

The Synthesis and Characterization of New, Fluorine-Containing
Polyacrylates Derived from
2-Hydroxyhexafluoroisopropylbenzene

Thesis

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Table of Contents

Table of Contents.....	page
List of Figures	iii
List of Tables	v
Acknowledgements.....	vi
1.0 Summay	1
2.0 Introduction and Background.....	3
2.1 Fluoropolymers.....	3
2.1.1 Historical background.....	3
2.1.2 Tetrafluoroethylene.....	4
2.1.3 Hexafluoroisopropylidene-containing Polymers.....	5
2.2 Polyacrylates.....	6
2.2.1 Historical Background	6
2.2.2 Structure-Property Relationships.....	8
2.2.3 Thermal Properties.....	9
2.2.4 Syntheses.....	10
2.3 Thesis Proposal.....	11
3.0 Experimental.....	12
3.1 General Considerations.....	12
3.2 Monomer Synthesis.....	13
3.2.1 Synthesis of Hexafluoro-2-phenyl-2-propyl Acrylate (HFAB)	13
3.2.2 Synthesis of Hexafluoro-2-(4-fluorophenyl)-2- propyl Allyl Ether	14
3.2.3 Synthesis of Hexafluoro-2-phenyl-2-propyl or -2-pentyl or -2-octyl Allyl Ether.....	14
3.2.4 Synthesis of 3-(Hexafluoro-2-phenyl-2-propoxy) -1-propanol or - 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentanol or - 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octanol.....	16
3.2.5 Synthesis of 3-(Hexafluoro-2-phenyl-2-propoxy) -1-propyl Acrylate or 5-(Hexafluoro-2-phenyl-2-propoxy) -1-pentyl Acrylate or 8-(Hexafluoro-2-phenyl-2-propoxy) -1-octyl Acrylate.....	18
3.3 Polymer Synthesis.....	20
3.3.1 Homopolymerization of 3-(Hexafluoro-2-phenyl-2-propoxy)- 1-propyl Acrylate in Toluene.....	20
3.3.2 Homopolymerization of 3-(Hexafluoro-2-phenyl-2-propoxy)- 1-propyl Acrylate in 1,3-Bis-(trifluoromethyl) Benzene: General Procedure.....	21
3.3.3 Homopolymerization of Methyl Acrylate in 1,3- Bis-(trifluoromethyl)Benzene.....	21

3.3.4 Copolymerization of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate with Methyl Acrylate.....	21
3.3.5 Attempted Bulk Polymerization of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate with Methyl Acrylate.....	22
4.0 Results and Discussion	23
4.1 Monomer Synthesis.....	23
4.1.1 Synthesis of Hexafluoro-2-phenyl-2-propyl Acrylate.....	23
4.1.2 Synthesis of Hexafluoro-2-phenyl-2-propyl Allyl or -4-pentenyl or-7-octenyl Ether.....	24
4.1.3 Synthesis of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propanol or 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentanol or 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octanol(HFPPO).....	26
4.1.4 Synthesis of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate or 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentyl Acrylate or 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octyl Acrylate.....	28
4.2 Polymer Synthesis.....	29
4.2.1 Attempted Bulk Polymerization of Hexafluoro-2-phenyl-2-propoxy-1-acrylate Derivatives.....	29
4.2.2 Solution Polymerization of the Different Acrylate Monomers.....	30
4.3 Copolymer Synthesis.....	32
4.4 Polymer Characterization.....	35
4.4.1 Thermal Analysis of Homopolymer and Copolymer.....	35
4.4.1.1 Thermogravimetric Analyses.....	35
4.4.1.2 Differential Scanning Calorimetry.....	38
4.4.2 Contact Angle.....	39
5.0 Conclusion.....	41
6.0 Suggestion for Future Research.....	42
References	79

List of Figures

Numbers	Page
1. ¹ H NMR of 1,3 Bis- HFAB.....	44
2. ¹³ C NMR of Monomethyl Ether of 1,3-Bis-HFAB.....	45
3. ¹ H NMR of Monomethoxy 1,3-Bis-HFAB Methacrylate.....	46
4. ¹ H NMR of 2-Hydroxyhexafluoroisopropylbenzene (HFAB).....	47
5. ¹³ C NMR of 2-Hydroxyhexafluoroisopropylbenzene (HFAB).....	48
6. ¹ H NMR of Hexafluoro-2-phenyl-2-propyl Allyl Ether.....	49
7. ¹³ C NMR of Hexafluoro-2-phenyl-2-propyl Allyl Ether.....	50
8. ¹ H NMR of 2-Hexafluoro-2 phenyl -2- pentyl Allyl Ether.....	51
9. ¹³ C NMR of 2-Hexafluoro-2 phenyl -2- pentyl Allyl Ether.....	52
10. ¹ H NMR of Hexafluoro-2-phenyl -2- octyl Allyl Ether.....	53
11. ¹³ C NMR of Hexafluoro-2-phenyl -2- octyl Allyl Ether.....	54
12. ¹ H NMR of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propanol.....	55
13. ¹³ C NMR of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propanol.....	56
14. ¹ H NMR of 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentanol.....	57
15. ¹³ C NMR of 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentanol.....	58
16. ¹ H NMR of 8-(Hexafluoro-2-phenyl-2-propoxy)-1- octanol.....	59
17. ¹³ C NMR of 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octanol.	60
18. ¹ H NMR of 3-(Hexafluoro-2-phenyl-2-propoxy)-1- propyl Acrylate.	61
19. ¹³ C NMR of 3-(Hexafluoro-2-phenyl-2-propoxy)-1- propyl Acrylate.....	62
20. ¹ H NMR of 5-(Hexafluoro-2-phenyl-2-propoxy)-1- pentyl Acrylate.....	63
21. ¹³ C NMR of 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentyl Acrylate.....	64
22. ¹ H NMR of 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octyl Acrylate.	65
23. ¹³ C NMR of 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octyl Acrylate.....	66
24. TGA Thermogram of Polymer 13 in nitrogen.....	67
25. TGA Thermogram of Polymer 13 in air.....	67
26. TGA Thermogram of Polymer 13a in nitrogen.....	68
27. TGA Thermogram of Polymer 13a in nitrogen.....	68
28. TGA Thermogram of Polymer 14 in nitrogen.....	69
29. TGA Thermogram of Polymer 14 in air.....	69
30. TGA Thermogram of Polymer 14a in nitrogen.....	70
31. TGA Thermogram of Polymer 14a in air.....	70
32. TGA Thermogram of Polymer 15 in nitrogen.....	71
33. TGA Thermogram of Polymer 15 in air.....	71
34. TGA Thermogram of Polymer 15a in nitrogen.....	72
35. TGA Thermogram of Polymer 15a in air.....	72
36. DSC Curve of Polymer 13	73
37. DSC Curve of Polymer 13a	73
38. DSC Curve of Polymer 13c	74
39. DSC Curve of Polymer 13d	74

40. DSC Curve of Polymer 14	75
41. DSC Curve of Polymer 14a	75
42. DSC Curve of Polymer 14b	76
43. DSC Curve of Polymer 14c	76
44. DSC Curve of Polymer 14d	77
45. DSC Curve of Polymer 15	77
46. DSC Curve of Polymer 15a	78
47. DSC Curve of Polymer 15b	78

List of Tables

Tables		Page
I.	Glass Transition Temperature of Some Typical Polymers.....	5
II.	Bulk and Solution Polymerization of the acrylate of 1-hexafluoro-2-hydroxy-2-propyl-3-hexafluoro-2-methoxy-2-propyl benzene...	29
III.	Solution Polymerization of Synthesis of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate (Compound 7) in 1,3-Bis-(trifluoromethyl) Benzene - Effect of Initiator Concentration and Temperature.....	30
IV.	Solution Polymerization of 3-(Hexafluoro-2-phenyl-2-propoxy)-propyl Acrylate (HFPA).....	31
V.	Solution Polymerization of the Acrylate of 5-(Hexafluoro-2-hydroxy-2-propyl)-1,1-dimethyl-3,3-bis(trifluoromethyl-2-oxa-1-silaindane).....	32
VI.	Solution Polymerization of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate (Compound 7).....	33
VII.	Solution Polymerization of 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentyl Acrylate (Compound 8).....	33
VIII.	Solution Polymerization of 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octyl Acrylate (Compound 9).....	34
IX.	Solution Polymerization of Compound 8 (20% wt. Solution).....	35
X.	Thermal Data and Water Contact Angles for Homopolymerization and Copolymerization of 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentyl Acrylate (Compound 7) with Methyl Acrylate.....	36
XI.	Thermal Data and Water Contact Angles for Homopolymerization and Copolymerization of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate (Compound 7) with Methyl Acrylate.....	37
XII.	Thermal Data and Water Contact Angles for Homopolymerization and Copolymerization of 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octyl Acrylate (Compound 9) with Methyl Acrylate.....	37
XIII.	Glass Transition Temperatures for Polymers 13, 14 and 15.....	38
XIV.	Water Contact Angles for Polymers 13, 14 and 15.....	39

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1.0 SUMMARY

Acrylate polymers are known for their clarity, lack of color and stability upon aging under severe conditions. These characteristics, along with the versatility and ability to tailor these polymers relatively easily to specific applications, have made them good candidates for numerous and diverse applications. Fluorinated polyacrylates are finding increased applications in a wide variety of functions including low dielectric coatings and water repellent prosthetic devices. These polymers have also been shown to be useful for dental, biomedical and optical applications.

The fluorinated alcohol, 4-fluoro-(2-hydroxyhexafluoroisopropyl) benzene (HFAB), had previously been studied and has been shown to be a highly useful starting material for the preparation of new monomers. Incorporation of the hexafluoroisopropylidene (HFIP) moiety into a polymer generally improves a number of properties including solubility, flame resistance, glass transition temperature, thermal stability and oxidative resistance.

The goal of this project was to synthesize new acrylate monomers and polymers in which the HFAB moiety was separated from the polymerizable vinyl group by a hydrocarbon spacer arm in order to facilitate the production of high molecular weight materials. This investigation was divided into three parts:

1. Synthesis and characterization of new monomers,
2. Synthesis of homopolymers and copolymers with methyl acrylate,
3. Characterization of the polymers.

The monomers were synthesized by reacting HFAB with an ω -bromo-alkene in the presence of an aprotic solvent (DMF) and a strong base (NaH). After purification of the intermediate ether by column chromatography, it was transformed to an alcohol by hydroboration. The monomers were synthesized by reacting the corresponding alcohol with acryloyl chloride in the presence of a tertiary amine using tetrahydrofuran as solvent. Purification of the crude monomers by column chromatography provided them as clear,

colorless liquids in yields up to 55% and with purities of 98% as determined by gas chromatography. The homopolymers and copolymers were synthesized by the solution, free radical polymerization technique using azobisisobutyronitrile (AIBN) as the initiator.

The second phase of the research was to study the thermal properties by TGA and DSC. The thermal stabilities of the polymers were as high as 380°C in nitrogen, and the glass transition temperatures were lower (11°C to -2°C) than the previously studied sterically crowded derivatives. These polymers had viscosities ranging from 0.23 to 0.76 dL/g.

2.0 INTRODUCTION AND BACKGROUND

Fluorine is the most electronegative element. On the Pauling scale, the electronegativity of fluorine (4.0) is well above the next two elements oxygen (3.4) and chlorine (3.2). Three interrelated factors explain why the chemistry of fluorine is different from the other elements: [1]

1. The low dissociation energy of the fluorine molecule;
2. The high strength of the bond between fluorine and metallic or non-metallic elements; and
3. The small size of both the fluorine atom and anion.

resulting in a higher effective nuclear charge, decreased overlap of the bonding orbital and increased repulsion between the non-bonding orbitals and electrons of the fluorine atom. [1]

Many attempts have been made to combine fluorine with organic compounds. Although some of the very early attempts to fluorinate such compounds as carbon tetrachloride, methane and chloroform met with success to produce compounds such as carbon tetrafluoride, many others were characterized by violent reactions and explosions. [2] The action of elemental fluorine on a carbon compound was compared to a combustion process where the reaction products are carbon tetrafluoride and hydrogen fluoride. [3,4,5]

2.1 Fluoropolymers

2.1.1 Historical background

Fluoropolymers have been found to be of considerable interest in applications where the unique values of their physical properties such as glass transition temperature, surface characteristics, and mechanical strength, among many others, can be exploited. An experimental fluoropolymer developed a number of years ago is an interesting case in point. This material contained sulfonic acid residues pendant to a fluorocarbon backbone. Subsequently, this pendant-functionalized fluoropolymer was found to have a number of interesting properties, the most important feature being its ability to selectively transport cations and serve as the membrane in chloroalkali cells. [6]

With the coming of "the space age", there has been a search for polymers capable of withstanding a working temperature above 300°C. These polymers must have high strength, rigidity, solvent and chemical resistance and serviceability at high temperatures. For these reasons, fluorocarbons and related fluorinated amines and ethers were targets and have long been essential components of many high technology industries. Unlike hydrocarbon analogs which exhibit extremely low polarizability, fluoropolymers have excellent electrical properties. Interest in fluoropolymers comes from the fact that the polymers have outstanding chemical and thermal resistance that result from the stability of the C-F bond. Other effects of fluorine substitution is the strengthening of adjacent C-C bonds, and the screening effect of the fluorine atoms, which because of their small size, may be tightly packed about the polymer backbone. [7]

Fluoropolymers have proven to be of great value in applications which require long operational lifetimes, resistance to chemicals and an ability to withstand temperature extremes, particularly elevated temperatures. As such, the demand for fluorinated materials has increased considerably during recent years. However, the high cost of most fluorinated compounds has considerably limited their use to specialized fields.

2.1.2 Tetrafluoroethylene

The synthesis of fluorine-containing polymers and their development as possible heat-resistant and low dielectric materials have been largely promoted by the very high thermal stability and low dielectric constant of polytetrafluoroethylene (PTFE). Polytetrafluoroethylene is a white solid with a waxy appearance and feel. It is a tough flexible material of moderate tensile strength with a tendency to creep under compression. [10] Comparative values for some properties of various fluoropolymers are given in Table I. The poor solubility and high melt viscosity of PTFE make processing so difficult that other structures are very often incorporated with tetrafluoroethylene to form copolymers. PTFE and its copolymers are

used whenever excellent toughness, electrical properties, heat resistance, or low coefficient of friction are required. Electrical applications include wire coatings and holders and spacers for use in aggressive conditions, while mechanical applications include gaskets, pump parts and laboratory equipment. Other uses include non-stick coatings for kitchen utensils, low friction linings for hoppers and diaphragms for low temperature equipment. [8]

Polytetrafluoroethylene has high thermal stability and retains its properties over a wide temperature range. The polymer may be used up to about 300°C for a long periods without loss of strength and thin sections remain flexible at temperature below -100°C. There is some weight loss when polytetrafluoroethylene is heated above about 200°C, but the weight loss is very small up to about 350°C. The glass transition temperature of PTFE is quite high when compared to non-fluorinated polymers such as polyethylene or polypropylene. This phenomenon is likely the result of the stiffness of the PTFE backbone resulting from the presence of the fluorine atoms. (Table I) Finally, it is noted that PTFE also has good weather resistance. [9]

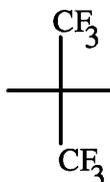
Table I: Glass transition temperature of some typical polymers. [10]

Polymer	Tg(°C)	Contributing Feature
polyethylene	-20	Flexible backbone
polypropylene	+5	CH ₃ group inhibits freedom of rotation
PVC (polyvinylchloride)	+80	Strong polar attraction between molecules
PTFE (polytetrafluoroethylene)	+115	Very stiff backbone

2.1.3 Hexafluoroisopropylidene-containing Polymers

Trifluoromethyl substituents, especially the 1,1,1,3,3,3-hexafluoroisopropylidene group (HFIP), also impart beneficial effects on polymer properties. The HFIP group was first incorporated into a

polymer in 1967 by Rogers who prepared polyimides from an HFIP bridged diamine. [11] Monomers and polymers containing the HFIP group are usually derived from the reaction of aromatic nuclei with hexafluoroacetone. A review article published in 1989 provides an extensive guide to the synthesis, properties and application of polymers derived from hexafluoroacetone. [12,13]



The HFIP Group

2.2 Polyacrylates

2.2.1 Historical Background

Polymers of lower n-alkyl acrylates have found some commercial use. The lowest member of this series, poly(methyl acrylate) has poor low-temperature properties and is water-sensitive. Therefore, its use is restricted to such applications as textile sizing and leather finishes. [14] Ethyl acrylates and butyl acrylates are among the most commonly used components of commercial acrylate rubbers. The important characteristics of acrylate rubbers are good oil resistance and good heat resistance. At this time, the majority of commercial acrylate rubbers are copolymers made of either ethyl or butyl acrylate and an alkoxyacrylate such as methoxyethyl or ethoxyethyl acrylate. It has been proven that the presence of a proportion of longer side-chains gives a rubber with greater flexibility at low temperature. [15]



Methoxyethyl Acrylate



Ethoxyethyl Acrylate

The most important method for the preparation of polyacrylates is emulsion polymerization. With this technique, the latex which is produced exhibits a lower viscosity than the corresponding solution and is consequently easier to handle. The high viscosity in solution polymerization arises because many branching and cross-linking reactions occur during polymerization of the acrylate monomers due to the ease with which hydrogen is abstracted from the polymer chain.[16]

Since acrylate monomers are easily hydrolyzed under basic conditions, [17] it is important that the polymerization reaction be conducted under neutral or acidic conditions. This is one of the reasons why fatty acid salts such as potassium oleates are not satisfactory emulsifying agents; however, salt of strong acids such as long chain sulfonic acids may be used. [17]

When the polyacrylate is intended for such uses as textile sizing, the latex is used directly; for the production of rubbers the latex must be vulcanized before they exhibit useful technological properties. It is possible to crosslink polyacrylate by various means. For example, treatment with a peroxide leads to abstraction of tertiary hydrogens and subsequent cross-linking. [17] Various basic compounds such as sodium hydroxide and sodium metasilicate are used to bring about vulcanization. In these cases, cross-linking is accompanied by the liberation of alcohol. However, vulcanizates of straight polyacrylates are usually weak and do not have good aging properties. For this reason, reactive sites are introduced into the polymer by copolymerization before the vulcanization process takes place. [17]

2.2.2 Structure Properties Relationships

The physical properties of polymeric materials are largely determined by molecular weight, strength of intermolecular forces, regularity of polymer structure and flexibility of the molecule. [18] The influence of these factors is illustrated by the different properties of various poly(n-alkyl methacrylates). In such a series where the alkyl group varies, as the length of the alkyl group increases, the polymer molecules become further spaced apart and intermolecular attraction is reduced. Therefore, as the side chain length becomes longer, the softening point decreases and the polymers become more rubbery at progressively lower temperatures. However, when the number of carbons in the side chain exceeds 12, side-chain crystallization becomes significant, and the polymers become less rubbery. This effect arises because of the better packing which is possible with the branched isomers and because the lumpy branched structure impedes rotation about the carbon-carbon bond in the main chain. Similarly, the X-methyl group present in the polymethacrylates have higher softening points than the corresponding polyacrylate. [19] The nature of the alkyl group in poly(alkyl methacrylates) also determines the mode of thermal decomposition of the polymer.

Initial research into acrylate polymers was concerned rather more with polyacrylates than polymethacrylates. The first acrylate polymer to be produced commercially was poly(methyl acrylate), which began in 1927 [20] by Rohm and Haas AG in Germany. About 1930, poly(methyl methacrylate) was found to be a potentially useful material, but was very difficult to create because of the high cost of the raw material. Some years later, a less costly synthesis based on acetone and hydrogen cyanide was developed to make the methacrylic acid. This is now by far the predominant synthetic route leading to poly(methyl methacrylate) which is preferred because of its relatively high softening point and strength. However, a few other poly(methyl acrylates) have found limited commercial use; n-butyl, n-octyl and n-nonyl esters are used as leather finishes and poly(lauryl methacrylate) is used to depress the pour point and improve viscosity-temperature characteristics of lubricating oils. [21]

2.2.3 Thermal Properties

The thermal stability of polymers has been described as the retention of certain physical properties over a defined temperature range. Thermal stability is measured using different methods, many of which monitor the change in weight, heat content or physical properties with respect to time and temperature. Common techniques are thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermal destruction of a polymer is accompanied by the evolution of volatile products which give rise to a loss of polymer mass. TGA measures the weight loss as a function of temperature over a period of time in air, argon or nitrogen atmospheres. By knowing the TGA decomposition behaviour of any material in both air and nitrogen, it is possible to make assertions about the type of decomposition that occurs in the sample.

DSC is used to determine phase transitions such as the crystalline and glass transition temperatures (T_g) in polymers. T_g is a phenomenon observed in amorphous polymers and occurs most often at well-defined temperatures when the bulk material ceases to be brittle and glassy and becomes less rigid and more rubbery. [22] Many physical properties change profoundly at the glass transition temperature, including coefficient of thermal expansion, heat capacity, refractive index, mechanical damping and electrical resistance. [23] All of these properties depend on the relative degree of freedom for molecular motion inside a given polymeric material and can be used to follow the point at which the glass transition occurs. The glass transition can be understood by considering the nature of the changes that occur at the temperature in question. The inherent mobility of a single polymer molecule is important and will cause differences in the value of T_g . But, interactions that occur between molecules can lead to restrictions in molecular mobility, thus altering the T_g of the resulting material. The T_g can be affected by the following factors:

1. The presence of groups pendant to the polymer backbone, since they increase the energy required for the molecule

to rotate about the primary bonds in the main polymer but also increase the free volume chain.

2. The presence of inherently rigid structures in the backbone of the molecule.
3. Crosslinking.
4. Hydrogen bonds between polymer chains.
5. The presence of plasticizers.

The effects of these different factors can be seen in the T_g values of some typical polymers. (Table I)

2.2.4 Syntheses

Free radical polymerization, which includes bulk, solution, emulsion, non-aqueous dispersion, and radiation-induced polymerization, is exclusively used for the preparation of acrylate and methacrylate polymers. Free radical polymerization can be divided into three distinct stages: initiation, propagation and termination. In the first stage, an initiator is used to produce free radicals which react with the olefinic monomer to initiate the polymerization. Each polymer chain propagates by rapid sequential addition of monomer molecules. Thus, upon every addition of monomer, the active center is transferred to a newly created chain end. Termination of the growing polymer chains result from reaction between the active center and other radical species without the formation of new radical species or by disproportionation or radical transfer or by quenching by an added agent

Most commercial polymers prepared by free-radical polymerization are, in fact, copolymers formed by simultaneous polymerization of two or more monomers. The inclusion of the second monomer, however, greatly complicates the reaction kinetics and brings additional requirements, the most important being the need to understand how differences in monomer reactivity affect copolymer composition and the sequence distribution of the different repeat units in the copolymer molecule being formed. Because the most reactive monomer is incorporated preferentially into the polymer chains, high molar mass copolymers are formed at low overall conversions of the comonomers, and the copolymer molecules

formed can have compositions which differ significantly from the composition of the initial comonomer mixture. The acrylates and methacrylates are outstanding in their ability to form copolymers from monomers of widely different polarities in order to improve the properties of the polymer.

2.3 Thesis proposal

Incorporation of the hexafluoroisopropylidene (HFIP) moiety into a polymer generally improves a number of properties including increased solubility, flame resistance, glass transition temperature, thermal stability and oxidative resistance. Fluorinated polyacrylates are finding increased applications in a wide variety of functions including low dielectric coatings and water repellent prosthetic devices. Therefore, it is the goal of this research to incorporate the HFIP group into polyacrylates. Simple acrylates of HFAB do not give high molecular weight polymers because of steric crowding of the reactive double bond. [8] The purpose of this research is to prepare new acrylate monomers and polymers in which the HFAB moiety is separated from the polymerizable double bond by a hydrocarbon spacer arm. It is anticipated that the new acrylates will give higher molecular weight polymers than the previously studied sterically crowded derivatives.

3.0 EXPERIMENTAL

3.1 General Consideration

Nuclear Magnetic Resonance

Unless otherwise specified, all ^1H and ^{13}C NMR spectra were obtained on a 400 MHz Varian Unity Inova Fourier Transform spectrometer using chloroform-d as solvent. Chemical shifts are expressed in δ downfield from internal tetramethylsilane(δ 0.0).

Splitting patterns are designated as follows:

s, singlet; d, doublet; (dd) doublet of doublets; t, triplet; q, quartet; m, multiplet.

Thin Layer Chromatography

Analytical thin layer chromatography (TLC) was performed on precoated silica gel plates (silica gel Ib2-F) obtained from VWR and column chromatography was performed with silica Ib2-F 150, 60-200 mesh obtained from Aldrich (75-250 microns).

Gas Chromatography

All gas chromatographic (GC) analyses were performed on a Varian Model 3000 equipped with a Hewlett Packard 3390A Integrator.

Gel Permeation Chromatography

All gel permeation chromatographic (GPC) analyses were performed using a Tracor 951LC pump at 1.0mL/min. with a Shodex k-80 packed column equipped with a Tracor 970A variable wavelength detector, set at 253 nm. The data were recorded with a Hewlett Packard integrator.

Thermal Analyses

All thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) analyses were performed with a model Rheometric Scientific DSC (Plus) and TGA 5700 (Plus).

Reagents

Hexafluoro-2-hydroxy-2-phenylpropane was obtained from Central Glass Company, Japan; allyl bromide (98%), 5-bromo-1-pentene (97%) and 8-bromo-1-octene (97%), supplied by Aldrich, were used without further purification. N,N-Dimethylformamide (DMF) and sodium hydride (NaH) were supplied by Aldrich and used as received. Tetrahydrofuran (THF) was purified by distillation from the sodium benzophenone ketyl. 2,2,1-Azobis(iso)butyronitrile (AIBN, Kodak) was recrystallized from spectrograde methanol. Triethylamine and acryloyl chloride were purchased from Aldrich Chemical Company and distilled before use. All reactions were carried out in a dry argon atmosphere. Unless otherwise indicated, MgSO₄ was used as a drying agent.

3.2 Monomer Synthesis

3.2.1 Synthesis of Hexafluoro-2-phenyl-2-propyl Acrylate (HFAB Acrylate)

The HFAB acrylate was synthesized as described by Gupta *et al.*(23) A 250 mL, three-neck, round-bottom flask was fitted with a gas inlet adapter, rubber septum, pressure-equalizing dropping funnel and magnetic stirring bar. The system was flushed with argon, flame dried, cooled to room temperature and maintained at a positive pressure of argon. The flask was charged with 5 g (0.21 mol) of hexafluoro-2-phenyl-2-propanol (HFAB) and 50 mL of dry THF . To this solution was added 4.28 mL (0.031 mol) of triethylamine, and the solution was cooled to 0°C. A solution of acryloyl chloride (3.30 mL, 0.041 mol, in 10 mL of THF) was added dropwise via an addition funnel while the reaction mixture was maintained at 0°C with an ice-water bath. The initially colorless reaction mixture gradually turned light orange as the addition was completed. The reaction remained in the ice-bath for an additional hour, and then the mixture was allowed to warm and stay at room temperature for 15 hours. The product was then poured into approximately 75 mL of distilled water. A yellow liquid was obtained and extracted three times with 50 mL portions of diethyl ether. All the ether layers were collected,

extracted twice with 20 mL of 10% sodium bicarbonate, once with 30 mL of distilled water, dried over magnesium sulfate and then filtered. The dry solution was filtered and concentrated under vacuum to yield 4.27g (70%) of crude monomer. The monomer was purified by column chromatography using a mixture of hexane and ethyl acetate (80/20 by volume) as eluent yielded 3.3g (55%) of the pure monomer.

3.2.2 Synthesis of Hexafluoro-2-(4-fluorophenyl)-2-propyl Allyl Ether

A dry, 500-mL, three-neck flask was equipped with a argon inlet adapter, a reflux condenser, a magnetic stirring bar and a pressure-equalizing dropping funnel. The system was flushed with argon, flame dried, cooled to room temperature and maintained under a positive pressure of argon. Dry THF (100 mL) was put into the flask. To that was added 4.126 g (0.017 mol) of hexafluoro-2-(4-fluorophenyl)-2-propanol (HFAF) and about 1 g (0.041 mol) of sodium hydride, which had been washed with hexane to remove the mineral oil. To this mixture 2.77 mL (0.032 mol) of allyl bromide was added dropwise from the addition funnel. The reaction mixture was heated to reflux for 15 hours and then cooled to room temperature. About 10 mL of isopropyl alcohol and 10 mL of distilled water were added successively, and very slowly (caution!) to destroy any unreacted sodium hydride. The solvent was evaporated, and the residue was taken into 100 mL of dichloromethane and washed with 100 mL of 1 M hydrochloric acid. The resulting product was washed with a saturated solution of sodium chloride (25 mL) and dried over magnesium sulfate. This solution was decanted from the desiccant and concentrated under reduced pressure, purified by column chromatography by using hexane as eluent to yield to yield 0.95g (20%) of material.

3.2.3 Synthesis of Hexafluoro-2-phenyl-2-propyl allyl (Compound 1) or-4-pentenyl (Compound 2) or 7-octenyl (Compound 3)

A dry, 500-mL, three-neck, round-bottom flask was charged with 100 mL of N,N-dimethylformamide (DMF). While the DMF was stirred

at ambient conditions under argon, 10 g (0.041mol) of hexafluoro-2-phenyl-2-propanol (HFAB) was added, and the mixture was stirred for 15 minutes. Sodium hydride, 2.45 g (0.10 mol), freed from protective mineral oil by three hexane washings, was added to the mixture. Shortly after starting the addition, an exothermic reaction caused an increase in temperature. Care should be taken not to add the sodium hydride too rapidly. After the addition was complete, stirring was continued for another 30 minutes at ambient temperature. To the stirred mixture was added allyl bromide, 5.32 g (0.044 mol) dropwise via an additional funnel. The reaction mixture was stirred at room temperature and then heated to reflux for about 10 h to give a yellow solution. The reaction mixture was allowed to cool to room temperature and isopropyl alcohol (5 mL) was added dropwise to the solution to destroy the remaining NaH (caution!). The resulting solution was poured into approximately 30 mL of water, and the mixture was stirred for 15 minutes before being poured into a 500 mL separatory funnel. The organic layer was separated and the aqueous layer was extracted with ether (2 x 50 mL). The combined organic layers were washed three times with water and one time with brine solution, and dried over magnesium sulfate. The drying agent was removed by filtration, and the solvent was removed under reduced pressure to give a crude product which was isolated by column chromatography using hexane as eluent to yield 10.47g (90%) of **1** as a colorless product.

Identical procedures were used to prepare analogues in which the allyl group was replaced respectively by the 4-pentenyl group in **2**, (from reaction with 5-bromo-1-pentene, yield=85%) and the 7-octenyl group, in **3** (from reaction with 8-bromo-1-octene, yield=80%). NMR data are summarized below.

Compound **1**

$^1\text{H NMR}(\text{CDCl}_3)$

δ : 7.600-7.448 (m 5H aromatic); 5.983-5.913 (m 1H, CH); 5.446-5.258 (dd 2H, (CH)₂); 4.104-4.094 (d 2H, O-CH₂);

$^{13}\text{C NMR}(\text{CDCl}_3)$

δ : 67.434; 117.721; 128.326; 129.054; 130.609; 132.877.

Anal: found/calculated for [C₁₂H₁₀F₆O], % C=50.79/50.71;

% H=3.66/3.52.

Compound 2

¹H NMR(CDCl₃)

δ: 7.98–7.452 (m 5H, aromatic); 5.829-5.812 (m 1H, CH); 5.093-4.986 (m, 2H CH₂ C=CH₂); 3.608-3.576 (t, 2H O-CH₂); 2.237-2.180 (m, 2H, CH₂-); 1.853-1800 (m, 2H CH₂-C)

¹³C NMR (CDCl₃)

δ: 29.285; 30.082; 66.001; 115.566; 128.394; 128.948; 130.442; 137.861.

Anal: found/calculated for [C₁₄H₁₄F₆O], % C=53.77/53.84;

% H=4.69/4.48.

Compound 3

¹H NMR (CDCl₃)

7.496-7.346 (m, 5H aromatic) 5.88-5.71(m, 1H-CH); 4.927-4.27-4.832(2H, (CH)₂); 3.481-3.299 m, 2H, OCH₂); 1.969-1.246 (m, 1OH, (CH₂)₅)

¹³C NMR (CDCl₃)

δ: 24.542; 27.023; 27.220; 27.220; 27.706; 27.782; 28.731; 31.787; 32.644; 32.682; 65.455; 113.295; 127.102; 127.603; 129.090; 137.92.

Anal: found/calculated for [C₁₇H₂₀F₆O], % C=57.55/57.62;

% H=5.69/5.54.

3.2.4 Synthesis of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propanol (Compound 4) or 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentanol (Compound 5) or 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octanol (Compound 6)

A 500-mL, three-neck, round-bottom flask was equipped with a magnetic stirring bar, 250-mL addition funnel, and a reflux condenser fitted with an inert gas (argon) inlet tube that was also attached to a mineral oil bubbler. The system was flushed with argon, flame dried, cooled to room temperature, and maintained under a positive pressure of argon. The reaction flask was charged with **1** (0.6 g, 0.037mol) dissolved in 250 mL of freshly distilled THF. To this was added dropwise 9-borabicyclo[3.3.1]nonane (9-BBN) (20.4 ml) over a period of 15 minutes. The reaction mixture was then heated to reflux for about 7 hours. After the reaction was allowed to

cool, the resulting organoborane was oxidized by adding successively 8.76 mL of absolute ethanol, 0.9 mL of 6 M sodium hydroxide and 1.8 mL of 30% hydrogen peroxide which was carefully added dropwise. The mixture was heated at 50°C for an additional twelve hours. The reaction mixture was cooled to room temperature, saturated with potassium carbonate and decanted into a 500-mL flask and extracted with diethyl ether. The organic portion was separated and the solvent was removed under vacuum to leave a colorless oil, compound **4**, which, after purification by column chromatography using a mixture of hexane and ethyl acetate (80/20 by volume) as eluent, was obtained in a yield of 7.9g (70%).

Identical procedures were used to prepare analogues in which the propylidene group was replaced respectively by the pentamethylene (from reaction with **2**, yield= 65%) and the octamethylene group (from reaction with **3**, yield =63%). NMR data are summarized below.

(Compound **4**)

¹H NMR (CDCl₃,δ)

δ: 7.566-7.399 (m, 5H, aromatic); 4.083-3.966 (m, 2H, OCH₂-); 3.779-3.675 (m, 2H, CH₂-O); 1.986-1.187 (m, 2H, CH₂-OH)

¹³C NMR (CDCl₃)

δ: 21.783; 23.624; 25.103; 59.873; 62.234; 124.396; 125.092; 126.705.

Anal: found/calculated for [C₁₂H₁₂F₆O₂], % C=48.77/47.68; % H=3.73/3.97.

(Compound **5**)

¹H NMR (CDCl₃,δ)

δ: 7.559-7.542 (m, 5H, aromatic); 3.840-3.807 (t, 2H, CH₂); 3.462-3.616 (t, 2H, CH₂)₃; 3.564-3.532 (t, 2H CH₂); 1.812-1.237 (m, 2H, CH₂-OH).

¹³C NMR (CDCl₃)

δ: 22.276; 22.337; 26.494; 26.714; 29.778; 29.801; 31.424; 32.312; 32.456; 32.585; 62.428; 62.428; 62.837; 66.554; 62.837; 66.554;

66.607; 71.204; 71.227; 128.310; 128.872; 128.895; 130.359;
130.397.

Anal: found/calculated for [C₁₄H₁₆F₆O₂], % C=51.07/50.90;
% H=4.79/4.84.

(Compound 6)

¹H NMR (CDCl₃, δ)

δ: 5.538-7.406 (m, 5H, aromatic); 4.363 (m, 1H, OH); 3.790-3.756 (t, 2H, O-CH₂), 3.521-3.488 (t, 2H, CH₂); 3.371-3.337 (t, 2H, CH₂); 1.831-1.291 (m, 10 H (CH₂)₅).

¹³C NMR (CDCl₃)

δ: 22.238; 22.321; 22.352; 23.179; 25.856; 25.887; 25.978; 26.016;
26.312; 26.478; 26.721; 26.752; 26.685; 29.407; 29.482; 29.528;
29.991; 31.720; 31.743; 32.145; 32.464; 32.517; 33.040; 34.353;
42.143; 62.663; 62.686; 66.661; 70.916; 71.075; 71.189; 128.280;
128.811; 130.298.

Anal: found/calculated for [C₁₇H₂₂F₆O₂], % C=54.66/54.83;
% H=6.02/5.91.

3.2.5 Synthesis of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate (Compound 7) or 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentyl Acrylate (Compound 8) or 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octyl Acrylate (Compound 9)

A dry, 500-mL, three-neck, round-bottom flask was equipped with a magnetic stirring bar, a 125 mL addition funnel fitted with an inert gas (argon) inlet tube that is attached to a mineral oil bubbler. The system was flushed with argon, flame dried, cooled to room temperature, and maintained under a positive pressure with argon. The reaction flask was charged with a solution containing 8.75g (0.029 mol) of **4** dissolved in 100 mL of freshly distilled THF. To the mixture was added 8.074 mL (0.058 mol) of triethylamine. The flask was cooled in an ice bath to 0°C and a second solution containing 4.71 mL (0.058 mol) of acryloyl chloride, dissolved in 20 mL of THF, was added over 1 hour from the addition funnel, while maintaining the reaction temperature at 0°C. After the addition was complete, a

light orange solution resulted which was maintained at 0°C for one additional hour. The ice bath was removed, and the resulting mixture was stirred at room temperature overnight. At the end of this time, a pale yellow solution resulted, to which approximately 100 mL of distilled water was added, resulting in an orange-yellow liquid. The reaction mixture was stirred for 15 minutes before being poured into a 500-mL separatory funnel. The solution was extracted with diethyl ether (2x50 mL). The layers were separated and the aqueous layer was extracted with ether (2x50 mL). The combined organic layers were washed with 10% sodium bicarbonate (50 mL) followed by 20 mL of distilled water and dried over magnesium sulfate. The filtered organic solvent was removed *in vacuo* and the product was purified by column chromatography using a mixture of hexane-ethyl acetate (80/20 by volume) as eluent to yield 5.46 g (53%) of a colorless clear liquid. Identical procedures were used to prepare analogues in which the alcohol group was replaced respectively by the 5-pentanol group, (from reaction with compound **5**, yield 52%), and the 8-octanol group (from reaction with compound **6**, yield 49%)

(Compound **7**)

¹H NMR (CDCl₃)

7.521–7.438 (m, 5H, aromatic); 6.395–6.321 (m, CH-); 6.116–6.046 (m, 1H, CH) 5.823–5.793 (m, 1H, CH); 4.341–4.310 (t, 2H, CH₂-O); 3.666–3.651 (t, 2H, CH₂-O); 2.072–1.501 (m, 2H, CH₂)

¹³C NMR (CDCl₃)

δ: 26.432; 27.654; 29.208; 32.651; 62.094; 62.876; 129.532 133.576; 134.871; 135.032; 166.054.

Anal: found/calculated for [C₁₅H₁₄F₆O₃], % C=50.42/50.56; % H=3.85/3.93.

(Compound **8**)

¹H NMR (CDCl₃)

7.555–7.455 (m, 5H, aromatic); 6.407–6.360 (m, CH-); 6.137–6.067 (m, 1H, CH-); 5.809–5.783 (m, 1H, CH); 4.149 (m, 2H, CH₂-O); 3.571–3.539 (m, 2H, CH₂-C-); 1.768–1.481 (m, 6H, CH₂-CH₂-CH₂-)

¹³C NMR (CDCl₃)

δ : 26.553; 26.803; 29.344; 30.680; 30.831; 65.392; 65.978; 122.021;
128.507; 129.417; 130.479; 131.404; 131.442; 131.768; 167.323.
Anal: found/calculated for [C₁₇H₁₈F₆O₃], % C=53.22/53.12;
% H=4.77/4.68

(Compound 9)

¹H NMR (CDCl₃)

7.561-7.442 (m, 5H, aromatic); 6.401-6.354 (m, 1H, CH=); 6.134-
6.065 (m, 1H, CH=); 5.803-5.773 (m, 1H, CH=); 4.15-4.118 (m, 2H, CH₂-
O); 3.547-3.514 (m, 2H, CH₂-O); 1.702-1.634 (m, 4H, CH₂-CH₂-);
1.390-1.333 (m, 6H (CH₂)₃)

¹³C NMR (CDCl₃)

δ : 21.182; 22.267; 22.342; 22.368; 23.426; 23.502; 24.527; 24.568;
24.627; 25.272; 62.182; 63.120; 121.048; 122.220; 124.270; 125.278;
125.372; 163.278.

Anal: found/calculated for [C₂₀H₂₄F₆O₃], % C=56.25/56.33;
% H=5.59/5.63.

3.3 Polymer Synthesis

3.3.1 Homopolymerization of 3-(hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate in Toluene.

Compound 7, 0.408 g (0.015 mol), and 0.0038 g (0.023 mmol) of AIBN were placed into a 25 mL flask. To this mixture was added 0.5 mL of freshly distilled toluene. The mixture was degassed by performing at least three successive freeze-pump-thaw cycles under vacuum. The polymerization was conducted in a constant temperature oil bath at 80°C. The mixture was heated for 24 hours, cooled to room temperature and poured into methanol. The white product was filtered and dried under vacuum at room temperature to give 0.26 g (63%) of polymer viscosity (0.3 dL/g)

3.3.2 Homopolymerization 3-(hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate in 1,3-Bis-(trifluoromethyl)Benzene: General Procedure.

1,3-Bis-(trifluoromethyl)benzene was used as solvent observing the same volumes and masses and the same procedure as described above. The resulting polymer was obtained in 51% yield and with an inherent viscosity of 0.48 dL/g. Identical procedures were used to prepare the other acrylates where $x=5$ (polymer 5) and $x=8$ (polymer 6). The resulting polymers were obtained in 71% and 37% yields with inherent viscosities of 0.68 and 0.71 for polymer 5 and polymer 6 respectively

3.3.3 Homopolymerization of Methyl Acrylate in 1,3-Bis-(trifluoromethyl)Benzene.

Freshly distilled methyl acrylate, 0.12g (0.014 mol), dissolved in 1,3-Bis-(trifluoromethyl)benzene (1.04 mL) along with AIBN, 0.0093 g (0.057 mmol), as initiator was degassed as previously described and heated in a constant temperature oil bath solution at 80°C for 10 minutes to give a viscous, colorless liquid. The product was dissolved in chloroform, and the mixture was poured into methanol. The product was filtered and dried under vacuum to provide 0.35 g (67%) of polymer.

3.3.4 Copolymerization 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate (Compound 7) with Methyl Acrylate.

Freshly distilled methyl acrylate 0.12 g (0.014 mmol), dissolved in 1,3-Bis-(trifluoromethyl)benzene (1.04 mL) was used along with compound 7 (0.408 g) using AIBN as initiator in a 1:50 mole ratio. The contents of the flask were degassed by performing three successive freeze-pump-thaw cycles under vacuum and poured into methanol to precipitate the polymer after the polymerization was conducted in a constant temperature oil bath at 80°C. for about 5-10 minutes. Then, the polymer was filtered and dried under vacuum overnight at room temperature.

Similar procedures were used to prepare a series of polymer 10 and 11 along with methylacrylate.

3.3.5 Attempted Bulk Polymerization with 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate (Compound 7).

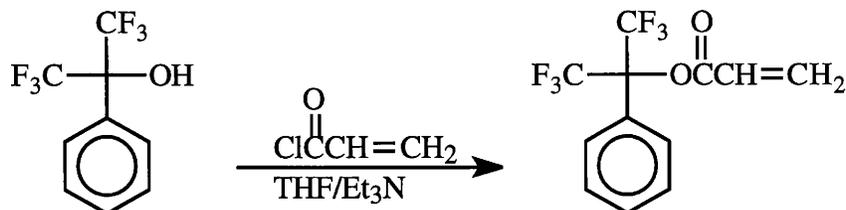
A similar procedure without the 1,3-bis-(trifluoromethyl) Benzene was performed as described above; unfortunately the polymer that resulted after precipitation into methanol gave rise to a gel which was only partly soluble in most organic solvents.

4.0 RESULTS AND DISCUSSION

4.1 Monomer Synthesis

4.1.1 Synthesis of Hexafluoro-2-phenyl-2-propyl Acrylate

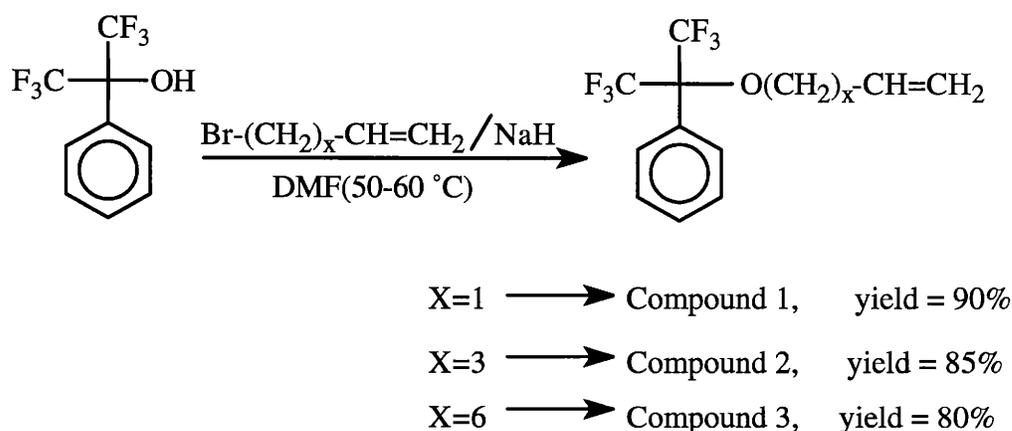
The synthesis of the monomer was performed according to the following general scheme.



Previous work has been reported in which 2-hydroxyhexafluoroisopropyl benzene (HFAB) was used as starting material. The increased acidity effect due to the electronegative inductive effect of the fluoroalkyl group facilitated its reaction with the acid chloride to produce the esters. The apparatus was kept dry to prevent the reaction between water and the acryloyl chloride and dry THF, distilled from sodium and benzophenone, was used as a solvent. The addition of the acryloyl chloride to the reaction mixture composed of HFAB, triethyl amine and tetrahydrofuran was performed very slowly and an external ice bath was applied during the addition because of the exothermic nature of the reaction. After the completion of the reaction, the solution was poured into water to remove the triethyl amine hydrochloride. A mixture of hexane and ethyl acetate (80/20 by volume) as the elution solvent was used to purify the crude monomer by column chromatography. The purity of the monomer was found to be 98% based on minimum detectable quantity by gas chromatography.

4.1.2 Synthesis of Hexafluoro-2-phenyl-2-propyl Allyl or-4-pentenyl or-7-octenyl Ether

The synthesis of the monomers was performed according to the scheme shown below. The reaction of HFAB with allyl bromide was first attempted using THF as solvent; but, the conversion was poor, giving about 50% of product. This nonpolar, aprotic solvent was apparently not effective in stabilizing the development of charge separation in order to facilitate the S_N2 reaction. The solvent was then changed to N,N-dimethyl formamide (DMF). DMF was a good solvent for the S_N2 reaction because the oxygen in the DMF acts as electron donor toward cations while the anion of the alcohol was weakly solvated and displayed high reactivity. The reaction was carried out readily between the salt and the organic reactant bearing a bromide leaving group. Three ether derivatives were prepared according to this method.



The apparatus was kept dry and flushed with argon. The addition of sodium hydride to the solution of HFAB and DMF was performed slowly at room temperature because of the exothermic nature of the reaction. After the addition was completed, the reaction was stirred for 30-45 minutes to allow the deprotonation to be complete. The addition of the organic reactant bearing the bromide was performed slowly. After the addition was completed,

the reaction flask was put into an oil bath. The reaction temperature was usually kept fairly low to minimize side reactions. The times of the experiment varied from 14h up to 24h depending on the length of the alkyl chain. After the completion of the reaction, isopropyl alcohol was added slowly to the reaction to destroy any remaining NaH. The solution was poured into water to remove the sodium salt formed during the reaction. Ethyl ether was used for the extraction. The light yellow crude material obtained after evaporation of the ether was found by gas chromatography to contain (0.5-1%) of starting material. Purification of the product by column chromatography resulted in a product of high purity (99.9%). Hexane was used as the elution solvent. The product obtained was in a yield of 90% for compound I, 85% for compound II and 80% for compound 3. The ^1H NMR spectrum of the compound I in CDCl_3 (Figure 3) shows peaks at about (7-8 ppm) for the aromatic region, (5-6 ppm) for the vinyl group and (1-3 ppm) for the aliphatic region. The percentage of signals varied depending on the number of the carbon atoms that were connected to the HFAB moiety. The aromatic region has three different signals distinguished as doublet of doublets (dd), triplet (t) and doublet (d). The doublet belonging to the proton bulky group split to a small extent. The doublet of doublets (dd) belonged to the proton *meta* with respect to the quaternary carbon, and the triplet belongs to the proton *para* to the substituent on the benzene group not nicely represented as (1,3,1) and deshielded certainly due to steric congestion.

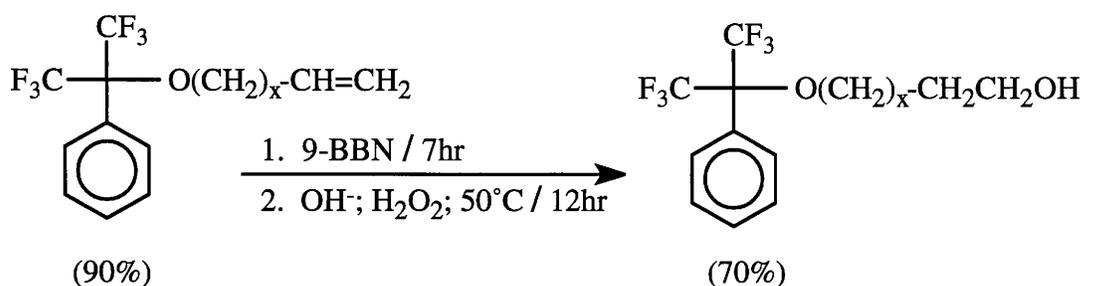
The vinyl group showed three types of signals, one peak was due to the geminal proton which appeared as a multiplet (5.3-3.8 ppm). The two protons appearing as doublet of doublets, were assigned to protons *cis* and *trans* with respect to the proton geminal. Both appearing at about 5 ppm were distinguished by the coupling constant, with the coupling constant *trans* being larger than the *cis*. The aliphatic region appeared between 1 and 4 ppm depending on the number of carbons present in the molecule.

The ^{13}C NMR spectrum shows different peaks. The sp^2 hybridized carbon appearing at about 124 ppm confirms the predicted shifts for (C=C). The substituted benzene exhibits four

different types of carbon resonance varying from 131 ppm up to 140 ppm. The quaternary carbon accounts for being the smallest of the four peaks. The alkyl carbon peak appears between 20 and 65 ppm depending on the number of carbons incorporated between the HFAB moiety and the vinyl group. The NMR spectra are presented in Figures 3 to 6.

4.1.3 Synthesis of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propanol, Compound 4, or 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentanol, Compound 5, or 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octanol, Compound 6.

The alkenyl ethers described above were used as starting materials in subsequent research. The reaction apparatus was kept dry and under nitrogen because 9-borabicyclo[3.3.1] nonane, 9-BBN reacts violently in the presence of water. The addition of 9-BBN to the solution containing the alkene and the THF was performed slowly at room temperature.



X=1 \longrightarrow Compound 4, yield = 70%

X=3 \longrightarrow Compound 5, yield = 68%

X=6 \longrightarrow Compound 6, yield = 65%

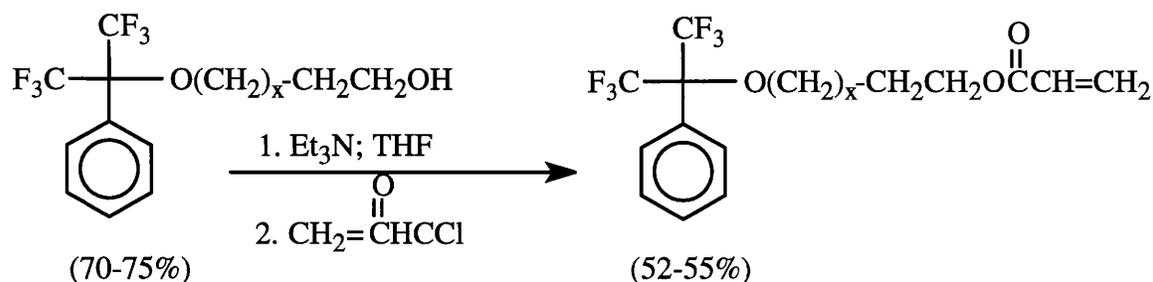
The alkenyl ether (1, 2, 3) was reacted with 9-BBN, then oxidized to compound 4, 5, or 6 in the presence of NaOH and H₂O₂. 9-BBN was selected for the hydroboration because it is more selective than borane itself, and the large steric requirement of the reagent results predominantly in a desirable regioselectivity.

between the two carbon atoms of the double bond. The usefulness of the hydroboration reaction in synthesis arises from the fact that the alkyl borane formed can be converted by further reactions into a variety of other products. A practical advantage of this reaction is that it is often unnecessary to isolate the intermediate organoborane. The time of the reduction step was twelve hours for 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propanol, 16 hours for the 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentanol and 24 hours for the 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octanol.

The oxidation of the organoborane to the alcohol was effected by 30% alkaline hydrogen peroxide which was carefully added dropwise. The reaction mixture was maintained at room temperature because of the exothermic nature of the reaction. After the completion of the reaction, the reaction mixture was saturated with potassium carbonate to neutralize the excess acid still present in the reaction. The reaction temperature was kept fairly low to minimize side reactions from occurring. The organic portion was extracted with diethyl ether, and a colorless oil was obtained after removal of the ether. The purification by column chromatography using a mixture of ethyl acetate hexane (80/20 by volume) as eluent resulted in a product of a sufficient purity for the next step.

The products were characterized by ^1H and ^{13}C NMR in CDCl_3 using TMS as an internal standard. The NMR spectra are shown in Figures 7 to 10. The aromatic region shows a pattern similar to the one described above for the ether precursors. The alkyl region shows two types of protons, one which appears at about 4-3 ppm, and the other at 1-3 ppm with the presence of the OH group making the peak very broad, due presumably to oxygen-hydrogen exchange. In the carbon spectrum, the aromatic region is similar to that discussed above for ether precursors. The estimation of the chemical shifts of carbon present in the aliphatic region are down-field due to the presence of electron withdrawing groups such as oxygen and fluorine atoms.

4.1.4 Synthesis of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate, Compound 7, or 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentyl Acrylate, Compound 8, or 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octyl Acrylate, Compound 9



Compound 7 (x=1), yield = 55%

Compound 8 (x=3), yield = 53%

Compound 9 (x=6), yield = 52%

The pure intermediate alcohol derived from the preceding reaction was used as starting material in the facile acrylate-forming reaction with acryloyl chloride. The addition of acryloyl chloride to the solution of 3-hexafluoro-2-phenyl propyl-1-alcohol, triethyl amine and tetrahydrofuran was performed very slowly and an external ice water bath was applied during the addition because of the exothermic nature of the reaction. After the completion of the reaction, the solution was poured into water to remove triethylamine hydrochloride. A solution of 10% sodium bicarbonate was added to the resultant mixture to neutralize any remaining acid and organic layers were extracted with diethyl ether. The purification of the product by column chromatography was made possible using a mixture of hexane and ethyl acetate (80/20 by volume) as eluent. The presence of the pure monomer was detected by thin layer chromatography, and the purity was found to be of 99% based on a minimum detectable quantity by gas chromatography. Similar procedures were used to synthesize the other acrylate monomers in which the alkyl spacer arm between the propoxy group and the acrylate group containing five and eight carbons. The

monomers were characterized by ^1H and ^{13}C NMR in CDCl_3 with TMS as an internal standard. The NMR spectra are shown in Figures 11 to 16.

4.2 Polymer Synthesis

4.2.1 Attempted Bulk Polymerization of Hexafluoro-2-phenyl-2-propoxy-1-acrylate Derivatives

The fluoroacrylate polymers without the alkyl chain between the HFAB moiety and the vinyl group have been previously reported and were found to be useful in biomedical applications.[20] Bulk and solution polymerization of the acrylate of 1-(hexafluoro-2-hydroxy-2-propyl)-3-(hexafluoro-2-methoxy-2-propyl) benzene (Compound A) were tried using 1,2,2-azobis(iso)butyronitrile (AIBN) as initiator. Different mole ratios of the initiator to monomer were used and the reactions were conducted with different reaction times and temperatures as indicated in Table II. [20] These polymerizations have resulted in low yield and low molecular weight polymers.

Table II: Bulk and Solution Polymerization of the acrylate of 1-Hexafluoro-2-hydroxy-2-propyl-3-hexafluoro-2-methoxy-2-propyl Benzene (A) [24]

Polymer	Mole % of A	Mole % of MA ^a	$[\eta]^b$ dL/g Bulk/Solution
10	100	---	0.32/0.29
10 a	75	25	0.33/0.31
10 b	50	50	0.39/0.36
10 c	40	60	0.46/0.41

(a) MA: methyl acrylate; (b) measured at 25°C in Chloroform at a concentration of 0.25-0.30 g/dL.

When bulk polymerization of the compound 7 was attempted, no significant changes were observed. All of these polymerizations resulted in either a gummy solid or milky solution when poured into methanol. Most of the resulting polymers were insoluble in most

organic solvents. It is unknown at this point why these polymerizations resulted in insoluble polymers. Some papers suggest that this insolubility appears when the polymers are above their gel point. [25]

4.2.2 Solution Polymerization of the Different Acrylate Monomers.

The unsatisfactory results obtained from bulk polymerization led to a study of the solution polymerization of the different monomers. AIBN was used as initiator and the reactions were conducted for different times and temperatures as shown in Table III.

Table III: Solution Polymerization of Synthesis of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate (Compound 7) in 1,3-Bis-(trifluoromethyl) Benzene - Effect of Initiator Concentration and Temperature.

Compound 7	Initiator	Initiator Monomer Ratio	Temperature (°C)	Viscosity ^a (dL/g)	Yield (%)
7	AIBN	1 : 50	100	0.35	40
			80	0.45	39
			50	0.29	7
7	AIBN	1 : 100	100	0.33	38
			80	0.40	39
			50	0.23	5
7	AIBN	1 : 150	100	0.36	41
			80	0.40	39
			50	0.32	50
7	AIBN	1 : 200	100	0.37	37
			80	0.39	38
			50	0.18	25

(a) measurement at 25°C in chloroform at a concentration of 0.25-0.30 g/dL.

The reactions were conducted at 50°C, 80°C and 100°C. At each of the indicated temperatures, a constant initiator to monomer mole ratio of 1/50, 1/100, 1/150, 1/200 was investigated in order to find the optimum reaction conditions. The polymer produced from reactions run at 80°C with a constant initiator-to- monomer mole ratio of 1:50 using 1,3-bis(trifluoromethyl) benzene resulted in the highest inherent viscosity (0.45 dL/g). The poorest results were obtained for monomers using a 1/200 and 1/100 mole ratio at 50°C which gave less than 10% yield due to the temperature being too low to initiate formation of radical of sufficient concentration for polymerization.

The solution polymerization of hexafluoro-2-phenyl-2-propyl acrylate (HPPA) was investigated (Table IV). As evidenced by the inherent viscosity values observed, low molecular materials were obtained. Polymerizations involving a silicon-substituted HFAB monomer, monomer B (Table V) also resulted in low molecular weight materials.

Table IV: Solution Polymerization of 3-(Hexafluoro-2-phenyl-2-propoxy)-propyl Acrylate (HFPA)

Polymer	Reaction Time (min)	Mole % of HPPA in Feed	Mole % of MA ^a in Feed	$[\eta]^b$ (dL/g)	yield (%)
11	35	100	---	0.14	65
11 a	35	80	20	0.16	62
11 b	35	60	40	0.17	75
11 c	35	40	60	0.19	58
11 d	35	20	80	0.22	59

(a) MA: methyl acrylate; (b) measured at 25°C in chloroform at a concentration of 0.25-0.30 g/dL.

Table V: Solution Polymerization of the Acrylate of 5-(Hexafluoro-2-hydroxy-2-propyl)-1,1-dimethyl-3,3-bis(trifluoromethyl-2-oxa-1-silaindane) [26]

Polymer ^a	Mole % of B	Mole % of MA ^b	[η] ^c dL/g
12	100	—	0.20
12 a	75	25	0.21
12 b	65	35	0.25
12 c	32	68	0.33

(a) AIBN: Monomer ratio = 1:50; (b) MA: methyl acrylate; (c) measured at 25°C in chloroform at a concentration of 0.25-0.30 g/dL.

Homopolymerization and copolymerization of compound **7**, **8**, and **9** were conducted by using 1,3-Bis(trifluoromethyl)benzene as a solvent and AIBN as initiator in a 1:50 mole ratio. Yields varied from 49% to 71%. The polymers obtained were soluble in most organic solvents. Inherent viscosity was determined using chloroform as solvent. The data are presented in Table VI, VII and VIII.

4.3 Copolymer Synthesis

Polymers derived from hexafluoro-2-phenyl-2-propoxyalkyl acrylate in which the hexafluoro-2-phenyl-2-propoxy alcohol moiety is attached by flexible spacer arms, exhibited greater molecular weights than the previously reported (2-fluorophenyl)-2-hexafluoropropylacrylate in which the sterically demanding HFAB-group is joined directly to the acrylate group. These results suggest that high molecular weight hydrophobic polymers can be obtained if the bulky hexafluoro-2-aryl-2-propoxy moiety is extended from the polymer backbone by a flexible alkyl bridge. See Tables (VI-VIII).

Table VI: Solution Polymerization of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate (Compound 7)

polymer	Reaction Time- (min)	Mole % of 7 in Feed	Mole % of MA ^a in Feed	$[\eta]^b$ dL/g	Molecular Weight ^c ($\times 10^5$)	Yield (%)
13	45	100	---	0.45	5.9	51
13 a	10	80	20	0.79	9.8	49
13 b	10	60	40	0.67	9.2	46
13 c	10	40	60	0.48	8.4	46
13 d	10	20	80	0.93	10.3	55

(a) MA: methyl acrylate; (b) measured at 25°C in chloroform at concentration of 0.25-0.30 g/dL; (c) GPC by comparison to polystyrene standards in THF.

Table VII: Solution Polymerization of 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentyl Acrylate (Compound 8)

Polymer	Reaction Time (min)	Mole % of 8 in Feed	Mole % of MA ^a in Feed	$[\eta]^b$ dL/g	Molecular Weight ^c ($\times 10^5$)	Yield (%)
14	14-17*	100	---	0.68	17.7	71
14 a	5-15	80	20	0.32	10.8	69
14 b	5-15	60	40	0.49	13.2	57
14 c	5-15	40	60	0.34	10.4	57
14 d	5-15	20	80	0.82	24.4	48

(a) MA: methyl acrylate; (b) measured at 25°C in chloroform at a concentration of 0.25-0.30 g/dL; c: GPC by comparison to polystyrene standard in THF.

(*) hours

Table VIII: Solution Polymerization of 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octyl Acrylate (Compound **9**)

Polymer	Reaction Time (min)	Mole % of 9 in Feed	Mole % of MA ^a in Feed	$[\eta]^b$ dL/g	Molecular Weight ^c ($\times 10^5$)	Yield (%)
15	14-17 *	100	---	0.71	19,3	37
15a	5-15	80	20	0.74	19.8	40
15b	5-15	60	40	0.80	17.6	32
15c	5-15	40	60	0.87	18.9	38
15d	5-15	20	80	0.94	27.5	45

(a) MA: methyl acrylate; (b) measured at 25°C in chloroform at a concentration of 0.25-0.30 g/dL; c: GPC by comparison to polystyrene standard in THF.

(*) hours

The copolymerizations of the HFAB-derived acrylate monomers with methyl acrylate were performed for the same length of time (36 minutes), and yields ranged from 58% to 75%. The results are reported in Tables (VI, VII, VIII). The viscosities of these polymers were found to increase with the concentration of methyl acrylate in the polymer.

Three more polymers were synthesized by reacting compound **8** with methyl acrylate by changing the monomer ratio in order to increase the percentage yield of the polymer. Since the optimum reaction conditions had already been determined, these polymerizations were carried out at 80°C using 1:50 monomer mole ratio. The reaction proceeded to provide a reasonable yield and a low inherent viscosity. Therefore, no attempt was made to synthesize other polymers using the composition of 20% weight solution. The details of these polymerizations are given in Table (IX)

Table IX: Solution Polymerization of Compound **8** (20% wt solution)

Polymer	Reaction Time	Mole % of 8 in Feed	Mole % of MA ^a in Feed	$[\eta]^b$ dL/g	Yield (%)
14	14-17hr*	100	—	0.18	79
14 a	10-30	60	40	0.22	72
14 c	10-30	—	100	0.41	77

(a) MA: methyl acrylate; (b) measurement at 25°C in chloroform at a concentration of 0.25-0.30 g/dL.

4.4 Polymer Characterization

4.4.1 Thermal Analysis of Homopolymer and Copolymer

4.4.1.1 Thermogravimetric Analyses (TGA):

The TGA thermogram in air and nitrogen of polymers **13**, **14**, and **15** containing three, six, and eight carbon spacer arms respectively are presented in Figures 17 to 28. The first weight loss region for the three homopolymers **13**, **14**, and **15** is between ambient temperature and 190°C-250°C likely because of free or bound water or residual oligomer degradation. At the primary decomposition, the 10 % weight loss is at 354°C and 369 °C for Polymer **13**, 352°C and 368°C for polymer **14** and 322°C-358°C for polymer **15** respectively in air and nitrogen. The thermal stability of the different polymers run either in air or nitrogen decreased of about 3% from polymer **13** to polymer **14** and about 30% from polymer **14** to polymer **15**. This is due to the presence of an aliphatic chain infused into the polymer backbone making it less thermally stable than the aromatic ones which require more heat for their bonds to be broken. As expected, these polymers decomposed more rapidly in air than in nitrogen. These differences can be

attributed to the formation and subsequent degradation of oxides in polymers run in air, while those oxides are not formed in nitrogen. The copolymers show a lower stability than the homopolymers. The values for copolymers in air ranged from 369°C to 308°C, and in nitrogen from 351°C to 325°C. In addition to the reason listed above, the mole % of methyl acrylate in feed will make the polymer less thermally stable as opposed to the corresponding homopolymer. The thermal stability of the different polymers run either in air or nitrogen decreased about 5% to 8% for the copolymer run in air, and about 10% to 20% for the polymer run in nitrogen. The char yield of all materials is essentially zero at 600°C. These data are presented in Tables X, XI, and XII.

Table X: Thermal Data and Water Contact Angles for Homopolymerization and Copolymerization of 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentyl Acrylate (Compound **8**) with MA

Polymer	Thermal Stability (°C) 10% Weight Loss		Char Yield (%) at 600°C in Nitrogen	Water Contact Angle(a)
	in air	in N ₂		
14	352	368	3	108°
14 a	335	337	3	111°
14 b	330	335	4	110°
14 c	320	332	3	105°
14 d	325	330	3	107°

(a): average of 10 measurements $\pm 2^\circ$

Table XI: Thermal Data and Water Contact Angles for Homopolymerization and Copolymerization of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate (Compound 7) with MA

Polymer	Thermal Stability (°C) 10% Weight Loss		Char Yield (%) at 600°C in Nitrogen	Water Contact Angle ^(a)
	in air	in N ₂		
13	354	369	4	111°
13 a	339	351	5	108°
13 b	330	340	2	105
13 c	327	345	3	104°
13 d	315	325	4	109°

(a) average of 10 measurements $\pm 2^\circ$

Table XII: Thermal Data and Water Contact Angles for Homopolymerization and Copolymerization of 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octyl Acrylate (Compound 9) with MA

Polymer	Thermal Stability (°C) 10% Weight Loss		Char Yield (%) at 600°C in Nitrogen	Water Contact Angle (a)
	in air	in N ₂		
15	322	358	3	106°
15 a	319	343	4	104°
15 b	321	353	4	105°
15 c	308	325	3	111°
15 d	302	313	3	104°

(a) average of 10 measurements $\pm 2^\circ$

4.4.1.2 Differential Scanning Calorimetry(DSC)

The glass transition temperatures for the different polymers were determined by DSC. Table XIII shows these observed values which vary from 12° to -8°C. The DSC thermogram of the polymer **13** has a glass transition of about 11 to 12°C. As the number of carbons increases in the polymer backbone, the glass transition decreases. This is shown in Table XIII. The T_g values for polymer series **14** and **15** vary from (-2° to -4°) and (-4° to -7°) respectively. The glass transition for the homopolymers **13**, **14** and **15** are 11°, -2° and -4° respectively. The presence of a long aliphatic chain increases the flexibility and the softness of the polymer backbone, resulting in the decrease in T_g . However, there is a deviation in the case of the copolymers, where this trend is not quiet pronounced.

Table XIII: Glass Transition temperatures of Polymers 13, 14, and 15.

Polymers	T_g (°C)
13	11
13 a	12
13 b	11
13 c	11
13 d	12
14	-2
14 a	-5
14 b	-8
14 c	-5
14 d	-7
15	-4
15 a	-8
15 b	-7
15 c	-7
15 d	-5

4.4.2 Contact angle

Wetting properties have been studied using contact angle measurement of sessile drops of pure liquids on smooth solid surfaces. Angles were obtained via a contact angle goniometer. In examining the wetting properties of the different solids surfaces of homoacrylate and copolyacrylate polymers, the values ranged from 104°C up to 111°C, which shows that these materials are less wettable, as was predicted. The lower contact angle found for polymer **13 c** (Table XIV) indicates that water has spread over this surface to a greater extent and thus reflects a more wettable surface than the other copolymer and homopolymers, and shows at the same time greater attractive forces between water and this particular copolymer.

Table XIV : Water Contact Angles for Polymers 13, 14, and 15

Polymers	Water Contact Angle (a)
13	111
13 a	108
13 b	105
13 c	104
13 d	109
14	108
14 a	111
14 b	110
14 c	105
14 d	107
15	106
15 a	105
15 b	111
15 c	106
15 d	102

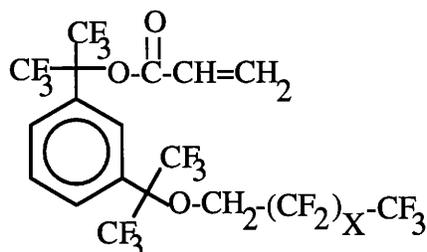
(a): average of 10 measurements $\pm 2^\circ$

The contact angle for the homopolymers **13**, **14** and **15** are 111°, 108°, and 106°, respectively. This reveals that the contact angle decreases with increasing the number of carbons in the aliphatic chain. The reason can be attributed to the introduction of methylene which decrease the concentration of the fluorinated monomer at the surface, resulting in the decrease of contact angle; however, there is a little deviation in the case of copolymer where the introduction of methyl acrylate into the polymer backbone should have resulted in the decrease of contact angle as well in this series.

5.0 Conclusion

New acrylate monomers and polymers derived from HFAB in which the HFAB moiety is separated from the polymerizable double bond by a hydrocarbon spacer arm were synthesized. Mono- and copolymerizations of these monomers were effected in solution by free radical techniques. High molecular weight polymers were obtained in yields up to 71% when the flexible spacer arm was incorporated between the HFAB moiety and the vinyl group. The inherent viscosity of these polymers ranged from 0.3 g/dL up to 0.9 g/dL. All the polymers formed colorless, transparent, tacky films and started decomposing at about 376 °C in N₂. The glass transition temperatures, ranged from -8°C to 47°C.

6.0 Suggestion For Future Research



A logical extension of this research is the synthesis of fluorinated acrylate derived from 1,3 (HFAB) with a fluorocarbon tail. The solubility of this model compound in supercritical carbon dioxide, (SC CO₂) could be studied. The presence of the fluorocarbon tail is anticipated to enhance the solubility of the compound in SC CO₂. In addition, the incorporation of the fluoroalkyl group into the polymer backbone can be used to study the polymer wettability. It is anticipated that in the main chain composition, the side chain length or size of among many other factors may influence the wettability of this kind of compound.

Further, It would be of interest to consider what effect if any, can be expected from compositional changes in the polymer main chain. Previous studies have shown that changing the composition of the backbone would influence the wettability. [27] The effect would be affected by using polymers with similar side chains, fluorine content, and fluorine atom arrangement, but differing in main chain composition. In addition to main chain composition, the pendant chain length may have an effect on the wettability. The critical surface tension may be studied using compounds of this sort. It was found that, in fact, in order to achieve the low critical surface tension value associated with completely fluorinated acids, for example, a fairly long fluorinated chain terminated by CF₃ was required. It might be interesting to further study the critical surface tension by varying the end chain of the fluoroalkyl group CF₃-CF₂-CFH₂ to know which factor will best influence the wetting properties and solubility of polymeric materials.

FIGURES 1-47

Figure 1:
 ^1H NMR of 1,3 Bis- HFAB

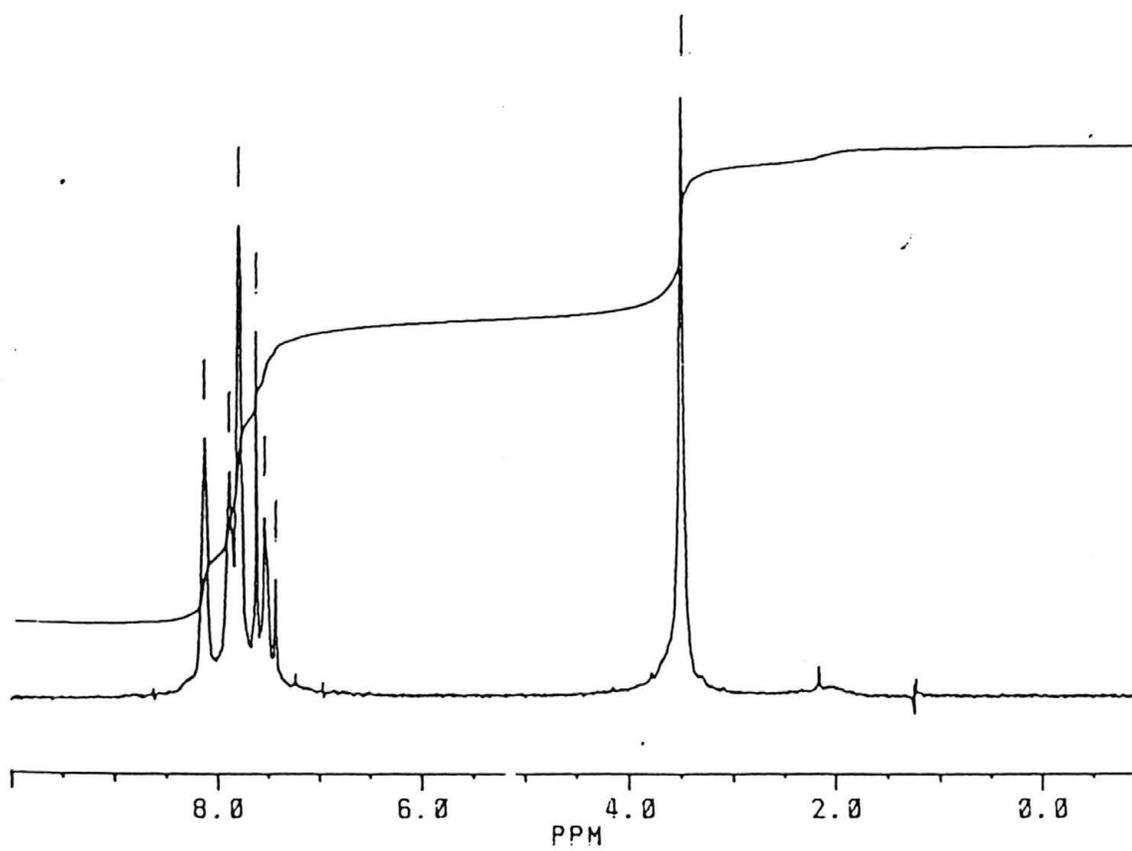


Figure 2:
 ^{13}C NMR of Monomethyl Ether of 1,3-Bis-HFAB

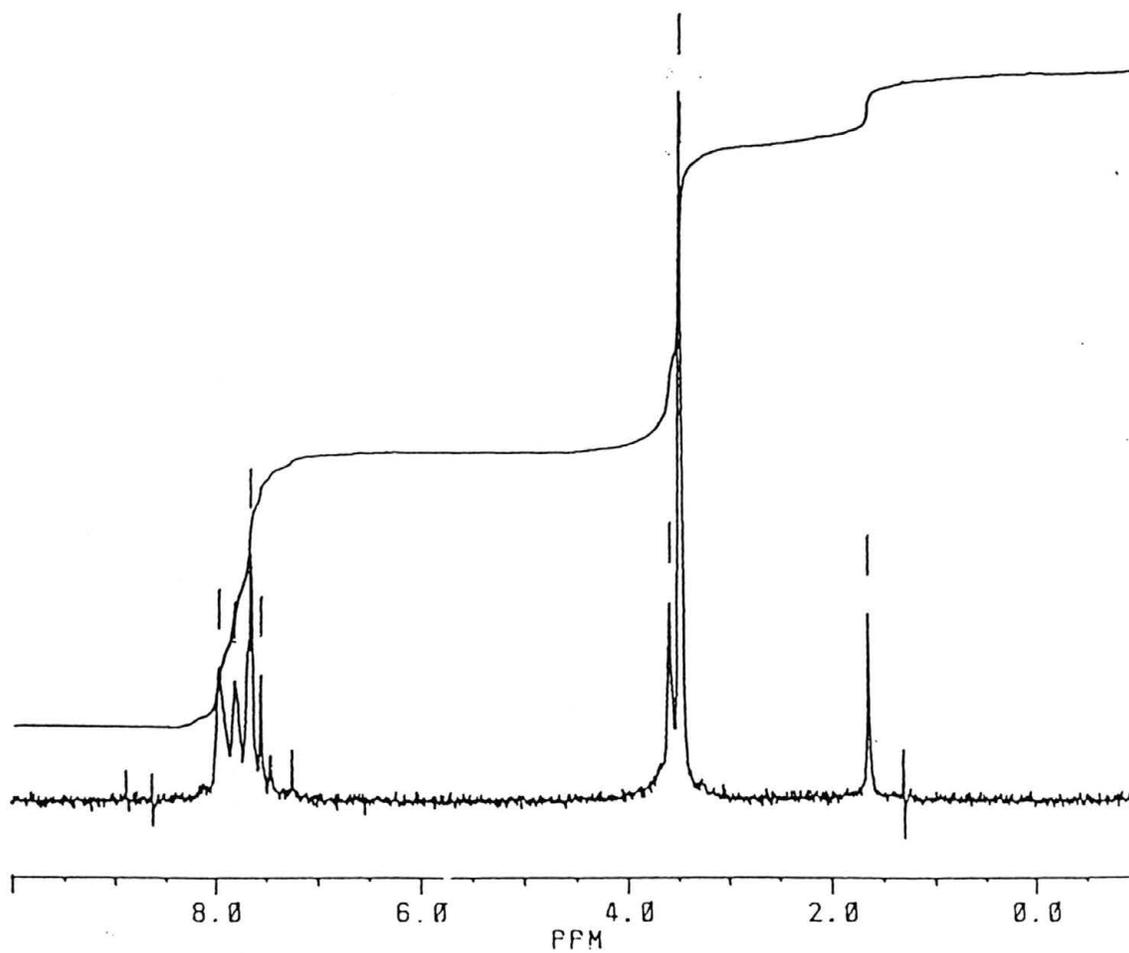


Figure 3:
 ^1H NMR of Monomethoxy 1,3-Bis-HFAB Methacrylate

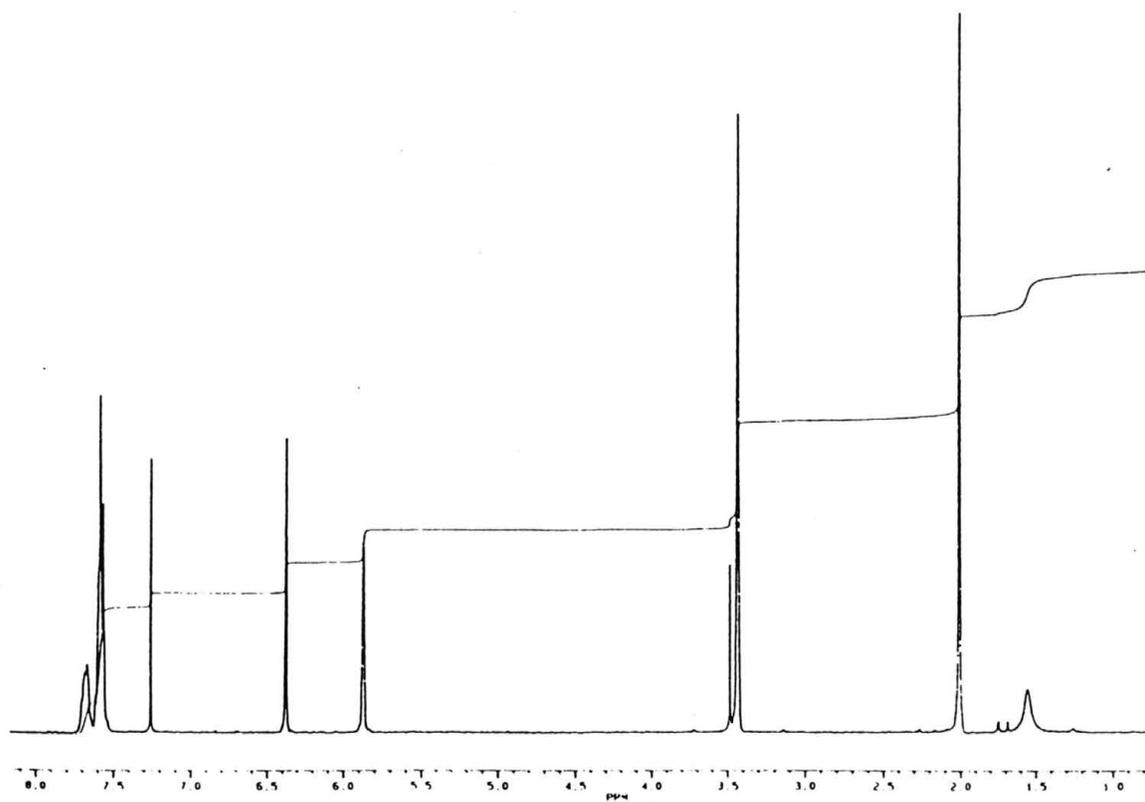


Figure 4:
 ^1H NMR of 2-Hydroxyhexafluoroisopropylbenzene (HFAB)

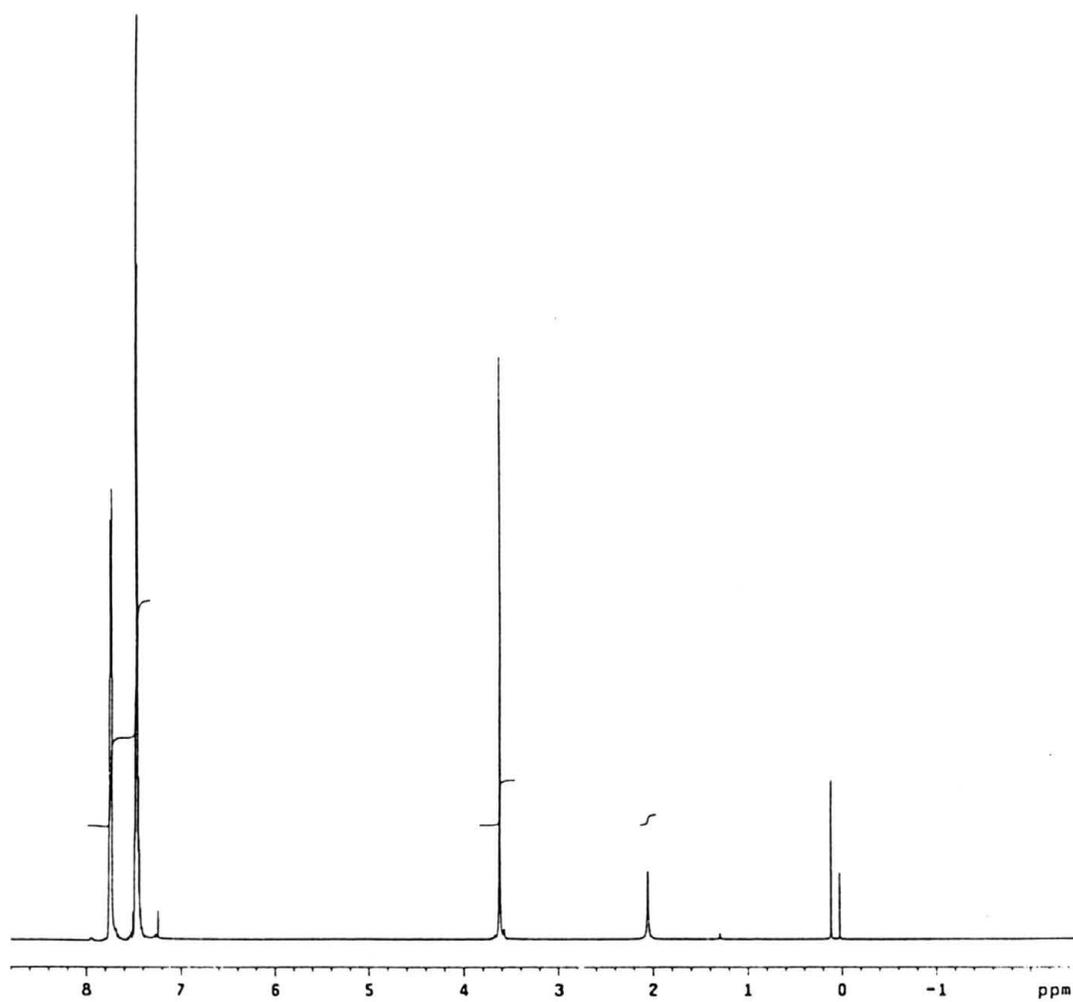


Figure 5:
 ^{13}C NMR of 2-Hydroxyhexafluoroisopropylbenzene (HFAB)

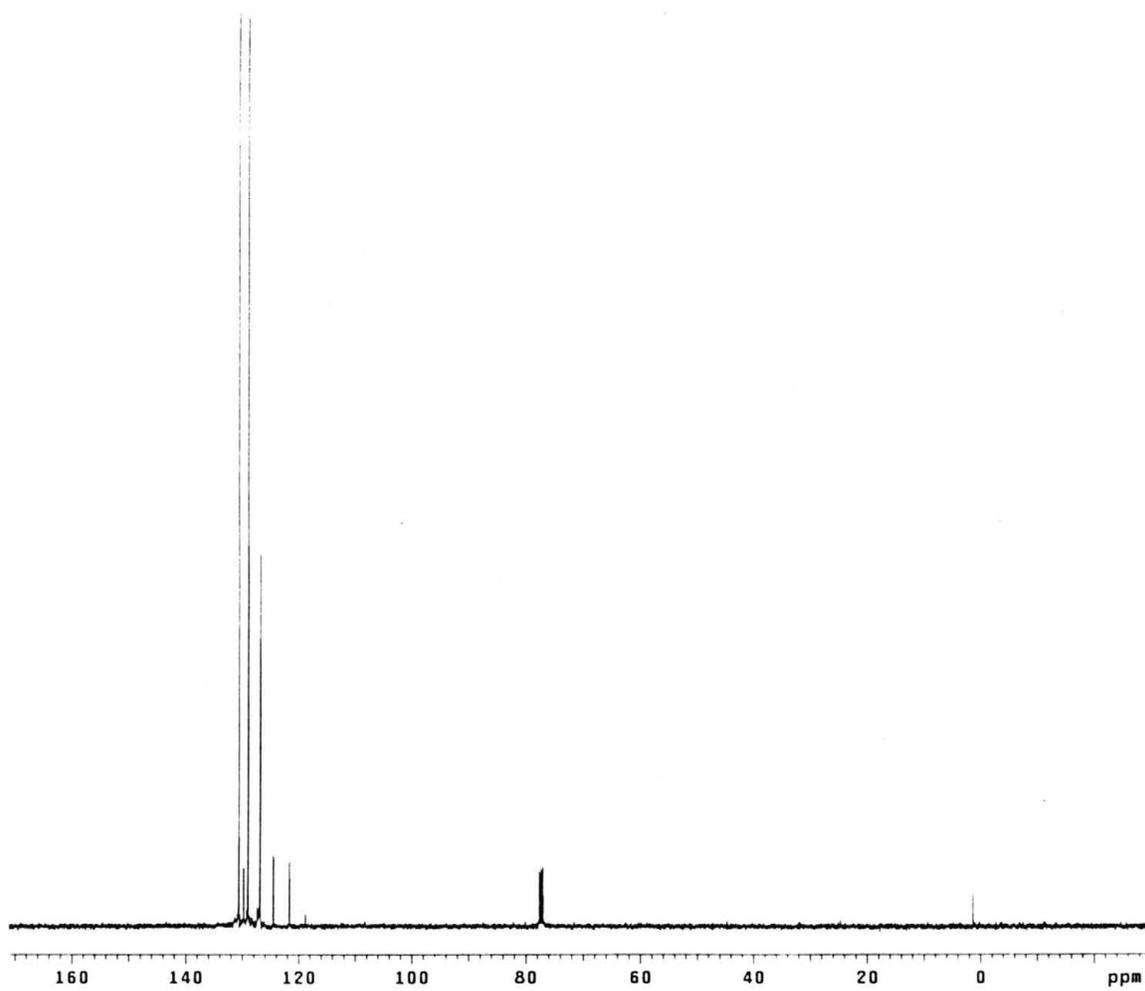


Figure 6:
 ^1H NMR of Hexafluoro-2-phenyl-2-propyl Allyl Ether

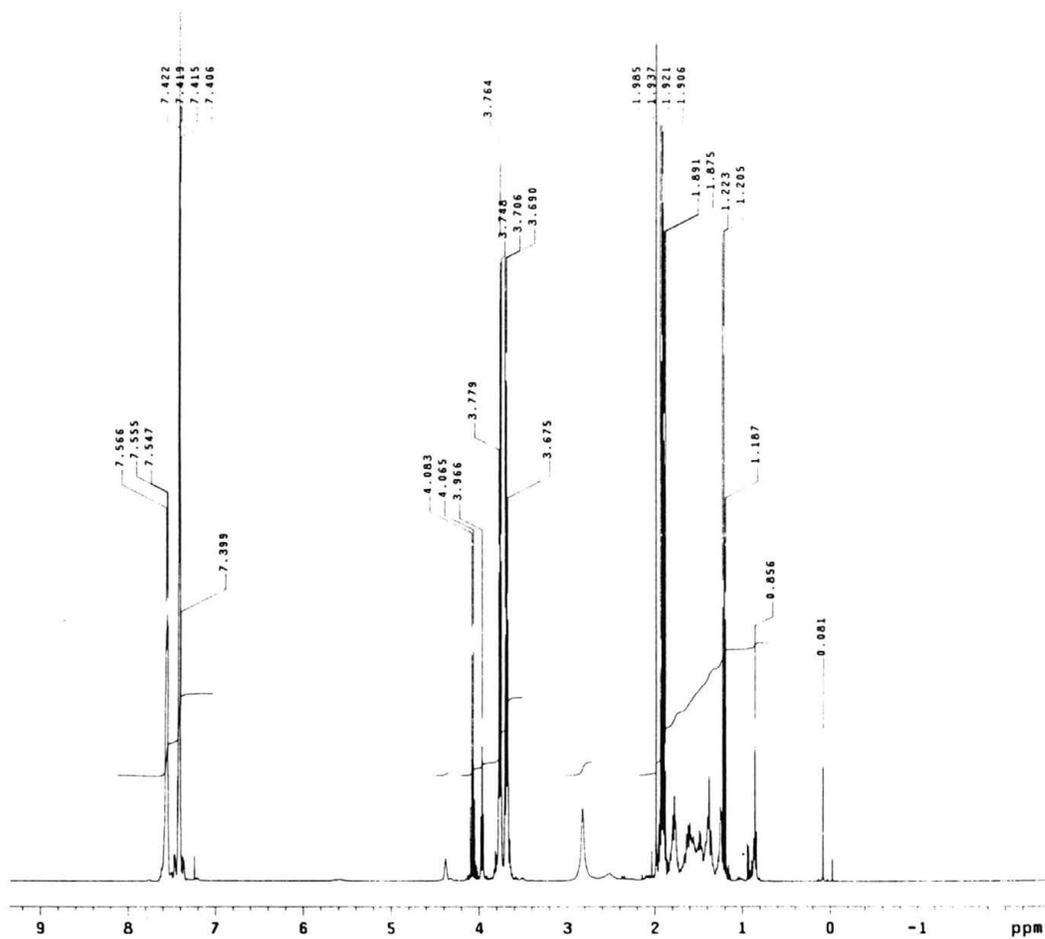


Figure 7:
 ^{13}C NMR of Hexafluoro-2-phenyl-2-propyl Allyl Ether

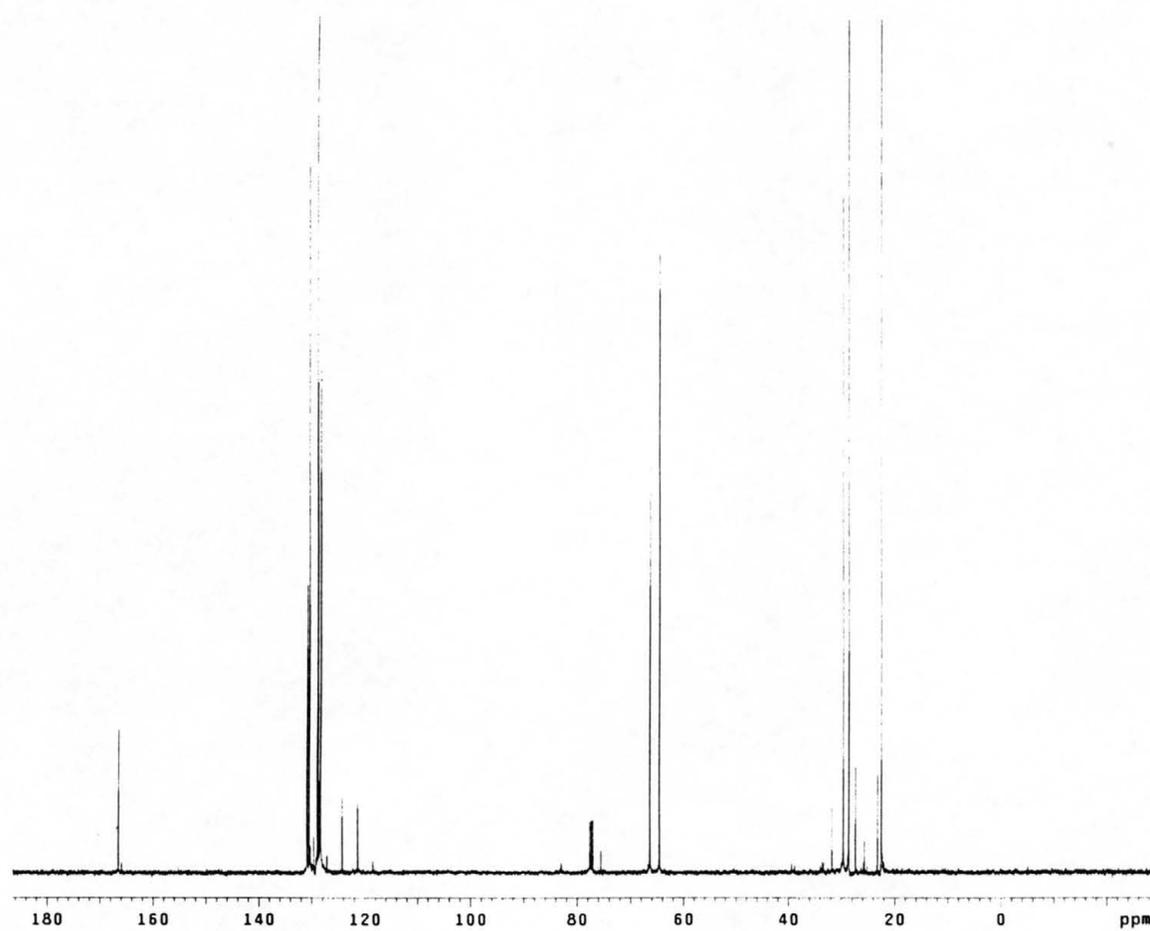


Figure 8:
 ^1H NMR of 2-Hexafluoro-2 phenyl -2- pentyl Allyl Ether

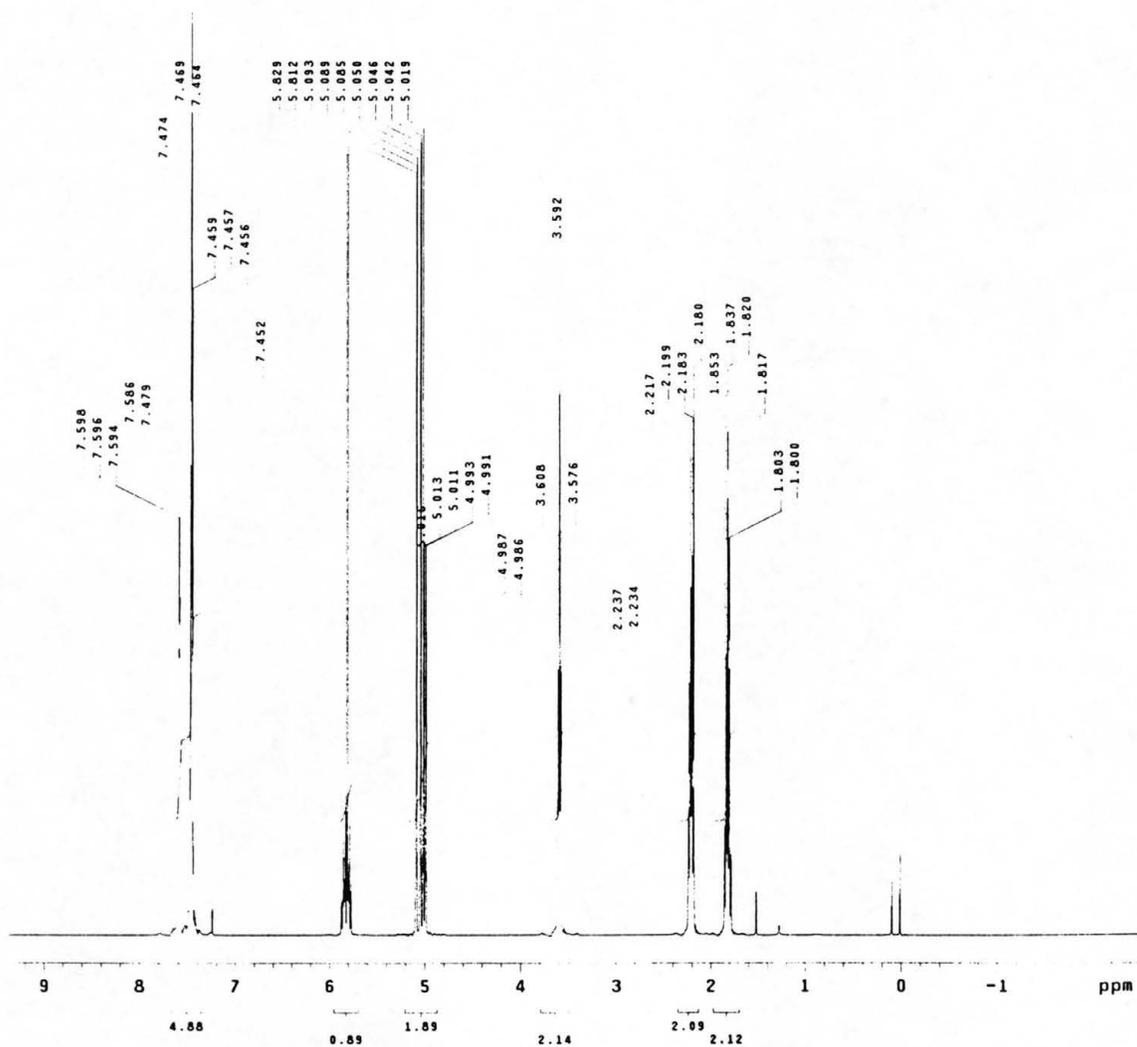


Figure 9:
 ^{13}C NMR of 2-Hexafluoro-2 phenyl -2- pentyl Allyl Ether

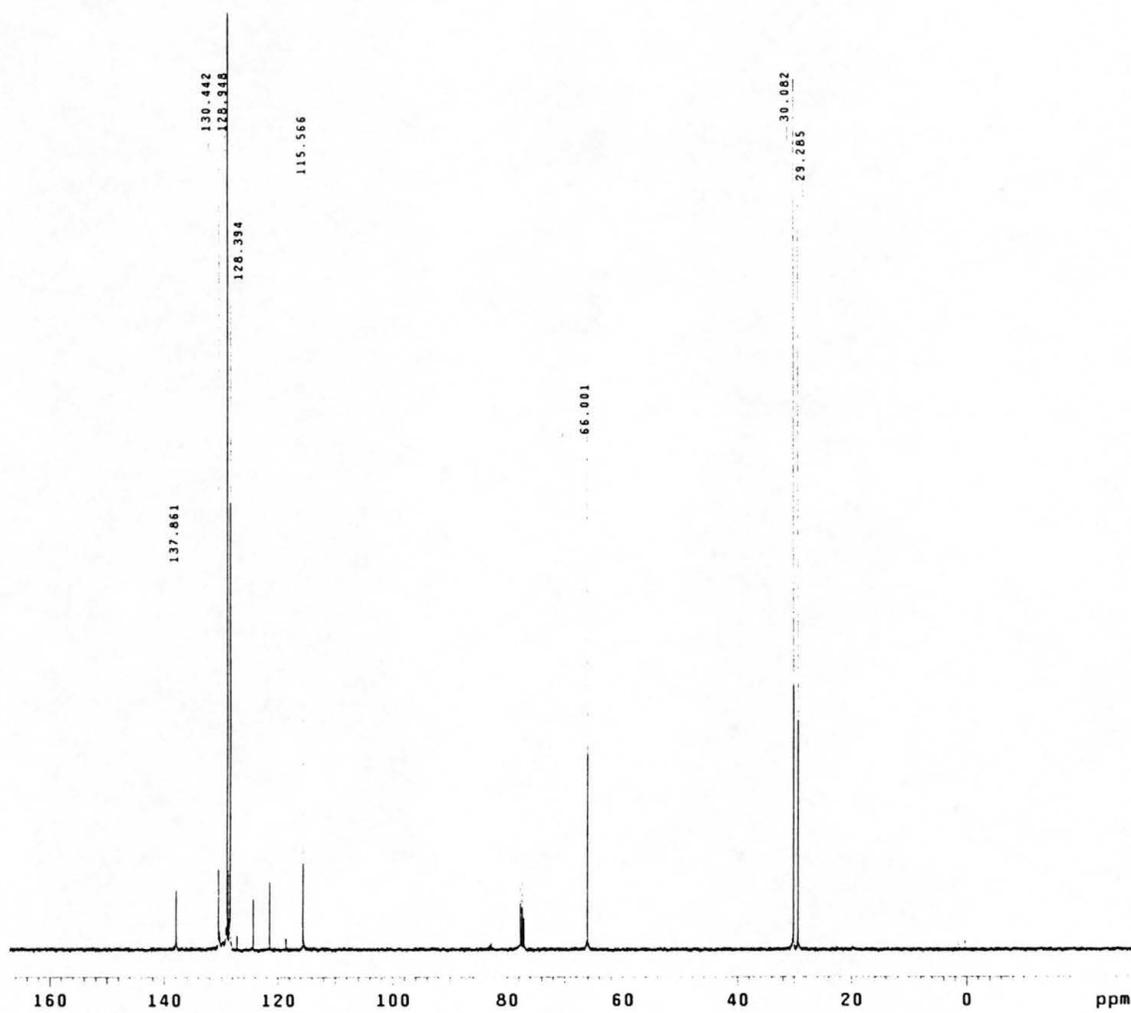


Figure 10:
 ^1H NMR of Hexafluoro-2-phenyl -2- octyl Allyl Ether

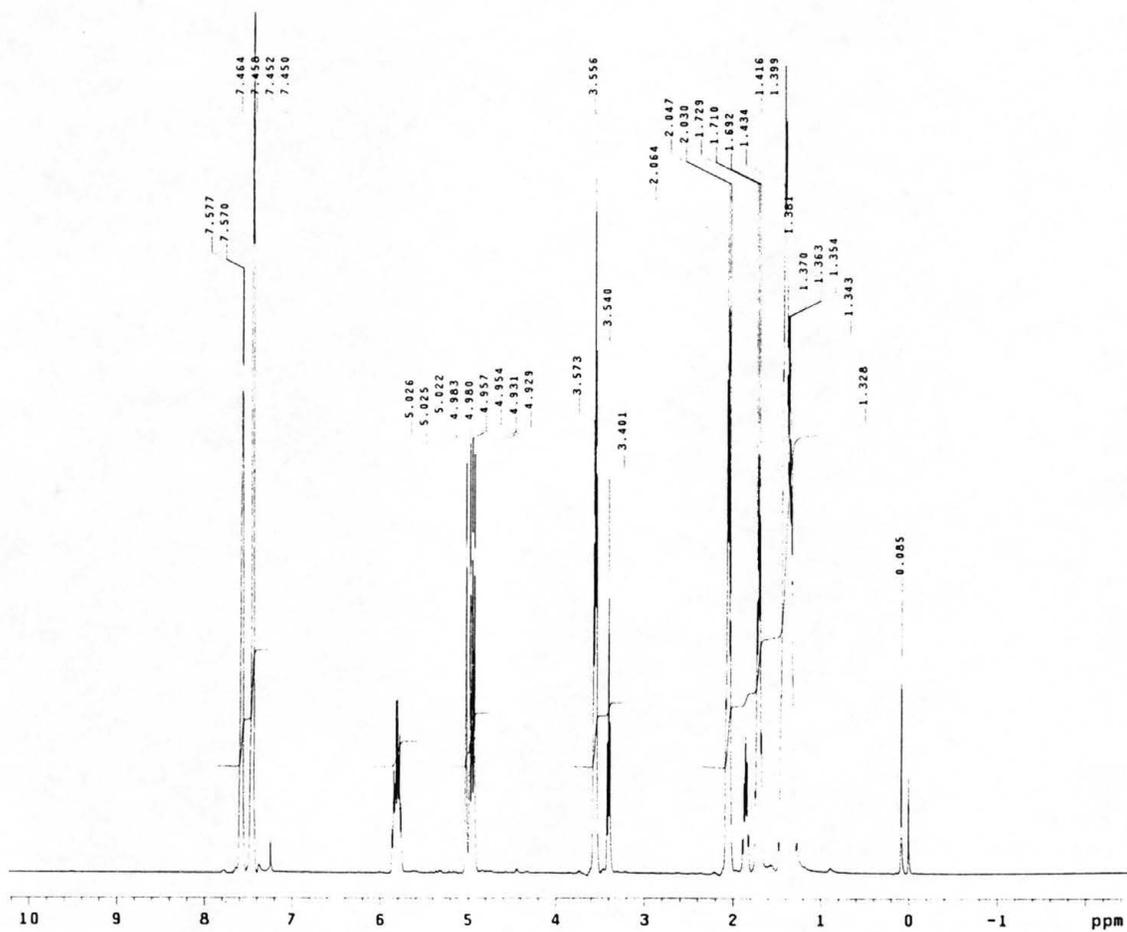


Figure 11:
 ^{13}C NMR of Hexafluoro-2-phenyl -2- octyl Allyl Ether

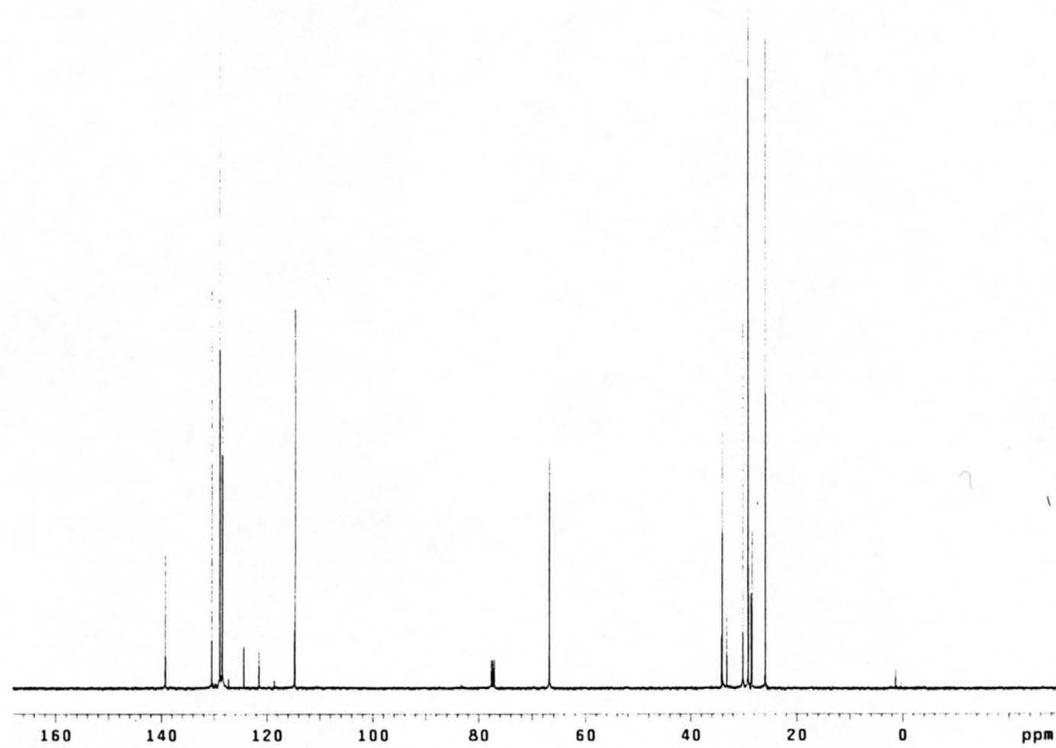


Figure 12:
 ^1H NMR of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propanol

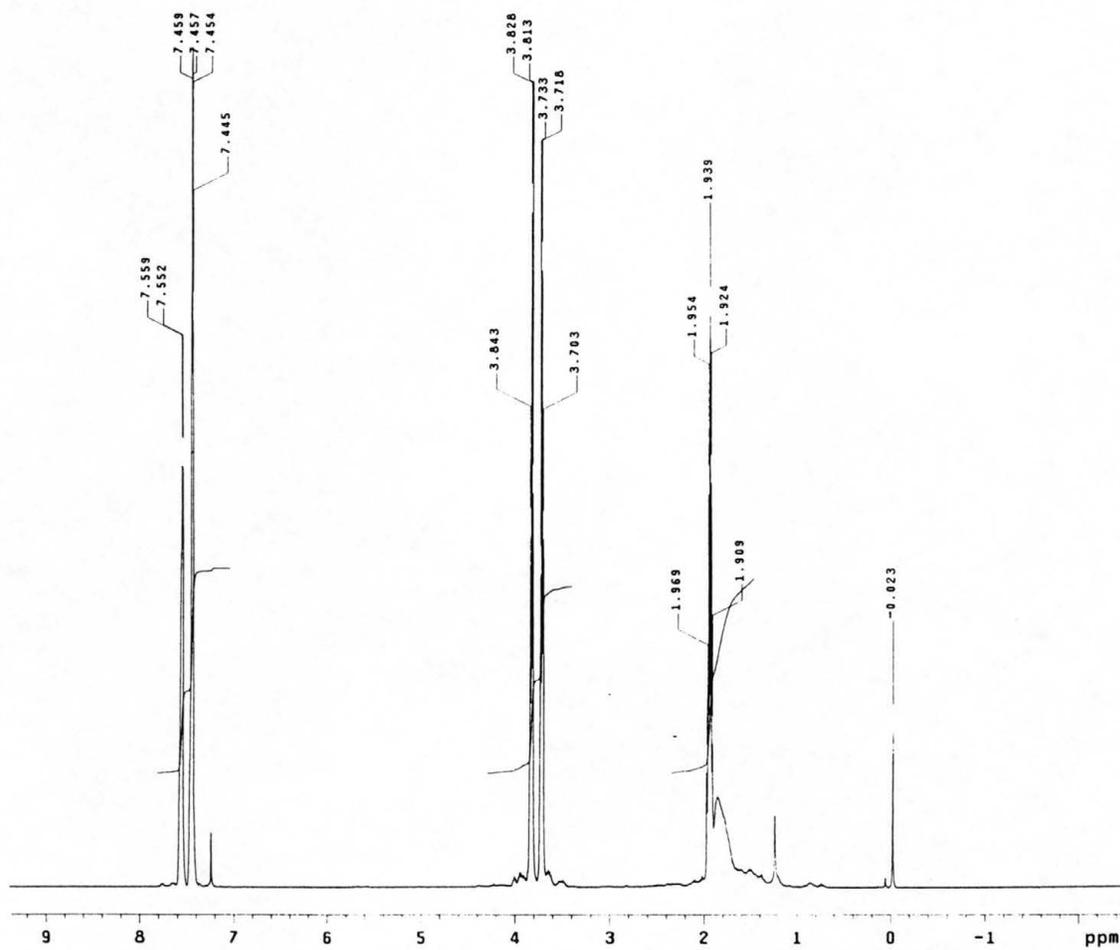


Figure 13:
 ^{13}C NMR of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propanol

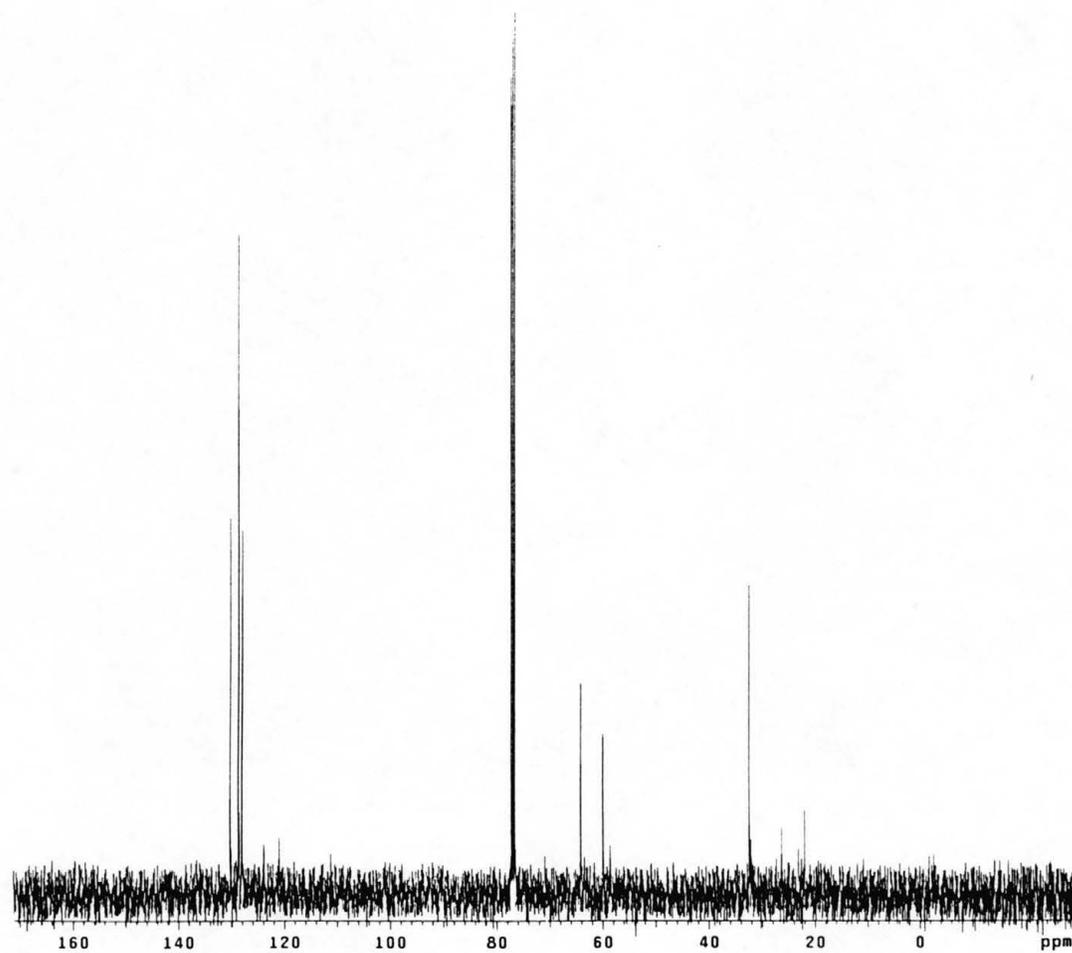


Figure 14:
 ^1H NMR of 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentanol

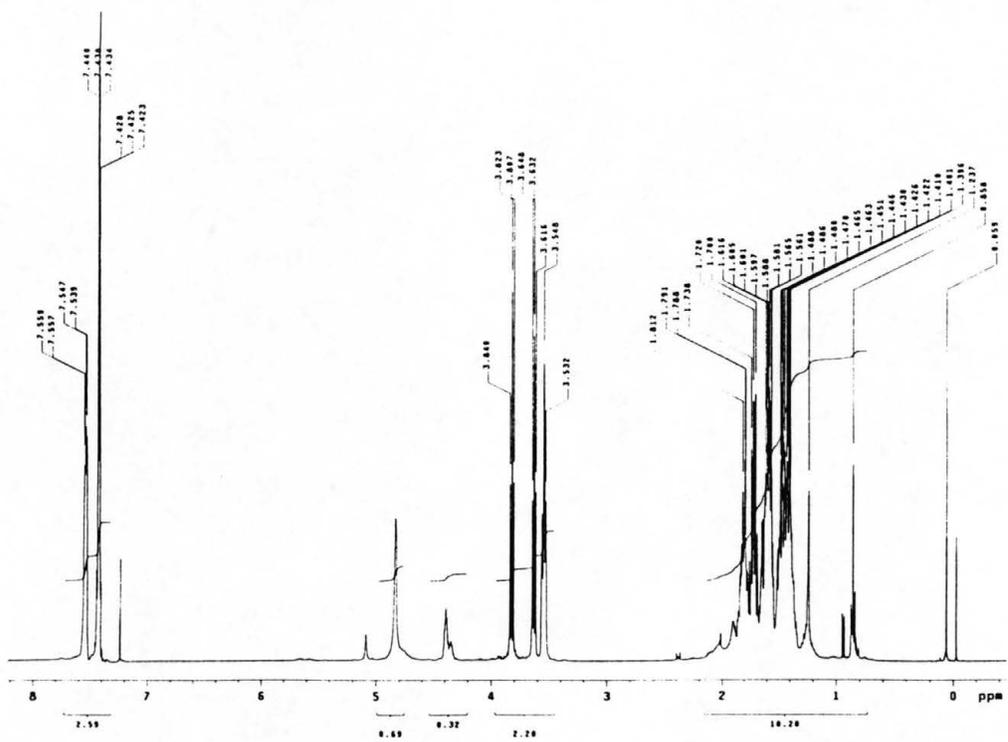


Figure 15:
 ^{13}C NMR of 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentanol

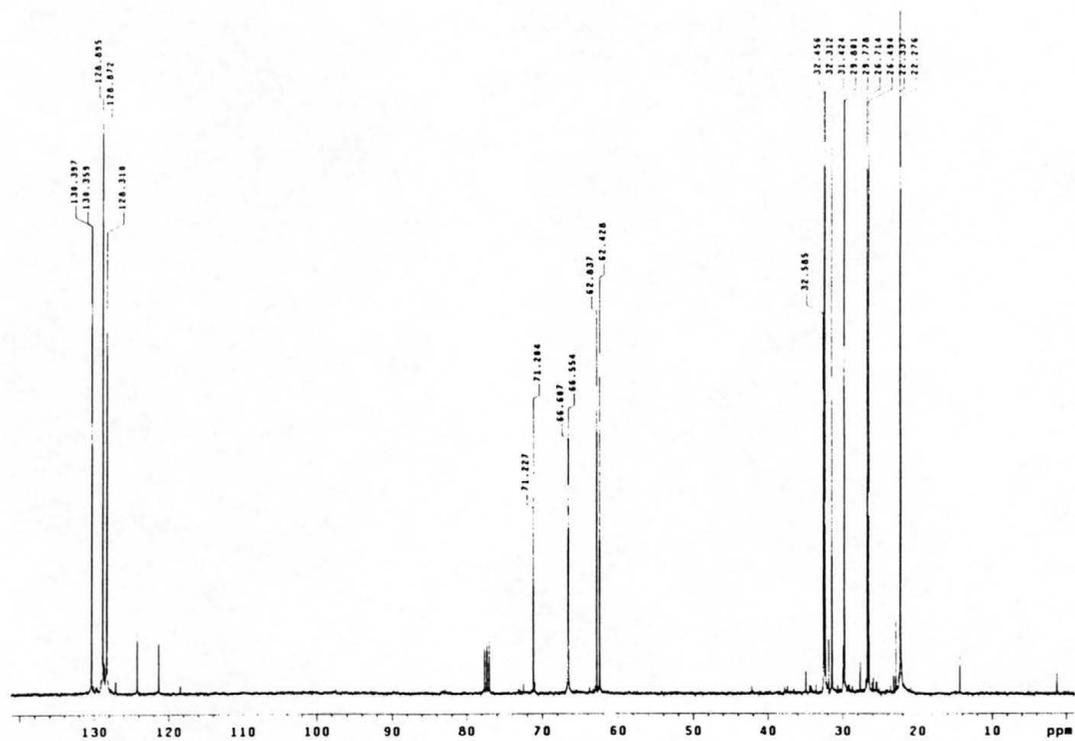


Figure 16:
 ^1H NMR of 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octanol

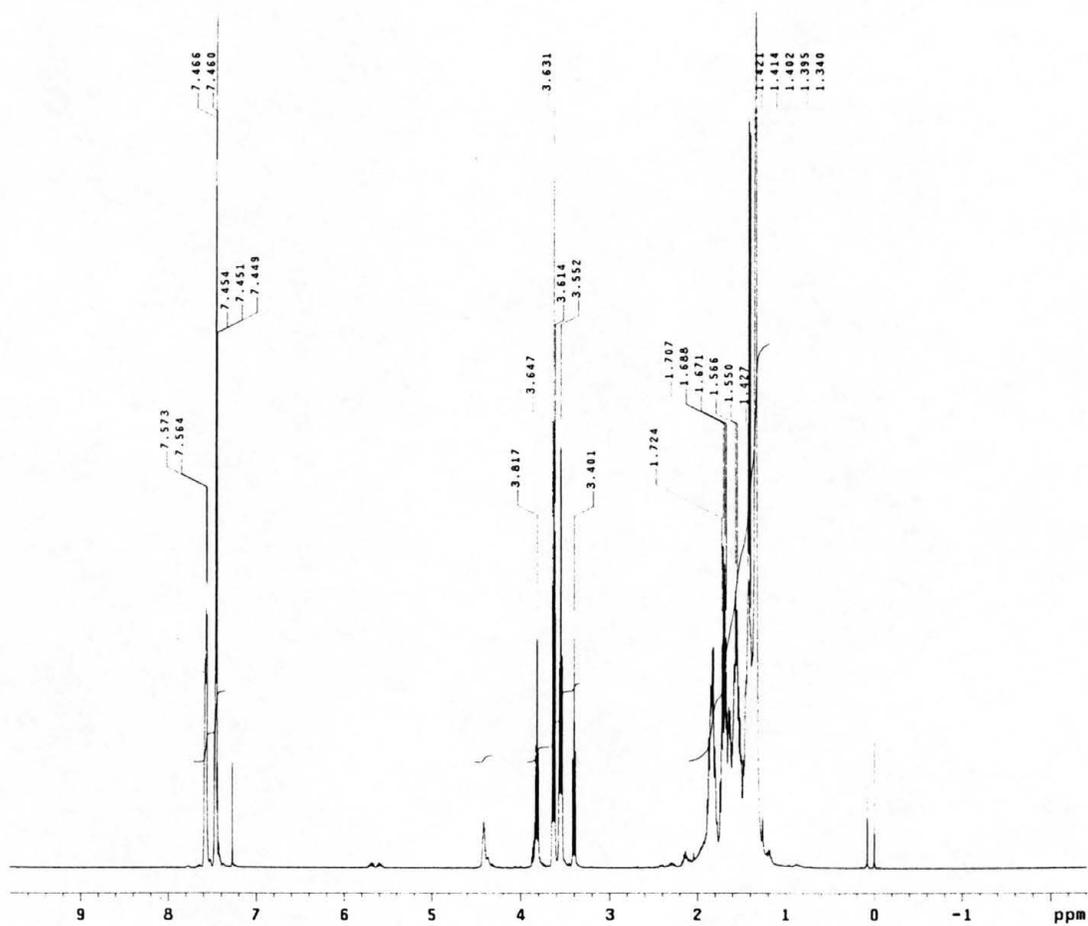


Figure 17:
 ^{13}C NMR of 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octanol

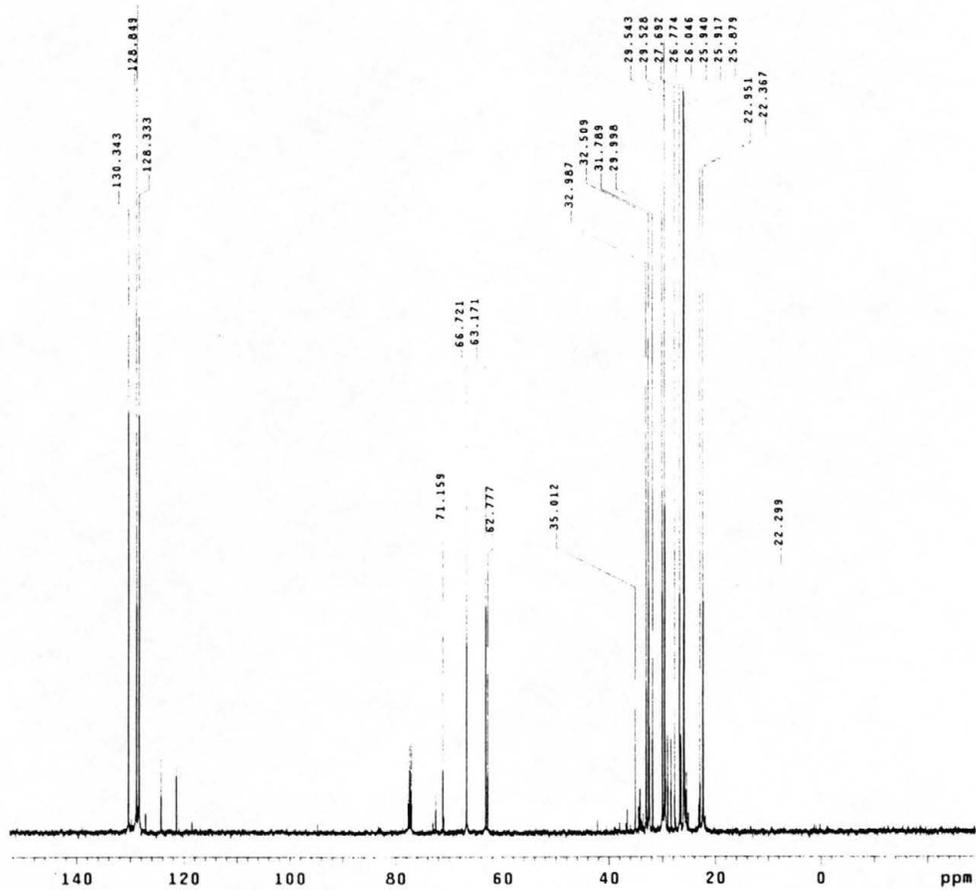


Figure 18:
 ^1H NMR of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate

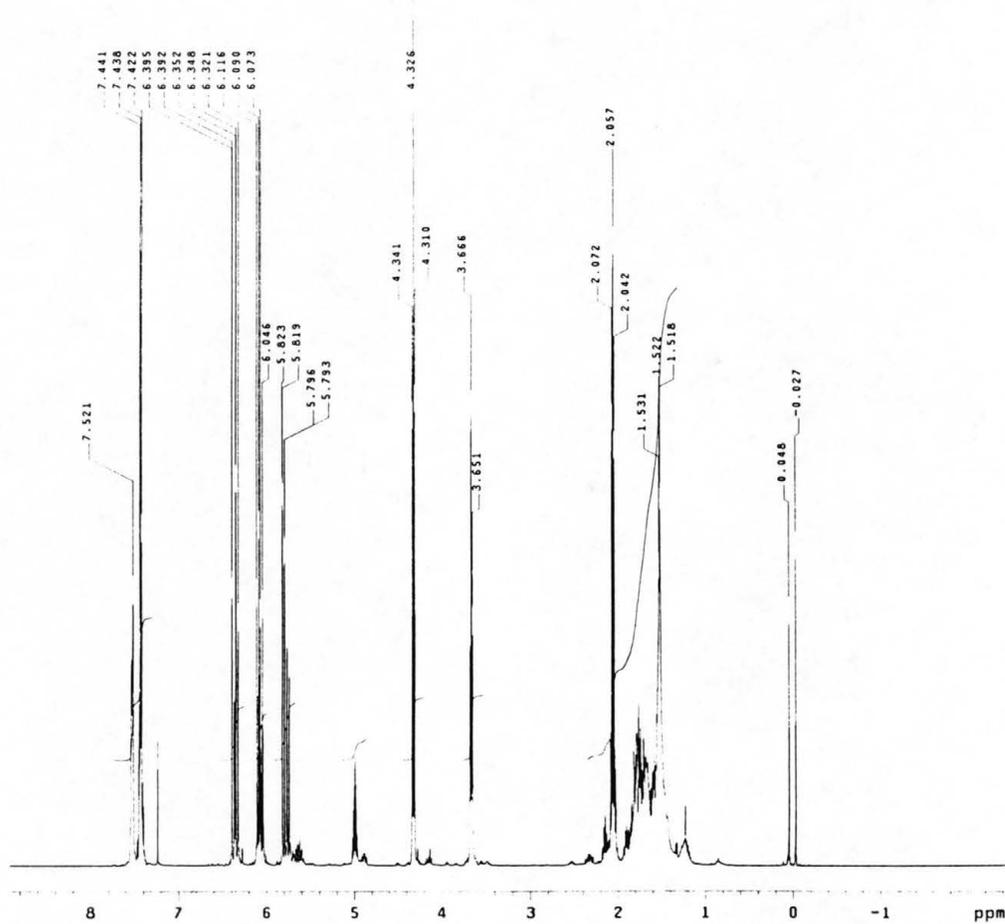


Figure 19:
 ^{13}C NMR of 3-(Hexafluoro-2-phenyl-2-propoxy)-1-propyl Acrylate

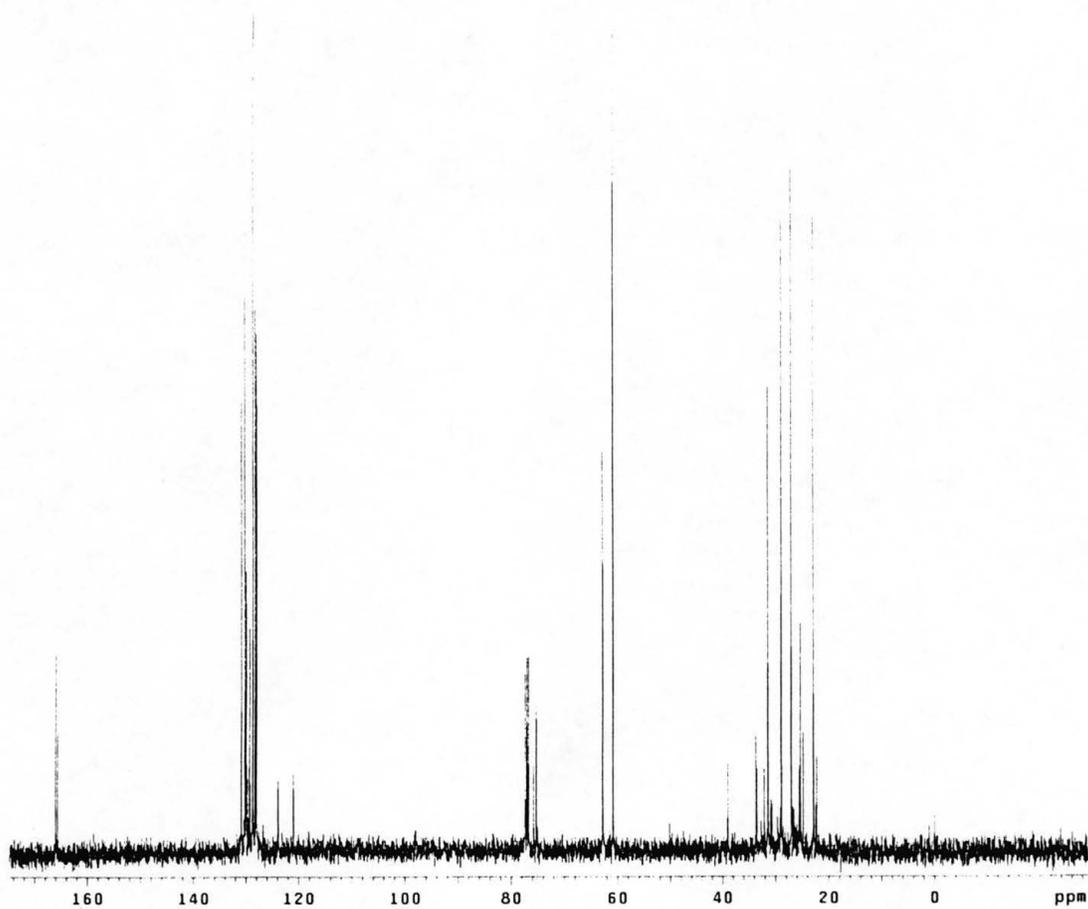


Figure 20:
 ^1H NMR of 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentyl Acrylate

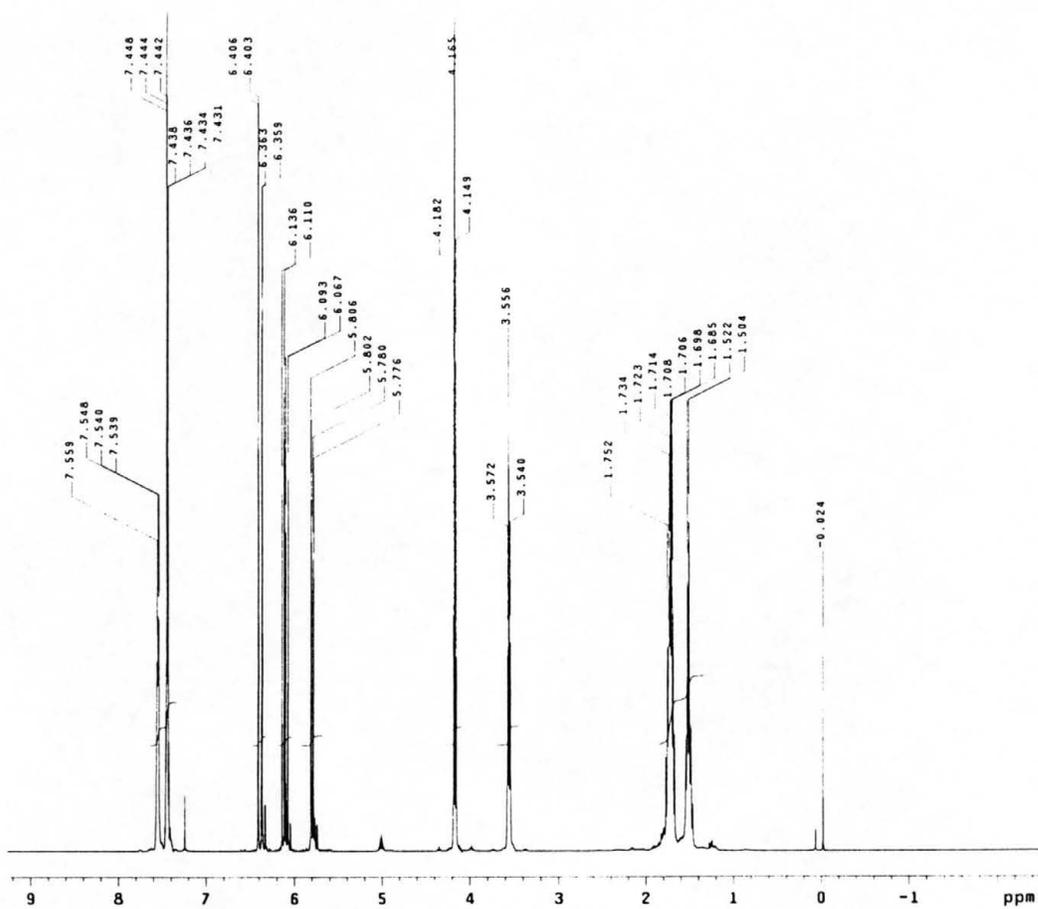


Figure 21:
 ^{13}C NMR of 5-(Hexafluoro-2-phenyl-2-propoxy)-1-pentyl Acrylate

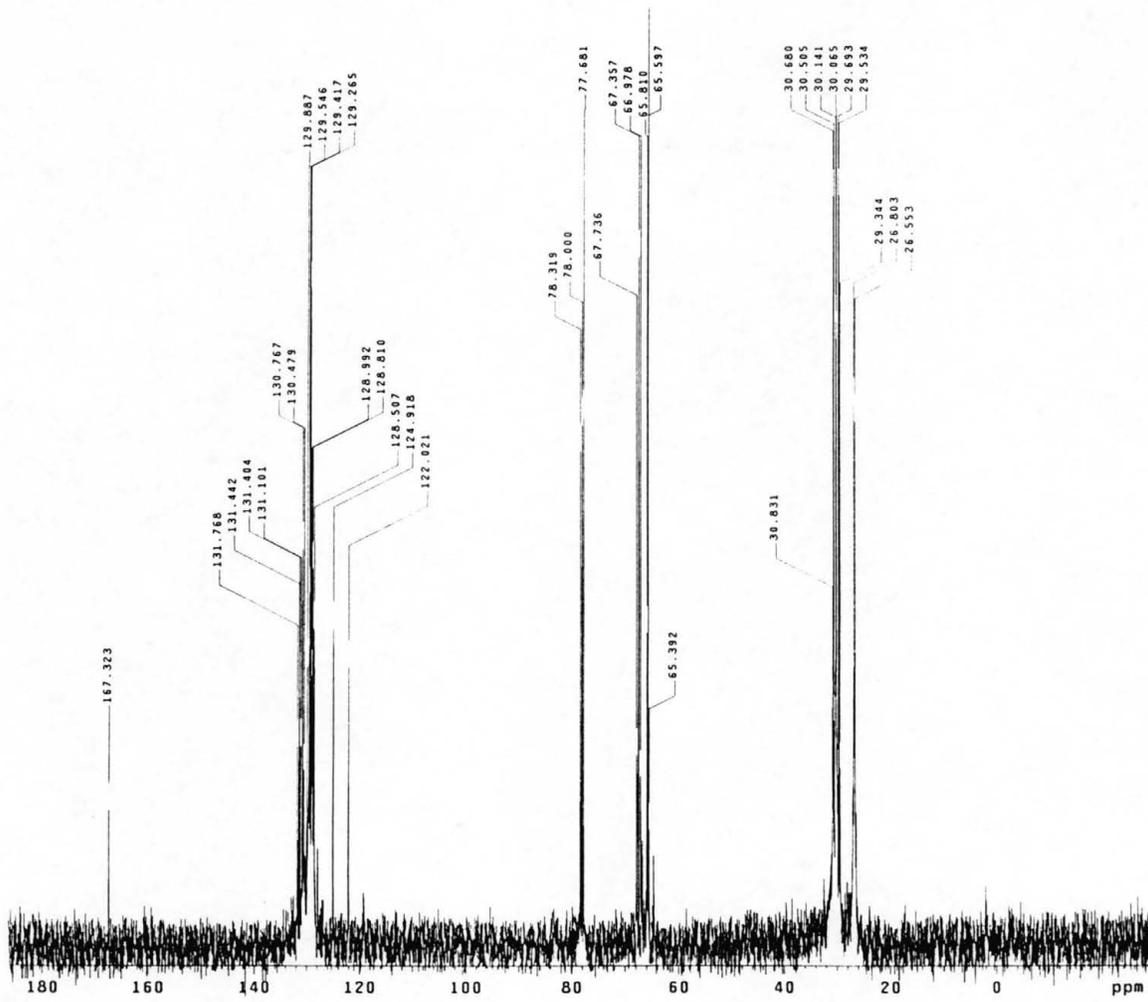


Figure 22:
 ^1H NMR of 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octyl Acrylate

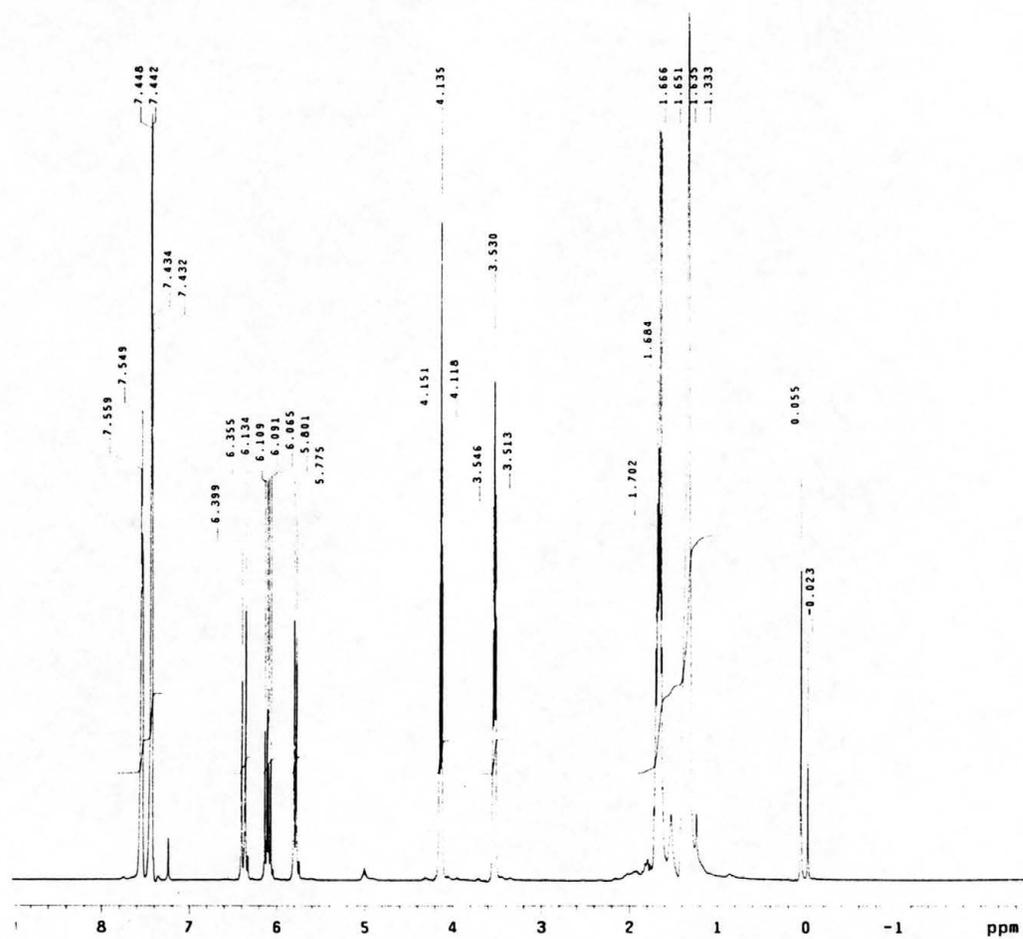


Figure 23:
 ^{13}C NMR of 8-(Hexafluoro-2-phenyl-2-propoxy)-1-octyl Acrylate

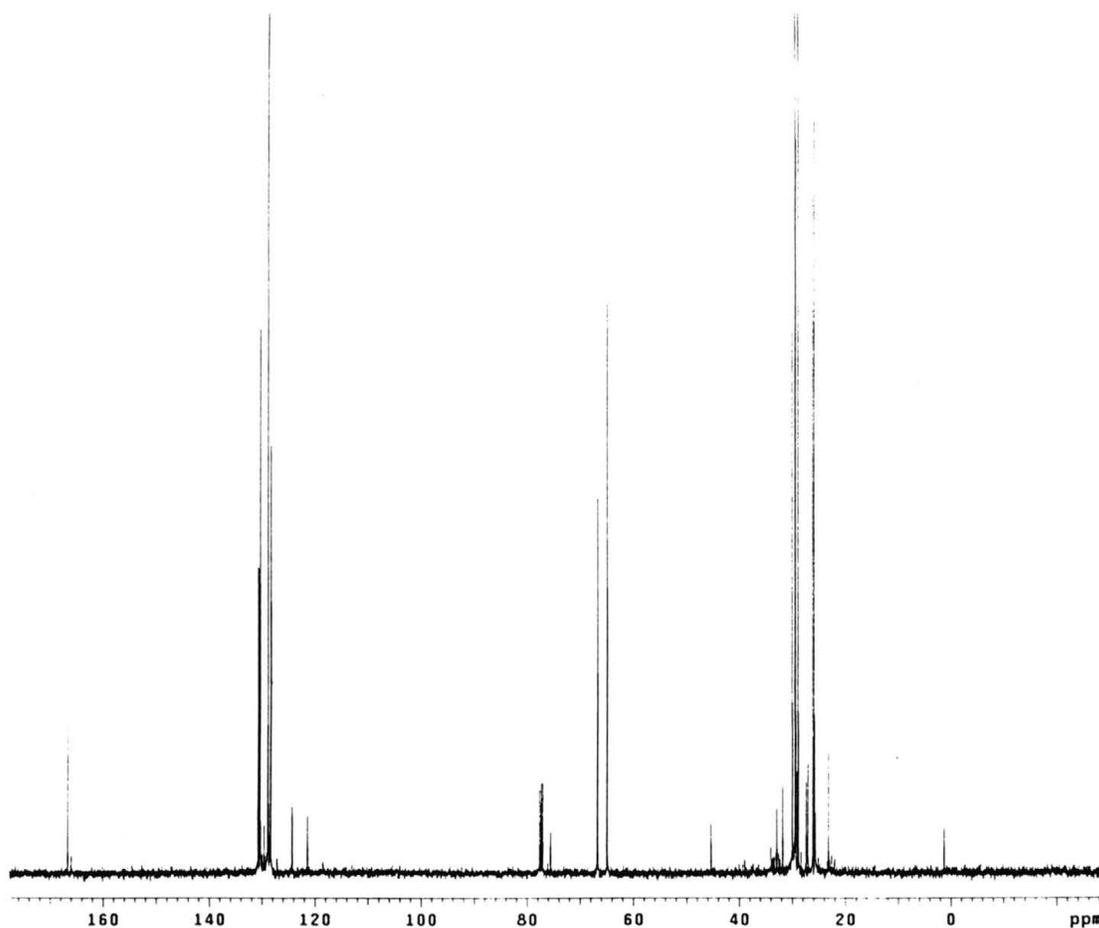


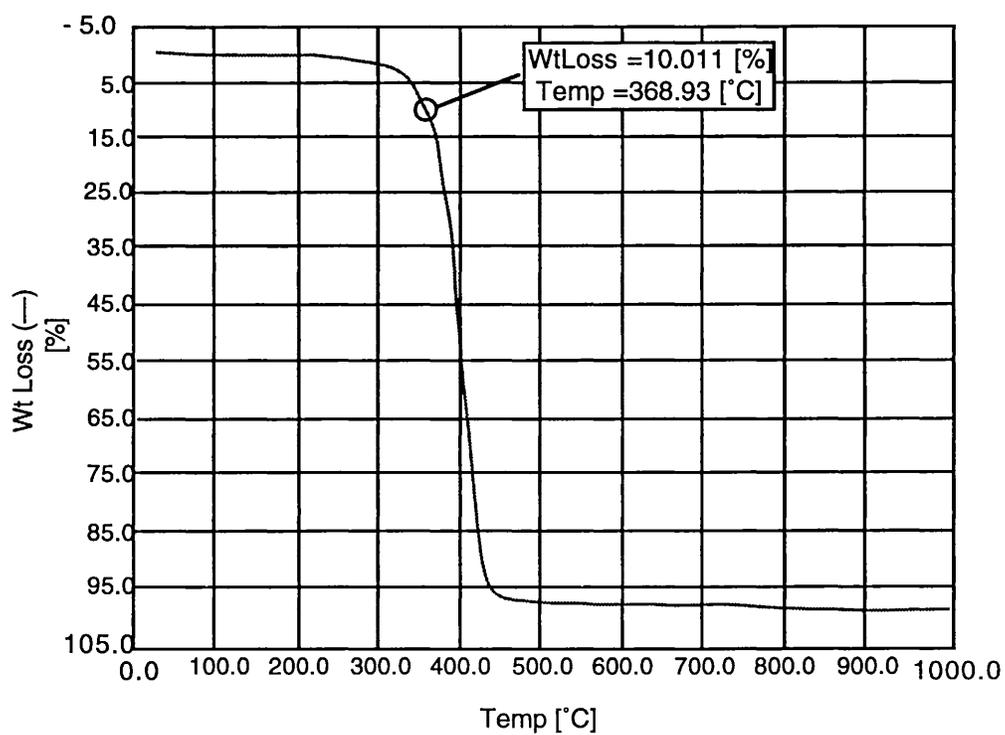
Figure 24: TGA Thermogram of Polymer 13 in N₂

Figure 25: TGA Thermogram of Polymer 13 in Air

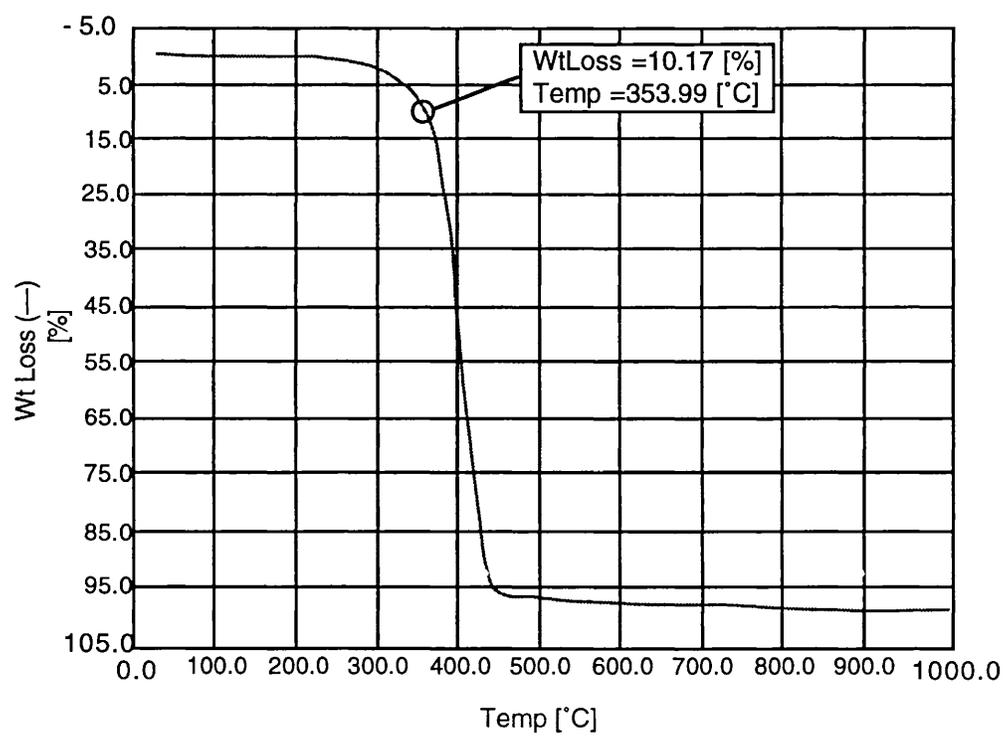


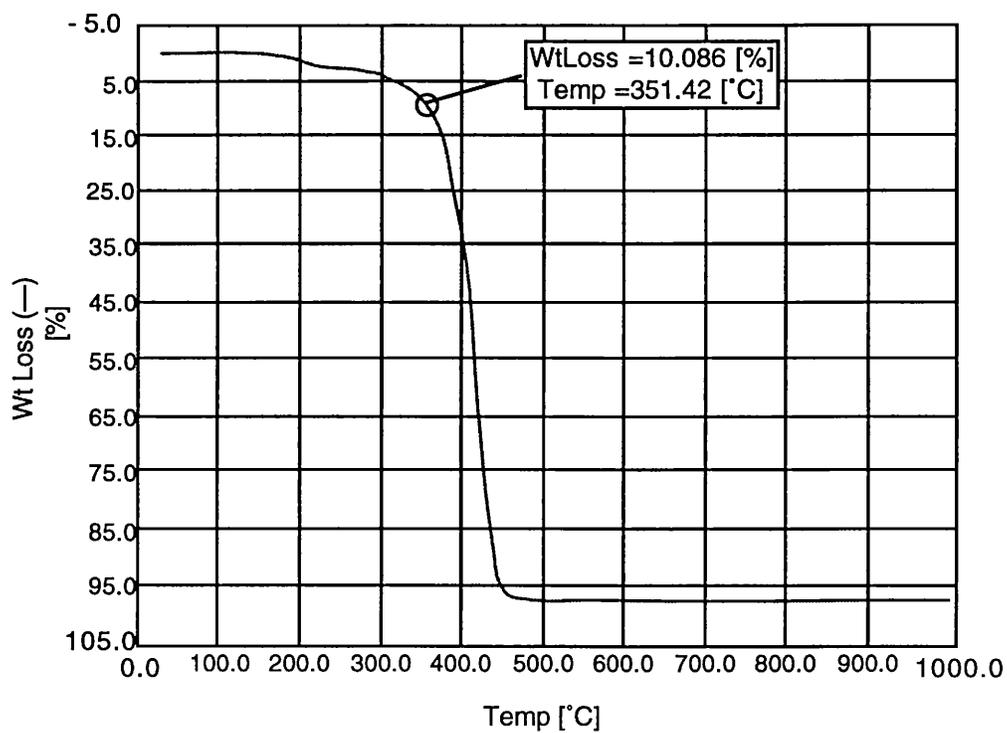
Figure 26: TGA Thermogram of Polymer 13a in N₂

Figure 27: TGA Thermogram of Polymer 13a in Air

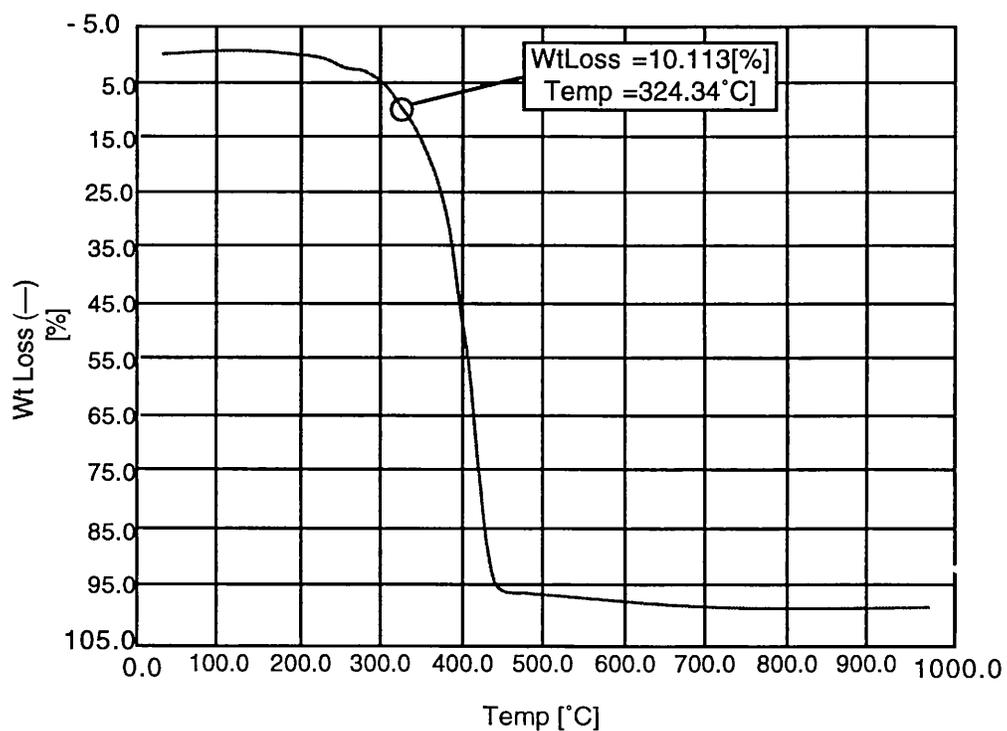


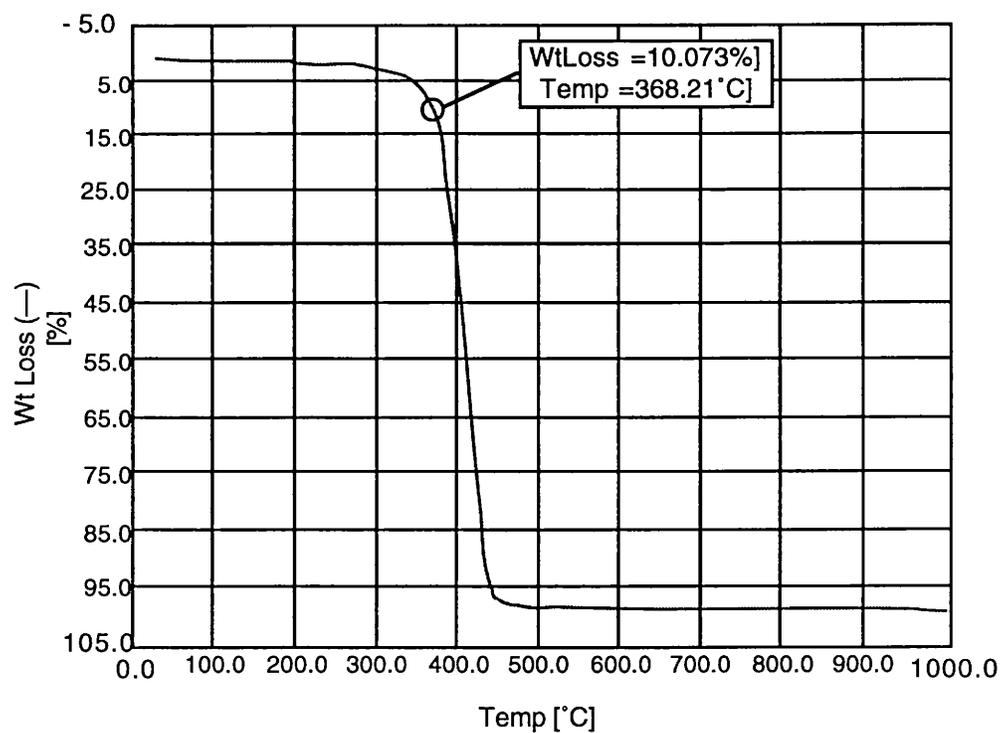
Figure 28: TGA Thermogram of Polymer 14 in N₂

Figure 29: TGA Thermogram of Polymer 14 in Air

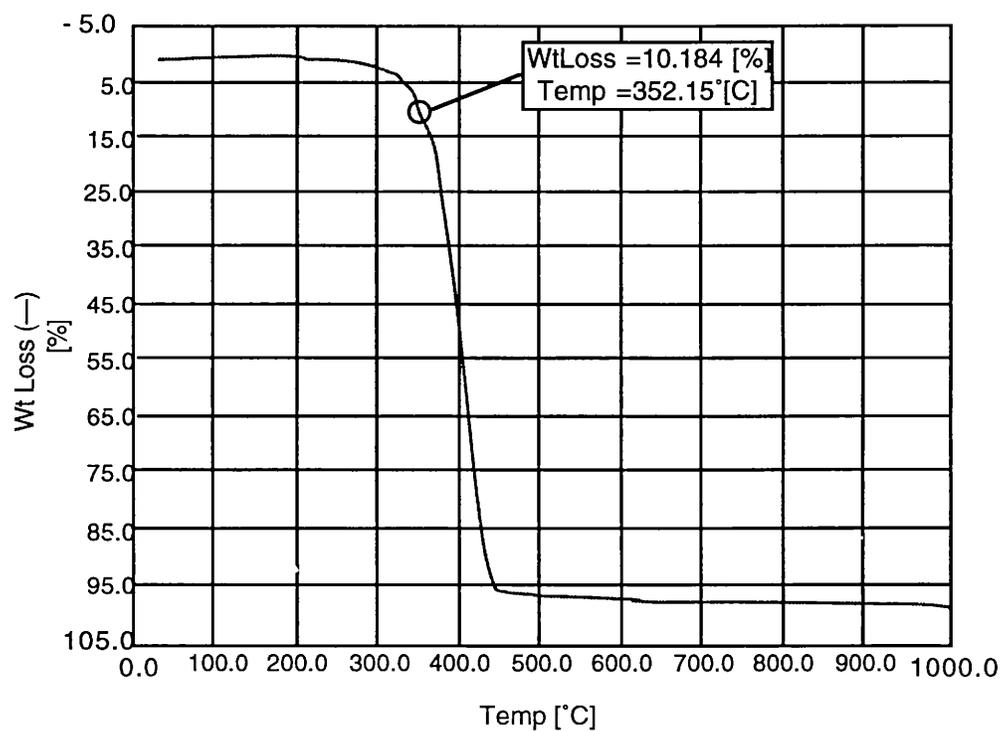


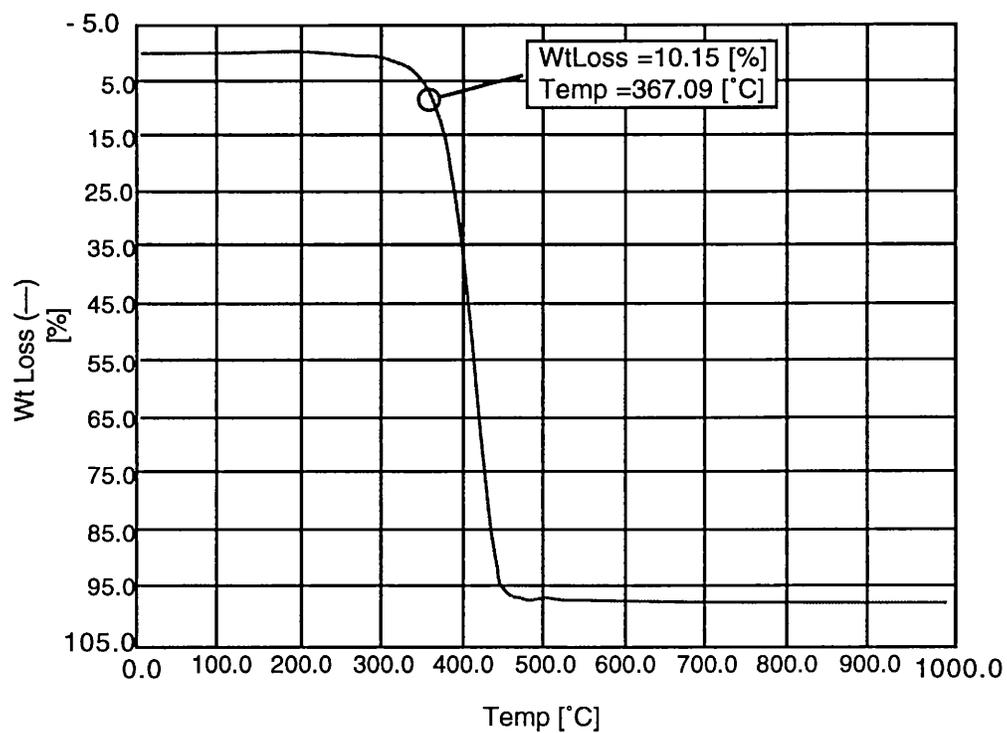
Figure 30: TGA Thermogram of Polymer 14a in N₂

Figure 31: TGA Thermogram of Polymer 14a in air

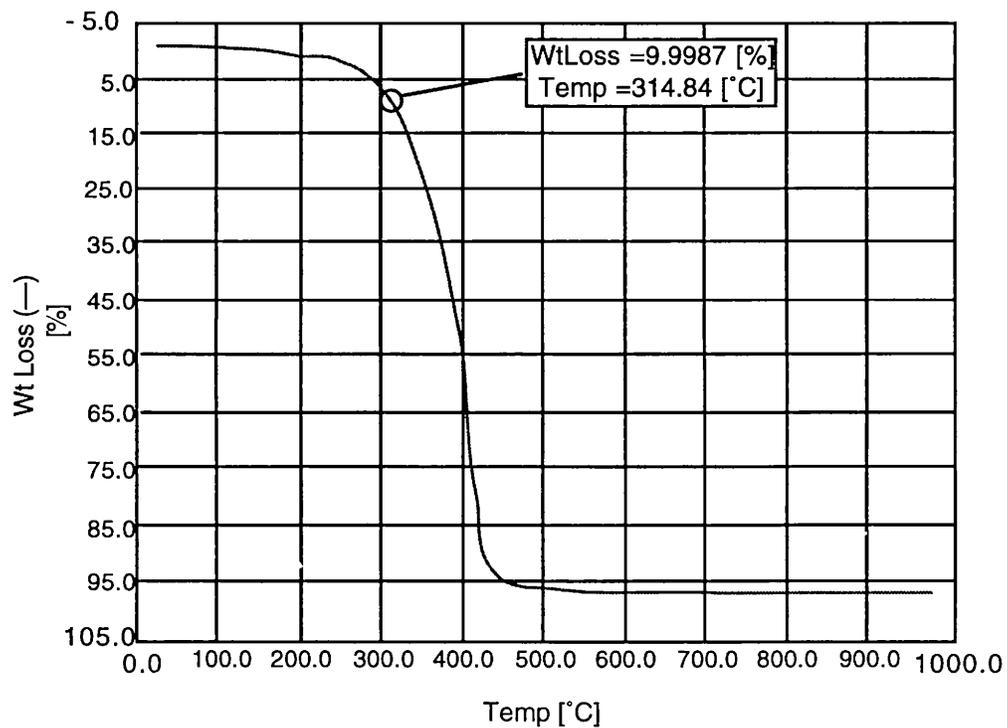


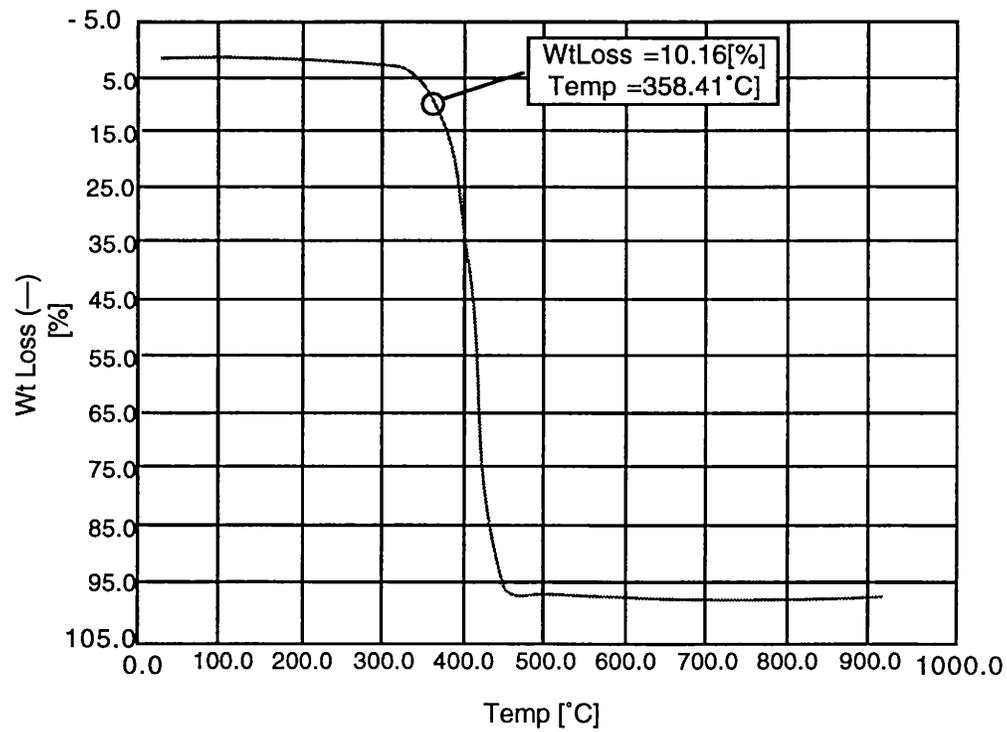
Figure 32: TGA Thermogram of Polymer 15 in N₂

Figure 33: TGA Thermogram of Polymer 15 in Air

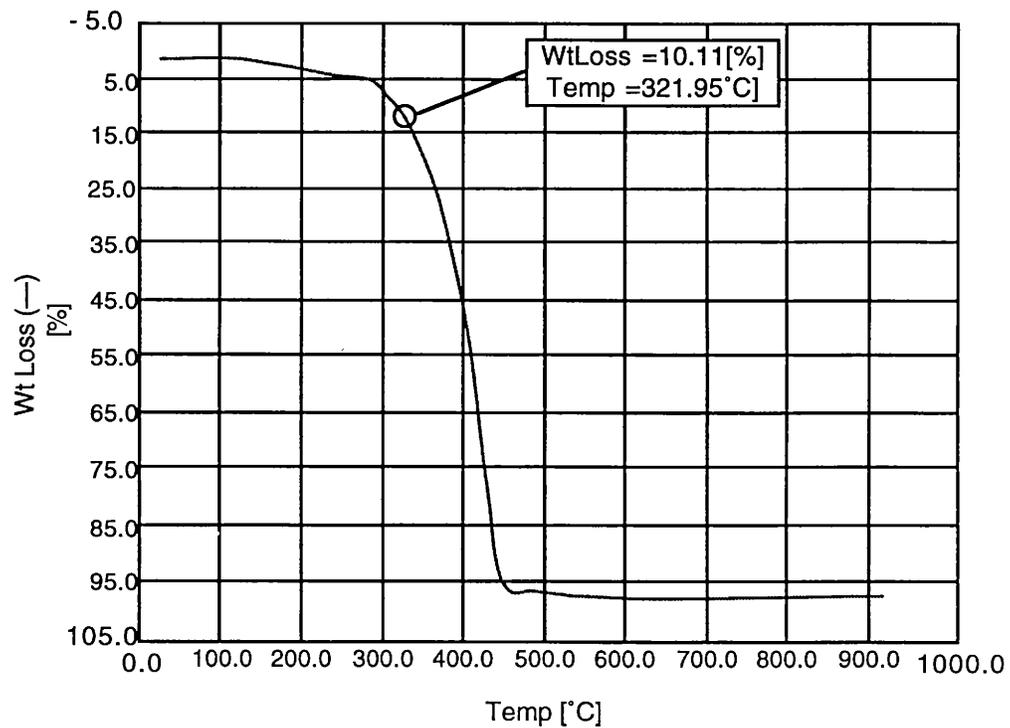


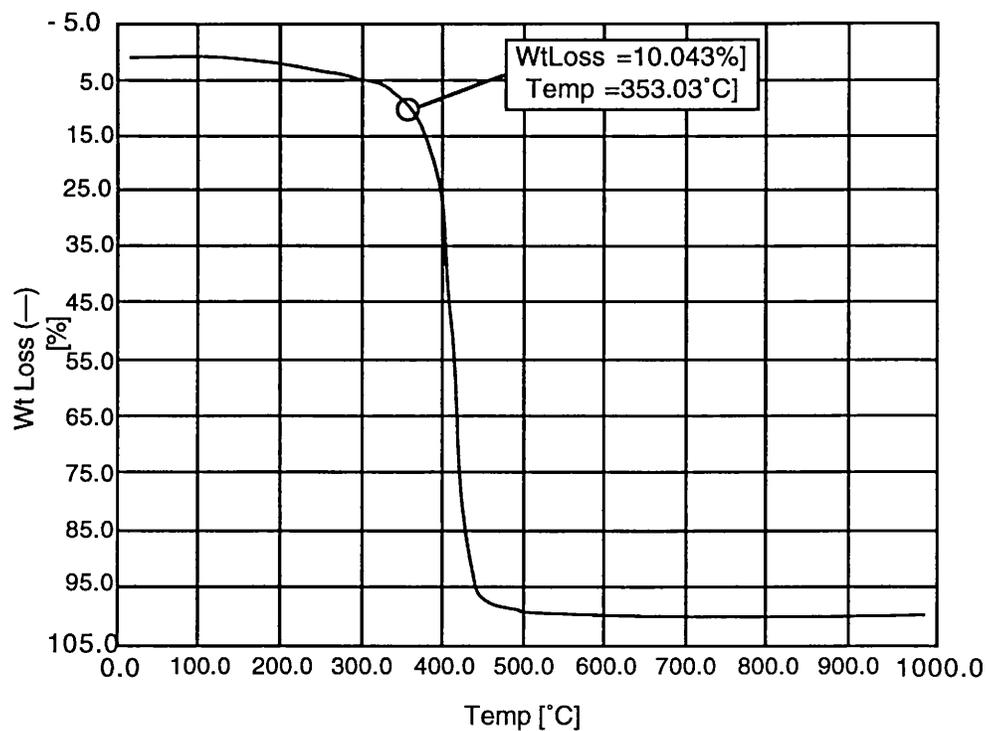
Figure 34: TGA Thermogram of Polymer 15a in N₂

Figure 35: TGA Thermogram of Polymer 15a in Air

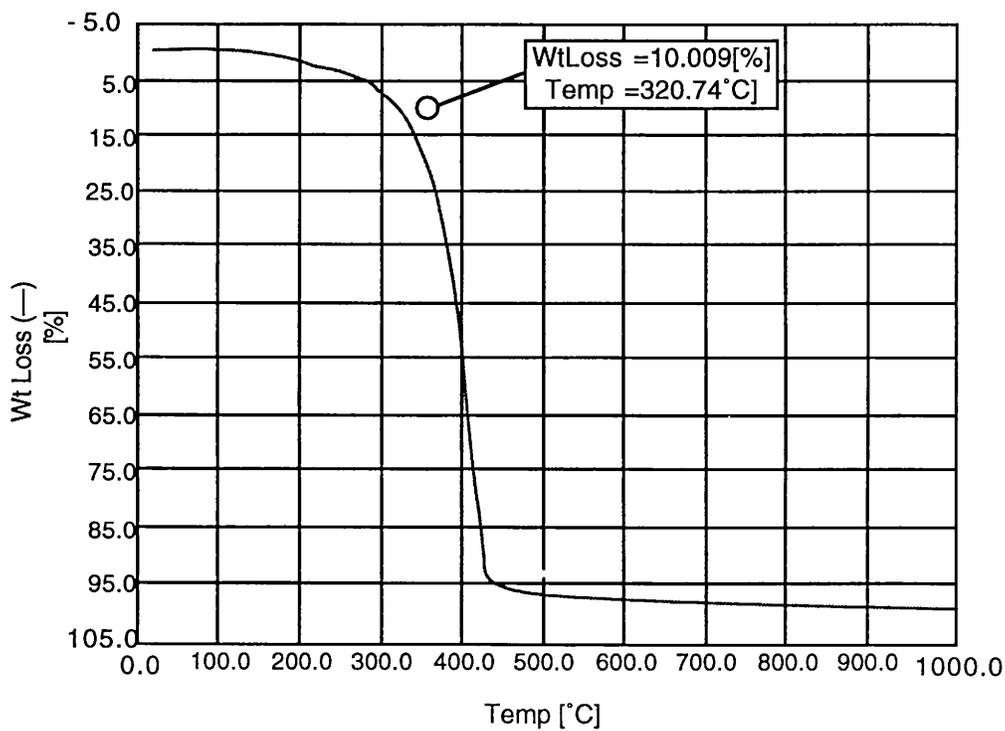


Figure 36: DSC Curve of Polymer 13

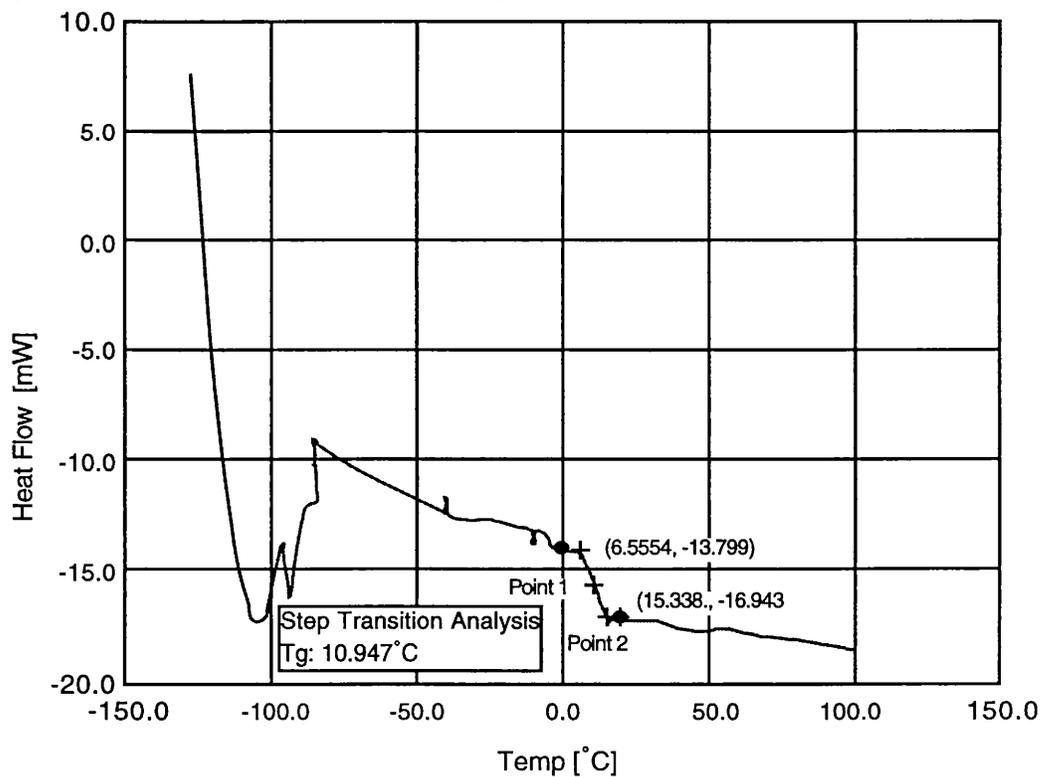


Figure 37: DSC Curve of Polymer 13a

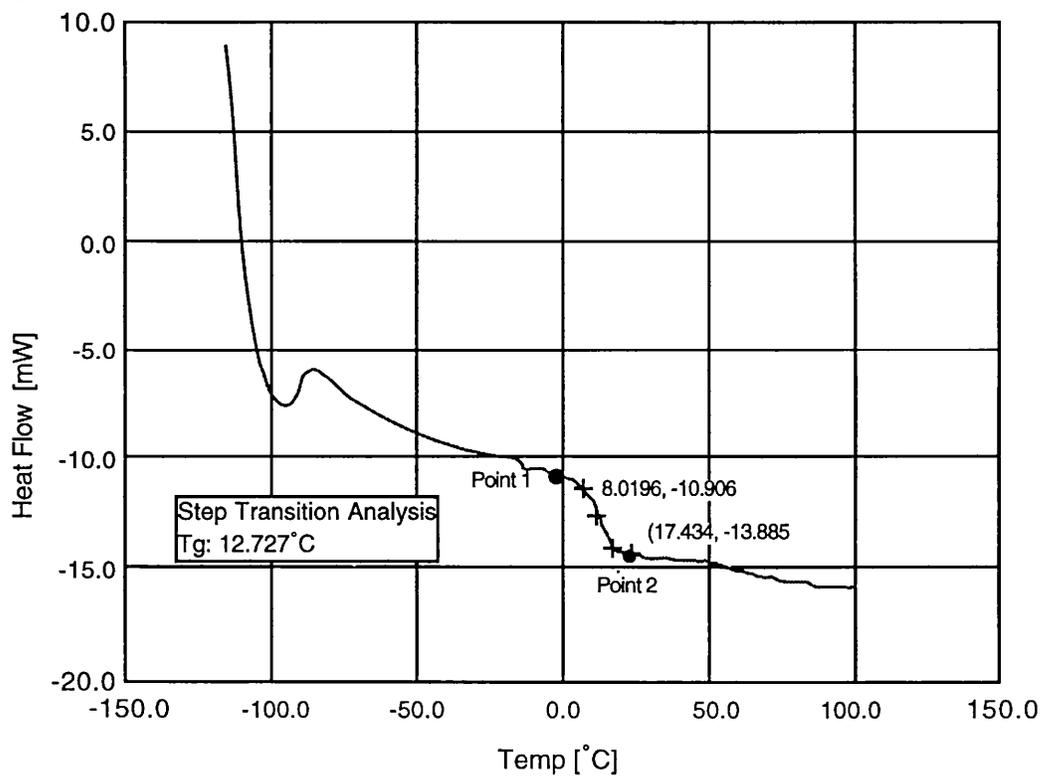


Figure 38: DSC Curve of Polymer 13c

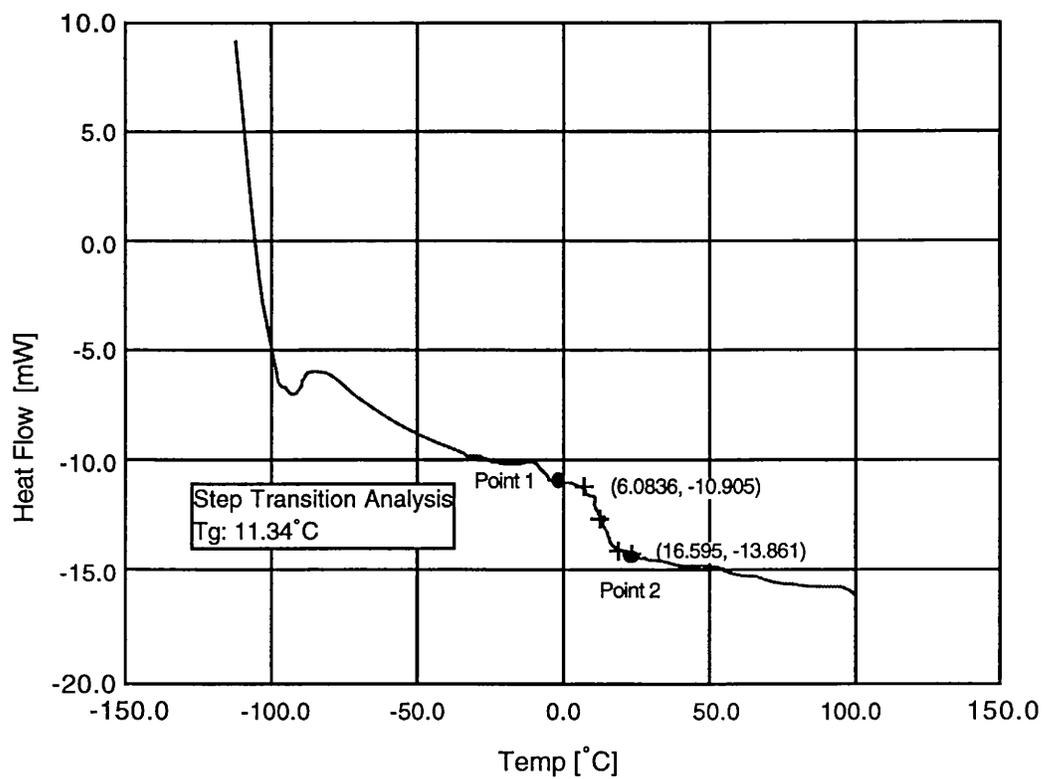


Figure 39: DSC Curve of Polymer 13d

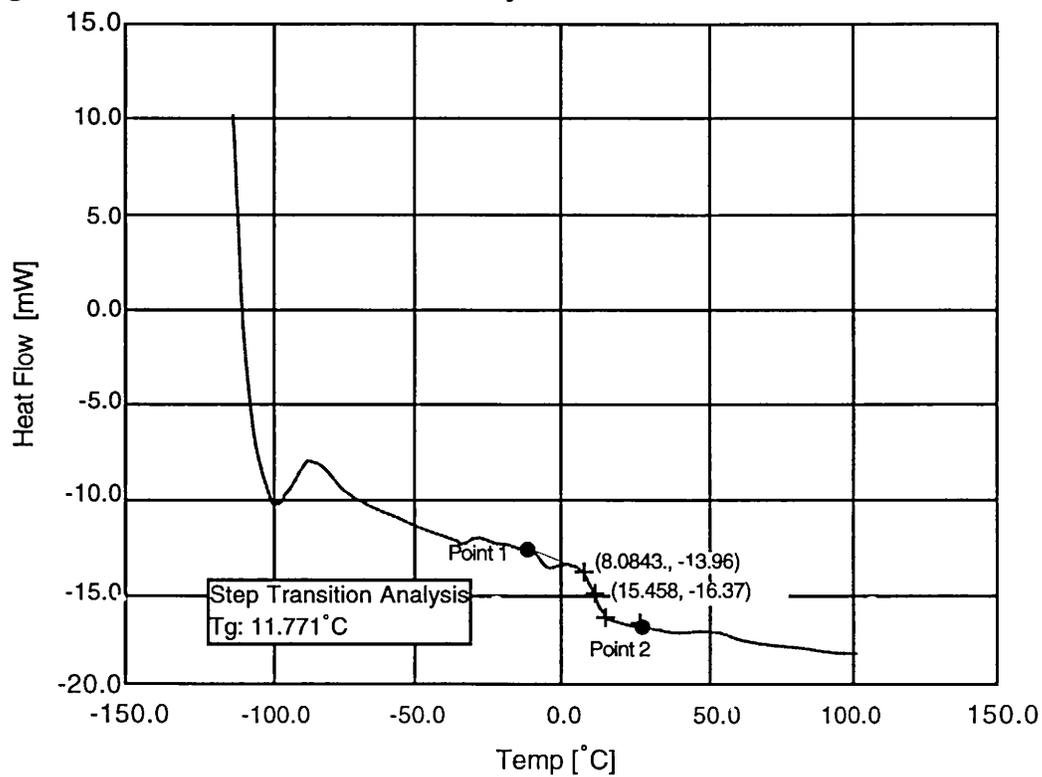


Figure 40: DSC Curve of Polymer 14

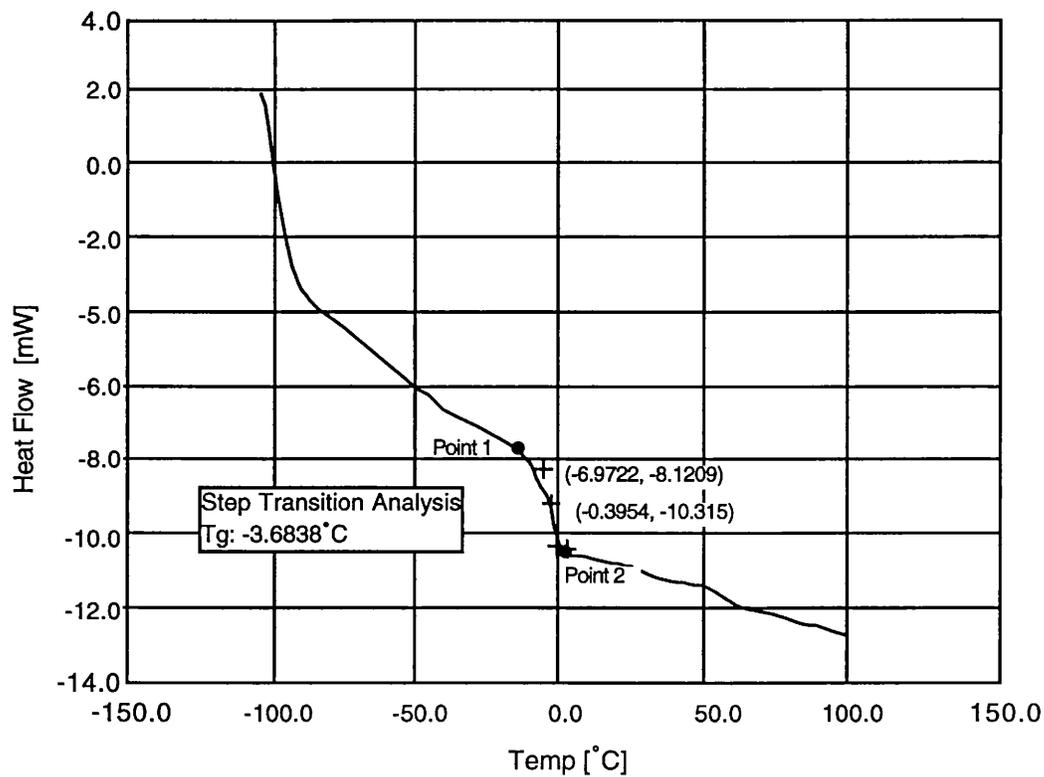


Figure 41: DSC Curve of Polymer 14a

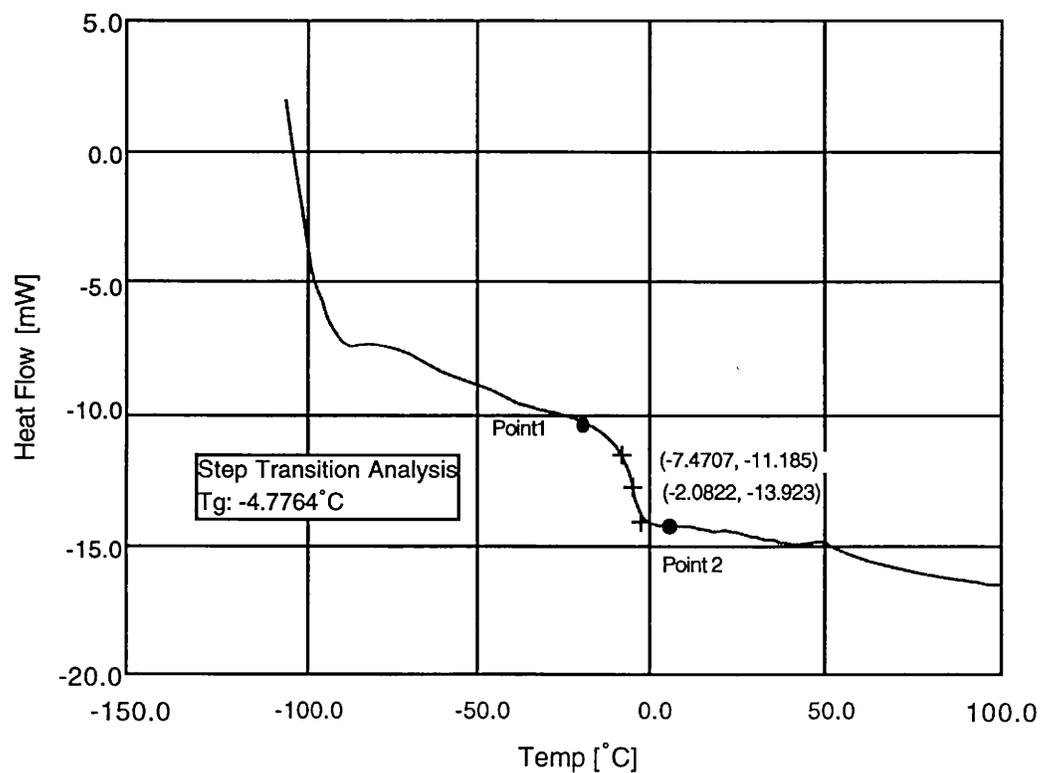


Figure 42: DSC Curve of Polymer 14b

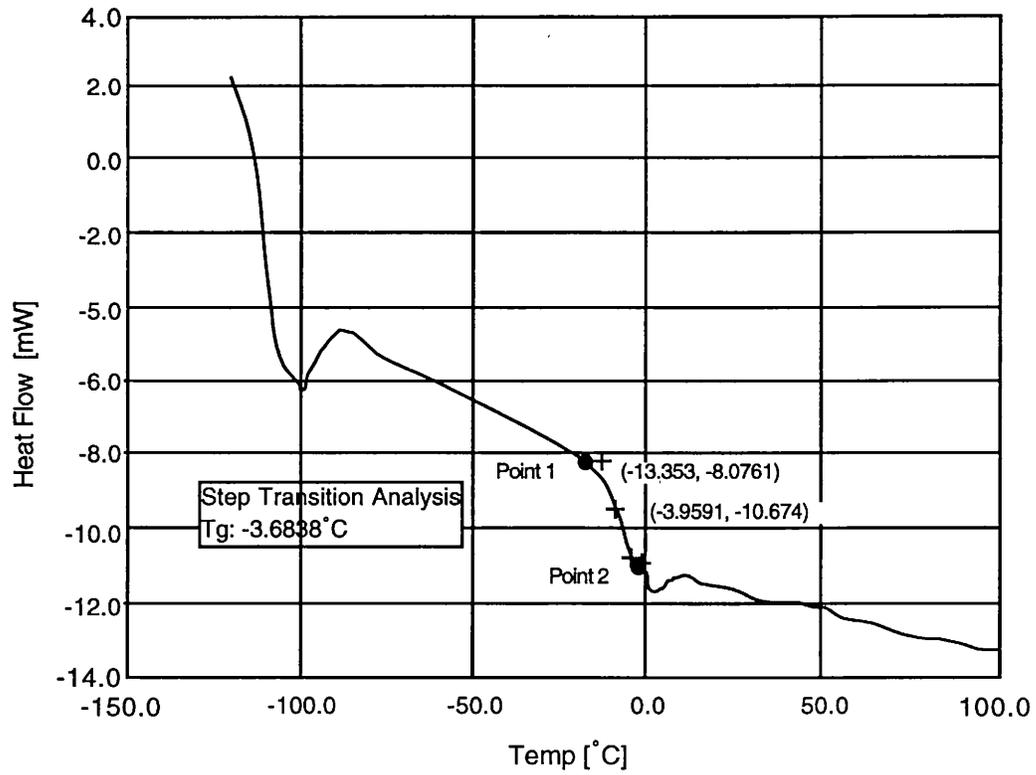


Figure 43: DSC Curve of Polymer 14c

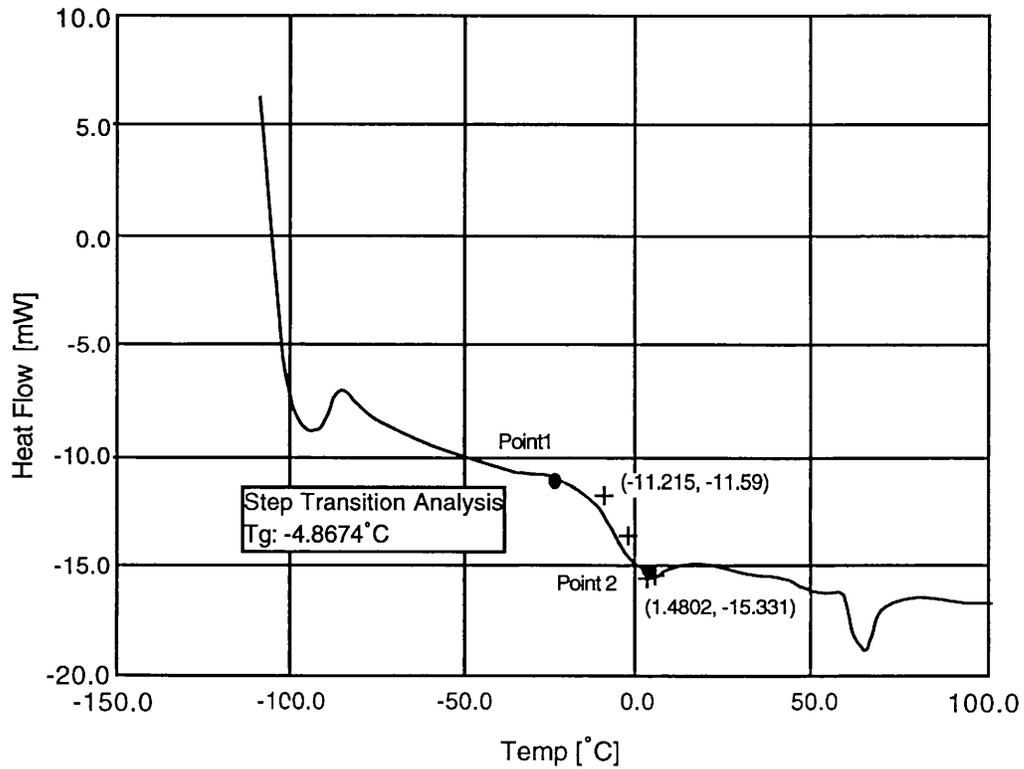


Figure 44: DSC Curve of Polymer 14d

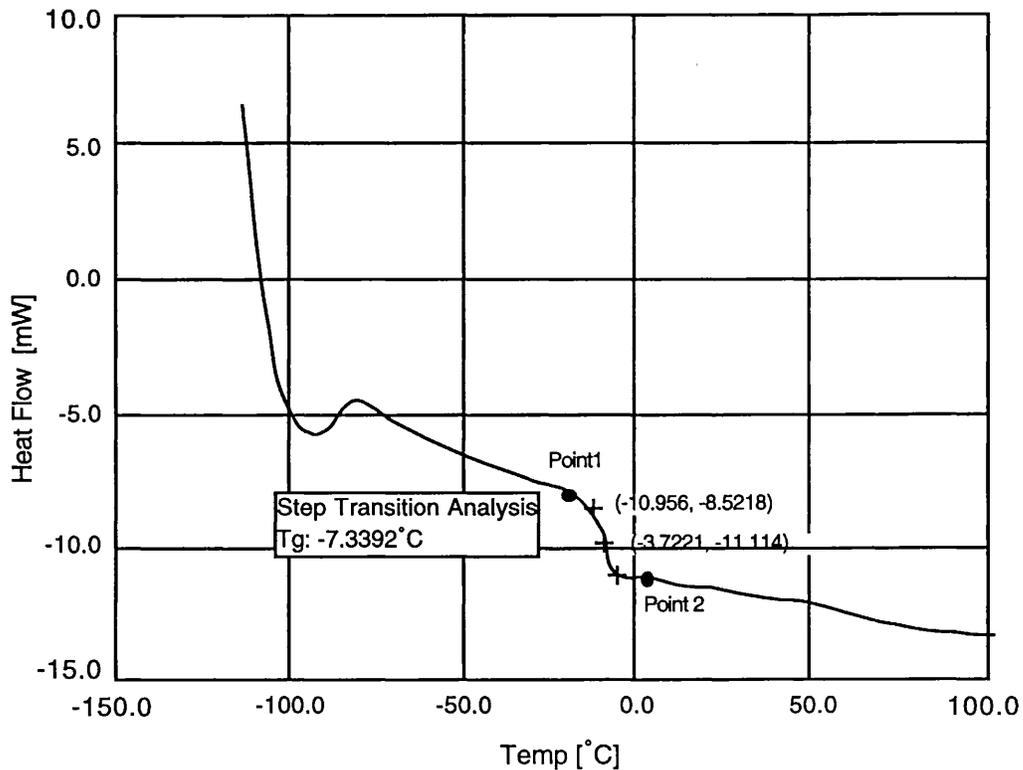


Figure 45: DSC Curve of Polymer 15

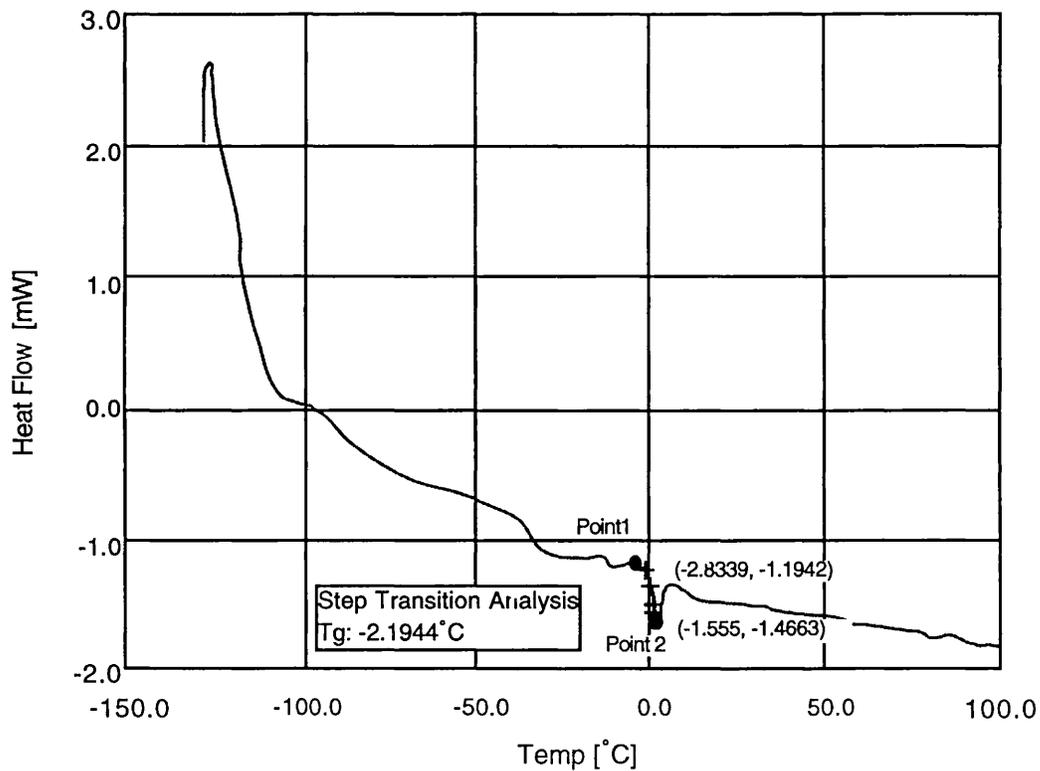


Figure 46: DSC Curve of Polymer 15a

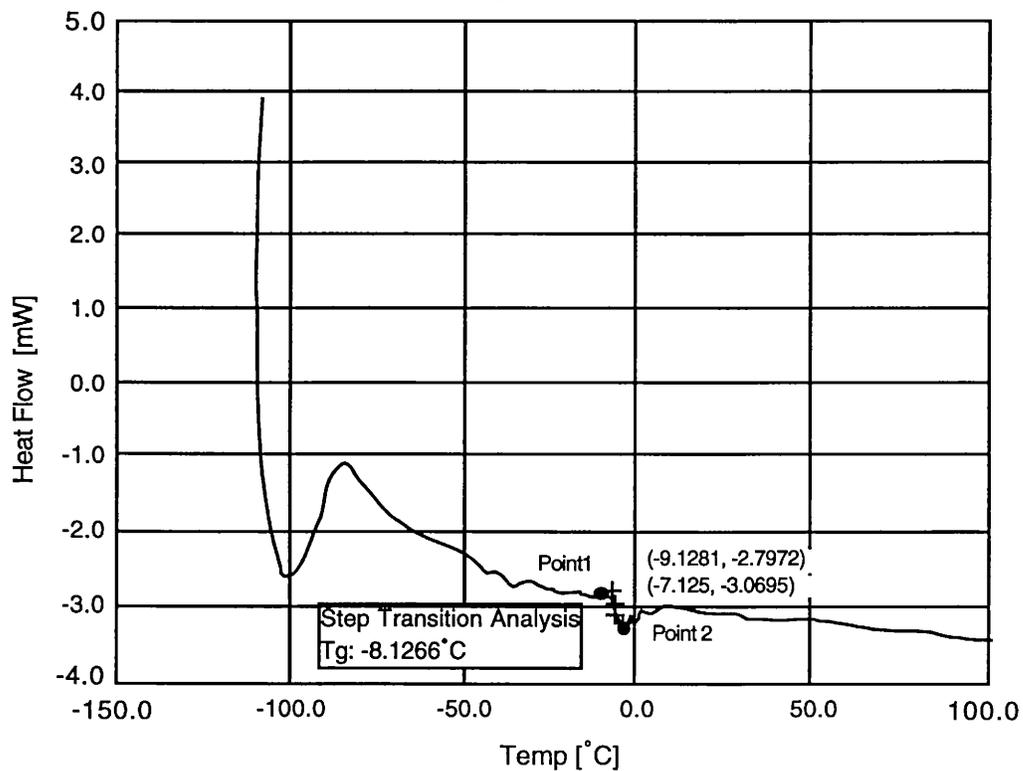
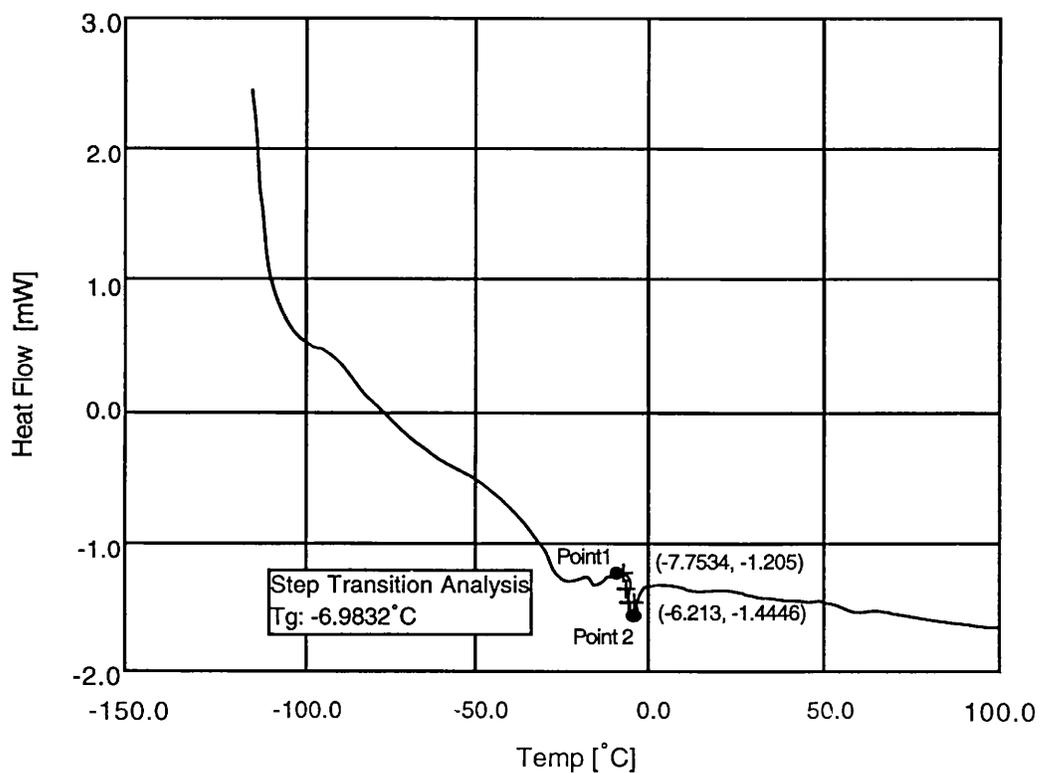


Figure 47: DSC Curve of Polymer 15b



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