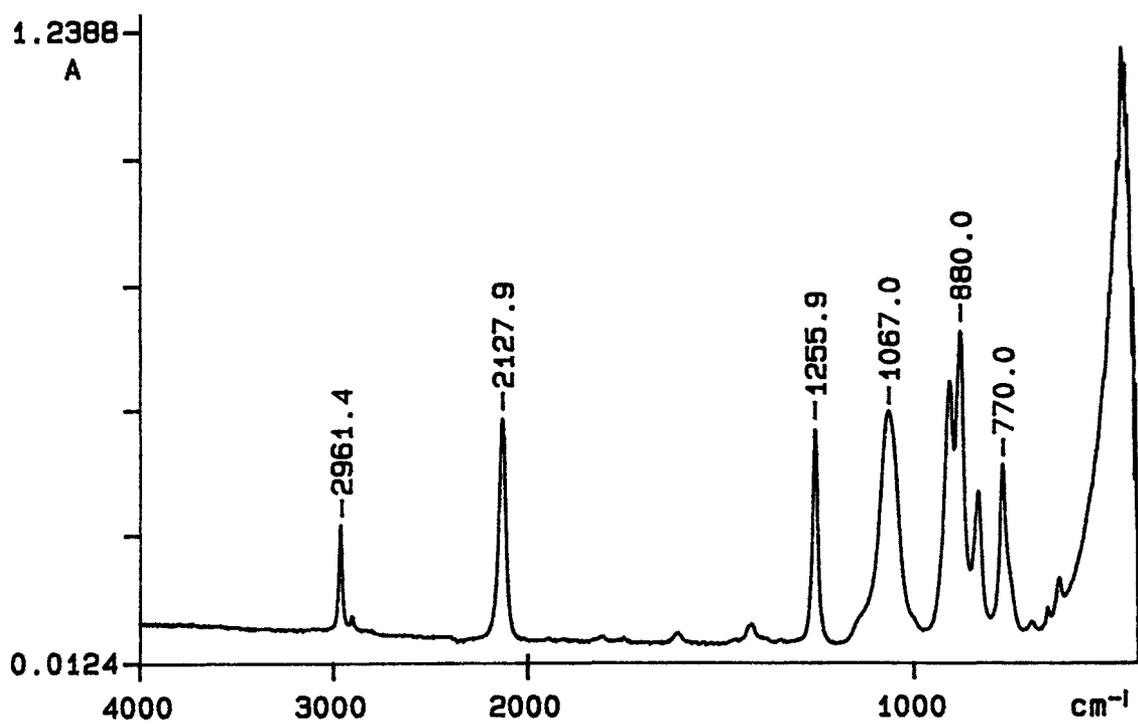
IR #1. 1,1,4,4-Tetramethyldiethylene, (Compound XV)



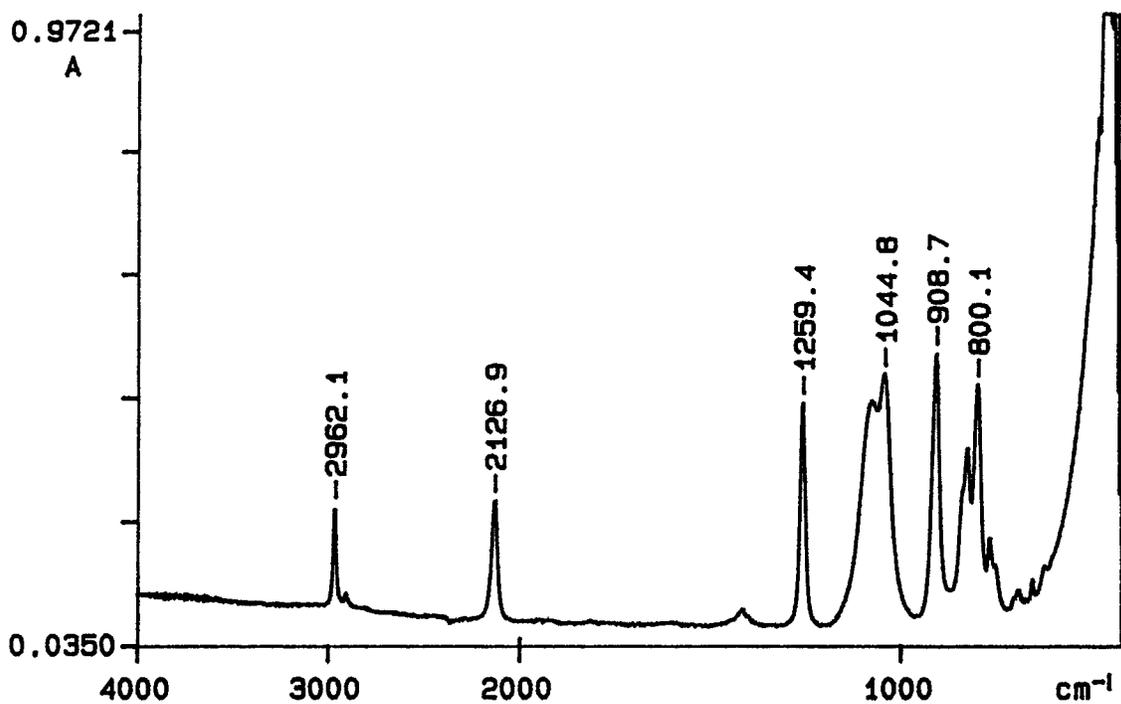
IR #2. 1,4 Bis(dimethylsilyl)benzene, (Compound XVI)



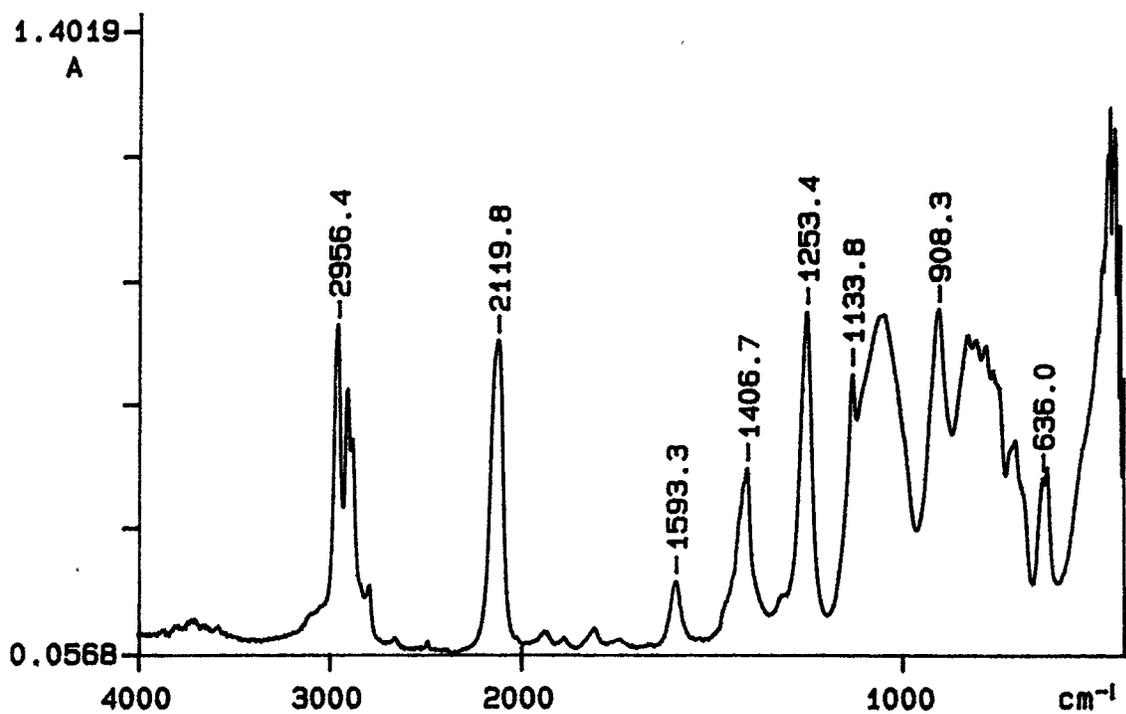
IR #3. Diphenylsilane, (Compound XVII)



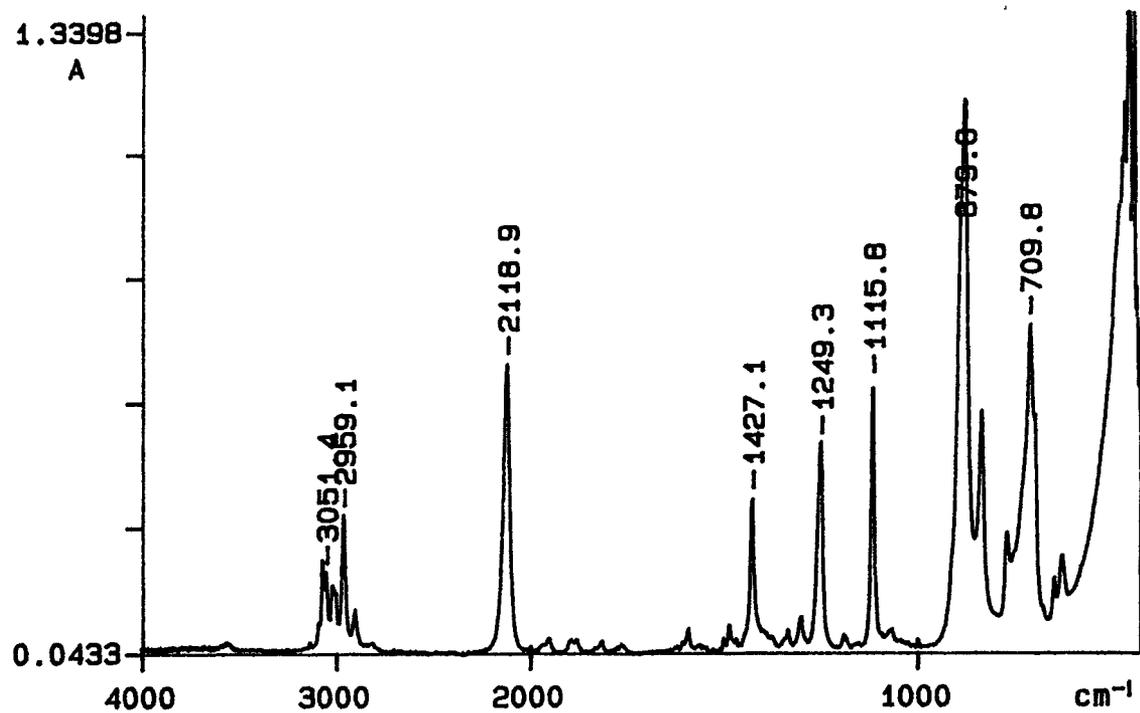
IR #4. 1,1,3,3-Tetramethyldisiloxane, (Compound XVIII)



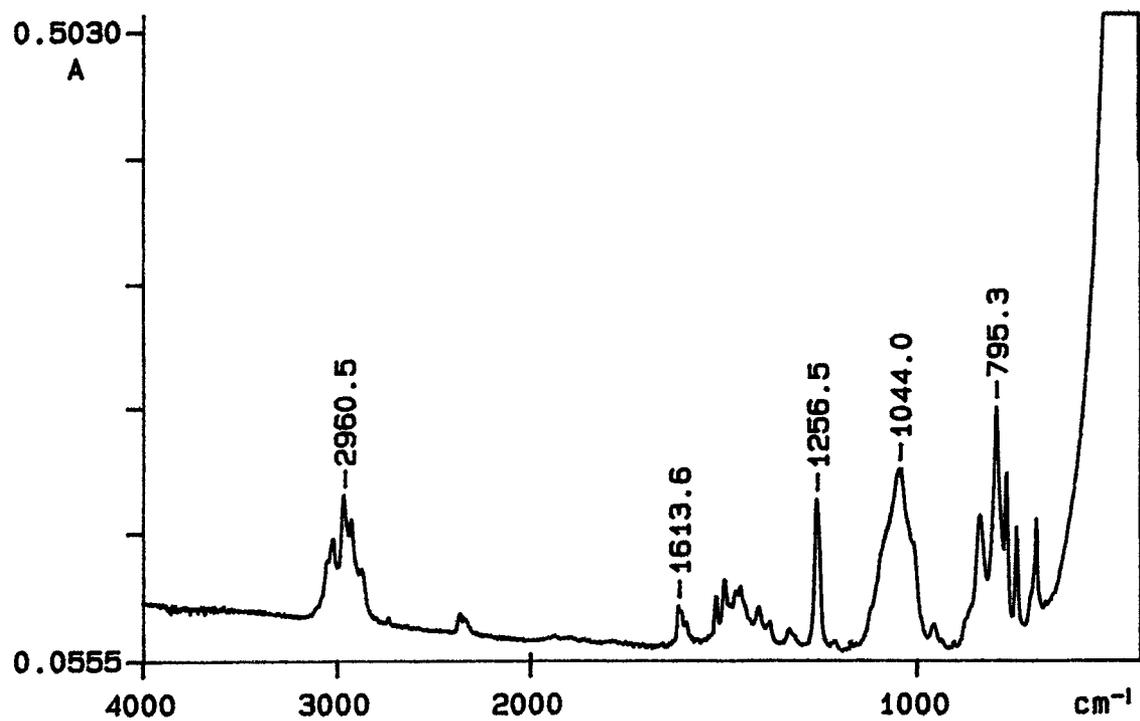
IR #5. 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane, (Compound XIX)

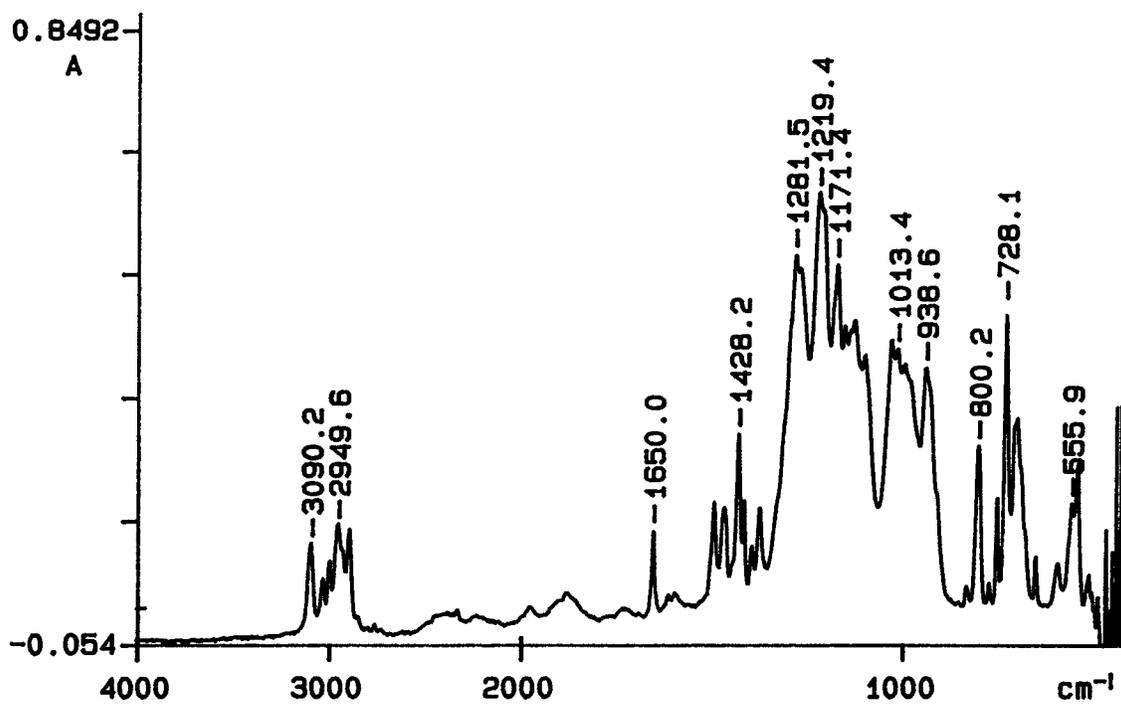


IR #6. 1-2-Bis(tetramethyldisiloxaneyl)ethane, (Compound XX)

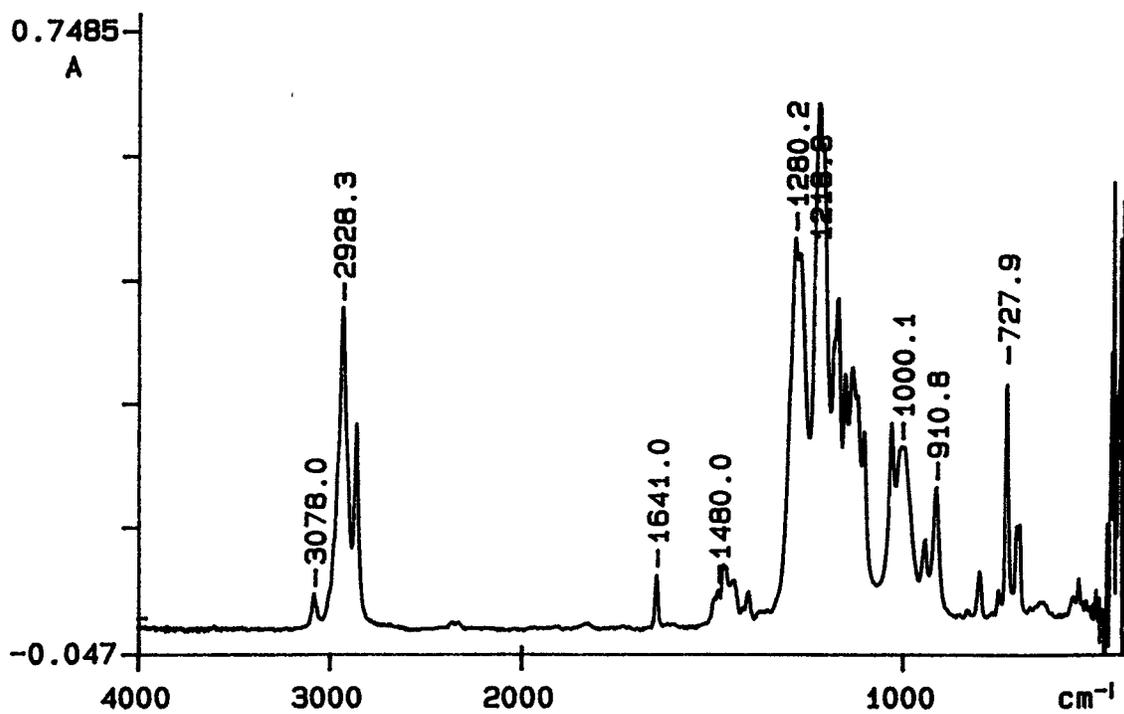


IR #7. Phenyltrimethylsilane, (Compound XII)

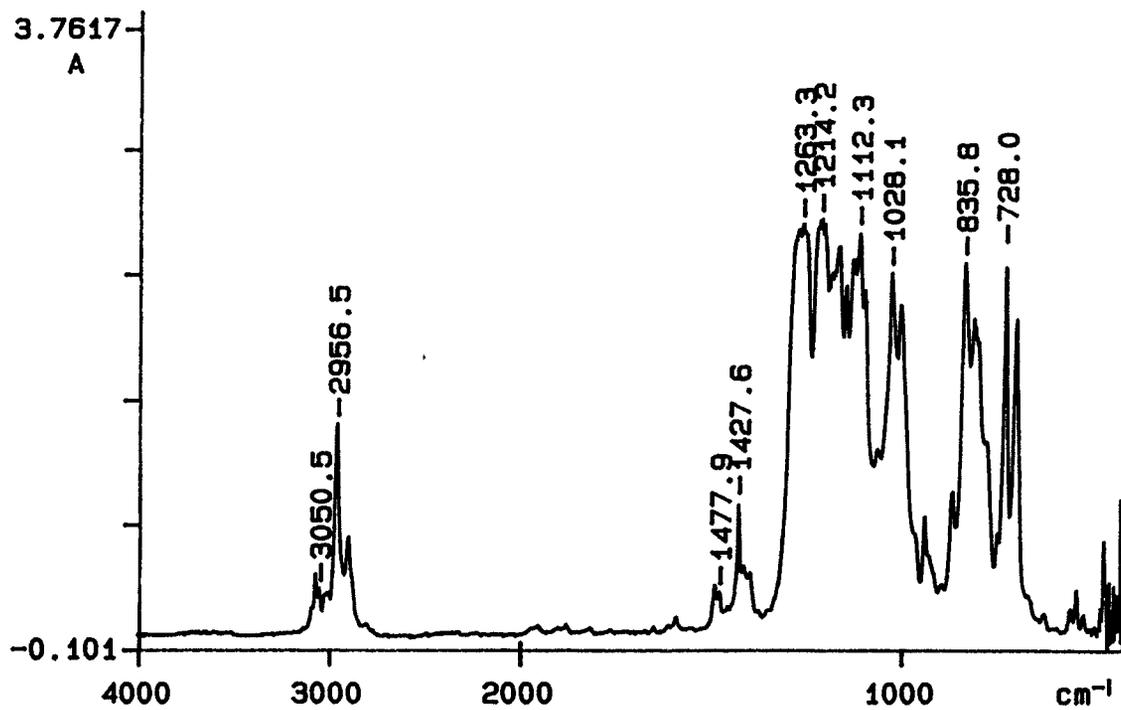
IR #8. Platinum Divinyltetramethyldisiloxane Complex in Xylene,
(3 to 3.5% Pt) (Catalyst)



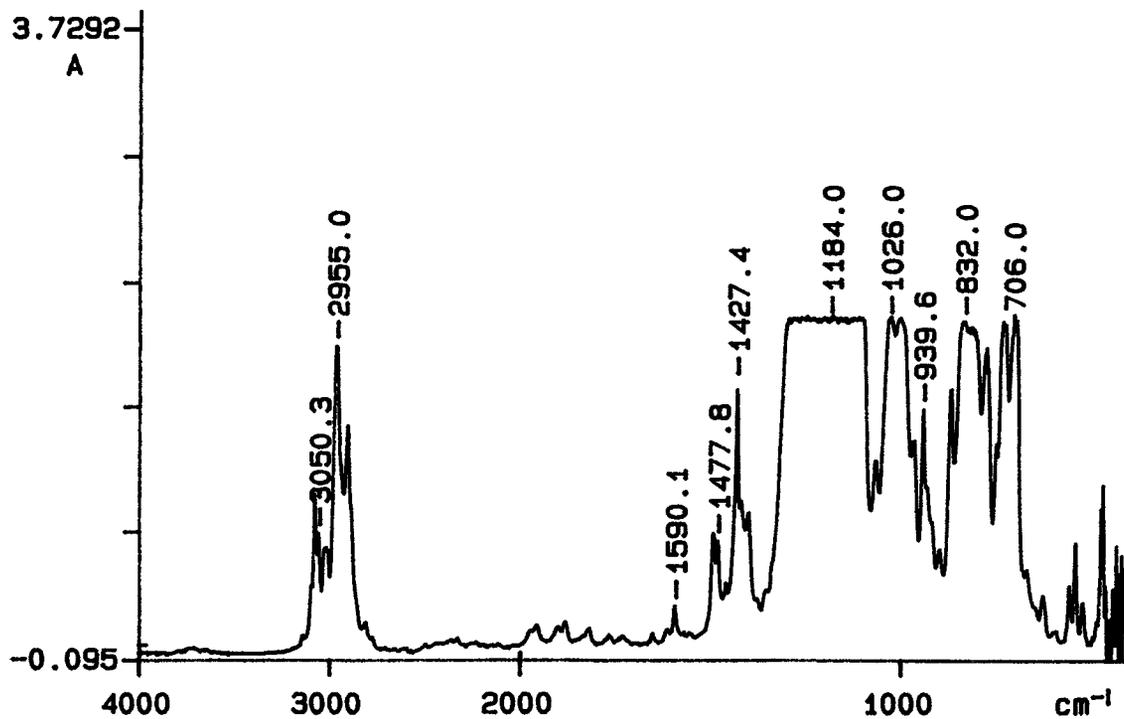
IR #9. 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene
(Propenyl Monomer), (Compound VII)



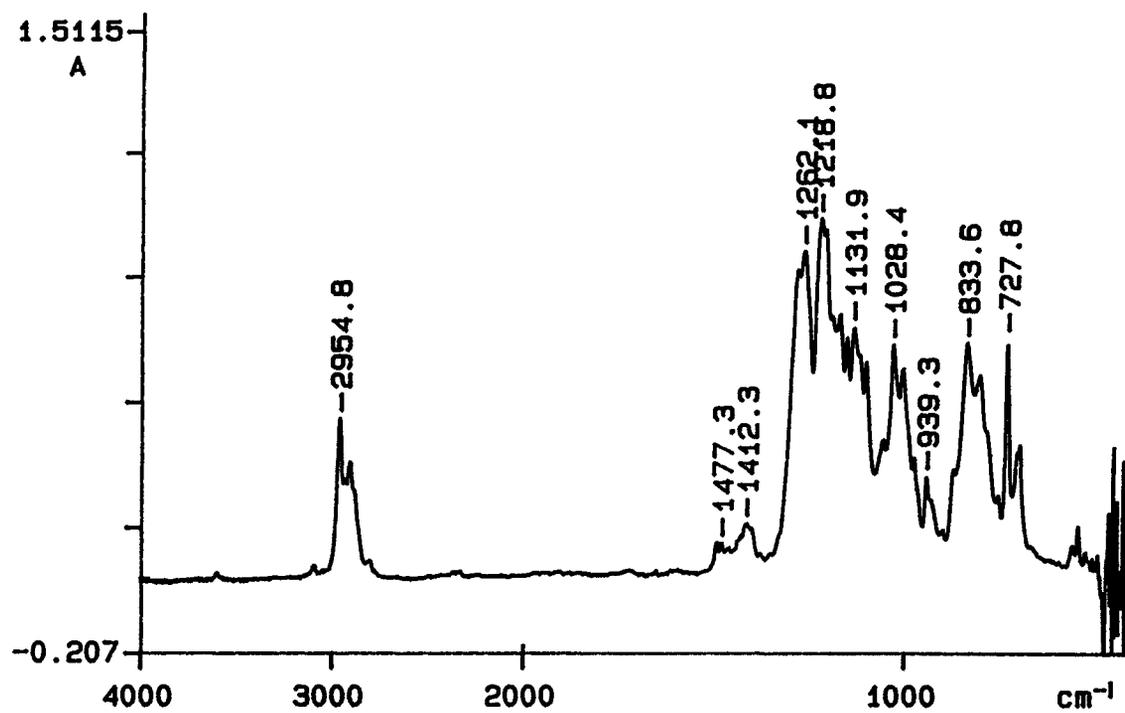
IR #10. 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene
(Decenyl Monomer), (Compound XI)



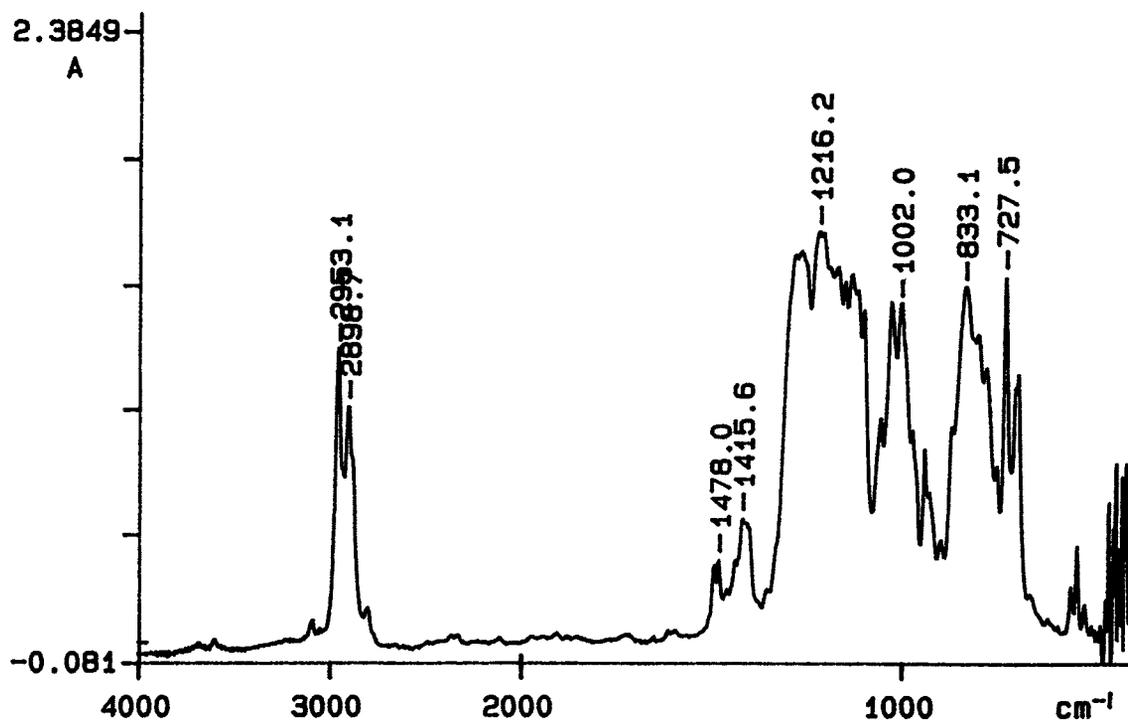
IR #11. (Propenyl Model Hydrosilation in Benzene),
(Compound XIIIb)



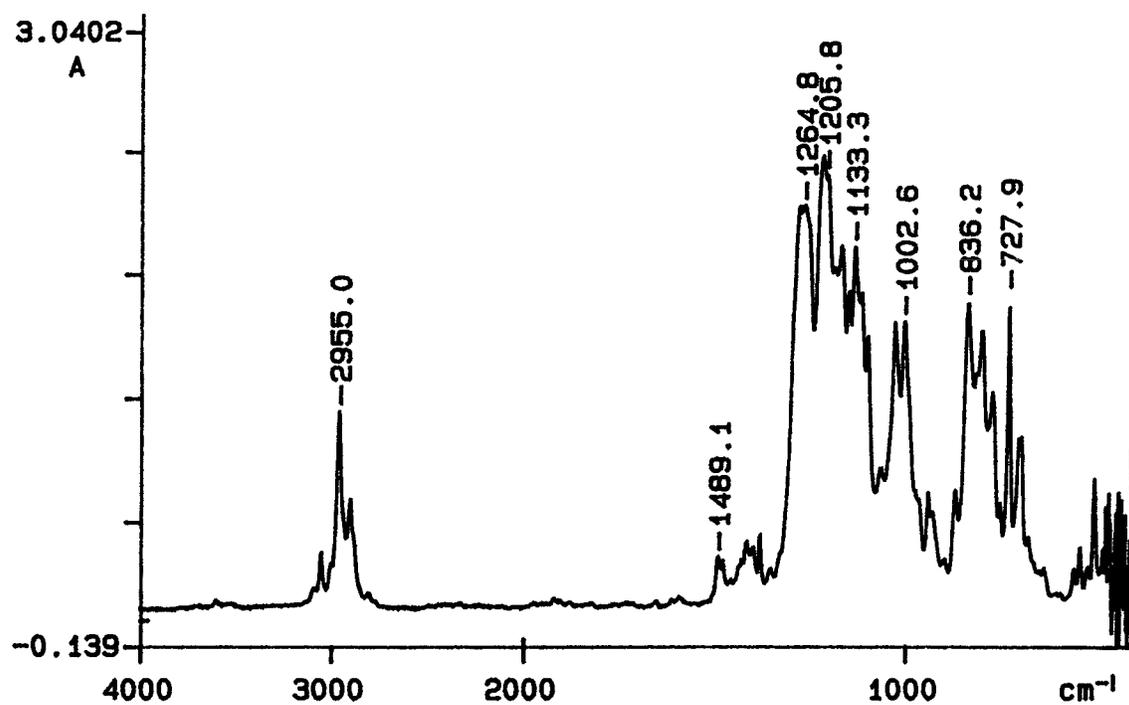
IR #12. (Propenyl Model Hydrosilation in ScCO₂), (Compound XIIIc)



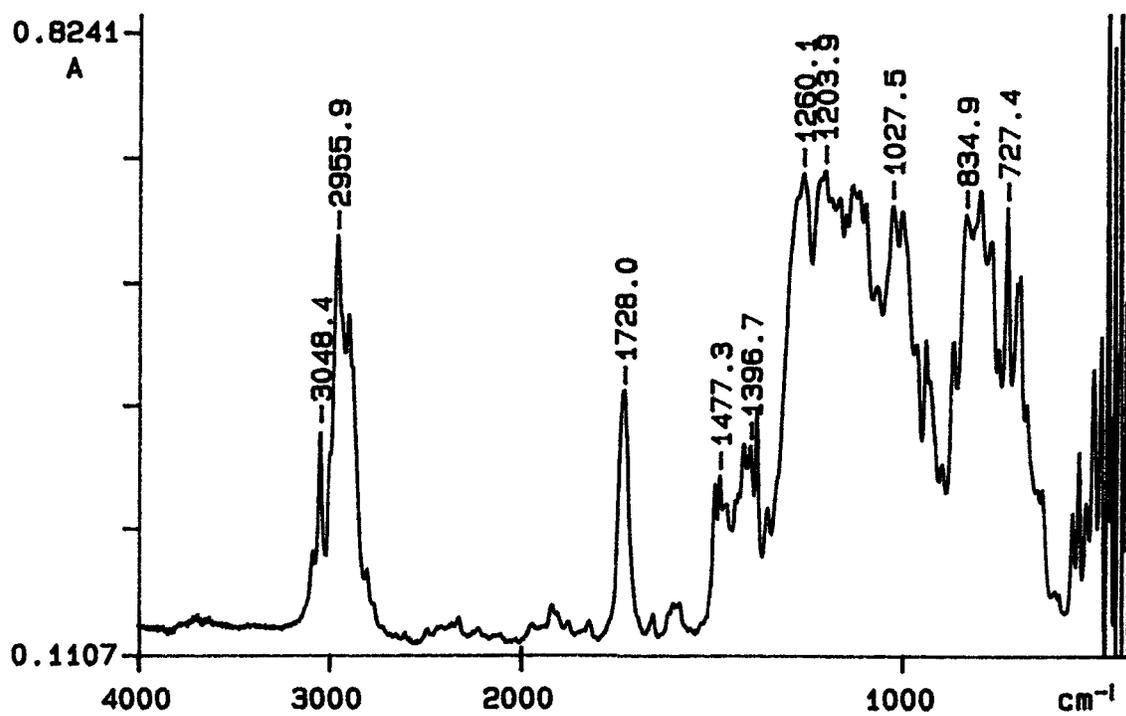
IR #13. (Compound XXI p-b)



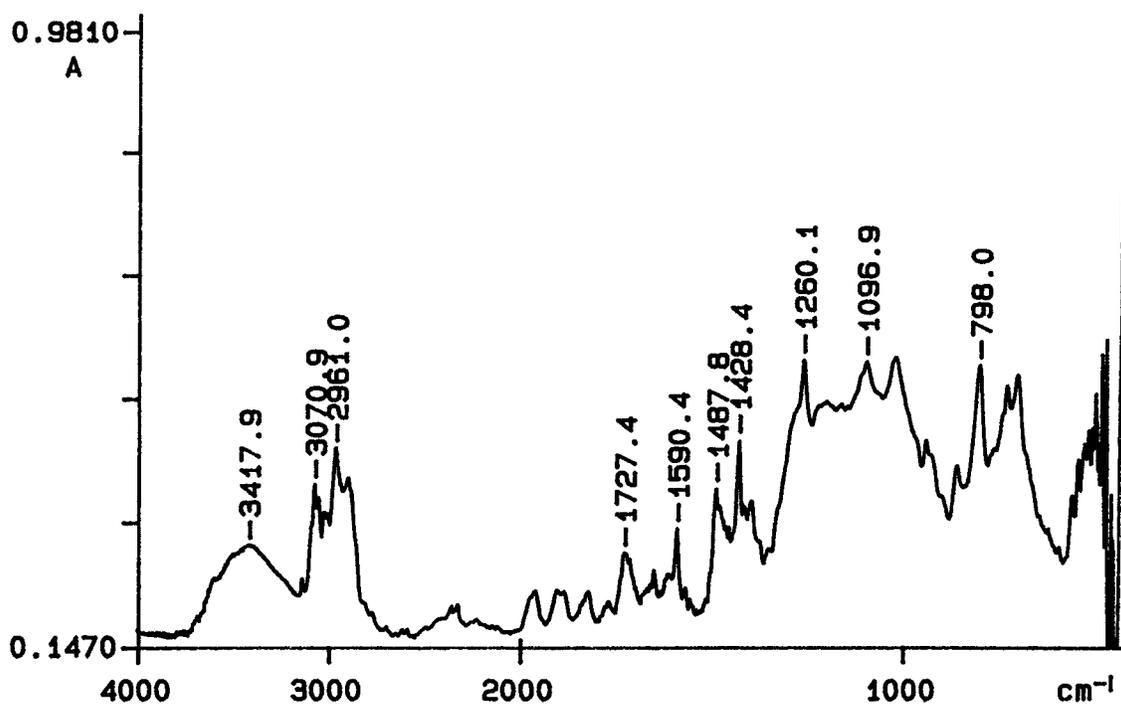
IR #14. (Compound XXI p-s)



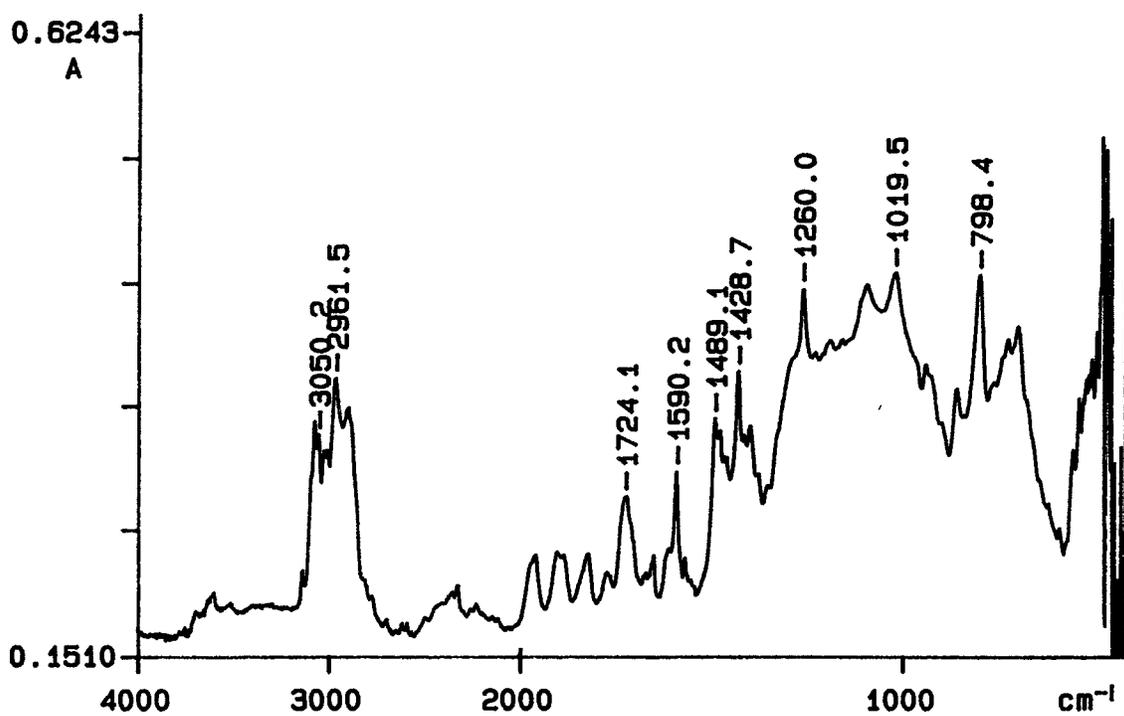
IR #15. (Compound XXIIp-b)



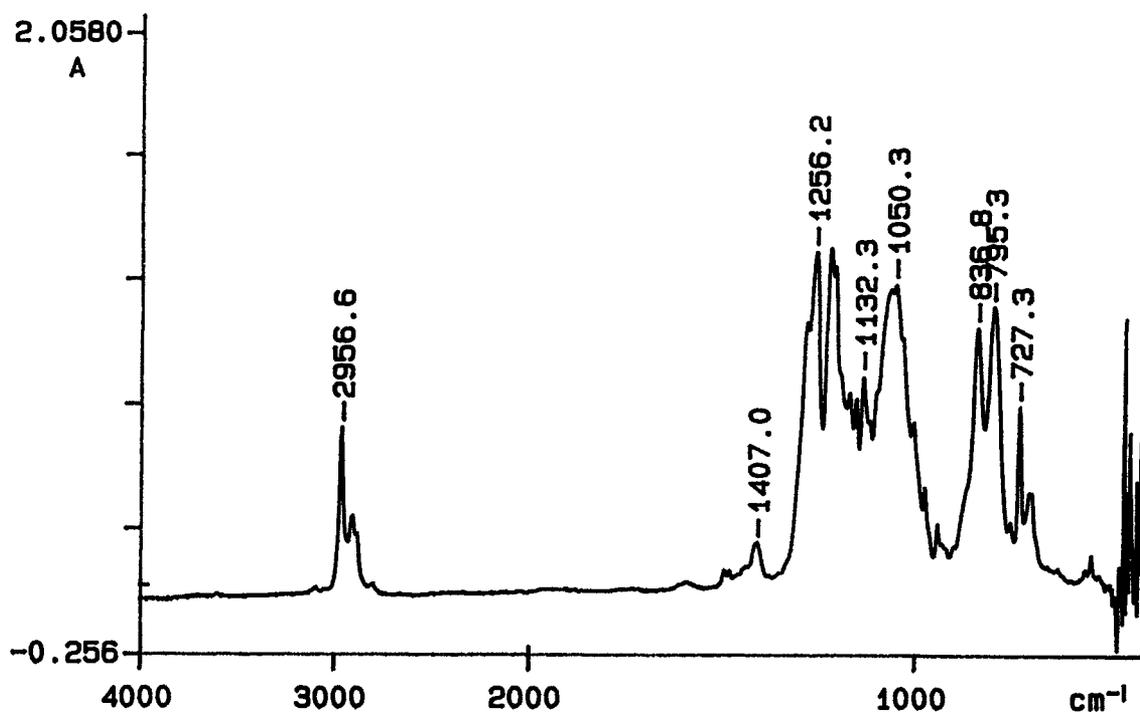
IR #16. (Compound XXIIp-s)



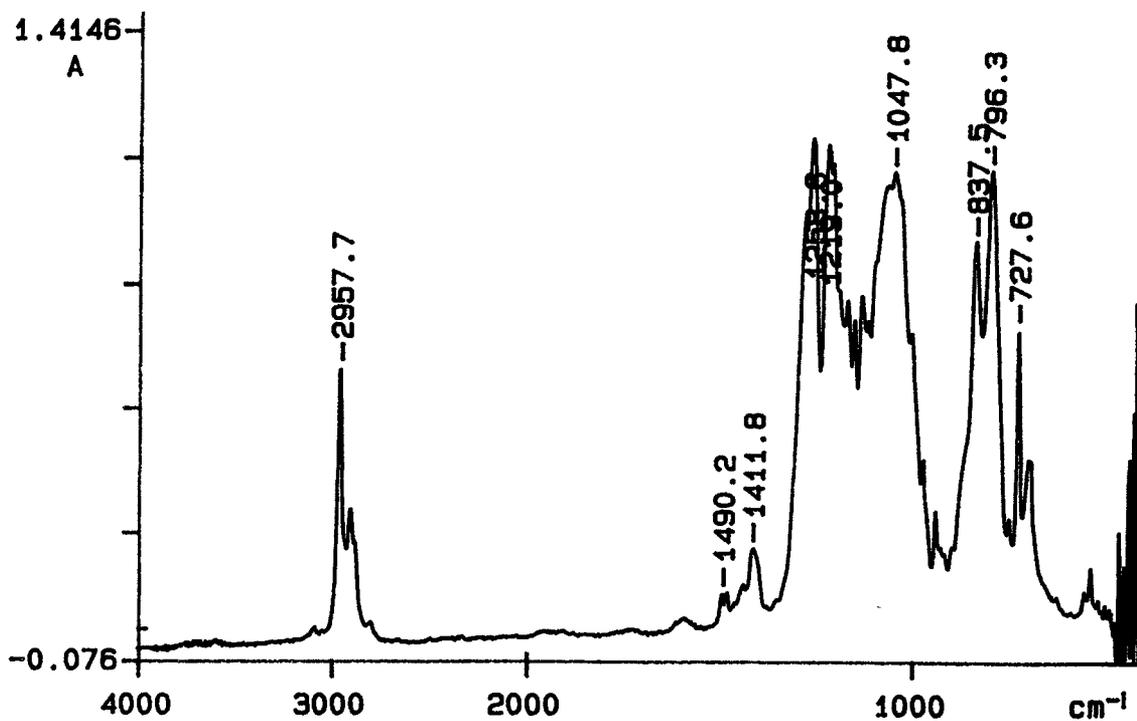
IR #17. (Compound XXIIIp-b)



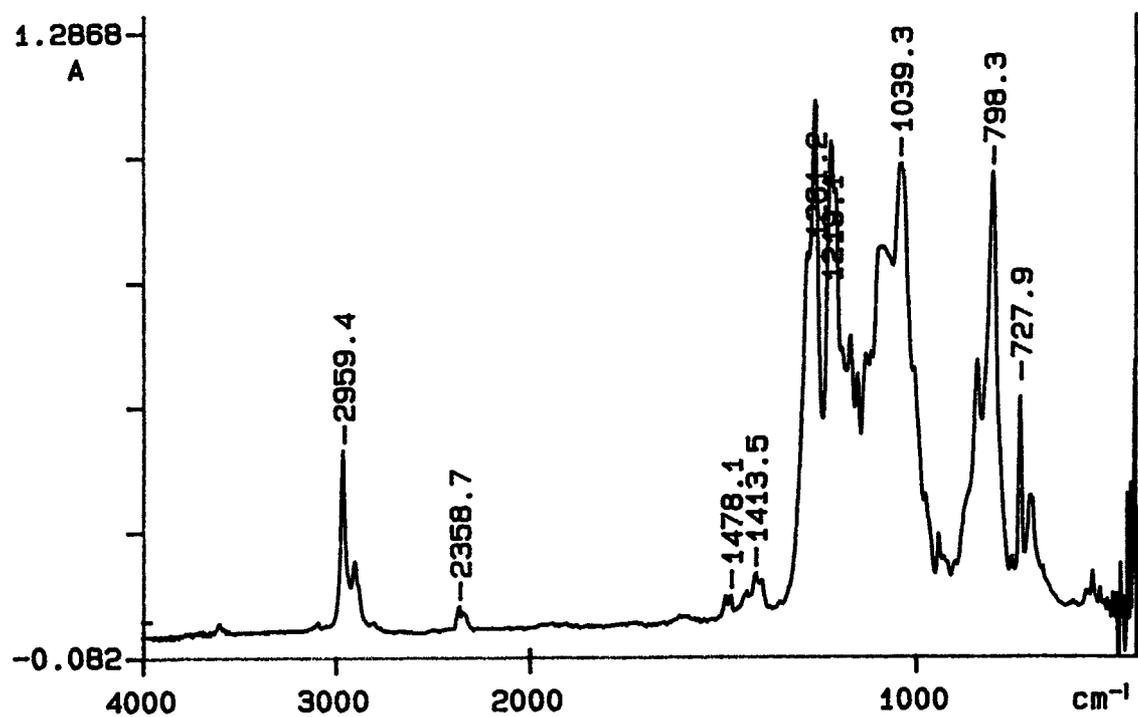
IR #18. (Compound XXIIIp-s)



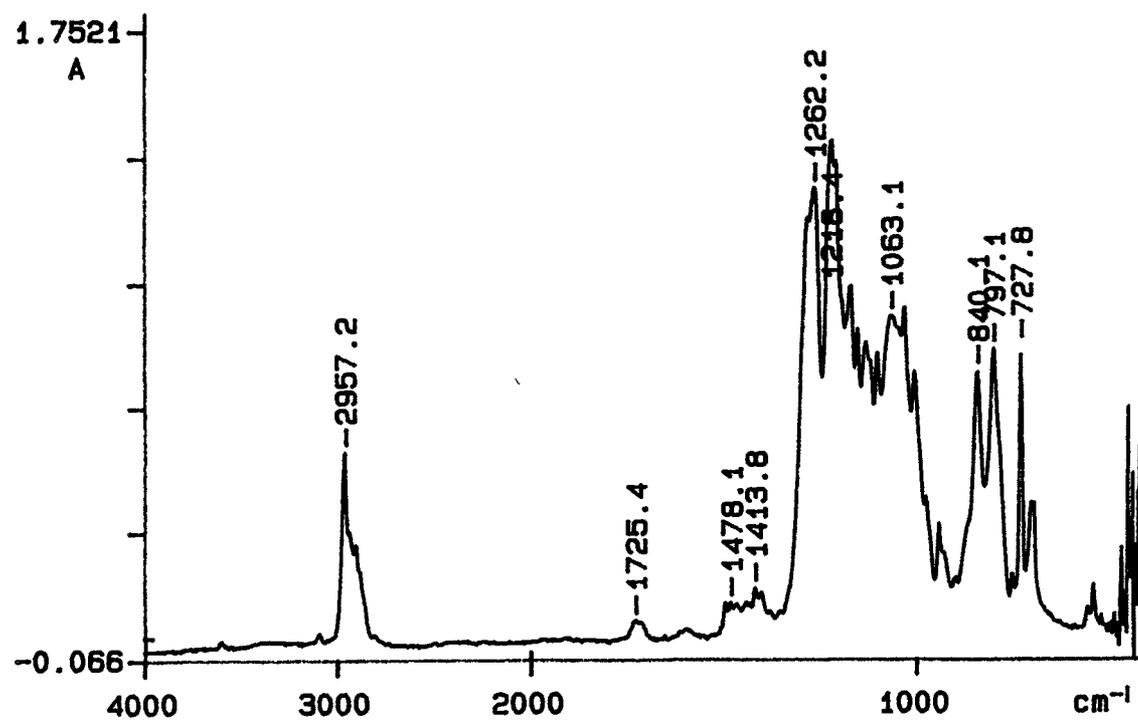
IR #19. (Compound XXIVp-b)



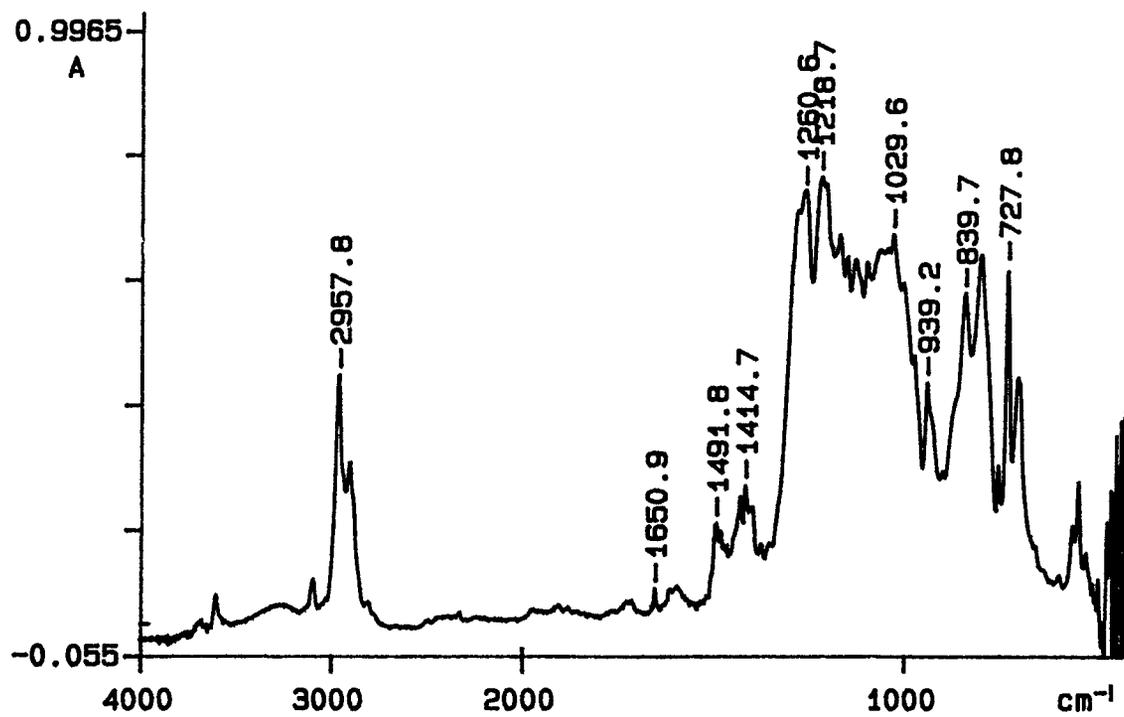
IR #20. (Compound XXIVp-s)



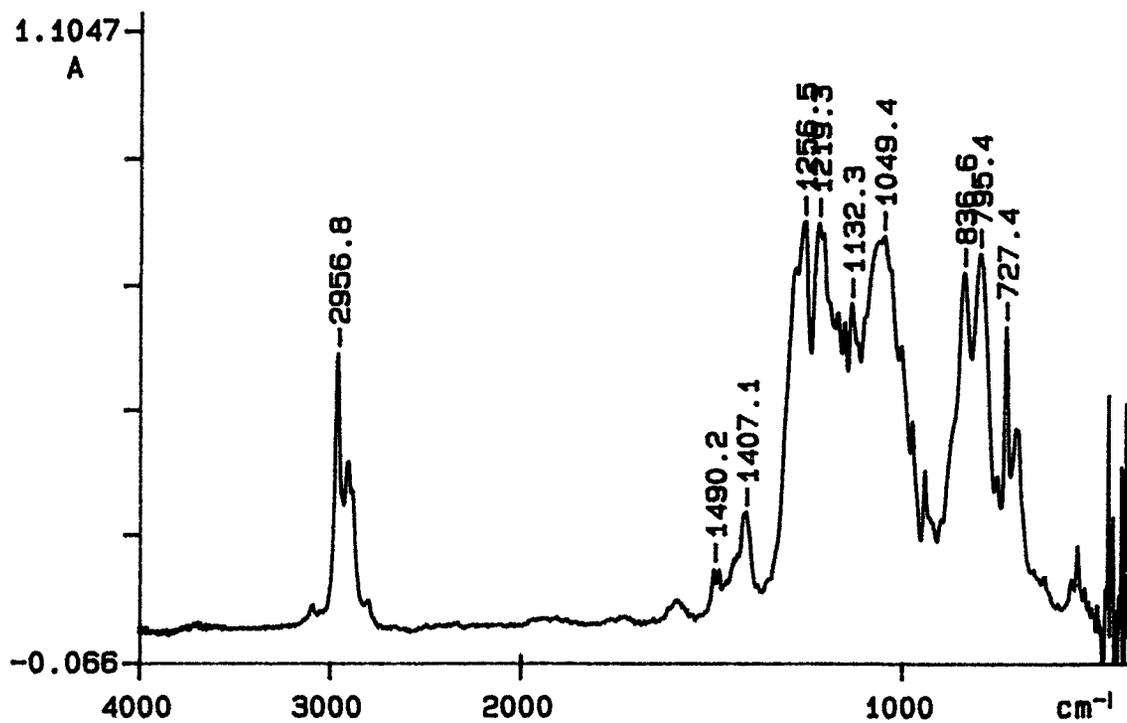
IR #21. (Compound XXVp-b)



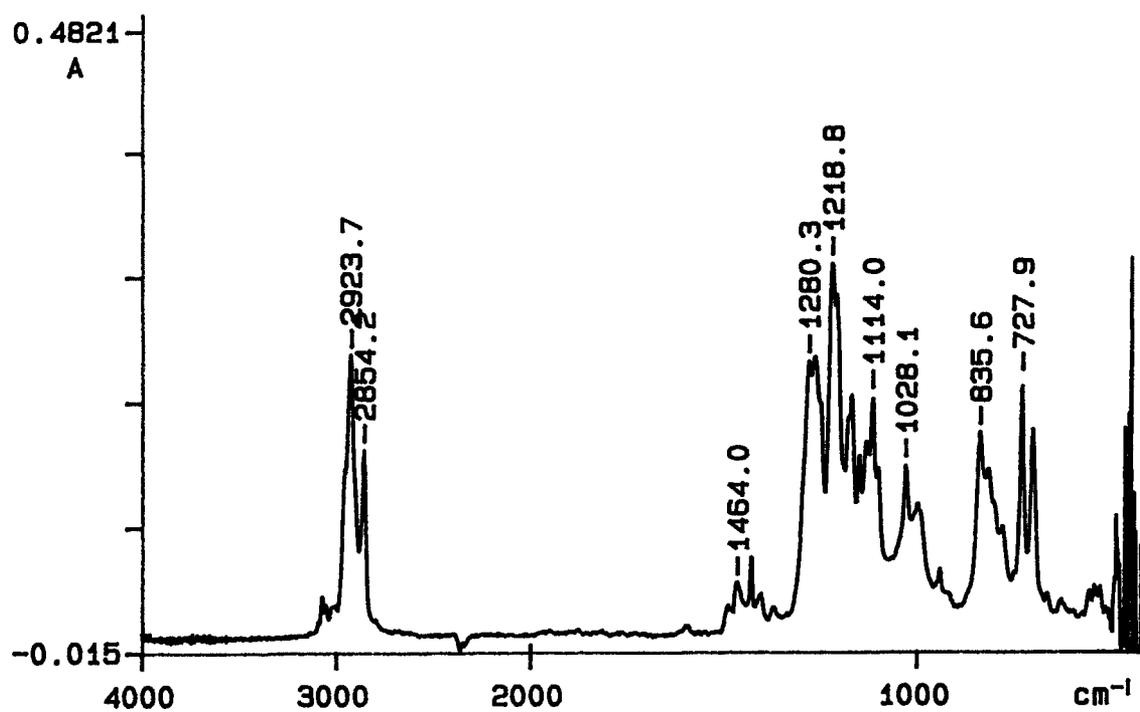
IR #22. (Compound XXVp-s)



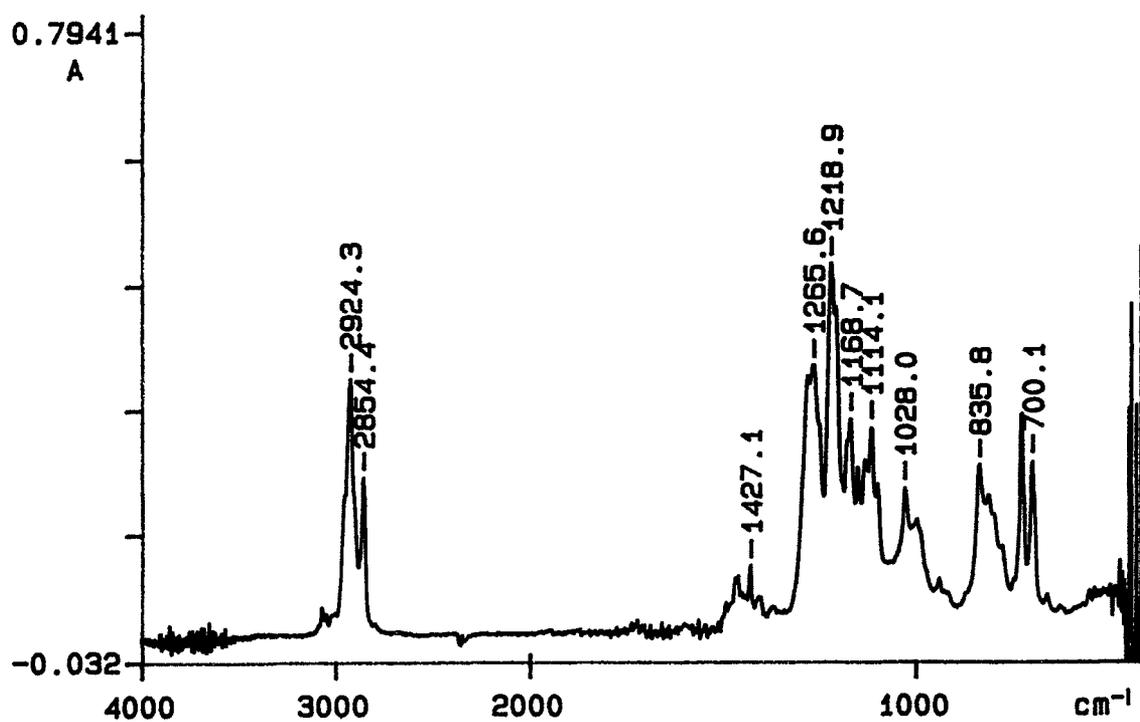
IR #23. (Compound XXVIp-b)

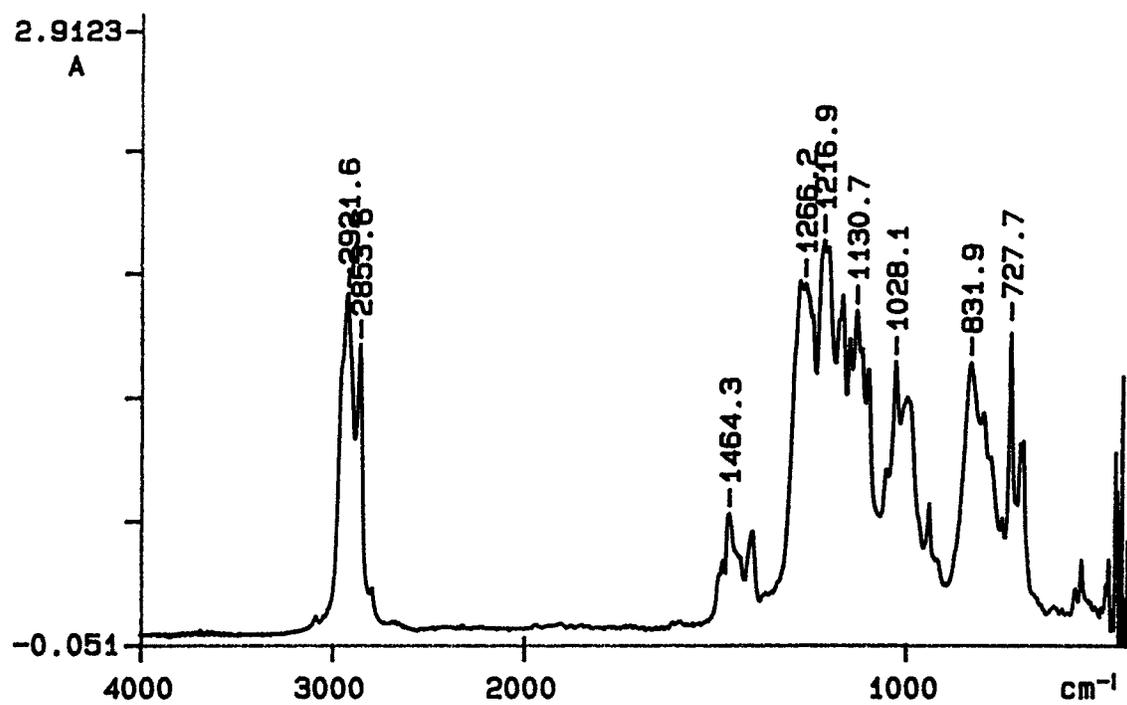


IR #24. (Compound XXVIp-s)

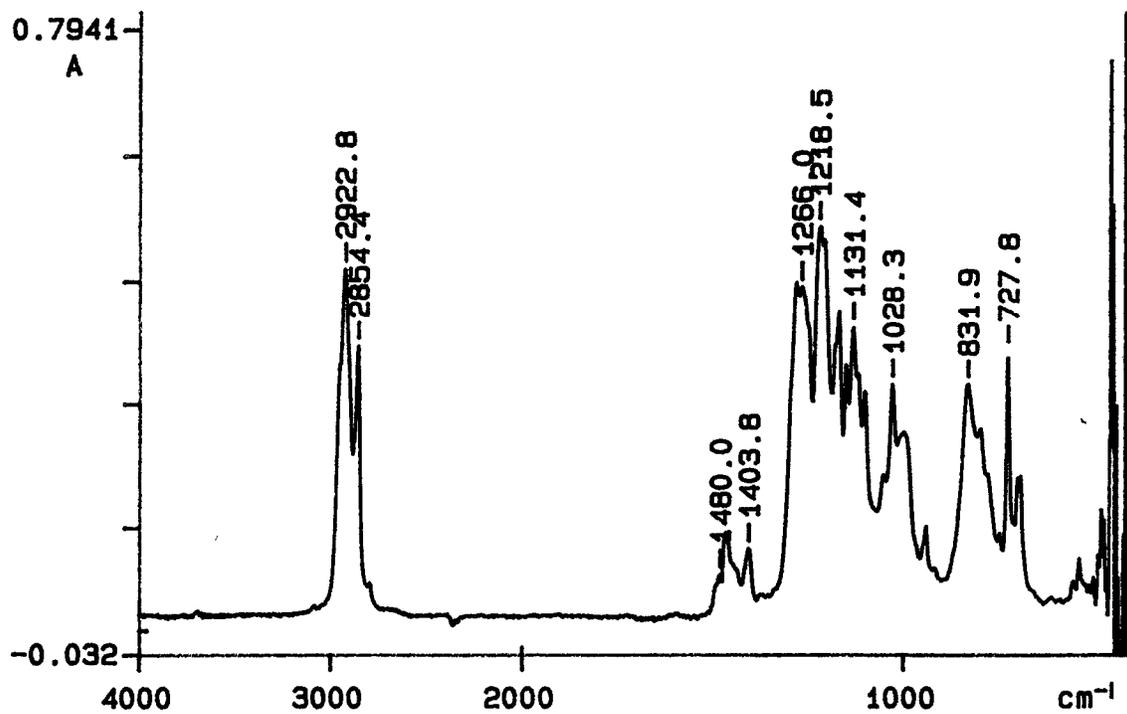


IR #25. (Decenyl Model Hydrosilation in Benzene), (Compound XIVb)

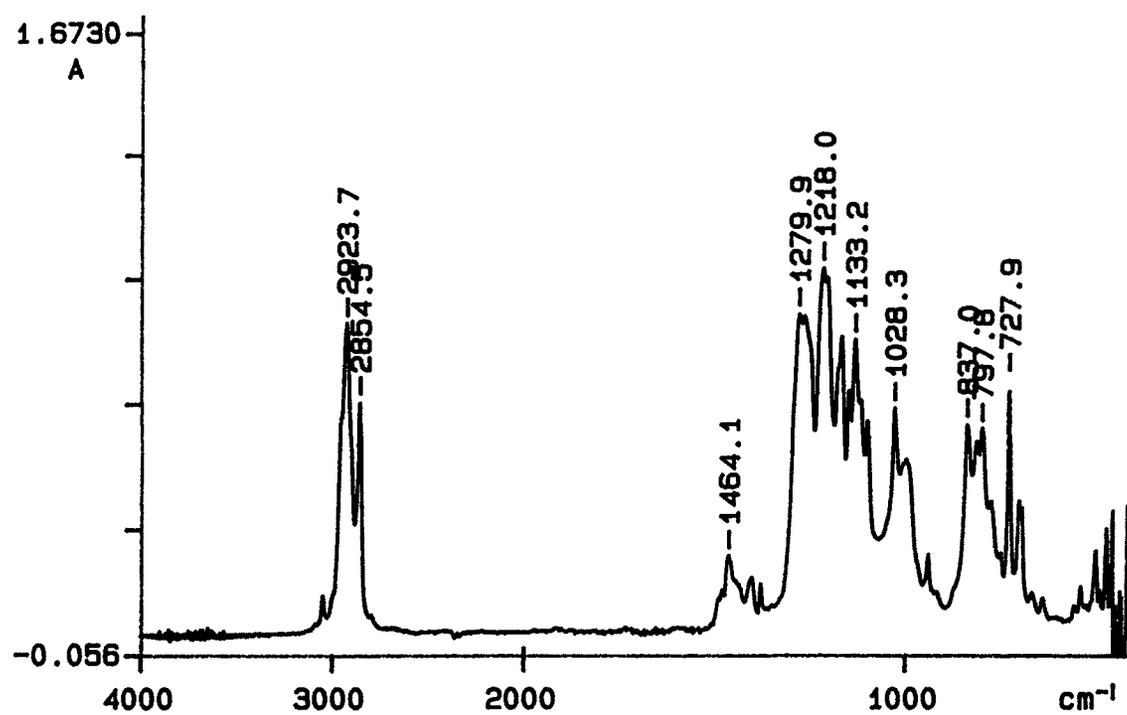
IR #26. (Decenyl Model Hydrosilation in ScCO₂), (Compound XIVs)



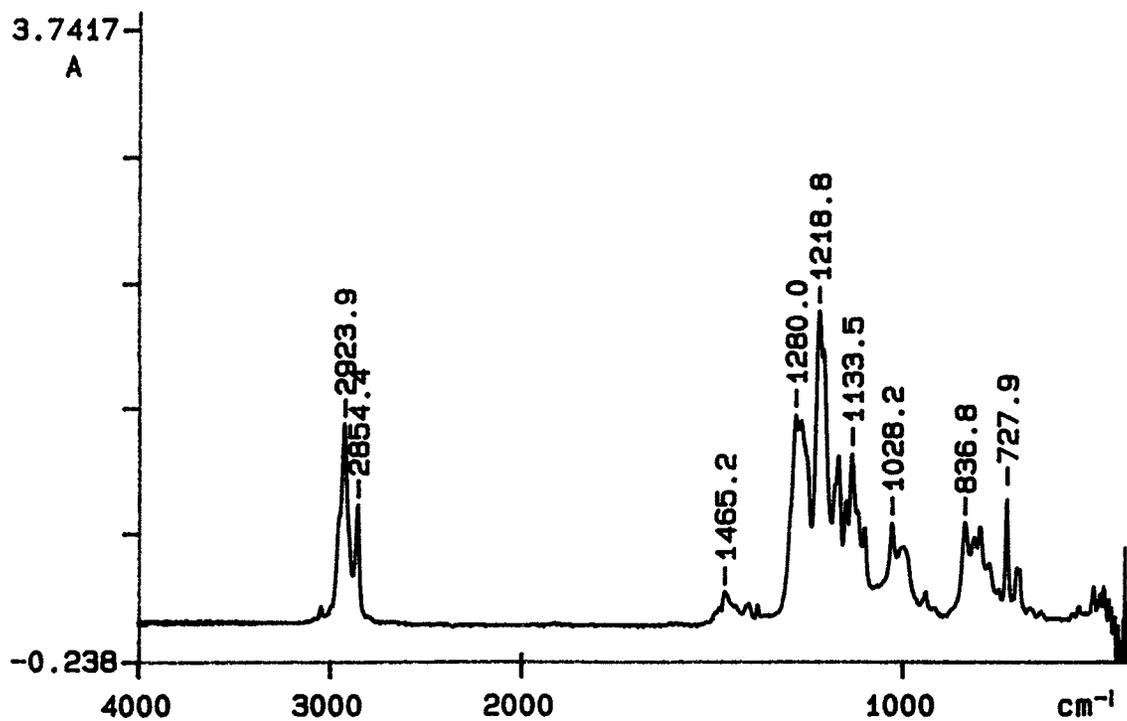
IR #27. (Compound XXIId-b)



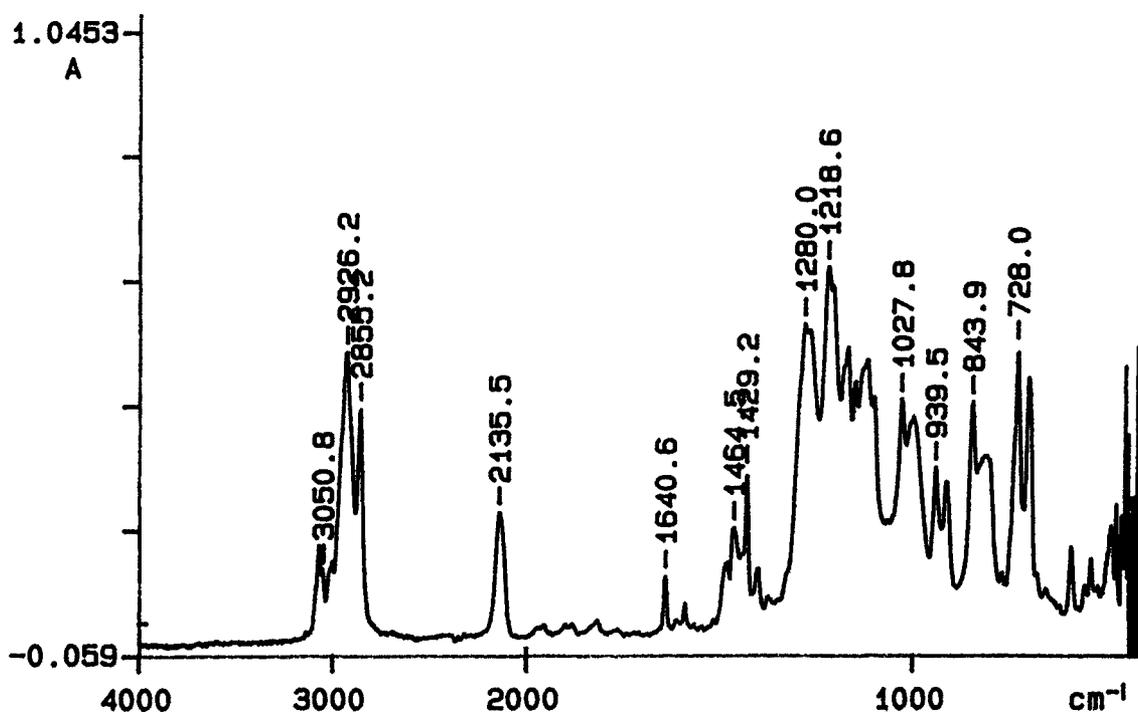
IR #28. (Compound XXIId-s)



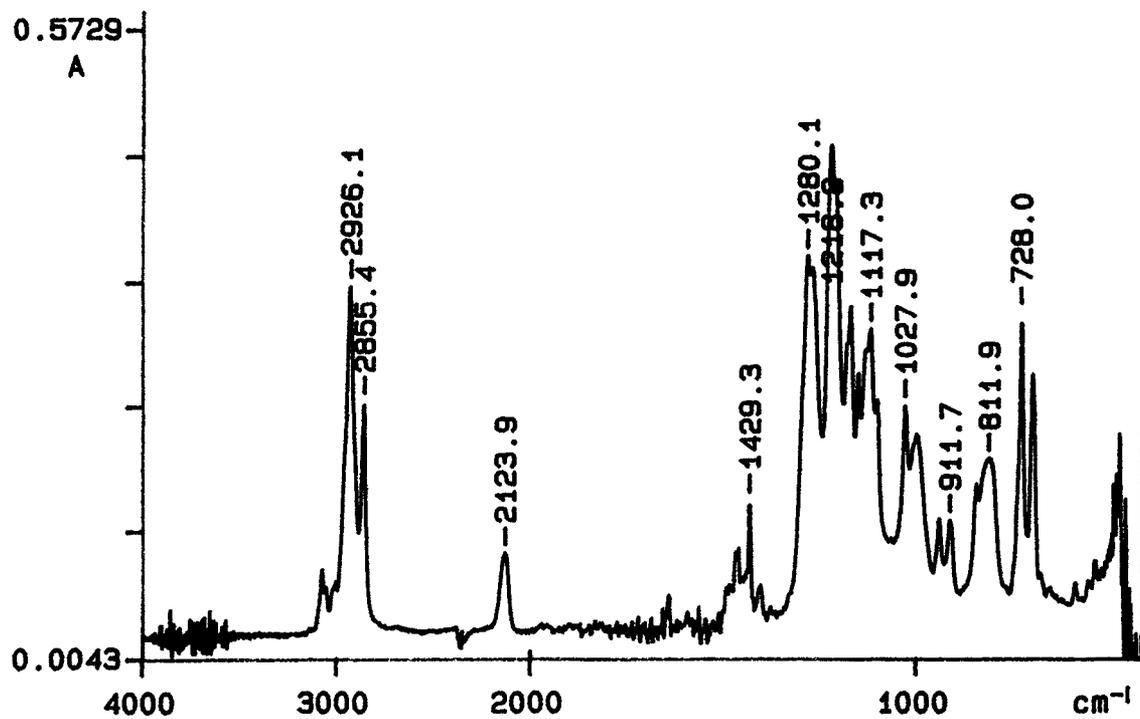
IR #29. (Compound XXII d-b)



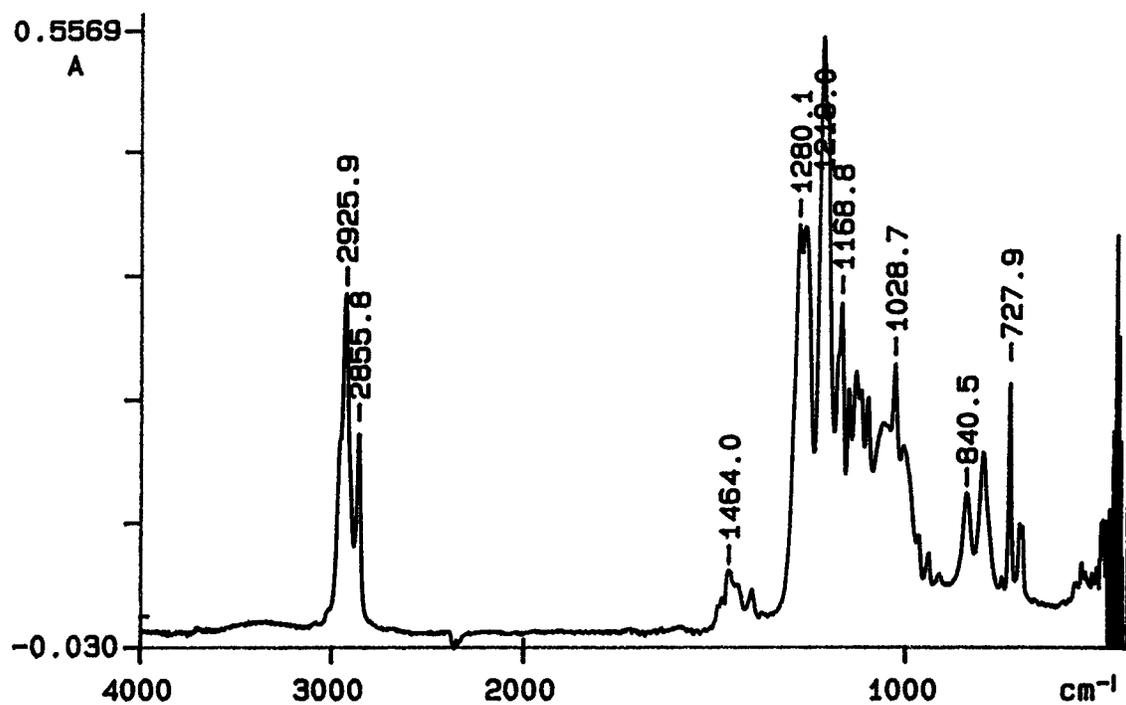
IR #30. (Compound XXII d-s)



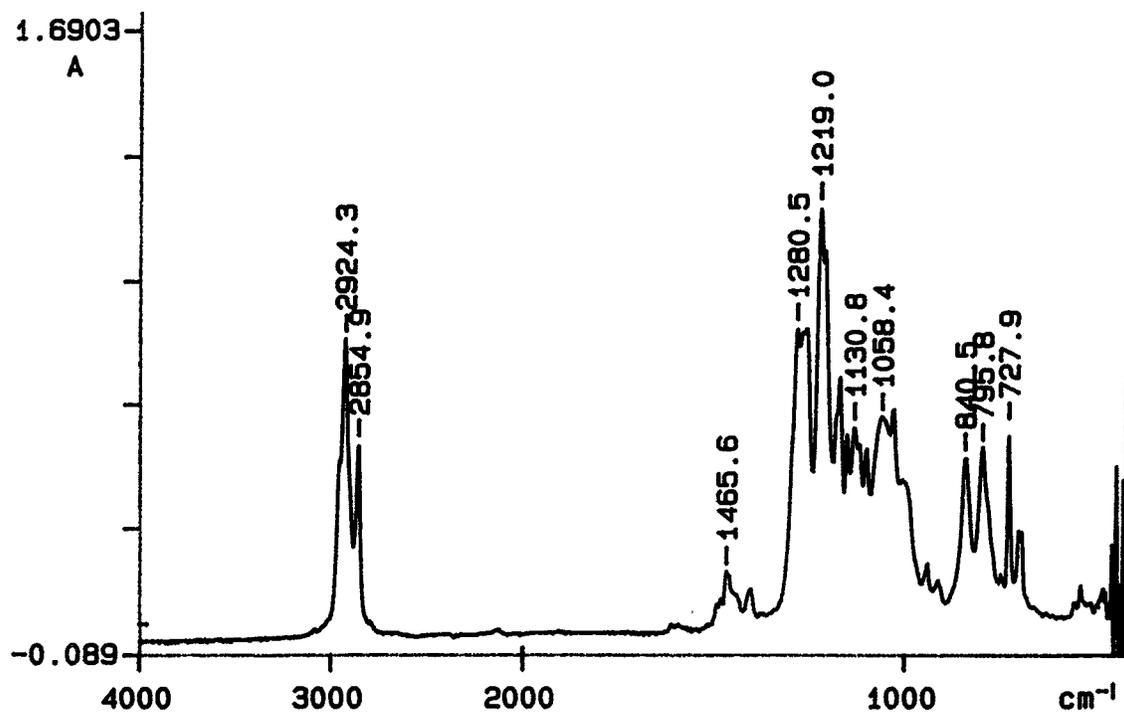
IR #31. (Compound XXIII d-b)



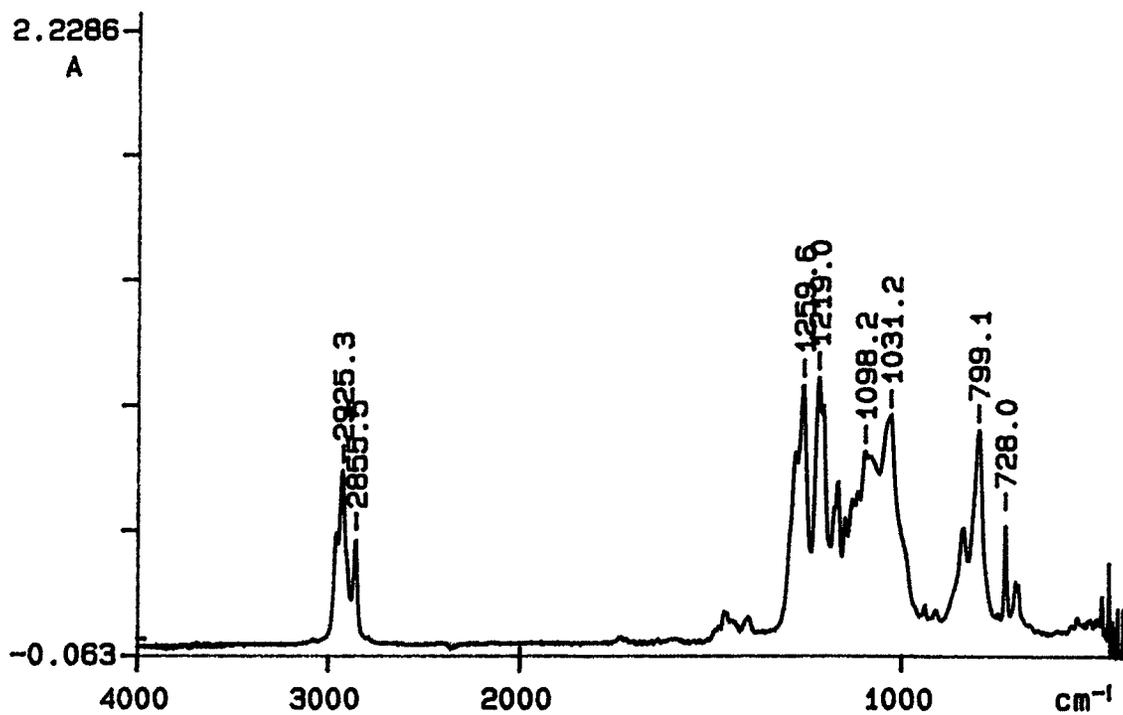
IR #32. (Compound XXIII d-s)



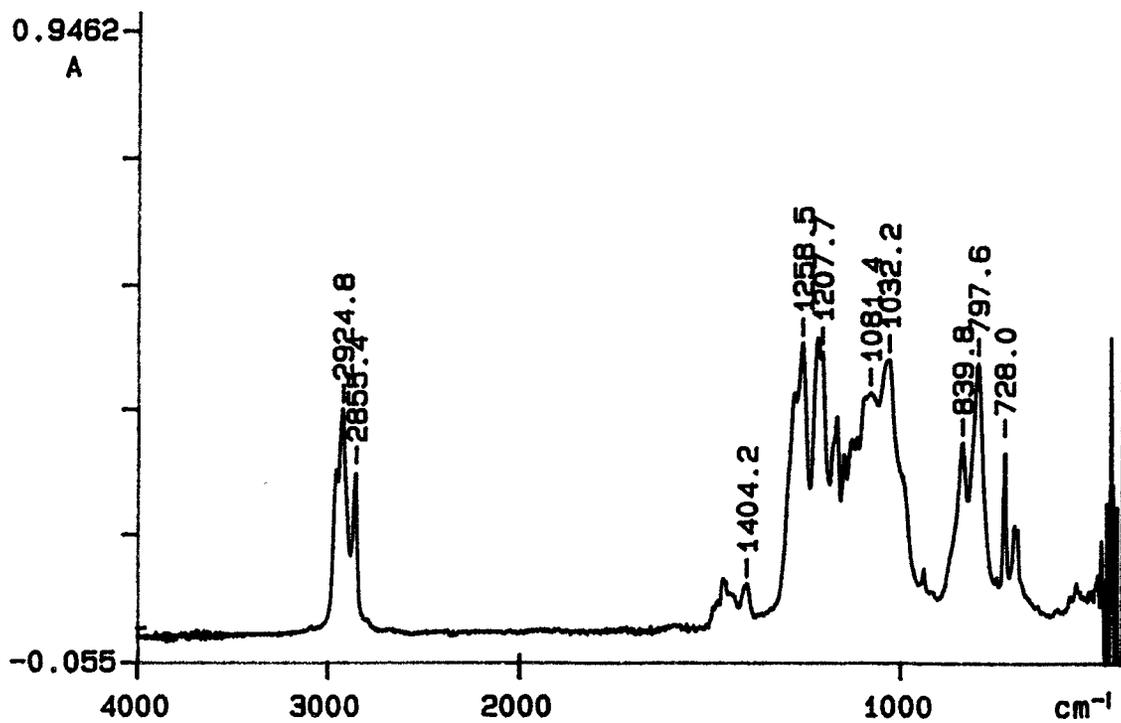
IR #33. (Compound XXIVd-b)



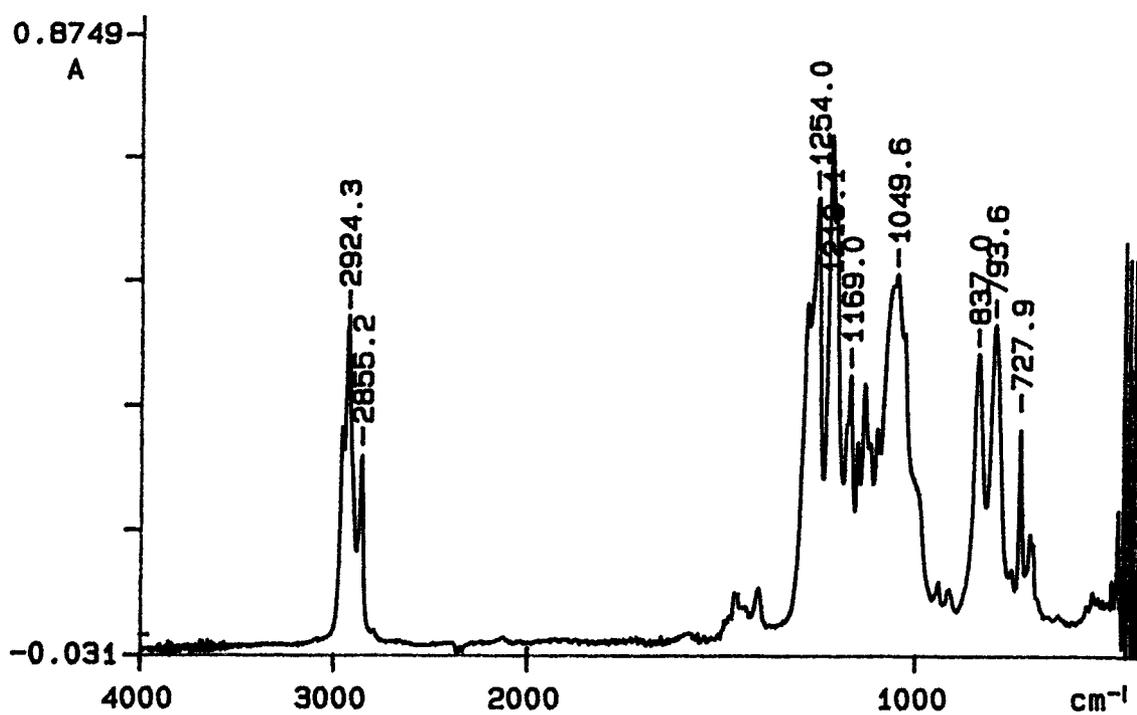
IR #34. (Compound XXIVd-s)



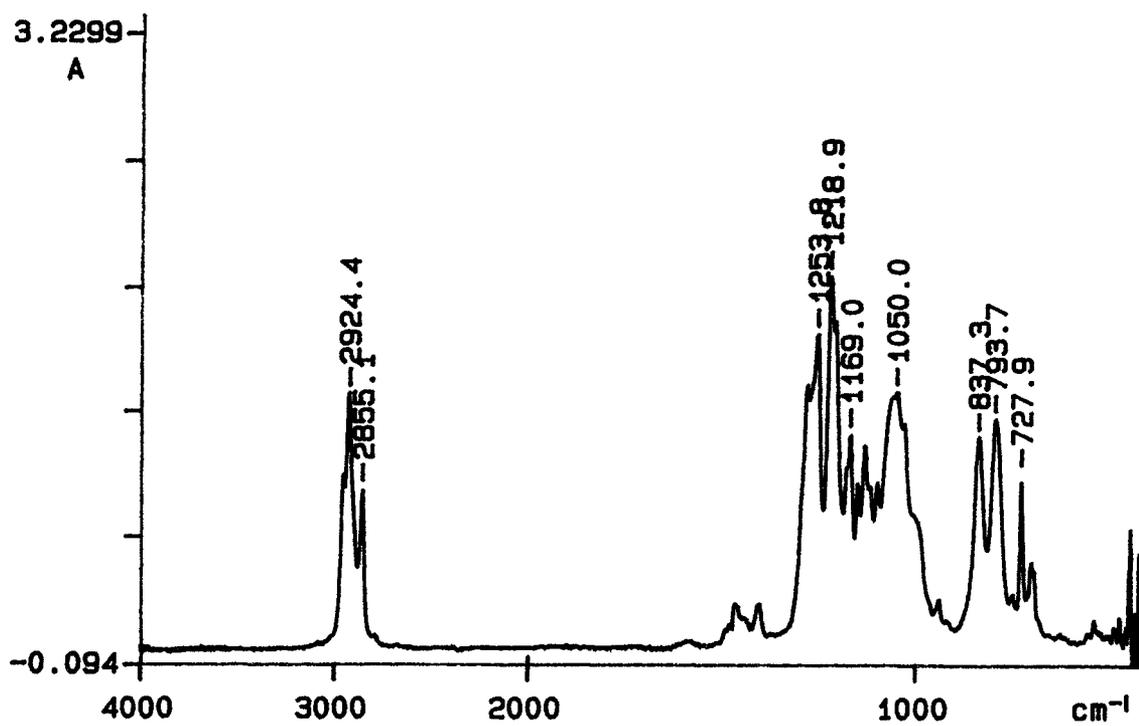
IR #35. (Compound XXVd-b)



IR #36. (Compound XXVd-s)



IR #37. (Compound XXVIId-b)



IR #38. (Compound XXVIId-s)

APPENDIX IV
TGA

Index for Appendix IV

Compound	TGA Number
1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene (Propenyl monomer), (Compound VII), (in Air)	1
(in Ar)	2
Compound derived from reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and Dimethyl Phenyl Silane; (Propenyl Model Hydrosilation in Benzene), (Compound XIII-b), (in Air)	3
(in Ar)	4
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,4,4-Tetramethyldisilethylene; in Benzene, (Compound XXI p-b), (in Air)	5
(in Ar)	6
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,4-bis dimethyl silyl benzene; in Benzene, (Compound XXII p-b), (in Air)	7
(in Ar)	8

Index for Appendix IV

(continued)

Compound	TGA Number
<hr/>	
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and Diphenyl-silane; in Benzene, (Compound XXIIIp-b), (in Air)	9
(in Ar)	10
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3-Tetramethyldisiloxane; in Benzene, (Compound XXIVp-b), (in Air)	11
(in Ar)	12
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane; in Benzene, (Compound XXVp-b), (in Air)	13
(in Ar)	14
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1-2-Bis(tetramethyldisiloxaneyl)ethane; in Benzene, (Compound XXVIp-b), (in Air)	15
(in Ar)	16
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(continued)

Compound	TGA Number
<hr/>	
Compound derived from reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and Dimethyl Phenyl Silane; (Propenyl Model Hydrosilation in ScCO ₂), (Compound XIII-s), (in Air)	17
(in Ar)	18
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,4,4-Tetramethyldisilethylene; in ScCO ₂ , (Compound XXIp-s) (in Air)	19
(in Ar)	20
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,4-bis dimethyl silyl benzene; in ScCO ₂ , (Compound XXIIP-s) (in Air)	21
(in Ar)	22
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and Diphenyl-silane; in ScCO ₂ , (Compound XXIIIp-s) (in Air)	23
(in Ar)	24
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Index for Appendix IV

(continued)

Compound	TGA Number
<hr/>	
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3-Tetramethyldisiloxane; in ScCO ₂ , (Compound XXIVp-s)	
(in Air)	25
(in Ar)	26
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane; in ScCO ₂ , (Compound XXVp-s)	
(in Air)	27
(in Ar)	28
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1-2-Bis(tetramethyldisiloxaneyl)ethane; in ScCO ₂ , (Compound XXVIp-s)	
(in Air)	29
(in Ar)	30

Index for Appendix IV

(continued)

Compound	TGA Number
<hr/>	
1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene (Decenyl monomer), (Compound XI)	
(in Air)	31
(in Ar)	32
Compound derived from the reaction of 1,3-bis decyl (10-oxyhexafluoroisopropylidene) benzene and Dimethyl Phenyl Silane; (Decenyl Model Hydrosilation in Benzene), (Compound XIV-b)	
(in Air)	33
(in Ar)	34
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,4,4-Tetramethyldisilethylene; in Benzene, (Compound XXId-b)	
(in Air)	35
(in Ar)	36
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,4-Bis(dimethylsilyl)benzene; in Benzene, (Compound XXIId-b)	
(in Air)	37
(in Ar)	38
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Index for Appendix IV

(continued)

Compound	TGA Number
<hr/>	
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and Diphenyl-silane; in Benzene, (Compound XXIII d-b)	
(in Air)	39
(in Ar)	40
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,3,3-Tetramethyldisiloxane; in Benzene, (Compound XXIV d-b)	
(in Air)	41
(in Ar)	42
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,3,3,5,5,7,7 tetramethyl disiloxane; in Benzene, (Compound XXV d-b)	
(in Air)	43
(in Ar)	44
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1-2-Bis(tetramethyldisiloxaneyl)ethane; in Benzene, (Compound XXVI d-b)	
(in Air)	45
(in Ar)	46
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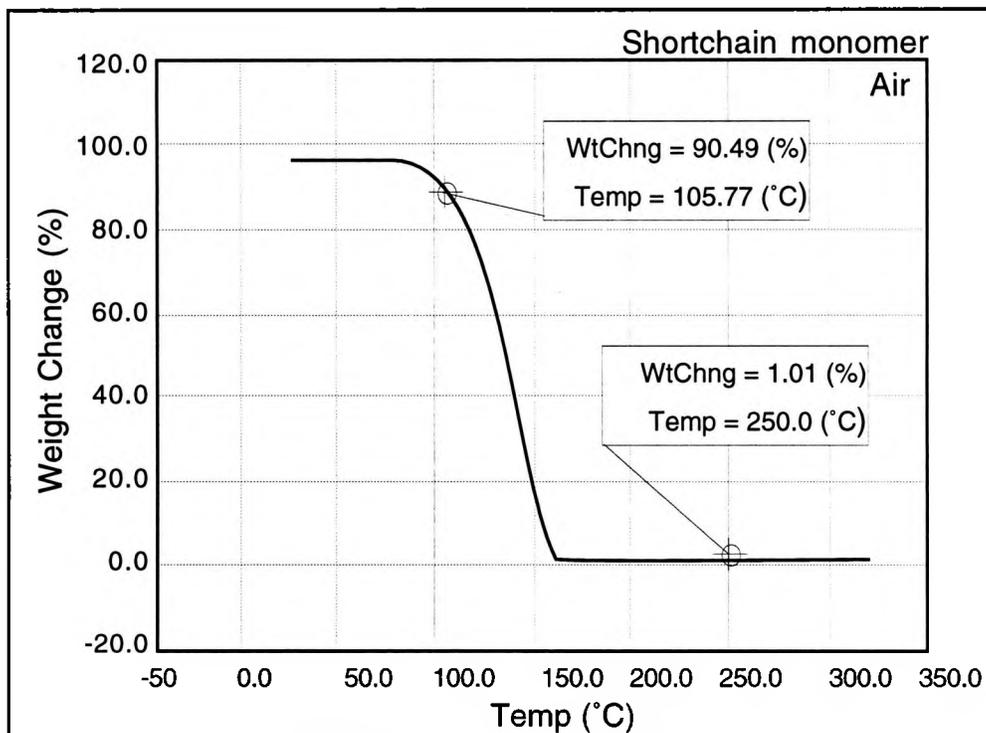
(continued)

Compound	TGA Number
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Compound derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene Dimethyl Phenyl Silane; Decyl Model Hydrosilation in ScCO ₂ , (Compound XIV-s)	
(in Air)	47
(in Ar)	48
 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,4,4-Tetramethyldisilethylene; in ScCO ₂ , (Compound XXId-s)	
(in Air)	49
(in Ar)	50
 Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,4-Bis(dimethylsilyl)benzene; in ScCO ₂ , (Compound XXIId-s)	
(in Air)	51
(in Ar)	52
 Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and Diphenyl-silane; in ScCO ₂ , (Compound XXIIIId-s)	
(in Air)	53
(in Ar)	54
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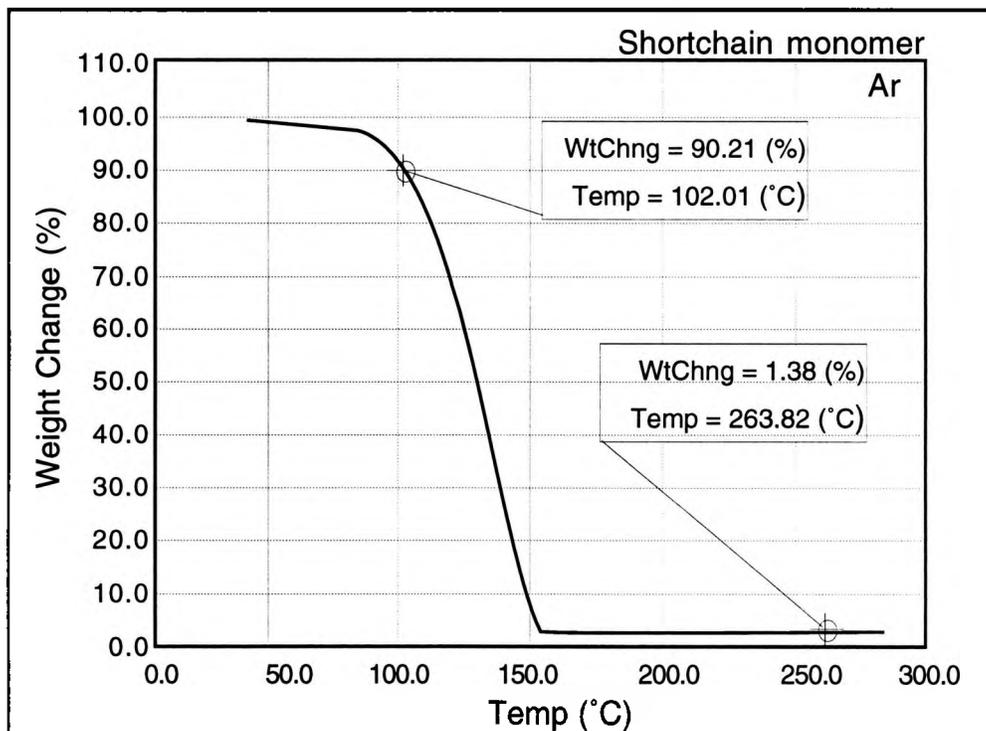
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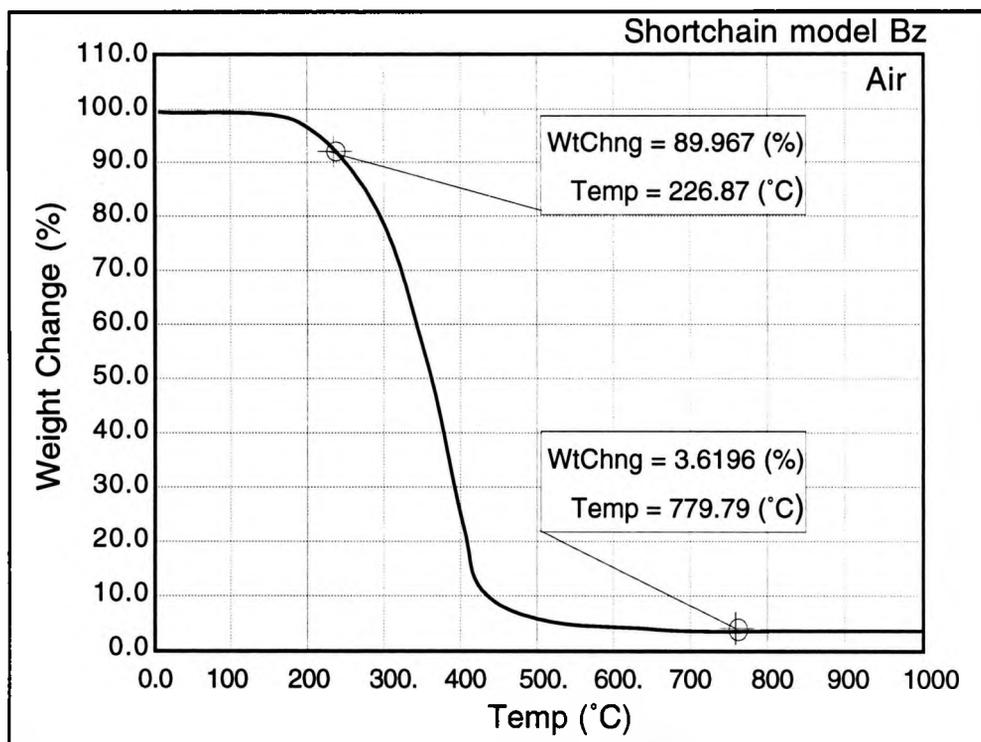
Compound	TGA Number
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,3,3-Tetramethyldisiloxane; in ScCO ₂ , (Compound XXIVd-s)	
(in Air)	55
(in Ar)	56
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1,1,3,3,5,5,7,7-Ttetramethyldisiloxane; in ScCO ₂ , (Compound XXVd-s)	
(in Air)	57
(in Ar)	58
Polymer derived from the reaction of 1,3-Bis[hexafluoro-2-(9-decenyloxy-2-propyl)] Benzene and 1-2-Bis(tetramethyldisiloxaneyl)ethane; in ScCO ₂ , (Compound XXVID-s)	
(in Air)	59
(in Ar)	60



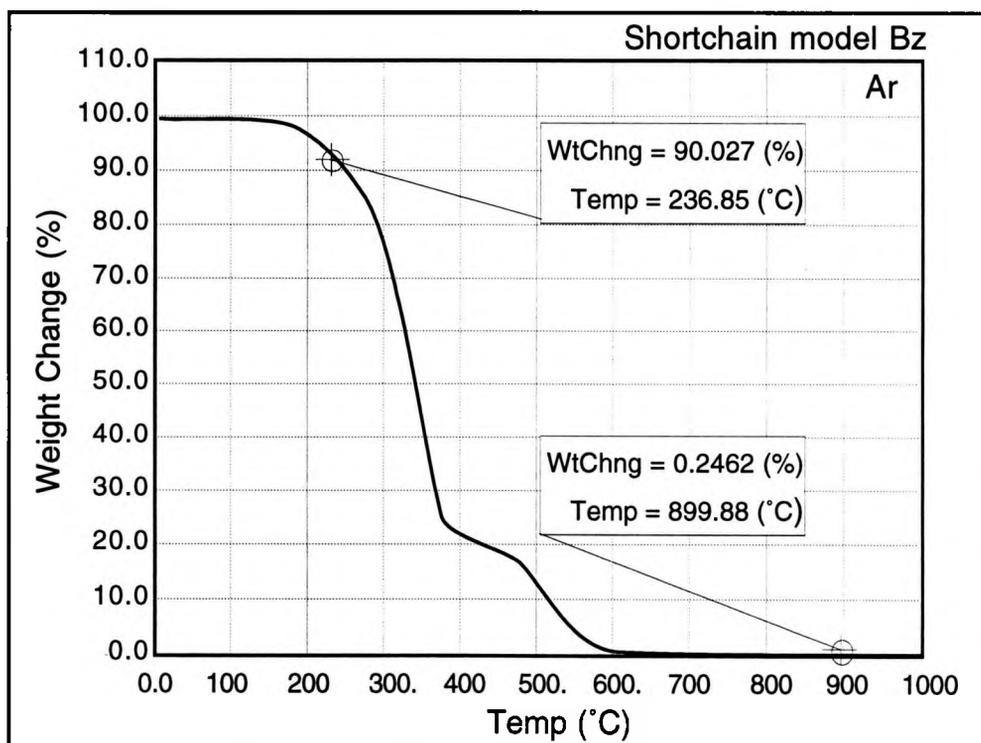
TGA #1. Air 1,3-bis (hexafluoro-2-propenyloxy-2-propyl) benzene (Propenyl monomer), (Compound VII)



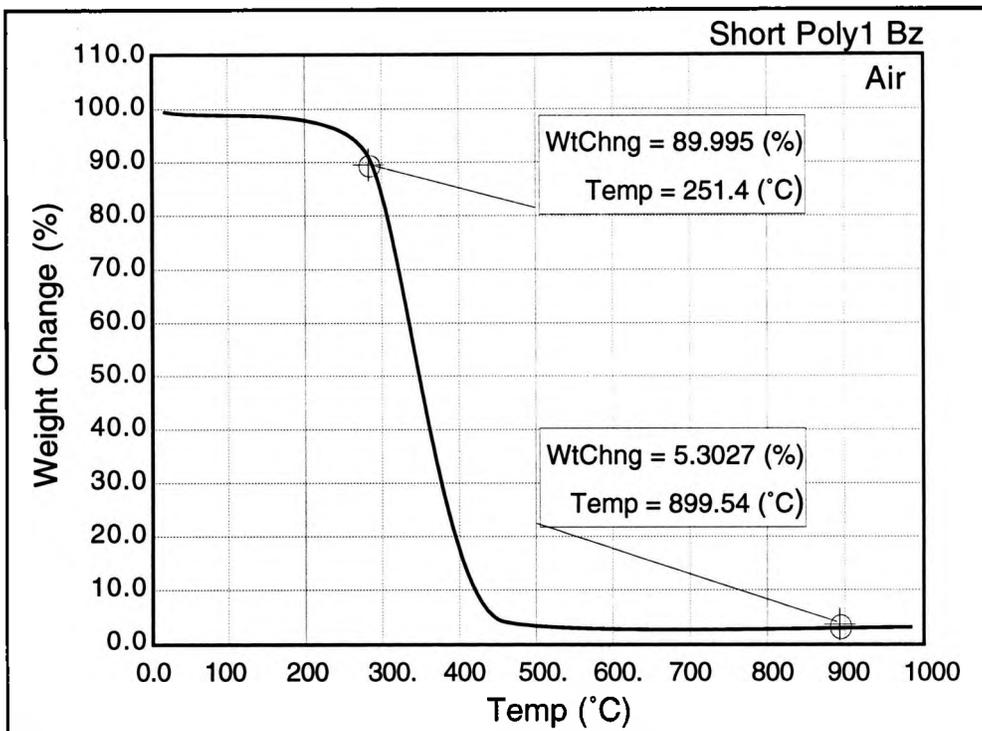
TGA #2. Ar 1,3-bis (hexafluoro-2-propenyloxy-2-propyl) benzene (Propenyl monomer), (Compound VII)



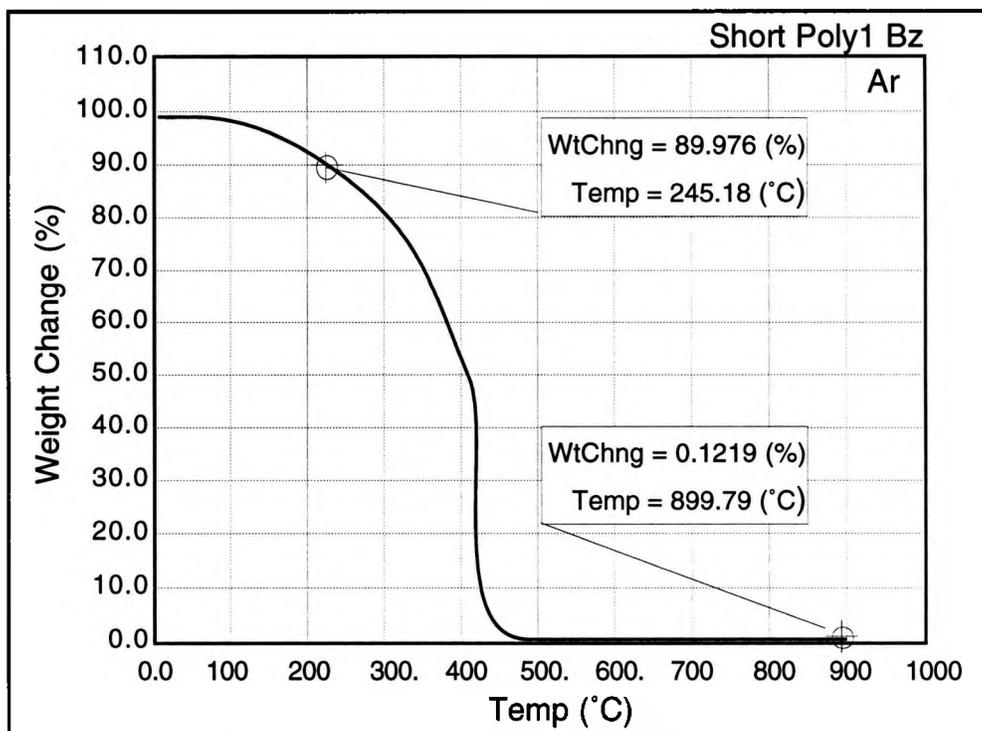
TGA #3. Air (Propenyl Model Hydrosilation in Benzene)
(Compound XIII-b)



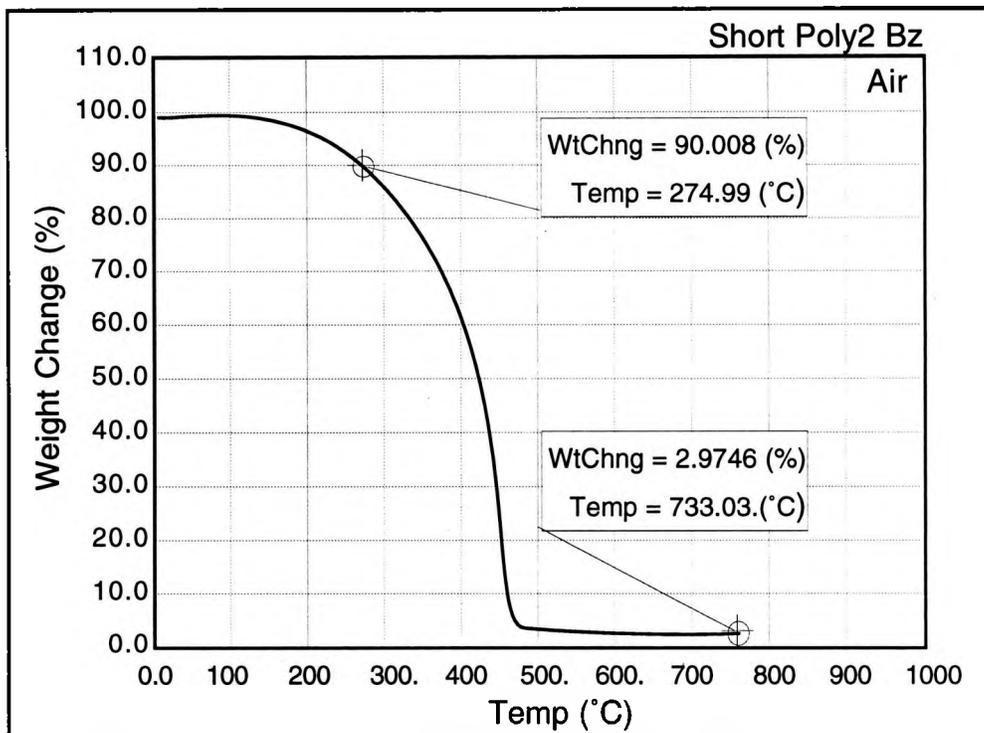
TGA #4. Ar (Propenyl Model Hydrosilation in Benzene)
(Compound XIII-b)



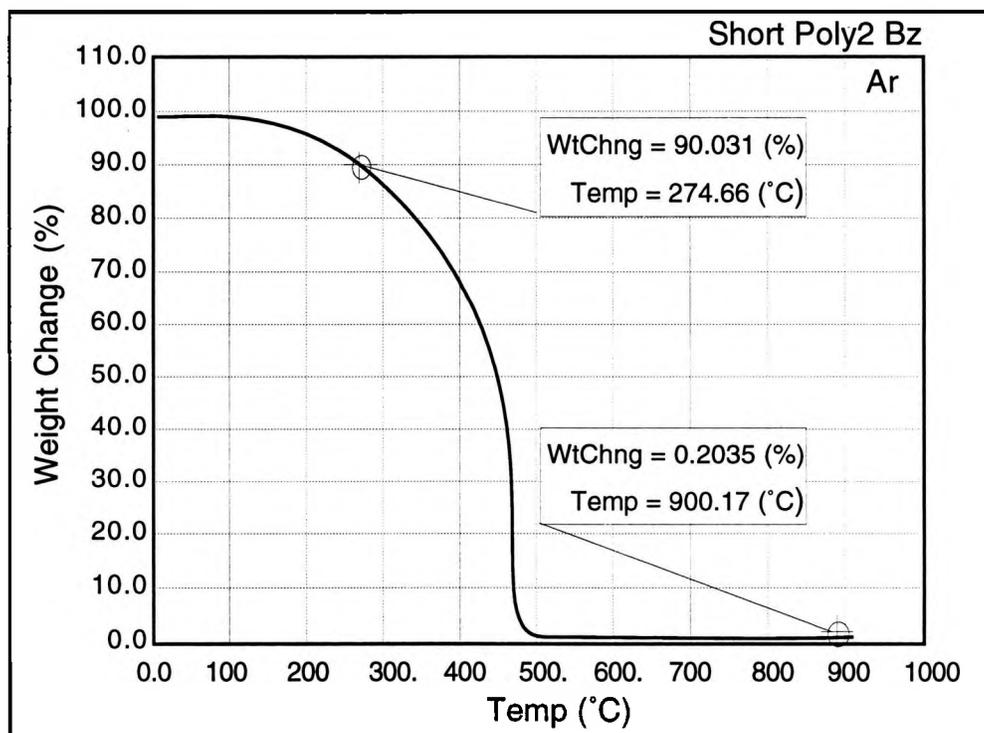
TGA #5. Air (Compound XXI**p**-b)



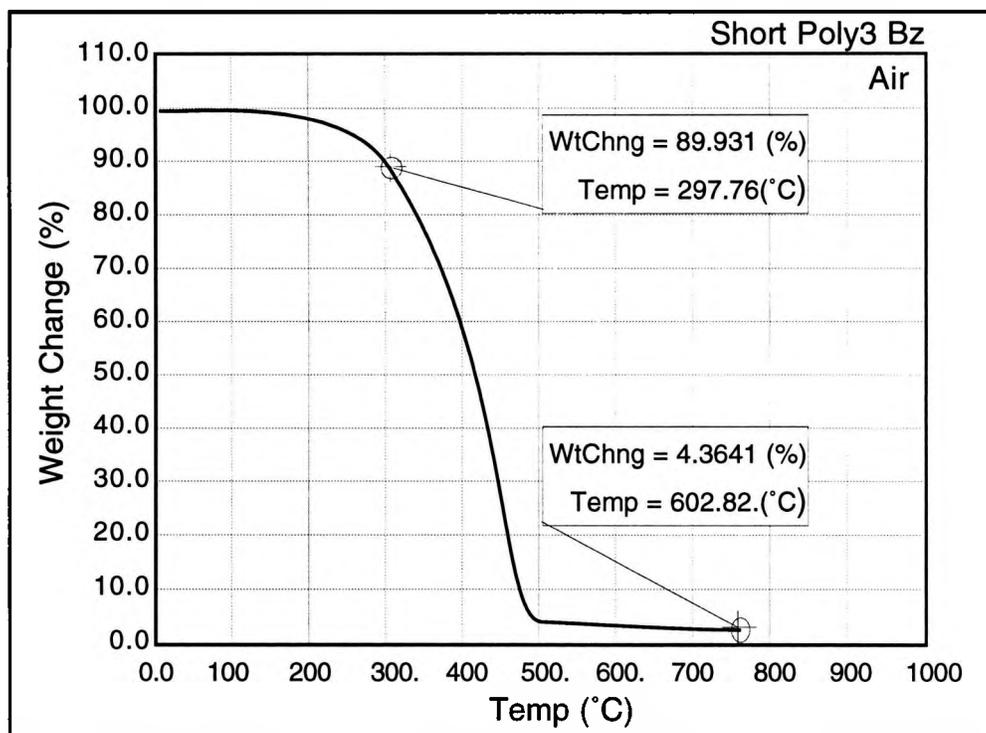
TGA #6. Ar (Compound XXI**p**-b)



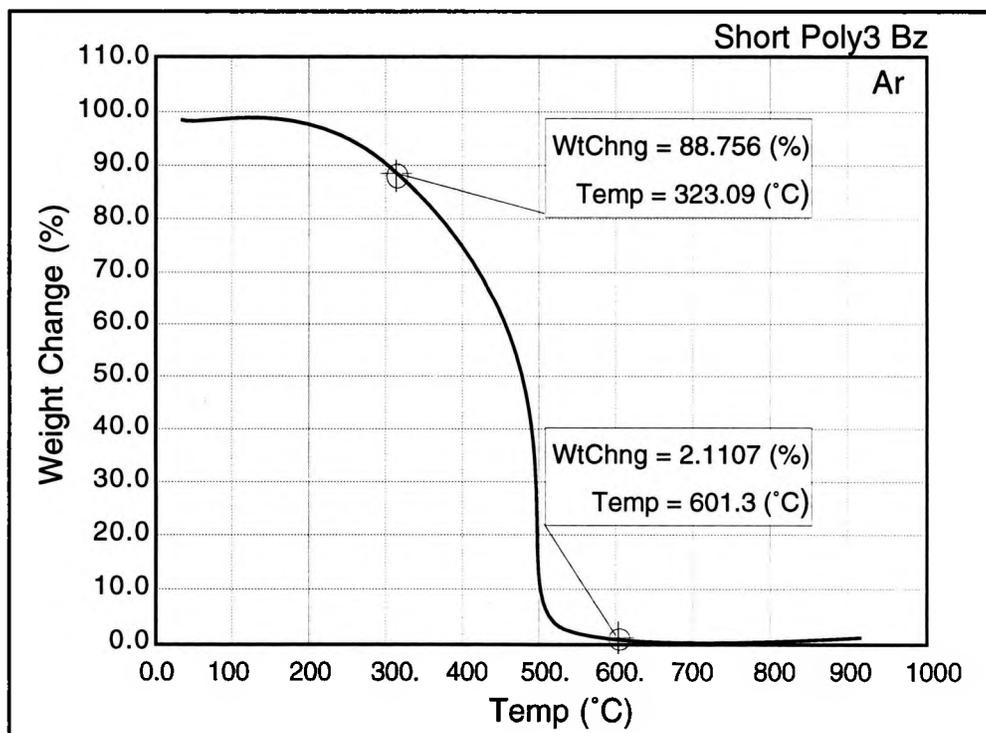
TGA #7. Air (Compound XXIIp-b)



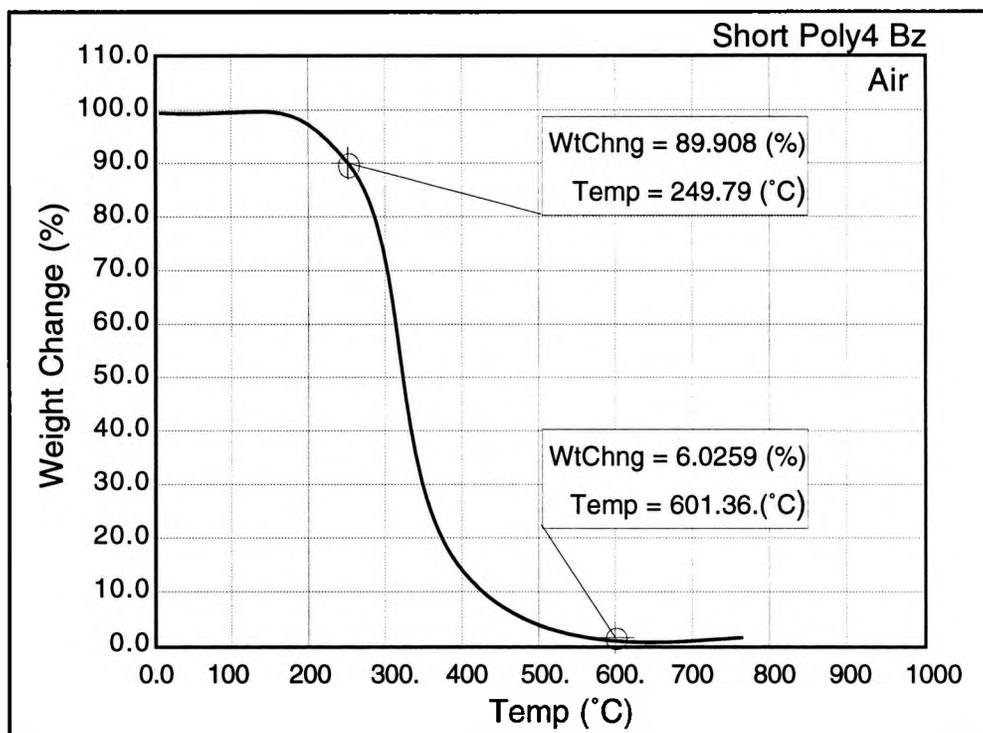
TGA #8. Ar (Compound XXIIp-b)



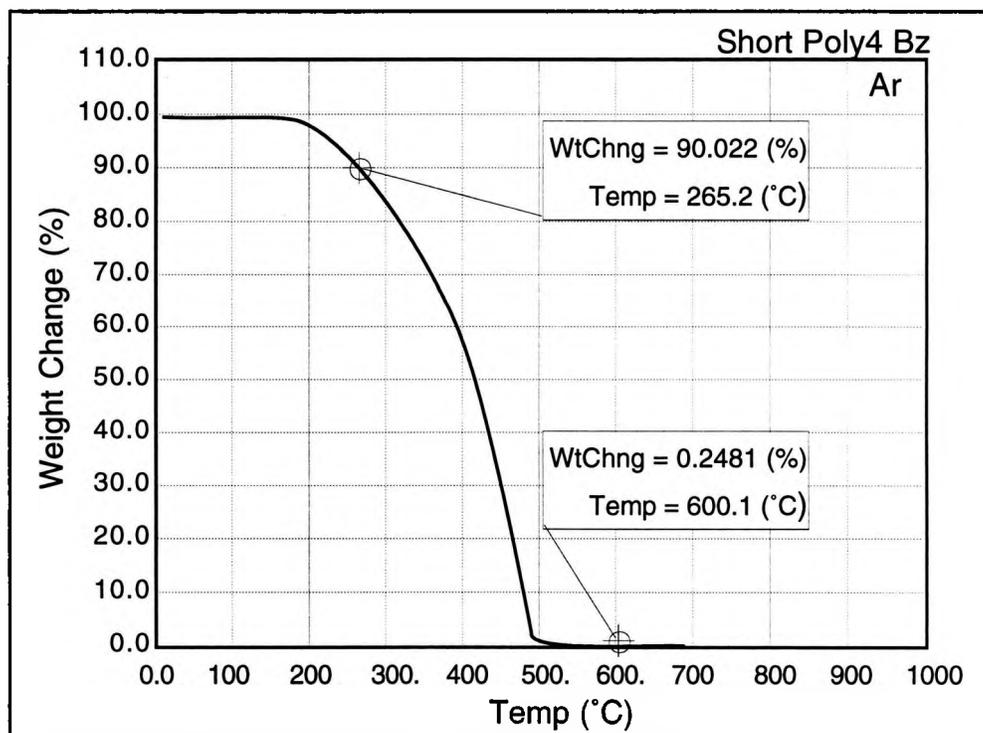
TGA #9. Air (Compound XXIIIp-b)



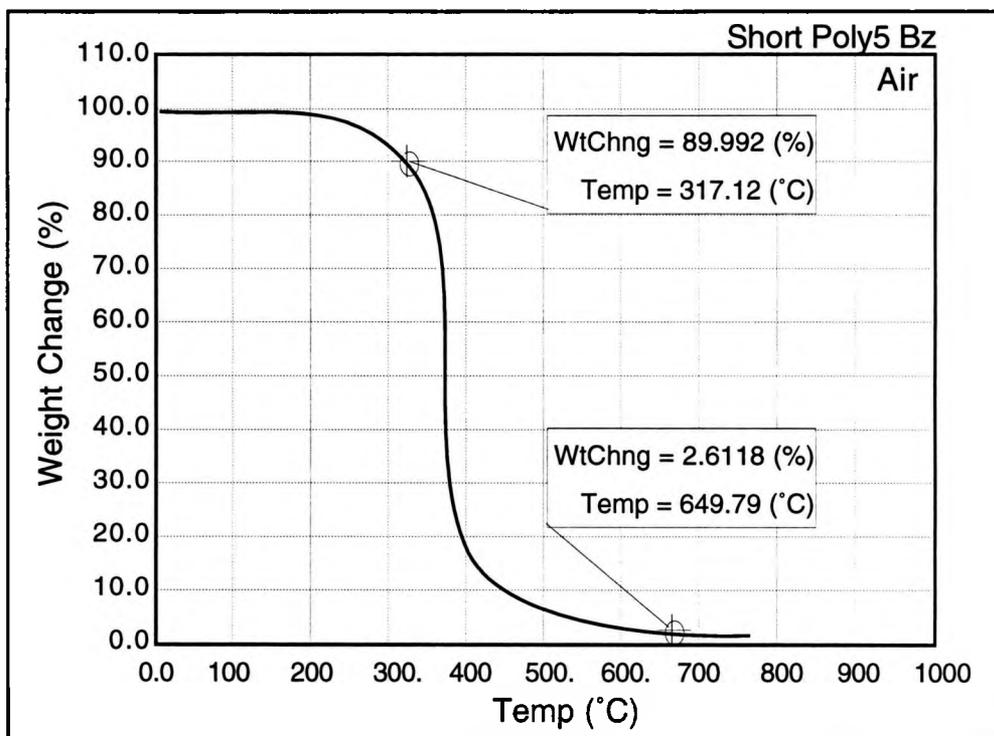
TGA #10. Ar (Compound XXIIIp-b)



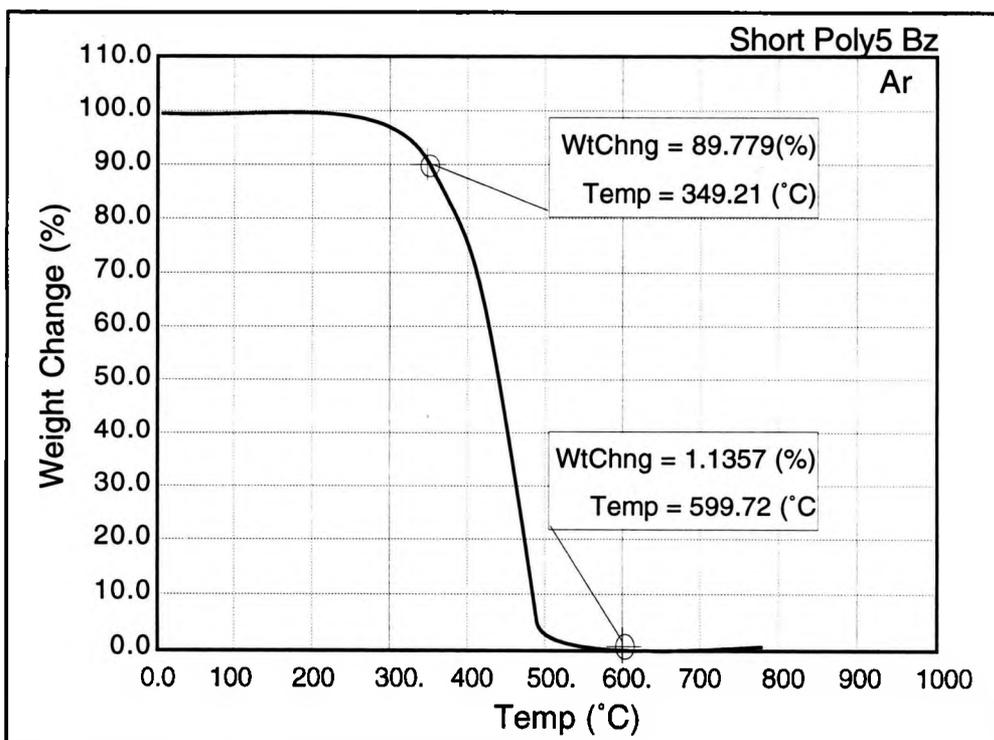
TGA #11. Air (Compound XXIVp-b)



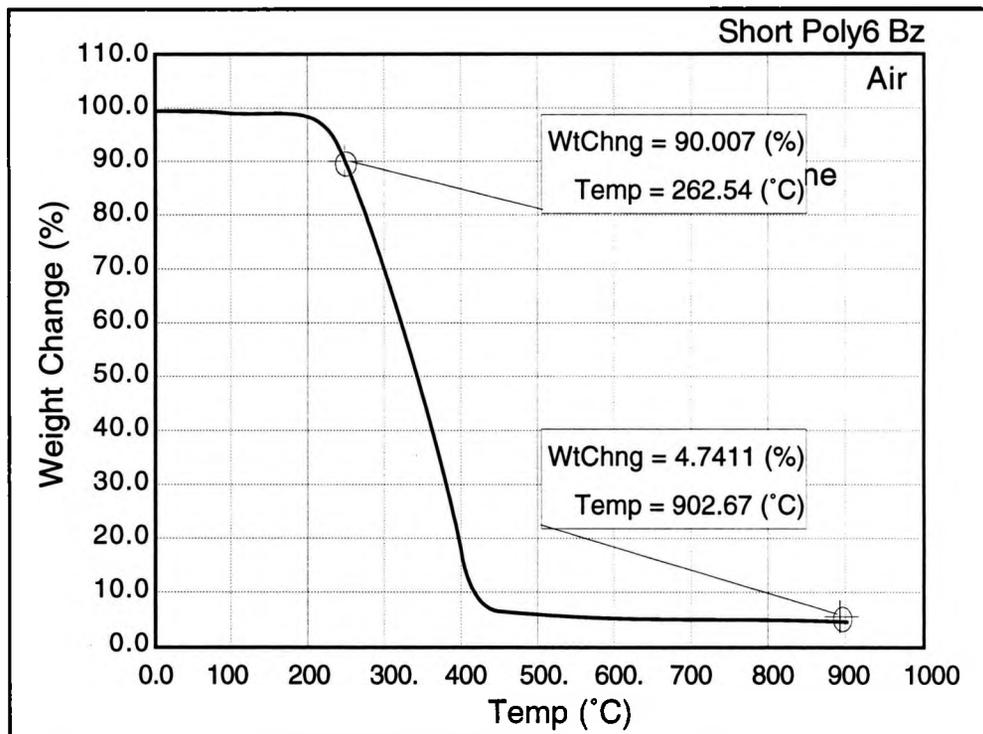
TGA #12. Ar (Compound XXIVp-b)



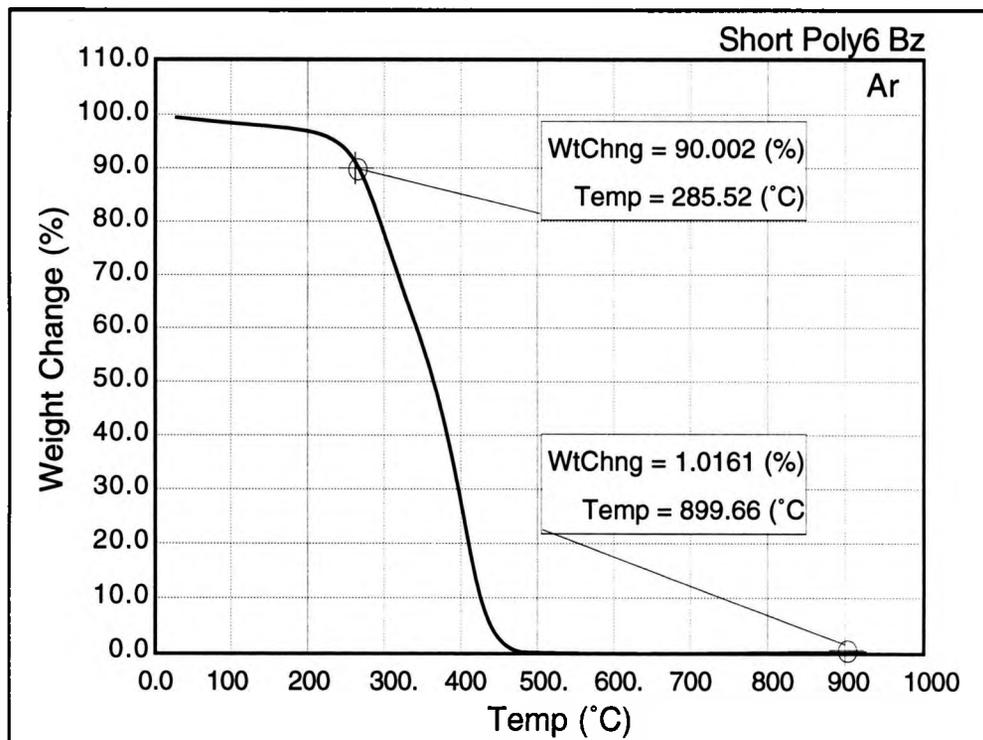
TGA #13. Air (Compound XXVp-b)



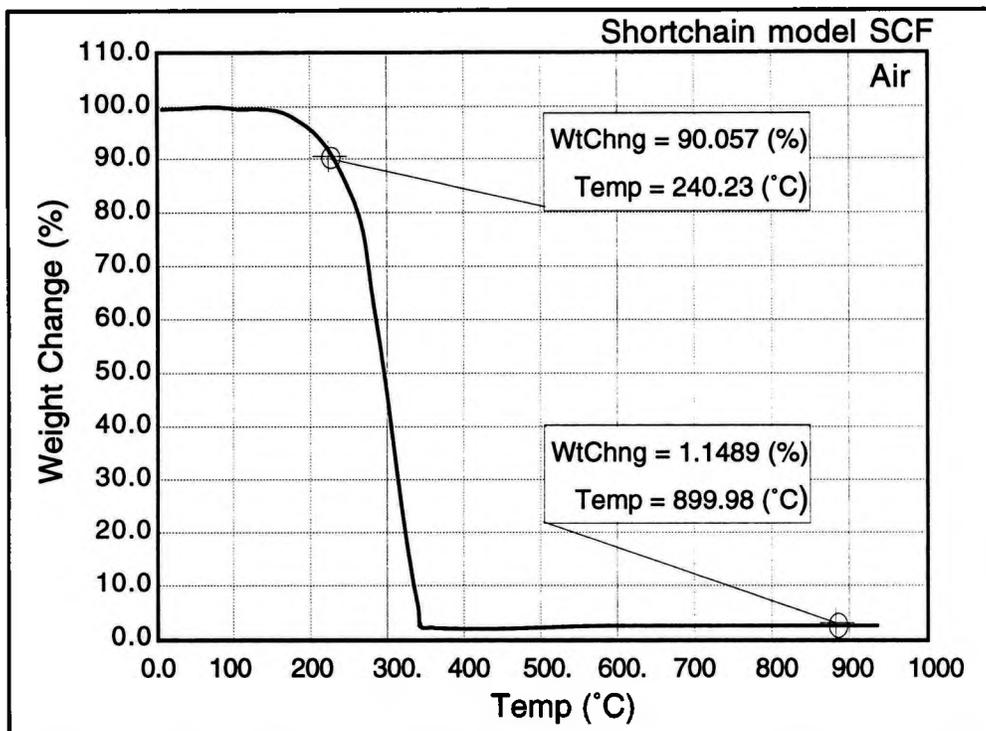
TGA #14. Ar (Compound XXVp-b)



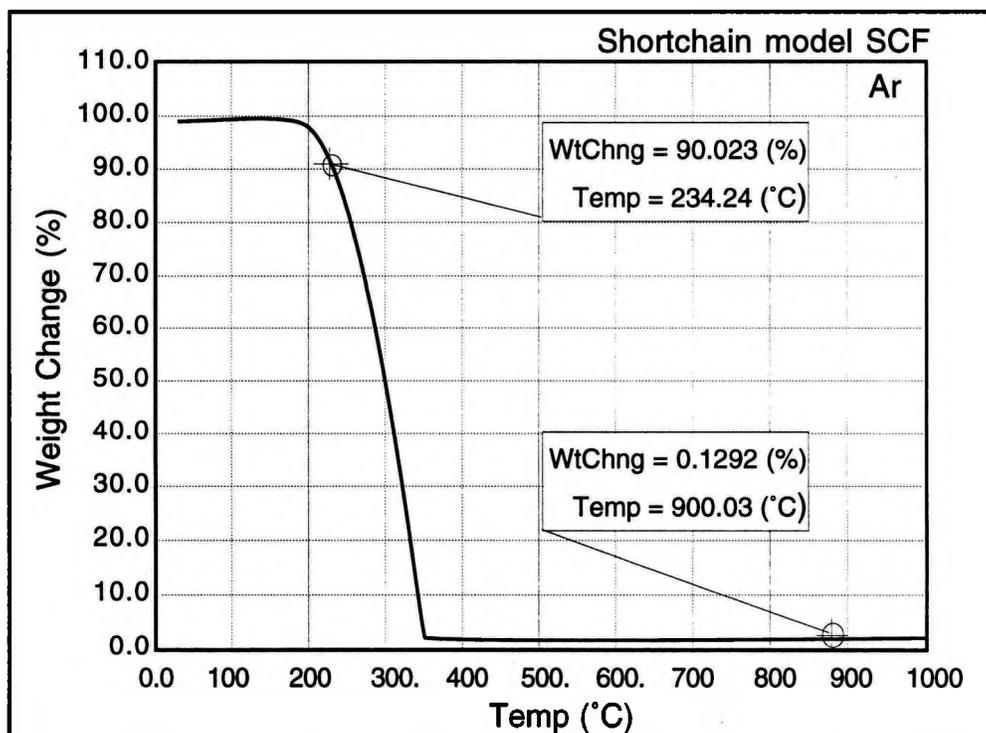
TGA #15. Air (Compound XXVIp-b)



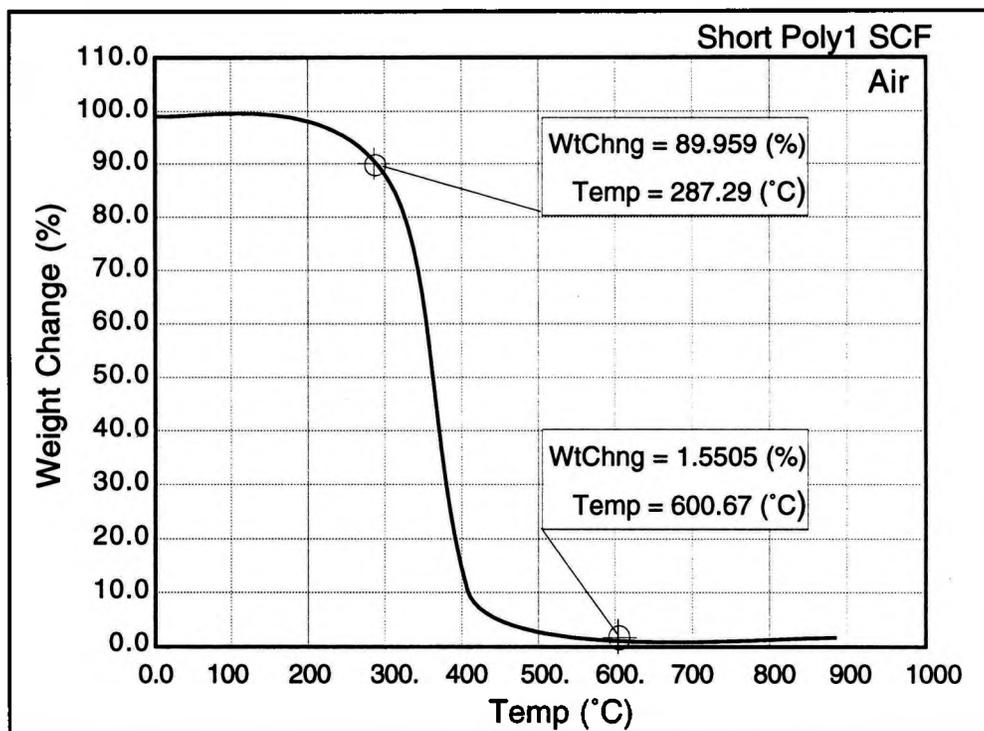
TGA #16. Ar (Compound XXVIp-b)



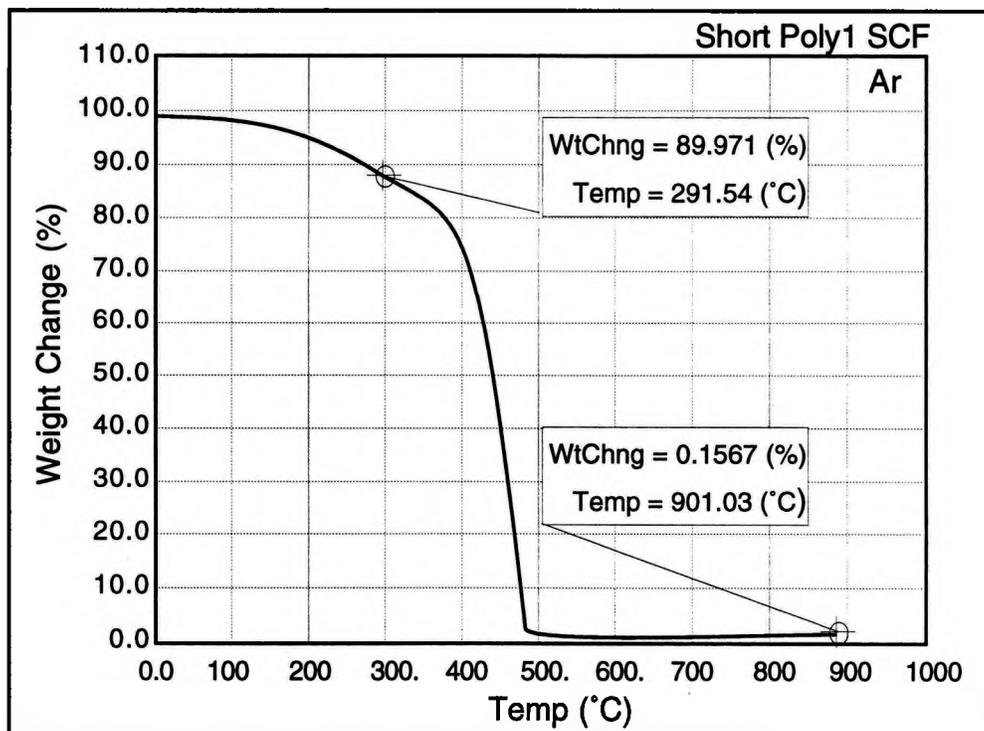
TGA #17. Air (Propenyl Model Hydrosilation in scCO₂),
(Compound XIII-s)



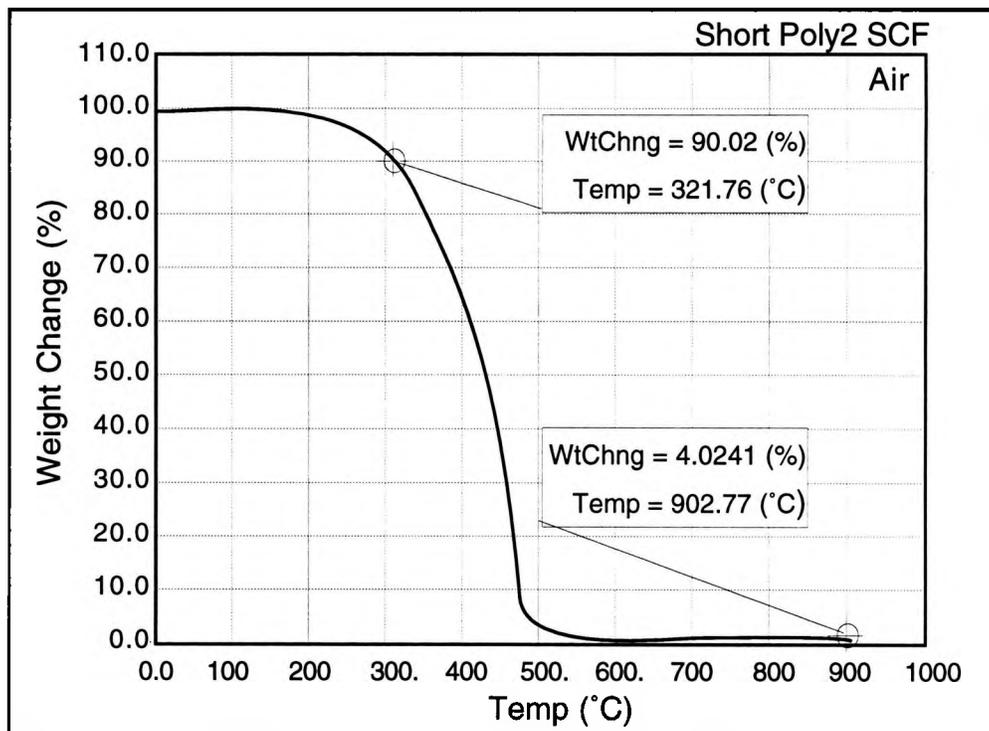
TGA #18. Ar (Propenyl Model Hydrosilation in scCO₂),
(Compound XIII-s)



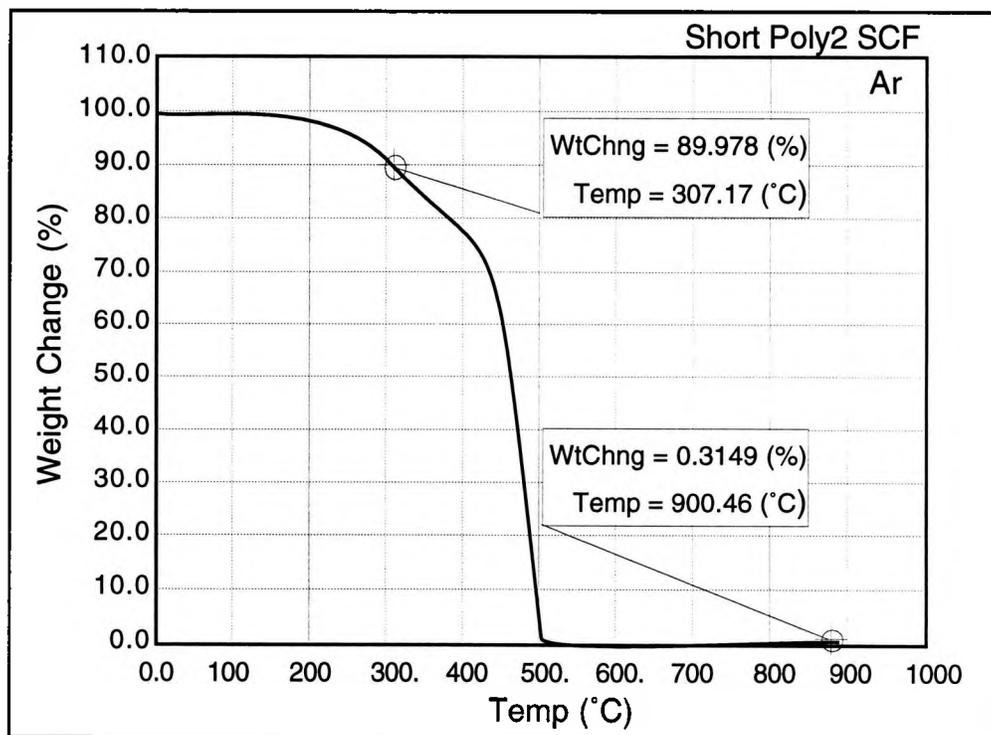
TGA#19. Air (Compound XXI_p-s)



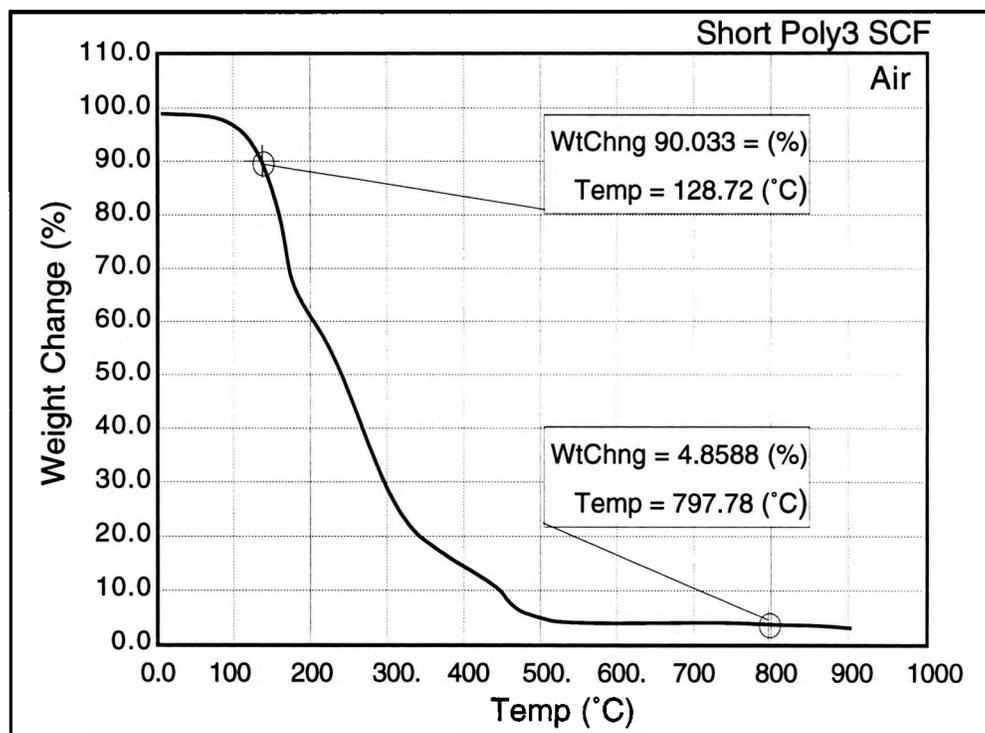
TGA #20. Ar (Compound XXI_p-s)



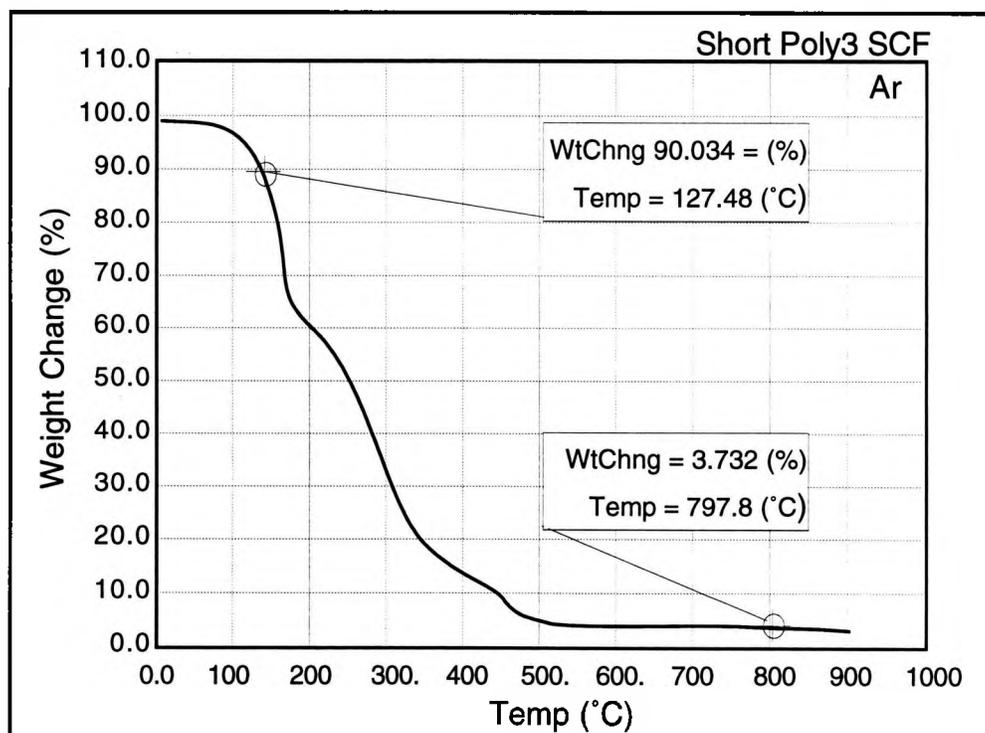
TGA #21. Air (Compound XXIIp-s)



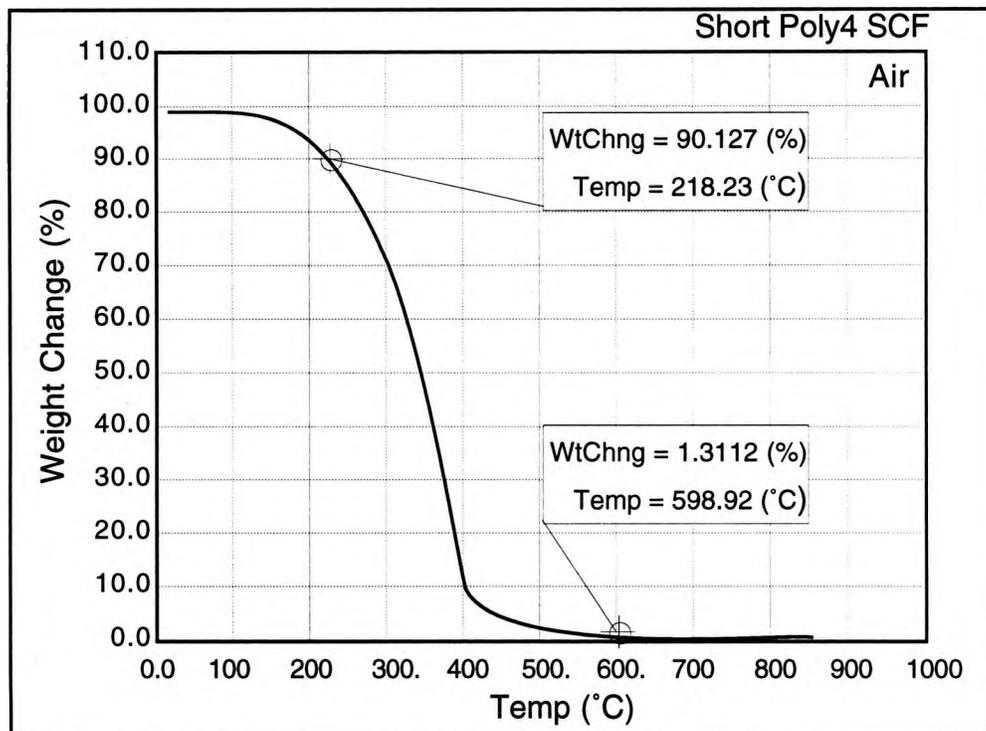
TGA #22. Ar (Compound XXIIp-s)



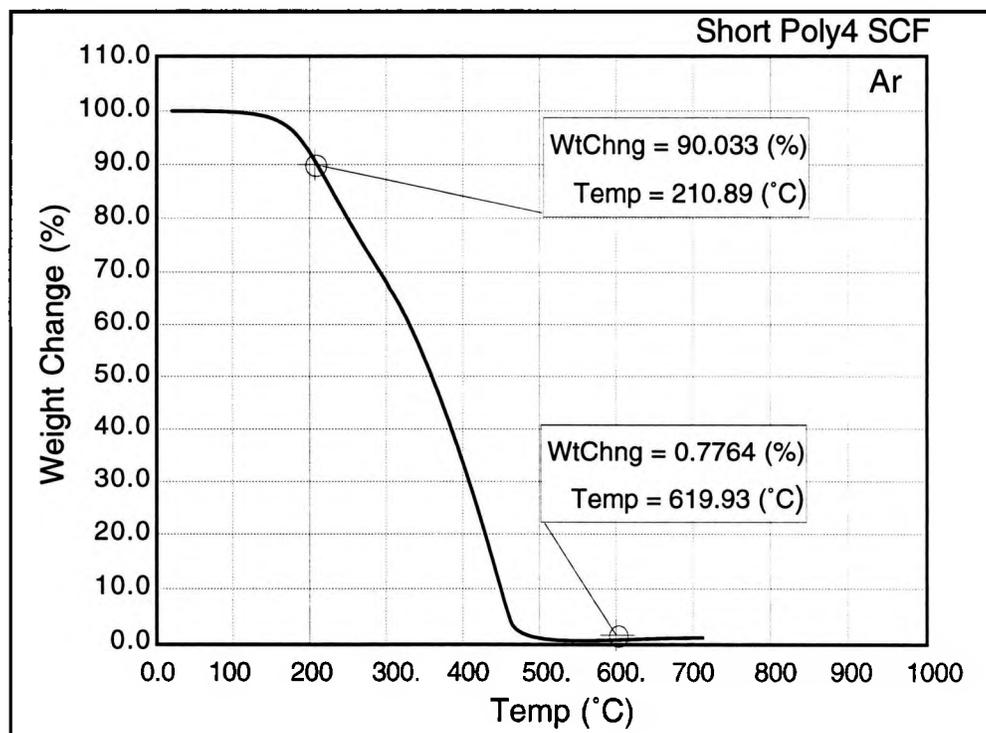
TGA #23. Air (Compound XXIIIp-s)



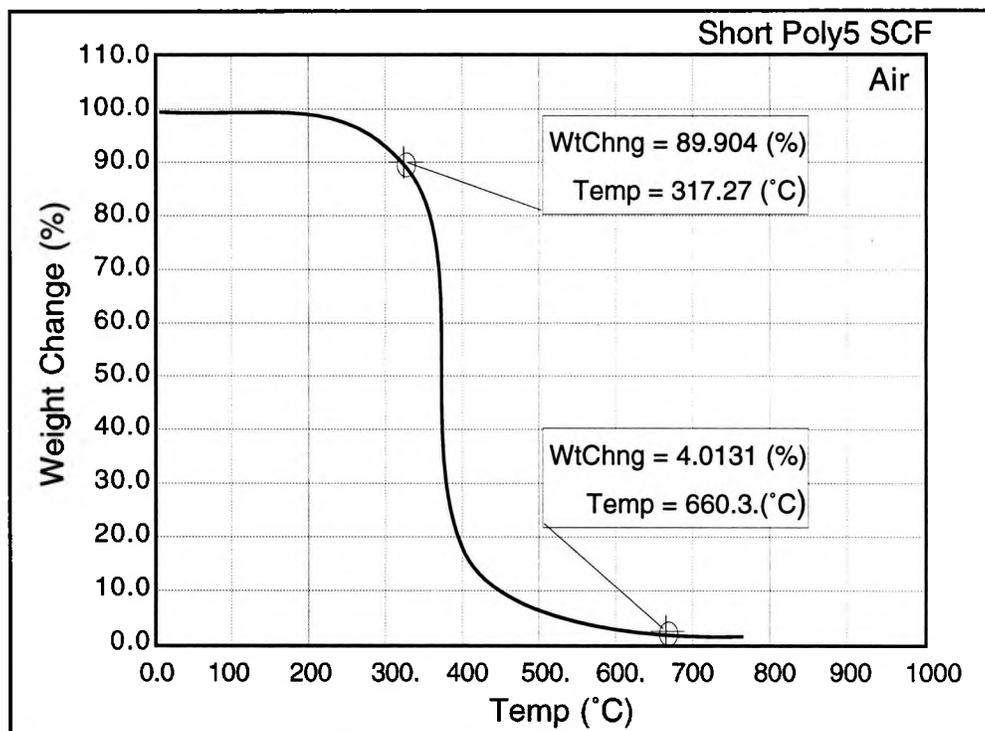
TGA #24. Ar (Compound XXIIIp-s)



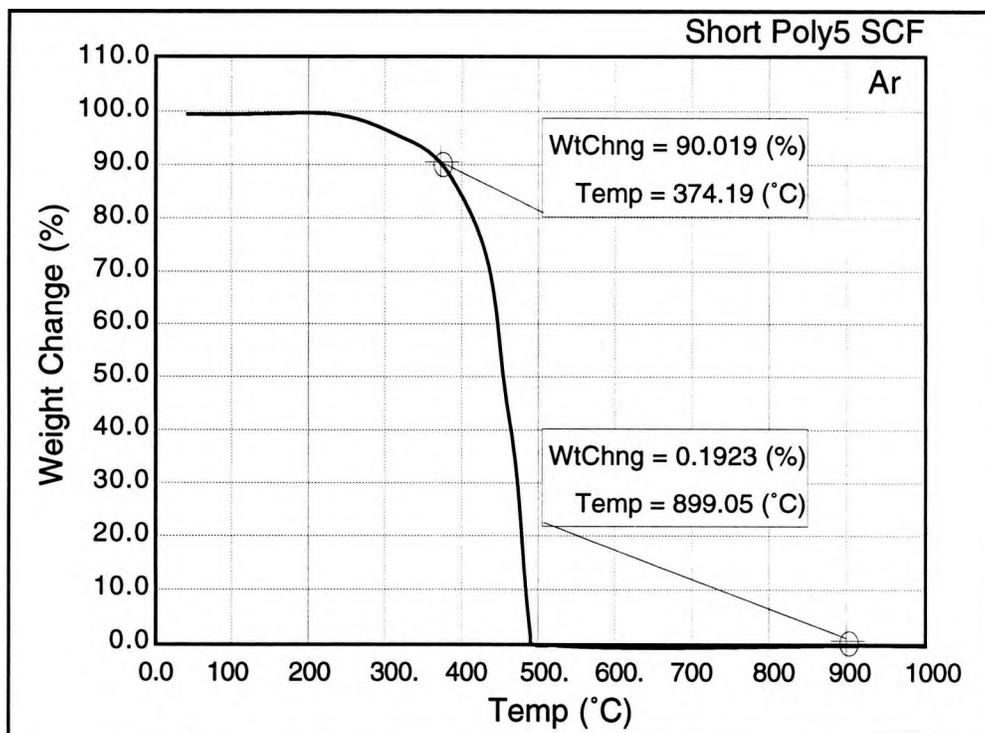
TGA #25. Air (Compound XXIVp-s)



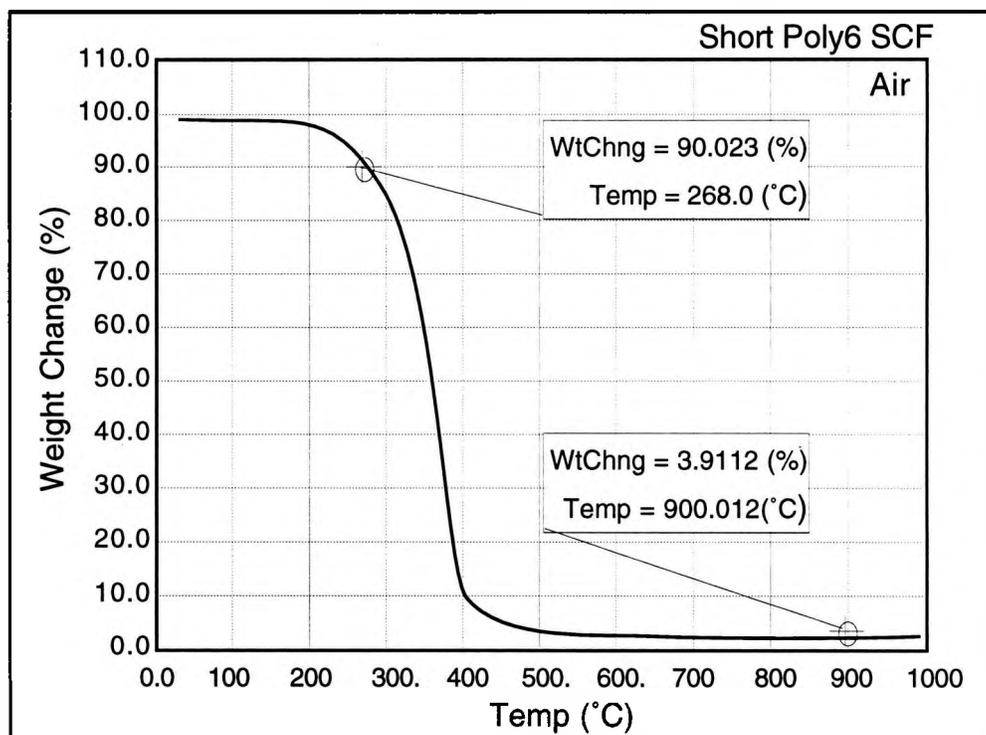
TGA #26. Ar (Compound XXIVp-s)



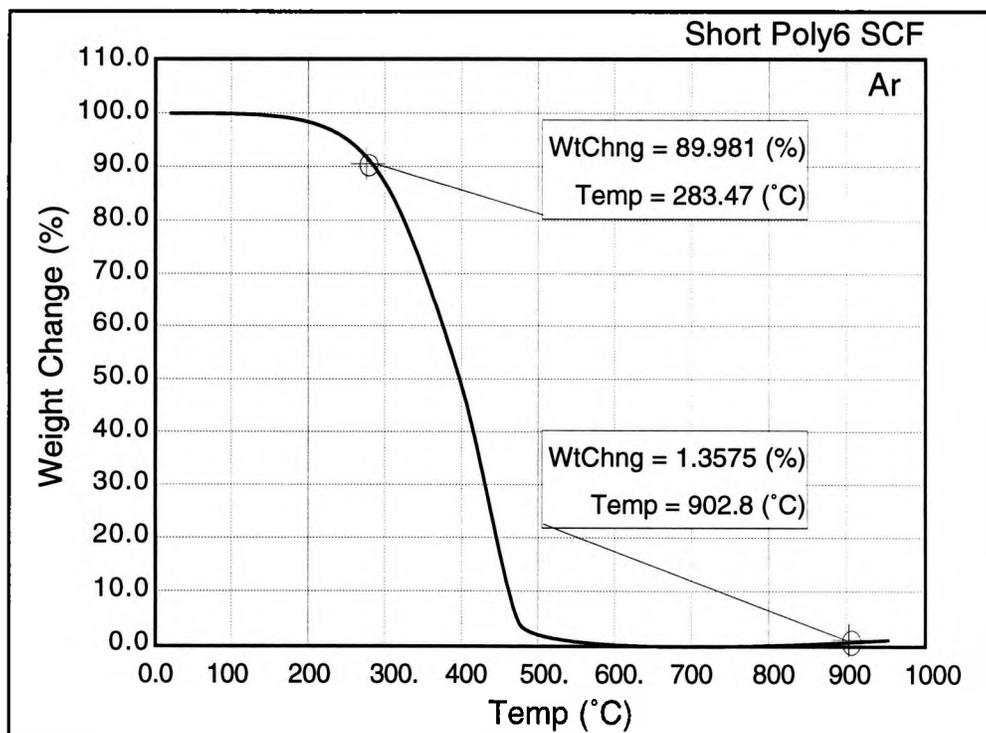
TGA #27. Air (Compound XXVp-s)



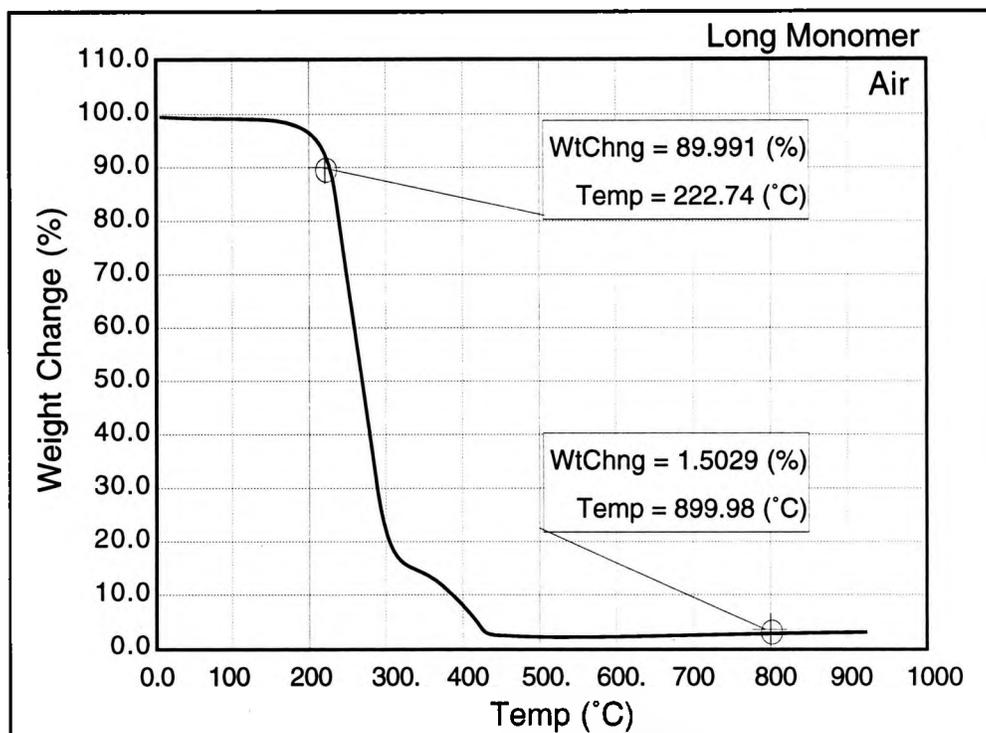
TGA #28. Ar (Compound XXVp-s)



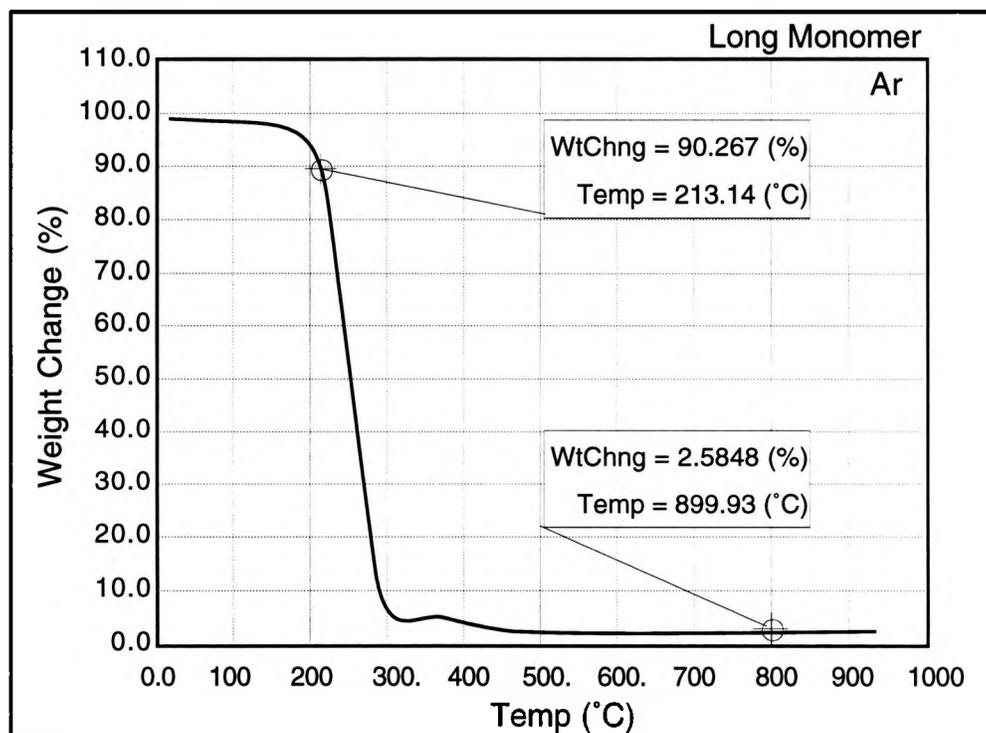
TGA #29. Air (Compound XXVIp-s)



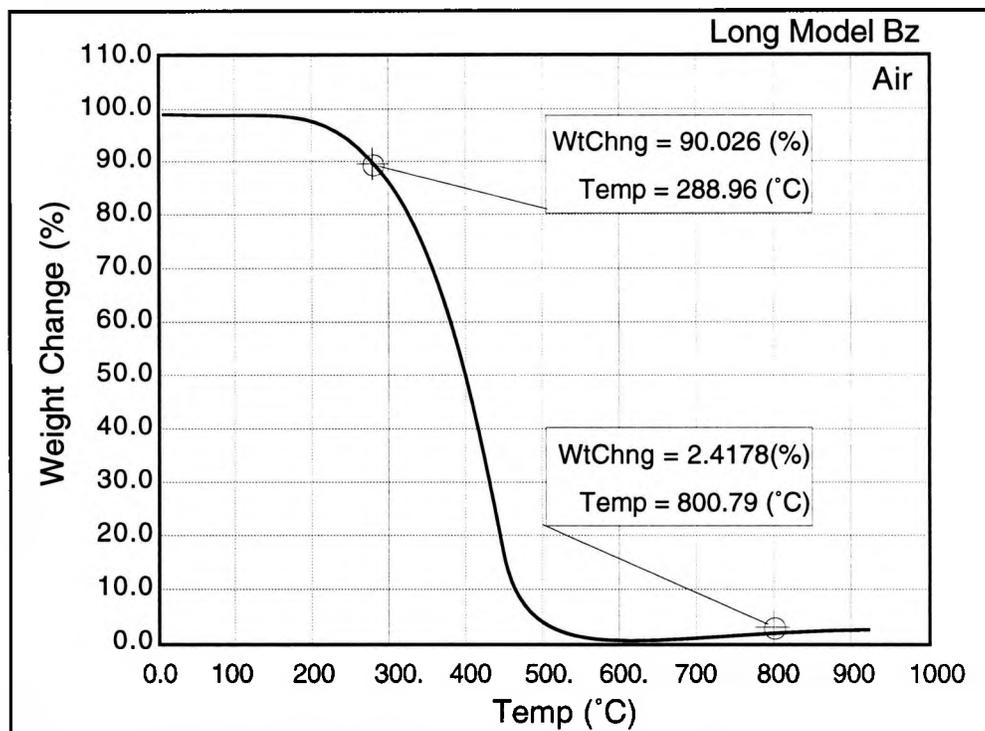
TGA #30. Ar (Compound XXVIp-s)



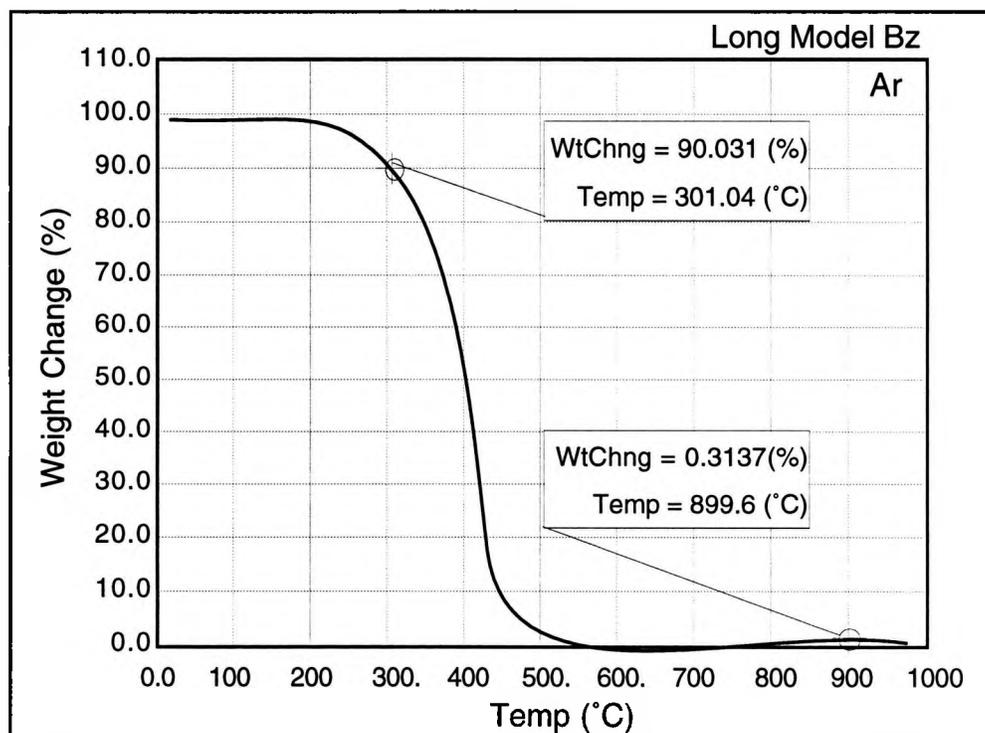
TGA #31. Air (Decenyl monomer), (Compound XI)



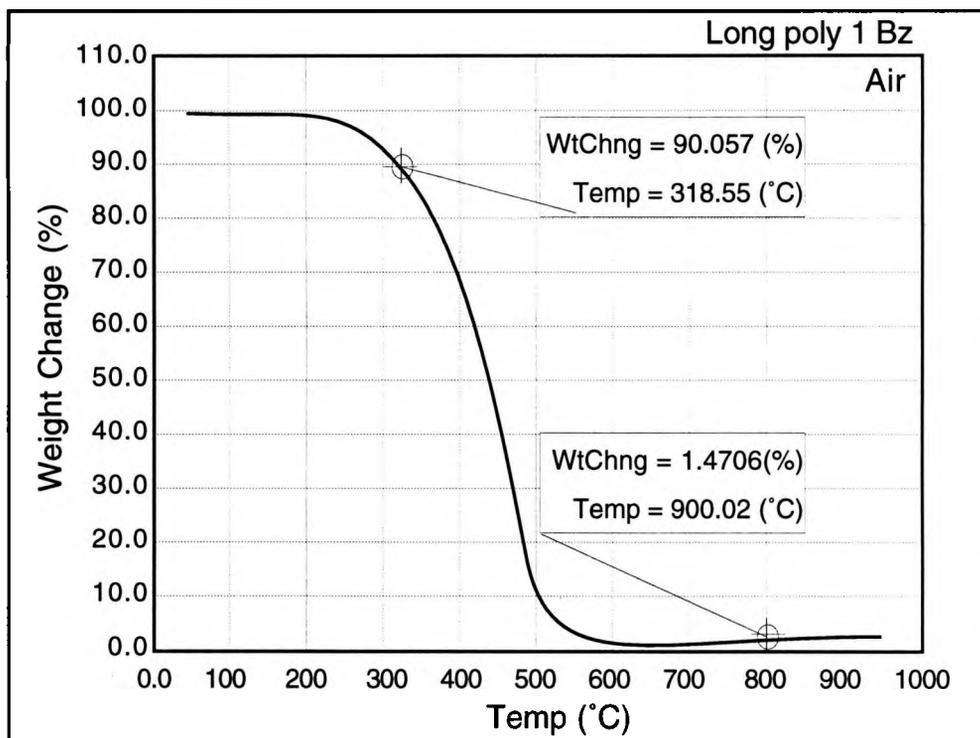
TGA #32. Ar (Decenyl monomer), (Compound XI)



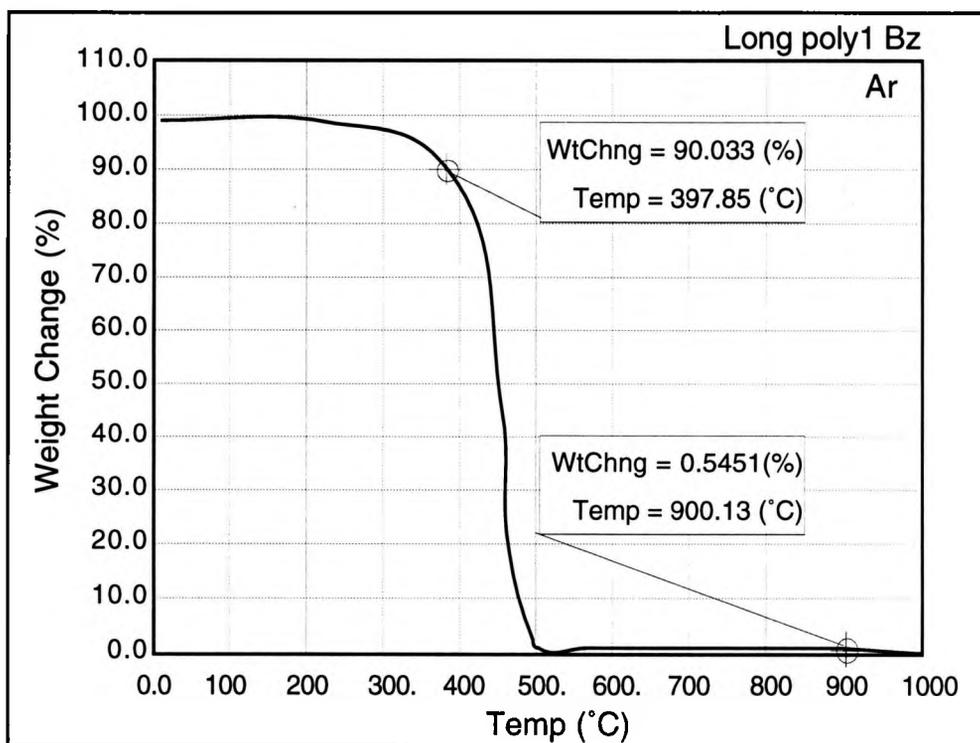
TGA #33. Air (Decenyl Model Hydrosilation in Benzene),
(Compound XIV-b)



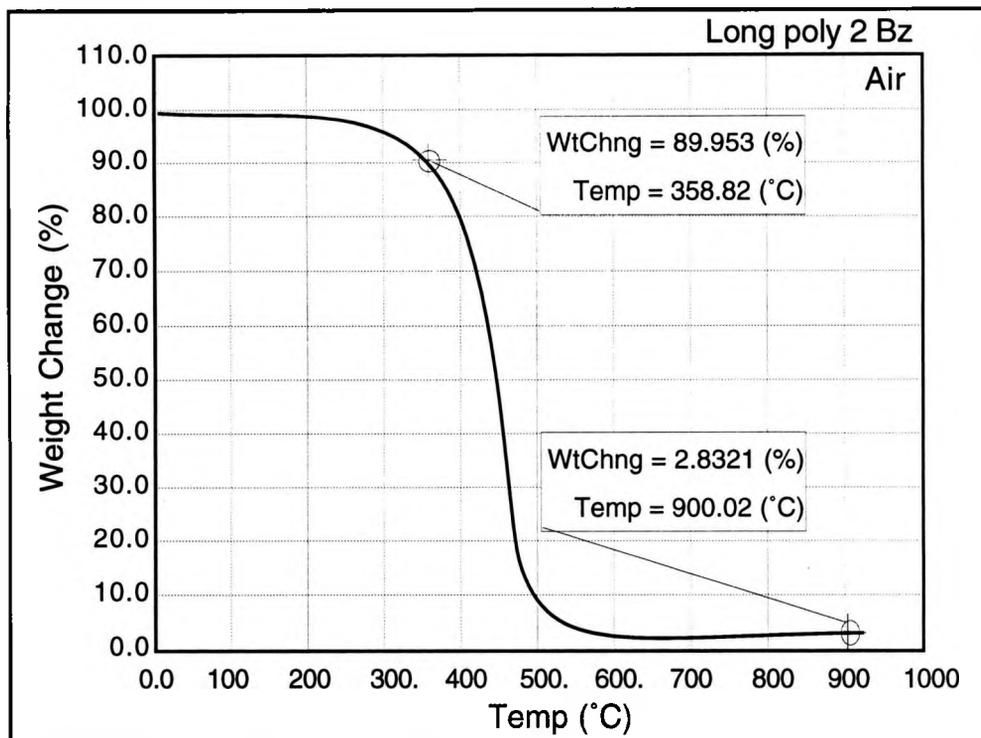
TGA #34. Ar (Decenyl Model Hydrosilation in Benzene),
(Compound XIV-b)



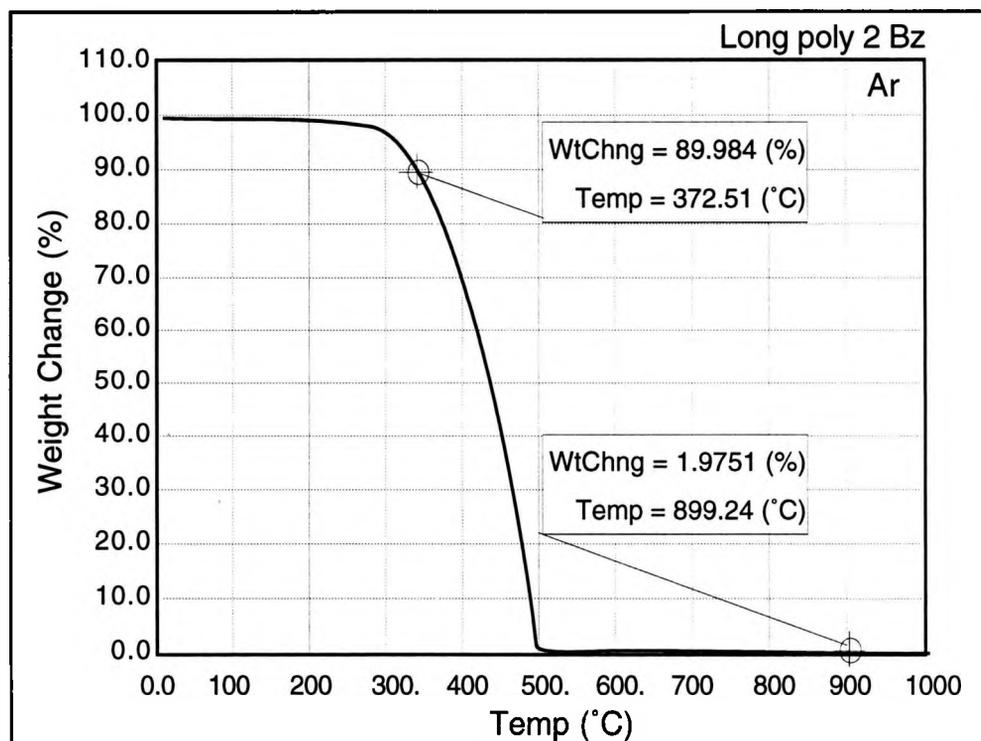
TGA #35. Air (Compound XXId-b)



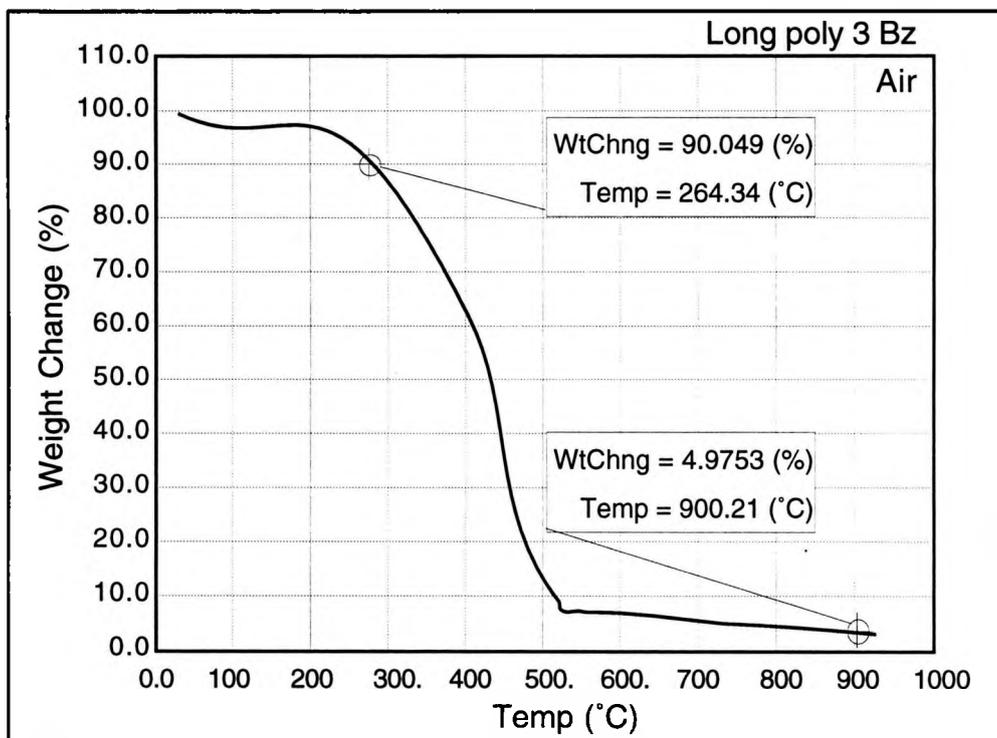
TGA #36. Ar (Compound XXId-b)



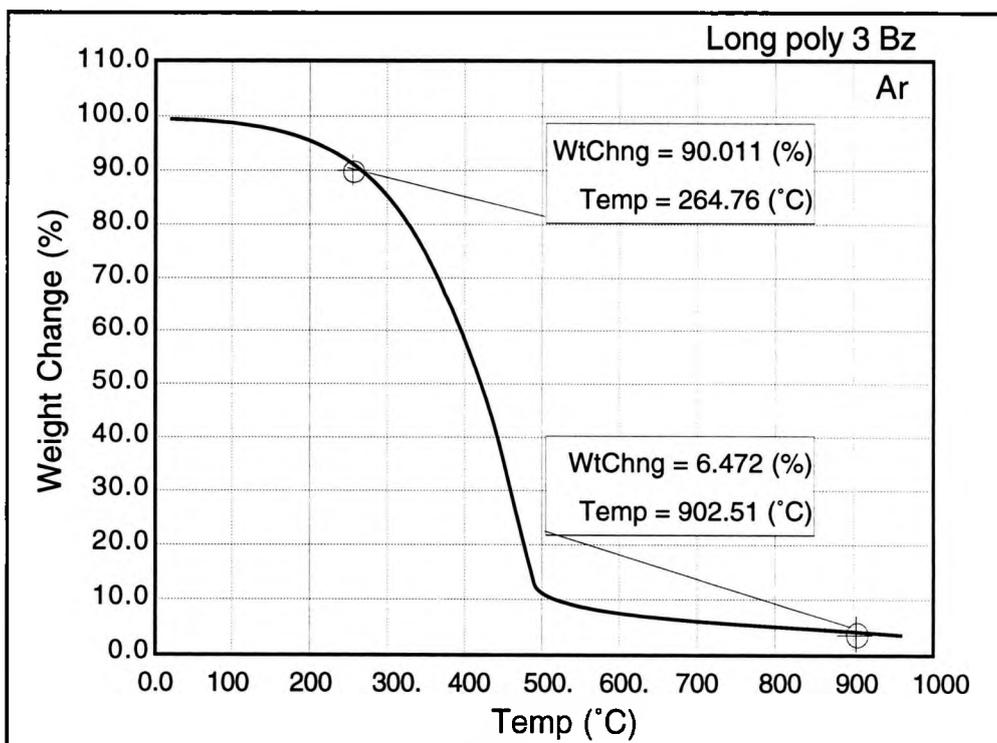
TGA #37. Air (Compound XXIIId-b)



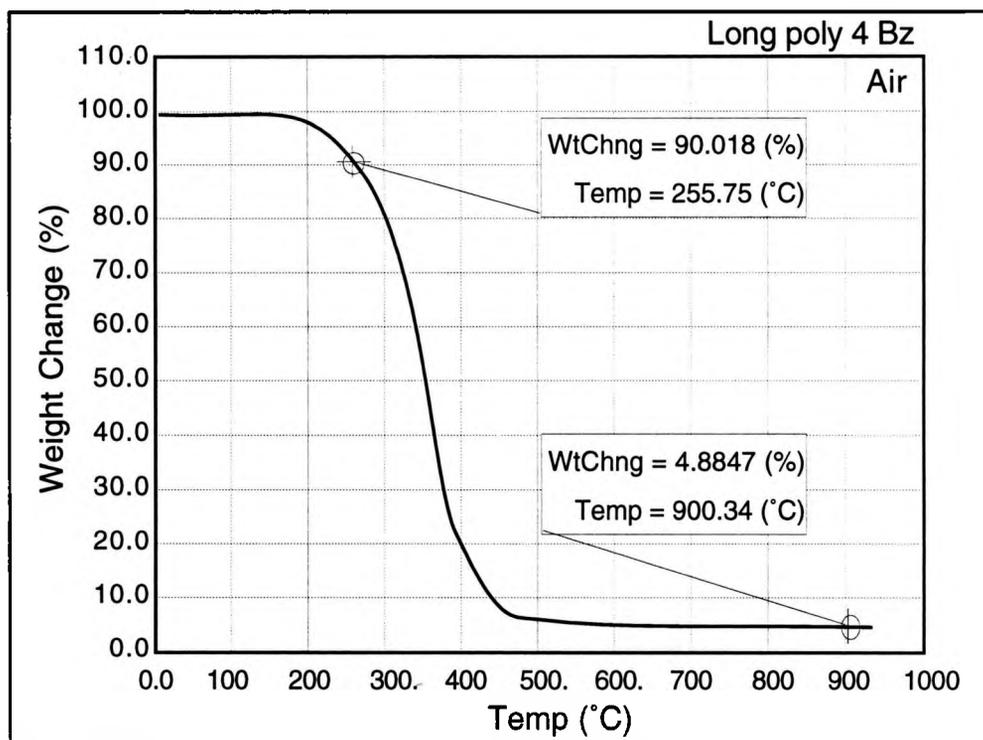
TGA #38. Ar (Compound XXIIId-b)



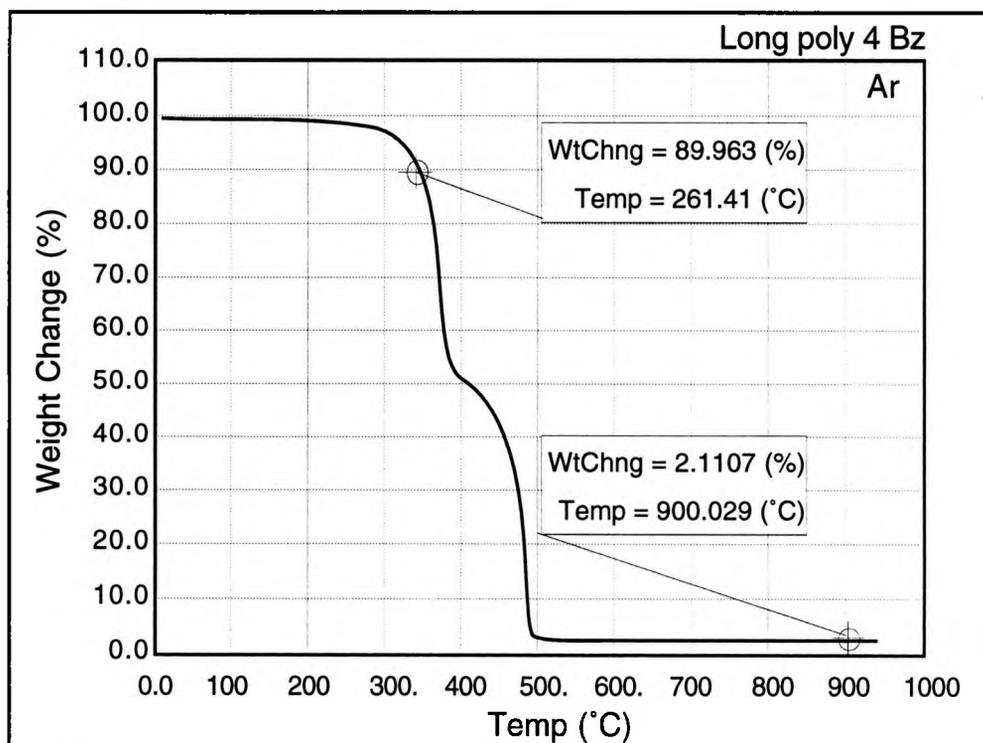
TGA #39. Air (Compound XXIIIId-b)



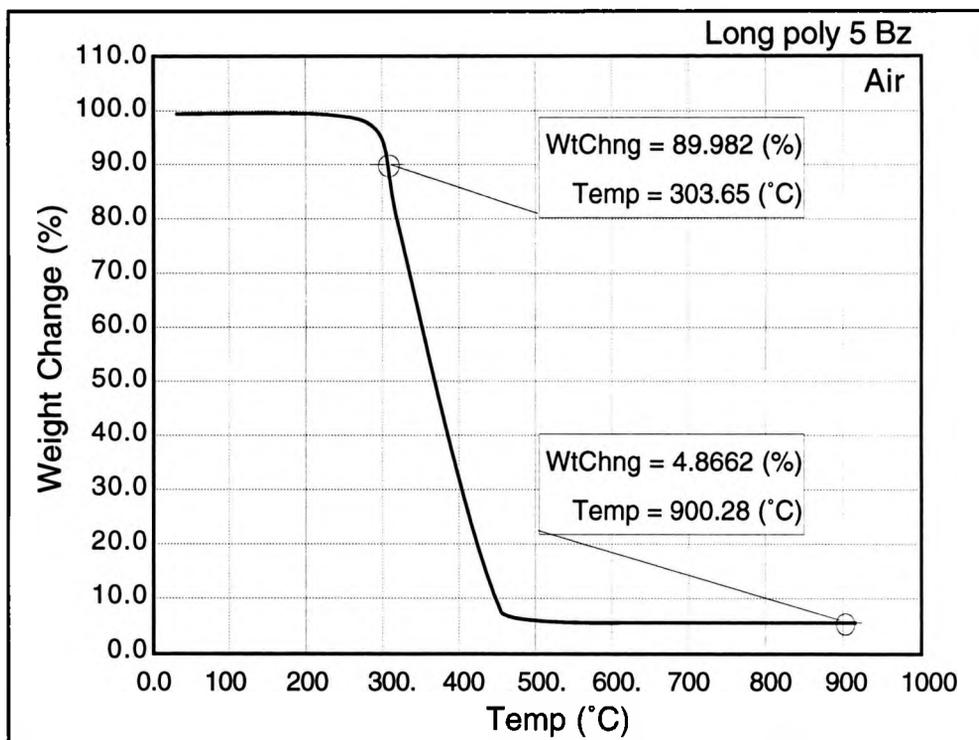
TGA #40. Ar (Compound XXIIIId-b)



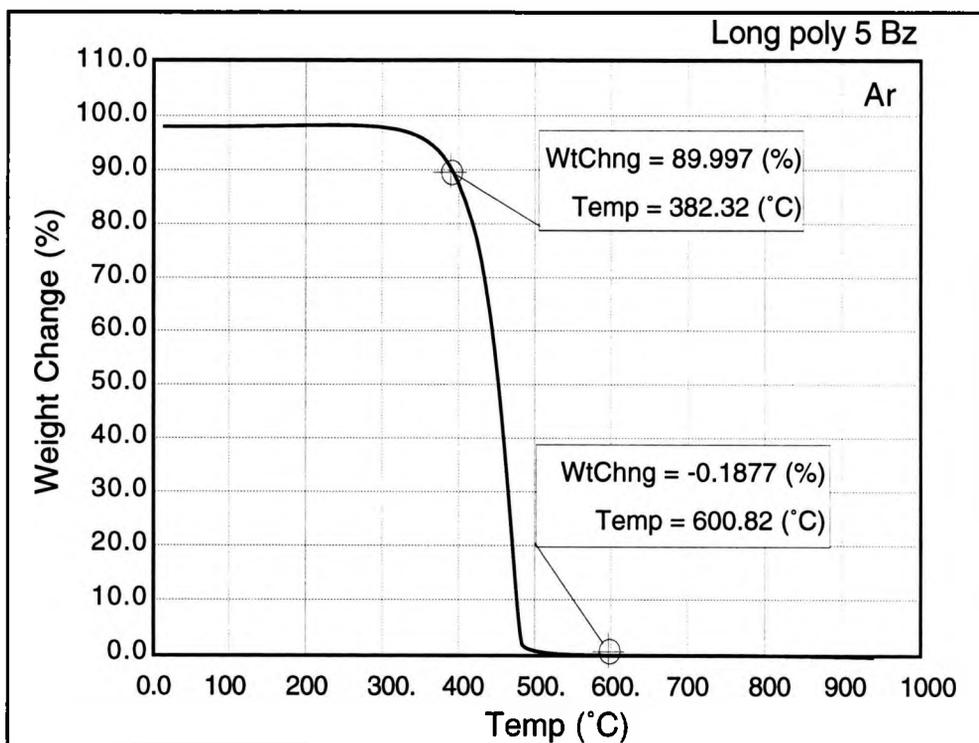
TGA #41. Air (Compound XXIVd-b)



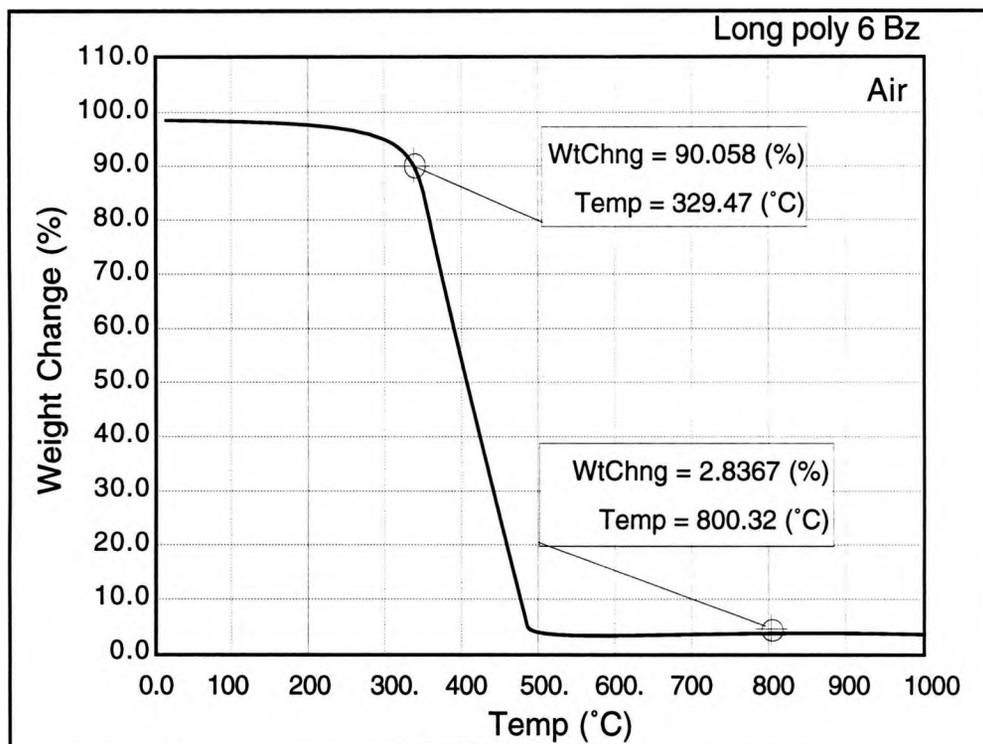
TGA #42. Ar (Compound XXIVd-b)



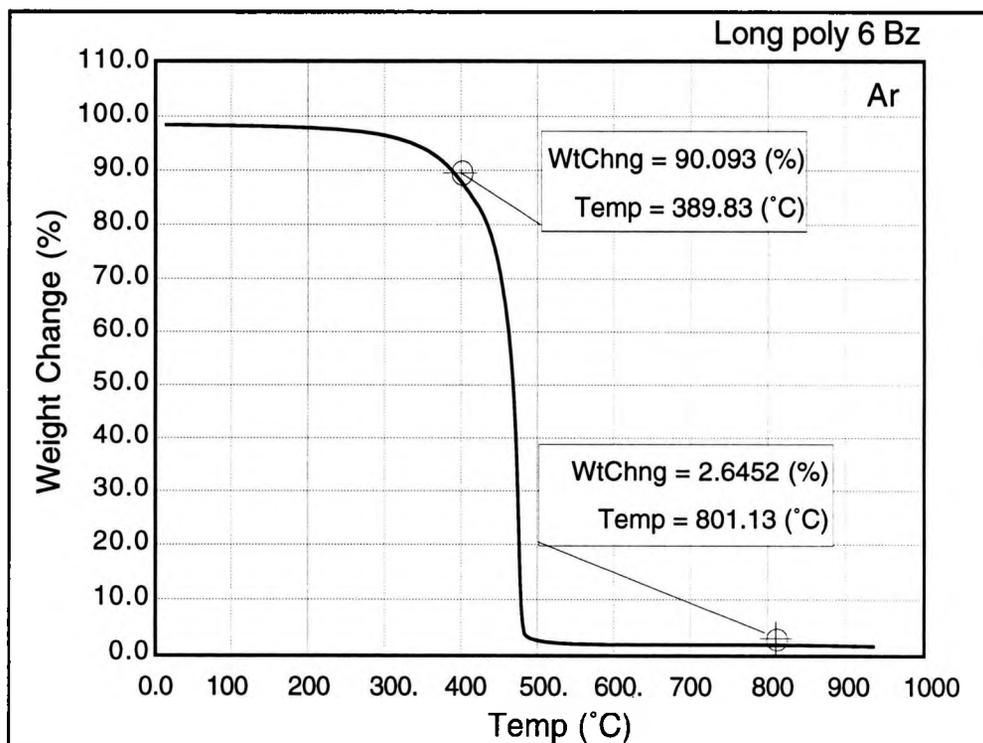
TGA #43. Air (Compound XXVd-b)



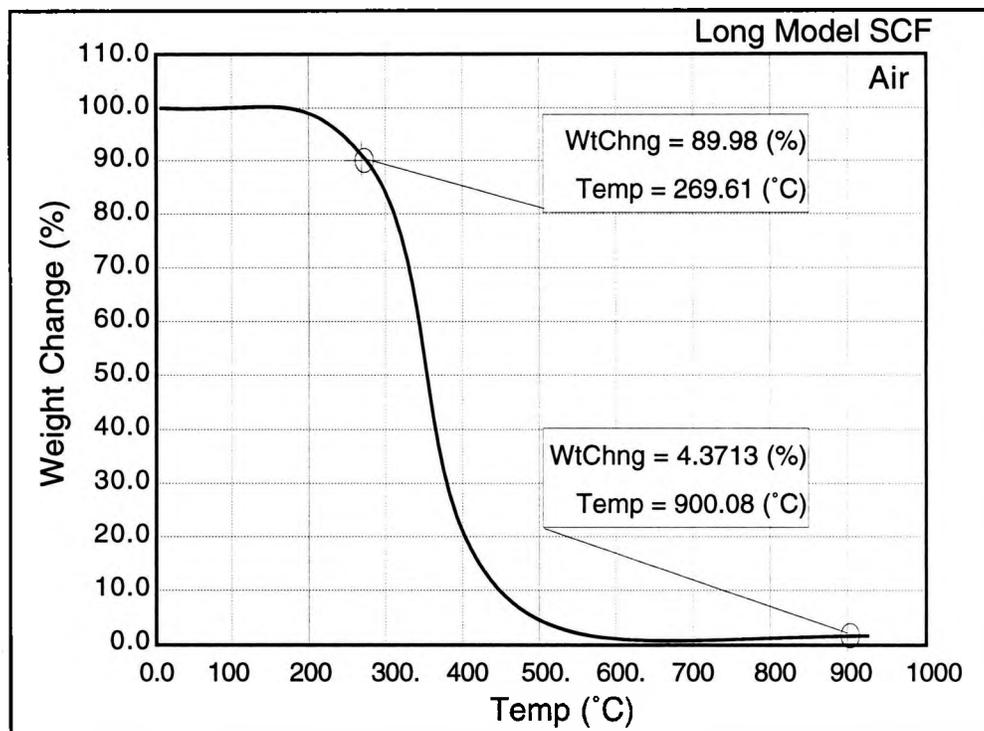
TGA #44. Ar (Compound XXVd-b)



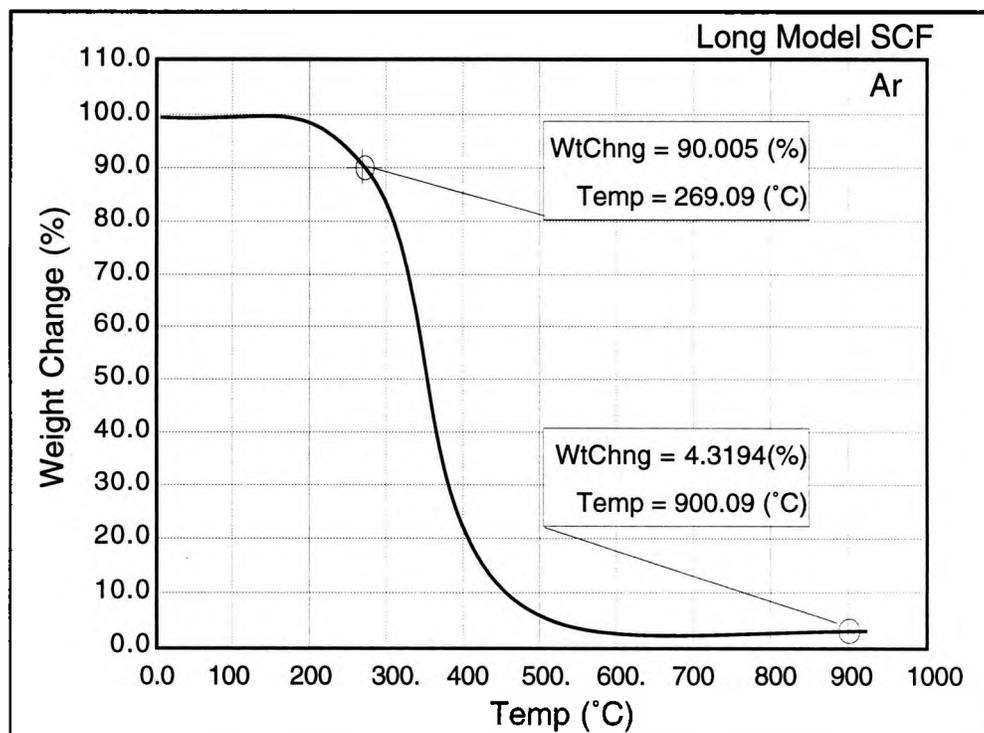
TGA #45. Air (Compound XXVIId-b)



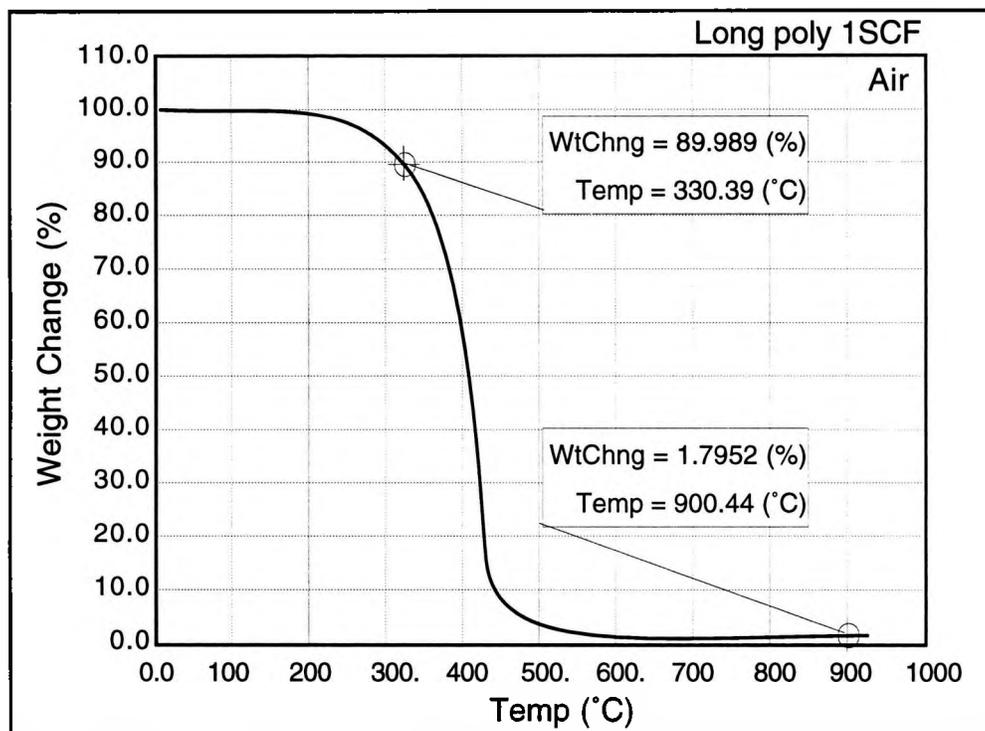
TGA #46. Ar (Compound XXVIId-b)



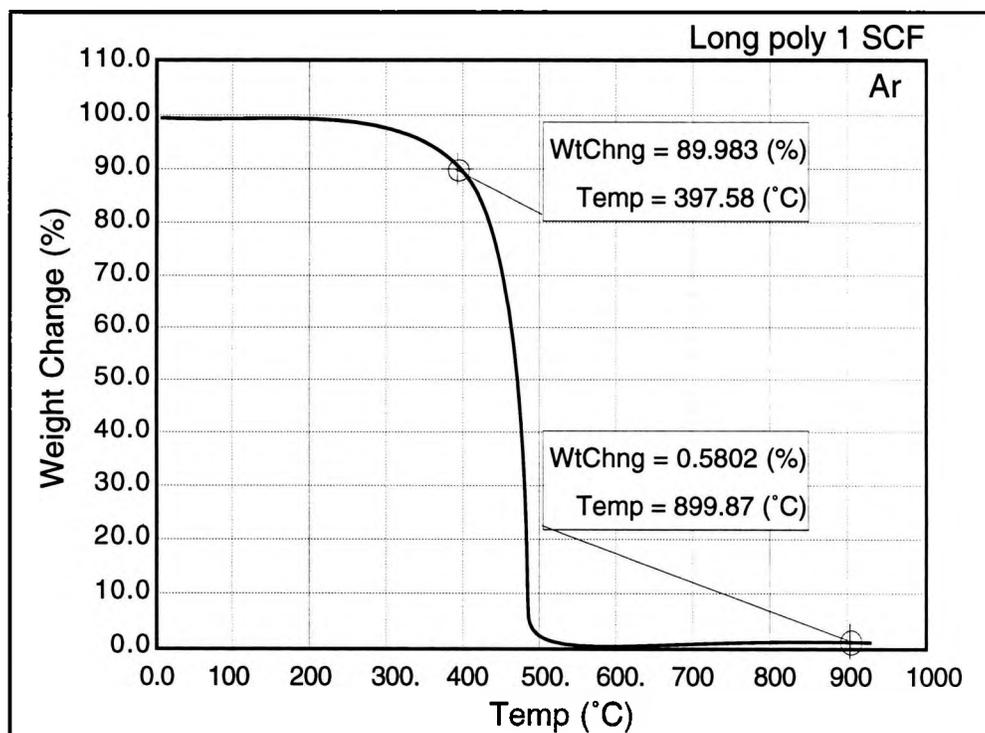
TGA #47. Air (Decenyl Model Hydrosilation in scCO₂),
(Compound XIV-s)



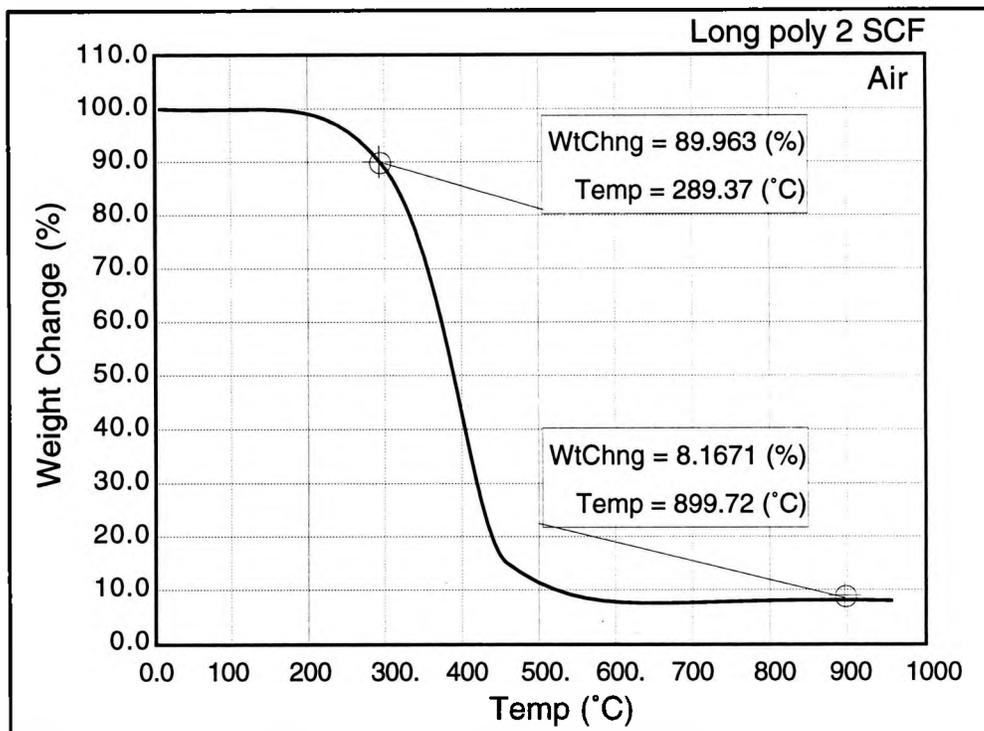
TGA #48. Ar (Decenyl Model Hydrosilation in scCO₂),
(Compound XIV-s)



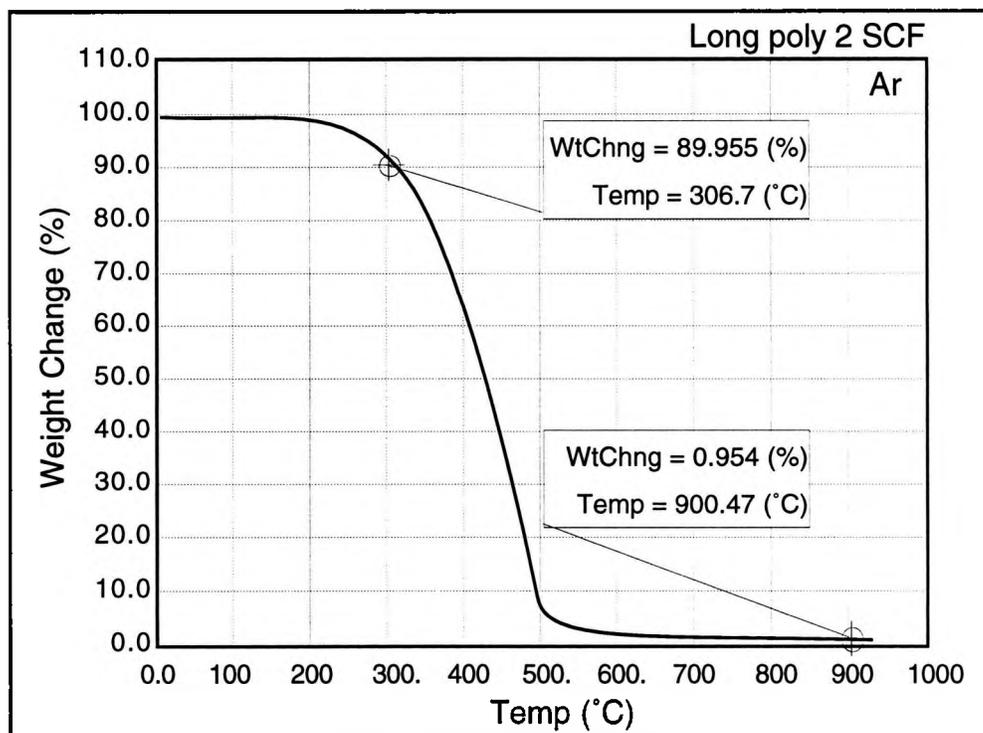
TGA #49. Air (Compound XXIId-s)



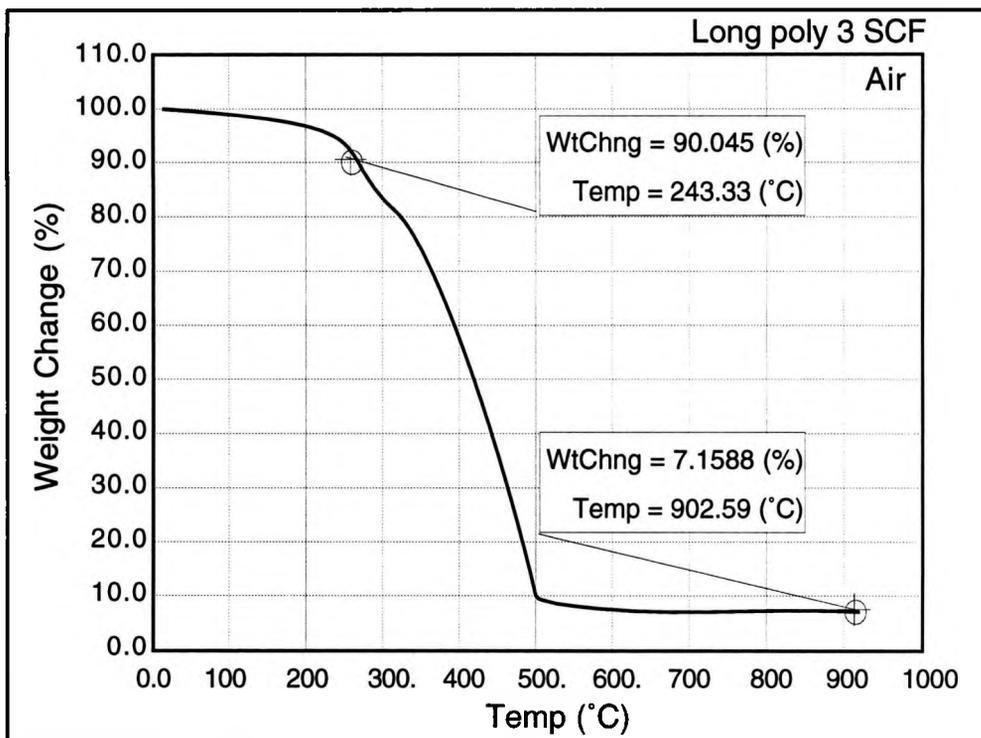
TGA #50. Ar (Compound XXIId-s)



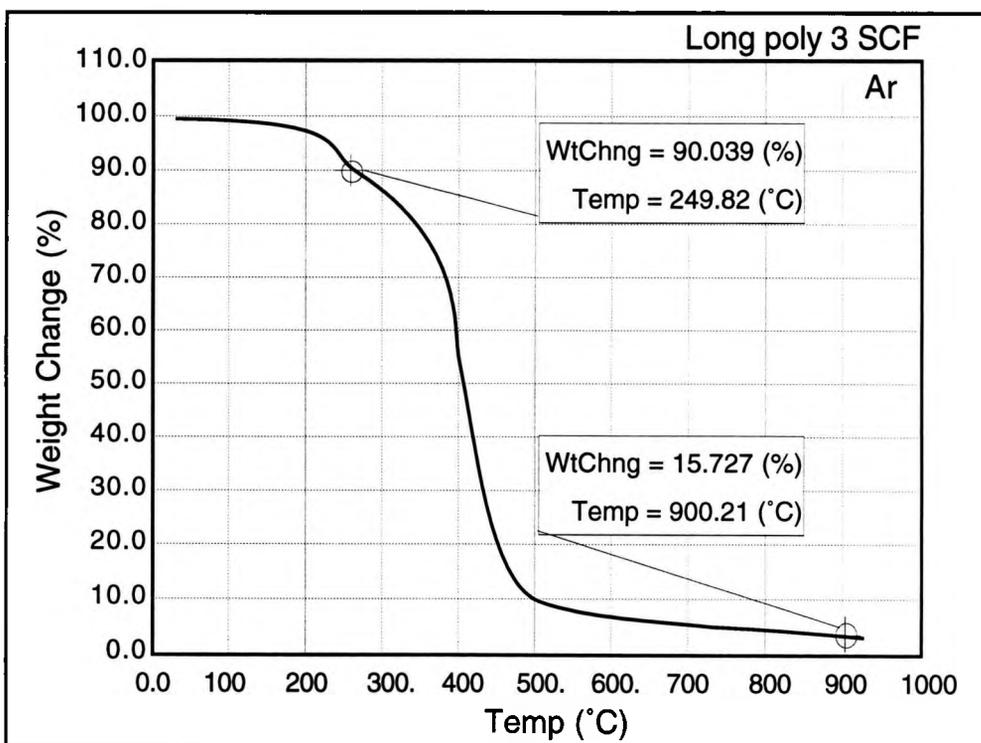
TGA #51. Air (Compound XXIIId-s)



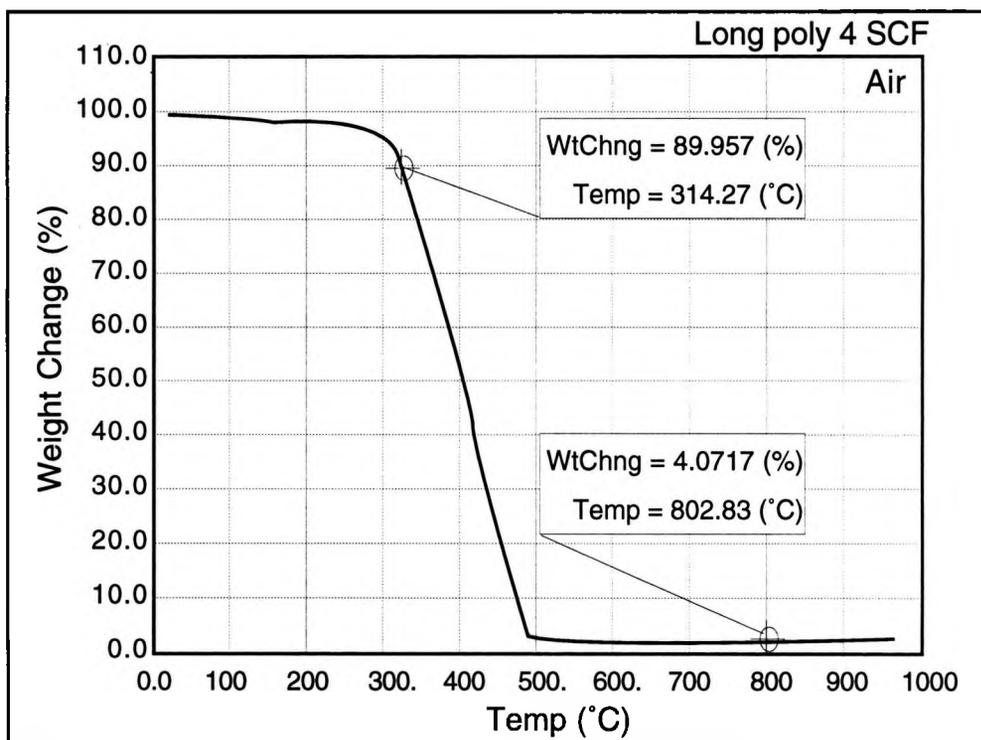
TGA #52. Ar (Compound XXIIId-s)



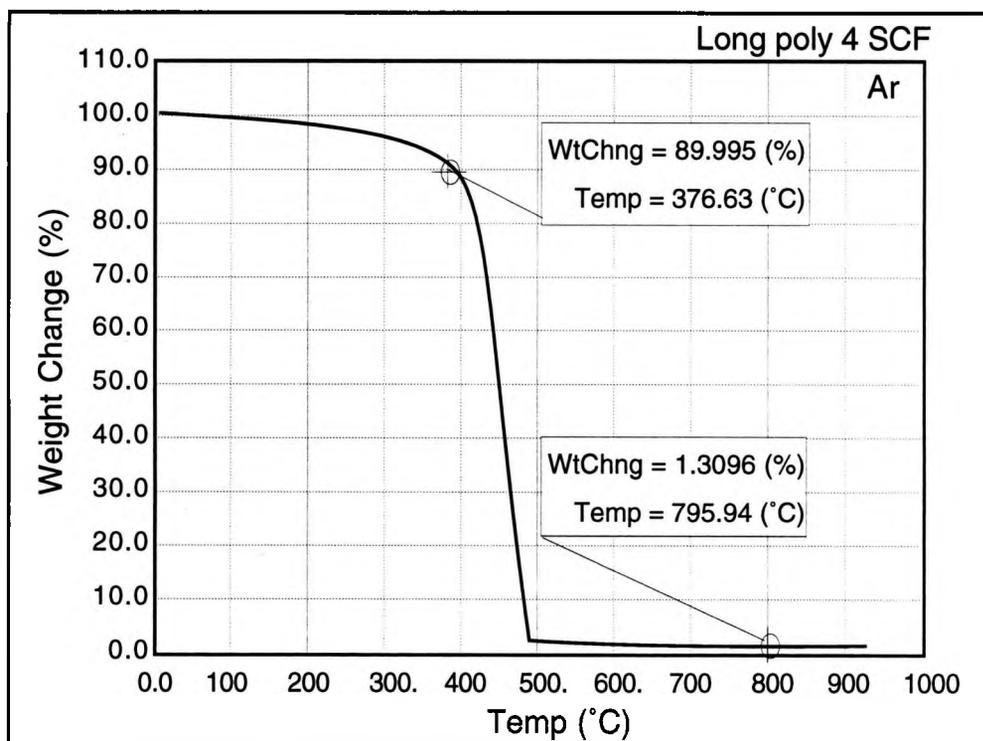
TGA #53. Air (Compound XXIIIId-s)



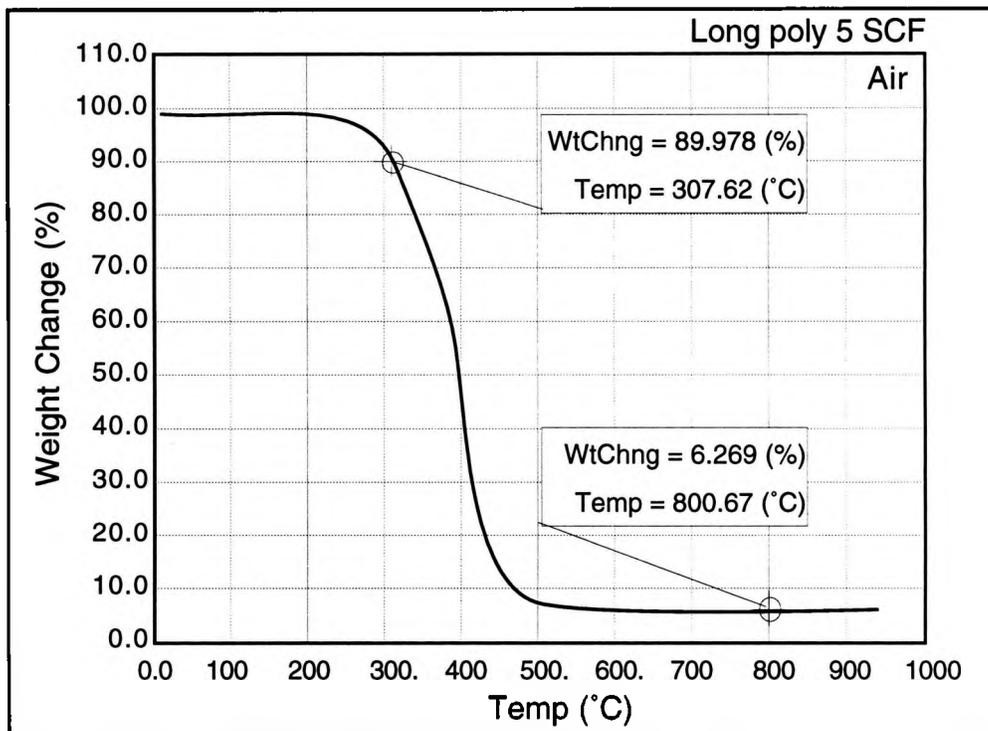
TGA #54. Ar (Compound XXIIIId-s)



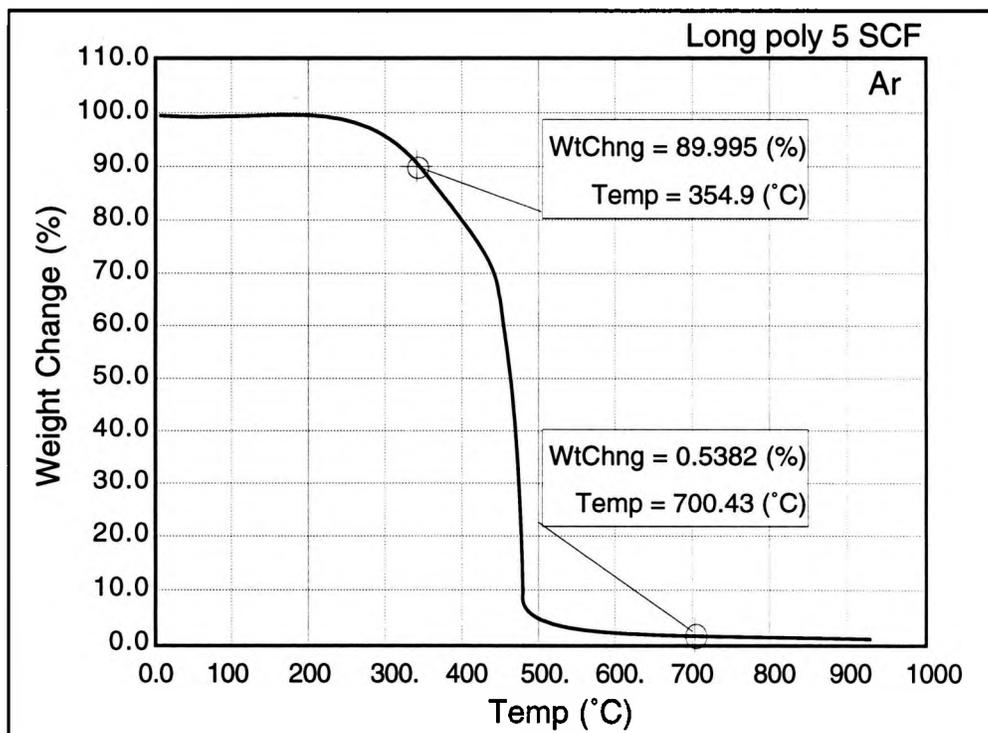
TGA #55. Air (Compound XXIVd-s)



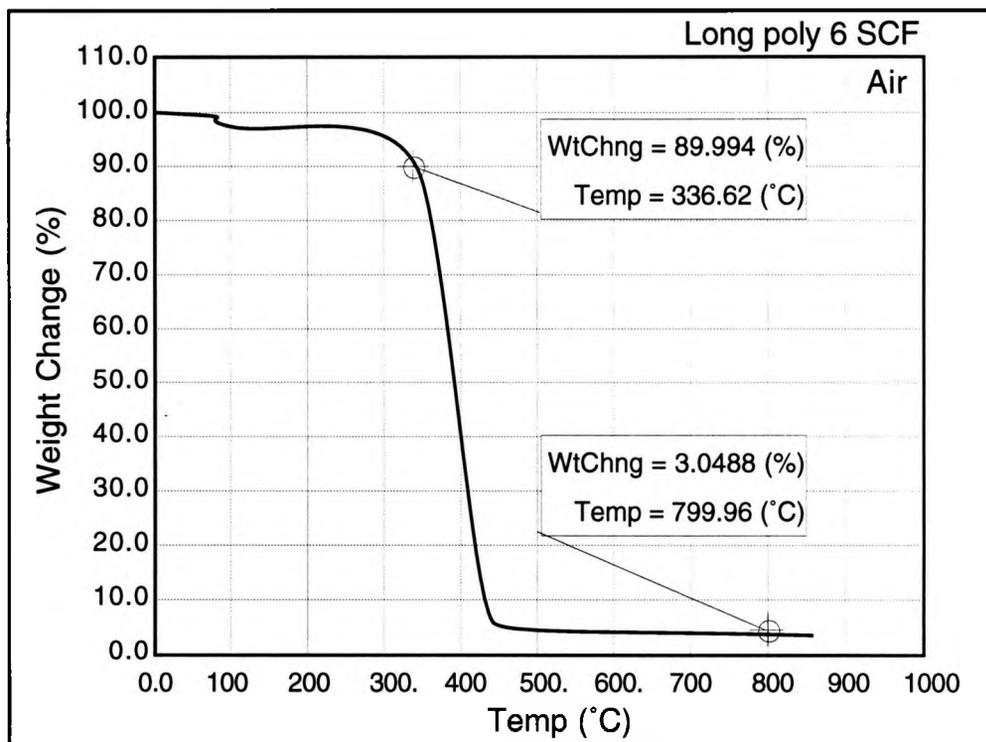
TGA #56. Ar (Compound XXIVd-s)



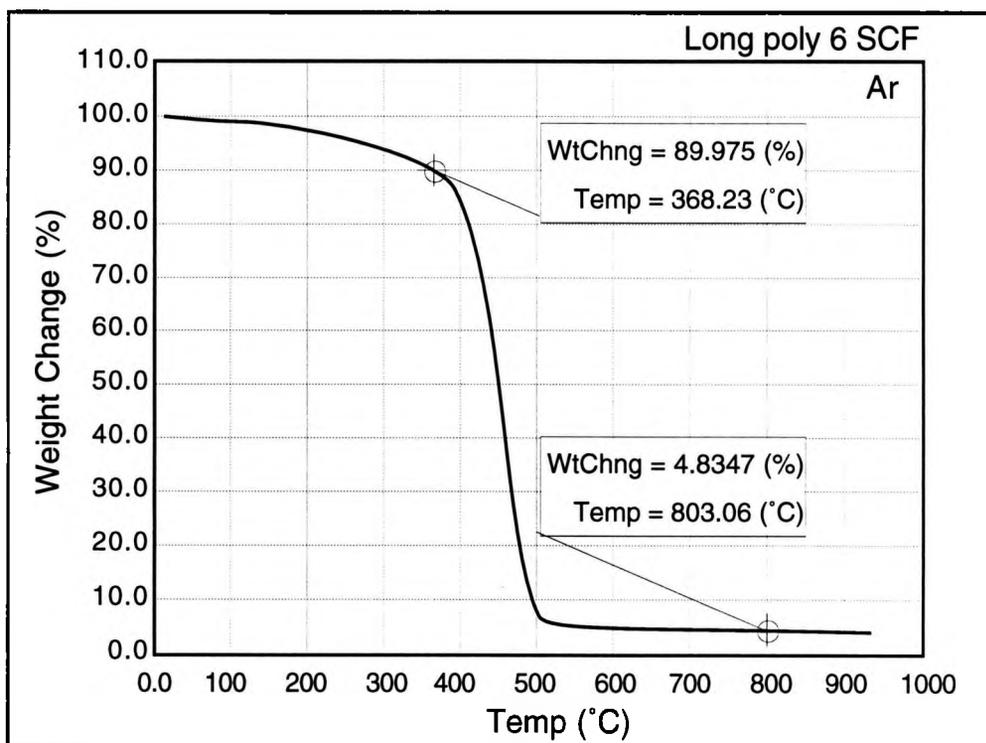
TGA #57. Air (Compound XXVd-s)



TGA #58. Ar (Compound XXVd-s)



TGA #59. Air (Compound XXVIId-s)



TGA #60. Ar (Compound XXVIId-s)

APPENDIX V
DSC

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Compound	DSC Number
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Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,4,4-Tetramethyldisilethylene; in Benzene, (Compound XXIp-b)	1
in ScCO ₂ , (Compound XXIp-s)	2
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,4-Bis(dimethylsilyl)benzene; in Benzene, (Compound XXIIp-b)	3
in ScCO ₂ , (Compound XXIIp-s)	4
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and Diphenyl-silane; in Benzene, (Compound XXIIIp-b)	5
in ScCO ₂ , (Compound XXIIIp-s)	6
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1,1,3,3-Tetramethyldisiloxane; in Benzene, (Compound XXIVp-b)	7
in ScCO ₂ , (Compound XXIVp-s)	8
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene	
<hr/>	

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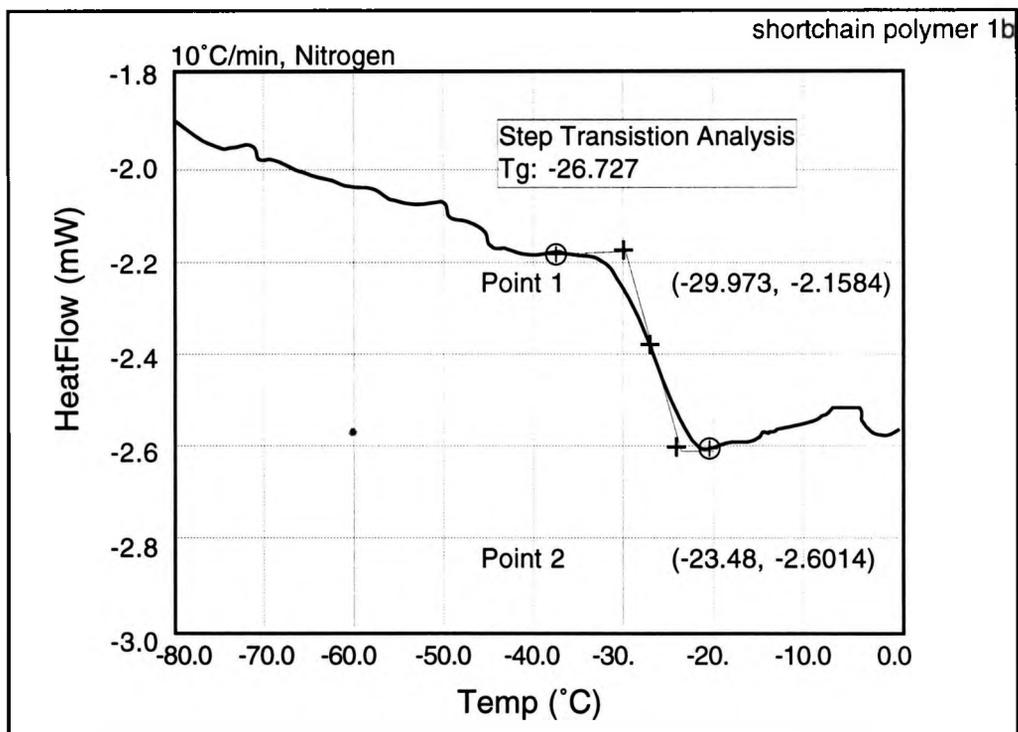
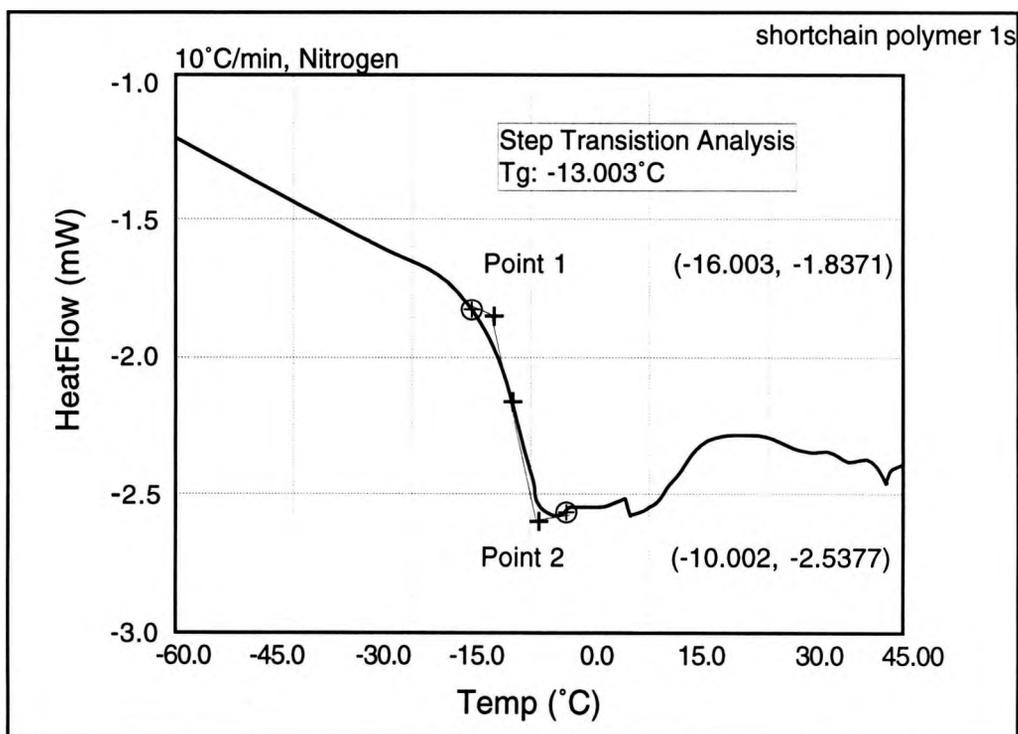
(continued)

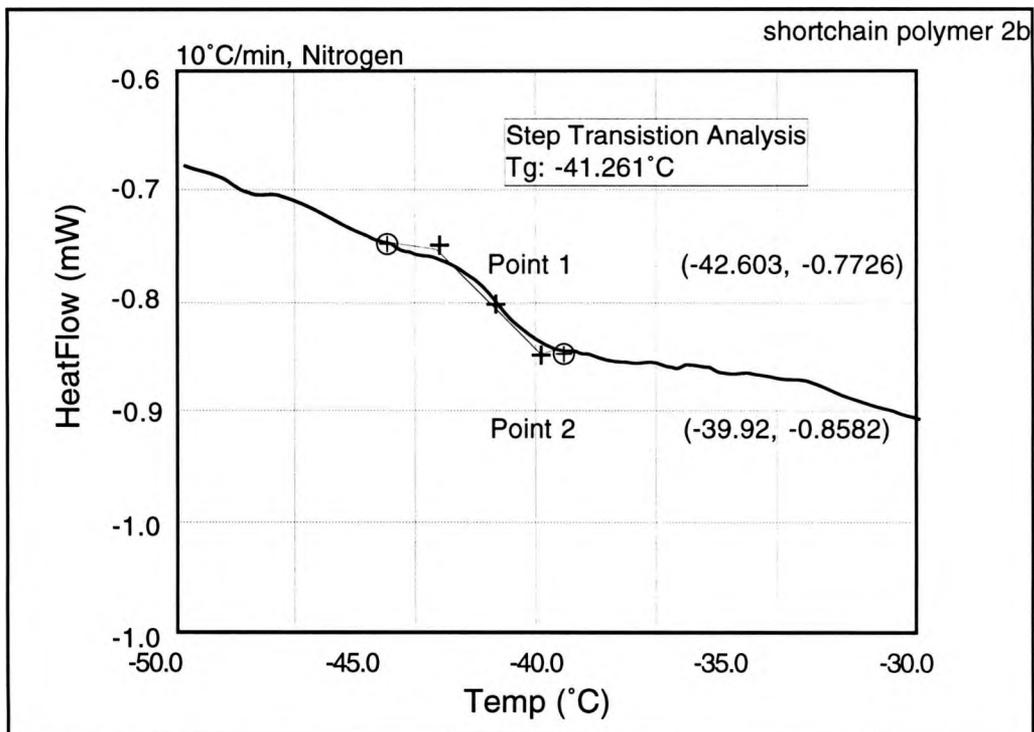
Compound	DSC Number
and 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane; in Benzene, (Compound XXVp-b)	9
in ScCO ₂ , (Compound XXVp-s)	10
Polymer derived from the reaction of 1,3-Bis(hexafluoro-2-propenyloxy-2-propyl) Benzene and 1-2-Bis(tetramethyldisiloxaneyl)ethane; in Benzene, (Compound XXVIp-b)	11
in ScCO ₂ , (Compound XXVIp-s)	12
Polymer derived from the reaction of 1,3-bis [hexafluoro-2-(9-decenyloxy-2-propyl)] benzene and 1,1,4,4-Tetramethyldisilethylene; in Benzene, (Compound XXId-b)	13
in ScCO ₂ , (Compound XXId-s)	14
Polymer derived from the reaction of 1,3-bis [hexafluoro-2-(9-decenyloxy-2-propyl)] benzene and 1,4-Bis(dimethylsilyl)benzene-silane; in Benzene, (Compound XXIIId-b)	15
in ScCO ₂ , (Compound XXIIId-s)	16
Polymer derived from the reaction of 1,3-bis [hexafluoro-2-(9-decenyloxy-2-propyl)] benzene and Diphenyl-silane; in Benzene, (Compound XXIIIId-b)	17
in ScCO ₂ , (Compound XXIIIId-s)	18

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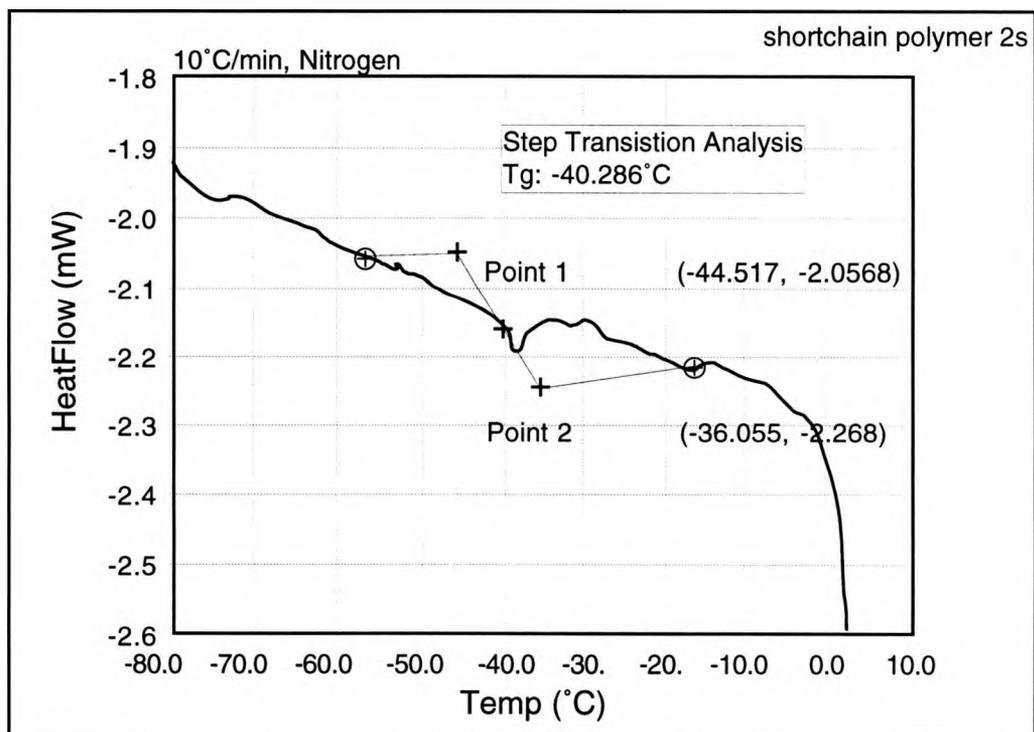
(continued)

Compound	DSC Number
<hr/>	
Polymer derived from the reaction of 1,3-bis [hexafluoro-2-(9-decenyloxy-2-propyl)] benzene and 1,1,3,3-Tetramethyldisiloxane;	
in Benzene, (Compound XXIVd-b)	19
in ScCO ₂ , (Compound XXIVd-s)	20
Polymer derived from the reaction of 1,3-bis [hexafluoro-2-(9-decenyloxy-2-propyl)] benzene and 1,1,3,3,5,5,7,7 tetramethyl disiloxane;	
in Benzene, (Compound XXVd-b)	21
in ScCO ₂ , (Compound XXVd-s)	22
Polymer derived from the reaction of 1,3-bis [hexafluoro-2-(9-decenyloxy-2-propyl)] benzene and 1-2-Bis(tetramethyldisiloxaneyl)ethane;	
in Benzene, (Compound XXVIId-b)	23
in ScCO ₂ , (Compound XXVIId-s)	24
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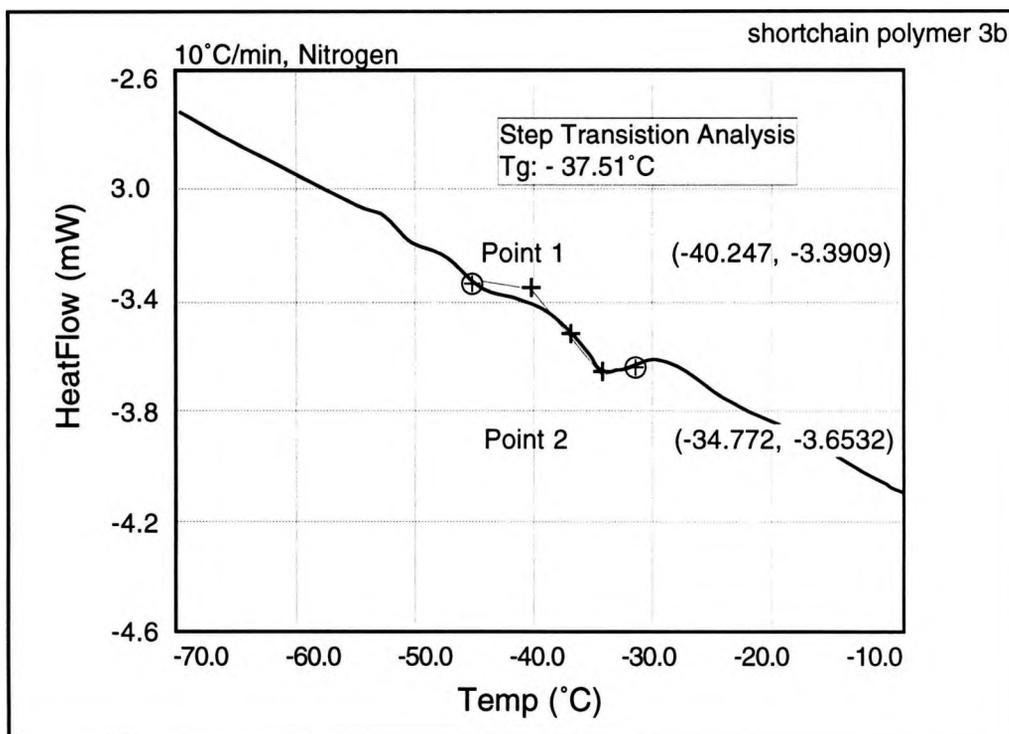
**DSC #1. (Compound XXI**p**-b)****DSC #2. (Compound XXI**p**-s)**



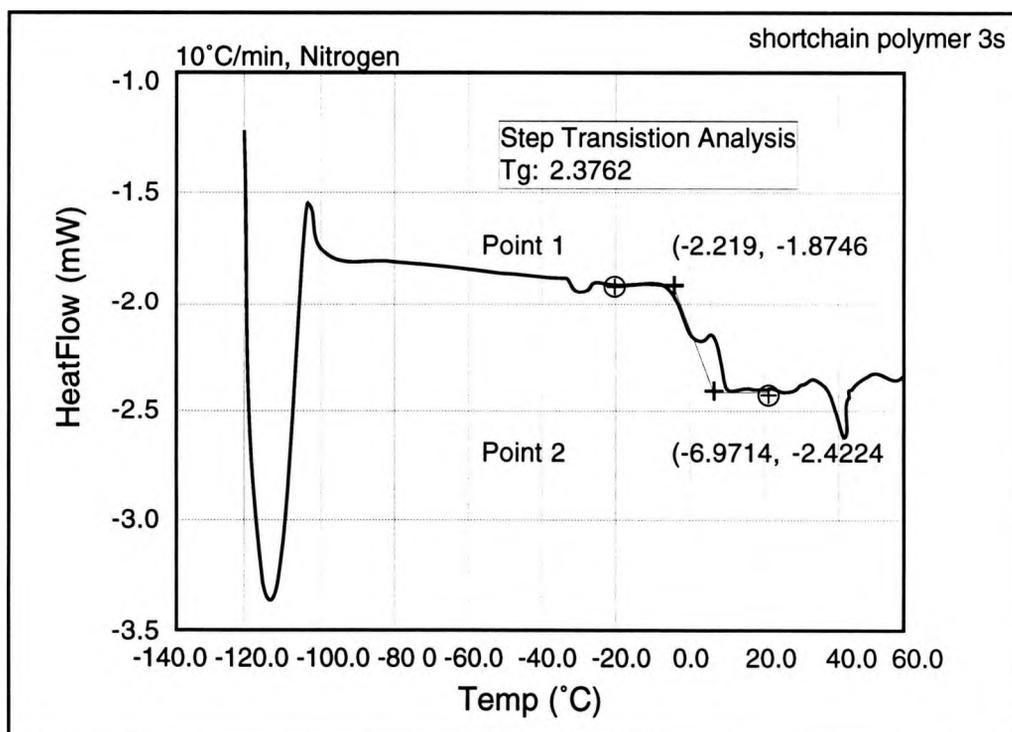
DSC #3. (Compound **XXIIp-b**)



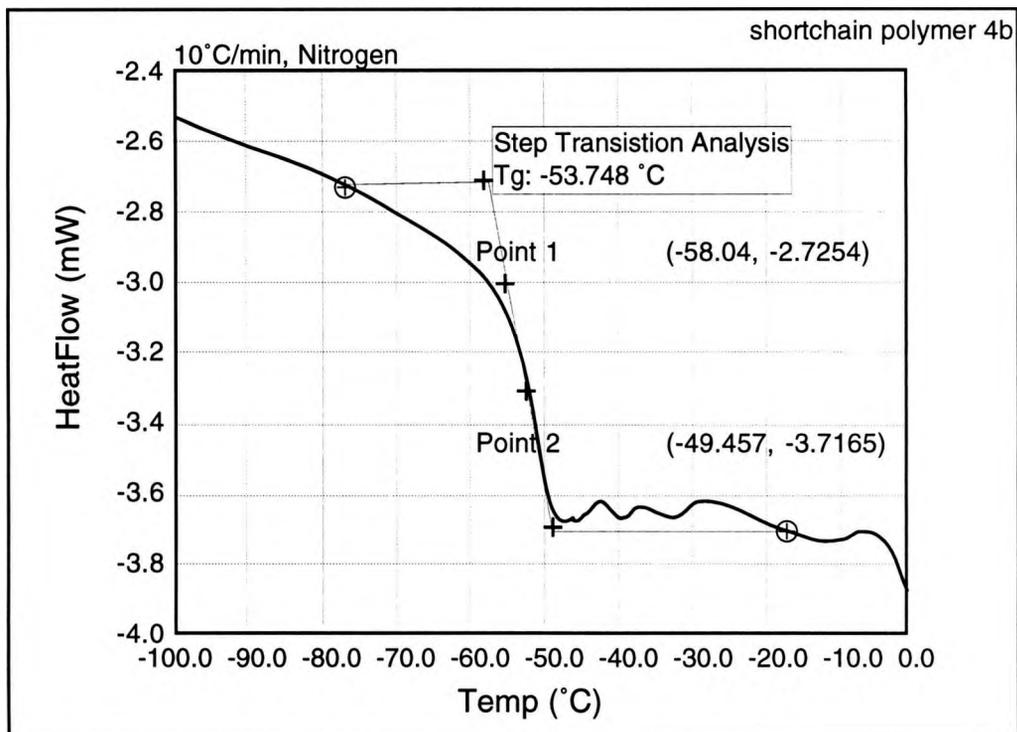
DSC #4. (Compound **XXIIp-s**)



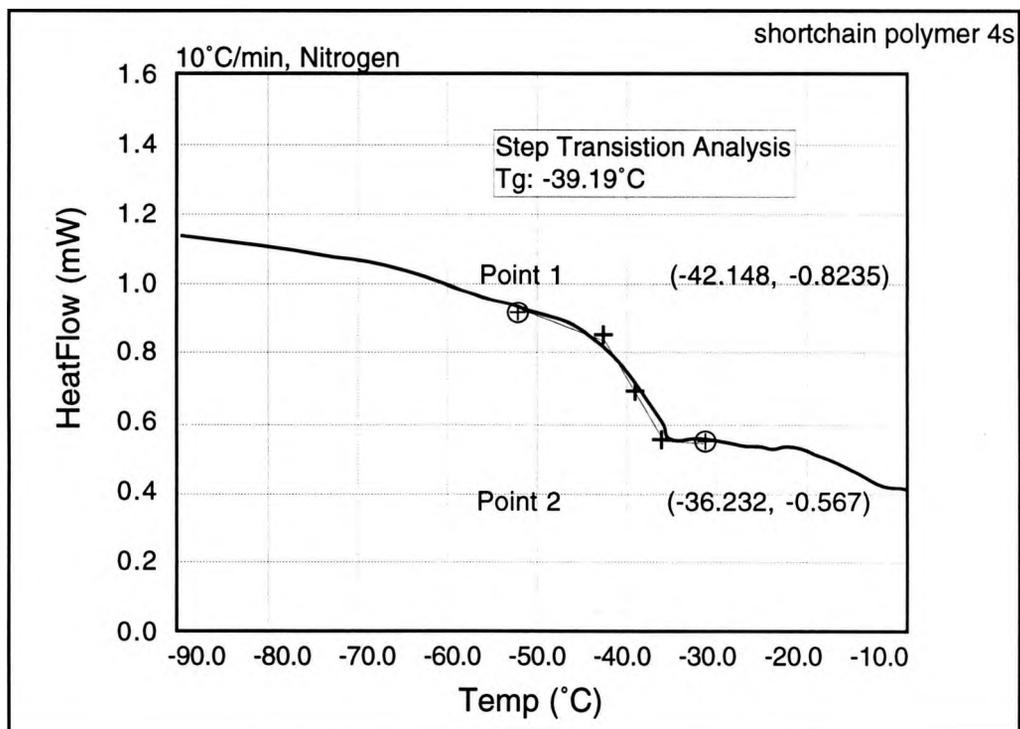
DSC #5. (Compound **XXIIIp-b**)



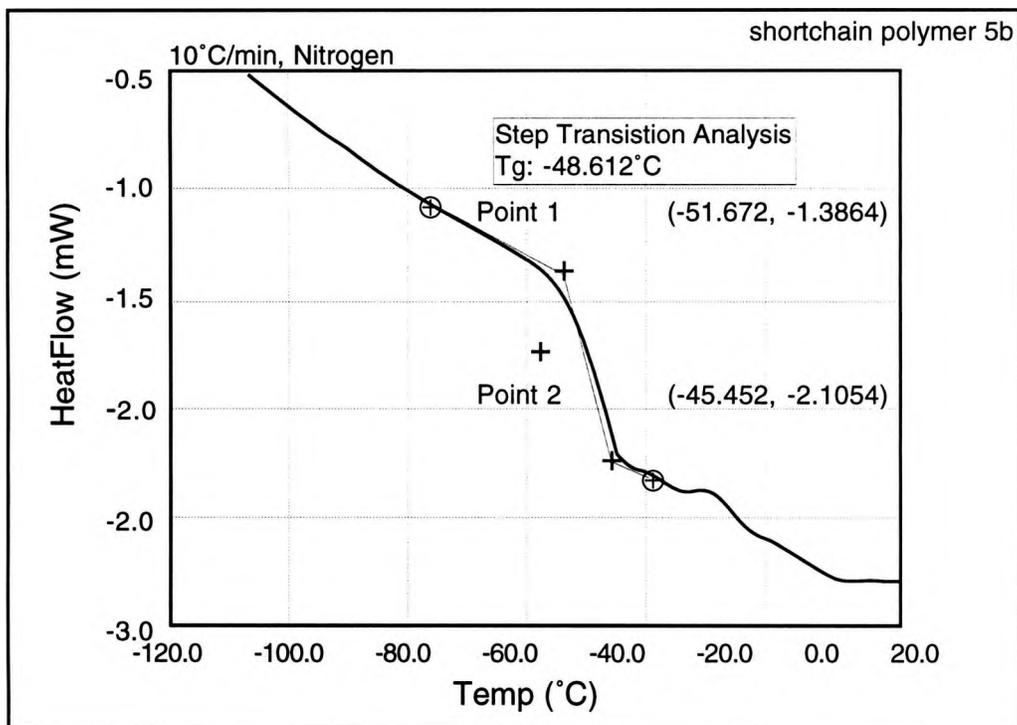
DSC #6. (Compound **XXIIIp-s**)



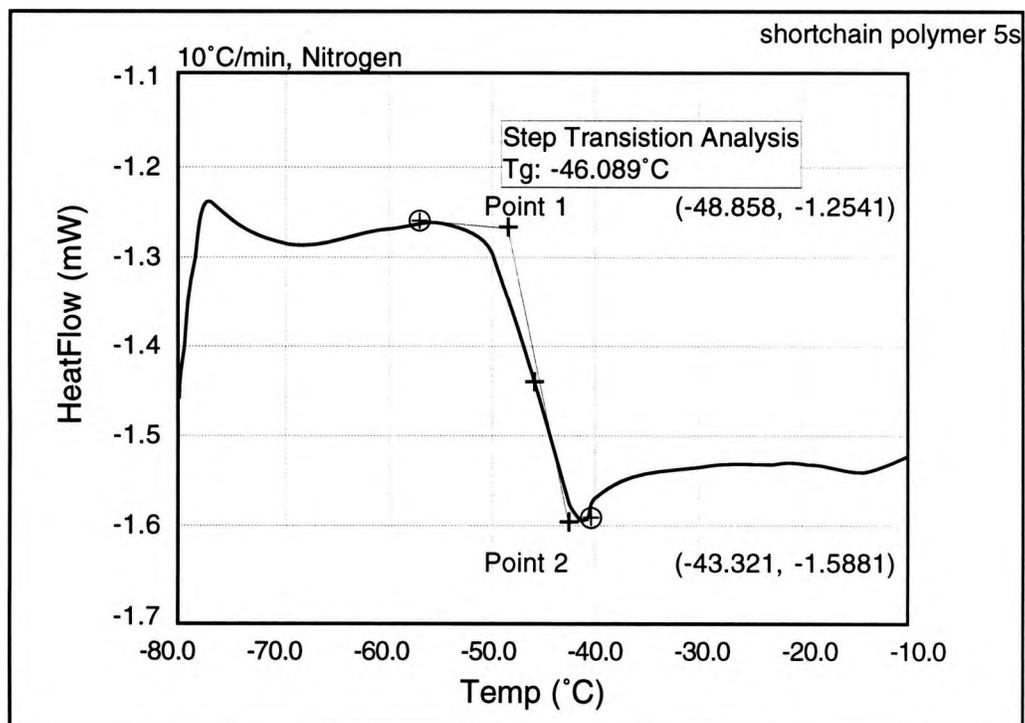
DSC #7. (Compound XXIVp-b)



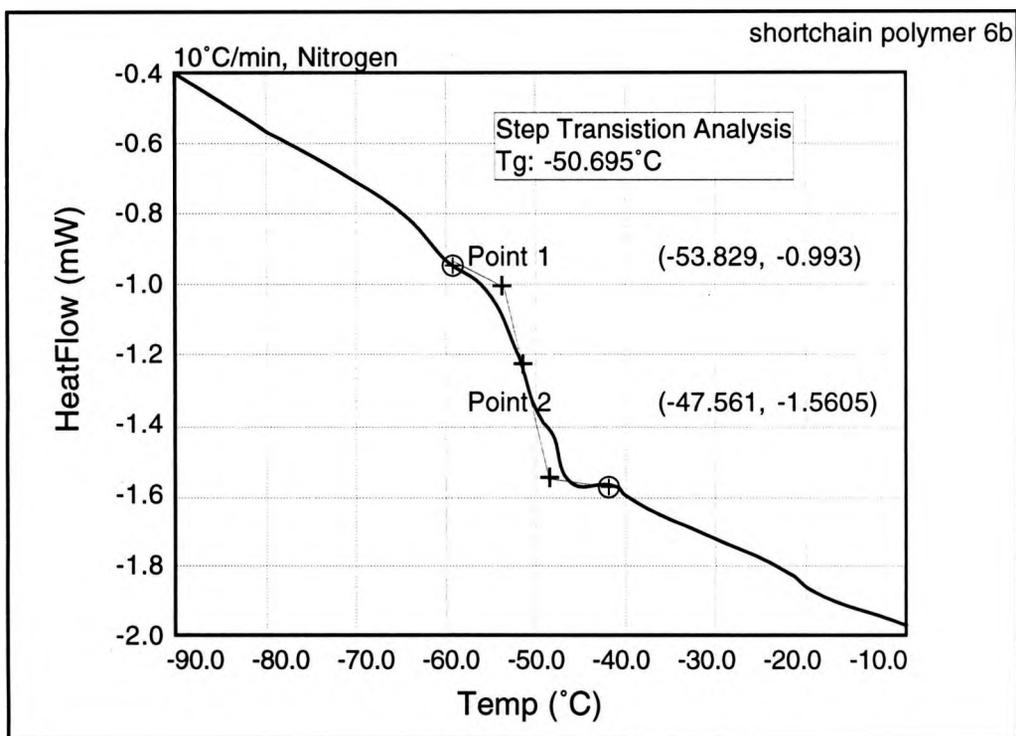
DSC #8. (Compound XXIVp-s)



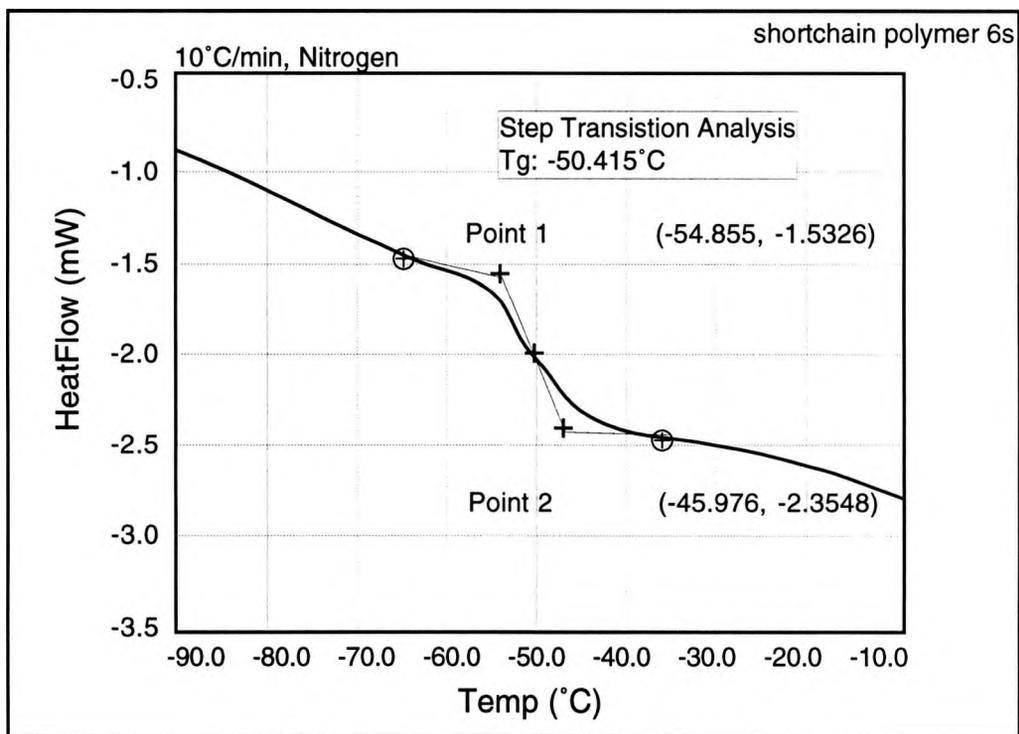
DSC #9. (Compound XXVp-b)



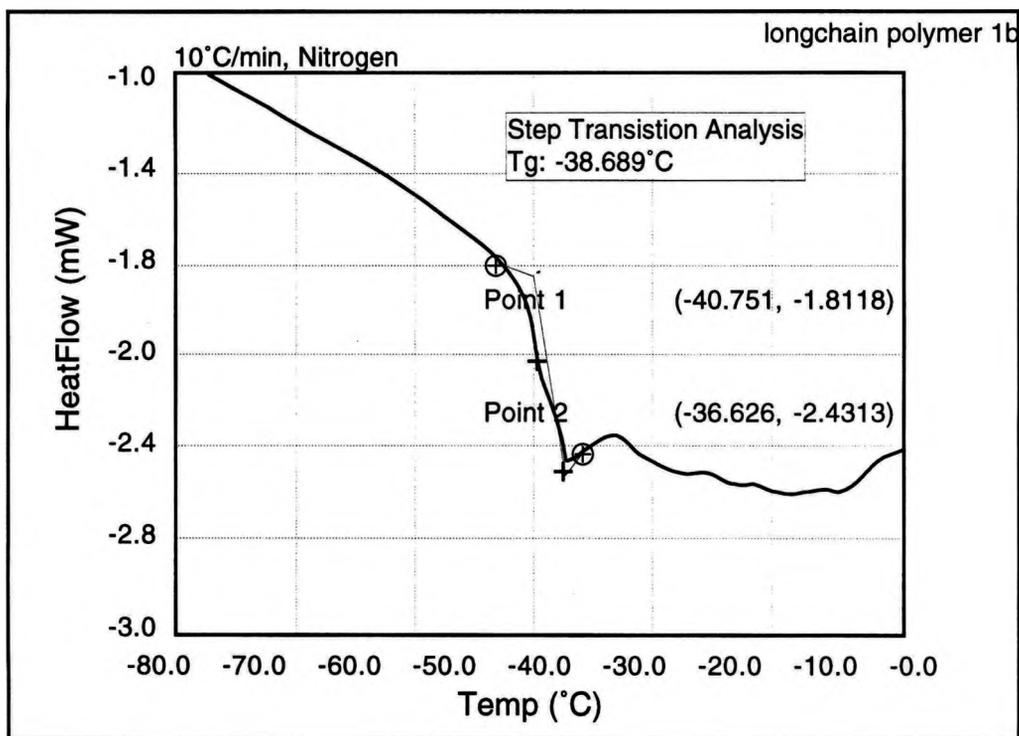
DSC #10. (Compound XXVp-s)



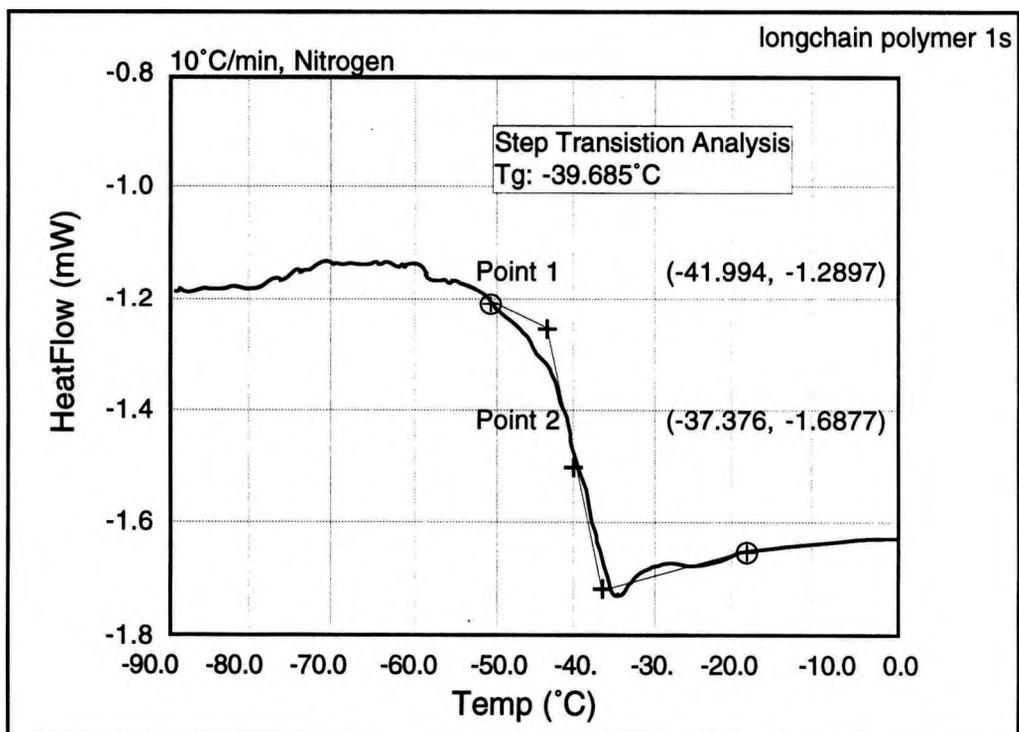
DSC #11. (Compound XXVIp-b)



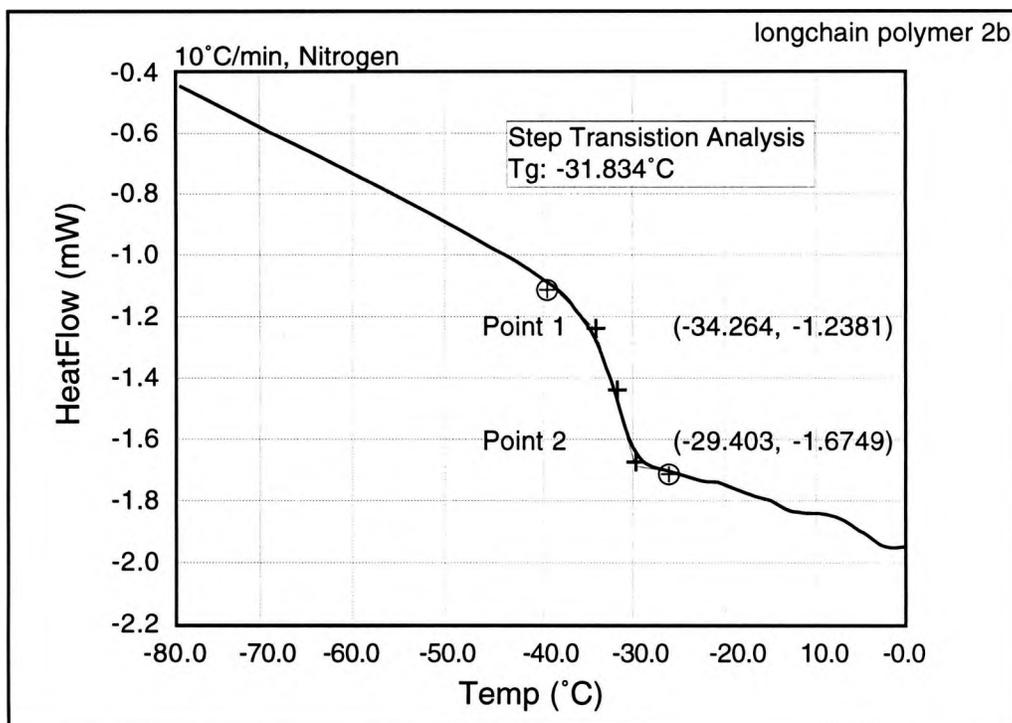
DSC #12. (Compound XXVIp-s)



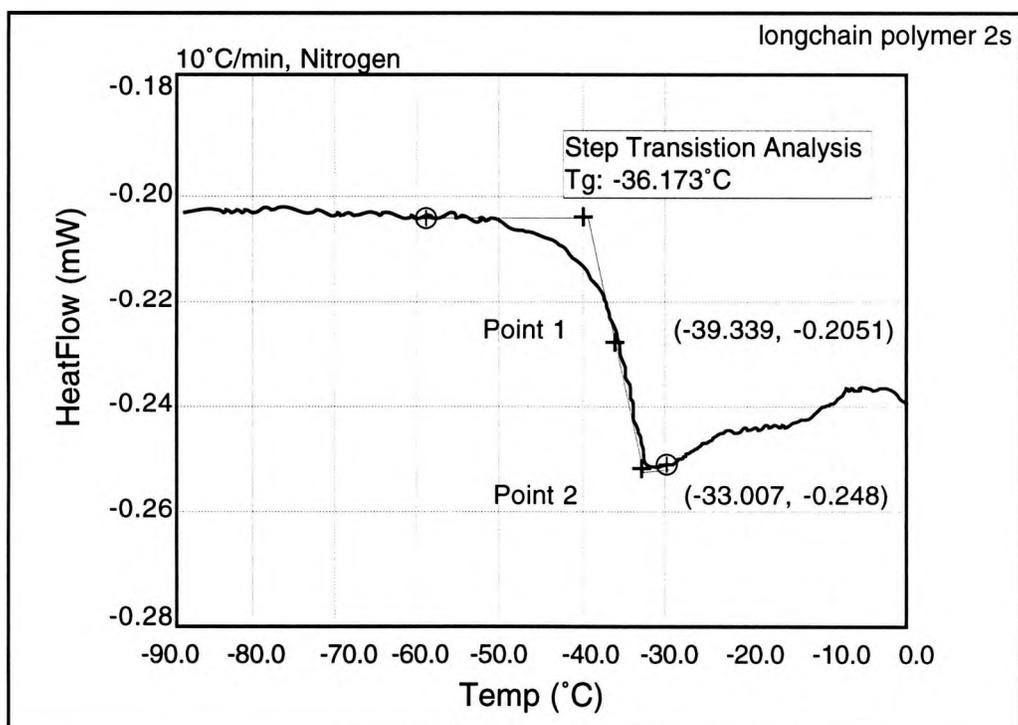
DSC #13. (Compound XXId-b)



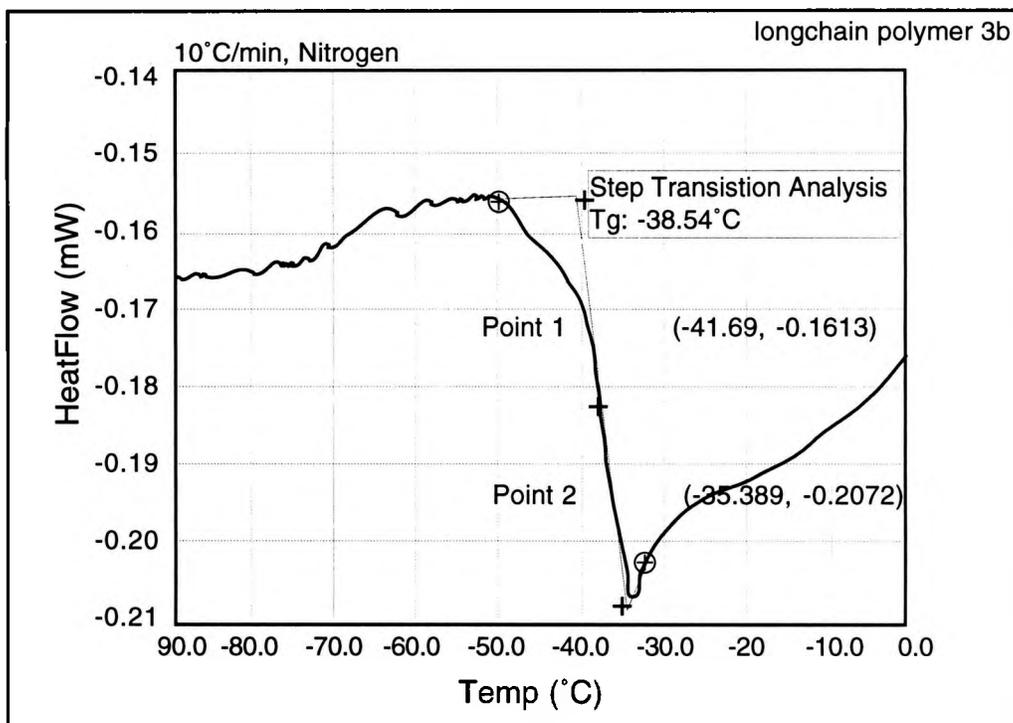
DSC #14. (Compound XXId-s)



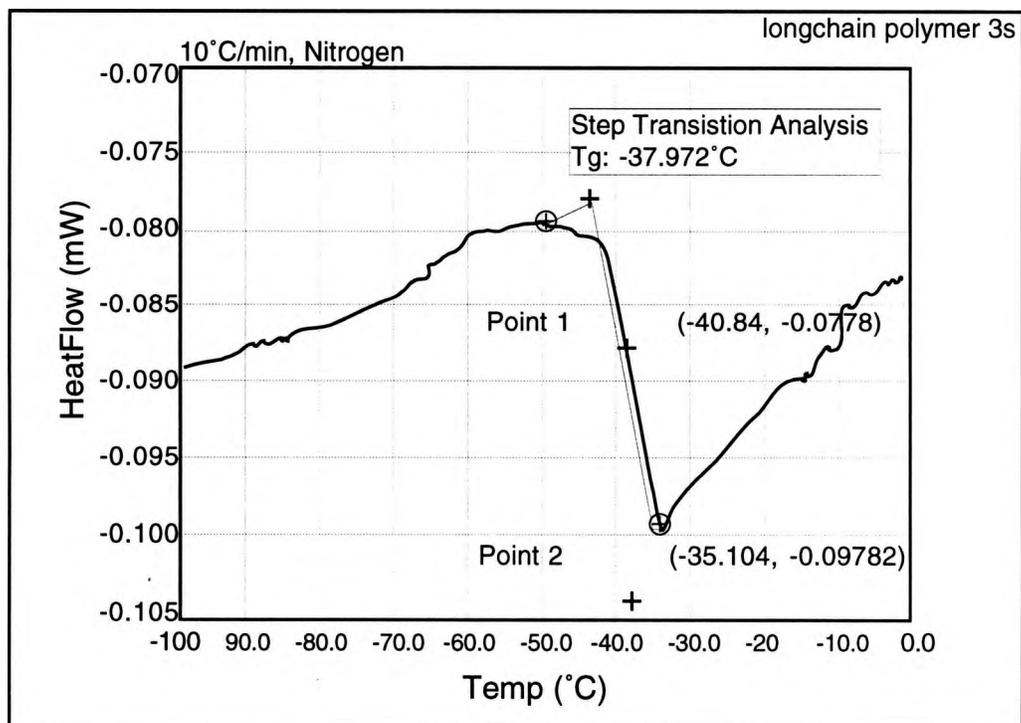
DSC #15. (Compound XXIIId-b)



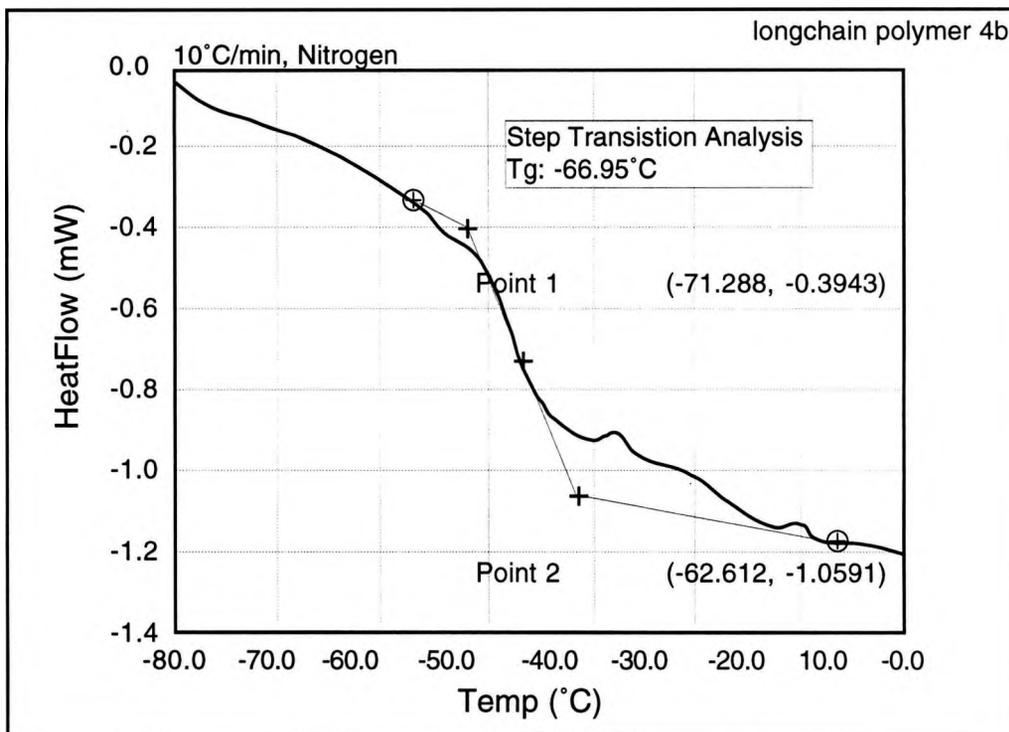
DSC #16. (Compound XXIIId-s)



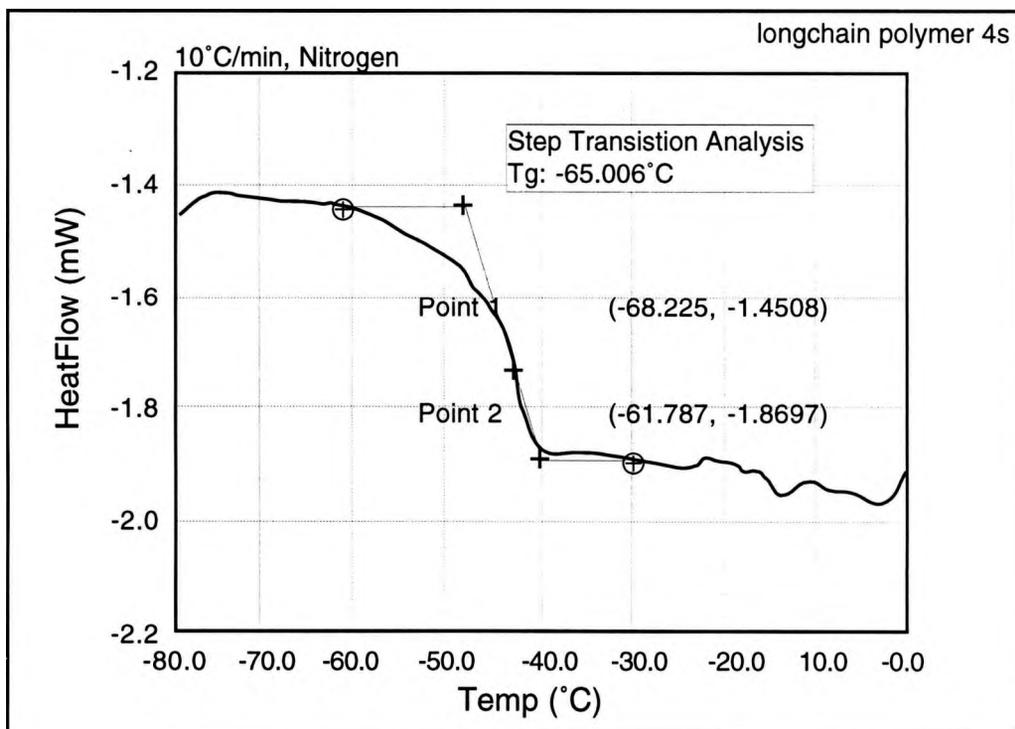
DSC #17. (Compound XXIIIId-b)



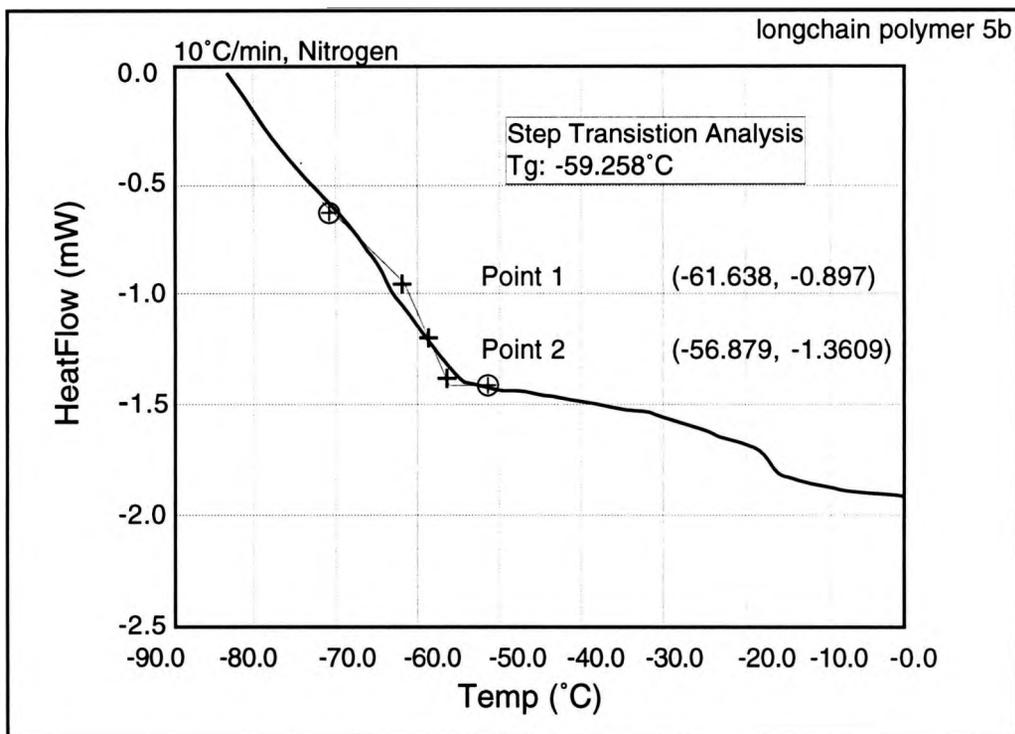
DSC #18. (Compound XXIIIId-s)



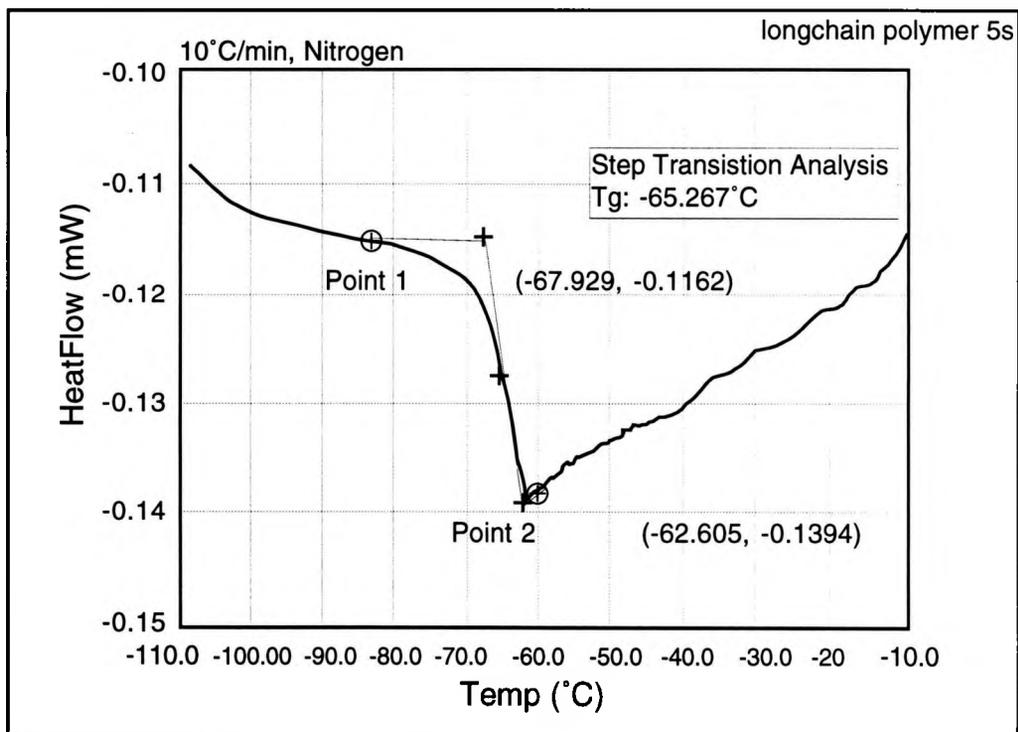
DSC #19. (Compound XXIVd-b)



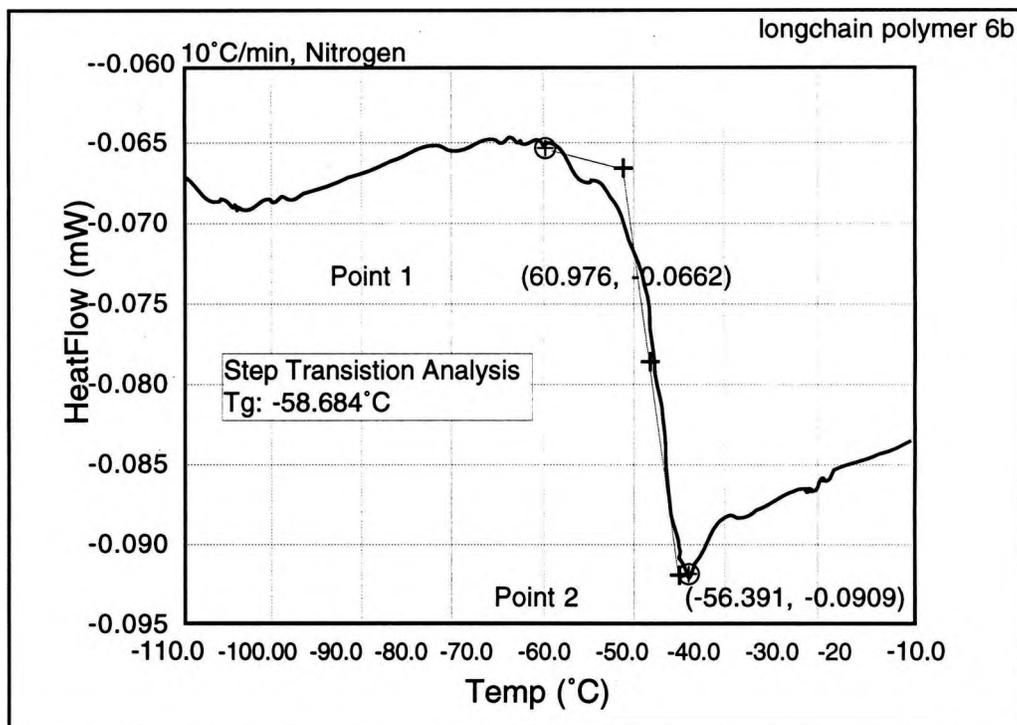
DSC #20. (Compound XXIVd-s)



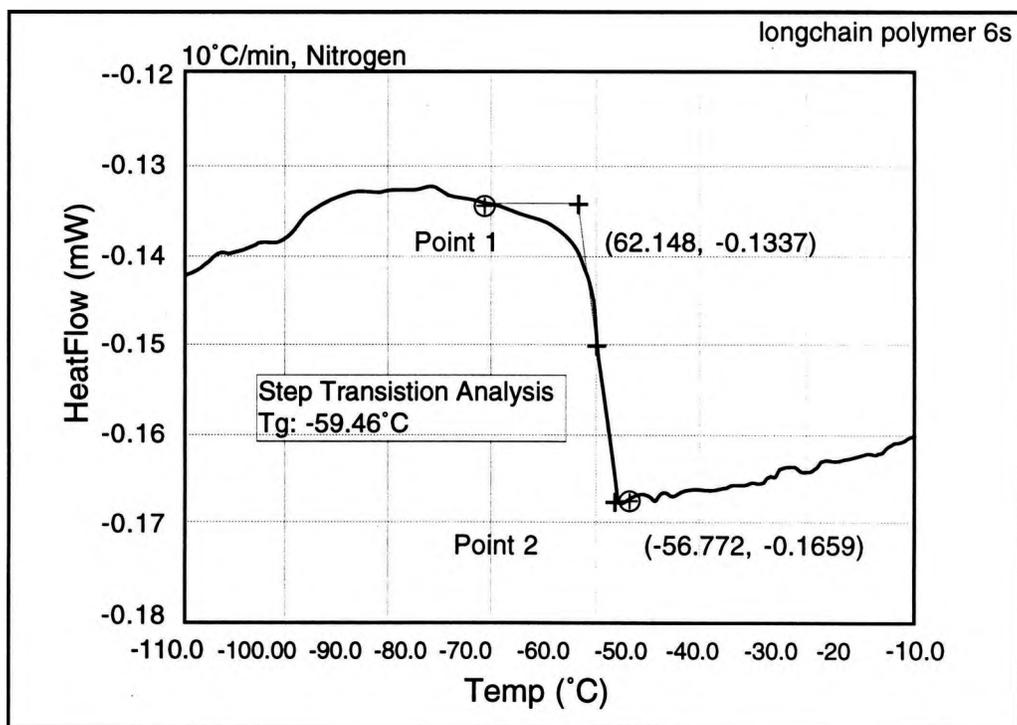
DSC #21. (Compound XXVd-b)



DSC #22. (Compound XXVd-s)



DSC #23. (Compound XXVIId-b)



DSC #24. (Compound XXVIId-s)

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