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ENHANCED SUPERCONDUCTORS

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PROJECT SUMMARY

ENHANCED SUPERCONDUCTORS

One of the major challenges facing high temperature superconductors is the making of non-brittle materials. Based on the successful discovery of high temperature perovskite superconductors, a new class of superconducting materials is hypothesized. The proposed class will be mechanically tough and may have high critical temperatures. The proposed material will be inexpensive to manufacture and easily formed into wires and bands.

This project's research goal was to detect a superconducting transition in a specific material within this proposed new class. Substantial progress was made toward this objective. In Phase I a major milestone, the bulk conversion of a precursor material, was successfully accomplished. This milestone had eluded researchers for nearly a decade.

New synthetic methods were demanded in Phase II to overcome the major problem of the Phase I material, high defect density. The high defect density is presumed to be responsible for an observed low normal-state conductivity.

In Phase II, two additional model conducting polymer systems were developed.

The second model precursor polymer, Polychlorofluoroethylene (PCFE), was synthesized for this study. We succeeded at making high molecular weight ($\sim M_n = 10^5$) material with good overall yield (10 grams per batch) (a first). Furthermore, with the high molecular weight PCFE we succeeded in forming a free standing film (via solvent casting).

The precursor polymer PCFE has a low defect density (as verified by NMR). This allowed the possibility of making low defect polyfluoroacetylene (but did not guarantee it). To assure that the low defect nature was maintained during chemical modification (when HCl is removed) a special sterically hindered phenoxide base was found. The sterically hindered chemical modification was successfully carried out. Both infra-red and visible spectral analysis indicate that very long conjugation lengths were achieved (an estimated 28 repeat units long).

This synthesis route yielded poly(fluoroacetylene) with a significantly lower defect density when compared to HF-eliminated fluoropolymer films. The poly(fluoroacetylene) could be doped by I_2 and exhibited conductivities up to $10^{-5} \Omega^{-1}$. This conductivity increase was reversible as the dopant could be removed by vacuum.

It is not fully understood why higher conductivities were not achieved since $10^{-3}\Omega^{-1}\text{cm}^{-1}$ had been reported for an alternative synthetic method (1)). Furthermore, normal state conductivities of doped non fluorinated polyacetylenes of $10^{+5}\Omega^{-1}\text{cm}^{-1}$ have been achieved. Thus our present results should not be construed as having established any strict upper limit to the conductivity of PFA.

The final phase of this work was directed to synthesis of poly(2,3,5,6-tetrafluoro-*para*-phenylene vinylene) (PTFPPV). The use of soluble precursor methods, commonly used for the preparation of high molecular weight PPV, was unsuccessful due to reactivity of the precursor salts to form side-products. A NaH polymerization of 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (BBMTFB) gave low molecular weight products with the proper chemical composition. UV-Vis-NIR spectroscopy indicates the polymer to have an electronic band gap of ca. 3 eV (absorption onset of 400 nm) as expected for a polymer substituted with electron withdrawing groups. Both oxidative (NOPF6) and reductive (sodium naphthalide) doping reactions were carried out. While some chemical evidence for doping was observed, no electrical conductivity increase was observed.

In summary, while making significant progress in synthesizing conducting polymers with polar or polarizable groups, this study did not reach its ultimate goal of producing a model compound with all of the necessary chemical properties to test the exciton model of superconductivity. Until such a model system is produced, the possibility of an inexpensive, processable, tough and strong high temperature superconductor will remain just that - a possibility.

REFERENCES

1. See Nov. 19, 1990 report.



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FOREWORD

This final report was prepared by Chronos Research Laboratories, Inc. for the U.S. Strategic Defense Command under Contract No. F49620-89-0100. The principle results were developed during the period 01 July 1989 to 15 April 1992.

The principal investigator was Randall B. Olsen. The SDI project manager was Harold Weinstock. Chemical synthesis was performed at the University of Texas at Arlington by V. Panchalingam under the direction of John R. Reynolds. We are grateful for the polymer extrusion work of Dean Wickwire, the technical support of Debbie McQuillan, Randall S. Millar, and the administrative support of Katherine L. Anderson. Discussions with Barry McQuillan and Lu Sham are also very much appreciated.

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IDENTIFICATION AND SIGNIFICANCE OF THE INNOVATION

A new class of superconducting materials is hypothesized. Based on the successful discovery of high temperature superconductors (HTSCs), the proposed class of

- * mechanically tough materials may yield comparably high critical temperatures. The
- * toughness of these materials stems from the fact that they naturally form as composites
- * of crystallites and amorphous regions.

The proposed materials can potentially solve the three biggest challenges facing high temperature superconductors:

- ◆ making non-brittle materials,
 - ◆ forming stable materials, and
 - ◆ achieving high critical currents.
- * The proposed Phase II research will make substantial progress toward solving all three of these challenges.
 - *

- * One solution to the inherent brittleness of present day high temperature superconductors is to form artificial composites containing a superconducting ceramic within a ductile host matrix. Since many research groups are following this approach (with difficulties that will be discussed later) it will not be pursued here.
- *

- * A truly innovative solution to this problem may be found by turning to a class of materials which naturally forms its own composites. This class comprises the semicrystalline polymers. These polymers contain both crystalline and amorphous regions. Since polymers contain another level of structure - the polymer chains - strength is maintained across the boundaries between the two types of regions. Since the strength stems from covalent bonds (along the polymer backbone chain), it is very high across these boundaries. This strength can be orders of magnitude larger than the strength of ceramic grain boundaries (1).
- *

- * Besides a tremendous strength advantage, the natural composite of a semicrystalline polymer offers another advantage. The morphology of the polymer can be varied over a wide range by changing its thermal-mechanical processing. This may be illustrated with a few examples. By rapidly cooling (quenching) a polymer from its melt point one can form a highly amorphous material. This process is similar to the formation of metallic

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* glass (2), but cooling rates need not be nearly as high. A quenched amorphous
* polymer can be annealed at a temperature somewhat below its melt point to induce
* crystallite growth. Polymers which are more than 90% crystalline can be made with such
* annealing. By varying the annealing time and temperature, and by applying mechanical
* stress, one can produce crystallite sizes varying from small fractions of a micron to tens
* of microns. The ability to make intimately mixed, strong composites may be unique to
* polymers. This degree of fabrication control allows tailoring of both the mechanical
* strength and the electrical transport properties. With polymers, it may be possible to
* make the amorphous regions so small that superconducting currents can tunnel across
* them (thus enabling high critical currents).

* The mechanical advantages of the polymers are clear, but what about the
* superconducting nature of the polymers? No high temperature superconducting
* polymers are presently known. (Before 1986 the same could have been said about all
* categories of materials.)

* Successful synthesis of a high temperature superconducting polymer is based on a
* strong hypothesis - a highly polarizable moiety (either atom or small molecular unit) is
* necessary for high temperature superconductivity.

* The hypothesis is based on a simple observation. All known high temperature
* superconductors contain a highly polarizable moiety (the oxygen). This polarizable
* moiety-HTSC connection is only beginning to be generally appreciated, but we believe
* that it provides one necessary condition for high temperature superconductivity. The
* polarizable moiety provides an electron-electron interaction (similar to the electron-
* phonon interaction in BCS theory (3)) which supports superconductivity even at high
* temperatures.

* The notion of polarization enhancement of superconductivity has been suspected for
* over 20 years(4),(5),(6),(7),(8),(9),(10).

* A related, though weaker, enhancement of the superconducting transition
* temperature was well established by the mid 1970's. Superconductivity enhancement
* arising from an interfacial interaction between a metal and a semiconductor has been
* studied (11). Superconducting T_c enhancements of metals by more than a factor of 5
* were observed as a result of alloying the metals with elemental semiconductors.

* One of the most easily understood (and earliest) explanations for high temperature
* superconductivity was presented in 1964 by Prof. Little of Stanford University (12).
* Little's calculations indicated that high superconducting transition temperatures could be
* obtained in specially constructed molecular systems. These systems, would rely on a

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* special electron-electron interaction. This interaction is more explicitly a conduction
* electron - "polarizable" electron interaction (13). The second electron corresponds to
* a polarizable localized molecular orbital. The polarizable electronic orbital state
* mediates an electron-electron coupling much like the phonon mediates the electron-
* electron coupling in standard BCS theory.

* This may seem a bit confusing - since there are several different electrons involved.
* The best way to view this is to review standard BCS theory and substitute the polarizable
* electronic orbital for the role of the phonon. When this is done, the possibility for much
* higher superconducting temperatures will become apparent.

* A good way to visualize the standard BCS mechanism is to imagine two marbles
* rolling on a drumhead. The two marbles represent the electrons and the drumhead
* represents the ionic lattice. As one marble rolls along the drumhead it depresses the
* surface. The other marble, sensing the depression made by the first, is attracted to it.
* The depression acts like the phonon in mediating the attractive force. It is the attraction
* of the electrons which allows them to pair up. The Cooper pairs thus formed (and the
* manner in which they handle scattering events) enable superconductivity to manifest
* itself.

* In the case of excitonic superconductivity as proposed by Prof. Little, the conducting
* electrons interact with electronically polarizable side groups (see Page 6, Figure 1, for a
* model of the system proposed by Little). A conduction electron traveling along the spine
* interacts with the polarizable side group via the conventional screened Coulomb
* interaction. The polarization of the side group in the excitonic case is similar to the
* displacement of the ionic lattice (phonon creation) in the standard BCS mechanism. At
* a latter time a second conduction electron passes down the spine by the polarized side
* group, and "feels" the impression made by the first conduction electron. Thus, the
* polarizable side group in the exciton model takes the place of the ionic lattice of
* standard BCS theory.

* It is now appropriate to ask why the transition temperature for the excitonic system
* should be any higher than for the standard lattice system. The reader will remember that
* one of the great successes of the BCS theory was the prediction of the isotope effect.
* That is, the transition temperature depends on the inverse of the square root of the mass
* of the ions in the lattice, or $[m_{\text{ion}}]^{-1/2}$. In the exciton case, the ions have been replaced by
* the polarizable side group. The items in the side group that are polarizable are
* electrons (or more precisely - the electronic orbital states). The mass of the electron is
* therefore substituted for the mass of an ion in the expression for the transition
* temperature. Thus, an enhancement of the transition temperature can be of order
* $(2000)^{0.5} = 45$ or more.

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* The exciton approach can potentially be applied to any highly polarizable system.
* As a broad class of materials, ferroelectrics are the most highly polarizable. Classical
* ferroelectrics are insulators. If they weren't insulators, their dipole nature would be
* unobservable, as it would be totally obscured by conduction current. Superconductors,
* on the other hand, are obviously conductors. Therefore, it may appear that
* superconductors and ferroelectrics (i.e. highly polarizable materials) are at opposite ends
* of the conductivity spectrum.

* We claim, however, that the high temperature superconductors are simply highly
* polarizable materials to which appreciable current carriers have been added. With
* conventional high temperature superconductors (e.g. the 1-2-3 compounds - see Page 6,
* Figure 2), the polarizable moiety is the oxygen atom. This crystal structure is composed
* of $\text{YBa}_2\text{Cu}_3\text{O}_7$. The oxygen atoms provide the polarizable moiety needed for high
* temperature superconductivity, while the oxygen deficiency provides the carriers (holes)
* for the current. Note that with the 1-2-3 superconducting system, if the compound is not
* oxygen deficient, it is not a good conductor, let alone a superconductor. The system we
* are proposing is shown in Figure 3, Page 6. This structure is poly(fluoroacetylene) (PFA).
* Fluorine provides the polarizable moiety for the proposed high temperature
* superconductor. The fluorine deficiency (relative to PVDF), along with doping, provides
* mobile holes to carry the current.

* Therefore, the suggested method of finding new high temperature superconductors is
* to start with established insulating ferroelectric materials (i.e. materials with highly
* polarizable moieties). The highly polarizable insulator should be modified to create a
* high mobility path for electrical current. The modification changes the insulator into a
* semiconductor (the structure becomes similar to polyacetylene).

* After modification to establish high mobility, carrier density must be increased to
* form a good normal-state conductor. The carrier density may be increased in a variety
* of ways, including (individually or in combination);

* doping
* proximity to a metal (i.e. Schottky barrier), and/or
* photoexcitation.

* The attainment of a good conductor (high mobility and high carrier density) in a
* polarizable host will set the stage for superconductivity.

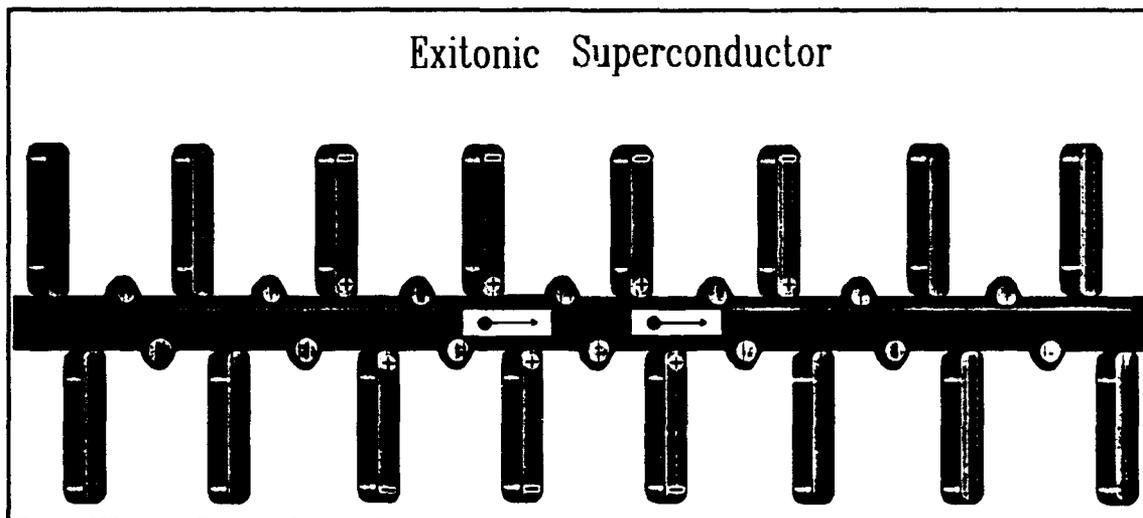
* Our research started with a highly polarizable (ferroelectric) polymer which we

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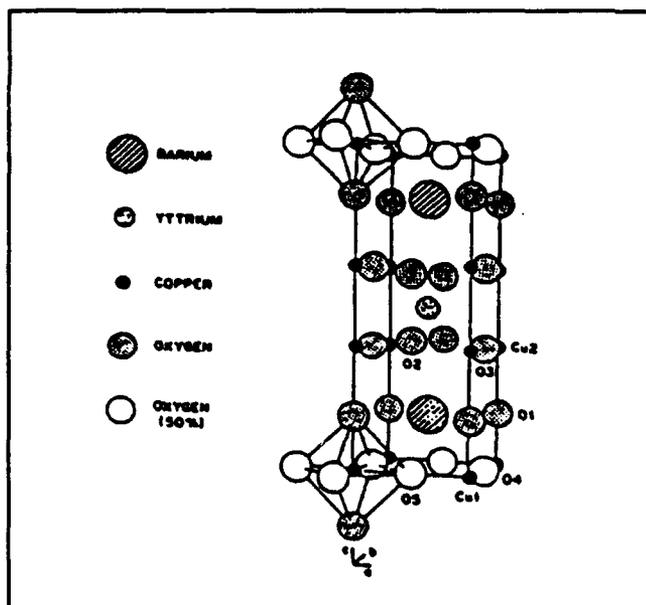
* chemically modified to various levels of conductivity. We expected to encounter some
* difficulty with the actual transport properties of the early materials due to the presence
* of amorphous regions. As noted earlier, with proper thermal-mechanical processing, the
* size and orientation of the amorphous regions can eventually be controlled and high
* critical current should result.

*
* Initially, we monitored magnetic and transport properties. The temperature
* dependence of the magnetic susceptibility was measured for a variety of chemical
* modification levels.

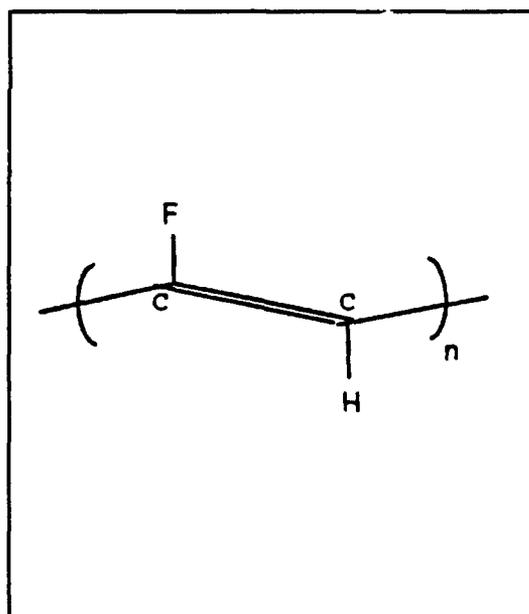
* We would like to make one general comment before turning to the technical details
* of this project. The histories of both superconductivity and ferroelectrics have been
* littered with many long held myths (e.g. "superconducting T_c s will never exceed 30 K",
* "hydrogen is essential for ferroelectricity", etc.). Because of this, we were willing (and
* still are willing) to take a radical departure from the main-line thinking and investigate a
* different system. Polymer ferroelectrics may be considered to be high risk, but that risk
* is more than warranted by the potential for very high engineering and economic payoffs.



- * Figure 1 - Electron pairs are conducted along the spine of a hypothetical
- * superconducting molecule by an attractive mechanism similar to that in a
- * superconducting metal.



- * Figure 2 - Crystal structure of $YBa_2Cu_3O_7$.
- * The oxygen atoms provide the polarizable moiety for superconductivity.



- * Figure 3 - Structure of
- * poly(fluoroacetylene) (PFA). Fluorine
- * provides the polarizable moiety for
- * the proposed high temperature
- * superconductor.

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REFERENCES

1. T. Baumeister, Marks' Standard Handbook for Mechanical Engineers, McGraw-Hill, New York 1978.
2. C.C. Tsuei, Electrical properties of liquid-quenched metals, Treatise on Materials Science and Technology, Academic Press, Vol. 20, p 395 1981.
3. J. Bardeen, L.N. Cooper, and J.R. Schrieffer, Phys. Rev. **106**, 162 (1957); **108**, 1175 (1957).
4. Ginzburg, V.L., and Kirzhnits, D.A., "High-Temperature Superconductivity," N.Y.-London: Consultants Bureau, 1982.
5. Ginzburg, V.L., "Waynflete Lectures on Physics," Chap. 2, Pergamon Press, 1983.
6. Dolgov, O.V., and Maksimov, E.G., Uspekhi fiz. **138**, 95(1982), Sov. Phys. Uspekhi.
7. Dolgov, D.A., Kirzhnits, D.A., and Maksimov, E.G., Rev. Mod. Phys., **56**, 81 (1981).
8. Proc. of Internat. Conf. on Low Modes Ferroel. and Supercond., Ferroelectrics, **16,17**, N 1/2 (1977).
9. Lefkowitz, I., and Bloomfield, P.E., Ferroelectrics, **51** 173 (1984).
10. Ginzburg, V.L., "Some Remarks on Ferroelectricity, Soft Modes and Related Problems," Ferroelectrics, **76**, p.3-22, 1987.
11. Tsuei, C.C., and Johnson, W.L., "Superconductivity in metal-semiconductor eutectic alloys," Phys. Rev. **9**, p. 4742-50, 1974.
12. W.A. Little, Possibility of synthesizing an organic superconductor, Phys. Rev. **134**, A1416 (1964).
13. We are trying to be careful not to confuse the reader with the notion of polarizable electron spin states. We are not describing polarizing the electron spin. Rather, we are talking about polarizing the orbital of the localized electron.

Chapter 1. Initial Studies - Poly(vinylidene fluoride-co-trifluoroethylene) (PVDF/TrFE) and Poly(Chlorofluoroethylene) (PCFE) Precursors and Their Conversions

Abstract

Dehydrofluorination reactions have been carried out on vinylidene fluoride/trifluoroethylene (VF_2/VF_3) copolymer in attempts to prepare conductive poly(fluoroacetylene) (PFA). Elemental analyses showed the incorporation of nitrogen functionalities into the PFA chain. The amount of nitrogen incorporation was greater when using tetrabutylammonium bromide (TBABr) as opposed to tetrabutylammonium hydrogen sulfate (TBAH) as a phase transfer catalyst (PTC). ESCA analyses showed the presence of oxygen functionalities in the dehydrofluorinated polymer which have been tentatively identified as carbonyl groups by solid state ^{13}C -NMR (CP-MAS) spectroscopy. A possible mechanism has been proposed for the incorporation of these carbonyl functionalities onto the PFA chain. TGA and DSC analyses showed differences in the materials prepared by the two different PTC systems. In addition, these thermal analyses provided information regarding the extent and completeness of the dehydrofluorination. Diffuse reflectance FT-IR spectra of the dehydrofluorinated VF_2/VF_3 copolymer as well as the homopolymer of VF_2 showed similarities in the newly formed functionalities.

Introduction

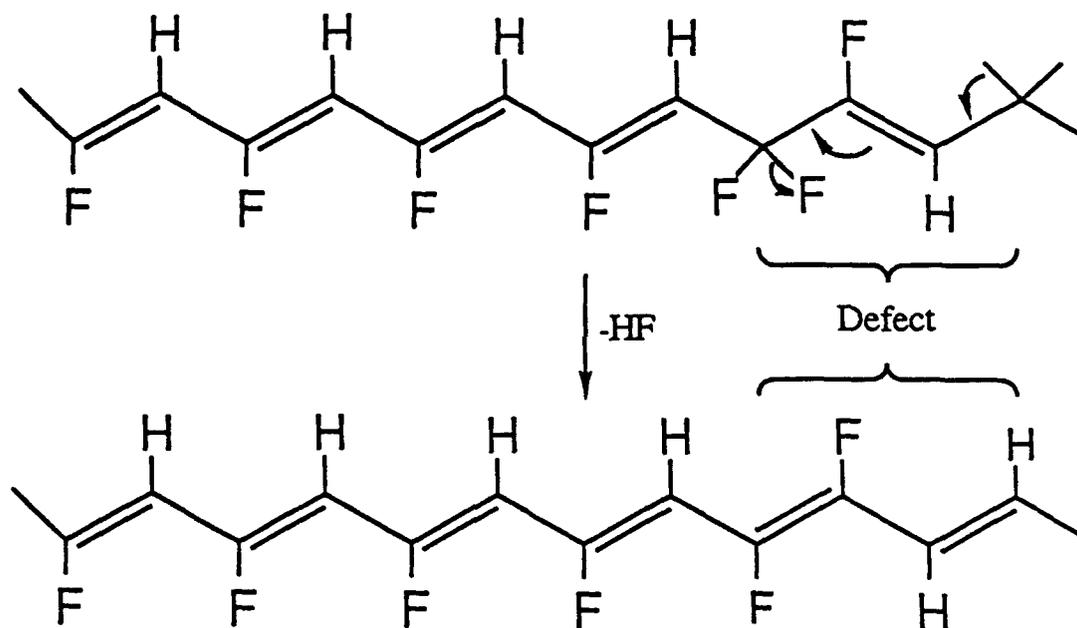
As part of Chronos Research Laboratories program entitled "Enhanced Superconductors" monitored by the Air Force Office of Scientific Research (contract # F49620-89-C-0100), we are preparing conjugated polymers which contain polar or polarizable side groups with the goal of obtaining low defect density conductors. Initially, our work is being directed to the synthesis of conjugated polymers containing either -F or -CN dipoles via elimination reactions or the direct polymerization of new dipole containing monomers.

In the first phase of this research, July 1, 1989 to September 30, 1989 we have investigated the base induced HF elimination of trifluoroethylene/vinylidene fluoride copolymer films produced by Pennwalt Inc. with a 40/60 composition. Characterization of the conjugated polymers has been accomplished using elemental analysis, diffuse reflectance FTIR spectroscopy, solid state ^{13}C NMR spectroscopy, thermogravimetric analysis, differential scanning calorimetry, and x-ray photoelectron spectroscopy. Initial experiments were carried out on the polymerization of chlorofluoroethylene to produce poly(chlorofluoroethylene) as a potentially low defect density polymer.

Polyacetylene has been extensively studied for its high electrical conductivity.¹ However, its instability and intractability limits its application. Dehydrohalogenation of poly(vinyl halides) or poly(vinylidene halides) is one potential method for preparing conjugated polymers. These can be processed from the soluble thermoplastics prior to chemical modification. For example, the dehydrochlorination of poly(vinyl chloride) and the copolymer of vinyl chloride and vinylidene chloride has been investigated under phase transfer catalysis (PTC) conditions.^{2,3} Although iodine doped dehydrochlorinated poly(vinyl chloride) exhibits high electrical conductivity, its applications are limited by its facile aerial oxidation. Dehydrofluorination of poly(vinylidene fluoride) (PVF₂) has been reported under PTC conditions⁴⁻⁶ and electrical conductivities as high as $10^{-3} \Omega^{-1} \text{cm}^{-1}$ have been reported for the resulting polyfluoroacetylene (PFA) after doping with iodine.⁴ The resistance of this PFA to aerial oxidation makes it worthwhile to study as a potential processable conducting polymer. FT-IR and UV spectroscopic techniques have been used to study the

structure of PFA prepared in this manner. The use of isopropanol/KOH for the dehydrofluorination has been shown to incorporate alcohol moieties into the resulting PFA thus reducing the conjugation length, despite a faster dehydrofluorination reaction.⁷ The use of NaOH in benzene in the presence of a catalytic amount of 1,8-diazabicyclo [5.4.0]-7-undecene (DBU) has been reported to result in facile HF elimination as shown by UV spectroscopy.⁴ However, the length of the polyene sequence was limited in this system due to the addition of DBU across the resulting double bonds.⁴ The influence of the catalyst structure for the PTC reaction has been investigated by Kise et al.⁷ who identifies hydrophobic and hydrophilic balances as playing an important role in dissolving the catalyst in the aqueous medium and penetrating into the organic polymer for the dehydrofluorination reaction.⁷ Tetrabutylammonium bromide (TBABr) has been shown to be the "best" PTC for the dehydrofluorination of PVF₂ resulting in a longer polyene sequence length as shown by FT-IR spectroscopy. However, the length of the polyene sequence decreased with increasing extent of HF elimination from a PVF₂ film with this PTC system. No explanation has been presented for the reduction of the conjugation length. Hahn et al.⁶ studied the HF elimination of PVF₂ using aq. NaOH and tetrabutylammonium hydrogen sulfate (TBAH) as PTC with added DMSO. The reaction rate was found to be slower at room temperature with this system and increased at 70 °C. However, when the reaction was carried out at 90 °C, a broad IR absorption signal around 2100 cm⁻¹ was observed which was assigned to a quaternary ammonium salt on the HF eliminated polymer chain. The formation of this salt has been attributed to a Hofmann elimination of the quaternary ammonium salt to form a free amine and a subsequent quaternization of the free amine with an allylic fluorine in the polymer chain. This quaternization does not reduce the conjugation length in the PFA, but the bulkiness of the amine group will reduce the interaction between adjacent conjugated segments. Kise et al.⁴ do not report such a quaternary ammonium salt in their HF eliminated sample despite an increased probability of their PTC (TBABr) to undergo Hofmann elimination. However, they have assigned a broad weak IR absorption signal around 2100-2150 cm⁻¹ for a C≡C triple bond due to the elimination of a second HF from the -CH=CF- unit. This signal may well be due to quaternary ammonium salt attached to the polymer chain.

Sequence lengths of 12 to 13 double bonds have been predicted in the PFA prepared by the NaOH/TBAH PTC system by UV spectroscopy.⁶ The sequence length limitations have been attributed to the presence of head to head (hh) and tail to tail (tt) linkages in PVF₂.⁶ Huhn et al.⁸ reported an IR absorption signal at 1613 cm⁻¹ for a -CH=CF- conjugated double bond and another signal at 1717 cm⁻¹ for a -CF=CF- double bond. The formation of this -CF=CF- double bond has been attributed to dehydrofluorination on either sides of a hh and tt defect structure and subsequent resonance between a conjugated region and a defect region as shown in Scheme I.⁸ Such a



SCHEME I

contribution from the -CF=CF- double bonds for the IR absorption signal is rather unlikely from a defect structure of only ~ 5%.⁸ The concentration of such a double bonds can be increased by the use of a vinylidene fluoride/trifluoroethylene (VF₂/VF₃) copolymer and its IR signal assignment verified in dehydrofluorinated polymer. Recently⁹ it has been reported that the VF₂/VF₃ copolymer undergoes facile HF elimination as shown by a significantly faster coloration when compared to the homopolymer of VF₂. In addition, it has been reported that the iodine doped dehydrofluorinated copolymer exhibited higher conductivity than the analog homopolymer.⁹

-CF=CF- double bonds can also be increased and its IR signal assignment can be verified by the dehydrofluorination of a VF₂/VF₃ copolymer. Here we report the dehydrofluorination of a VF₂/VF₃ copolymer and the structural analyses of the resulting PFA by elemental analyses, thermal analyses, FT-IR, ESCA, and solid state ¹³C-NMR spectroscopic techniques.

ELIMINATION OF VF₂/VF₃ COPOLYMER

Experimental Section

Materials and General Techniques. Pennwalt vinylidene fluoride/trifluoroethylene (VF₂/VF₃) copolymer of 60/40 mol % composition and 0.17 mm thick films were used for the dehydrofluorination reactions. The films were extracted by refluxing in methylene chloride for 1 h to remove plasticizers. The elimination reactions were carried out with 33.3% (w/v) aq. NaOH (8.3 M NaOH) and 47 mM tetrabutylammonium hydrogen sulfate (TBAH) as phase transfer catalyst (PTC) containing 20% (v/v) DMSO at 70°C. The reactions were also carried out with 5 M aq. NaOH and 25 mM tetrabutylammonium bromide (TBABr) as PTC with no added DMSO at 70 and 90°C. The chemical reactions and the subsequent washing of the materials were carried out according to the following methods:

Handling Method A: Distilled water, ethanol, and DMSO were deoxygenated with bubbling nitrogen for 0.5 h. Reactions were carried out under a nitrogen atmosphere but the films were exposed to air during washing.

Handling Method B: Distilled water was deoxygenated by boiling to reduce the volume to 90% and cooled under nitrogen. Ethanol and DMSO were deoxygenated by three freeze-pump-thaw cycles. All reactions and washings were carried out under a nitrogen atmosphere. All handling of the films were performed with exclusion of air.

Diffuse reflectance FT-IR spectra of the HF elimination products were obtained on a Digilab model FTS-40 spectrometer as a 1.5% powder in KBr. For comparison KBr pellet transmission spectra were also obtained. Solid state ¹³C-NMR (CPMAS) spectra of the HF elimination products were obtained on a Bruker 300 MSL spectrometer. Thermal stabilities and melting properties of the materials were determined under nitrogen atmosphere using a 951 TGA module and 910 DSC module on a model 9900 DuPont thermal analyzer. TGA samples were heated at 20°C/min and DSC samples were heated at 10°C/min. X-ray photoelectron spectroscopy (ESCA) of the samples was kindly provided by Surface Science Instruments.

Syntheses. HF elimination reactions were carried out in a 1L round bottom flask or in a 150 ml Schlenk flask. The reactions carried out in the round bottom flask using handling method A, afforded better mixing of the aqueous and organic (DMSO) layers. Stirring problems were encountered in the reactions carried out in Schlenk flasks using handling method B. After the reaction, the films were rinsed with distilled water until the rinses were neutral to litmus paper. Subsequently, the films were soaked and washed with ethanol 3 times for 3 h to 3 days and dried under vacuum overnight at 70 °C. The films treated with no DMSO appeared black and even colored. On the other hand the films treated with aq. NaOH containing DMSO appeared brownish black with uneven color.

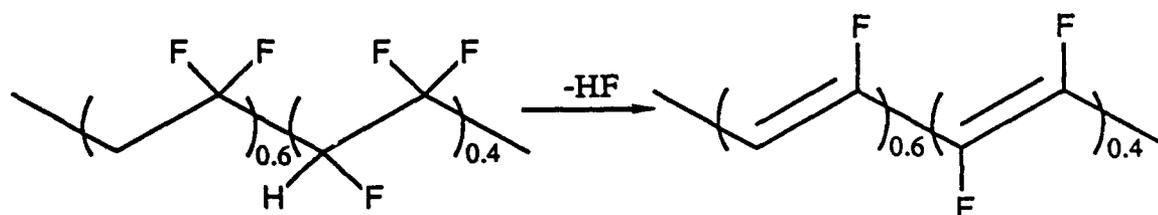
Results and Discussion

An XPS survey scan of unreacted VF₂/VF₃ copolymer is shown in Figure 1. In general it is as expected except for a relatively high concentration of Si and O which can be most likely attributed to a coating of poly(dimethylsiloxane). This sample was thoroughly extracted with CH₂Cl₂ prior to analysis and thus it is expected that the as received film is highly surface contaminated. Experiments are underway to determine this. It should be pointed out that our HF elimination reactions remove the Si from the polymer surface and thus the poly(fluoroacetylene) obtained is not contaminated.

It has been reported that poly(fluoroacetylene) undergoes no ambient oxidation.⁴ Our preliminary ESCA experiments on the HF eliminated samples showed considerable amounts of oxygen functionalities. Consequently, the reactions and handling of the materials were carried out under rigorous exclusion of air.

The addition of 33.3% (8.3 M) aq. NaOH containing 47 mM TBAH onto the VF₂/VF₃ films at 70°C resulted in the immediate release of a dark brown colored material from the films into the aqueous layer. After the addition of DMSO into the solution, the brown colored liquid enters the top organic layer. Subsequently, there is no apparent formation of brown colored liquid from the films. The light brown colored DMSO layer and the clear aqueous layer remain the same over a

period of 12 h. Overnight, the aq. layer also becomes brown and ultimately becomes more intensely colored than the organic layer. During rinsing, several water rinses were brown colored. Chain degradation leading to pitting and corrosion of the polymer surface may be occurring here. Electron microscopy studies are presently underway to evaluate this. On the other hand, the reactions carried out with 5 M NaOH/25 mM TBABr with no DMSO, either at 70 or 90°C showed a smaller amount of brown coloration initially and the solution became only slightly colored with the extent of the reaction. Extents of conversion for the HF elimination products were determined gravimetrically and are summarized in Table 1 with reaction conditions. The % conversions were calculated based on a 28% weight loss for the complete (100% conversion) elimination of HF from the copolymer and no chain cleavage as shown in Scheme II.



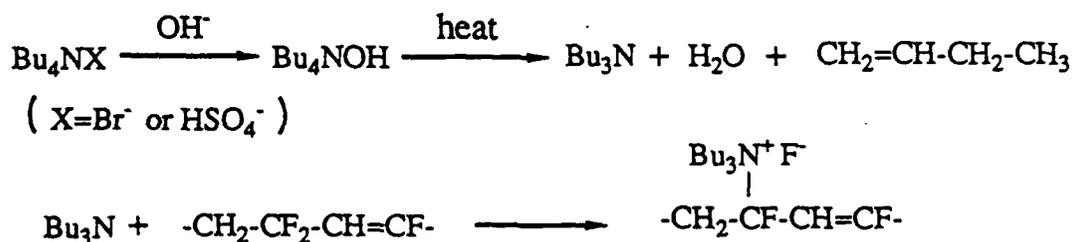
SCHEME II

The HF elimination results in Table 1 shows that the phase transfer catalyzed (PTC) reaction with TBAH at 70°C with no mixing of aqueous and organic layers undergoes an induction period. The reactions carried out for 8-11 h show only 5% conversion. When the reaction was carried out with mixing of the aq. and organic layers for an additional 9 h (VPC-56) reaction rates increase considerably. When the reaction was carried out with vigorous mixing of the layers from the start for 9 h (VPC-62), 10% conversion was obtained. These results show the need for thorough mixing of the aq. and organic layers to avoid an induction period for the reaction. A direct comparison of VPC-37 and VPC-75 shows the importance of mixing the aq. and organic layers as Method A had better mixing. The runs VPC-65 and VPC-87 indicate that the reactions can be conveniently carried out in a homogeneous medium with no mixing of the aqueous and organic layers but with an extended period of time. The treatment of the VF₂/VF₃ copolymer with 5 M NaOH/25 mM TBABr with no DMSO at 90 °C, as reported for the HF elimination of PVF₂,⁴

seemed to be a faster reaction. The initial elemental analysis results for these elimination reactions showed the presence of nitrogen in the elimination product. Consequently, the reaction with this PTC system was carried out at 70 °C in an attempt to decrease the extent of the side reaction. As we will see in the elemental analyses of these copolymers, a small amount of nitrogen was still found in the HF eliminated product, though the side reaction proceeds quite slowly.

Elemental Analyses. The C, H and N analyses of the virgin and HF eliminated copolymers are shown in Tables 2 and 3. Though the virgin copolymer shows the presence of 0.32% nitrogen this is within experimental error for no nitrogen (no nitrogen was detected in the virgin sample by ESCA). The elimination of HF from the copolymer is expected to increase the carbon content from 33.71% to 46.88% for complete reaction while the hydrogen content decreases.

The results in Table 2 show that the carbon content steadily increases with the extent of HF elimination. However, the content of H and N (to a small extent) also increases with the extent of the reaction. The incorporation of N into the sample is most likely due to the formation of free amine, via a Hofmann elimination, from the quaternary ammonium salt (PTC) and its subsequent reaction with an allylic fluorine as shown in Scheme III.⁶ The elemental analyses show that the reaction proceeds very slowly at 70°C with the TBABr PTC system compared to a significantly



SCHEME III

faster reaction at 90°C. The analyses also show that the incorporation of nitrogen is almost the same at 70 and 90°C for the same extent of reaction (compare VPC-29-3 and VPC-70). The results in Table 3 for the HF elimination product by the TBAH PTC system show low amounts of nitrogen at levels lower than the sensitivity of the technique. It should be noted that 47 mM TBAH

was used as opposed to 25 mM TBABr. The structure of the HF elimination product cannot be formulated from the content of nitrogen in the sample.

Differential Scanning Calorimetry (DSC). The VF₂/VF₃ (60/40) copolymer exhibits two endothermic peaks in the DSC as shown in Figure 2. The low temperature peak is due to the ferroelectric to paraelectric transition and the high temperature peak is due to the melting of the semicrystalline copolymer.¹⁰ DSC traces for the HF eliminated samples are presented in Figures 2 and 3. With increased extent of HF elimination, the crystalline content in the sample decreases as evident by the decrease in the intensity of the melting endotherm at *ca.* 145 °C. On the other hand, the signal due to the paraelectric to ferroelectric transition moves to higher temperature. This may be due to an increase in the content of VF₂ units in the copolymer with increasing HF elimination. The HF elimination may be postulated to occur faster in the VF₃ units, as opposed to the VF₂ units, as evident by the more rapid coloration during elimination of the VF₂/VF₃ copolymer when compared to PVF₂. It has been reported that the paraelectric to ferroelectric transition temperature increases with increase in the VF₂ content in the VF₂/VF₃ copolymer.¹¹ Based on the DSC analysis samples VPC-29-4 and VPC-70 underwent incomplete HF elimination, despite containing ~ 48% carbon (Table 2) as expected for complete HF elimination. The samples VPC-14-2 (Table 2) and VPC-65 (Table 3) underwent almost complete HF elimination and loss of crystallinity. Therefore, DSC analysis may actually be a useful tool for determination of the extent and completeness of HF elimination from these fluoropolymers.

Thermogravimetric Analyses (TGA). The TGA traces of virgin and HF eliminated VF₂/VF₃ copolymers are shown in Figures 4 (NaOH/TBAH System) and 5 (NaOH/TBABr System). It should be noted that the virgin copolymer is more stable than the HF elimination products. The virgin copolymer undergoes depolymerization to the starting monomer at *ca.* 450 °C resulting in no residue. The initial weight loss in the thermograms of eliminated samples are probably due to the loss of water and ethanol in the samples. The remainder of the thermograms generated from the NaOH/TBABr system can be divided into three regions. The weight loss between ~ 225-300 °C can be attributed to the loss of quaternary ammonium salt attached to the

polymer chain (Figure 5e). The weight loss in this region is proportional to the content of nitrogen in the HF elimination products (Tables 2 and 3). The second weight loss between ~ 300 - 400 °C is probably due to HF elimination from the $-\text{CH}=\text{CF}-$ linkages. The third weight loss between ~ 400 - 525 °C is due to the depolymerization of the unreacted monomer units to the starting monomer.

With increased extent of HF elimination catalyzed by TBABr there is a substantial and constant char residue found in the thermally analyzed samples (Fig. 5). However, there is a steady increase in the char residue with extent of HF elimination in the NaOH/TBAH PTC system (Fig. 4). These differences may be due to the differences in the sequence distribution of the unreacted monomer units present in the HF eliminated samples obtained by the two PTC systems or the effectiveness of the PTC to penetrate into the film and give a more homogeneous reaction. Thus, these TGA studies provide a wealth of information regarding the extent of HF elimination, extent of Hofmann elimination of the PTC (and its subsequent quaternization with the allylic fluorines of the polymer chain) and the different modes of HF elimination by the two PTC systems.

Solid State ^{13}C -NMR (CPMAS). The solid state ^{13}C -NMR spectrum of an HF eliminated sample (VPC-37) is shown in Figure 6. Elemental analysis indicates HF elimination to be essentially complete in this sample (Table 3). The peaks between 0-65 ppm are assigned to the sp^3 carbons of the quaternary ammonium salts attached to the polymer chain, while the broad peaks between 65-150 ppm are assigned to the $-\text{CH}=\text{CF}-$ and $-\text{CF}=\text{CF}-$ carbons. The two sets of weak resonances further downfield between 150-200 ppm are assigned to carbonyl carbons along the polymer chain. A possible mechanism for the formation of these carbonyl carbons is shown in Scheme IV. These carbonyl carbons are probably formed by the addition of H_2O across the double bond followed by HF elimination to give an enol via tautomerization. If these assumptions are correct, the oxygen functionality in the HF elimination products are not due to ambient oxidation of the sample, but can be attributed to side reactions during elimination and serve as the most important defects in this system. The two types of carbonyl peaks (170 and 190 ppm) are

probably due to extents of fluorination on neighboring carbons which originate from the VF₂ or VF₃ units in the copolymer chain.

FT-Infrared spectroscopy. Diffuse reflectance FT-IR spectra of the HF elimination products are shown in Figures 7-9. For comparison, HF elimination product of PVF₂ (Fig. 7) and a KBr pellet transmission spectrum of an eliminated copolymer sample are also included (Fig. 10). All the spectra show -OH signals due water or attached -OH groups (Scheme IV) in the sample. A broad weak signal at ~2200-2100 cm⁻¹ is evident and is assigned to the quaternary ammonium salts attached to the polymer chain.⁶ It should be noted that no such peak was reported by Kise et al.⁴ in the poly(fluoroacetylene) prepared using the TBABr PTC system. However, our elemental analyses and ESCA results support these IR studies. There are three major peaks between 2000 and 1500 cm⁻¹ in all the diffuse reflectance spectra. The peak ~ 1760-1750 cm⁻¹ is assigned to the carbonyl peak illustrated earlier in Scheme IV. The strong signal at ~ 1590 cm⁻¹ is assigned to the stretching vibration of the -CH=CF- conjugated double bonds.⁴ It has been reported⁸ that a signal at ca. 1717 cm⁻¹ is due to the -CF=CF- group in the HF elimination product of PVF₂. This is in agreement with an IR signal at 1724 cm⁻¹ which was reported for the -CF=CF- group in poly(hexafluoro-1,3-butadiene).¹² We expected an increase in the amount of -CF=CF- group in our eliminated copolymer formed from the VF₃ units. On the other hand, the concentration of -CH=CF- groups will decrease due to the presence of -CF=CF- neighboring units since the copolymer is random. Therefore, the exact position of the IR signals for the -CF=CF- and -CH=CF- groups cannot be determined accurately from our IR results. By comparison with the literature,^{4,8} the signal at ~ 1590 cm⁻¹ is assigned to the -CH=CF- group and the shoulder between the signals at 1750-1590 cm⁻¹ are assigned to the -CF=CF- groups in the polymer chain. It should be noted that only a single peak was found in this region in the KBr pellet transmission spectrum (Fig. 10). Others workers^{4,8} could not identify the carbonyl group in the HF elimination product of PVF₂ using the same spectroscopic technique.

X-ray photoelectron spectroscopy (ESCA, XPS). The ESCA (C1s) of virgin copolymer is shown in Fig. 11. There are four major peaks. A minor peak at 290.4 eV is

assigned to the CF_2 carbon in $\text{CF}_2\text{-CF}_2$ units *due to head-head defects* by comparison with the C1s spectrum of PTFE.¹³ Binding energies were not compensated for charging effects and thus further experimentation is required to determine exact energies. The peaks at 287.9 eV and 285.7 eV are assigned to the CF_2 and CHF carbons of the VF_2 and VF_3 units in regular head to tail linkages.¹³ The other two signals at 283.4 eV and 281.6 eV are tentatively assigned to the $-\text{CH}_2-$ carbon of the VF_2 units and the $-\text{CH}_3$ carbon of the silicone surfactant. These assignments were made by comparing samples with different silicone contents. There are 3 peaks seen in the C1s spectrum of the HF elimination product (Fig. 12). It should be noted that the x-ray irradiation removed extensive amount of fluorine from the virgin sample. However, the technique identified other elements such as sodium (NaOH), N(quaternary ammonium salts), S(from Bu_3NHSO_4 or DMSO) and oxygen in the HF eliminated samples (Table 4). The concentrations of O, N and S are overestimated here due to the large decrease in F content. Irrespective of how the sample was handled (presence of air or not), all the HF eliminated samples showed O1s peaks. Assuming some oxygen content can arise from NaOH and HSO_4^- , the remainder of the oxygen was determined from the total contribution and the results are shown in Table 4. Consequently, all the samples show an oxygen contribution of 9-11% and this oxygen is tentatively assigned to the carbonyl and alcohol groups whose structure is presented in Scheme IV. If this suggestion is correct then the alcohol and carbonyl moieties on the backbone of the PFA chain are present in extremely high concentrations. It should be noted that not all of the nitrogen present in the samples are due to free Bu_4NHSO_4 (PTC) trapped in the polymer, but are also due to the quaternary ammonium salt attached to the polymer chain. The O1s spectrum of the HF eliminated samples showed 2-3 signals and the results are summarized in Table 5. These peaks are tentatively assigned to the oxygen in carbonyl groups, NaOH and free phase transfer catalyst (Bu_4NHSO_4).

I_2 Doping. The room temperature vapor phase iodine doping results are summarized in Table 6. The low weight increase in samples VPC-29-3 and VPC-40 over 7 days may be due to a leak in the system. In general quite small irreversible I_2 uptake is observed and conductivity increases are negligible.

Poly(1-chloro-1-fluoroethylene) (PCFE)

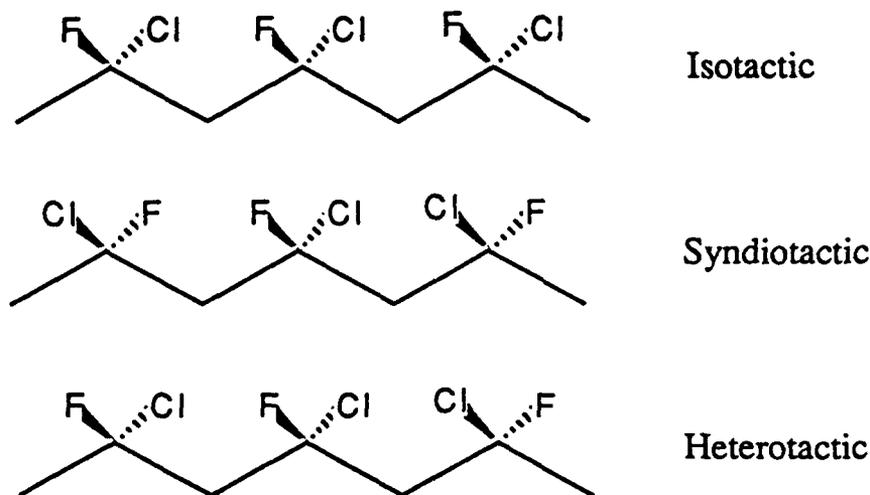
Experimental Section

Materials and methods. The monomer 1-chloro-1-fluoroethylene (CFE) was obtained from PCR Research Chemicals Inc., and purified by drying and removal of inhibitor (if present) by passage through columns of silica gel and molecular sieves, followed by degassing by freeze-pump-thaw cycles. The 75.47 MHz ^{13}C -NMR spectrum and 282.36 MHz ^{19}F -NMR spectrum of the polymer sample were obtained on a Bruker 300 MSL spectrometer at room temperature. The NMR sample was prepared as a solution in acetone with D_2O insert as a lock solvent. Chemical shifts were calibrated with respect to C_6F_6 (-163 ppm) and acetone- d_6 (29.8 ppm) as external references for the ^{19}F -NMR and ^{13}C -NMR spectra respectively.

Synthesis of PCFE. The polymerization was carried out at 45°C from bulk monomer sealed in a glass ampule with 1 mol% AIBN as initiator. The resulting polymer is soluble in solvents such as acetone and DMSO. Purification of the polymer proved difficult in that precipitation in solvents such as ether, methanol and pentane was unsuccessful. The polymer solution was precipitated in water with difficulty. The polymer showed a film forming ability with an elastic nature.

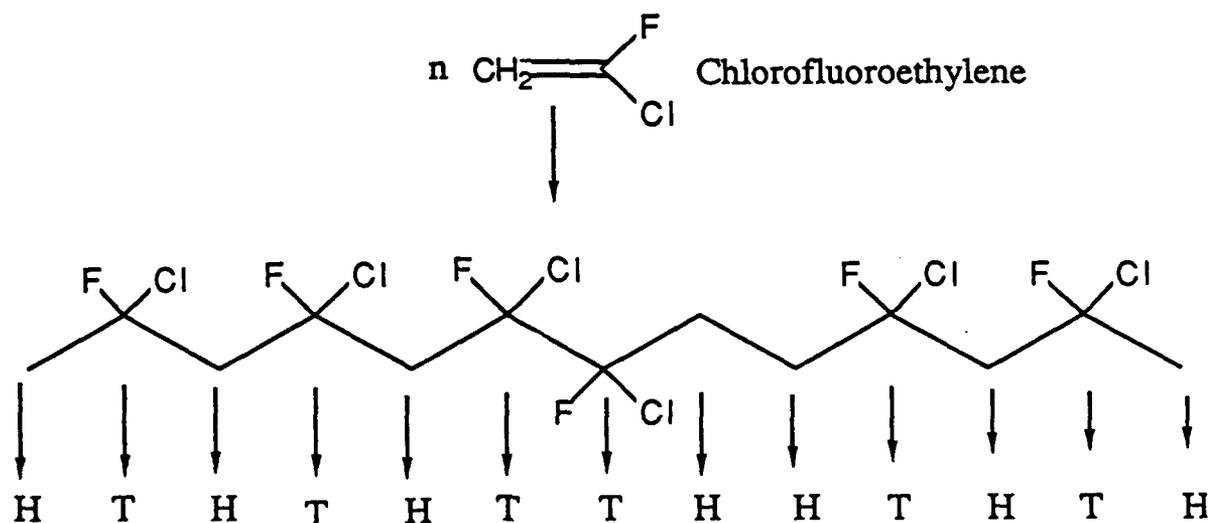
Results and Discussion

Structural analyses of PCFE. The ^{19}F -NMR spectrum of the sample (Fig. 13) showed it to be atactic with an isoregic monomer sequence as desired for a low defect precursor. The spectrum consists of a simple triplet with components at -98.58, -99.93, and -101.20 ppm, corresponding to isotactic, heterotactic, and syndiotactic triads.¹⁴ (Scheme V)



SCHEME V

The ^{13}C -NMR spectrum of the sample (Fig. 14) showed a doublet (109.38 and 106.05 ppm) for the $-\text{CFCl}$ carbon and a multiplet ~ 52.58 ppm for the $-\text{CH}_2$ carbon in the polymer chain. The absence of other signals in the ^{19}F -NMR and ^{13}C -NMR spectra of the sample indicate that it contains regular head-to-tail linkages (isoregic) in the polymer chain with no detectable head-to-head and tail-to-tail (aregic) linkages. (Scheme VI)



SCHEME VI

Preliminary HF elimination results. The treatment of PCFE in 5 M aq. NaOH containing 25 mM TBABr as PTC at room temperature showed immediate coloration of the sample

indicating facile HCl elimination to form isoregic poly(fluoroacetylene). The facile HCl elimination at room temperature indicates that the structural irregularities, such as the incorporation of quaternary ammonium salt on the side chain and carbonyl group formation, may be eliminated and a higher order for the material should be achieved.

References

1. Fromer, J. E.; Chance, R. R.; *Conducting Polymers*, Encyclopedia of Polymer Science and Engineering, Wiley: New York, Vol. 5, 1985.
2. Kise, H. *J. Polym. Sci. Polym. Chem. Ed.*, 1982, 20, 3189.
3. He, F. F.; Kise, H. *J. Polym. Sci. Polym. Chem. Ed.*, 1983, 21, 1729.
4. Kise, H.; Ogata, H.; Nakata, M. *Angw. Makromol. Chem.* 1989, 168, 205.
5. Dias, A.; McCarthy, T. *J. Polym. Sci. Polym. Chem. Ed.*, 1985, 23, 1057.
6. Hahn, B.; Percec, V. *J. Polym. Sci. Polym. Chem. Ed.*, 1987, 25, 783.
7. Kise, H.; Ogata, H. *J. Polym. Sci. Polym. Chem. Ed.*, 1983, 21, 3443.
8. Huhn, K. J.; Hahn, B.; Percec, V.; Urban, M. W. *Appl. Spectrosc.* 1987, 41(5), 843.
9. Olsen, R. B. Chronos Laboratories, Private Communications.
10. Stack, G. M.; Ting, R. Y. *J. Polym. Sci. Polym. Phys. Ed.*, 1988, 26, 55.
11. Tashiro, K.; Takano, K.; Kobayashi, M.; Chatani, Y.; Tadokoro, H. *Polymer*, 1984, 25, 195.
12. Narita, T.; Hagiwara, T.; Hamana, H.; Sezaki, M. *Macromolecules*, 1989, 22, 3183.
13. Radner, B. D. *Proc. 2nd Int. Conf. on Polymers in Medicine*, Chiellian, E. Ed., Plenum: New York, 1986.
14. Cais, R. E.; Kometani, J. M. *Org. Coat. Appl. Polym. Sci. Proc.* 1983, 48, 216.

Table 1
Dehydrofluorination Results of VF₂/VF₃ (60/40) Copolymer

Ref. #	Catalyst ^a	Reaction Temp. (°C)	Method	Time(h)	Weight (g)		% Conversion ^b
					Initial	Final	
VPC-37	NaOH/TBAH	70	A	15	0.8191	---	> 100 ^f
VPC-50-1		70	B	8	4.3704	4.3107	5
VPC-50-2		70	B	11	4.1205	4.0620	5
VPC-56		70	B	21 ^c	4.4250	3.4855	76
VPC-62		70	B	9 ^d	3.6357	3.5362	10
VPC-65		70	B	36	1.8271	---	> 100 ^f
VPC-75		70	B	16 ^e	0.5715	0.5063	40
VPC-87		70	B	24	2.6143	2.0757	74
VPC-70	NaOH/TBABr	90	B	24	1.3181	1.1017	59
VPC-14-2		90	A	24	0.4186	---	> 100 ^f

^aNaOH/TBAH = 33.3% aq. NaOH (w/v)/47 mM TBAH containing 20% (v/v) DMSO.
 NaOH/TBABr = 5 N. aq. NaOH/25 mM TBABr.

^bBased on 28% weight loss corresponds to 100% elimination of HF.

^cFor 12 h both aqueous and organic layers were non-mixed and for an additional 9 h both layers were mixed.

^dAqueous and organic layers were mixed for 9 h.

^eAfter 0.5 h. of reaction, oxygen was bubbled for 5 minutes.

^fConversions greater than 100% are due to corrosive action and a second HF elimination.

Table 2

Elemental Analysis Results of VF₂/VF₃ copolymer prepared by Elimination Reactions with 5 M. aq. NaOH/25 mM. TBABr

Ref. #	Temp. (°C)	Reaction Time(h)	Method	% weight		
				C	H	N
VPC-29-1	70	10.0	A	36.34	2.50	0.24
VPC-29-2	70	22.0	A	37.21	2.60	0.32
VPC-29-3	70	61.5	A	47.15	3.46	0.75
VPC-29-4	70	96.0	A	48.85	4.06	1.00
VPC-14-1	90	8.0	A	41.32	3.23	0.54
VPC-14-2	90	24.0	A	55.05	5.10	1.25
VPC-70	90	24.0	B	47.34	3.66	0.73
(VF ₂ /VF ₃) ^a (60/40)				33.27 (33.71)	2.14 (2.25)	0.32 0
(VF ₂ VF ₃ -HF) ^b				46.88	1.17	0

^aValues within the brackets are calculated for a copolymer of VF₂/VF₃ with molar composition of 60/40.

^bCalculated for complete HF elimination.

Table 3

Elemental Analysis Results of VF₂/VF₃ copolymer prepared by
Elimination Reactions with 33.3% (w/v) aq. NaOH/47 mM.
TBAH containing 20% (v/v) DMSO.

Ref. #	Temp. (°C)	Reaction Time(h)	Method	% weight		
				C	H	N
VPC-39	70	5	A	41.31	2.58	0.20
VPC-40	70	7	A	42.79	2.66	0.06
VPC-37	70	15	A	49.73	3.54	0.21
VPC-56	70	21	B	44.90	2.75	0.23
VPC-65	70	36	B	56.38	3.72	0.38

Table 4
ESCA results for VF₂/VF₃ copolymer and its HF elimination products.

Sample (Ref. #)	%Atomic concentration							
	C	F	O	N	Na	Si	S	(C=O) ^c
VF ₂ /VF ₃ (60/40)	50.14	42.14	4.45			3.27		
	45.45	54.55	(Theoretical)					
(VPC-40) ^a	67.13	4.84	18.15	1.30	5.98		0.72	9.29
(VPC-50-2) ^b	80.40	4.39	13.16	0.69	0.99		0.37	10.69
(VPC-56) ^b	71.35	4.48	16.96	1.82	5.04	0.15	0.19	11.00

^aSample was exposed to oxygen under the experimental condition.

^bSample was handled under rigorous exclusion of air during the HF elimination and handling.

^cCalculated for the concentration of carbonyl group in the sample assuming other oxygen in the sample are due to NaOH, Si-O and HSO₄⁻.

Table 5
ESCA O1S results of HF elimination products of VF₂/VF₃ copolymer.

Sample #	% HF elimination	Peak binding energy(eV)	%
VPC-50-2	5	527.09	32.0
			528.99
68.0			
VPC-40	70	527.75	42.7
			529.50
57.3			
VPC-56	76	527.71	43.4
			529.51
47.3			
	9.3		531.86

Table 6
Vapor phase iodine doping results of the HF elimination products
of the VF₂/VF₃ copolymer and PVF₂ fiber.

Sample	% HF elimination	Doping Time (days)	% weight increase
VPC-29-3	46	7	0.4
		15	8.0
VPC-40	70	7	0.5
		15	13.8
VPC-56	76	5	7.2
VPC-62	11	5	0.27
VPC-59 ^a	~100	5	4.9

^a)HF elimination product of PVF₂ fiber.

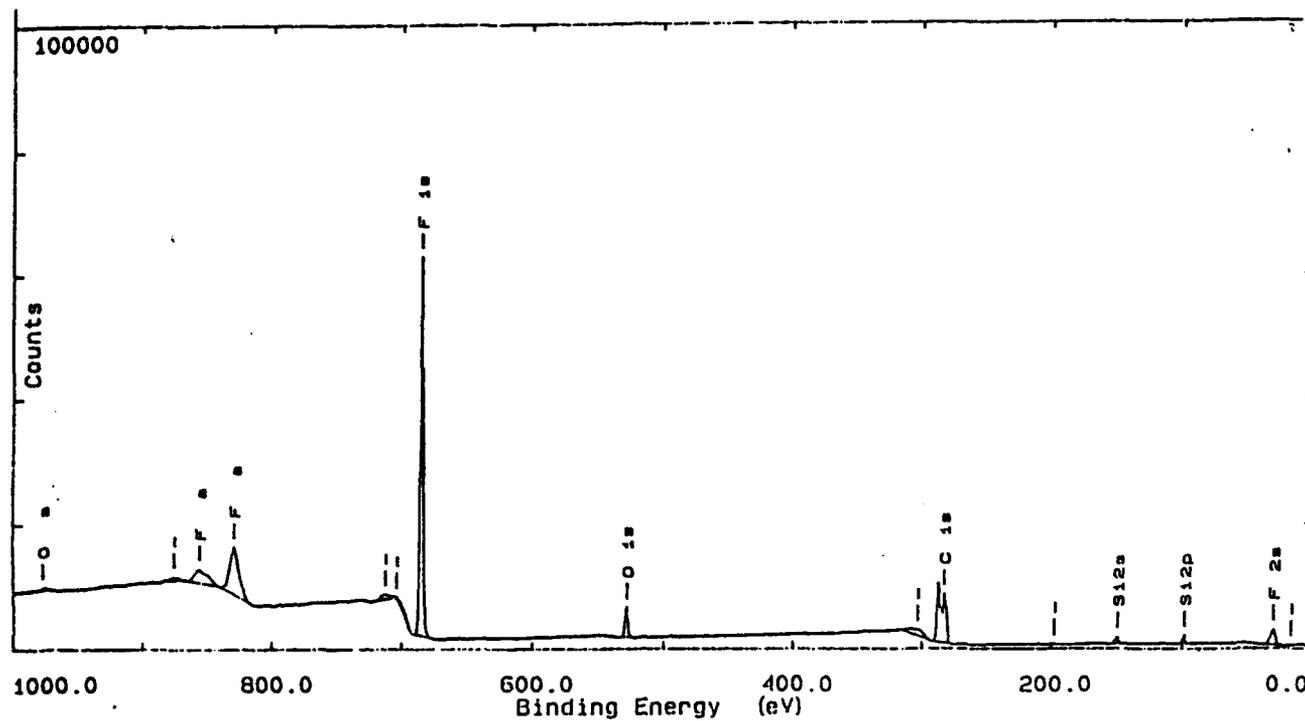


Figure 1. XPS Survey spectrum of VF_2/VF_3 copolymer.

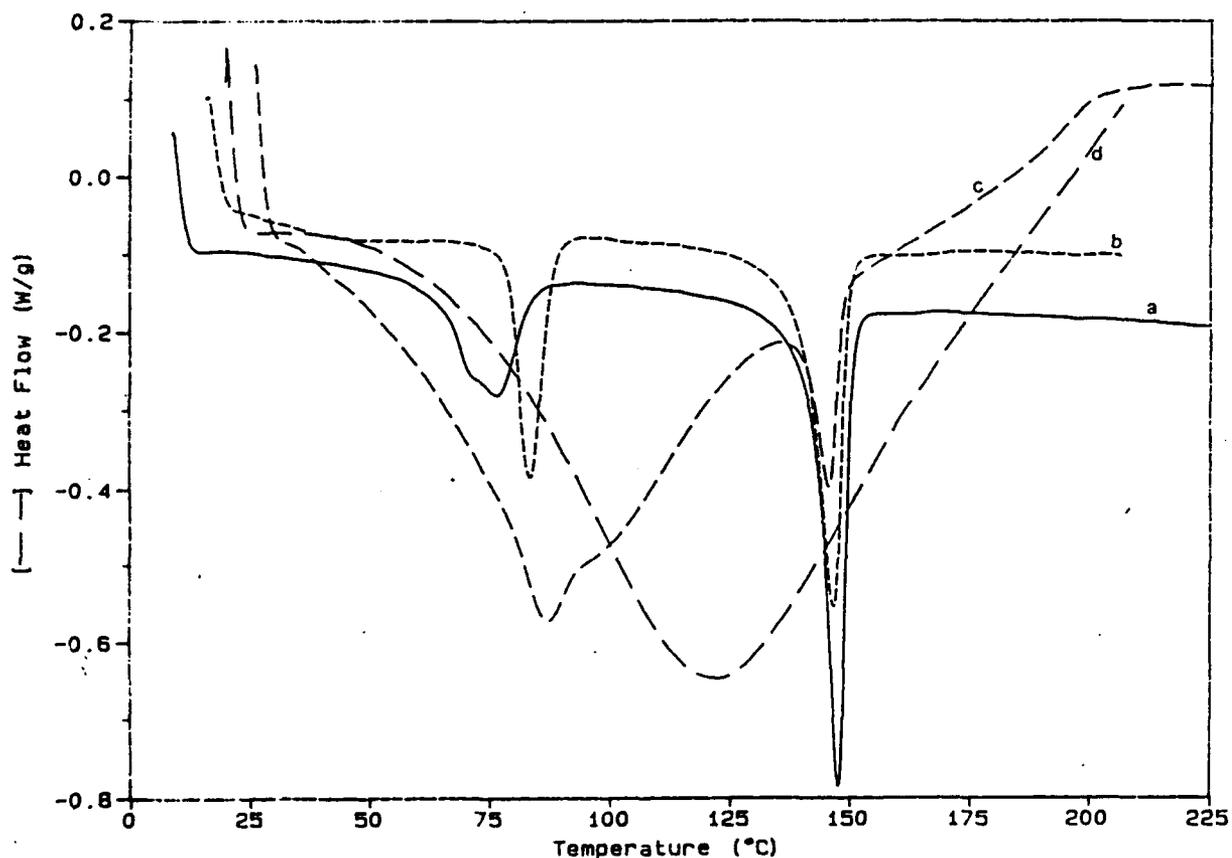


Figure 2. DSC traces of VF_2/VF_3 copolymer and its HF elimination products by NaOH/TBAH PTC system at 70°C : (a) VF_2/VF_3 copolymer, (b) VPC-50 (5% HF elimination); (c) VPC-56 (76% HF elimination); and (d) VPC-65 (~100% HF elimination).

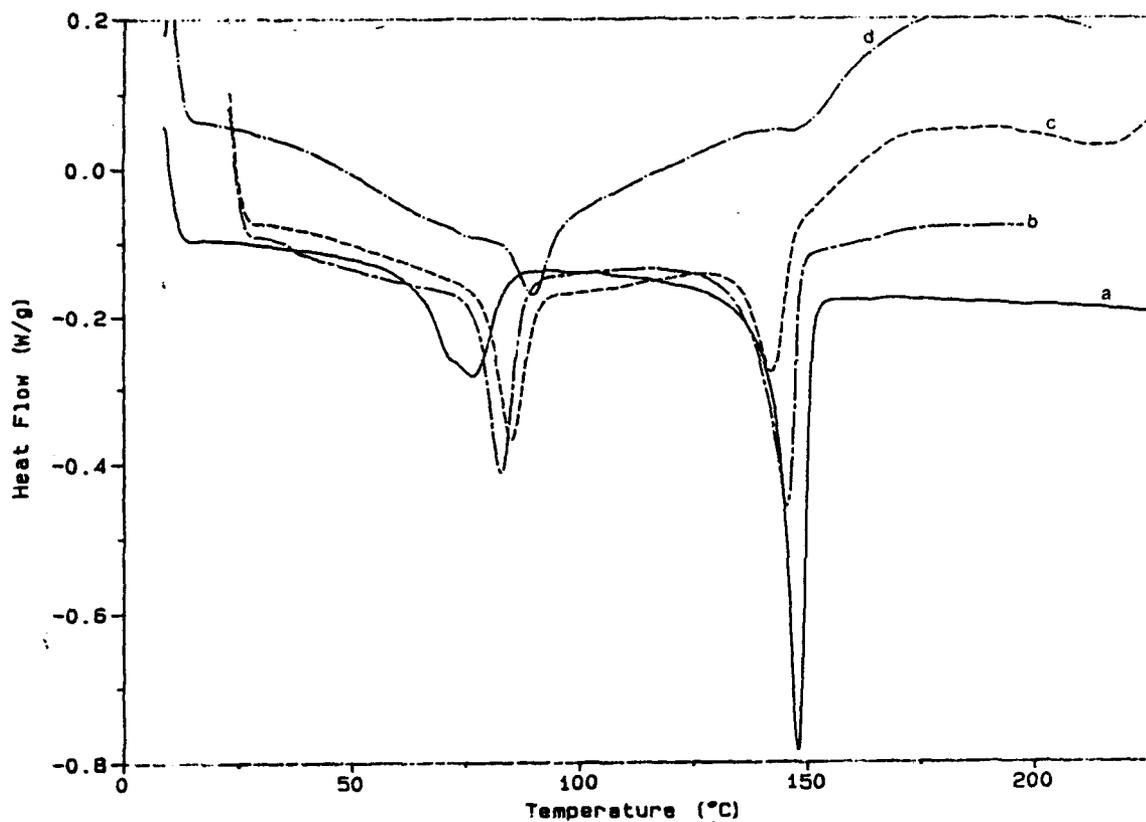


Figure 3. DSC traces of VF₂/VF₃ copolymer and its HF elimination products by NaOH/TBABr PTC system at 70 °C (% HF elimination N/A): (a) VF₂/VF₃ copolymer; (b) VPC-29-2 (22 h); (c) VPC-29-3 (61.5 h); and (d) VPC-29-4 (96 h).

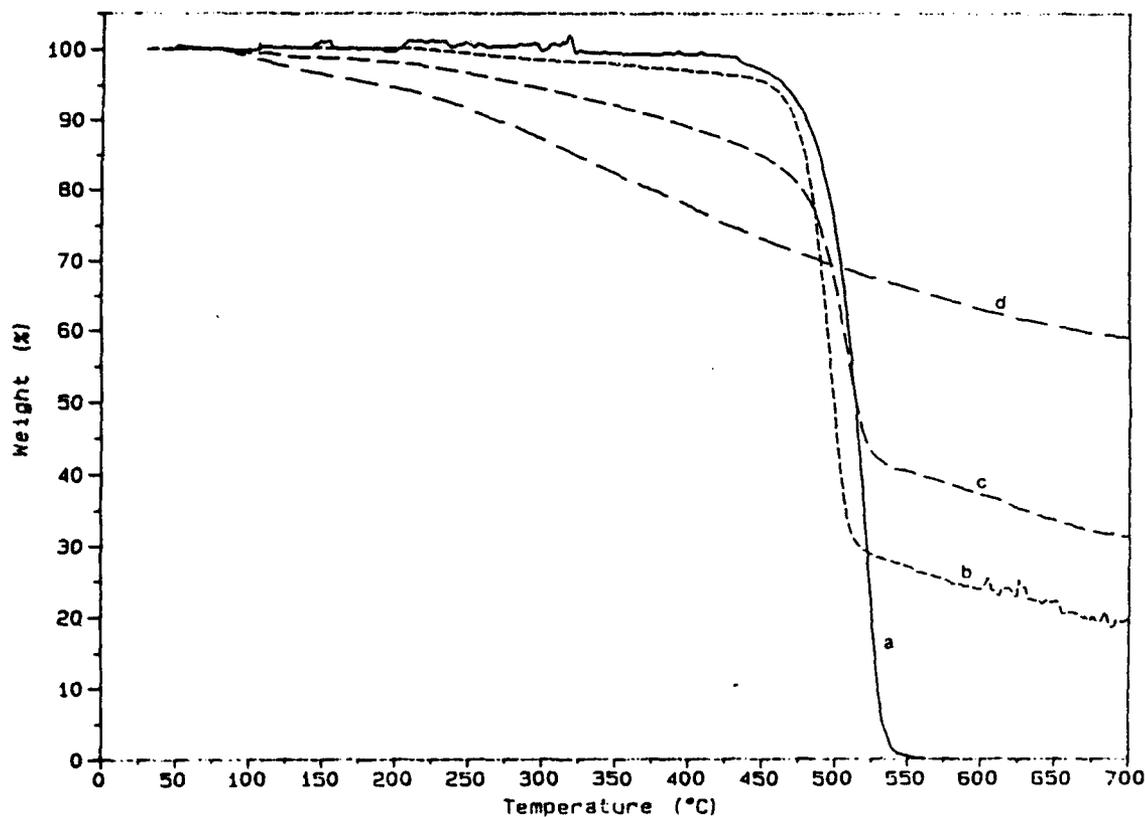


Figure 4. TGA traces of VF₂/VF₃ copolymer and its HF elimination products by NaOH/TBAH PTC system at 70 °C: (a) VF₂/VF₃ copolymer; (b) VPC-62 (10% HF elimination); (c) VPC-56 (76% HF elimination); and (d) VPC-65 (~100% HF elimination).

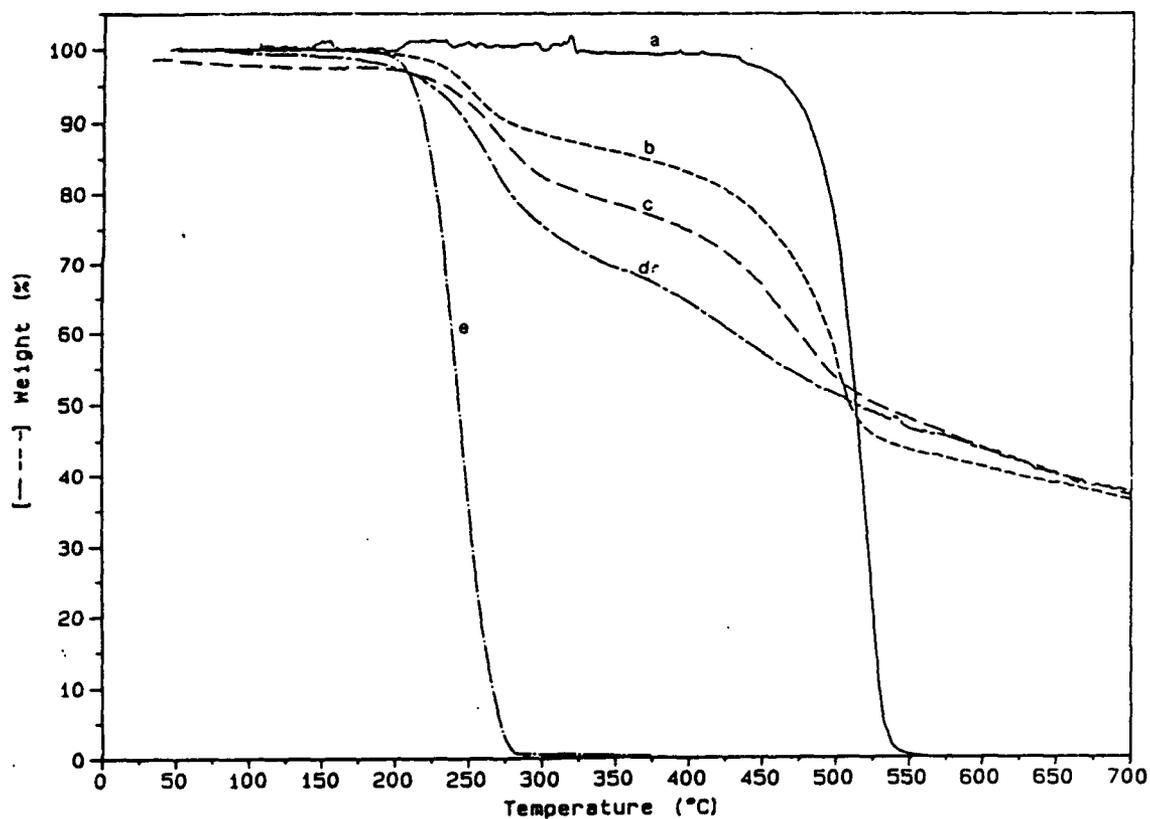


Figure 5. TGA traces of VF_2/VF_3 copolymer and its HF elimination products by NaOH/TBABr PTC system at 70 and 90 °C (see Tables 1 & 2): (a) VF_2/VF_3 copolymer; (b) VPC-14-1 (% HF elimination N/A); (c) VPC-70 (59% HF elimination); (d) VPC-14-2 (~ 100 % HF elimination); and (e) TBABr.

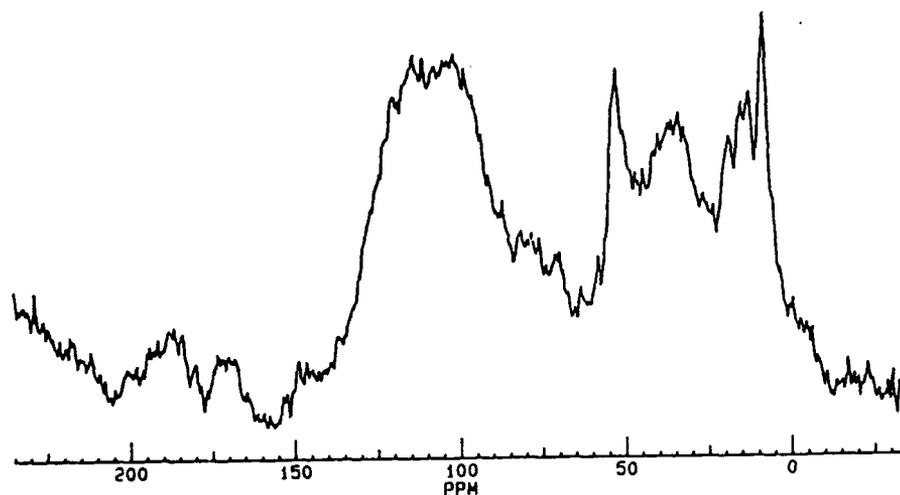


Figure 6. 75.47 MHz solid state (CP-MAS) ^{13}C -NMR spectrum of ~ 100% HF eliminated product of VF_2/VF_3 copolymer (VPC-37).

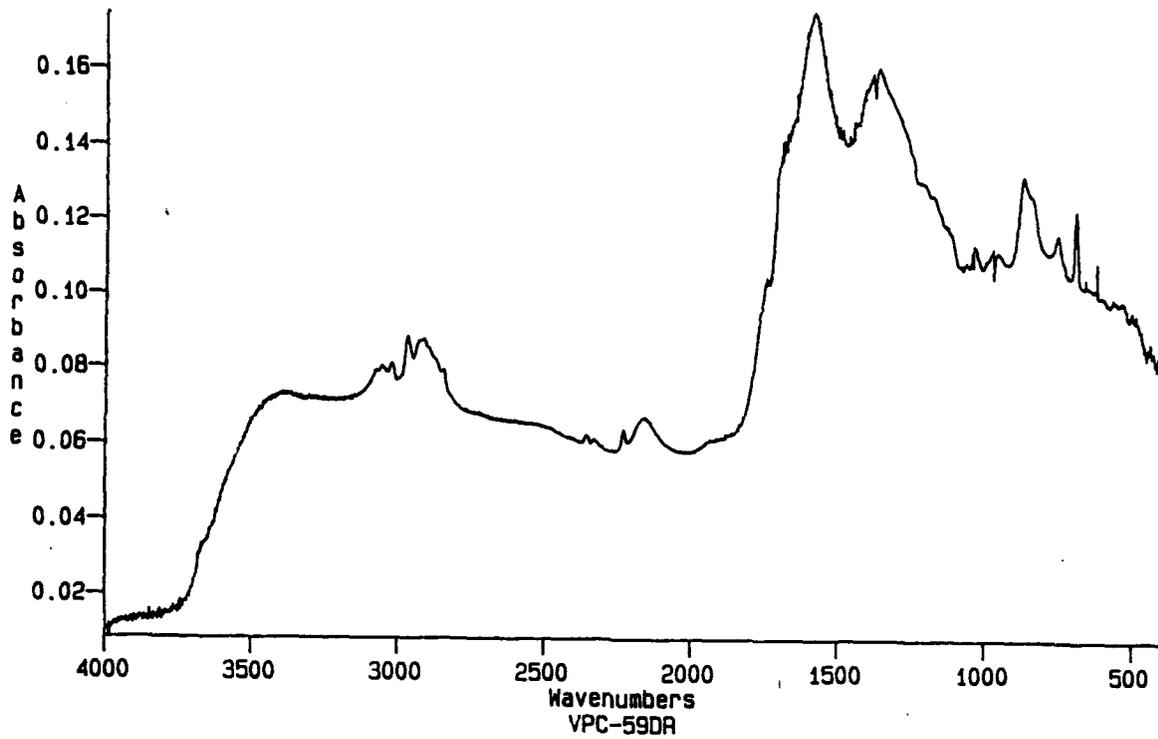


Figure 7. FT-IR (diffuse reflectance) spectrum of VPC-59 (~ 100% HF elimination from PVF₂ fiber by NaOH/TBAH PTC system).

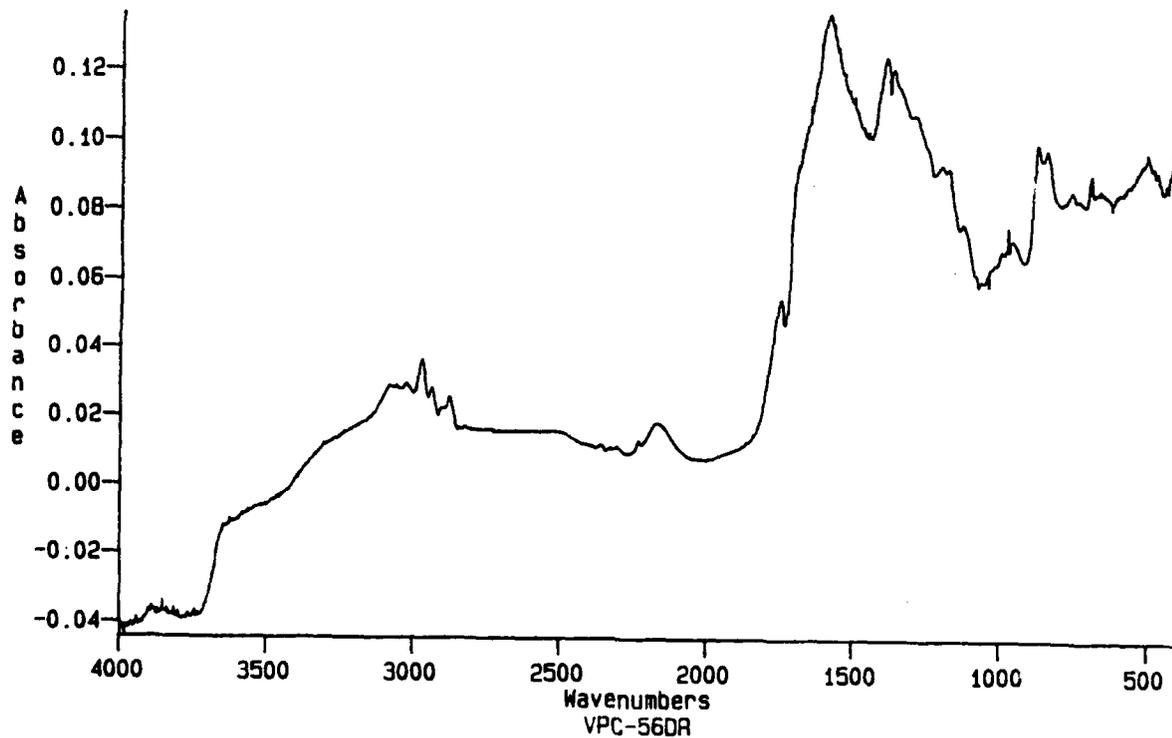


Figure 8. FT-IR (diffuse reflectance) spectrum of VPC-56 (76% HF elimination by NaOH/TBAH PTC system).

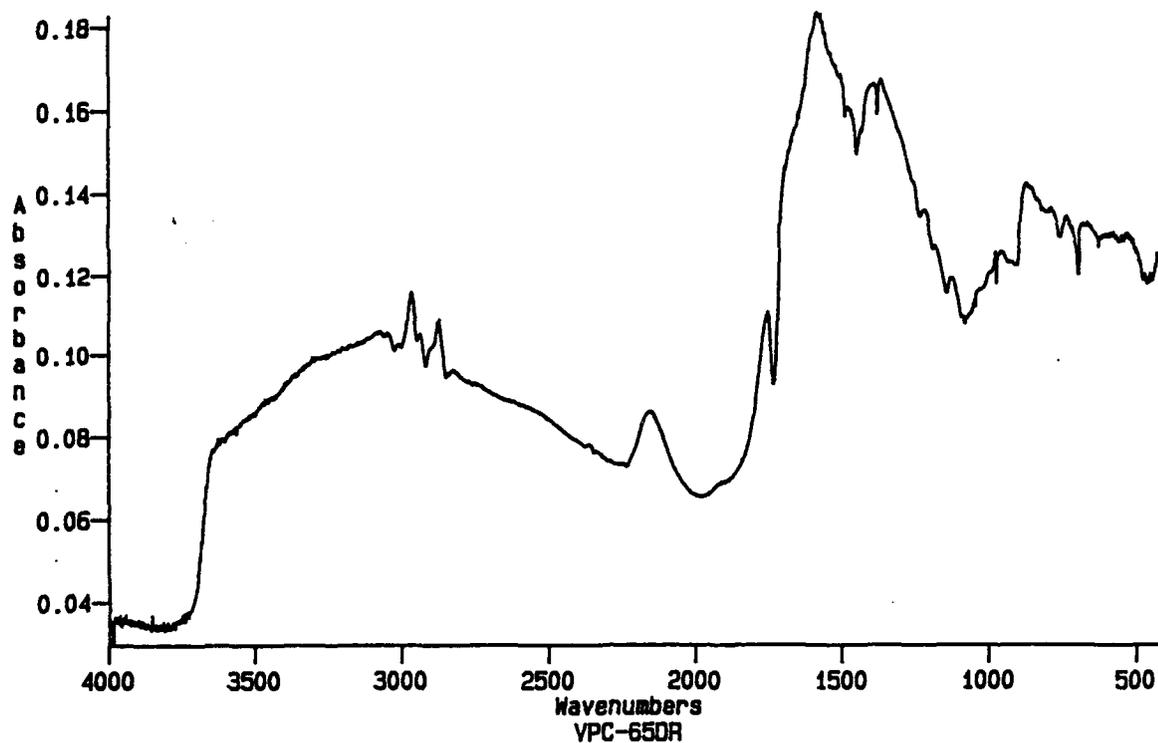


Figure 9. FT-IR (diffuse reflectance) spectrum of VPC-65 (~ 100% HF elimination by NaOH/TBAH PTC system).

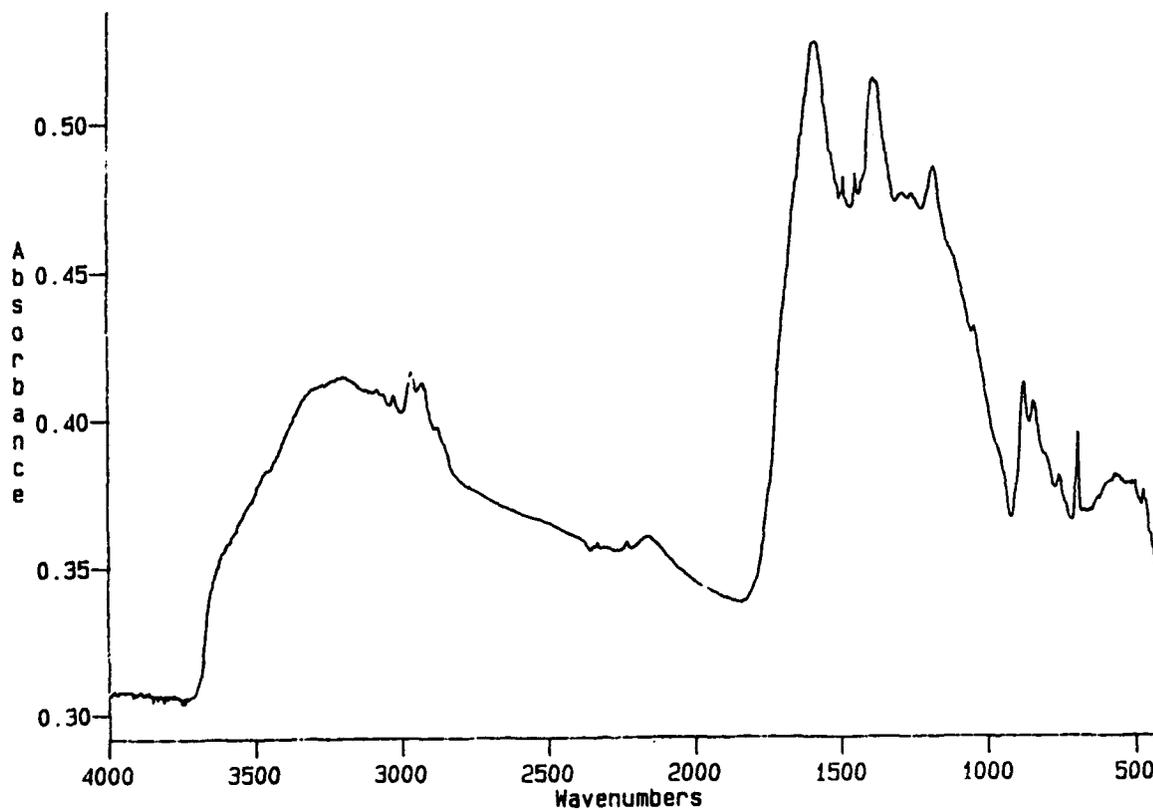


Figure 10. FT-IR (transmittance; KBr pellet) spectrum of VPC-56 (76% HF elimination by NaOH/TBAH PTC system).

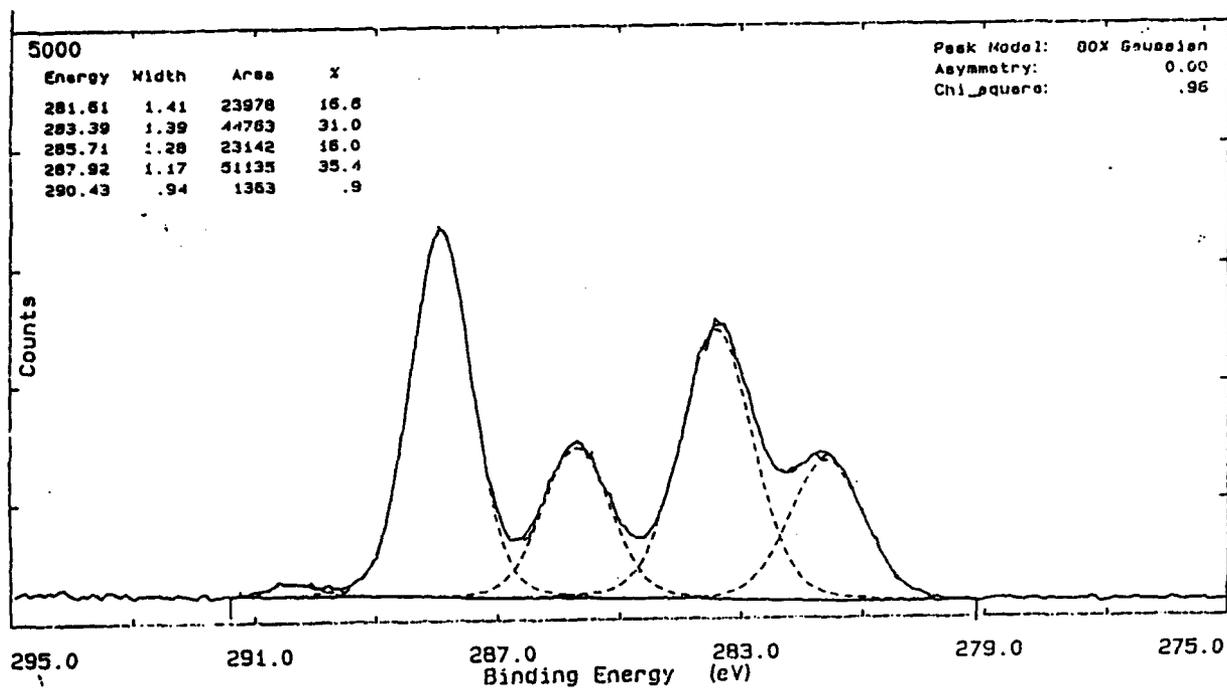


Figure 11. C1s XPS spectrum of VF₂/VF₃ copolymer.

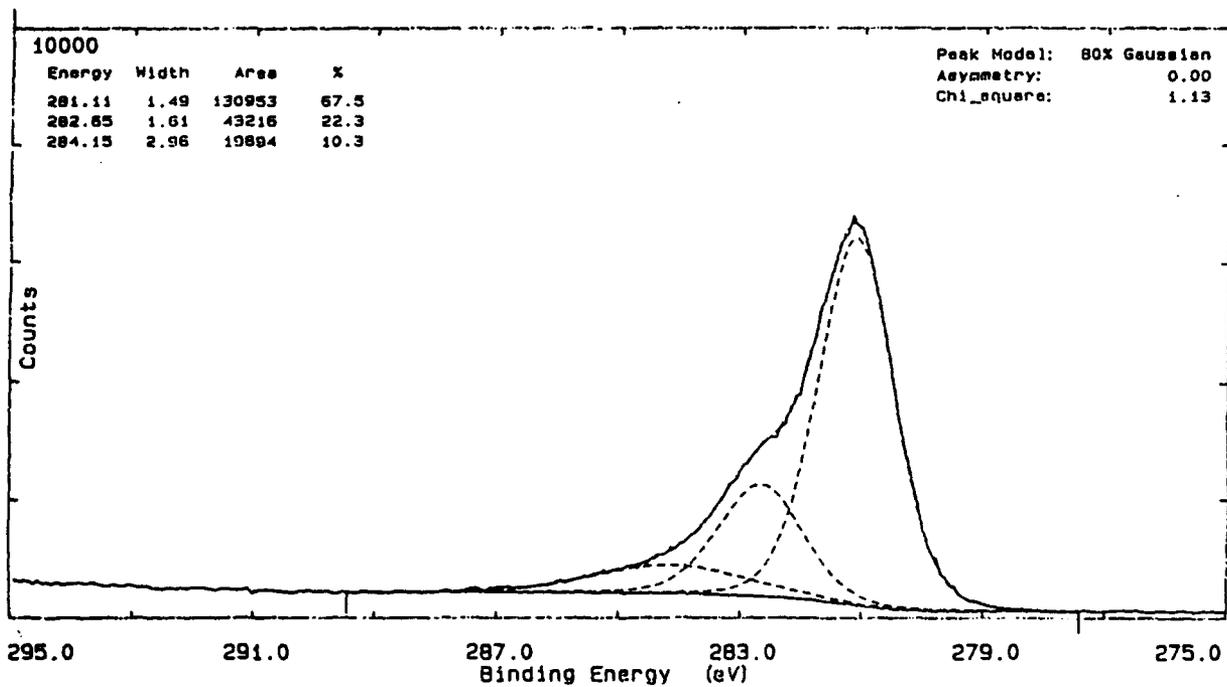


Figure 12. C1s XPS spectrum of VPC-50 (5% HF elimination by NaOH/TBAH PTC system).

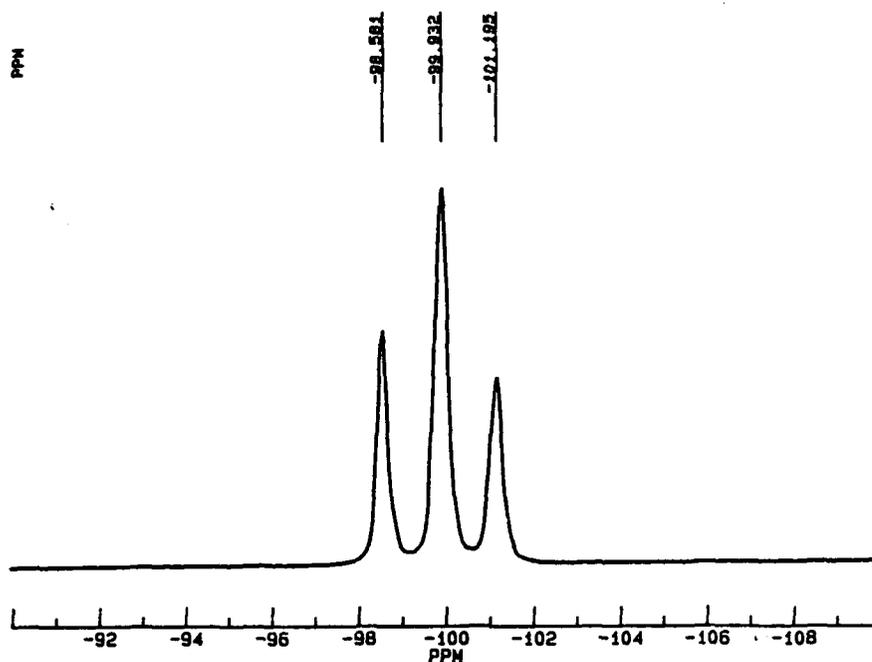


Figure 13. ^{19}F -NMR spectrum (282.36 MHz) of poly(1-chloro-1-fluoroethylene) in acetone (with D_2O insert as a lock solvent).

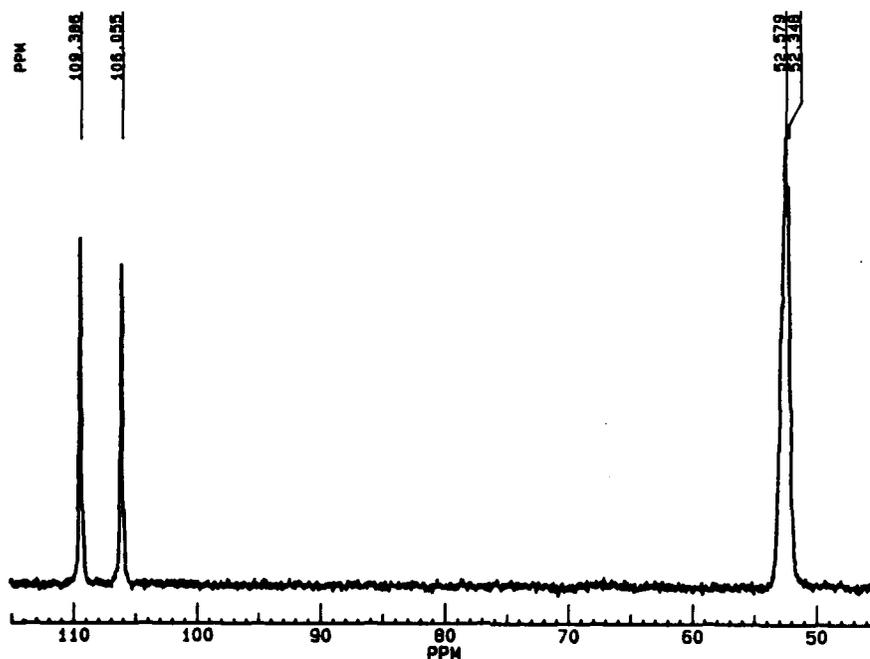


Figure 14. ^{13}C -NMR spectrum (75.47 MHz) of poly(1-chloro-1-fluoroethylene) in acetone (with D_2O insert as a lock solvent).

Chapter 2. Advanced Studies - Poly(vinylidene fluoride-co-trifluoroethylene) (PVDF/TrFE) and Poly(Chlorofluoroethylene) (PCFE) Precursors and Their Conversions

Abstract

Electron microscopic studies of the HF elimination products of VF₂/VF₃ copolymer exhibited extensive cracking of the film surfaces. The low conductivity of the HF eliminated doped samples have been attributed to this surface cracking. A slower drying process of the HF elimination products showed that the surface cracking occurs during the HF elimination of the copolymer with the presence of highly concentrated (5.0-8.3 M)NaOH and the phase transfer catalyst at all reaction temperatures. Consequently, milder reaction conditions were attempted for the HF elimination of the VF₂/VF₃ copolymer. The use of 18-crown-6 ether as a phase transfer catalyst with either KF or KOH as base in benzene at 80°C have been attempted for the HF elimination of the copolymer. The significantly lower concentration of the crown ether complexes of the bases (~10⁻³M)resulted in HF elimination yielding relatively smooth film surfaces.

Poly(chlorofluoroethylene) (PCFE) has been prepared in bulk with high molecular weight ($M_n \sim 10^5$)and good film forming properties. The PCFE underwent facile HCL elimination to produce a black material with 18-crown-6 ether in combination with KF or KOH at room temperature. We have found a highly sterically hindered non-nucleophilic phenolic anion as a base for the HCL elimination of PCFE in a homogeneous reaction medium. The hindered phenolic anion has been prepared by the reaction of 2,6-di-*t*-butyl-4-methylphenol and *n*-butyl lithium in THF. FT-IR spectral analyses of the HCL elimination products of PCFE by these bases show a higher degree of conjugation in the resulting conjugated polymer than the one prepared from PVF₂. The UV-VIS spectral analyses of the material prepared from PCFE and the phenolic anion exhibit a λ_{max} of 504 nm compared to a value of 364 nm reported for the conjugated polymer prepared from PVF₂. The VF₂/VF₃ copolymer undergoes slower HF elimination than PCFE with this phenolic anion in THF at room temperature. The UV-VIS spectral analyses of the conjugated polymer prepared from VF₂/VF₃ copolymer exhibit only shoulders at low wavelength, probably due to a lower degree of conjugation.

Introduction

We have previously reported the HF elimination reactions of VF₂/VF₃ copolymer. Our preliminary measurements of the doped samples indicated relatively low conductivities. Electron microscopic studies of the HF eliminated samples showed cracking of the film surfaces. This cracking can adversely affect the conductivity measurements and milder reaction conditions were attempted to reduce these effects. It has been reported that 18-crown-6 ether in benzene can be used as a phase transfer catalyst with either KOH or KF/CaO as bases for the dehydrohalogenation of poly(vinylidene chloride).¹ The use of CaO with KF neutralizes the evolved HCl. The concentration of the reactive bases in the crown ether of a 0.1M solution in benzene is of the order of 10⁻³M. The use of the crown ether complexes for the HF elimination of PVF₂ was found to be ineffective.² However, the facile dehydrohalogenation of the VF₂/VF₃ copolymer and the poly(chlorofluoroethylene) (PCFE) when compared with PVF₂ showed that this crown ether system may be an efficient elimination catalyst. Here, we report the dehydrohalogenation results of PCFE and VF₂/VF₃ copolymer with this crown ether system. In addition the HF elimination reactions of the VF₂/VF₃ copolymer has been attempted at room temperature to avoid the cracking of the film surfaces. Iodine and bromine doping experiments were carried out on the HF elimination products of VF₂/VF₃ copolymer and the results are presented. It has been reported that a hindered phenolic anion can be used for the deprotonation of α -methylene ketones.³ Due to the solubility of this anion in THF and ether, we have exploited this anion for the dehydrohalogenation of PCFE and VF₂/VF₃ copolymer. The progress of this dehydrohalogenation reaction has been monitored by UV-VIS spectroscopy.

Results and Discussion

Dehydrofluorination of VF₂/VF₃ Copolymer

Dehydrofluorination at room temperature shows the copolymer to undergo a slow color change compared to the high temperature reactions in which a rapid color change was observed with the NaOH/TBAH phase transfer catalyst system. The reactions with 18-crown-6 ether and KOH or KF/CaO systems at 80°C also undergo a slow color change of the films. However, the final color of the films is darker than when treated with NaOH/TBAH at room temperature. Due to a low extent of HF elimination with the crown ether system and the NaOH/TBAH system at room temperature, thin films were used under these conditions. The dehydrofluorination results of VF₂/VF₃ copolymer are presented in Table 1 under various conditions. For comparison, some previous results are also included in the Table.

The reaction VPC-136 in Table 1 with no added DMSO shows a 5% HF elimination compared to a complete reaction with added DMSO under similar conditions (VPC-111). This explains the importance of the mixing of both organic and aqueous layers for the reaction with NaOH/TBAH system. The difference in the extent of HF elimination in VPC-62, VPC-111 and VPC-134 are clearly due to the extent of mixing of the two layers under the stirring condition for the reaction. The HF eliminated sample in VPC-111 was dried slowly in air and then under vacuum. The sample VPC-134 was critical point dried by replacing the ethanol soaked film in liquid CO₂. Other films were dried directly under vacuum. In all cases the film surfaces were cracked due to the strong alkaline concentrations and high temperature for the reaction. Consequently, the reactions were carried out with the NaOH/TBAH system at room temperature using thin films. Due to a lower extent of reaction, the HF eliminated films at room temperature appeared smoother. The use of 18-crown-6 ether in combination with KOH or KF/CaO in benzene at 80°C for reaction of the copolymer also exhibits slow HF elimination. The electron micrographs of the films treated with these system show smooth surfaces and the films are more colored than the ones treated with the NaOH/TBAH system at room temperature. The use of the hindered phenolic anion in THF for the HCl elimination of poly(chlorofluoroethylene) (PCFE)

at room temperature was found to be very successful as will be described later. The use of this anion for the VF₂/VF₃ copolymer at room temperature in THF in a homogeneous reaction medium resulted in slower HF elimination. We will attempt this reaction at room temperature in ether in which the copolymer is not soluble so that HF eliminations can be carried out on the copolymer film. The use of a lower temperature and quantitative amount of anion may produce high quality HF eliminated films compared to the use of higher temperatures and excess reagents in the case of NaOH/TBAH and 18-crown-6 ether catalytic systems.

Doping of HF eliminated VF₂/VF₃ films

Our initial doping experiment with iodine at room temperature resulted in low doping levels. The presence of an electron withdrawing fluorine atom in the poly(fluoroacetylene) may lead to lower extents of oxidation by the weaker oxidizing iodine. Consequently, the doping of the HF eliminated films were carried out at higher temperatures and with a stronger oxidizing agent; bromine. The iodine doping results are summarized in Table 2. It appears that the increase in the doping temperature does not influence the doping level very much. For completeness of the doping, the experiments at higher temperatures were also carried out for a longer period of time. Hence, the doping at higher temperatures may occur more quickly, but to the same extent as the one for the lower temperatures. The thin films show a higher molar doping level than the thick films of comparable extent of HF elimination. This is due to the increased surface to volume ratio for the doping in the thin films. However, the films treated with aqueous NaOH/TBAH system at room temperature (sample VPC-138-2) show a 4.4% weight increase with iodine doping compared to a 13% weight increase with iodine doping for the films treated with the crown ether system in benzene (sample VPC-125-2). Both samples underwent the same extent of HF elimination (~7.5%) and the reason for this different doping behavior is not clear at this point.

The bromine doping results of the HF elimination products of VF₂/VF₃ copolymer are shown in Table 3. The doping level is seen to decrease with the increase of temperature. At 40°C, the bromine doping is more effective than the iodine doping of the samples of comparable HF elimination. The higher molar uptake may be due to the stronger oxidizing ability of bromine for the electron deficient poly(fluoroacetylene). We will optimize the doping temperature if elevated conductivities and reliable measurements are obtained for these films.

Dehydrohalogenation of Poly(chlorofluoroethylene).

The polymer is soluble in common organic solvents such as THF, acetone, CHCl₃, benzene, and even ether. It is insoluble in hydrocarbon solvents. The polymer undergoes facile HCl elimination with aqueous NaOH/TBAH system. Due to the ease of HCl elimination from PCFE when compared to HF elimination from PVF₂ or VF₂/VF₃ copolymer, the NaOH/TBAH system was not further investigated. Side reactions reported previously would be a major problem. The use of KF alone as a base in benzene (soluble polymer) results in slow color development over a week. The use of powdered CaO causes brown coloration of the sample overnight. The coloration occurs in the solid CaO surface in the bottom of the beaker and not in the solution. This may be due to the binding of the chlorines of the PCFE with the Ca atom of the CaO and subsequent HCl elimination. These observations suggest that at least two conjugated double bonds may be formed on the polymer chain rather than isolated double bonds due to the binding of two adjacent chlorines in the polymer chain with the calcium. The combined use of KF and CaO for the HCl elimination of PCFE in benzene results in immediate solution color change and the color is darker in the solid phase (CaO) than in solution. The use of 18-crown-6 ether with the KF/CaO system results in immediate coloration of the whole solution. The KF and CaO reaction mechanism does not involve any nucleophilic addition reactions with the double bonds of the resulting polyene to lower the conjugation length. This was believed to be a problem with the aqueous NaOH/TBAH system used for the HF elimination from VF₂/VF₃ copolymer in our early work. However, the removal of CaO from

To facilitate the isolation of the reaction products, the reaction was initially carried out at room temperature for 12 h and then heated at 40°C overnight to complete the reaction. With this system the polymer solution turns to light yellow to light brown and then purple color. The FT-IR spectra of the conjugated polymer prepared by different methods are presented in Figure 1. The spectra of the conjugated polymer prepared from PCFE by the reaction of 18-crown-6/KOH and phenolic anion are shown in Figure 1a and 1c respectively, while the spectrum of the sample prepared from PVF₂ is shown in Figure 1b. For comparison, the spectrum of PCFE is also presented in Figure 2. The absorption signals between 1800-1500 cm⁻¹ are due to the -CH=CF- stretching vibrations of the polyene with varying degrees of conjugation. It has been reported that the signals around 1700 cm⁻¹ are due to the stretching vibration of the -CF=CF- bonds arising from the presence of irregular head-to-head linkages in the polymer. In our early studies, we determined that the PCFE polymer contains no detectable amount of irregular linkages by NMR compared to 5% of these linkages in PVF₂. The results in Fig.1 indicates that this spectral assignment is unlikely due to the similarity of the spectra in this region. The dehydrohalogenated polymer prepared from PCFE and the hindered phenolic anion exhibits an IR absorption signal at 1512 cm⁻¹ (Fig. 1c) characteristic of the C=C stretching vibration of a conjugated polyene. This is the lowest IR absorption frequency reported to date for polyfluoroacetylene. With an increase in conjugation, the double bond character in a C=C bond decreases due to the resonance forms between the double bond and its neighboring single bond. This reduces the force constant (f) between the C=C bond which in turn reduces the IR absorption frequency (ν) of the conjugated double bond ($\nu \propto f^{1/2}$). Consequently, it appears that the use of our hindered phenolic anion as a base gives rise to higher degree of conjugation to the eliminated polymer. We attribute this to the high isoregic sequences in our precursor polymer and low amount of side reactions during elimination.

We have investigated the HCl elimination of PCFE with the hindered phenolic anion in THF at room temperature using UV-VIS spectroscopy. The results are presented in Figures 3a&b. The signals at 282 nm and 314 nm are due to the phenol and phenolic anion respectively. The broad signal with λ_{\max} at 504 nm is due to the conjugated polymer. The λ_{\max} value of 504 nm is the highest reported for an eliminated fluoropolymer to date. The HF elimination PVF₂ film exhibited a λ_{\max} of 364 nm due to a lower degree of conjugation.⁴ The decrease of the λ_{\max} with the extent of the reaction is probably due to side reactions. One of these side reactions may be a cyclization to form benzene rings which is facilitated by the mobility of the polymer chain in the solution. The UV-VIS spectra of the HCl elimination product of PCFE film in isooctane with 18-crown-6 ether/KOH system is shown in Figure 4. This film also shows a λ_{\max} of ~ 500 nm indicating a long conjugation length. We are going to use the phenolic anion as a base in isooctane for the film to achieve a more complete HCl elimination and higher degree of conjugation. The use of a film rather than a solution will freeze the mobility of the polymer chain and cyclization reactions should be minimized.

The UV-VIS spectra of HF eliminated product of VF₂/VF₃ copolymer in THF with this phenolic anion is shown in Figure 5. As expected, the HF elimination from this copolymer is slower than the HCl elimination from the PCFE. A lower absorption frequency, resulting in a shoulder as opposed to a well defined peak, is observed for this system may be due to a lower degree of conjugation in this polymer.

References

1. Yie-Shun, C.; Jagur-Grodzinski, J.; Vofsi, D. *J. Polym. Sci. Polym. Chem. Ed.*, 1982, 23, 1193.
2. Kise, H.; Ogata, H. *J. Polym. Sci. Polym. Chem. Ed.*, 1983, 21, 3443.
3. Corey, E. J.; Chen, R. H. K. *Tet. Lett.*, 1973, 39, 3817.
4. Urban, M. W.; Salazar, E. M. *Macromolecules*, 1988, 21, 372.

Table 1
Dehydrofluorination Results of VF₂/VF₃ (60/40) Copolymer

Sample	Catalyst	Rn Temp. (°C)	Rn Time (h)	% Conversion ^a
VPC-50	NaOH/TBAH ^{b,c}	70	8.0	5.0
VPC-56	NaOH/TBAH ^{b,d}	70	21.0	76.0
VPC-62	NaOH/TBAH ^{b,e}	70	9.0	10.0
VPC-111	NaOH/TBAH ^{b,e}	70	9.0	23.2
VPC-112	NaOH/TBAH ^{b,e}	70	9.0	107.0 ^f
VPC-116	18-crown-6/KF/CaO ^g	80	92.0	5.5
VPC-125-1	18-crown-6 /KOH ^h	80	5.0	5.0
VPC-125-2	"	80	48.0	7.8
VPC-131	"	80	144.0	9.3
VPC-134	NaOH/TBAH ^{b,e}	70	9.0	18.1
VPC-136	NaOH/TBAH ⁱ	70	15.0	5.0
VPC-138-1	NaOH/TBAH ^{b,e}	RT	24.0	2.6
VPC-138-2	NaOH/TBAH ^{b,e}	RT	48.0	7.6
VPC-138-3	NaOH/TBAH ^{b,e}	RT	144.0	13.9

^aBased on 28% weight loss corresponds to 100% elimination of HF.

^b8.3 M aq. NaOH/47 mM TBAH containing 20% (v/v) DMSO.

^cSeparate aqueous and organic layers

^dFor 12 h both aqueous and organic layers were non-mixed and for additional 9 h both layers were mixed.

^eAqueous and organic layers were mixed throughout the reaction.

^fConversions greater than 100% are due to corrosive action and a second HF elimination.

^g0.1M 18-crown-6 ether in benzene with excess solid KF and CaO.

^h0.1M 18-crown-6 ether in benzene with excess solid KOH.

ⁱ8.3 M aq. NaOH/47 mM TBAH containing no DMSO.

Table 2
Vapor Phase Iodine Doping Results of the HF Elimination Products of
VF2/VF3 (60/40) Copolymer.

Sample ^a	% HF elimination ^b	Doping Temp.(°C)	Doping Time (days)	% weight increase
VPC-50	5.0 (TK)	RT	6	2.6
		90	4	3.8
VPC-56	76.0(TK)	70	6	20.2
VPC-62	10.0 (TK)	RT	6	5.7
		70	6	6.8
		90	4	6.0
VPC-112	107.0 (TK)	RT	6	28.1
VPC-116	5.5 (TN)	90	4	14.7
VPC-125-1	5.0 (TN)	90	4	12.4
VPC-125-2	7.8 (TN)	90	4	13.0
VPC-131	9.3 (TN)	90	5	10.4
VPC-136	5.0 (TK)	90	5	3.9
VPC-138-1	5.0 (TN)	90	5	2.5
VPC-138-2	7.6 (TN)	90	5	4.4

^aRefer Table 1 for details of these samples.

^bTK = Thick film; TN = Thin film.

Table 3
Bromine Doping Results of the HF Elimination Products of VF2/VF3 (60/40)
Copolymer.

Sample ^a	% HF elimination ^b	Doping Temp.(°C)	Doping Time (days)	% weight increase
VPC-50	5.0 (TK)	40	5	3.1
VPC-56	76.0 (TK)	40	5	36.0
		90	6	17.5
VPC-62	10.0 (TK)	40	5	5.9
		90	6	4.9
VPC-29-3	46.0 (TK)	40	5	18.9
VPC-131	9.3 (TN)	90	6	3.9
VPC-138-2	7.6 (TN)	90	6	0.7

^aRefer Table 1 for details of the samples.

^bTK = Thick film; TN = Thin film.

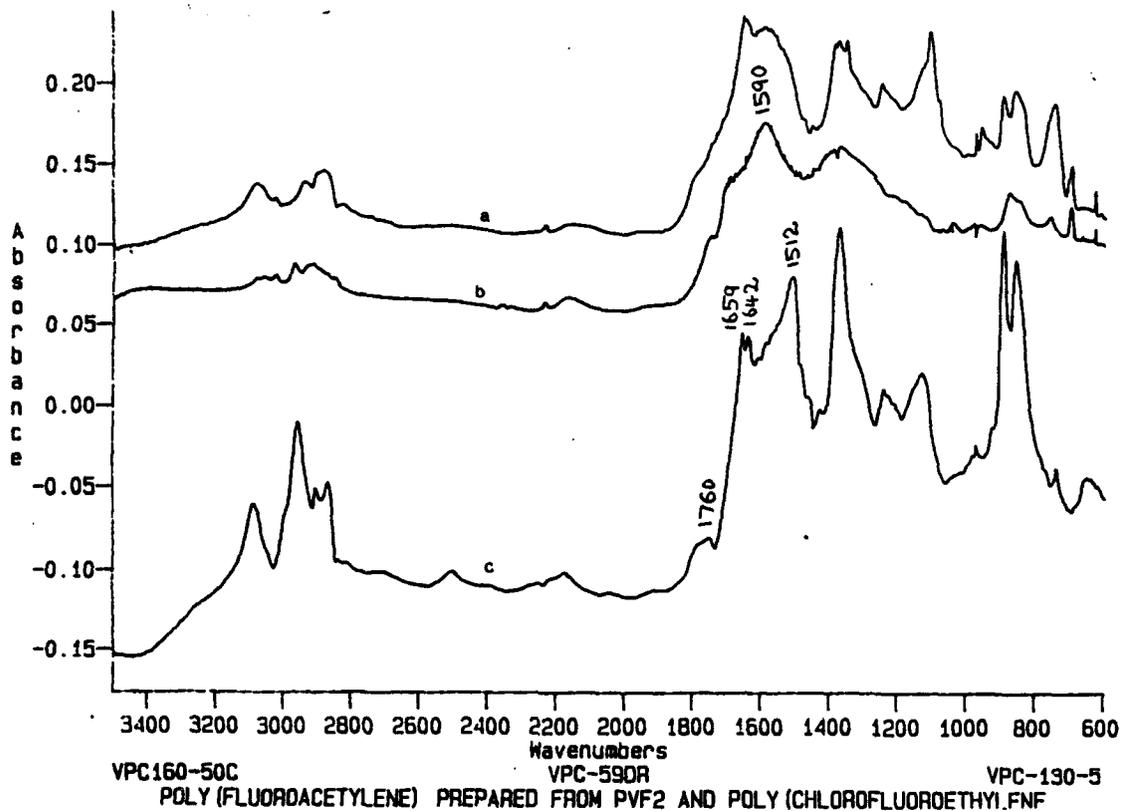


Figure 1. Diffuse reflectance FT-IR spectra of poly(fluoroacetylene) prepared from poly(vinylidene fluoride) (PVF₂) and poly(chlorofluoroethylene) (PCFE): (a) From PCFE by the reaction of 18crown-6 ether and KOH in benzene at room temperature; (b) From PVF₂ by the reaction of aq. NaOH/TBAH at 70°C; (c) From PCFE by the reaction of hindered phenolic anion in THF at room temperature.

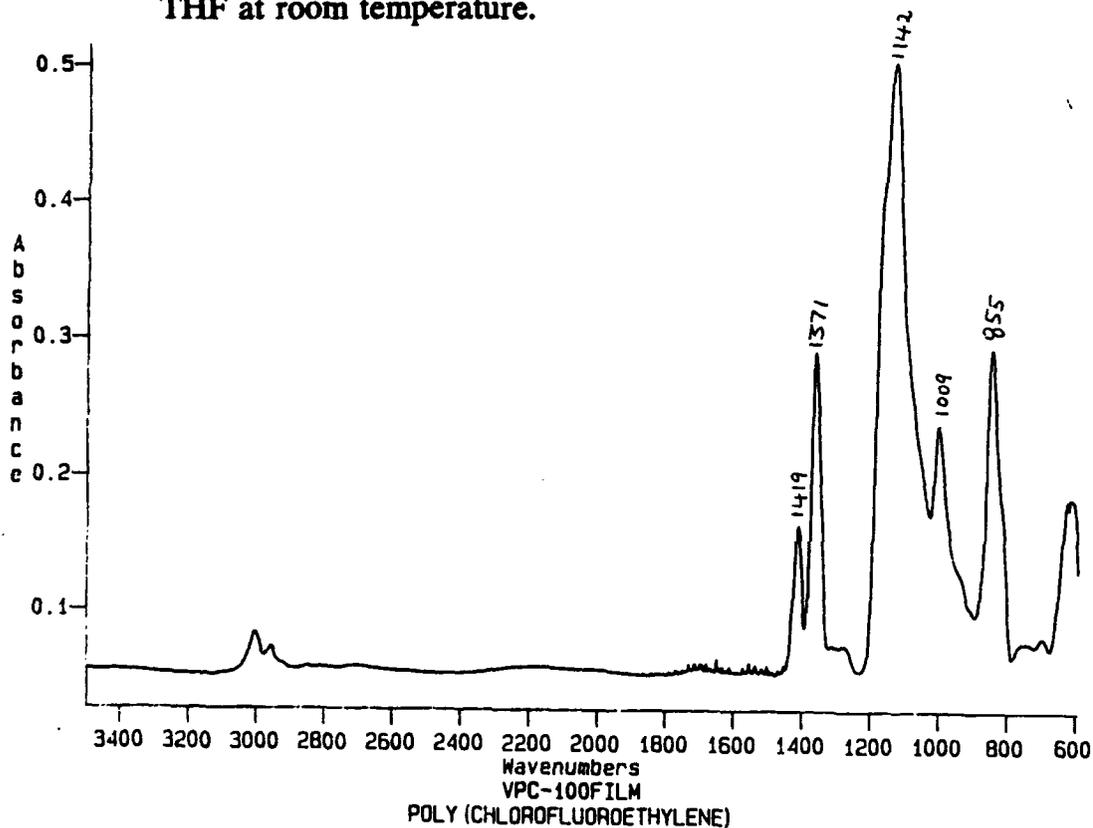


Figure 2. FT-IR transmission spectrum of poly(chlorofluoroethylene).

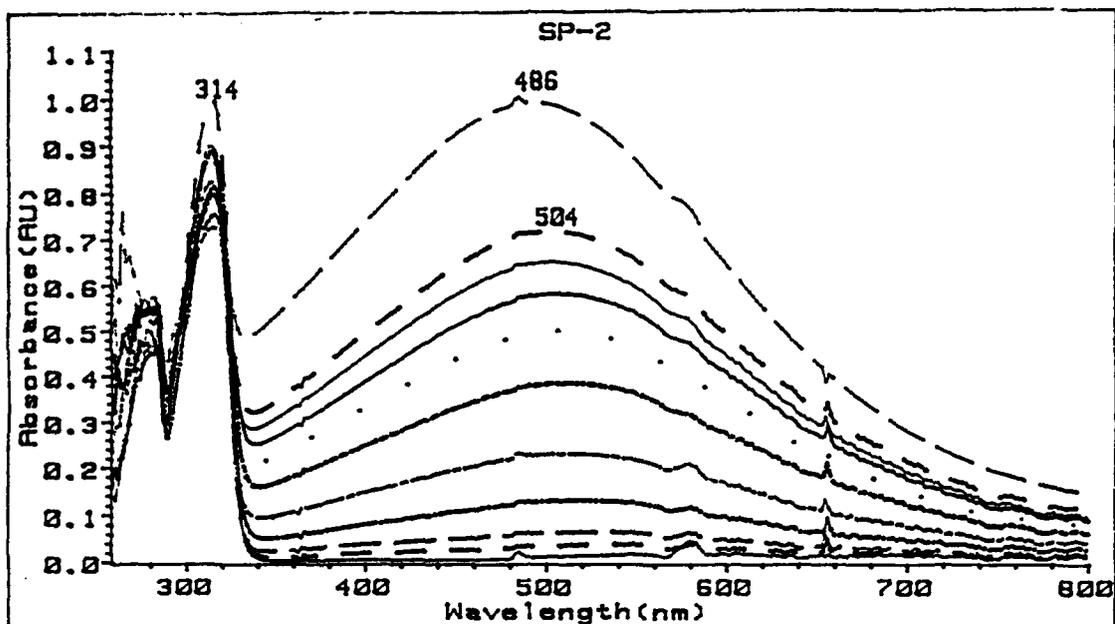


Figure 3a. UV-VIS spectra of poly(chlorofluoroethylene) treated with hindered phenolic anion in THF at room temperature at various time intervals (minutes): (bottom to top) 10, 20, 25, 35, 45, 60, 75, 90, 105, 120, and 210.

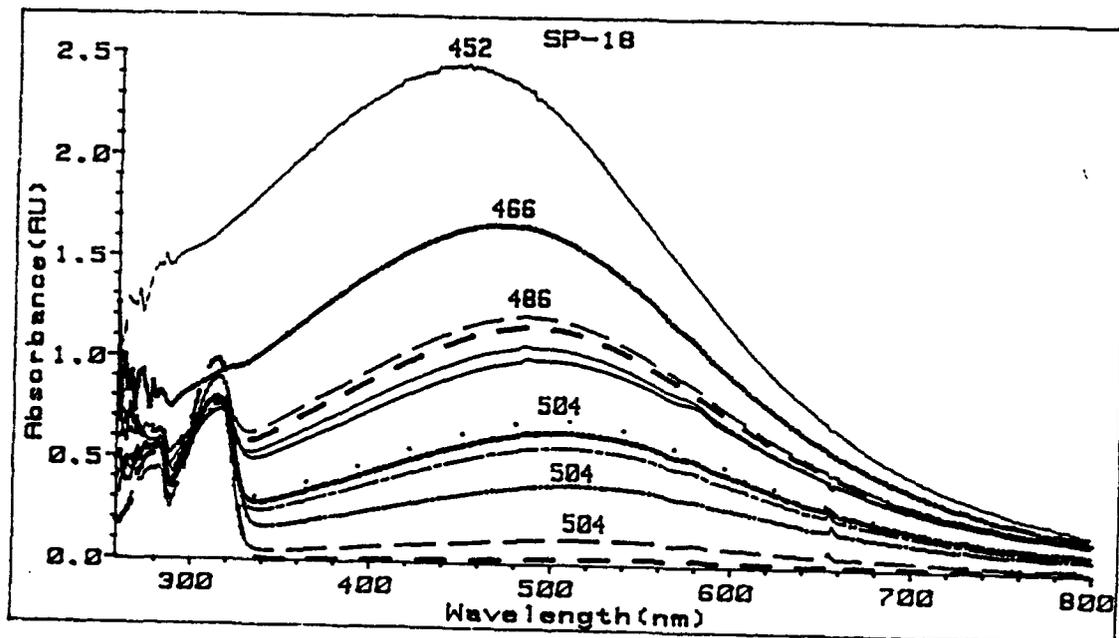


Figure 3b. UV-VIS spectra of poly(chlorofluoroethylene) treated with hindered phenolic anion in THF at room temperature at various time intervals (minutes): (bottom to top) 20, 35, 60, 90, 105, 120, 210, 240, 300, 330, 900, and 2340.

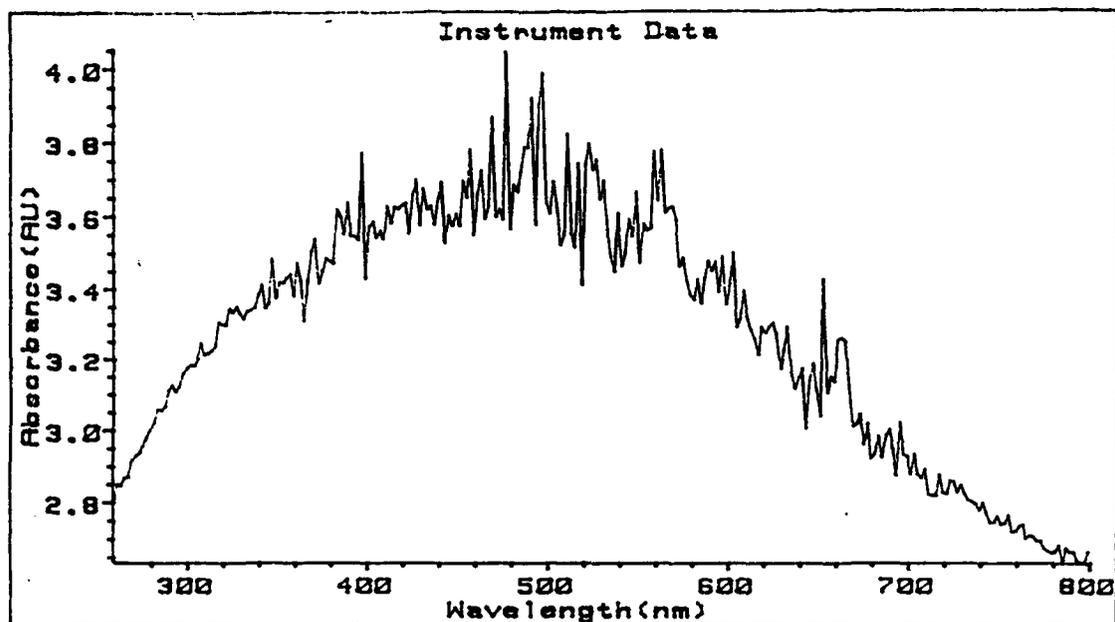


Figure 4. UV-VIS spectrum of poly(chlorofluoroethylene) treated with 18-crown-6 ether and KOH in isooctane.

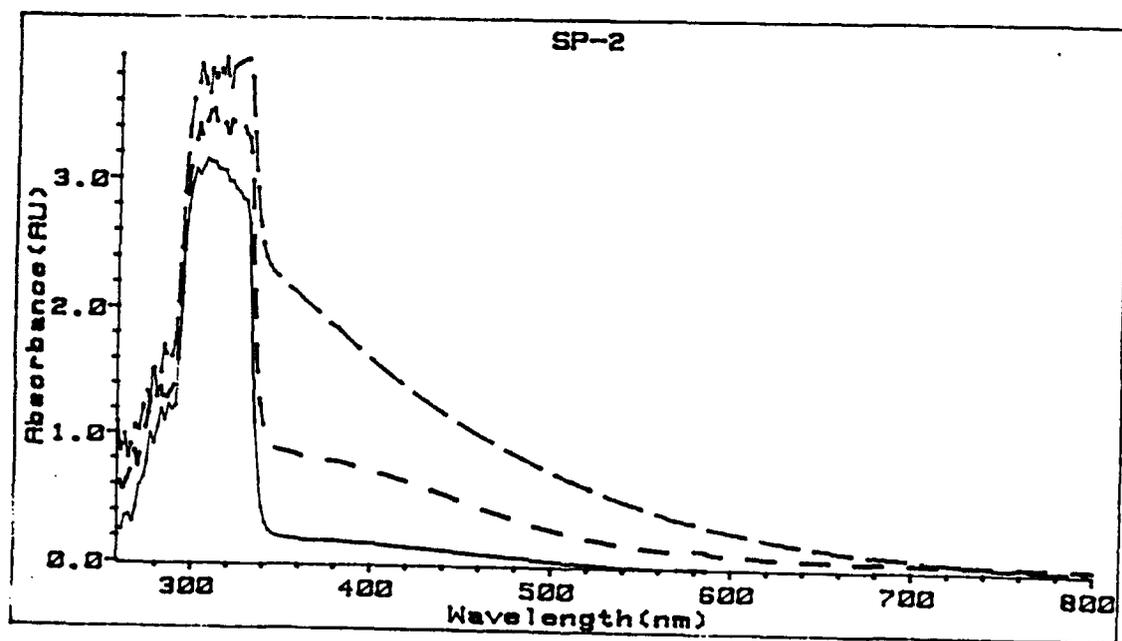


Figure 5. UV-VIS spectra of VF_2/VF_3 copolymer treated with hindered phenolic anion in THF at room temperature at various time intervals (hours): (bottom to top) 7, 17, and 40.

Chapter 3. Poly(Chlorofluoroethylene) (PCFE) Conversions and Doping Experiments

Abstract

Poly(chlorofluoroethylene) (PCFE) films have been reacted with phenolic anion to prepare poly(fluoroacetylene) in a mixture of isooctane and tetrahydrofuran (THF). Vapor phase iodine doping studies showed that the conductivity of the material increases from $10^{-8}\Omega^{-1}\text{cm}^{-1}$ to $10^{-5}\Omega^{-1}\text{cm}^{-1}$. However, the conductivity drops to the original value upon the removal of iodine. The results were compared with the vapor phase iodine doping of poly(3-decylthiophene)/poly(ethylene) blended fibers in which the conductivity increases by 6 orders of magnitude. The conductivity decreases only by two orders of magnitude upon the removal of iodine. The PCFE films have been treated with 1,8-diaza-bicyclo-7-undecene (DBU) in solution as well as in solid state. The UV-VIS analysis of the reaction system indicates similar behavior to the previously reported phenolic anion and 18-crown-6/KOH, but with a faster elimination reaction. The FT-IR analysis of HCL elimination products with DBU show similar spectral features to the phenolic anion reaction. The HCL elimination reaction with DBU for the films seem to be a better method to prepare poly(fluoroacetylene) (PFA) films due to the formation of no insoluble side reaction products. This seems to be a problem with the HCL elimination by the use of phenolic anion in which LiCl, a side reaction product, is insoluble in the reaction medium and created holes in the resulting PFA films.

In general, PFA prepared by elimination of PCFE has been more fully structurally characterized than the PFA obtained from PVF_2 and VF_2/VF_3 copolymers. While the PFA prepared using the PCFE precursor is superior to that from the pure fluoropolymers, it still contains a number of defects. The difficulties encountered in removing these defects suggests a new direction should be pursued for the synthesis of dipole containing conjugated polymers.

Introduction

It has been reported that the conductivity of poly(fluoroacetylene) (PFA) prepared from poly(vinylidene fluoride) increases to $10^{-3} \Omega^{-1}\text{cm}^{-1}$ upon doping with iodine.¹ The conductivity measurements were made in an iodine chamber and the excess iodine was not removed. Our initial attempts to prepare PFA showed no improvement in conductivity for approximately 5 HCl elimination products of PCFE upon doping with iodine and removal of excess iodine. It is well known that the conductivity of poly(acetylene) increases up to 12 orders of magnitude on doping and only decreases slightly upon the removal of the excess iodine. Therefore we have attempted to study the in situ vapor phase iodine doping of the HCl elimination products of PCFE as a function of time and also measured the conductivity with the removal of excess dopant. To gain experience in these conductivity measurements, we also studied the vapor phase iodine doping of poly(3-decylthiophene)/poly(ethylene) blended fibers which had a higher conductivity than the HCl elimination product of PCFE. The polythiophene blends were selected in our study due to their air stability. Our previous studies showed oxygen impurities in the HCl elimination product of PCFE. Attempts were made to eliminate the oxygen impurities. Here we also report the HCl elimination of PCFE in solution as well as in solid state by the use of a new base, 1,8-diaza-bicyclo-7-undecene (DBU).

Results and Discussion

The vapor phase iodine doping results of the the HCl eliminated PCFE film by the use of phenolic anion is shown in Figure 1. The conductivity of the material increases from $10^{-8} \Omega^{-1}\text{cm}^{-1}$ to $10^{-5} \Omega^{-1}\text{cm}^{-1}$. However, the conductivity drops to the original value upon the removal of iodine. (If further interest is shown in these materials by the physics collaboration, measurements will require experiments in ampules of iodine). The results were compared with the vapor phase iodine doping of poly(3-decylthiophene)/poly(ethylene) blended fibers (Figure 2) in which the the

conductivity increases by 6 orders of magnitude. The conductivity decreases only by two orders of magnitude upon the removal of iodine. The PCFE films for these conductivity measurements were prepared by the reaction of PCFE films supported on glass slides in isooctane containing 30% THF. During the reaction of these films with phenolic anion, LiCl is a side product which is insoluble in the reaction medium and precipitates out of the solution. In addition, it creates small holes in the HCl eliminated films shown by electron microscopy. LiCl is soluble in diglyme and therefore we are planning to carry out the phenolic anion reaction in a mixture of isooctane and diglyme. We have previously shown, by elemental analysis, that the reaction of the PCFE film in a mixture of isooctane and THF with phenolic anion results in selective and complete elimination of HCl. At the same time, oxygen impurities are incorporated.

ESCA analysis of an HCl eliminated film (utilizing phenolic anion) is shown in Table 1. It is clear there is a reduction in the expected fluorine content at the surface of the eliminated product. For comparison, the surface atomic compositions of our precursor poly(chlorofluoroethylene), poly(vinylidene fluoride) (PVF₂) and a copolymer of VF₂ and VF₃ (VF₂:VF₃=60:40) are also included in Table 1. It is clear from Table 1 that the ESCA determined fluorine contents in the virgin polymers are within experimental error. It should be noted that the bulk elemental analysis of the HCl eliminated PCFE show a 37-40% fluorine (Table 2). The ESCA analysis of atomic compositions of the HCl eliminated PCFE film is confined to the surface (10-100 Å²) whereas the elemental analysis reflect the bulk composition. In both solution and film reactions, quantitative amounts of bases were used for the elimination of HCl. The lower amounts of fluorine at the surface as determined by ESCA may be due to the loss of both HF and HCl at the polymer/reactant interface. This may be due to the availability of surface fluorine which are eliminated more easily than chlorine in the film bulk. This was also observed in the dehydrofluorination of the VF₂/VF₃ copolymer in which a drastic loss of surface fluorine occurred. To check this

hypothesis, solution reactions were carried out with excess amount of base and the results will be discussed later.

Dehydrohalogenation Reaction of PCFE with 1,8-diaza-bicyclo (5,4,0)-7-undecene (DBU)

DBU was selected as a suitable base for the HCl elimination of PCFE due to the absence of any oxygen functionality in the molecule. The other bases used for the HCl elimination reactions contained oxygen functionality. The oxygen defect found in the ESCA of HCl eliminated PCFE films may be due to trapped bases in the film, attachment of the bases to the backbone of the polymer film, or oxidation of the sample itself. The use of DBU eliminates the first two possibilities and therefore was selected for the HCl elimination reactions. In addition, the side reaction product DBU·HCl is soluble in THF thus eliminating the problem of hole formation in the film reaction which resulted with the phenolic anion. It was found that no solid colored products were brought into the solution during the reaction of PCFE film with DBU in the THF/isooctane mixture.

The UV-VIS spectra of the HCl elimination products of PCFE in THF with DBU is similar to the spectra of the reaction with the other bases. The variation of absorbance at λ_{\max} with time is shown in Figure 3. For comparison, the data for phenolic anion, 18-crown-6/KOH, and t-BuOK are also presented in Figure 3. It should be noted that the PCFE and the bases were 0.1 mM concentration for all the reactions except for the phenolic anion reaction wherein both were doubled. The results indicate that the HCl elimination is faster with DBU than with either phenolic anion or 18-crown-6 ether/KOH systems. The initial HCl elimination with t-BuOK seemed to be faster than with any other bases. However, t-BuOK resulted in the elimination of both HCl and HF shown by FT-IR analysis and thus ruined (over dehydrochlorinated) the PCFE to PFA conversion.

**FT-IR analysis of the HCl elimination product of PCFE
with DBU in solution**

The reaction was carried out in benzene in a 1:1 molar ratio of PCFE and DBU at room temperature overnight. The reaction seemed to be complete as all of the polymer precipitated. The reaction was carried out in benzene to avoid any oxygenated solvents. The product was Soxhlet extracted with benzene for 24 h to remove the side reaction product DBU·HCl. The FT-IR spectral analysis of the product showed DBU moiety in the sample. The sample was further Soxhlet extracted with THF for two days to remove any DBU moiety. The FT-IR spectrum shown in Figure 4 is similar to the spectra we reported previously with the other bases. This clearly shows the need for THF to remove any side reaction products from the reaction medium. Subsequently the reaction was carried out in THF in a 1:1 and 1:3 molar ratio of PCFE and DBU to examine whether the second HX elimination occurs to form a triple bond in the polymer chain. Such second HX elimination can explain the drastic loss of fluorine in the HF eliminated VF₂/VF₃ copolymer film as we previously discussed in the ESCA analysis. The reaction was allowed to proceed for 30 h and the filtered product was Soxhlet extracted for overnight. Gravimetric analysis showed that the reaction of PCFE and DBU in a 1:3 molar ratio resulted in quantitative HCl elimination. It should be noted that the gravimetric response of a possible second HX elimination (HF) to form triple bonds in the presence of the excess DBU may be counter balanced by a possible reaction of DBU with the resulting polyene chain. The elemental analysis results for the 1:1 and 1:3 molar ratio (PCFE:DBU) reactions are shown in Table 2. The presence of nitrogen in the samples are due to DBU moiety still trapped in the sample or attached to the polyene backbone representing a minor defect structure. Elimination of an HF from the polyene chain to form a C≡C triple bond or benzene ring will result in an increase in the carbon content and decrease in the fluorine content compared to the elimination of only HCl to form poly(fluoroacetylene). The results in Table

2 indicate that the absence of HF elimination to form the undesired triple bonds and benzene ring formation. The molar ratio of C:F = 2:1 in Table 2 clearly indicates the presence of $(-\text{CH}=\text{CF}-)_n$ repeat unit corresponding to poly(fluoroacetylene) in the dehydrohalogenated PCFE. The FT-IR spectra of the products obtained in the 1:1 and 1:3 molar ratio are presented in Figures 5 and 6 respectively. There is no major differences over the full range of $4000-400\text{ cm}^{-1}$ in both spectra. The $2200-2100\text{ cm}^{-1}$ region is characteristic of the carbon-carbon triple bond stretching vibration in a polyene and shows a minor difference in the two samples. The similarities of the IR spectra under reaction conditions suggest the elimination of predominantly one HX molecule from the polymer chain even in the presence of an excessive amount of base.

The formation of $\text{C}\equiv\text{C}$ triple bonds or benzene rings on the polyene chain require higher energy to eliminate HF and form these defect structures. The use of a lower temperature for the HCl elimination reaction will prevent the above mentioned unfavorable and undesirable side reactions. The DBU was able to eliminate HCl from PCFE in THF at $0-5^\circ\text{C}$ and the FT-IR spectrum of the product shown in Figure 7 was similar to the reactions carried out at room temperature (Figures 5 and 6). This experiment also supports the absence of the elimination of HF to form the undesired side reactions. We have been concerned about the ambient oxidation of the dehydrohalogenated PCFE to form defect structures during the reaction and handling procedures. To examine such possibility, the HCl elimination reaction with DBU in THF was carried out by bubbling oxygen into the solution for 5 minutes. The FT-IR spectrum of the product is shown in Figure 8. The spectrum is similar to the products obtained in the absence of oxygen (Figures 5, 6, and 7) except the line broadening of the signals indicating the absence of any oxygen functionalities in the polymer. We are awaiting an elemental analysis result to check any decrease in the total content of C, H, N, and F in the product compared to the reactions carried out in the absence of oxygen to indicate any increase in the oxygen content in the product.

HCl elimination reaction of PCFE film in isooctane/THF mixture with DBU

The reaction was carried out in isooctane containing 30% THF at room temperature for 48 h. The films were then rinsed with water, THF and finally with pentane to remove any unreacted DBU and side reaction products and dried under vacuum. The ESCA of the film supported on a glass slide is shown in Figure 9. The ESCA shows the presence of nitrogen, oxygen, and chlorine in addition to the expected carbon and fluorine. The nitrogen may be due to DBU not removed from the film or DBU reacted with the polyene. The presence of chlorine indicates an incomplete elimination of HCl from the PCFE film. The presence of oxygen suggests a major problem. This is complicated by the use of oxygenated solvents to rinse the HCl eliminated PCFE film. Without the use of these oxygenated solvents, the unreacted DBU and side products could not be removed. To check whether the oxygen impurities are due to the oxygenated solvents, a depth profile experiment was carried out in the ESCA. A lower angle probes less of the surface while a higher angle probes more deeply. We might expect more oxygen inside the bulk, if it is due to entrapped solvent impurities which are still not removed from the sample. The data in Table 3 indicate inconclusive results. A complete elimination of HCl from the PCFE film is necessary to obtain a better ESCA and meaningful atomic composition.

We have shown previously that the absence of $C\equiv C$ triple bond formation in the solution reactions by the combined use of elemental analyses and FT-IR spectroscopy. The $C\equiv C$ triple bond in a poly(fluoroacetylene) is symmetrically substituted and stretching vibration of such a bond will not result in any change in dipole moment. Consequently, the triple bond will be IR inactive and no signal is expected in the range of $2200-2100\text{ cm}^{-1}$. The minor signals in these range are therefore due to overtones of some vibrations appearing at lower frequencies. For example an IR absorption signal at 1075 cm^{-1} (ν) may have an overtone at 2150 cm^{-1} (2ν). However, these symmetrically substituted triple bonds are Raman active and expected to give strong signals in the range of

2200-2100 cm^{-1} . The Raman spectra of (a) PCFE, (b) partially HCl eliminated PCFE, and (c) completely HCl eliminated PCFE films are shown in Figure 10. The partially and completely HCl eliminated films show similar signals due to the poly(fluoroacetylene). No signal was found in the range of 2200-2100 cm^{-1} indicating the absence of $\text{C}\equiv\text{C}$ triple bonds in the polyene as defect structures.

Conclusions

PCFE film has been reacted with a new base, DBU, to obtain HCl eliminated films which have a superior surface morphology than the previous ones. FT-IR, elemental analysis and gravimetric analyses indicate that the use of excessive amount of DBU to eliminate HCl from the the PCFE essentially results in the loss of quantitative amount of HCl and no significant loss of HF from the polymer. These results coupled with the reaction carried out at 0-5°C indicate the absence of side reactions to form defect structures such as $\text{C}\equiv\text{C}$ triple bonds and benzene rings in our poly(fluoroacetylene). The total elemental analysis of the dehydrohalogenated PCFE accounted only about 90% indicating about 10% oxygen in the sample probably due to oxidation of the material. The ESCA analysis shows that no drastic loss of surface fluorine in the HCl eliminated film occurs. In addition, the ESCA analysis indicates the presence of oxygen impurities in the poly(fluoroacetylene). However, the dehydrohalogenation reactions carried out in the presence of oxygen and the subsequent FT-IR analysis of the product does not provide evidence for the oxidation of the polyene. The HCl eliminated PCFE films with DBU are going to be doped and will be available for microwave measurements if improvement in conductivities are achieved.

References

1. Kise, H.; Ogata, H. *J. Polym. Sci. Polym. Chem. Ed.*, 1983, 21, 3443.

Table 1: ESCA data for the HCl elimination product of PCFE film with phenolic anion, virgin PCFE, PVF₂, and VF₂/VF₃ (60/40) copolymer.

Sample	Atomic composition (%) ^a				
	C _{1s}	Cl _{2p}	F _{1s}	O _{1s}	Si _{2p}
PCFE-HCl	56.87(66.67) ^b	3.37(0)	8.40(33.33) ^b	21.05(0)	10.31(0)
PCFE	52.63(50.0)	20.89(25.0)	26.48(25.0)		
PVF ₂	50.09(50.0)	-	39.70(50.0)	10.22(0)	-
VF ₂ /VF ₃ copolymer	38.25(45.45)	-	61.0(54.55)	0.75(0)	-

^a Values within the brackets indicate the calculated values

^b Calculation based on (C₂FH)_n for poly(fluoroacetylene)

Table 2: Elemental Analyses Results of PCFE and Dehydrohalogenated PCFE.

Sample	Composition (%) (wt)							Total
	Carbon	Hydrogen	Nitrogen	Fluorine	Chlorine	Metals		
PCFE (Virgin Polymer)	30.51 (29.81)	2.57 (2.48)	-	23.63 (23.60)	44.23 (44.10)	-		100.94
PCFE-HCl/18C6/KOH (Solution Reaction)	46.02 (54.55) ^a (3.83) ^b	1.35 (2.27) ^a (1.35) ^b	-	37.01 (43.18) ^a (1.95) ^b	1.48 (0.0)	1.32(K)		87.18
PCFE-HCl/ArOLi (Solution Reaction)	50.36 (4.20) ^b	1.51 (1.51) ^b	-	40.01 (2.11) ^b	0.41	0.0(Li)		92.29
PCFE-HCl/DBU(1:1) (Solution Reaction)	54.28	2.85	0.93	n/a	n/a	-		n/a
PCFE-HCl/DBU(1:3) (Solution Reaction)	54.63 53.51	3.04 2.65	1.97 2.10	n/a 38.33	n/a 0.26	- -		n/a 96.57
PCFE-HCl/ArOLi (Film Reaction)	48.23 (4.02) ^b	2.03 (2.03) ^b	-	39.01 (2.05) ^b	0.12	0.09(Li)		89.48

^a Values within the brackets indicate the calculated values

^b Molar amount of carbon, hydrogen, and fluorine; C:F=2:1 (-CH=CF-)_n

Table 3: ESCA data for the HCl elimination product of PCFE film with DBU as a function of depth angle

Depth Angle	Atomic composition (%) ^a				
	C _{1s}	Cl _{2p}	F _{1s}	O _{1s}	N _{1s}
75	56.39(66.67) ^b	7.66(0)	21.44(33.33) ^b	12.14(0)	2.38(0)
45	57.17(66.67) ^b	9.96(0)	22.68(33.33) ^b	7.43(0)	2.76(0)
30	62.54(66.67) ^b	8.78(0)	14.04(33.33) ^b	10.36(0)	4.28(0)
15	55.32(66.67) ^b	9.58(0)	17.95(33.33) ^b	10.71(0)	6.44(0)

^a Values within the brackets indicate the calculated values

^b Calculation based on (C₂FH)_n for poly(fluoroacetylene)

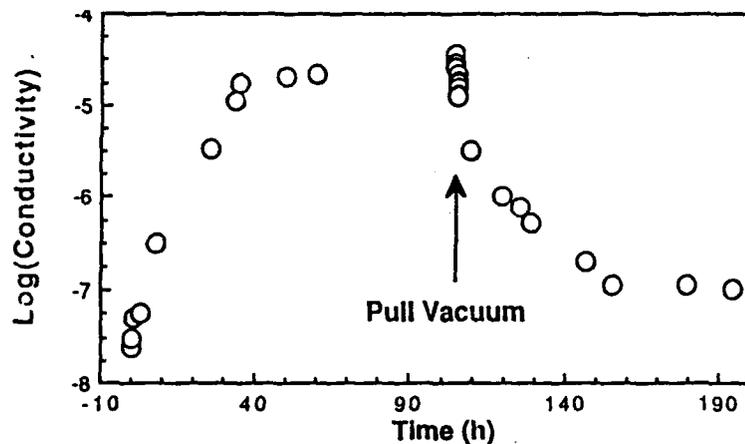


Figure 1. The vapor phase iodine doping results of the HCl eliminated PCFE film by the use of phenolic anion.

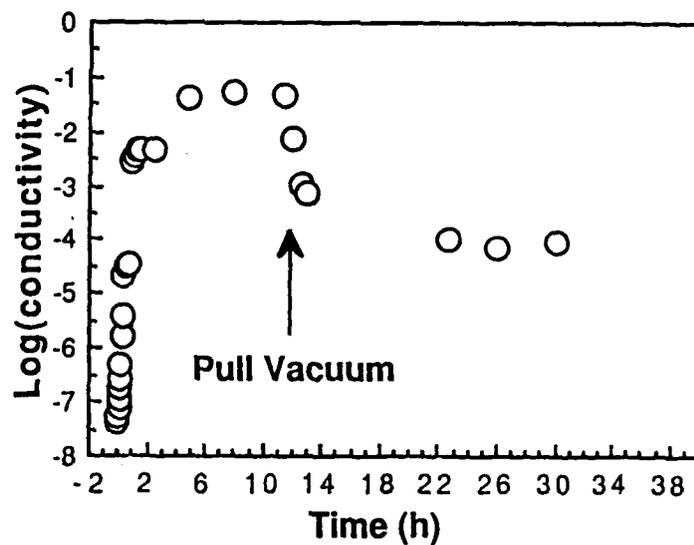


Figure 2. The vapor phase iodine doping of poly(3-decylthiophene)/poly(ethylene) blended fibers.

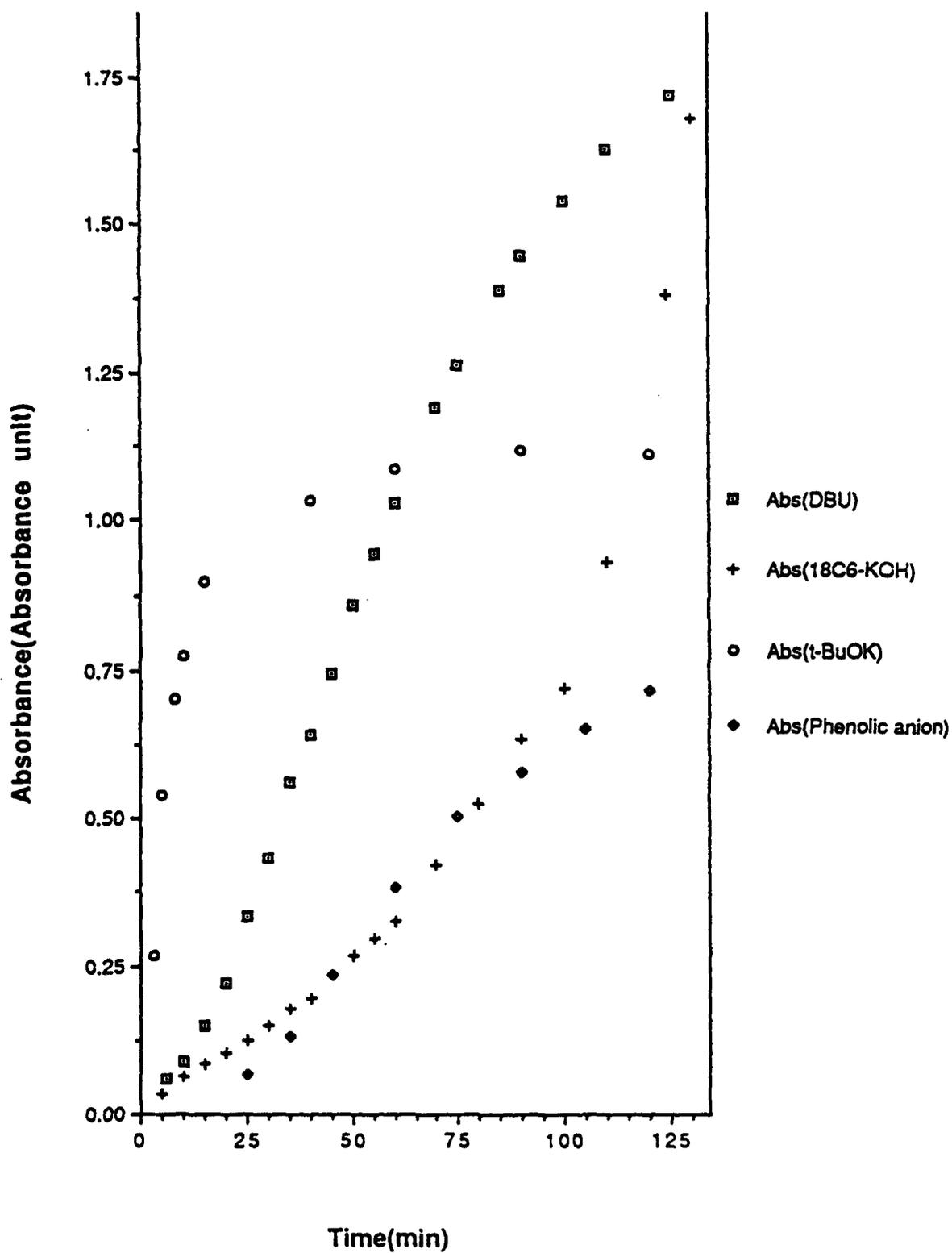


Figure 3. Uv-VIS analysis of PCFE treated with various bases in THF.

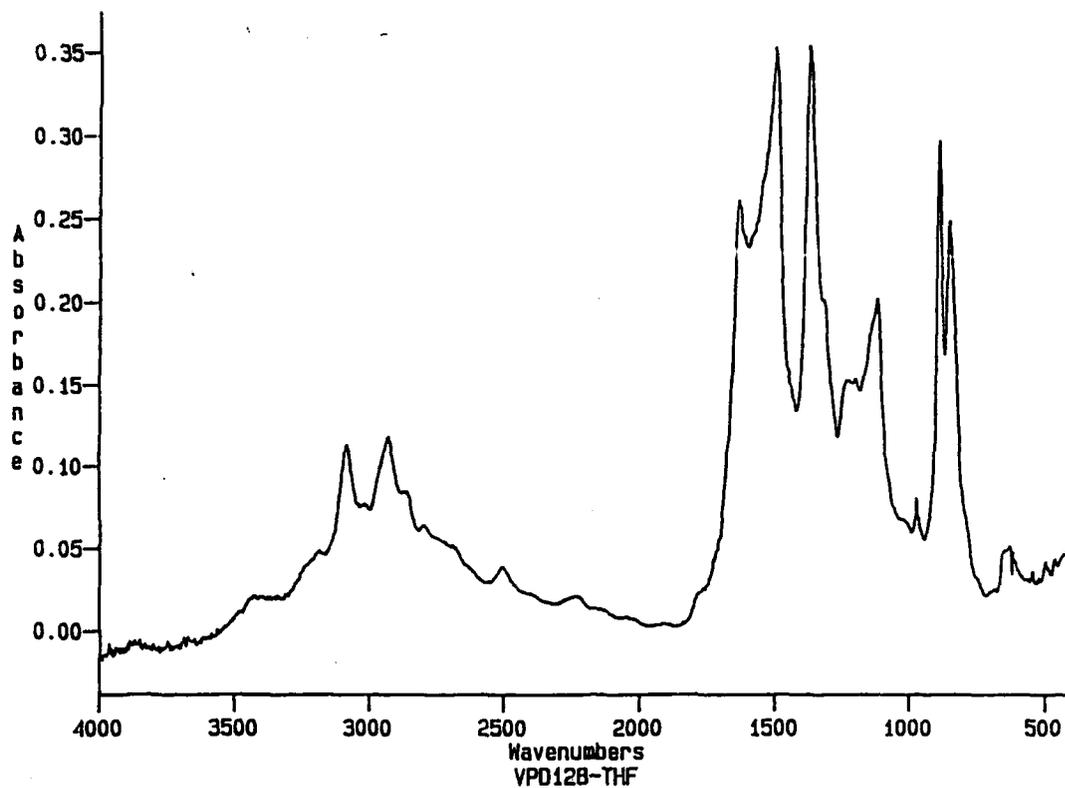


Figure 4. PCFE treated with DBU in Benzene at room temperature overnight.

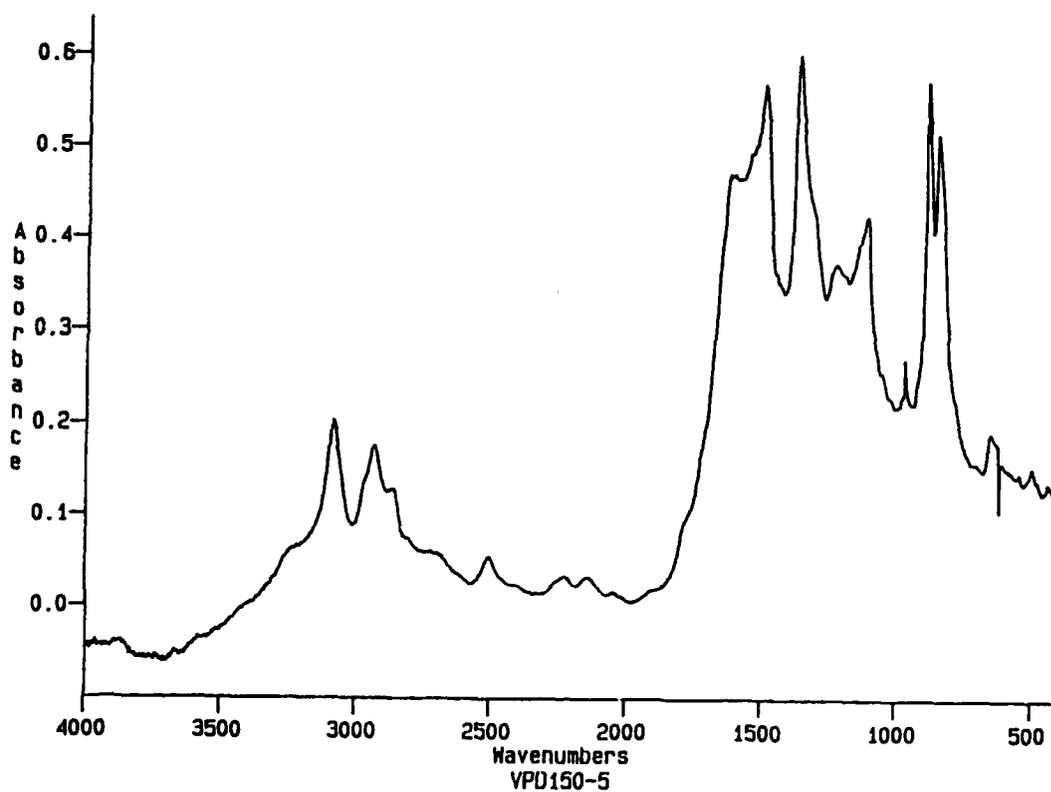


Figure 5. The FT-IR spectra of the products obtained in the 1:1 molar ratio.

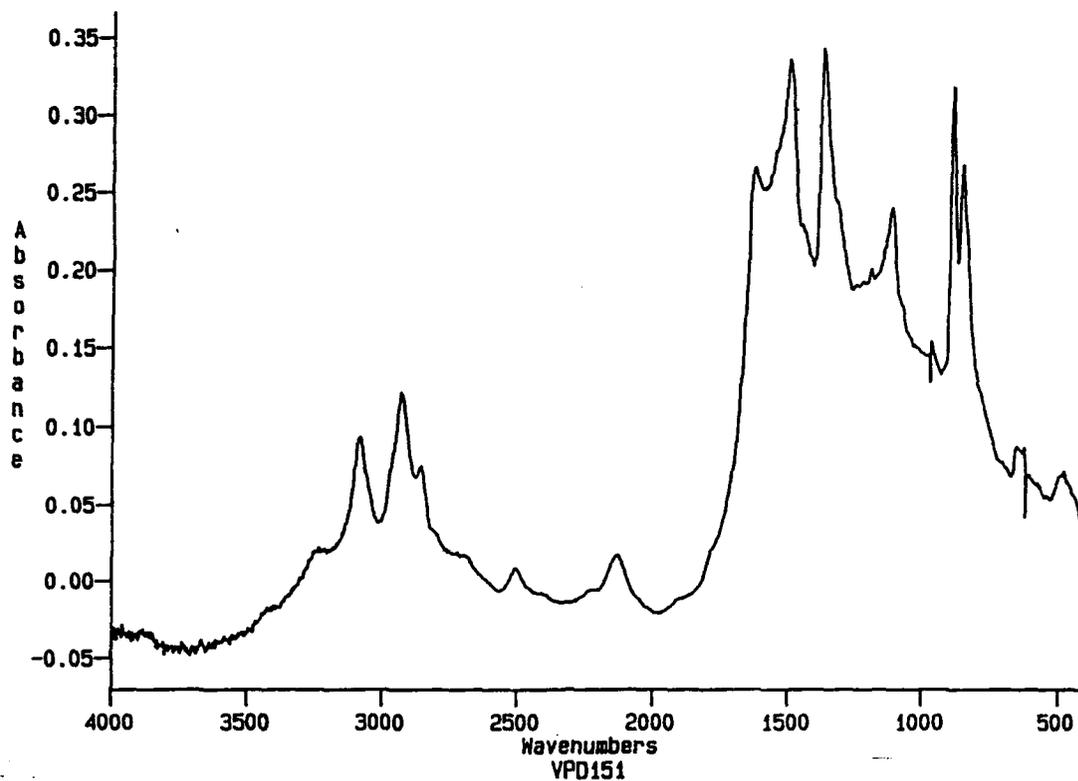


Figure 6. The FT-IR spectra of the products obtained in the 1:3 molar ratio.

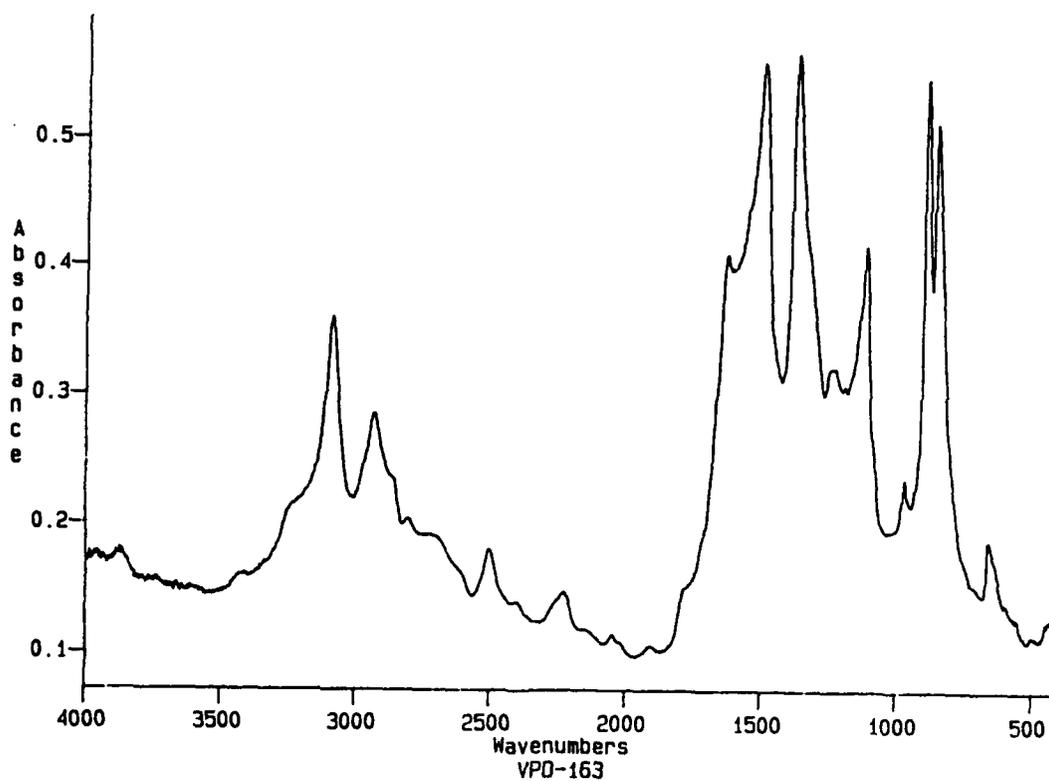


Figure 7. PCFE treated with DBU at $\sim 5^\circ\text{C}$ in THF.

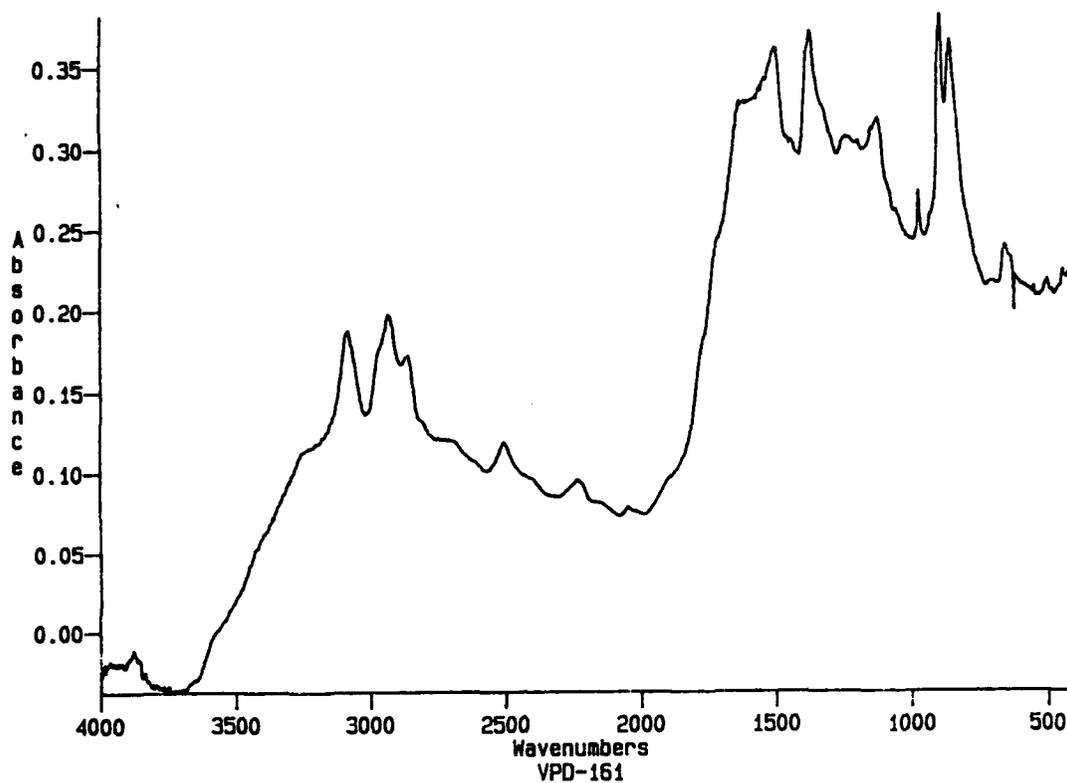


Figure 8. PCFE treated with DBU in THF with bubbled oxygen.

ESCA SURVEY 10/9/90 ANGLE= 75 deg ACQ TIME=18.34 min
 FILE: VPD1532 PCFE TREATED WITH DBU IN ISOCTANE CONTAINING 30% THF
 SCALE FACTOR= 1.151 k c/s, OFFSET= 0.029 k c/s PASS ENERGY= 89.450 eV NI 400 W

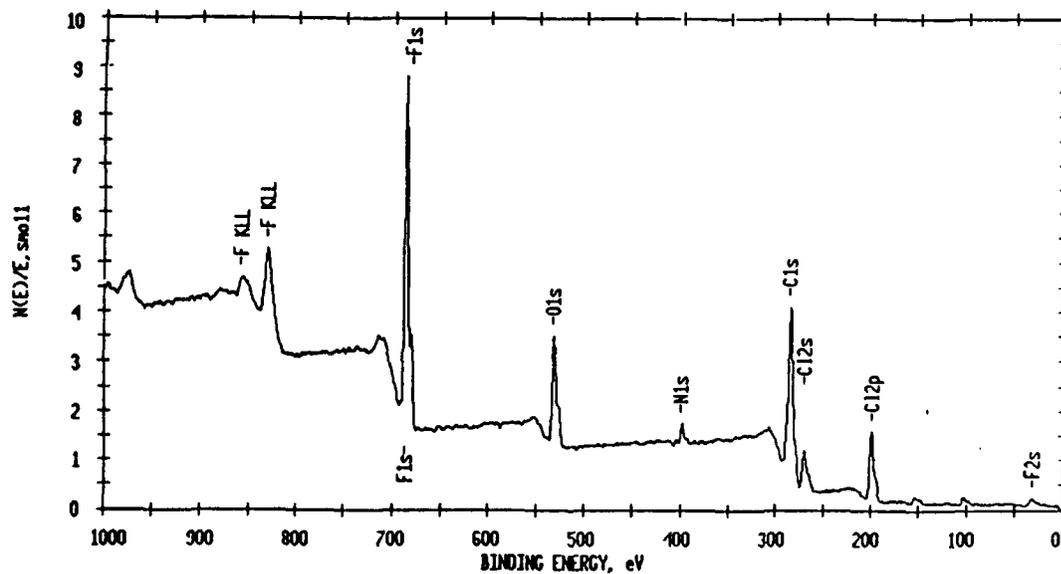


Figure 9. PCFE treated with DBU in Isooctane containing 30% THF.

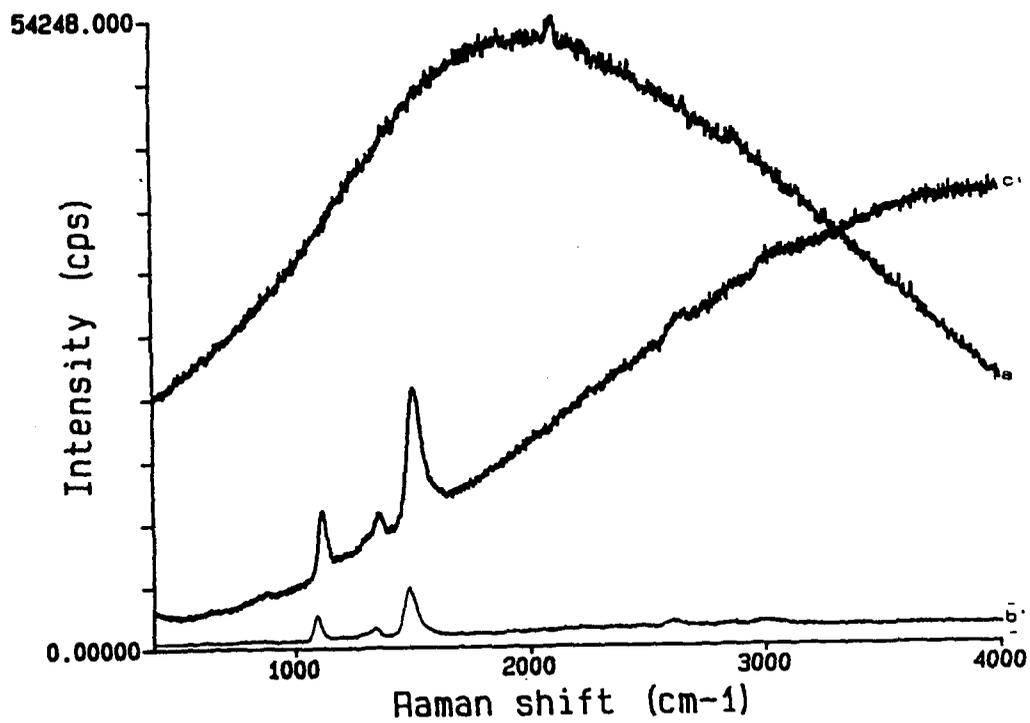


Figure 10. Raman Spectra of (a) PCFE, (b) partially HCl eliminated PCFE, and (c) completely HCl eliminated PCFE.

Chapter 4. Poly(2,3,5,6-Tetrafluoro-*para*-Phenylene Vinylene) (PTFPPV)**Abstract**

Poly(2,3,5,6-tetrafluoro-*para*-phenylene vinylene) (PTFPPV) has been prepared by two different methods. In reactions expected to yield low molecular weight polymers, 1,4-bis(chloromethyl)-2,3,5,6-tetrafluorobenzene (BCMTEFB) and 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (BBMTEFB) have been treated with sodium hydride in DMF. The resulting products have been characterized by elemental analysis, FT-IR, and thermogravimetric analysis (TGA). Elemental analysis and FT-IR spectroscopy indicates the formation of PTFPPV by this method. In reactions expected to yield higher molecular weight polymers, a water soluble precursor monomer was prepared by the reaction of BBMTEFB in DMSO with an excess of dimethyl sulfide (DMS). The resulting salt was treated with equimolar amounts of either NaOH or tetrabutylammonium hydroxide (TBAOH) at 0-5 °C to obtain a polyelectrolyte. The polyelectrolyte was dialysed in water to remove low molecular weight oligomers and unreacted materials. Water was removed from the polyelectrolyte by a freeze drying technique and the resulting light yellow polymer was thermally treated at 250 °C with a subsequent change in color to brown. FT-IR analysis indicates the formation of PTFPPV from the thermally treated sample. The FT-IR analysis also indicates that the light yellow coloration in the precursor polymer was due to a small amount of HX elimination.

Introduction:

Polyacetylenes containing polar or polarizable side groups and no defect structures have been predicted to be superconductive polymeric materials.¹⁻³ We have thus prepared such a fluorinated polyacetylene by the chemical dehydrochlorination of an isoregic poly(chlorofluoroethylene).⁴ Even though this polymer contained a higher degree of conjugation than previously reported fluorinated polyacetylenes⁵⁻⁷ due to facile HCl elimination under mild reaction conditions and the isoregic nature of the precursor polymer, it still contained defect structures. One possible point of origin of these defects is statistical elimination of HCl leaving unsaturated linkages. Jen et al.⁸ reported the synthesis of a poly(*p*-phenylene vinylene) (PPV) containing an electron donor side group by a condensation type reaction. The resulting polymer is insoluble, low molecular weight, and non-processable. Orienting the polymer by stretching to improve the conductivities are not possible with this polymer. Recently, Blumstein et al.^{9,10} have reported a synthesis of polyacetylene containing pyridine as a polarizable side group which is soluble in organic solvents and thus processable. To date, no conductivity results have been reported on these polymers.

PPV's are easily synthesized using a water soluble precursor polymer.¹¹⁻¹⁴ This soluble precursor polymer can be purified by dialysis to remove low molecular weight oligomers and cast into films. The final conjugated polymer is then obtained by thermal treatment of the film with elimination to form the conjugated double bond. Stretch oriented films have conductivities greater than $2000 \Omega^{-1}\text{cm}^{-1}$ after doping.^{13,15} Using this background, we directed syntheses to to prepare a conjugated PPV containing fluorine as the polarizable side groups on the conjugated polymer.

Experimental:

Materials and Methods: Tetrafluoro-*para*-xylene (TFPX) (99%, Aldrich Chemicals), sulfuryl chloride (SO₂Cl₂) (practical grade, J. T. Baker Chemical Co.), dimethyl sulfide (DMS, 99%, Aldrich Chemicals), tetrahydrothiophene (THT, 99%, Aldrich Chemicals), tetrabutylammonium hydroxide (TBAOH, 40% by weight in methanol, Aldrich Chemicals), and benzoyl peroxide (BPO, Aldrich Chemicals) were used as received. *N*-bromosuccinimide (NBS, 98%, Aldrich Chemicals) was recrystallized from water.

FT-NMR spectra were recorded on a Nicolet 200 NMR spectrometer operating at 200.06 MHz for ¹H- and 50.3 MHz for ¹³C-nuclei. The spectra obtained in CDCl₃ were referenced to TMS (for ¹H) and 77 ppm (for ¹³C). The spectra obtained in D₂O were referenced to HOD (at 4.67 ppm for ¹H) and 39.5 ppm (for ¹³C) using DMSO as an external reference. Diffuse reflectance FT-IR spectra were recorded as a dispersion in KBr on a Digilab FTS-40 FT-IR spectrometer. Mass spectra were recorded on a Finnigan Mat model TSQ 70 instrument. Thermal analyses were carried out on a DuPont model 9900 thermal analyzer containing model 951 TGA module and model 910 DSC module. XPS spectra were recorded on a Perkin Elmer model 5000 instrument.

Initial reactions to synthesize PTFPPV were carried out as shown Schemes I-III. The polymer synthesis method shown in Scheme IV¹⁶ is expected to yield low molecular weight PTFPPV as the partially conjugated polymer precipitates during reaction. The second polymer synthesis method shown in Scheme V is expected to yield higher molecular weight PTFPPV, as it proceeds via a soluble precursor method and subsequent dialysis removes low molecular weight oligomers (Refer to Schemes I-V at end of report).

1,4-Bis(chloromethyl)-2,3,5,6-tetrafluorobenzene (BCMTFB)¹⁷: To a 250 ml three necked flask equipped with an addition funnel and a reflux condenser were added 4.5 g TFPX (25 mmol), benzoyl peroxide (BPO) (30 mg), and 100 ml CCl₄. 13 g sulfuryl chloride (SO₂Cl₂) (96 mmol) was slowly added over 3h at 90°C at reflux under a nitrogen

atmosphere. Reflux was maintained for two days. Additional BPO (30 mg) was added on the second day. The unreacted SO_2Cl_2 and CCl_4 were removed under vacuum at room temperature. The resulting white solid product is soluble in common organic solvents. The mono-chlorinated product was removed by sublimation under vacuum at room temperature. Yield: 2 g (32%), Mass spectra (m/z): 246 (M^+), 211 (M^+-Cl), and M^+-2Cl . $^1\text{H-NMR}$ (CDCl_3): δ 4.67 (s, $-\text{CH}_2\text{Cl}$). $^{13}\text{C-NMR}$ (CDCl_3): δ 31.55 ($-\text{CH}_2\text{Cl}$), 147.07, 142.12 (d, $=\text{CF}-$), 117.21 (C-quart). The ^1H - and ^{13}C -NMR spectra are shown in Figures 1a and 1b respectively.

1,4-Bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (BBMTFB)¹⁸: To a 250 ml three necked flask equipped with a reflux condenser was added 17.4 g NBS (0.098 mol) and CCl_4 (150 ml). 7.82 g TFPX (0.044 mol) and 30 mg BPO were added and the mixture was stirred at 80°C under a nitrogen atmosphere. An additional 30 mg BPO was added on the next day and the reaction was carried out for a total of 48h. After the reaction, the contents were cooled in ice water and the clear solution was decanted. The residual solid product was further extracted with CCl_4 and the combined extract was rotoevaporated to remove the solvent and a white solid product was obtained. The mono-brominated material was removed by vacuum sublimation at room temperature by stirring the solid product. Yield :12.45 g (85%), mp $126-128^\circ\text{C}$ (Lit.¹⁹ $68-70^\circ\text{C}$). $^1\text{H-NMR}$ (CDCl_3): δ 4.51 (s, $-\text{CH}_2\text{Br}$). $^{13}\text{C-NMR}$ (CDCl_3): δ 16.22 ($-\text{CH}_2\text{Br}$), 146.89, 141.12 (d, $=\text{CF}-$), 117.52 (C-quart). The ^1H - and ^{13}C -NMR spectra are shown in Figures 2a and 2b respectively.

2,3,5,6-Tetrafluoro-*para*-phenylenedimethylene-bis-(tetramethylene sulfonium chloride)¹⁴: 0.5 g TFPX (2.02 mmol) and 25 ml methanol were added to a 50 ml round bottom flask. An excess amount of tetrahydrothiophene (THT) was added to the flask and closed by a rubber septum. The contents were stirred at 50°C overnight. The

reaction mixture became light redish brown color. The reaction solution was concentrated and the ^1H - and ^{13}C -NMR spectral analysis indicated several signals for the aliphatic protons and carbons. The target product is expected to show three types of protons and carbons signals in the aliphatic region. The presence of several signals in this region indicates that the THT undergoes ring opening during the salt formation and hence the precursor monomer salt cannot be prepared using the THT. The ^1H - and ^{13}C -NMR spectra of the reaction mixture are shown in Figures 3a and 3b respectively. A similar reaction was also observed with the BBMTFB monomer.

2,3,5,6-Tetrafluoro-*para*-phenylenedimethylene-bis-(dimethyl sulfonium bromide)¹⁴: 11.15 g BBMTFB (33.4 mmol) was dissolved in DMSO (150 ml) in a 250 ml round bottom flask. ~6 g dimethyl sulfide (7ml, 97 mmol) was added and the flask closed by rubber septum. The contents were stirred at 35°C overnight. In a few minutes, a precipitate starts to form. Then the reaction mixture was cooled to room temperature and the clear light yellow solution was decanted. The solid product was rinsed with more DMSO until the filtrate was colorless. Then the white solid was stirred with cold acetone and the product was isolated by centrifugation and dried under vacuum at room temperature overnight. Yield 8.7 g (58%). Elemental analysis: calc (found) C: 31.44 (31.35), Br: 34.50 (34.77), F: 16.59 (16.72), H: 3.49 (3.37), S: 13.97 (14.15). ^1H -NMR (D_2O): δ 4.78 (s, $-\text{CH}_2-$), 2.89 [s, $-\text{S}^+(\text{CH}_3)_2$]. ^{13}C -NMR (D_2O): δ 22.20 [$-\text{S}^+(\text{CH}_3)_2$], 31.98 ($-\text{CH}_2-$), 146.00, 140.80 (d, $=\text{CF}-$), 107.32 (C-quart). The ^1H - and ^{13}C -NMR spectra are shown in Figures 4a and 4b respectively.

Polymerization:

PTFPPV from BCMTFB using NaH: To a suspension of 0.12 g NaH (80% in mineral spirits, 2.02 mmol) in anhydrous DMF (25 ml) was added 0.5 g BCMTFB (2.02 mmol) in anhydrous DMF (15 ml) using an addition funnel under a nitrogen atmosphere.

The reaction mixture was stirred at 70°C for 2h. A yellow precipitate was formed. Methanol (5 ml) was added to quench any unreacted NaH and the precipitate redissolved. The solution was concentrated and the polymer was precipitated as a light brown powder using pentane. The product was dried to remove pentane and washed with water and dried under vacuum. Yield 80 mg (23%). Elemental analysis (weight %): calc (found) C: 55.17 (5.73), F: 43.68 (n/a), H: 1.15 (0.88), Cl: 0 (n/a), N: 0(0.07).

PTFPPV from BBMTFB using NaH #1: To a suspension of 0.29 g NaH (80% in mineral sprit, 9.7 mmol) in anhydrous DMF (40 ml) was added 1.5 g BBMTFB (4.5 mmol) in anhydrous DMF (35 ml) using an addition funnel under a nitrogen atmosphere. The reaction mixture was stirred at 80°C overnight. A brownish yellow precipitate was formed. The product was filtered and stirred with water to remove any inorganic salts. The filtered product was dried under vacuum. Yield 0.34 g (44%). Elemental analysis (weight %): calc (found) C: 55.17 (51.15), F: 43.68 (41.68), H: 1.15 (2.58), Br: 0 (2.26). Upon isothermal treatment at 275°C for 0.5 h, the Br content drops to 1.89%.

To increase the yield of the polymer, the above reaction was carried out with 30% (mole) excess of NaH. The elemental analysis of the above reaction product showed the presence of ~1.5% nitrogen probably due to trapped DMF in the polymer. Therefore, the reaction product was soxhlet extracted with THF to remove any residual DMF.

PTFPPV from BBMTFB using NaH #2: To a suspension of 0.68 g NaH (80% in mineral sprits, 22.7 mmol) in anhydrous DMF (50 ml) was added 3.0 g BBMTFB (9.0 mmol) in anhydrous DMF (50 ml) using an addition funnel under a nitrogen atmosphere. The reaction mixture was stirred at 80°C overnight. A brownish yellow precipitate was formed. The product was filtered and stirred with water to remove any inorganic salts. The filtered product was dried under vacuum. This product was soxhlet extracted with THF overnight to remove any residual DMF and then dried under vacuum. Yield 0.74 g

(65%). Elemental analysis (weight %): calc (found) C: 55.17 (50.68), F: 43.68 (n/a), H: 1.15 (2.65), Br: 0 (n/a). This product showed saturated linkages in the polymer as shown by infrared spectroscopy and hence it was heated under vacuum at 225°C for 4 days.

Elemental analysis (weight %): calc (found) C: 55.17 (53.79), F: 43.68 (33.87), H: 1.15 (2.00), Br: 0 (0.18), N: 0(0.90), Na:0(1.22).

PTFPPV from BBMTFB-dimethyl sulfide (DMS) salt and NaOH by soluble precursor route: To a 100 ml three necked flask equipped with an addition funnel and an attached pH electrode was added 1.0 g BBMTFB-DMS (2.18 mmol) in water (18 ml). 0.1 N NaOH (22 ml) was added to the addition funnel. Both solutions were bubbled with deoxygenated nitrogen for 0.5h and the flask was cooled to 0-5°C. The NaOH solution was added to the flask slowly and the progress of the reaction was monitored (qualitatively) by pH meter. A white cloudy solution was formed and a light yellow coloration was also observed. The reaction mixture became more viscous and, when the temperature drops below 0°C (~-5°C), the product solidifies (no gel). After 9 h of reaction, the pH of the medium was ~10.18 and polymerization was quenched by adding 0.1 N HCl (~2 ml) to bring the pH to ~6. Then the contents were transferred to a dialysis tube (3500 MW cut off) with an additional 20 ml water and the polymer was dialysed for 48 h at 0°C with the exchange of dialysis water after 24 h. The water was removed from the dialysed polymer by freeze drying under vacuum ($\sim 10^{-3}$ torr) at 0°C. The color of the polymer was not changed at room temperature. Yield 0.1 g (14%). The yield of the polymer is 26%, if it is considered to be converted to poly(2,3,5,6-tetrafluoro-para-phenylene vinylene) under the experimental conditions. The wet polymer was found to be soluble in methanol. However, upon removal of solvent, the polymer became insoluble in methanol.

PTFPPV from BBMTFB-dimethyl sulfide (DMS) salt and tetrabutyl ammonium hydroxide (TBAOH) by soluble precursor route: To a 100 ml three

necked flask equipped with an addition funnel and an attached pH electrode was added 1.0 g BBMTFB-DMS (2.18 mmol) in water (18 ml). 1.4 g TBAOH (40% by weight in methanol) diluted to 22 ml with distilled water was added to the addition funnel. Both solutions were bubbled with deoxygenated nitrogen for 0.5h and the flask was cooled to 0-5°C. The TBAOH solution was added to the flask slowly and the progress of the reaction was monitored (qualitatively) by pH meter. A white cloudy solution was formed and stayed white in most of the early stage of the reaction. In the latter stages of the reaction a light yellow coloration was also observed. The reaction mixture became more viscous and when the temperature drops below 0°C (~-5°C), the product solidifies (no gel). In the latter stage 20 ml of water was added to dissolve the polymer. After 9 h of reaction, the pH of the medium was ~9.47 and polymerization was quenched by adding 0.1 N HCl (~0.5 ml) to bring the pH to ~6. Then the contents were transferred to a dialysis tube (3500 MW cut off) and the polymer was dialysed for 48 h at 0°C with the exchange of dialysis water several times. The water was removed from the dialysed polymer by freeze drying under vacuum (~10⁻³ torr) at 0°C. The color of the polymer was not changed at room temperature. Elemental analysis (precursor polyelectrolyte): calc (found) C: 37.97 (46.99), H: 2.85 (5.82), N: 0(1.58), Br: 34.50 (n/a), F: 16.59 (n/a), S: 10.13 (n/a). Elemental analysis calculated for the polyelectrolyte being converted to the final poly(2,3,5,6-tetrafluoro-para-phenylene vinylene) (PTFPPV): C: 55.17, H: 1.15, F: 43.68. The increased contents of C and H are due to the presence of residual tetrabutyl ammonium bromide in the sample as shown by the presence of nitrogen.

The polymer yield in the above two methods were found to be too low. One possible reason for this is that the target precursor polyelectrolyte is partially converted to PTFPPV. The other possibilities are the occurrence of undesirable side reactions. If this is the case, the use of only one equivalent of base for the preparation of polyelectrolyte polymer results in unreacted monomer and this can explain the low yield. This is due to the

consumption of the base for the conversion of polyelectrolyte to PTFPPV. Consequently, two equivalents of base were used to obtain the PTFPPV in one step. The above polymerizations in water resulted in precipitation of the polymer during the reaction. The monomer is not soluble in methanol and the wet polymer is found to be soluble in methanol. Therefore, we attempted the above polymerization by dissolving the monomer in a minimum amount of water and added a sufficient amount of methanol to keep the monomer in solution at the polymerization temperature. To confirm this hypothesis, and to improve the polymer yield, an in-situ $^1\text{H-NMR}$ experiment was also carried out using deuterium oxide (D_2O) as solvent and NaOD in D_2O as base at room temperature. In another experiment at $-5\text{-}0^\circ\text{C}$, a controlled amount of base was used at intervals of time and the progress of the reaction was followed by $^1\text{H-NMR}$.

PTFPPV from BBMTFB-dimethyl sulfide (DMS) salt and NaOH (2 equivalent) using water methanol mixed solvent system: To a 150 ml three necked flask was added 3.11 g BBMTFB-DMS (6.79 mmol) in water (20 ml). The solution was cooled to $-5\text{-}0^\circ\text{C}$ and methanol (70 ml) was added to the solution. NaOH (0.27g, 6.79 mmol) was dissolved in water (10 ml) in a test tube at $-5\text{-}0^\circ\text{C}$. Both solutions were bubbled with deoxygenated nitrogen for 0.5h. The NaOH solution was added over a period of 1 h. and the reaction mixture was allowed to stir at $-5\text{-}0^\circ\text{C}$ for another 9 h. The solution was concentrated by rotoevaporation of the solvent. The product was filtered and washed with water to remove NaBr. The final product was isolated into an acetone soluble (liquid) and insoluble components.

Results and Discussion.

Precursor monomer salt synthesis: The $^{13}\text{C-NMR}$ spectrum of the reaction product of BBMTFB and THT is shown in Figure 5. The spectrum shows several signals at 50-10 ppm for the aliphatic carbons. A simple salt formation between BBMTFB and THT is

expected to show only three signals for the aliphatic carbons (*one for BBMTFB and two for THT ring*). A ring opening of the THT unit will result in the formation of $-\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-Br}$. Formation of this unit is expected to show five signals for the aliphatic carbons. The presence of more than five signals in this region suggests that some other reactions may also be occurring in addition to the ring opening of the THT unit. The reaction of dimethyl sulfide with BBMTFB may also result in the formation of side products as shown by less than 100% (58%) yield. In the case of the non-fluorinated analogue, the reaction rate was increased by the addition of water¹⁴ by increasing the rate of the SN_1 type reaction. The use of a polar aprotic solvent, such as DMSO ($\epsilon=46.68$), will facilitate the reaction to occur by an SN_2 type reaction. Consequently the yields were ~40% for the reactions in methanol ($\epsilon=32.2$) and in acetonitrile ($\epsilon=37.5$). It has been reported¹⁴ that the use of tetrahydrothiophene (THT) to prepare the sulfonium salt precursor monomer results in increased yield of water soluble precursor polymer of non-fluorinated PPV compared to the use of the corresponding DMS salt. In addition, the molecular weight of the polymer was also higher with this sulfonium salt. The thermal elimination of the THT and HX ($\text{X}=\text{Br}$ or Cl) also occurs at a lower temperature. The ^1H - and ^{13}C -NMR chemical shifts data are presented in Table 1 along with the non-fluorinated analogues and side reaction products for comparison. The data in Table 1 clearly indicate that the proton chemical shifts are deshielded in the fluorinated compounds. However, the carbon chemical shifts show some shielding effects despite having electron withdrawing fluorines on the benzene rings. This is due to the fact that carbon chemical shifts are affected by electron density around that carbon atom as well as substituent effects and space effects.

The FT-IR spectra of BCMTFB, BBMTFB, and BBMTFB-DMS salts all exhibit four signals $800\text{-}500\text{ cm}^{-1}$ due to C-X ($\text{X}=\text{Cl}$ or Br) stretching vibrations. The introduction of DMS to form the salt with BBMTFB alter the intensities of the BBMTFB

signals. In all samples, there was a strong signal $\sim 1490\text{ cm}^{-1}$ assignable to the C=C stretching vibration of C=C-F of the benzene ring. The presence of a strong electron withdrawing fluorine makes the C=C bond more polar and results in an intense signal. These samples exhibit several signals which are difficult to assign. For comparison, the FT-IR spectra of TFPX, BCMTFB, BBMTFB and BBMTFB-DMS salt are presented in Figures 6-9 respectively.

PTFPPV Prepared by the reaction of BBMTFB and NaH in DMF as Shown in Scheme IV

The FT-IR spectrum of PTFPPV obtained from BBMTFB and NaH in the first and second preparations are shown in Figures 10 and 11 respectively. The signals at 2948, 2887, 2828, and 2779 cm^{-1} are due to the C-H stretching vibrations. On heating this PTFPPV results in the loss of signals at 2828 and 2779 cm^{-1} and increase in the signal intensities $\sim 1660\text{ cm}^{-1}$ (Figure 12). Consequently, the signals at 2948 and 2887 cm^{-1} are assigned to the C-H stretching vibration of the vinylene unit in the PTFPPV. The signals $\sim 1660\text{ cm}^{-1}$ are due to the C=C stretching vibration of the vinylene unit. The signal at 1711 cm^{-1} is probably due to a carbonyl functional group. The signal intensity for this peak increased in intensity as the sample was heated under vacuum. Elemental analysis indicate only a trace amount of bromine indicating the formation of PTFPPV as expected. The elemental analysis also indicates the presence of $\sim 10\%$ oxygen in the PTFPPV.

PTFPPV obtained using this method is brown in color. The DMF soluble component is also brown in color. The UV-VIS spectrum (Figure 13) shows a broad strong absorption centered $\sim 300\text{ nm}$. This λ_{max} value is lower than other conjugated polymers which is expected due to the electron withdrawing fluorines attached to the conjugated polymer. The XPS spectrum of PTFPPV obtained after thermal treatment was recorded as a powder on a scotch tape. Spectra are shown for scotch tape (as a background) and PTFPPV powder in Figures 14 and 15 respectively. The XPS spectrum

in Figure 15 indicate the absence of bromine (~ 90 eV). The TGA of PTFPPV obtained in the chemical reaction is shown in Figure 16 and the thermally treated sample in Figure 17. The PTFPPV obtained using this method was doped with sodium naphthalide in THF. The blue color of the sodium naphthalide disappeared during the doping indicating a chemical reaction. The FT-IR spectrum of the doped sample is shown in Figure 18 and indicates a slight splitting of the signal ~ 1485 cm^{-1} and a small decrease in intensity of the signals ~ 984 - 945 cm^{-1} compared to the undoped sample (Fig. 12). The signal at 1485 cm^{-1} is due to the C=C stretching of fluorinated benzene ring which may be reacting with the fluorine. It is unlikely that the changes are due to doping of the conjugated polymer as a significantly higher absorption throughout the IR region would be expected. (Conductivity measurements carried out for the sodium naphthalide and NOPF_6 doped samples show no improvement).

PTFPPV Prepared by the Soluble Precursor Route as Shown in Scheme V.

The FT-IR spectrum of the PTFPPV precursor polymer, prepared from the BBMTFB-DMS salt and NaOH by the soluble precursor route, is shown in Figure 19. Compared to Figure 10 of the BBMTFB-DMS salt, there is a reduction of the signals in the 900 - 500 cm^{-1} region due to the loss of HBr. On heating this sample to 250°C for 15 min., the IR spectrum (Figure 20) shows the formation of conjugated C=C bonds as seen by the increased signal intensity at ~ 1600 cm^{-1} . In addition, the C-H stretching vibrations ~ 3000 cm^{-1} decrease to indicate the formation of PTPTFPPV units by this method. It should be noted that the increased signal intensity in Figure 20 indicates that the formation of vinylene units in the first base treatment of the precursor salt occurs only to a small extent despite appearing as a light yellow color. It has been reported¹³ that an IR signal exists at ~ 965 cm^{-1} for the trans vinylenic protons and we observe a signal in that region. Unfortunately, the presence of too many signals in this region in our fluorinated polymer makes it difficult to make full assignments.

Using the soluble precursor method to prepare high molecular weight PTFPPV, the yields are lower than the NaH coupling polymerizations. Unlike the other non-fluorinated soluble precursor polymers, our fluorinated analogue starts to precipitate from water. This is likely to decrease the molecular weight of the polyelectrolyte as it will not continue to polymerize in the solid state. Our pH titrations which follow this reaction indicate that a quantitative amount of base has been consumed. However, this pH titration may only indicate that the initial formation of ylide and not the actual polymerization.

An in-situ $^1\text{H-NMR}$ experiment was carried out using $\text{NaOD/D}_2\text{O}$ and one equivalent base at room temperature. Spectra were recorded every 10 minutes for 60 minutes. The spectra are shown in Figure 21. The signal at ~ 2.9 ppm is due to methyl groups of the sulfonium salt. The signal at ~ 4.8 ppm is due to the methylenic protons adjacent to the benzene ring in the salt. The peaks at ~ 4.7 ppm are due to HOD in the solvent (D_2O) and possibly a $-\text{CHD}-$ unit which is formed by the exchange of one of the protons. Upon the addition of NaOD, the signals ~ 2.9 and 4.7 ppm show additional peaks and new signals ~ 2 ppm. The formation of $(\text{CH}_3)_2\text{S}$ is the first step in this reaction as shown in Scheme V. One of the signals in this region is due to the methyl group in the $(\text{CH}_3)_2\text{S}$. A likely cause of the other signal in this region is due to a $-\text{S}-\text{CH}_3$ group which could have formed by the loss of CH_3Br from the dimethyl sulfonium salt. If this reaction occurs, the targeted soluble precursor polymer is not a salt and the organic polymer is going to be insoluble in water as we have observed. The relative intensities of all the signals remained the same with the extent of the reaction up to 60 minutes. Upon the addition of the second equivalent of base, the relative intensities were changed and the peaks at ~ 2.9 ppm were disappeared. After bubbling the NMR solution with nitrogen, all the peaks disappeared leaving only the HOD peak of the solvent at ~ 4.7 ppm. This experiment clearly shows that side reactions, other than the reactions shown in Scheme V, consume the base. An in-situ reaction was also carried out in a mixture of $\text{D}_2\text{O/CD}_3\text{OD}$ so

that the methanol could dissolve the non-polyelectrolyte component of the polymer. The experiment was carried out at $\sim -5^{\circ}\text{C}$ by the addition of a controlled amount of base at various time intervals. Here again the spectral features were similar to the reaction without methanol except the signals ~ 2 ppm had three components instead of 2 as observed in the previous case.

A large scale experiment was therefore carried out in a mixture of water/methanol so to cause the dimethyl sulfonium salt to stay in solution. The product was isolated as an acetone soluble light yellow polymer and an acetone insoluble dark orange polymer. The FT-IR spectrum of the acetone soluble component is shown in Figure 22. Surprisingly an intense signal at 1104 cm^{-1} was observed which is not present in the polymer prepared without methanol. This signal is due to the presence of $-\text{OCH}_3$ group which was formed by the replacement of sulfonium group by methanol. This type of reaction has been observed in the preparation of both PPV and poly(thienylene vinylenes). The broad signals between $3500\text{--}3200\text{ cm}^{-1}$ are due to $-\text{OH}$ groups formed by the replacement of sulfonium group by the base (OH^-). The weak signal at 1643 cm^{-1} is due to the $\text{C}=\text{C}$ stretching vibration of the vinylene units. The ^{13}C -NMR spectrum of the acetone soluble polymer is shown in Figure 23. The assignments were confirmed by a coupling experiment. Accordingly the signal at ~ 15 ppm is due to the $-\text{S}-\text{CH}_3$ carbon and the signals at ~ 30 ppm are due to the $-\text{CH}_2-$ carbon. The signals ~ 60 ppm are due to the $-\text{OCH}_3$ carbon which has been shown to be present by FT-IR also. The presence of a $-\text{OCH}_3$ carbon should show the presence of a $-\text{OCH}-$ carbon in the polymer chain. In general, $-\text{OCH}-$ carbons are more deshielded than $-\text{OCH}_3$ carbons. However, the CH_2 carbon adjacent to the benzene ring in the fluorinated compounds are more shielded than the non-fluorinated compounds as seen in Table 1. Therefore, the $-\text{OCH}-$ carbons are appearing in the same region as the $-\text{OCH}_3$ carbons. The FT-IR spectrum of the acetone insoluble component is shown in Figure 24. This spectrum is very similar to the PTFPPV prepared by the reaction of BBMTFB/NaH in DMF (Fig. 12). The main difference is the presence of a signal $\sim 1100\text{ cm}^{-1}$ characteristic

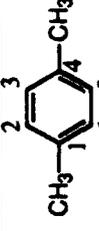
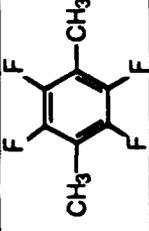
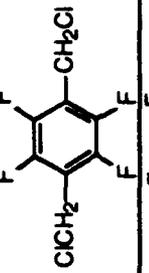
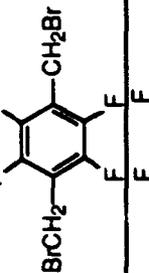
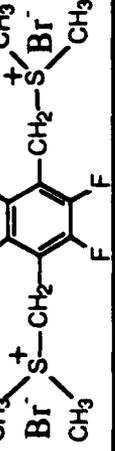
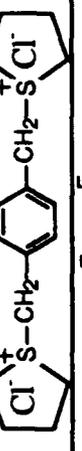
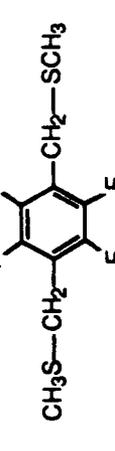
of -OCH₃. These results indicate that our soluble precursor method proceeded as shown in Scheme VI. By thermal treatment the polymer shown in Scheme VI can be converted to fully conjugated PTFPPV with no other defect structures. However, the use of BBMTFB and NaH in DMF resulted in higher yields.

References:

1. Little, W. A.; Gutfreund, H. *Phys. Rev. B* **1971**, *4* (3), 817.
2. Davis, D.; Gutfreund, H.; Little, W.A. *Phys. Rev. B* **1976**, *13* (11), 4766.
3. Little, W. A. *Science*, **1988**, *242*, 1390.
4. Panchalingam, V.; Reynolds, J. R.; Lopez, L. E.; Arnott, H. J. *Amer. Chem. Soc. Div. Polym. Chem., Polym. Prepr.*, in press.
5. Dias, A.; McCarthy, T. J. *J. Polym. Sci. Polym. Chem. Ed.*, **1985**, *23*, 1057.
6. Kise, H.; Ogata, H.; Nakata, M. *Angew. Makromol. Chem.* **1989**, *168*, 205.
7. Swei, S. W.; Rickert, S. E.; Lando, J. B. in "*Polymers for Advanced Technologies, IUPAC International Symposium*", Lewin, M. ed.; VCH publishers, Inc., New York, **1988**, 285.
8. Jen, K. Y.; Cava, M. P. *Synthetic Metals*, **1986**, *15*, 155.
9. Blumstein, A.; Subramanyam, S. in "*Organic Super Conductivity*" V. Z. Kresin and W. A. Little Eds., Plenum Press, New York, **1990**, pp 335-340.
10. Subramanyam, S.; Blumstein, A. *Mackromol. Chem. Rapid Commun.* **1991**, *12*, 23.
11. Wessling, R. A.; Zimmerman, R. G. *US Patent*, **1968**, 3401152.
12. Gagnon, D. R.; Capistran, J. D.; Karasz, F. E.; Lenz, R. W. *Polym. Bull.* **1984**, *12*, 293.
13. Bradley, D. D. D. *J. Phys. D. Appl. Phys.* **1987**, *20*, 1389.
14. Lenz, R. W.; Han, C. C.; Smith, J. S.; Karasz, F. E. *J. Polym. Sci. Polym. Chem. Ed.*, **1988**, *26*, 3241.
15. Machado, J. M.; Masse, M. A.; Karasz, F. E. *Polymer*, **1989**, *30*, 1992.
16. Horhold, V. H-H.; Opfermann, J. *Makromol. Chem.* **1970**, *131*, 105.

17. The reaction used to chlorinate benzylic protons is utilized for the chlorination of TFPX.
18. The reaction used to brominate benzylic protons is utilised for the bromination of TFPX.
19. Filler, R.; Cantrell, G. L.; Wolanin, D.; Naqvi, S. M. *J. Fluorine Chem.*, 1986, 30, 399.

Table 1: ^1H and ^{13}C -NMR data of *p*-xylene, tetrafluoro-*p*-xylene and their halogenation products^a

Sample	Chemical Shift (ppm)				
	C1,C4	C2,C3,C5,C6	-CH ₃	-CH ₂ X	-S ⁺ (CH ₃) ₂ X-
	134.50	128.85	20.83 (1.39)	-	-
	137.57	128.89	-	45.66 (3.03)	-
	112.94	147.12 142.34 (d)	7.33 (2.23)	-	-
	117.21	147.07 142.12 (d)	-	31.55 (4.67)	-
	117.517	146.889 141.810 (d)	-	16.216 (4.51)	-
	109.725	148.379 143.292 (d)	-	34.403 (4.78)	24.605 (2.89)
	130.419	131.572 (7.52)	-	45.119 (4.46)	42.723, 28.30 (3.4, 2.2)
			-	24.906 (3.76)	15.589 (2.13)

^aValues within the brackets indicate the ^1H -NMR chemical shifts.

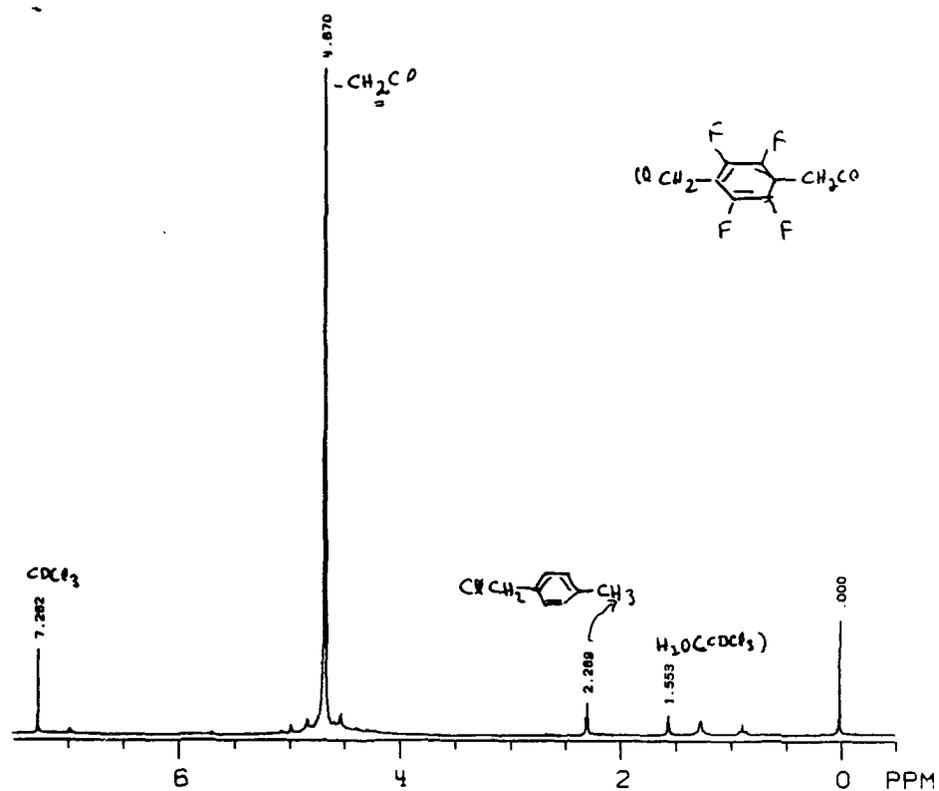


Figure 1a. $^1\text{H-NMR}$ spectrum of 1,4-bis(chloromethyl)-2,3,5,6-tetrafluorobenzene.

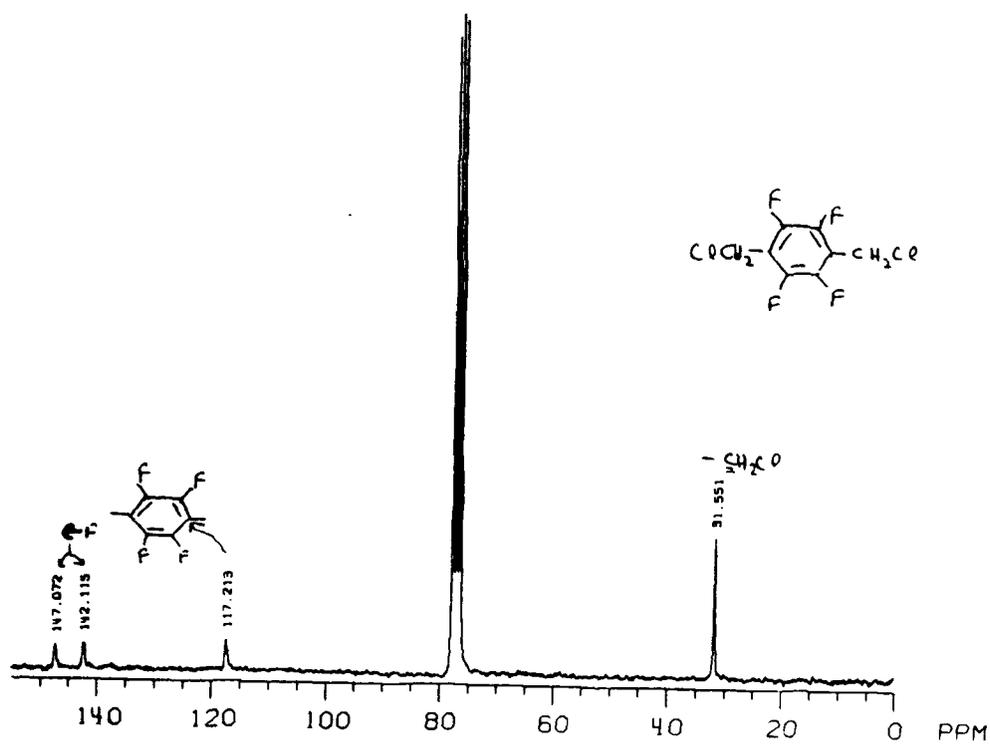


Figure 1b. $^{13}\text{C-NMR}$ spectrum of 1,4-bis(chloromethyl)-2,3,5,6-tetrafluorobenzene.

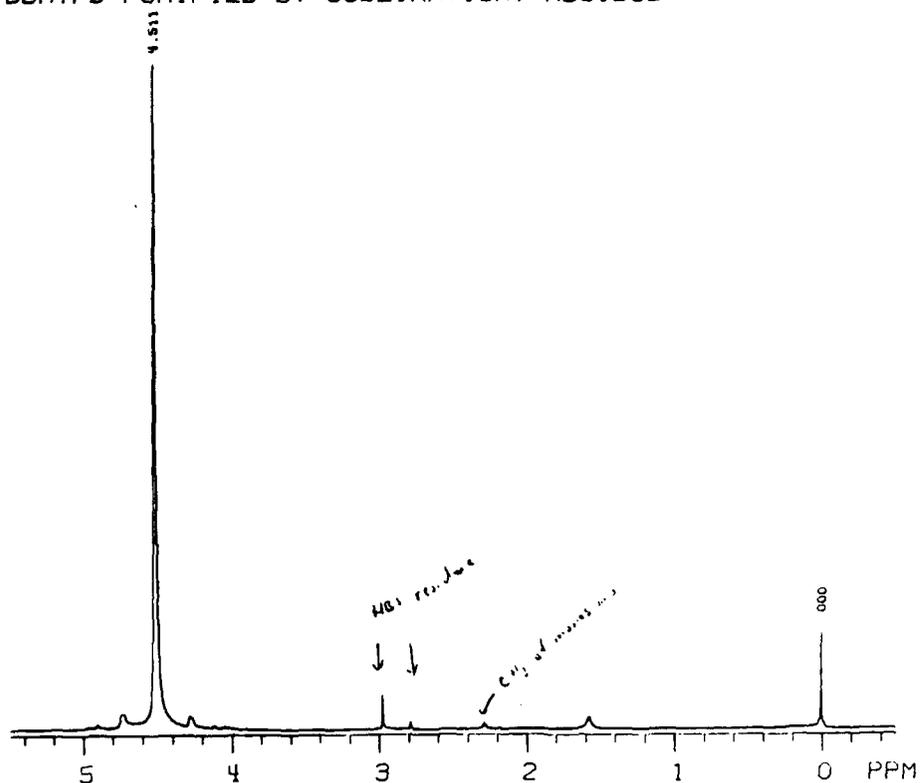


Figure 2a. $^1\text{H-NMR}$ spectrum of 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene.

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BBMTFB-SUBLIMED PDT: RESIDUE

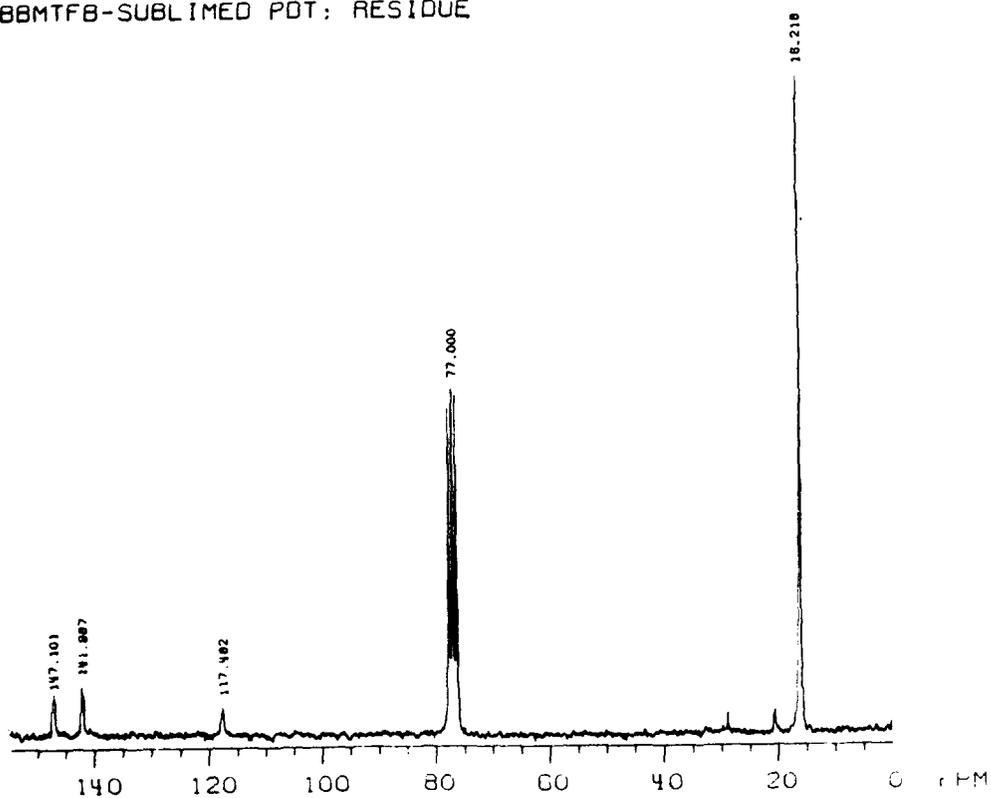


Figure 2b. $^{13}\text{C-NMR}$ spectrum of 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene.

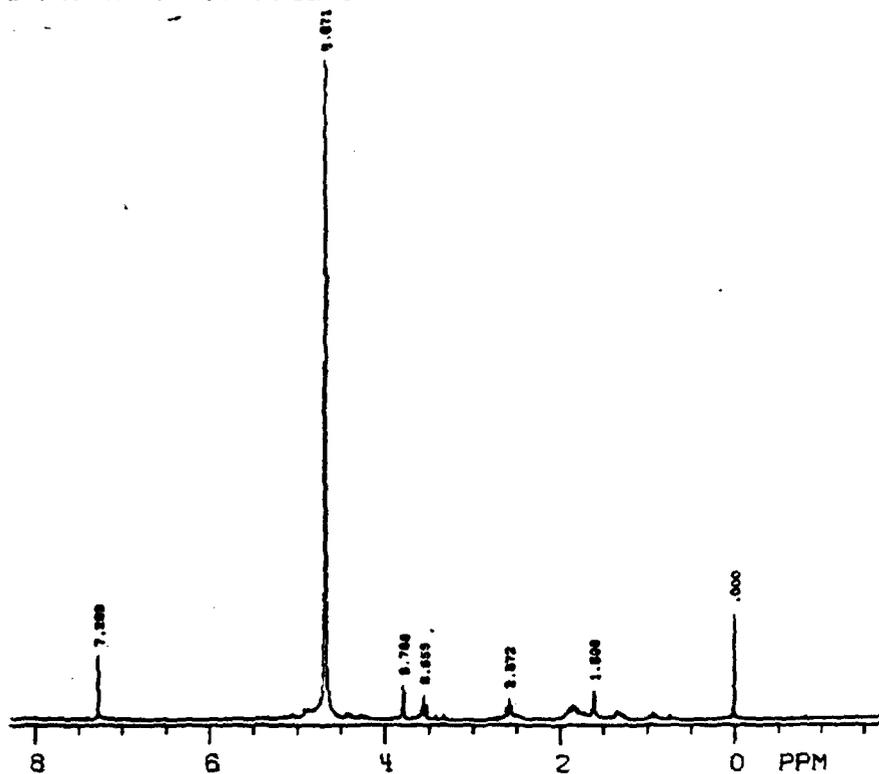


Figure 3a. ¹H-NMR spectrum of 2,3,5,6-tetrafluoro-para-phenylenedimethylene-bis-(tetramethylene sulfonium chloride).

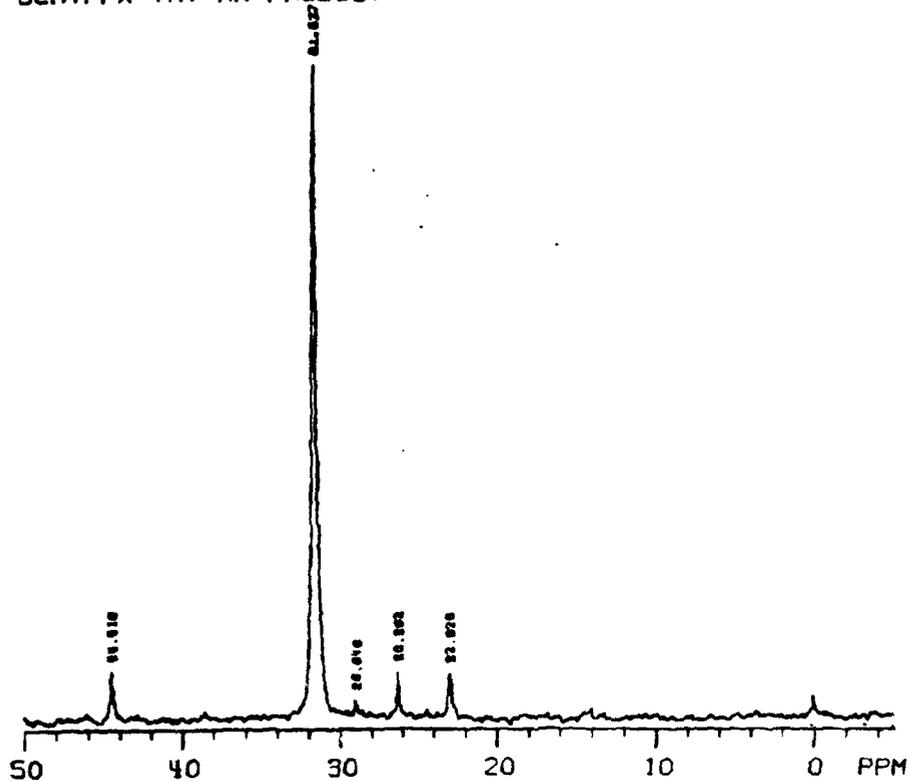


Figure 3b. ¹³C-NMR spectrum of 2,3,5,6-tetrafluoro-para-phenylenedimethylene-bis-(tetramethylene sulfonium chloride).

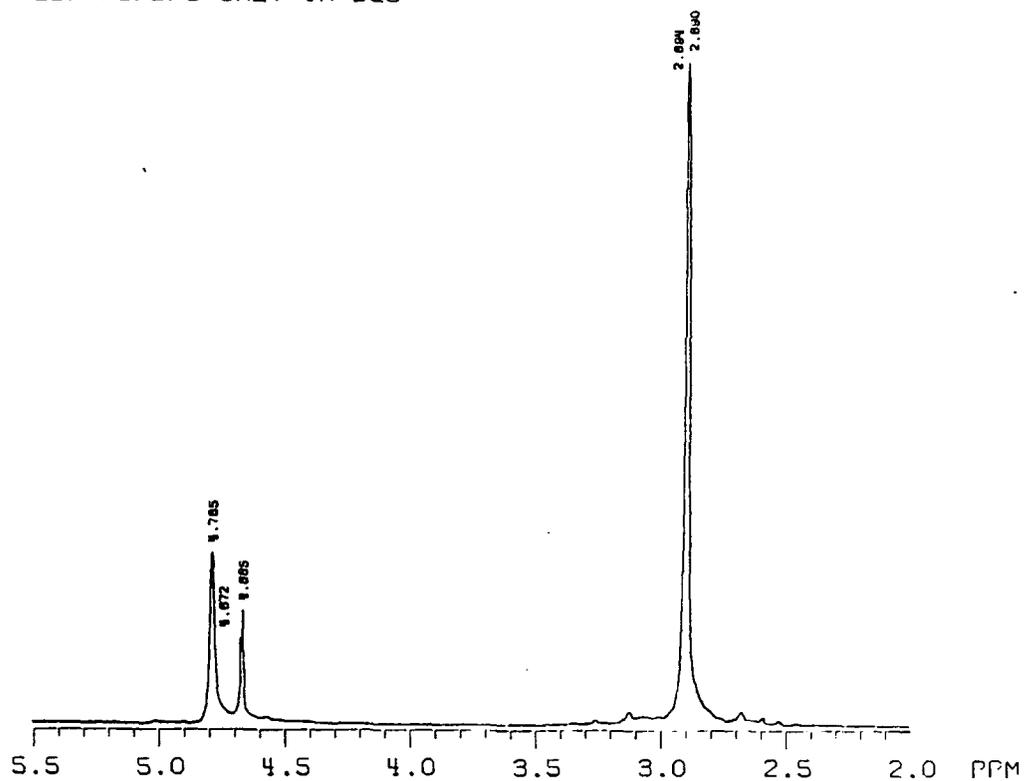


Figure 4a. ^1H -NMR spectrum of 2,3,5,6-tetrafluoro-para-phenylenedimethylene-bis-(dimethyl sulfonium chloride).

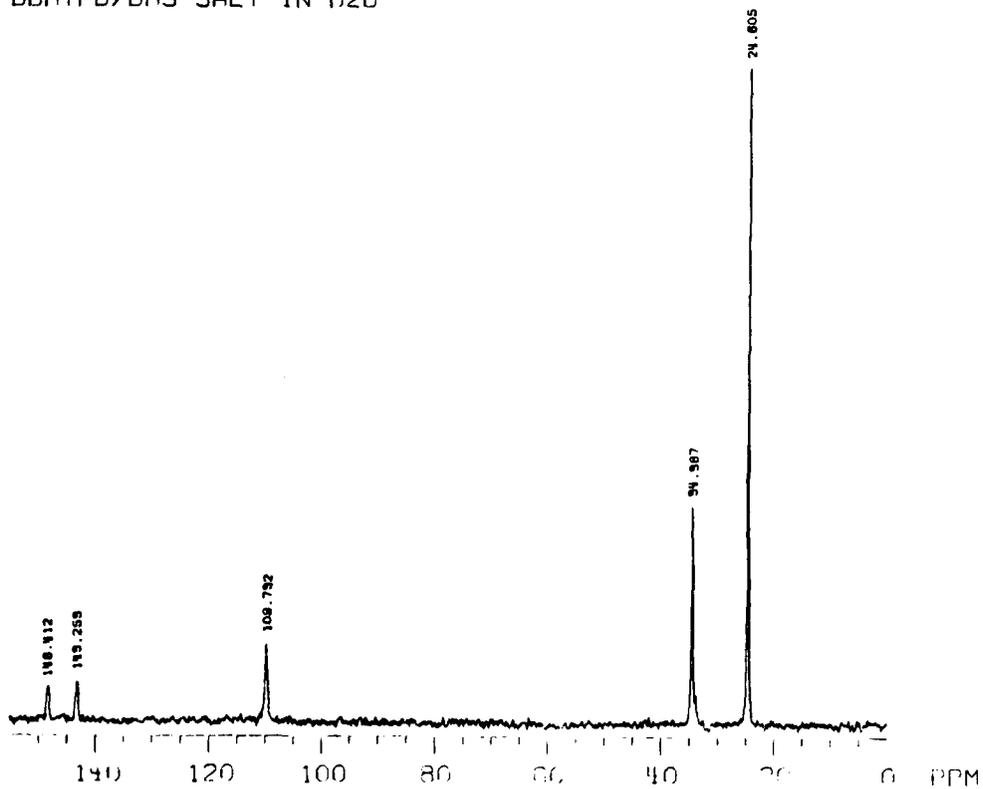


Figure 4b. ^{13}C -NMR spectrum of 2,3,5,6-tetrafluoro-para-phenylenedimethylene-bis-(dimethyl sulfonium chloride).

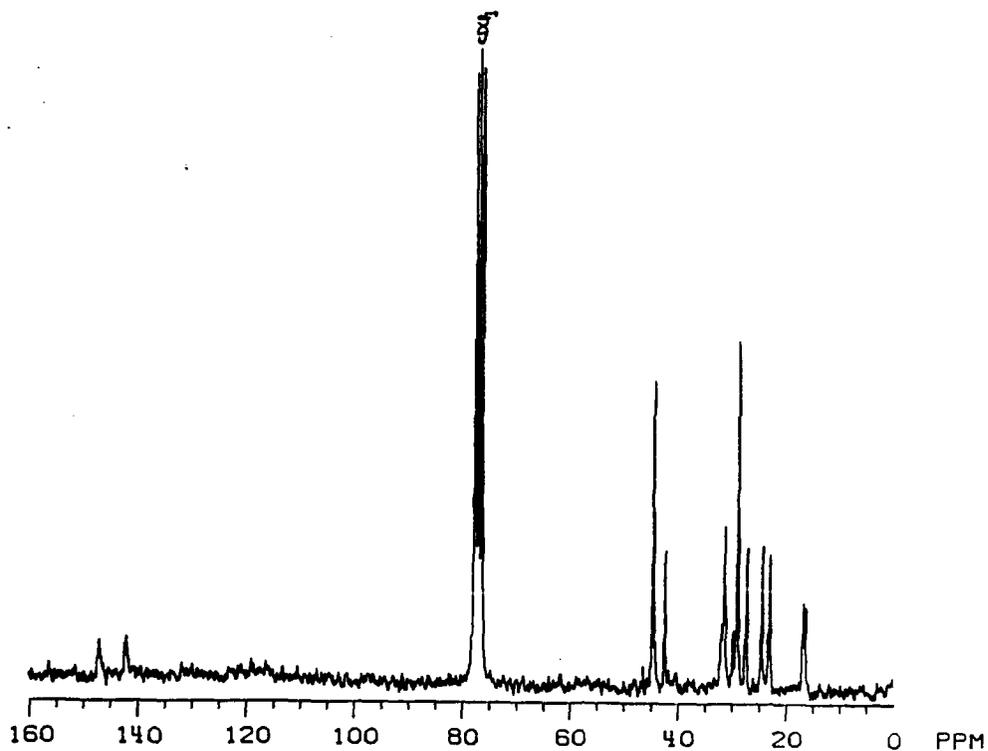


Figure 5. ¹³C-NMR spectrum of the reaction product between BBMTFB and tetrahydrothiophene (THT).

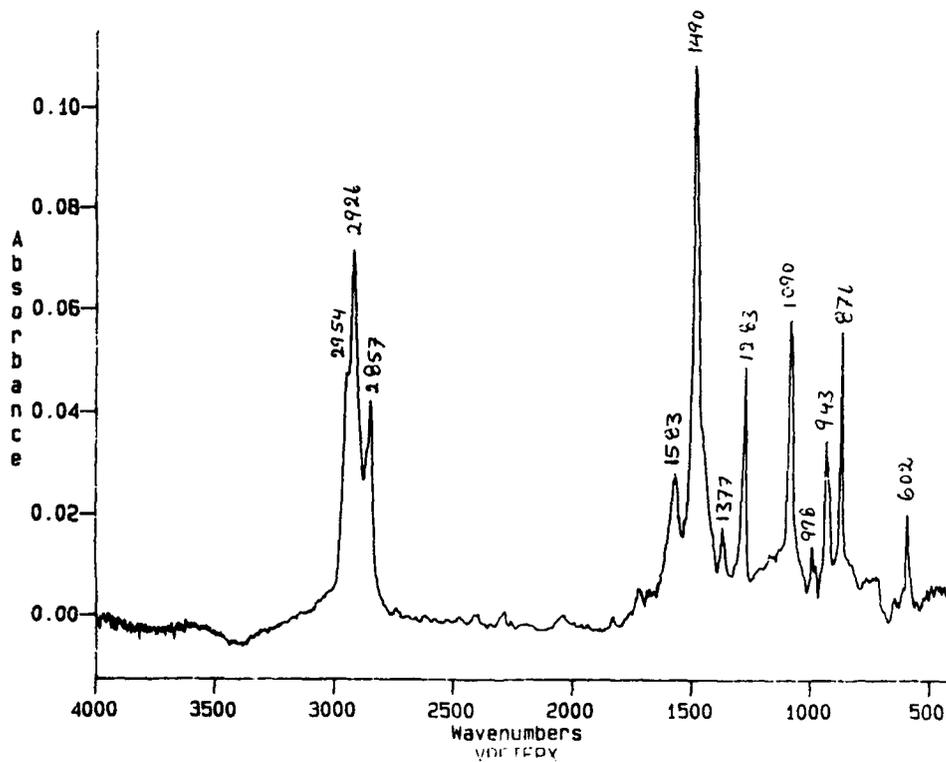


Figure 6. FT-IR spectrum of tetrafluoro-para-xylene (TFPX).

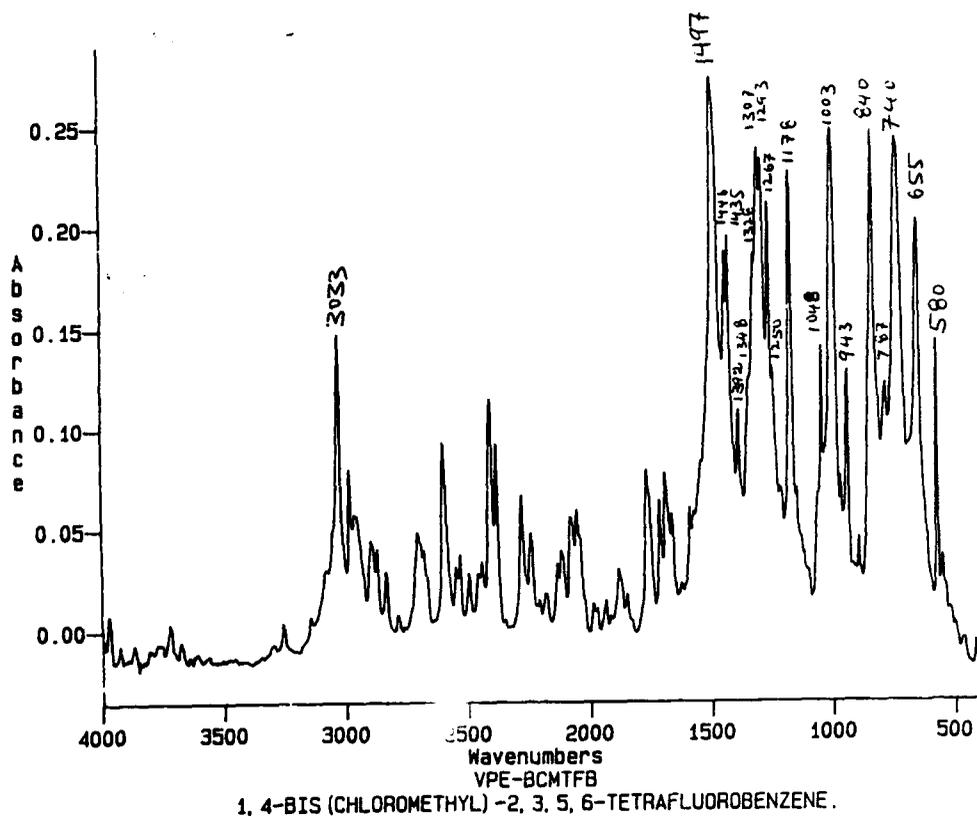


Figure 7. FT-IR spectrum of 1,4-bis(chloromethyl)-2,3,5,6-tetrafluorobenzene (BCMTFB).

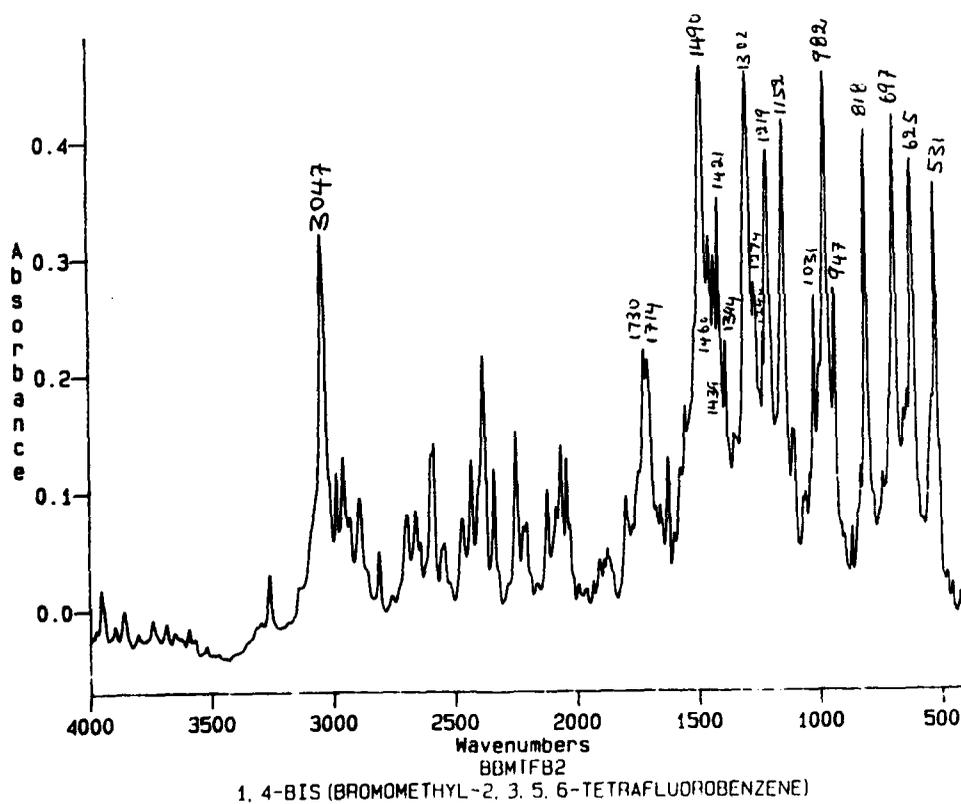


Figure 8. FT-IR spectrum of 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (BBMTFB).

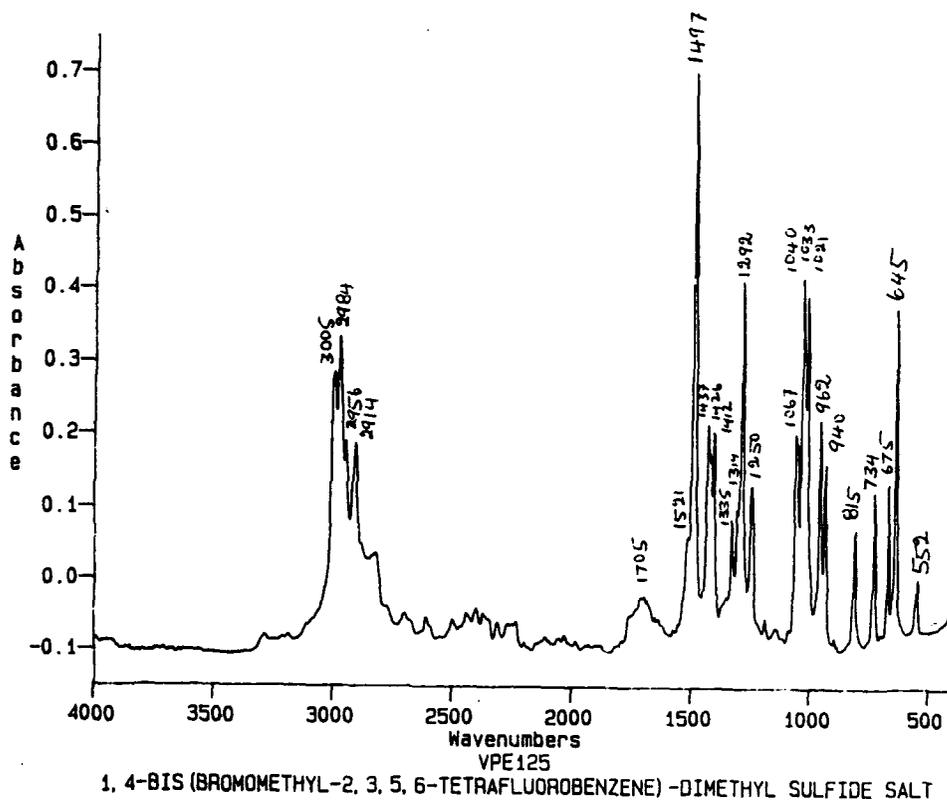


Figure 9. FT-IR spectrum of 2,3,5,6-tetrafluoro-*para*-phenylenedimethylene-bis-(dimethyl sulfonium chloride) (BBMTFB-DMS salt).

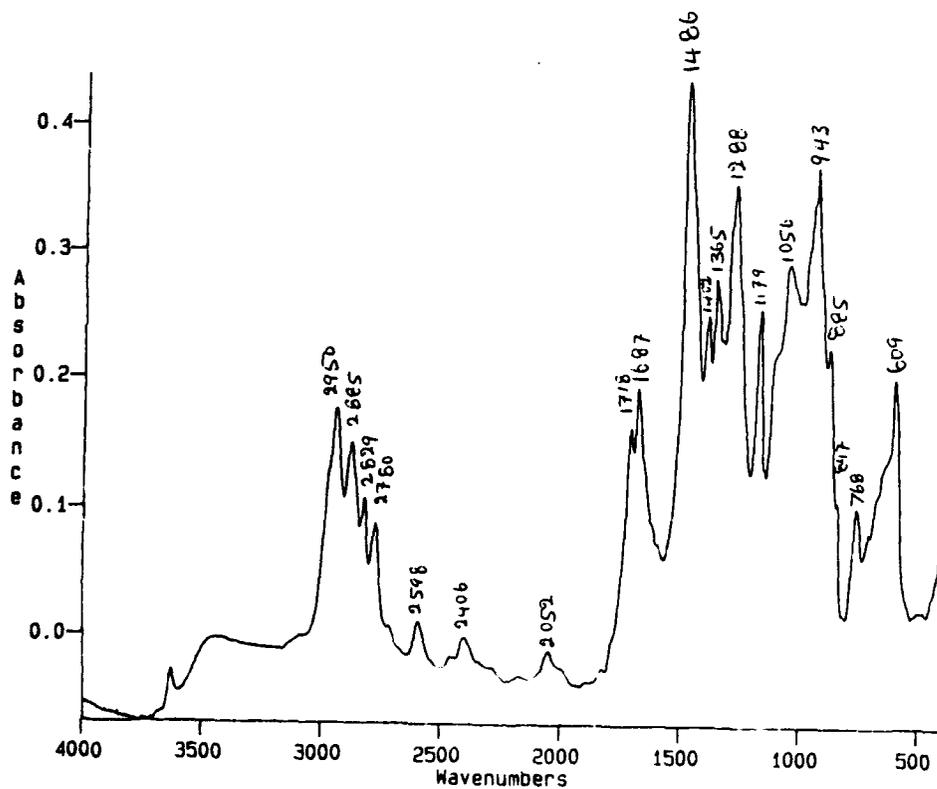


Figure 10. FT-IR spectrum of PTFPPV obtained from the reaction of BBMTFB and NaH in the first preparation.

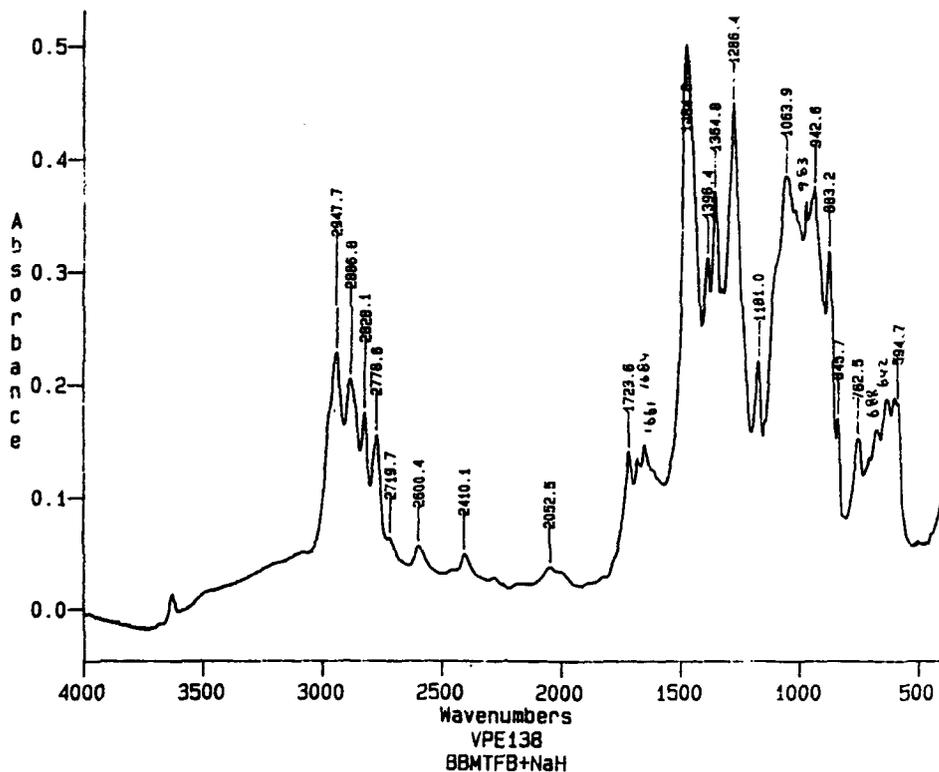


Figure 11. FT-IR spectrum of PTFPPV obtained from the reaction of BBMTFB and NaH in the second preparation.

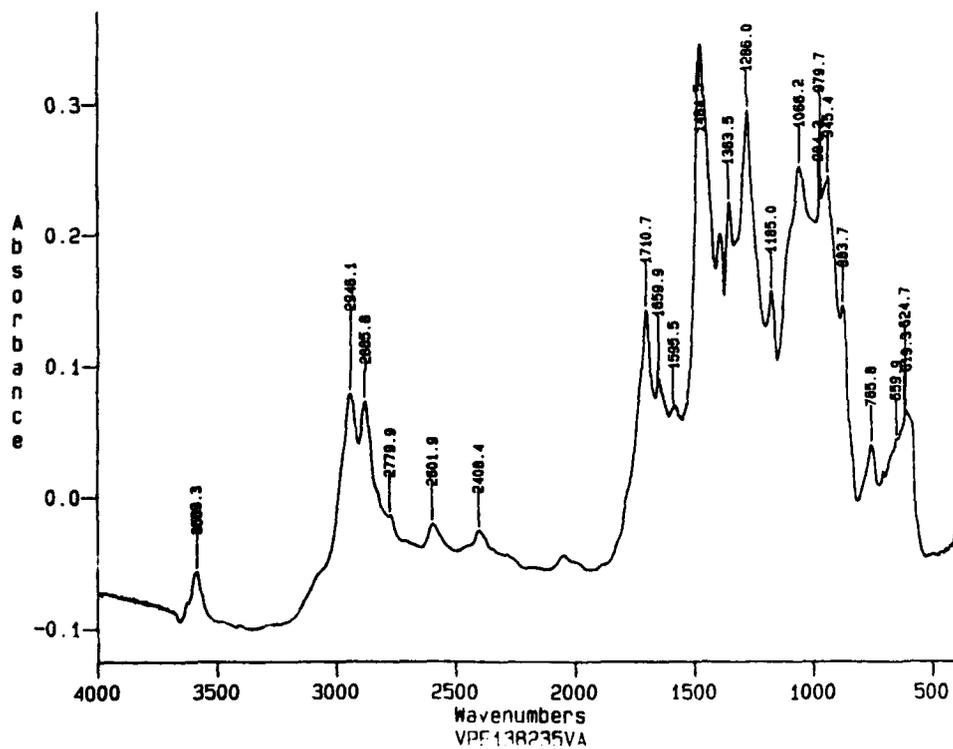


Figure 12. FT-IR spectrum of PTFPPV obtained from the reaction of BBMTFB and NaH in the second preparation and heated under vacuum at 225 °C.

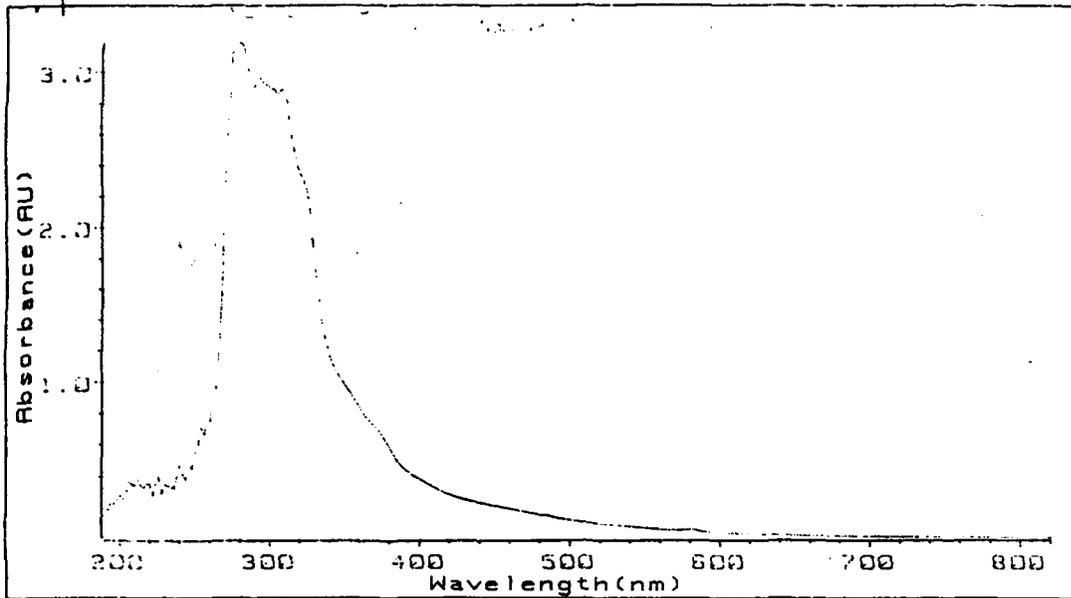


Figure 13. UV-VIS spectrum of DMF soluble PTFPPV polymer prepared by the reaction of BBMTFB and NaH.

ESCA SURVEY 6/24/91 ANGLE= 45 deg ACO TIME=25.01 min
 FILE: WPE1381 SCOTCH TAPE SURVEY TO COMPARE WITH PONDRE ON TAPE
 SCALE FACTOR= 0.311 k c/s, OFFSET= 0.007 k c/s PASS ENERGY= 89.450 eV Al 300 W

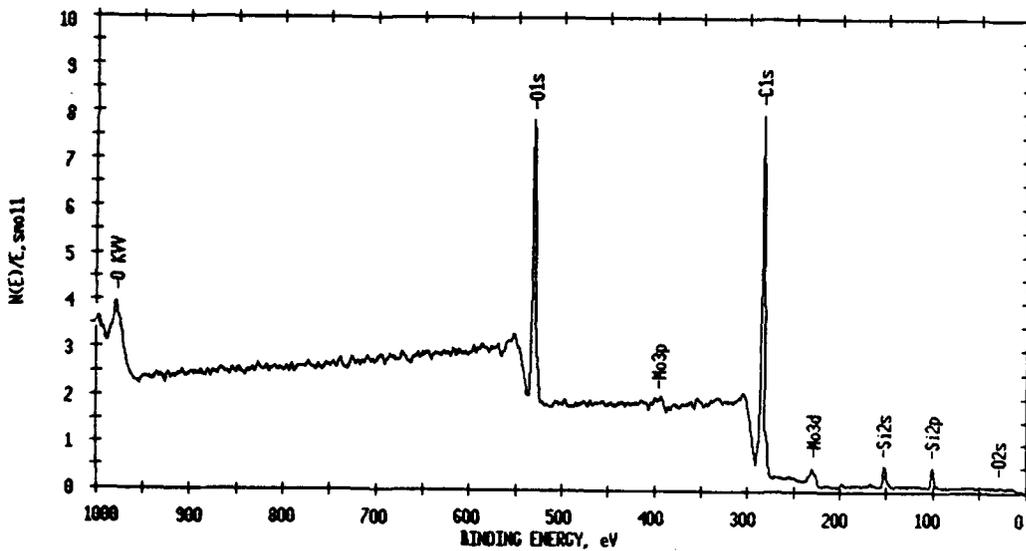


Figure 14. XPS survey spectrum of scotch tape.

ESCA SURVEY 6/24/91 ANGLE= 45 deg ACO TIME=15.01 min
FILE: VPE1382 POWDER SAMPLE ON SCOTCH TAPE
SCALE FACTOR= 0.666 k c/s, OFFSET= 0.002 k c/s PASS ENERGY= 89.450 eV Al 300 W

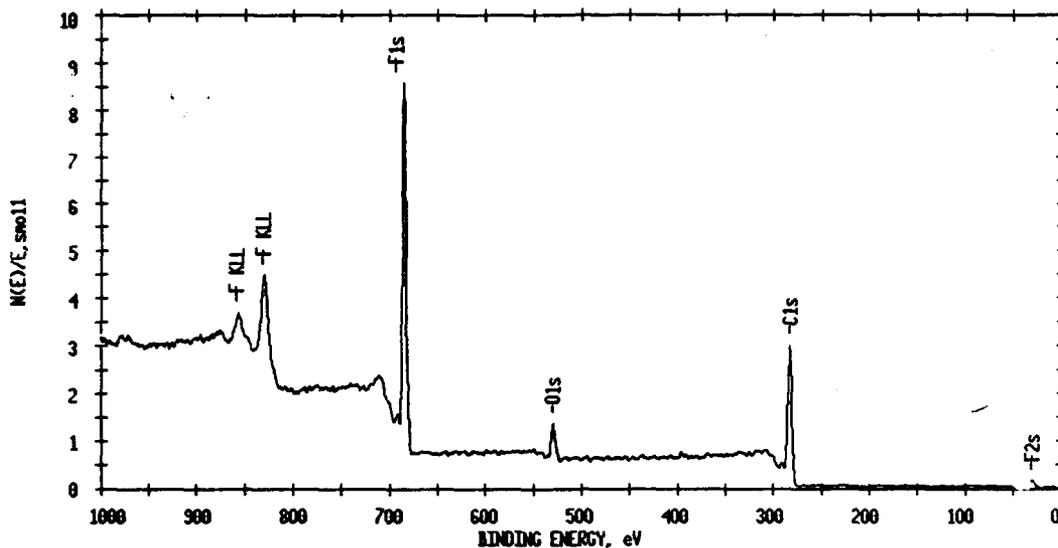


Figure 15. XPS survey spectrum of PTFPPV obtained from the reaction of BBMTFB and NaH in the second preparation and heated under vacuum at 225 °C.

Sample: VPE138
Size: 11.3140 mg
Method: TGA
Comment: BBMTFB+NaH IN DMF AT 80 DEG.C

TGA

File: VPE138TGA.01
Operator: PANCH
Run Date: 06/09/91 00:56

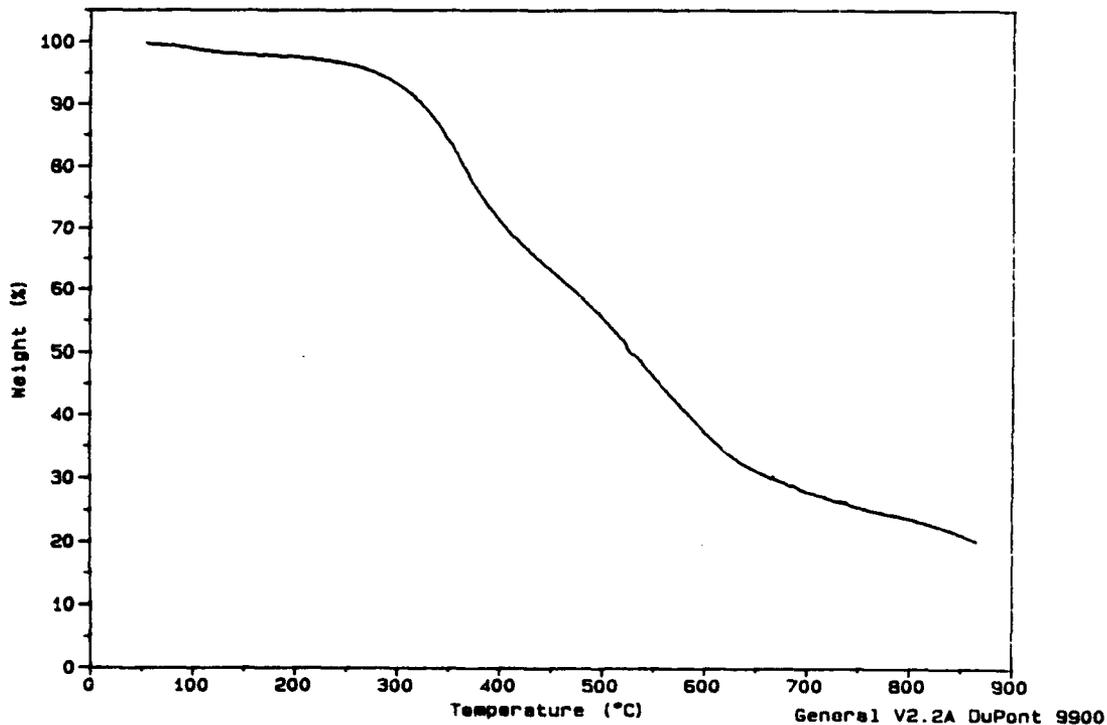


Figure 16. TGA trace of PTFPPV obtained from the reaction of BBMTFB and NaH in the second preparation.

Sample: VPE138
 Size: 8.6500 mg
 Method: TGA
 Comment: F-PPV ; BBMTFB+_NaH IN DMF; SAMPLE HEATED UNDER VACUUM AT 225

TGA

File: VPE138225V.01
 Operator: PANCH
 Run Date: 06/22/91 12:18

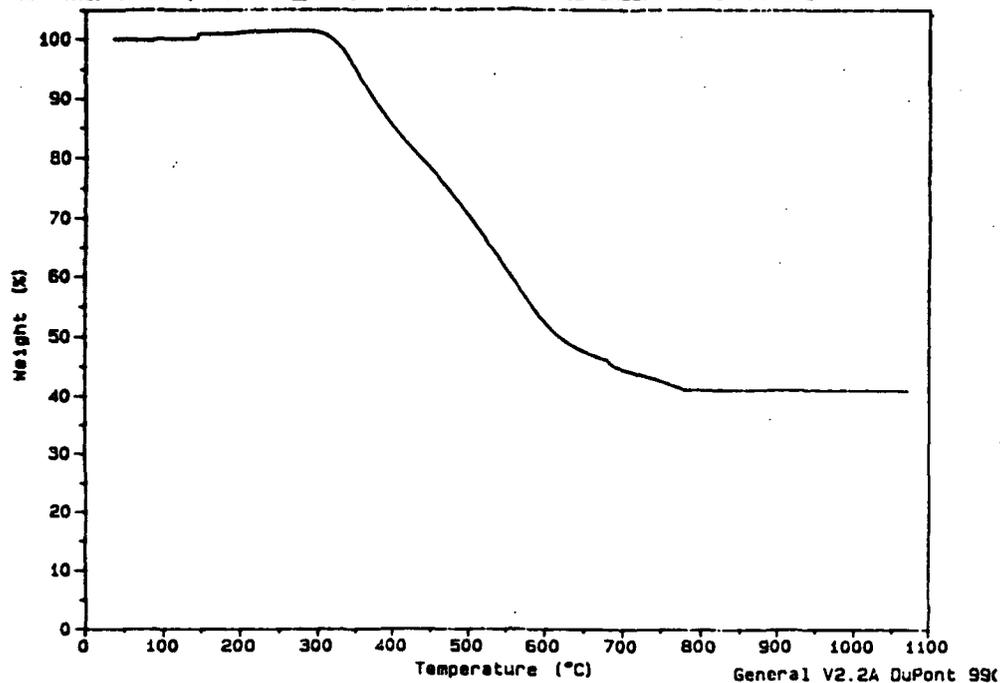


Figure 17. TGA trace of PTFPPV obtained from the reaction of BBMTFB and NaH in the second preparation and heated under vacuum at 225°C.

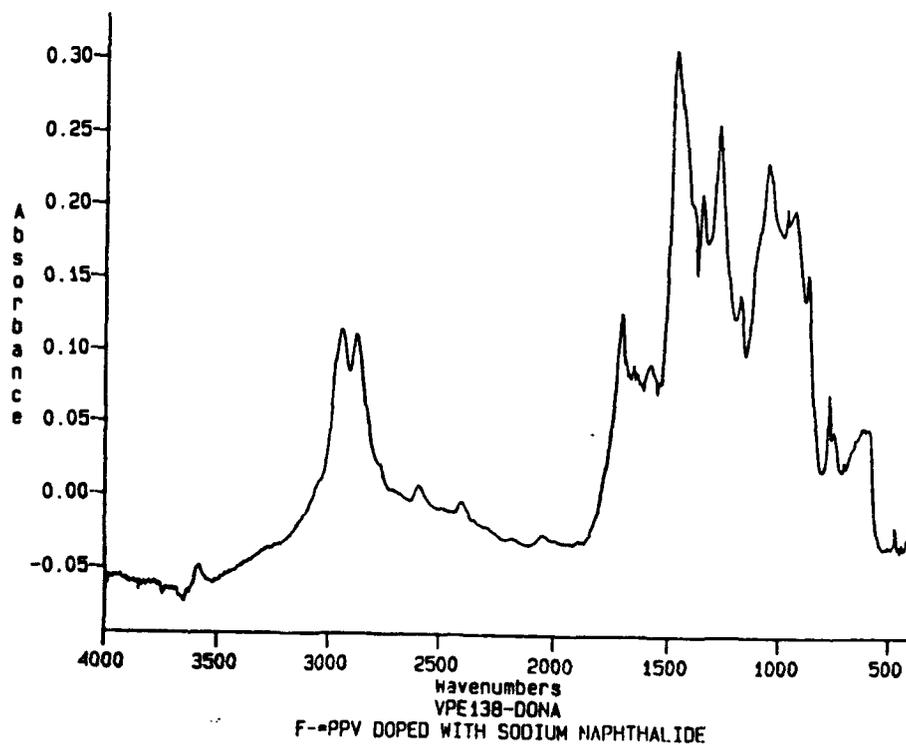


Figure 18. FT-IR spectrum of sodium naphthalide doped sample of PTFPPV obtained from the reaction of BBMTFB and NaH in the second preparation and heated under vacuum at 225°C.

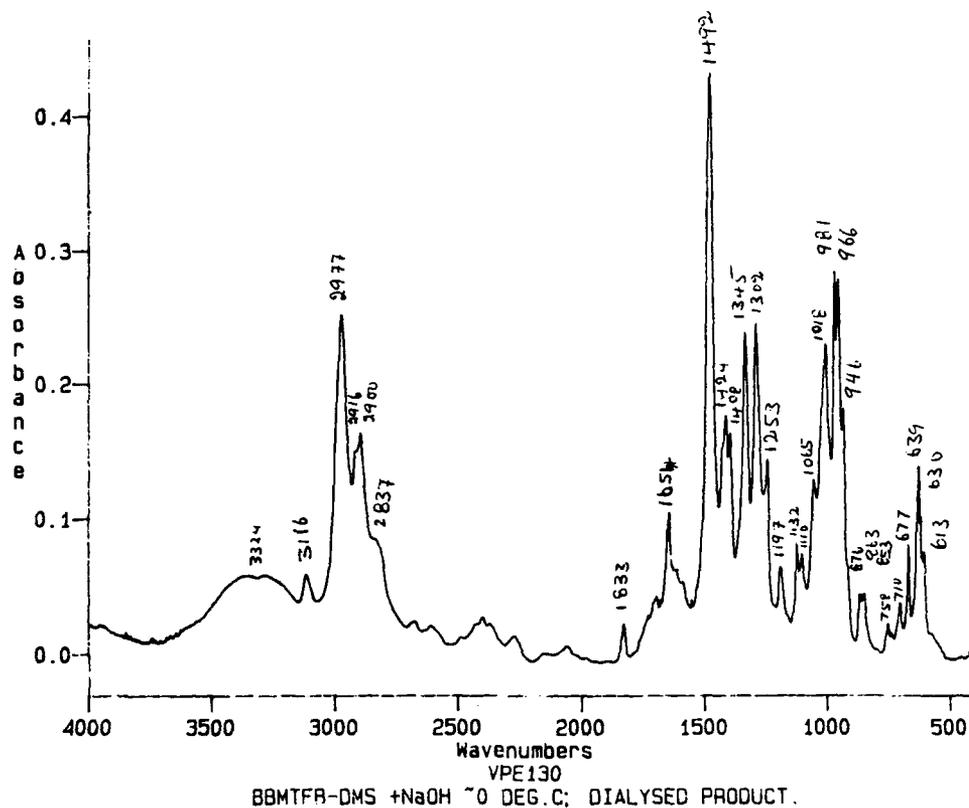


Figure 19. FT-IR spectrum of PTFFPV precursor polymer obtained from BBMTFB-DMS salt and NaOH.

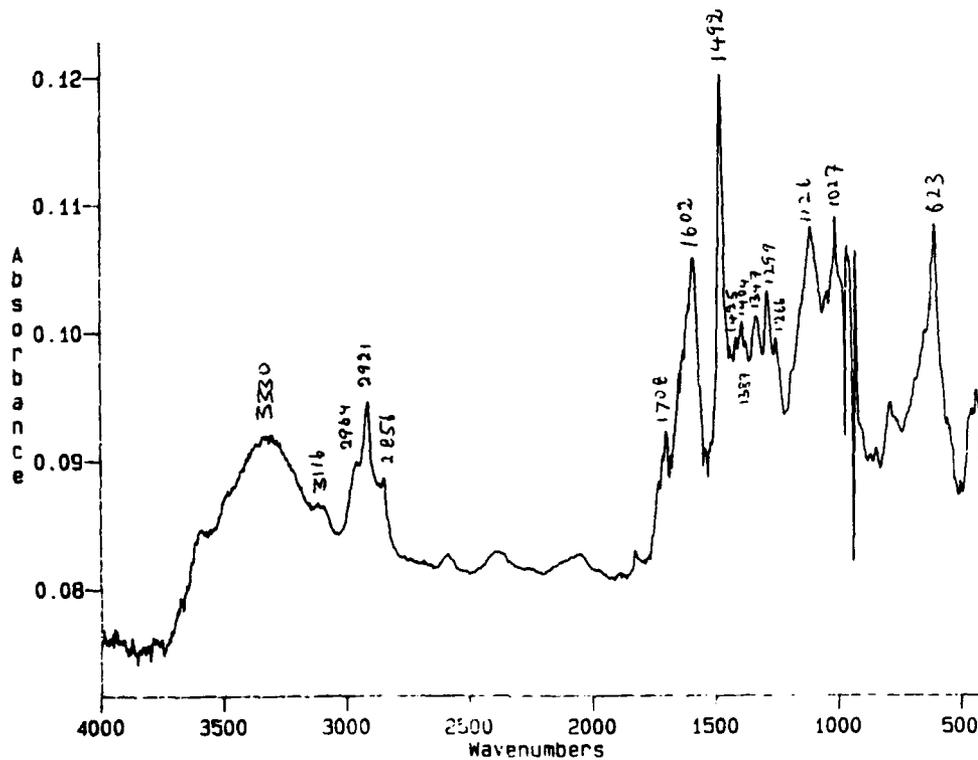


Figure 20. FT-IR spectrum of PTFFPV precursor polymer obtained from BBMTFB-DMS salt and NaOH and heated to 250°C.

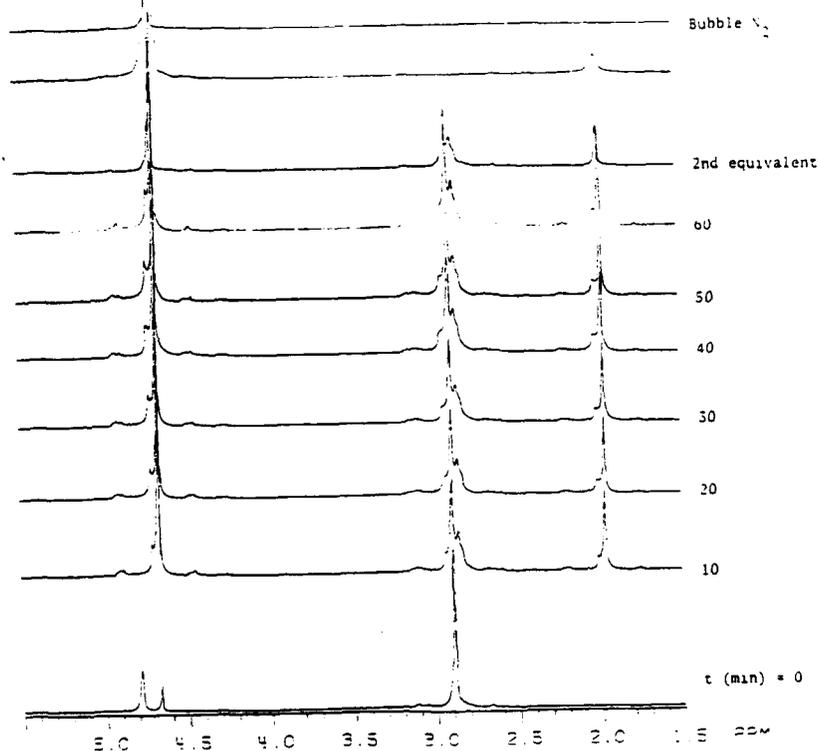


Figure 21. In-Situ $^1\text{H-NMR}$ spectra of BBMTFB-DMS salt reacted with NaOD in O_2O at room temperature.

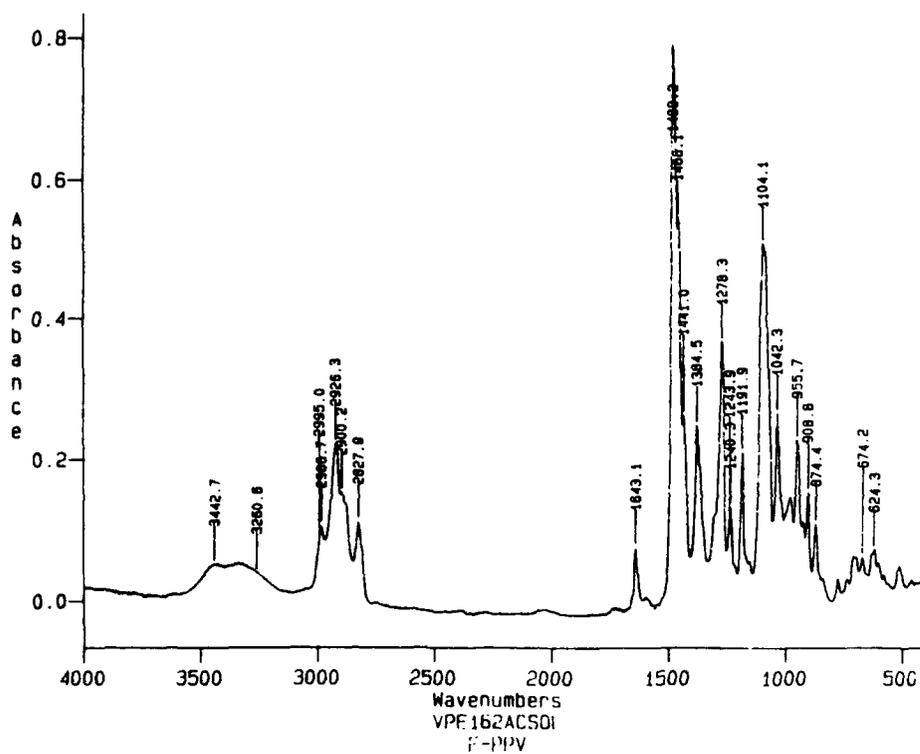


Figure 22. FT-IR spectrum of acetone soluble polymer prepared by the reaction of BBMTFB-DMS salt and 2 equivalent of NaOH in a mixture of water and methanol.

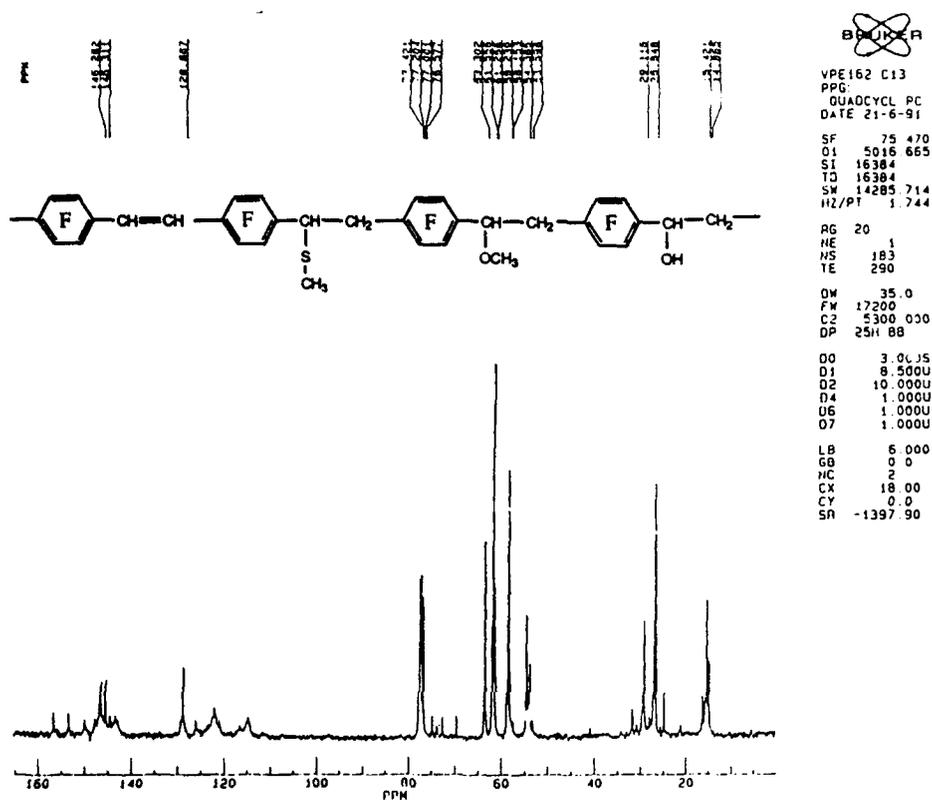


Figure 23. ^{13}C -NMR spectrum of acetone soluble polymer prepared by the reaction of BBMTFB-DMS salt and 2 equivalent of NaOH in a mixture of water and methanol.

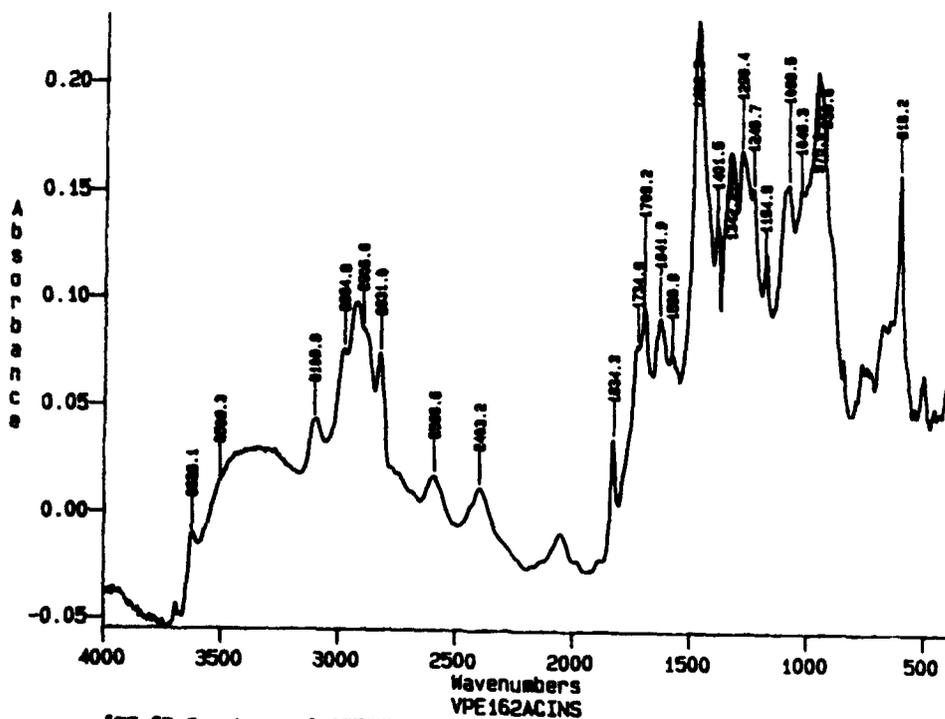
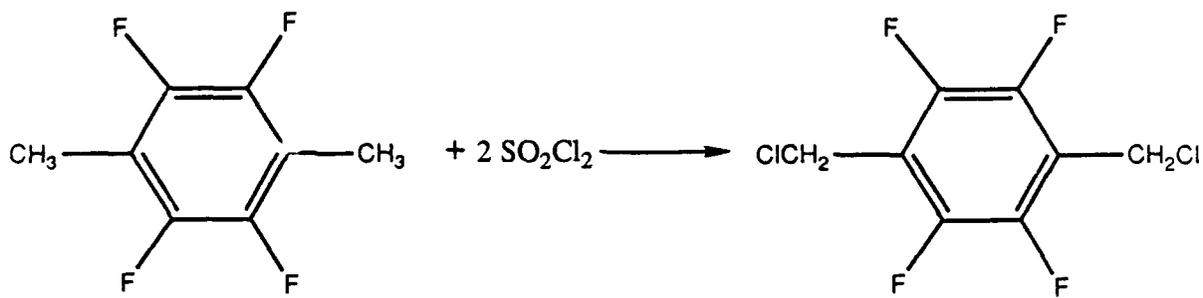
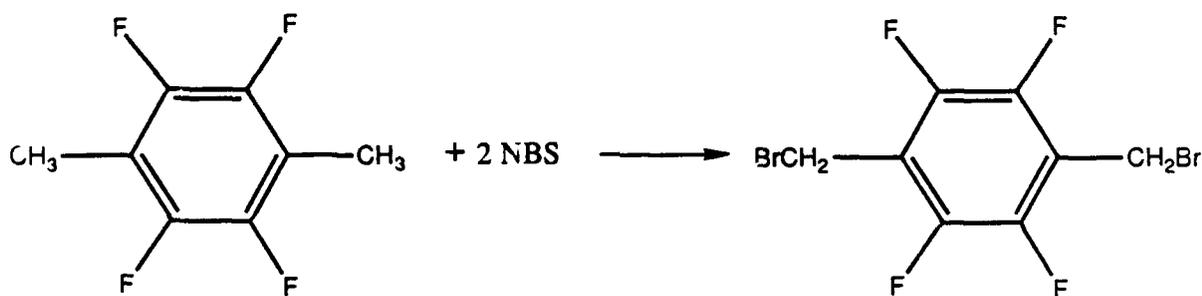


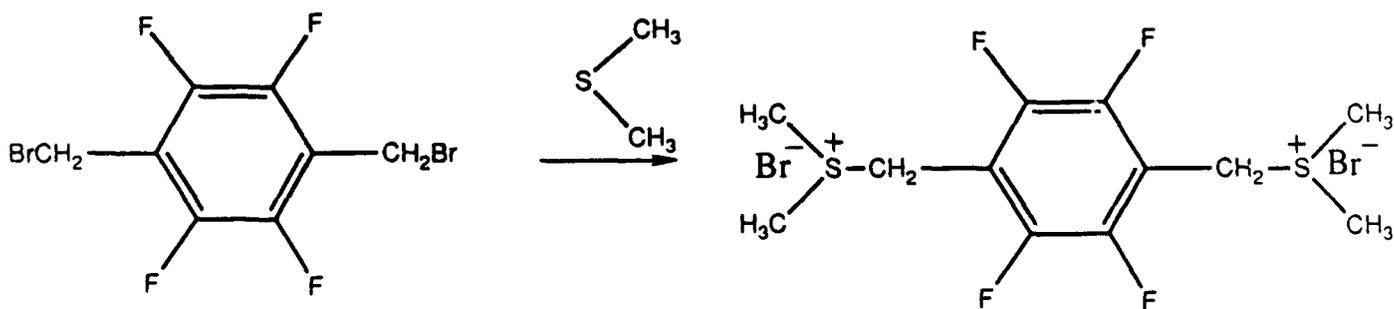
Figure 24. FT-IR spectrum of acetone insoluble polymer prepared by the reaction of BBMTFB-DMS salt and 2 equivalent of NaOH in a Mixture of water and methanol.

2,3,5,6-Tetrafluoro-*p*-Xylene (TFPX)1,4-Bis(Chloromethyl)-2,3,5,6-Tetrafluorobenzene
(BCMTFB)

Scheme II

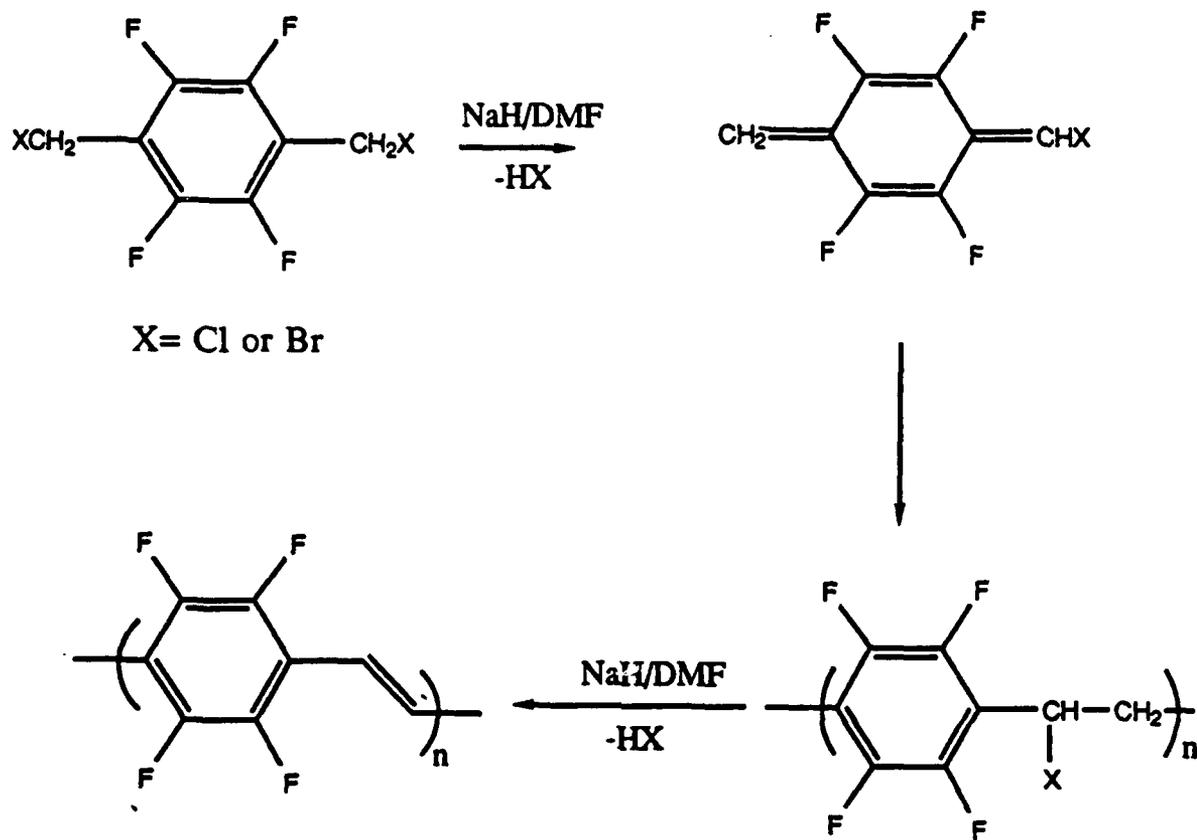
2,3,5,6-Tetrafluoro-*p*-Xylene (TFPX)1,4-Bis(Bromomethyl)-2,3,5,6-Tetrafluorobenzene
(BBMTFB)

Scheme III

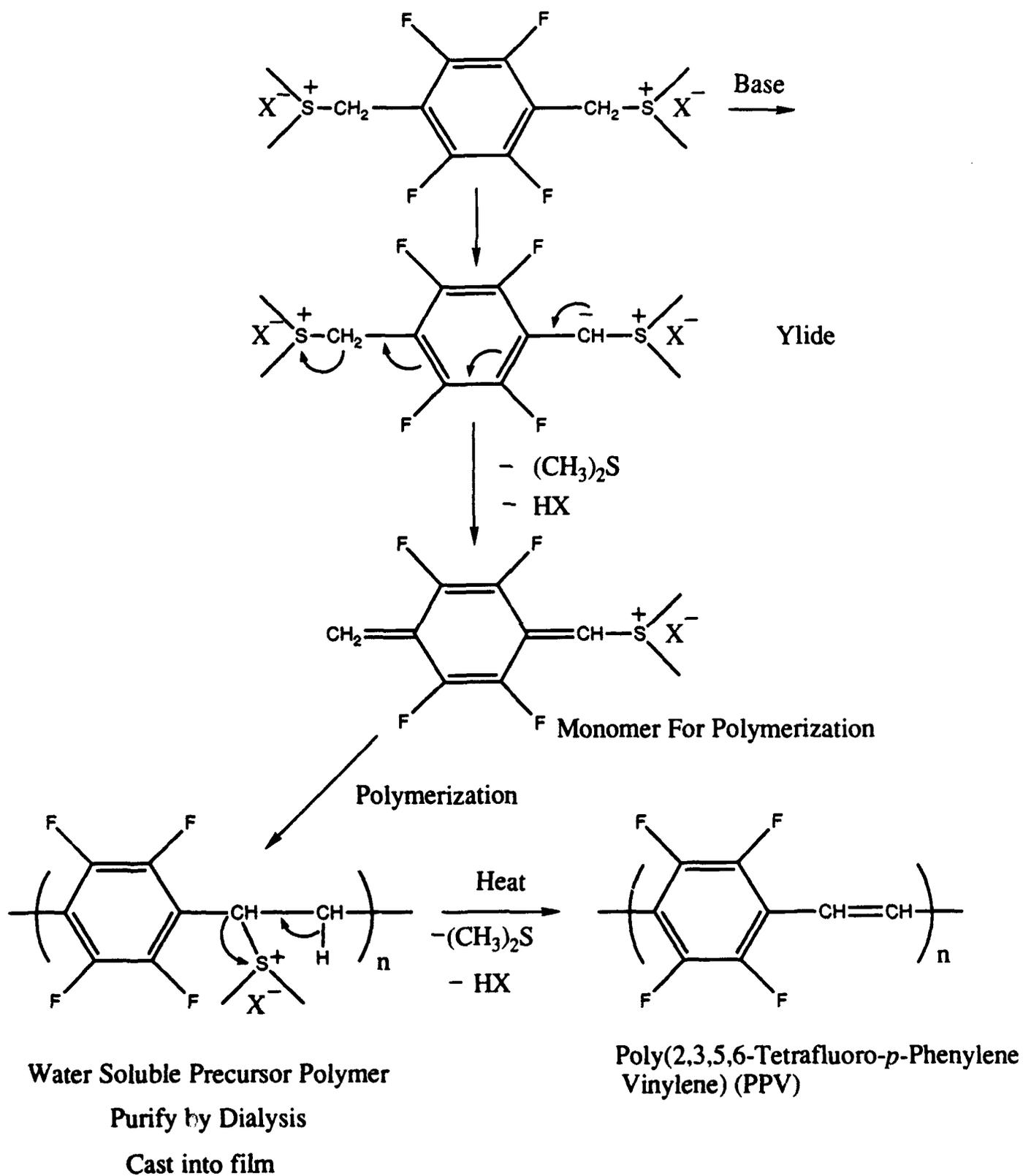
1,4-Bis(Bromomethyl)-2,3,5,6-Tetrafluorobenzene
(BBMTFB)

BBMTFB-DMS Salt

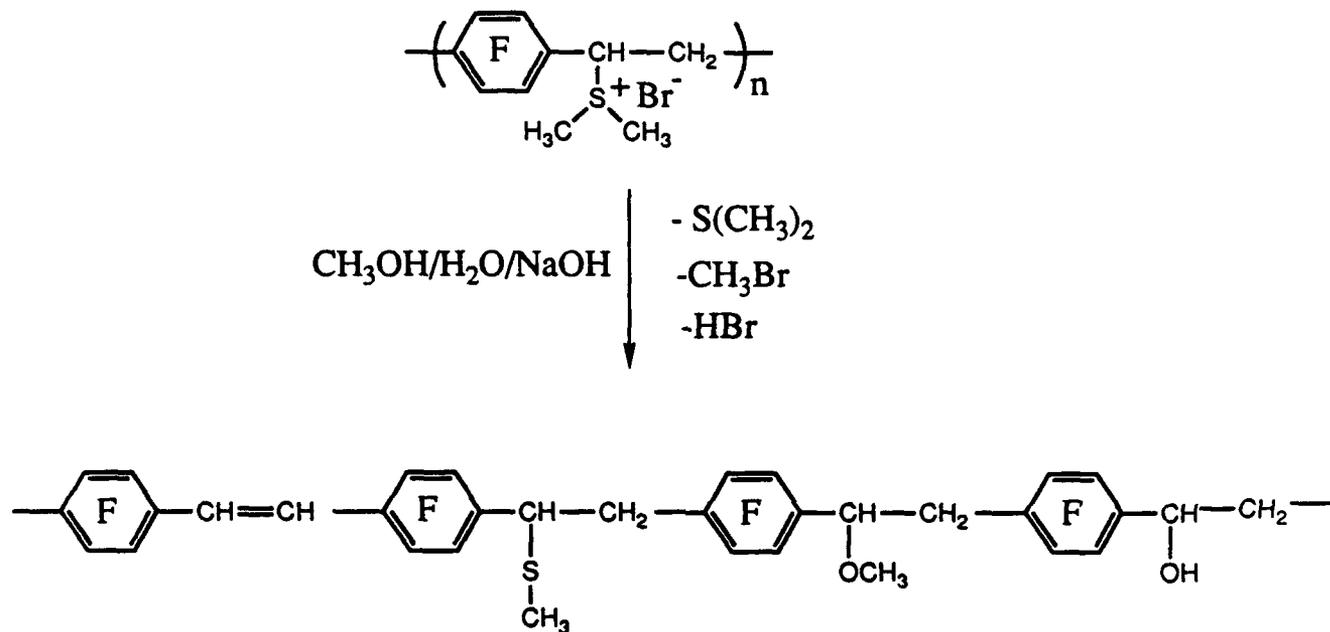
Scheme IV



Scheme V



Scheme VI



*** CONCLUDING REMARKS**

* The most direct solution to the inherent brittleness of present day high temperature
* superconductors is to form artificial composites containing the superconductor ceramic
* within a ductile host matrix. The only method that has been successful so far involves
* compaction of superconducting powder inside silver tubes, followed by drawing out
* (swaging) and annealing in an oxygen atmosphere. The oxygen can be provided by
* inclusion of a substance which releases O₂ upon heating, or by using a tube which is both
* oxygen permeable and oxygen resistant and heating in an external O₂ atmosphere.
* Results thus far have been scattered, but a wire with an I_c of about 10³ A/cm² at 77 K
* has been described (1). Problems include oxygen loss, formation of amorphous
* material, lowered density of the superconducting phase, and thick, non-superconducting
* outer layers on the grains.

* Since the properties of the material are strongly anisotropic, a method for aligning
* the grains to yield a common crystalline orientation would be useful. This is a difficult
* problem for the swaged materials. Some small amount of orientation occurs during the
* draw-down process, but significant alignment has not been reported.

* In the proposed polymer system, high degrees of orientation are possible.
* Orientation of crystallites is firmly established throughout the polymer processing
* industry. For example, oriented polystyrene forms the support tray of many see-through
* meat packages. Oriented nylon gives strength to fishing line. Bi-axially oriented Mylar
* (Dupont) is used for high strength film applications. Crystallite orientation is so
* commonly performed with polymers because it is inexpensive to accomplish and greatly
* enhances the mechanical properties. The fundamental reason for the ease of orientation
* of polymers stems from the long chain nature of the basic polymeric unit. The chains
* extend throughout both the crystalline regions and the amorphous regions. Most
* importantly, the chains extend across the boundaries between the two types of regions.
* During drawing, the chains straighten out and then pull on the sides of the crystallites to
* orient them.

* The ease of orientation gives polymeric superconductors two important advantages
* over ceramic materials. First, orientation gives the polymer great strength in the
* machine direction. The second, and even more important aspect of orientation, has to
* do with critical currents. As is well known in ceramic superconductors, the critical
* depends on orientation. Since polymers can be very highly oriented, they have the
* potential for high critical currents which so far have been seen only in thin films of the
* ceramic superconductors.

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- * A recent breakthrough in polyacetylene work gives additional support to our notions
- * on polymeric superconductors. By modifying the Shirakawa method, a group at BASF
- * (Germany) produced highly oriented, low defect density material with a normal-state
- * conductivity almost equal to that of copper.

REFERENCES

1. 1st European Workshop on High T_c Superconductors and Potential Applications, Genoa, Italy (3 July 1987).