SYNTHESIS AND CHARACTERIZATION OF MONOACETYLFERROCENE ADDED SULFONATED POLYSTYRENE IONOMERS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
THE MIDDLE EAST TECHNICAL UNIVERSITY

BY

ARZU BÜYÜKYAĞCI

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
OF
MASTER OF SCIENCE
IN
THE DEPARTMENT OF CHEMISTRY

JANUARY 2004

Approval of the Graduate School of Natural and Applied Science

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Hüseyin İşçi
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. Leyla Aras
Supervisor

Examining Committee Members

Prof. Dr. Duygu Kısakürek (Chairman)

Prof. Dr. Leyla Aras

Prof. Dr. Zuhal Küçükyavuz

Prof. Dr. Ali Usanmaz

Assist.Prof. Dr. Göknur Bayram

ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF MONOACETYLFERROCENE ADDED SULFONATED POLYSTYRENE IONOMERS

Büyükyağcı, Arzu
M.Sc., Department of Chemistry
Supervisor: Leyla Aras, Prof. Dr.

January 2004, 59 pages

Incorporation of monoacetylferrocene to the sulfonated polystyrene ionomers imparted some changes in the properties of sulfonated polystyrene. Sulfonation was carried out by acetic anhydride and concentrated sulphuric acid. The sulfonation reaction and the degree of sulfonation were determined by analytical titration and adiabatic bomb calorimeter .

For this purpose, sulfonated polystyrene (SPS) samples with varying percentages of sulfonation were prepared between 0.85% and 6.51%. Monoacetyl ferrocene was used in equivalent amount of sulfonation through addition procedure.

FTIR Spectroscopy was one of the major techniques used to support the successful addition of AcFe to the SPS samples. Altering the sulfonation degree did not change the characteristic peak positions, but increased the peak intensities with increasing the degrees of sulfonation.

Mechanical properties of resultant polymers were investigated. As a result, elastic modulus of polymers decreased by the amount of monoacetylferrocene.

Thermal characteristic were found by Differential Scanning Calorimeter (DSC). Thermal analysis revealed that sulfonated polystyrene samples after addition of monoacetylferrocene displayed lower values of T_g.

Microscopic analysis were made by Scanning Electron Microscopy (SEM) and single phase for each sample was observed. Besides, energy dispersed micro analysis showed an increase in the intensity of the iron (II) peaks that is related to the amount of monoacetylferrocene added to the SPS samples.

Flame retardancy for each polymer was also examined and found that addition of monoacetylferrocene to sulfonated polystyrene does not change the Limiting Oxygen Index value (LOI)(17). However, LOI value for polystyrene is 18.

Keywords: Ionomer, Sulfonated Polystyrene, Monoacetylferrocene, Adiabatic Bomb Calorimeter, Elastic Modulus, Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM).

ÖZ

MONOASETİLFERROSEN EKLENMİŞ SULFONLANMIŞ POLİSTİREN İYONOMERLERİNİN SENTEZİ VE KARAKTERİZASYONU

Büyükyağcı, Arzu
Yüksek Lisans, Kimya Bölümü
Tez Yöneticisi: Prof. Dr. Leyla Aras

Ocak 2004, 59 sayfa

Sülfonlanmış polistiren iyonomerlerine monoasetilferrosen katılması bu malzemelerin özelliklerinde büyük değişikliklere neden olabilmektedir. Polistirenin sülfonlanması asetik anhidrid ve konsantre sülfürik asit kullanılarak gerçekleştirilmiştir ve sülfonlanma derecesi analitik titrasyon ve adyabatik bomba kalorimetresi ile tayin edilmiştir.

Bu amaç için, sülfonlanma dereceleri %0.85 ile %6.51 arasında değişen sülfonlanmış polistiren örnekleri hazırlanmış ve sülfonlanma miktarına eşdeğer oranda monoasetilferrosen ilave edilmiştir.

FTIR Spektrofotometresi, monoasetilferrosenin başarılı bir şekilde sulfonlanmış polistiren örneklerine katılmasını destekleyen en önemli tekniklerden biridir. Sülfonlanma derecelerini değiştirmek karakteristik bant pozisyonlarını değiştirmemiş ancak bant şiddetlerini arttırmıştır.

Elde edilen polimerlerin mekanik özellikleri ölçülmüş ve elastik modül değerlerinin monoasetilferrosen miktarı ile ters orantılı olduğu saptanmıştır.

Isıl özellikleri DSC ile tayin edilmiş ve monoasetilferrosen katılmış sülfonlanmış polistiren örneklerinin T_g değerlerinin sülfonlanmış polistiren örneklerinin T_g değerlerinden düşük olduğu gözlenmiştir.

SEM analizi sonuçlarında, örneklerin homojen bir karışım olduğu saptanmış ve enerji dağılımlı mikro analiz sonuçlarından monoasetilferrosen miktarı arttıkça demir(II) sinyal şiddetinin arttığı görülmüştür.

Örneklerin yanmazlık özellikleri LOI tayini ile incelenmiş ve polistirenden (LOI 18) pek farklı olmadıkları görülmüştür (LOI 17).

Anahtar kelimeler: İyonomer, Sülfonlanmış Polistiren, Monoasetilferrosen, Adyabatik Bomba Kalorimetresi, Elastik modül, DSC, SEM.

To my family...

ACKNOWLEDGEMENTS

I deeply present my gratitude to my Supervisor Prof. Dr Leyla Aras for her guidance, inspiration and encouragement throughout my M.S study. Not only did I benefit from her profound knowledge and enermous enthusiasm, but I also profited from her wonderful personality.

I would like to express my special thanks to my lab-mates, Cemil Alkan, Funda Çelebi, Evrim Şen, Tuba Ecevit, Özlem Akın and Ahu Dumanlı for their endless helps and friendships and Güralp Özkoç for his helps through the mechanical testing of my samples.

I would like to thank to Park Teknik Elektrik Maden San. Ve Tic. A.Ş. and the personal for their support and technical assistance.

Finally, I would like to thank to my family for their never ending encouragement, support and love.

TABLE OF CONTENTS

ABSTRACT... iii
ÖZ.. v
DEDICATION... vii
ACKNOWLEDGEMENS... viii
TABLE OF CONTENTS... ix
LIST OF TABLE.. xi
LIST OF FIGURES.. xii

CHAPTER

1. INTRODUCTION.. 1
  1.1 Ionomers…………………….. 1
    1.1.1 Ionomer Structures.. 2
    1.1.2 Synthesis of Ionomers.. 3
  1.2 Homogeneous Sulfonation of Polymers... 4
    1.2.1 Sulfonation of Small Organic Molecules..................................... 5
    1.2.2 Sulfonation of Polymers………………………………………. 6
  1.3 Organometallic Compounds…………………………………………… 6
  1.4 Methods of Characterization of Ionomers.. 8
    1.4.1 Thermal Analysis of Polymers……... 8
    1.4.2 Mechanical Analysis of Polymers 10
  1.5 Adiabatic Calorimetry…………………....................................... 12
  1.6 Aim of the Study…………………………………………………... 17

2. EXPERIMENTAL... 18
- 2.1 Chemicals.. 18
- 2.2 Instrumentation.. 19
- 2.3 Preparation of Samples.. 20
  - 2.3.1 Synthesis of Sulfonated Polystyrene 20
  - 2.3.2 Sulfonation Degree Determination.. 20
  - 2.3.3 Addition of Monoacetylferrocene to Sulfonated Polystyrene.. 21
- 2.4 Calorimetric Analysis... 21
- 2.5 Preparation of Samples for FTIR Analysis.................................. 23
- 2.6 Preparation of Samples for Mechanical Analysis........................ 23
- 2.7 Limiting Oxygen Index Test.. 23

3. RESULTS AND DISCUSSION... 25
- 3.1 FTIR Analysis Results... 25
- 3.2 Sulfonation Degree Determination.. 29
  - 3.2.1 Titration Method.. 30
- 3.3 Adiabatic Bomb Calorimeter Measurements................................ 31
- 3.4 Differential Scanning Calorimeter Results.................................. 32
- 3.5 Limiting Oxygen Index Test Results... 34
- 3.6 Mechanical Analysis Results.. 35
- 3.7 Scanning Electron Microscopy Results....................................... 37

4. CONCLUSIONS.. 41

REFERENCES... 44

APPENDICES.. 50
- A. Fourier Transform Infrared (FTIR) Spectrums................................. 50
- B. Differential Scanning Calorimetry (DSC) Thermograms................... 54
- C. Mechanical Analysis Data... 59

LIST OF TABLES

TABLE

3.1. Some characteristic peaks for PS and SPS.. 25
3.2. Some characteristic peaks for Monoacetylferrocene.............................. 26
3.3. Titration results of SPS samples.. 30
3.4. T_g values from DSC.. 33
3.5. LOI values of the polymers.. 34
3.6. Modulus of elasticity values... 35
C.1. Mechanical property data……………………………………………… 59

LIST OF FIGURES

FIGURE

1.1. Restricted mobility model of Eisenberg et.al.. 2
1.2. Idealized stress-strain curve………………... 11
1.3. Schematic representation of the oxygen bomb..................................... 12
1.4. Adiabatic bomb calorimeter... 13
2.1. The limiting oxygen index apparatus... 24
3.1. FTIR spectrum of AcFe... 27
3.2. FTIR spectrum of (a) 3.66 % SPS/AcFe, (b) 3.66 % SPS..................... 28
3.3. Calorific values vs. % SPS and % AcFe/SPS graphs........................... 32
3.4. Modulus of elasticity vs. Sulfonation degree graph.............................. 36
3.5. Modulus of elasticity vs. % amount of AcFe.. 36
3.6. SEM photograph of 0.845 % SPS... 38
3.7. SEM photograph of 0.845 % AcFe/SPS.. 38
3.8. SEM photograph of 2.21 % SPS... 39
3.9. SEM photograph of 2.21 % AcFe/SPS.. 39
3.10. SEM photograph of 3.66 % SPS... 40
3.11. SEM photograph of 3.66 % AcFe/SPS.. 40
4.1. The most probable structure of the resultant polymer........................... 43
A.1. FTIR spectrum for PS.. 50

A.2. FTIR spectrum of (a) 0.845 % AcFe/SPS, (b) 0.845 % SPS................ 51
A.3. FTIR spectrum of (a) 2.21 % AcFe/SPS, (b) 2.21 % SPS................... 51
A.4. FTIR spectrum of (a) 0.845 % AcFe/SPS, (b) 0.845 % SPS................ 52
A.5. FTIR spectrum of (a) 2.21 % AcFe/SPS, (b) 2.21 % SPS................... 52
A.6. FTIR spectrum of (a) 3.66 % AcFe/SPS, (b) 3.66 % SPS................... 53
B.1. DSC thermogram of PS.. 54
B.2. DSC thermogram of 0.95 % SPS... 55
B.3. DSC thermogram of 0.95 % AcFe/SPS.. 55
B.4. DSC thermogram of 1.87 % SPS... 56
B.5. DSC thermogram of 1.87 % AcFe/SPS.. 56
B.6. DSC thermogram of 2.21 % SPS... 57
B.7. DSC thermogram of 2.21 % AcFe/SPS.. 57
B.8. DSC thermogram of 3.98 % SPS... 58
B.9. DSC thermogram of 3.98 % AcFe/SPS.. 58

CHAPTER 1

INTRODUCTION

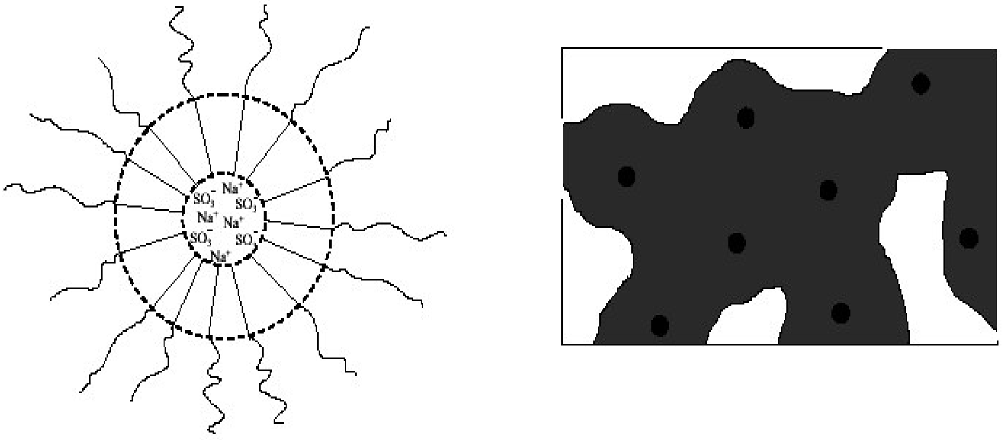
1.1. Ionomers

During the last 30 years, scientists have been fascinated by the class of polymers known as ionomers. Ionomers are normally defined as ion-containing polymers with a maximum ionic group content of about 15 mol % or less [1]. The literature in this field has grown exponentially and a large number of conferences on the topics have been held [2-8]. Many reviews, articles [9-13] and edited volumes have also been published on the subject of ionomers [14-20]. The wide range of compositions, molecular architectures, and morphologies present in ionomeric systems are of great interest to experimentalists as well as theoreticians. As expected, polymer scientists are particularly interested in the potential application of these materials, based on an understanding of their fundamental principles. The common thread in most of the research efforts to date was the knowledge that the presence of ionic groups, even in small amounts, dominates the viscoelastic behavior of ionomers, their thermal stability and mechanical properties, their transport properties, and their ability to sorb a variety of solvents.

As reported in many papers, review articles, [21-22] and books, [23-24], ionomers are extremely complex systems, sensitive to changes in structure and composition, and therefore not easily amenable to modeling and to the derivation of general patterns of behavior.

1.1.1. Ionomer Structures

Ionomers can be interpreted in the context of such as restricted mobility (RM) model of Eisenberg and co-workers [25]. The basic assumption of the RM model is that at low ionic concentrations, ionic moieties aggregate into loosely defined multiplets consisting typically of 2-8 ion pairs (Figure 1.1). The formation of these aggregates is induced by electrostatic forces associated with the ionic moieties, which must overcome the entropic and elastic forces exerted by the hydrocarbon chains to which they are attached.



Multiplet
(2-8 ion pairs, < 50 Å)

Ionic clusters
(phase separation, > 50 Å)

Figure 1.1. Restricted mobility model of Eisenberg et al.: left, a schematic of a multiplet and its restricted mobility shell; right, a schematic two-dimensional representation of a cluster. Solid spheres are the ionic multiplets, the hatched area is the restricted mobility domain, and the unmarked area is the unclustered hydrocarbon matrix [27].

This restricted mobility “corona” surrounding the multiplet core is distinct from the bulk polymer matrix, and its size is dependent on the aggregation number of the multiplet and the stiffness of the polymer backbone. Typically, the size of this corona/core entity is too small (<50 Å) to form a distinct phase and, thus, its effect is limited to that of a physical cross-link. As the ion content is increased, the number of multiplets grows and the restricted mobility “corona” of neighboring multiplets start to overlap and coalesce until a point is formed whose size is sufficiently large to be considered as a distinct phase (Figure 1.1). This aggregate of several multiplets is known as a *cluste*r. In a cluster structure, two glass transition temperatures can often be observed due to phase separation [26].

1.1.2. Synthesis of Ionomers

Ionomers have been prepared by two general routes:

i) copolymerization of a low level of functionalized monomer with an olefinically unsaturated comonomer

ii) direct functionalization of a preformed polymer. Almost all ionomers of practical interest have contained either carboxylate or sulfonate groups as the ionic species. Other salts, such as phosphonates, sulfates, thioglycolates, ammonium, and pyridinium salts have been studied.

Typically, carboxylate ionomers are prepared by direct copolymerization of acrylic or methacrylic acid with etylene, styrene or similar comonomers by free radical copolymerization [28]. Recently, a number of copolymerization involving sulfonated monomers have been described. For example, Weiss et al. [29-32] prepared ionomers by a free-radical, emulsion copolymerization of sodium sulfonated styrene with butadiene or styrene. Similarly, Allen et al. [33] copolymerized n-butyl acrylate with salts of sulfonated styrene. The ionomers prepared by this route, however were reported to be ‘blocky’ with regard to the incorporation of the sulfonated styrene monomer.

The second method used to prepare ionomers involves functionalizing a preformed polymer. This has been the more common strategy for obtaining sulfonate-ionomers. Makowski et al. [34-35] prepared lightly sulfonated polystyrene (SPS) ethylene-propylene-diene terpolymers (SEPDM) by a reaction of the polymers with acetyl sulfate in homogeneous solution. This chemistry yields a controlled concentration and a random distribution of sulfonate groups. Bishop et.al [36,37] described the sulfonation of poly(ether ether ketone) with chlorosulfonic acid or sulfuric acid.

1.2. Homogeneous Sulfonation of Polymers

Sulfonation is defined as a substitution reaction used to attach the $-SO_3$ group on a molecule of an organic compound via chemical bond to carbon or, less frequently to a nitrogen atom of the organic compound. Compounds such as H_2SO_4, SO_3 and its complexes, such as acyl and alkyl sulfates and chlorosulfonic acid are commonly used as sulfonating agents.

Sulfonation precedes easily for the aromatics, even though the dissociation energy of the C-H bond is higher in aromatic (428 kj/mol) than aliphatic(374 kj/mol) compounds. This phenomenon is assumed to be caused by the two-step reaction mechanism where the rate of SO_3 insertion to hydrocarbon alone cannot control the reaction rate. While only one SO_3H group can attach to aromatic ring, in aliphatic chains one, two or three SO_3H groups can be attached.

Sulfonated ionomers are defined as macromolecular compounds containing sulfonic ($-SO_3$) groups. These compounds are utulized satisfactorily, because of their interesting chemical and mechanical properties, in a number of industrial applications e.g. for production of compatible blends of nonmiscible polymers, ion exchange materials, membranes for reverse osmosis and ultrafiltration, plasticizers for macro-defect-free concretes, and conductive composites [38].

1.2.1. Sulfonation of Small Organic Molecules

Conventional methods for the preparation of sulfonated low molecular weight aromatic compounds by homogeneous sulfonation in a solution, is frequently done by H_2SO_4 as the sulfonating agent. An aromatic ring can be sulfonated in a reaction with sulfonic cation (SO_3H^+), which arises from concentrated sulfuric acid. Acetic acid, acetic anhdyride, tetra chloromethane or an excess of substrate were the preferred solvents used in these sulfonation reactions. Eq 1.1. and 1.2. show the origin of sulfonic cation by disproportination of H_2SO_4.

$$2H_2SO_4 \longrightarrow H_3SO_4^+ + HSO_4^- \qquad \text{Eq 1.1.}$$

$$H_3SO_4^+ \longrightarrow H_2O + HSO_3^+ \qquad \text{Eq 1.2.}$$

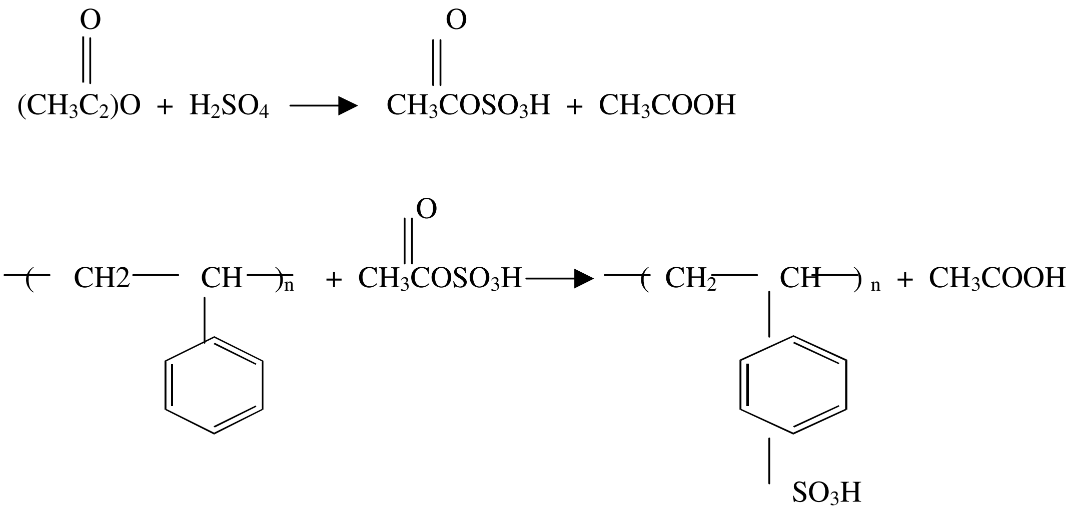
The addition of stabilizing acetic acid was used to reduce the formation of sulfones in this reaction. The concentration of free SO_3 decreased after addition of the acetic acid and sulfur trioxide; the acetyl sulfate, and sulfuric acid were found to exist in equilibrium. Equation 1.3. describes the mechanism of acetic acid effect on the sulfonation agent [39].

$$CH_3COOH + SO_3 \longleftrightarrow CH_3COOSO_3H + CH_3COOH \longleftrightarrow (CH_3CO)_2 + H_2SO_4$$

Eq 1.3.

1.2.2 Sulfonation of Polymers

The principles of the sulfonation reactions with molar mass compound and polymers are identical. Sulfonation kinetics is however, altered and some hindrances to sulfonation arise as a result of steric effects caused by the size of substrate molecules. Equation 1.4. describes the appropriate reaction scheme for sulfonation of Polystyrene.



$$(CH_3C_2)O + H_2SO_4 \longrightarrow CH_3COSO_3H + CH_3COOH$$

Eq 1.4.

1.3. Organometallic Compounds

Since the early 1950s, the rapid development of the organometallic chemistry of the transition elements has resulted in a tremendous variety of new and often remarkable molecular structures and a range of novel catalytic species [40]. Recently, interest in organotransition metal compounds has been extended to the materials science interface. For example, in the past decade or so, organometallic materials with novel magnetic, electrical, and liquid crystalline properties have attracted considerable attention [41]. As it is well known the properties of polymers can be modified dramatically by subtle changes in chemical structure, the possibility of using organometallic structural moieties to prapare macromolecular materials with interesting and possibly useful characteristics is a very attractive one.

On the basis of these considerations, since the 1950s, the incorporation of organometallic groups into polymer structures has attracted growing attention.

The discovery of ferrocene (cyclopentadienyliron) in 1951 [42,43] has provided access to the fascinating chemistry of a class of organometallic compounds commonly called metallocenes. This class, in the generally accepted terminology, comprises transition metal complexes with one or more π-cyclopentadienyl ligands; in a somewhat broader sense, complexes with other π-bonded aromatic ring systems as ligands, may be included in this classification. The challenging synthetic and structural possibilities of the metallocenes, coupled with a highly attractive technological potential in areas such as radiation protection, combustion catalysis, rubber vulcanization, polymerization acceleration, and in a variety of reduction-oxidation reactions, have spurred considerable research activities, which are documented in an abundance of publications in the scientific, patent, and government report literature.

The structure and chemistry of ferrocene, the prototype metallocene complex, and its congeners, ruthenocene and osmocene, have been discussed profoundly by Rosenblum [44], one of the pioneering contributors to the field.

In ferrocene, the two cyclopentadienyl rings, are arranged in parallel planes, are bonded in sandwich fashion to the centra iron atom; the cyclopentadienyl C-C bond length approximates 1.43 A^o, and the distance between metal and ring C atoms is about 2.06 A^o. The rings are staggered in the crystalline compound, which is of D_{5d} symmetry; in the dissolved or gaseous states, there is substantially free rotation of the rings around the molecular axis. The metal-to- ring bonds, essentially of the dπ-pπ type, are strongly delocalized, and the aromatic character of ferrocene (and other metallocenes) results from the appreciable π-electron density remaining in the vicinity of the rings.

In macromolecular derivatives of ferrocene, the electronic absorption characteristics of the metallocene system in the visible region are essentially retained (unless highly conjugated bridging segments are present). Ferrocene polymers, as a consequence, are generally colored yellow, tan-brown, or reddish-brown, depending on the degree of conjugation achieved between metallocene and subtituent link.

Ferrocene-containing polymers possess very useful properties including high thermal stability, radiation resistance, and electroconduction. These interesting features have made them suitable for a wide spectrum of applications including heat resistant lubricants and thermally stable and heat resistant elastomers.

1.4. Methods of Characterization of Ionomers

1.4.1 Thermal Analysis of Polymers

Whenever a sample of material is to be studied, one of the easiest tests to perform is to heat it. The observation of the behavior of the sample and the quantitative measurement of the changes on heating can yield a great deal of useful information on the nature of the material. Thermal methods of analysis have developed out of the scientific study of the changes in the properties of a sample, which occur on heating. Some sample properties may be obvious to the analyst such as color, shape and dimensions or may be measured easily, such as mass, density and mechanical strength. There are also properties, which depend on the bonding, molecular structure and nature of the material. These include the thermodynamic properties such as heat capacity, enthalpy and entropy. Transformations, which change the materials in a system, will alter one or more of these properties. The change may be physical such as melting, crystalline transition or vaporization or it may be chemical involving a reaction. Which alters the chemical structure of the material. Even biological processes such as metabolism, interaction or decomposition may be included [45].

Several methods are commonly used – these are distinguished from one another by the property, which is measured. Some common thermal analysis methods are: Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Dynamic Mechanical Analysis (DMA), Thermomechanical Analysis (TMA), Dielectric Analysis (DEA).

Calorimetry is also another method for thermal characterization which is defined as the measurement of the flow of heat or work, energy arising from chemical or physical changes in a material. Calorimeters can be broadly classified in three categories: Isothermal, Adiabatic and Temperature Scanning.

- Isothermal Calorimeters: Heat energy is exchanged from a heat sink maintaining the reaction environment at a constant temperature. Modern isothermal calorimeters have a very high degree of sensitivity and can detect enthalpy changes in the order of 5 nJ.

- Adiabatic Calorimeters: These calorimeters allow a rise in temperature of the reaction temperature of the reaction system for exothermic reactions or a decrease in temperature change as a function of time. In this work, adiabatic bomb calorimeter is used to determine the sulfonation degree of sulfonated polystyrene and addition of monoacetylferrocene profile to the polystyrene ionomers.

- Temperature Scanning Calorimeters: These calorimeters provide a constant change in heat energy to pass between the samples. Two types of temperature scanning instruments are used: heat flux and power compensation [46].

1.4.2. Mechanical Analysis of Polymers

There are a number of fundamental techniques used to characterize the mechanical properties of polymers, including tensile, flexural, tear strength, fatigue, impact and hardness tests.

The degree to which a material will strain depends on the magnitude of the imposed stress. This stress (σ) is defined as the load (F) per unit area (A), given as follows:

$$\sigma = F / A \qquad \text{Eq 1.5.}$$

There are three basic types of stress measurements- *tensile stress* is the resistance of a material to streching forces, *compressive stress* is the resistance of a material to ‘ squashing ’ forces, while *shear stress* is the resistance of a material to ‘ push-pull ’ forces.

The strain (ε) is the amount of deformation per unit length of the material due to the applied load, and is given as follows:

$$\varepsilon = (l_i - l_0) / l_0 = \Delta l / l_0 \qquad \text{Eq.1.6.}$$

where l_0 is the original length of the sample before any load is applied, l_i is the instantaneous length, and Δl is the amount of elongation.

Deformation where the stress and strain are proportional is called *elastic deformation.* In such a case, a plot of stress against strain produces a linear graph.

The slope of such a plot provides the *Young's modulus* (also known as the *modulus of elasticity* or the *tensile modulus*) (*E*) of the material, a proportionality constant. The modulus can be thought of as the 'stiffness' of a polymer. The parameter *E* can be evaluated from the slope of the linear elastic portion of a force-extension curve where:

$$E = (\text{slope x gauge length}) / (\text{cross-sectional area}) \qquad \text{Eq.1.7}$$

The data derived from stress-strain measurements on thermoplastics are important from a practical viewpoint, providing as they do, information on the modulus, the brittleness, and the ultimate and yield strengths of the polymer. By subjecting the specimen to a tensile force applied at a uniform rate and measuring the resulting deformation, a curve of the type shown in figure 1.2 can be constructed.

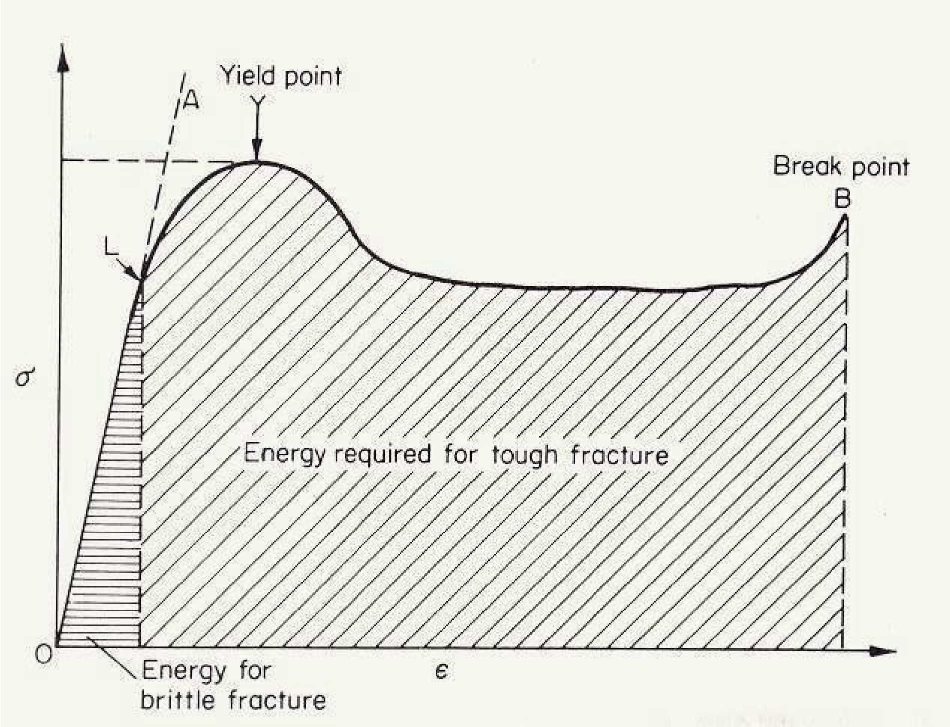


Figure 1.2. Idealized stress-strain curve. The slope of line OA is a measure of the true modulus.

1.5. Adiabatic Calorimetry

Precision measurements of the heat capacity are normally carried out in adiabatic calorimeters. The principle construction of a typical adiabatic calorimeter used for the measurements of specific heat capacities consists of an electrical source of heat, which supplies an exactly known amount of heat into the sample under study, and a temperature-measuring instrument, which determines precisely the change in temperature of the sample. In order to minimize the heat losses, the calorimeter itself is surrounded by a radiation shield, the temperature of which is electrically controlled to be very close to that of the calorimeter. The smaller the temperature difference can be kept between calorimeter and shield, the smaller is the heat loss. Normally, calorimeter and jacket are located in an evacuated insulated container. Energy input to the calorimeter is chosen in such a way as to arrive at heating rates of less than 1K/min after heating periods. The energy input is usually correlated to the heat leakage and water value of the calorimeter itself [48].

Figures 1.3. and 1.4. show schematic representations of an oxygen bomb and adiabatic bomb calorimeters respectively.

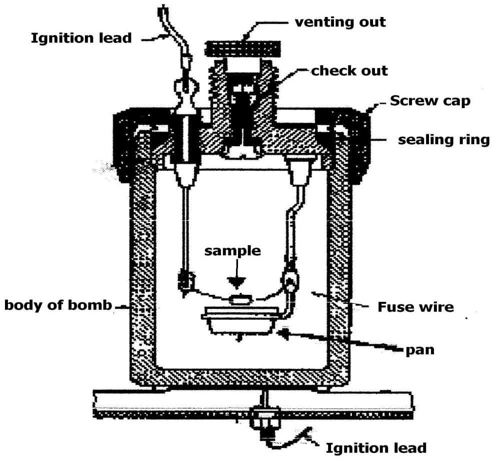


Figure 1.3. Schematic representation of the oxygen bomb [49]

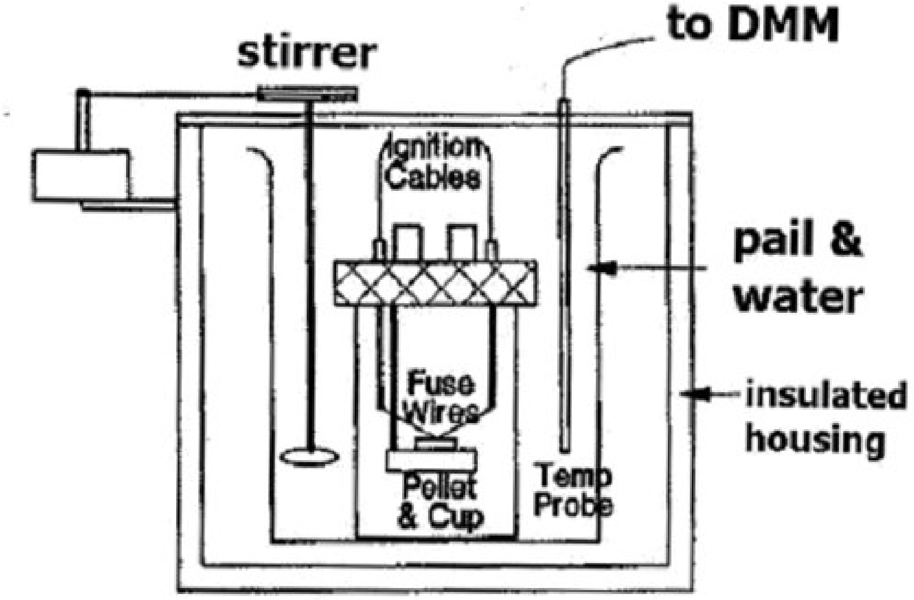


Figure 1.4. Adiabatic bomb calorimeter [49]

An average heat capacity for the heating interval for the sample of known mass m is;

$$Cp = \Delta Q / m\Delta T \quad \text{Eq 1.8.}$$

Where Cp is the mean value of the heat capacity for the given temperature rise is ΔT, ΔQ is the corrected energy input. The overall precision of typical adiabatic calorimeters is 0.1-0.5 %.

Depending on the temperature interval of operation, the adiabatic calorimeters used for the measurements of the heat capacity of polymers can be subdivided into two groups; low temperature calorimeters, which operate below 300 K and high temperature ones working in the temperature region 250-600 K.

Heat capacity measurements below about 10 K need special cryostats and low temperature thermometry.

The heat capacity measurements of polymers by means of the adiabatic calorimeters of both these groups involve some difficulties closely related to the low thermal conductivity of polymers, their low density, which lead to a very unfavorable ratio of the heat capacity of the sample and the calorimeter and, finally, the possibility of a slow temperature drift occuring resulting from the slow relaxational processes in polymers. For the high temperature measurements a very important aspect is the oxidation and degradation of polymers. The precise data on heat capacities of most polymers especially at low temperatures have been obtained by means of adiabatic calorimetry. Adiabatic calorimeters for heat capacity measurements of polymers have been described in many papers [50-52].

Adiabatic calorimetry is the most precise method of direct measurement of heat capacity of polymers, and indeed this method was used for the determination of the heat capacity of polymers such as phenolic resins [52], it has, nevertheless, some disadvantages. First of all, polymers are not perfectly suitable for adiabatic calorimetry because of their metastability and sensitivity to thermal pretreatment.

In addition, adiabatic calorimetry is rather slow and needs large samples. These problems stimulated the development of dynamic calorimetry, which is widely used nowadays for the thermal analysis of polymers including the heat capacity measurements [49].

Another feature of adiabatic calorimeters is the determination of gross and net calorific value of materials. In order to determine these values experimentally, one should know the definitions and equations for the adiabatic bomb calorimeter system;

Heat Capacity: the heat capacity C of the calorimeter system is the amount of heat which is required to raise the temperature of the measuring system by 1 K.

The heat capacity of the calorimeter system, which is required for the computation of subsequent analyses, must be determined under the same conditions as prevail in the tests by burning a standart substance of a known gross calorific value (benzoic acid) [53].

$$C = (H_{OB} \times m_B + Q_F) / \Delta T \qquad (cal / {}^{o}C) \qquad \text{Eq 1.9.}$$

Where;

H_{OB} : gross calorific value of the standart substance (cal/g)

m_B : weight of the sample weighed in air (g)

Q_F : sum of all quantities of extraneous which do not stem from the combustion of the standart (e.g. ignition energy, ignition aids, chemical reactions) (cal)

ΔT : temperature increase in the calorimeter system (${}^{o}C$) [53].

Gross Calorific Value : Gross Calorific Value is the heat produced by combustion of unit quantity of a solid or liquid fuel when burned at constant volume in an oxygen bomb calorimeter under specified conditions, with the resulting water condensed to a liquid.

The gross calorific value of the samples are calculated as;

$$Q_v(gross) = [(t \text{x} C) - e_1 - e_2 - e_3] / g \qquad \text{Eq 1.10.}$$

Where;

Q_v(gross) : gross calorific value

t : corrected temperature rise (°C)

C : heat capacity (cal/°C)

e_1 : correction for the titration of the bomb solution with Na_2CO_3 (cal)

e_2 : correction for heat of combustion of ignition wire (cal)

e_3 : correction for heat of formation of H_2SO_4 (cal)

g : mass of sample (g)

Net Calorific Value : The net calorific value is the heat produced by combustion of unit quantity of a solid or liquid fuel when burned, at a constant pressure of 1 atm (0.1 MPa), under conditions such that all the water in the products remain in the form of vapor.

The net calorific value is technically the more important parameter for the energy content of substances, since in all important technical applications it is only the net calorific value which can be utilized as energy.

The net calorific value of the samples are calculated according to the equation below;

$$Q_{v(net)} = Q_{v\ (gross)} - 24.41 \times H \qquad \text{Eq 1.11.}$$

Where;

$Q_{v(net)}$: net calorific value at constant pressure (cal/g)

$Q_{v\ (gross)}$: gross calorific value at constant volume

H : total hydrogen which includes the hydrogen in sample moisture (%) and 24.41 is a constant for the adiabatic bomb calorimeter system [53].

1.6. Aim of the Study

In this study a novel method of incorporating a ferrocene derivative into the sulfonated polystyrene ionomers was carried out.

It is well known that, the properties of polymers may be modified by the insertion of ions into the system, the synthesis of ionomers and their characterization have gained importance in many research fields. Our laboratory has worked on this subject as well and in this research it is desired to see if metallocene polymers can be synthesized by the same technique and to characterize the resulting polymers.

CHAPTER 2

EXPERIMENTAL

2.1. Chemicals

2.1.1. Tetrahydrofuran, THF is Merck grade and used to prepare monoacetylferrocene/sulfonated polystyrene polymers.

2.1.2. 1,2-dichloro ethane, **$C_2H_4Cl_2$**: is Merck grade and used to dissolve PS so that it will be sulfonated.

2.1.3. Acetic anhydride, $(CH_3CO)_2O$ is reagent grade and used to make H_2SO_4 to H_2SO_3.

2.1.4. Sulfuric Acid, H_2SO_4 is reagent grade and used to sulfonate Polystyrene.

2.1.5. Methanol, CH_3OH is Merck grade and used to prepare Methanolic NaOH.

2.1.6. **Ethanol, C_2H_5OH** is Merck grade and used as non solvent.

2.1.7. **Polystyrene, PS** is Aldrich grade (M_n= 118,000)

2.1.8. Monoacetylferrocene, is Merck grade.

2.2. Instrumentation

2.2.1. Fourier transform infrared radiation spectrophotometry (FTIR): Nicholet 510 model Fourier Transform Infrared Radiation Spectrophotometer was used in the wavenumber range of 400-4000 cm^{-1}.

2.2.2. Adiabatic Bomb Calorimeter: IKA-Calorimeter System-C4000 adibatic was used for the determination of calorific values. The thermal and thermochemical corrections applied was in accordance with the ASTM D 2015.

2.2.3. Differential Scanning Calorimetry (DSC): The thermal analysis of the samples were made by using Perkin Elmer (DSC) Differential Scanning Calorimeter. Samples were scanned in the temperature range of 0-400 ^{o}C at 5 ^{o}C/min. They were cooled and scanned for the second time.

2.2.4. Limiting Oxygen Index Apparatus (LOI): A limiting Oxygen Index apparatus fulfilling the demands set by standards was used to determine the minimum percentage volume of oxygen in a flowing mixture of oxygen and nitrogen that will just support combustion of the material.

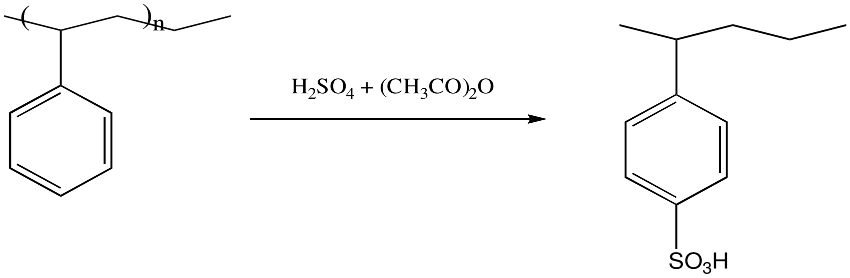
2.2.6 Lloyd 30K Universal Testing Machine: Tensile tests were performed according to ASTM D 882-91 with a crosshead speed of 2mm/min.

2.2.7. Scanning Electron Microscopy (SEM): JSM-6400 Scanning Electron Microscope of Noran Instruments Inc. in Metallurgical Engineering department of the Middle East Technical University was used. Because of unconsiderable conductivity of blends, samples to be analyzed by SEM were covered by a gold salt and made conductive. Then analysis of appearance could be performed.

2.3. Preparation of samples

2.3.1. Synthesis of Sulfonated Polystyrene (SPS)

10 g of PS was weighed and dissolved in 125 ml of 1,2-dicholoro ethane. Stoichiometric amounts of H_2S0_4 and acetic anhydride are added to this solution to obtain the desired percentage of sulfonation. It is known that yield in sulfonation of polystyrene is about 80%. Solution is mixed at 50 ^{o}C for 1 hour and poured to boiling deionized water. Special care must be taken because of sudden foaming. SPS is boiled for about two hours and precipitated in deionized water. It is dried under vacuum at room temperature till constant weight [54].



Eq 2.1.

2.3.2. Sulfonation Degree Determination

The sulfonation degree is determined by titration of SPS in a mixture of toluene/methanol (1/9 v/v) solution with phenolphtalein as an indicator against 0.045N, 0.01885N, and 0.0154N NaOH solution. NaOH solution is standardized with primary standard potassium hydrogen phthalate ($KHC_8H_4O_4$) according to ASTM E 200 – 91 [55].

2.3.3. Addition of Monoacetylferrocene (AcFe) to Sulfonated Polystyrene (SPS)

Addition of monoacetylferrocene to the sulfonated polystyrene samples were caried out by following procedure; sulfonated polystyrene samples were dissolved in tetrahydrofuran (THF). Monoacetylferrocene in equivalent amount of sulfonation was also dissolved in THF in another beaker. When the SPS samples and monoacetylferrocene dissolution was completed, the monoacetylferrocene solution was added to the SPS solution. Resultant solution was mixed for about 8 hours at room temperature, and purified by solution precipitation method and dried at room temperature till constant weight.

2.4. Calorimetric Analysis

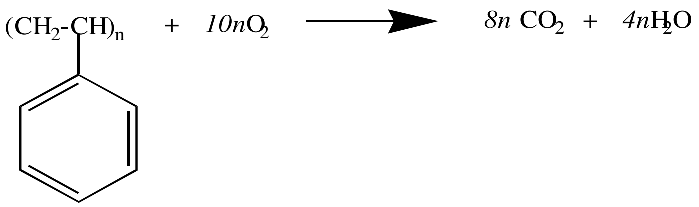
An IKA-Calorimeter System-C4000 adiabatic was used for the determination of calorific values. The thermal and thermochemical corrections applied was in acordance with the ASTM D 2015.

Description of Measuring Principle of Calorimeter: An accurately weighed amount of the substance to be determined is enclosed in a pressure vessel (calorimetric bomb). The substance is put into contact with an ignition device. Since it is chemically bound energy (combustion energy) which is to be determined, it must be ensured that the substance is completely burnt. This means that the substance must be offered an excess supply of oxygen to achieve complete combustion. Therefore, after closing the bomb, it is filled with 30 bar pure oxygen. This amount of oxygen ensures complete combustion of even quite large weighed-in quantities of substance.

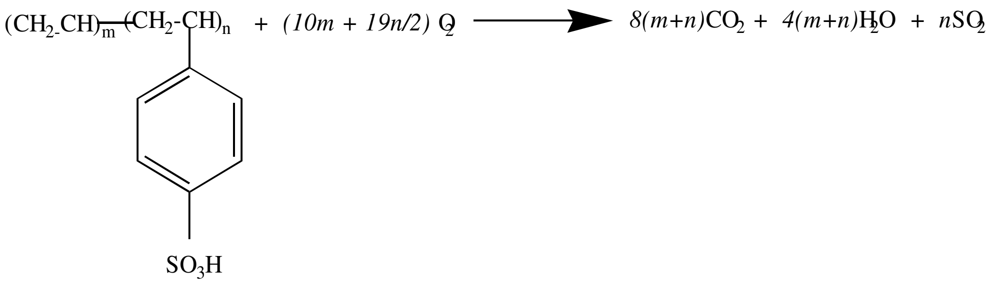
The bomb is then placed in a vessel filled with a known amount of water, which is supplied with a highly accurate thermometer. Moreover, this water is permanently stirred so as to avoid local temperature differences. The sample is ignited and the heat evolved is absorbed by the bomb and water.

The heat of combustion produced increases the temperature of the calorimeter system. About 10 to 15 minutes after ignition the heat exchange between the calorimeter bomb and the water surrounding it in the inner vessel is completed. The temperature rise is then measured and serves to calculate the gross calorific value H_o. This calculation is possible only if under the same test conditions the capacity C of the adiabatic system has been determined previously by burning a reference substance.

The calorific value determination of sulfonated polystyrene and monoacetylferrocene added samples are carried as described above. The measurements are corrected according to the equations 2.2 and 2.3.



Eq 2.2.



Eq 2.3.

2.5. Preparation of Samples for FTIR Analysis

Thin films with thickness of < 25 mm were prepared by compression moulding at 130 ^{o}C. A Nicholet 510 model Fourier Transform Infrared Radiation Spectrophotometer was used to obtain the spectra of the samples.

2.6. Preparation of Samples for Mechanical Analysis

Tensile tests were performed according to ASTM D 882-91 with a crosshead speed of 2mm/min by using a Lloyd 30K Universal Testing Machine. The specimens were in the form of thin sheeting (gauge-length=25 mm, thickness=0.20 mm, and width=5.25 mm) and prepared by a compression moulding machine.

2.7. Limiting Oxygen Index Test

The oxygen index apparatus consits of an igniter, holding assembly, oxygen and nitrogen rotameters and a test column connected to the nitrogen-oxygen gas line from the bottom as seen in Figure 2.1.

The ignition source is a tube with small orifice (1 to 3 mm in diameter) having a gas flame that can be inserted into the open end of the column to ignite the test specimen. The ignition time is about 30 seconds [56].

In LOI test, a bar specimen is placed vertically in an up-stream atmosphere of oxygen and nitrogen and is ignited at the top. The minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen thatwill just support combustion is measured and LOI is stated as by the mole fraction of oxygen in the mixture:

$$\text{LOI} = \frac{[\,O_2\,]}{[\,O_2 + N_2\,]} \times 100$$

Where;

$[\,O_2\,]$: Oxygen concentration

$[\,O_2 + N_2\,]$: Concentration of Oxygen and Nitrogen in the mixture.

The material is normally considered as self extinguishable if the LOI is larger than 26.

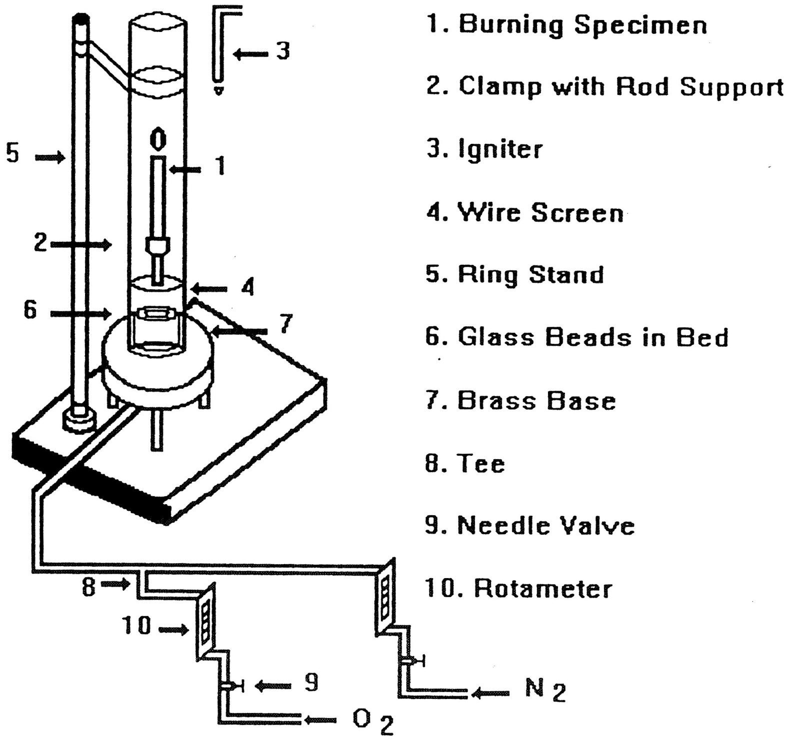


Figure 2.1. The limiting oxygen index apparatus.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. FTIR Analysis Results

When FTIR spectrum of PS is compared with the spectrum of SPS with various degrees of sulfonation, some of the characteristic peaks that belong to SPS overlap with the peaks of PS. These similar and characteristic peaks for PS and SPS are summarized in Table 3.1.

Table 3.1. Some characteristic peaks for PS and SPS [57].

PS		SPS	
546cm^{-1}	Out of plane bending of the phenyl ring	543cm^{-1}	S=O=S angle deformation
678cm^{-1}	C-H out of plane bending of the phenyl ring	690cm^{-1}	Ring vibration of para-substituted benzene
906cm^{-1}	Aromatic C-H streching	907cm^{-1}	S-O streching
2920cm^{-1} 2850cm^{-1}	CH_2 asymmetric stretching CH_2 symmetric stretching	1183cm^{-1}	S=O=S streching antsym.
1602cm^{-1} 1492cm^{-1} 1453cm^{-1}	C-C in plane vibration	1670cm^{-1} 970cm^{-1}	Streching, p-subst. benzene

The FTIR spectra of SPS and corresponding AcFe/SPS derivative are given together in the same figure to achieve simplicity in observing the changes in absorptions. Pure PS FTIR spectrum is given in Appendix A Figure A.1.

In Figure 3.1 the FTIR spectrum of pure AcFe is given and its characteristic peaks are summarized in Table 3.2.

Table 3.2. Some characteristic peaks of monoacetylferrocene [58]

Peak position	**Vibration mode**
3077 cm^{-1}	CH stretching
1454 cm^{-1}	Aromatic C-C strecthing
1100 cm^{-1}	Ring breathing mode of π-bonded cyclopentadienyl rings
1670 cm^{-1}	C=O stretching
1369 cm^{-1}	CH_3 symmetrical deformation
1180 cm^{-1} 1115 cm^{-1}	Vibration mode of skelatal ketones
1280 cm^{-1}	one cyclopentadienyl stretching

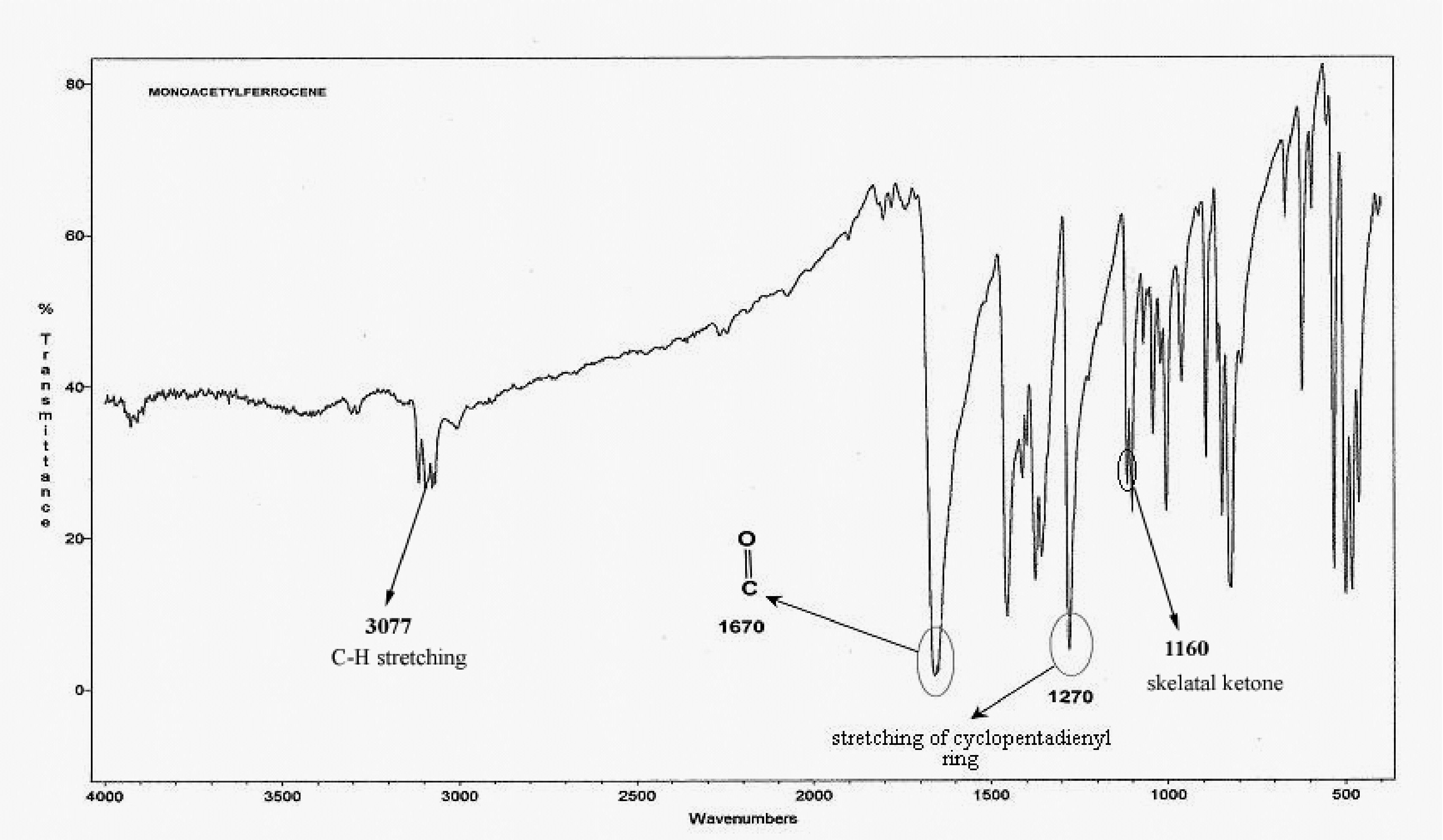


Figure 3.1. FTIR Spectrum of AcFe

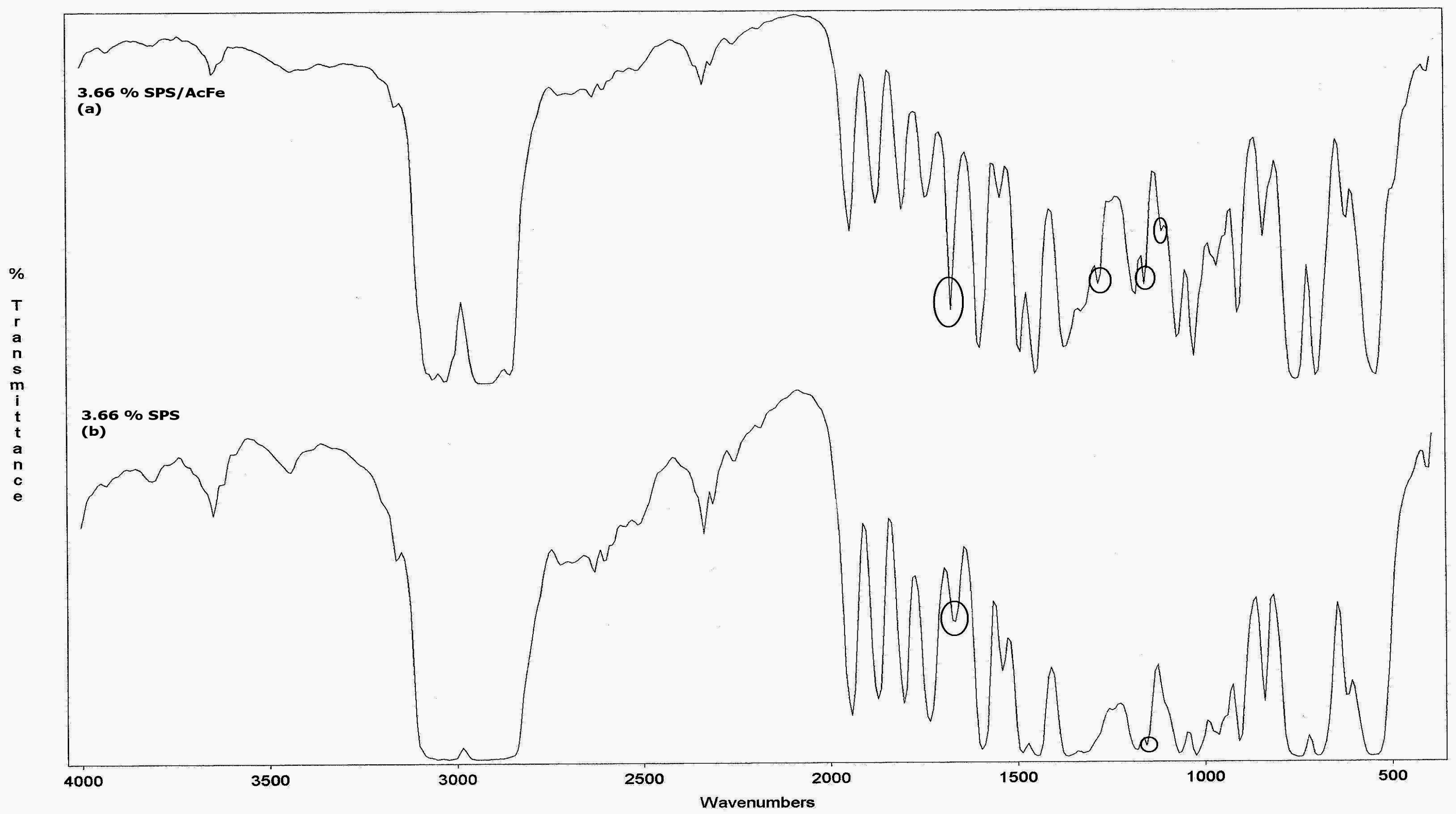


Figure 3.2. FTIR Spectrum of (a) 3.66 % SPS/AcFe

(b) 3.66 % SPS

Figure 3.2 (a) and (b) show the FTIR spectra for 3.66% AcFe/SPS and 3.66% SPS respectively in the wavenumber range of 400-4000 cm^{-1}.

In Figure 3.2 (a) the major bands appearing after sulfonation treatment on PS are observed at 1670 cm^{-1} and 1160 cm^{-1}. Where band at 1670 cm^{-1} results from the stretching vibration of the p-substituted benzene ring, while the band at 1160 cm^{-1} is due to the symmetric stretching vibration of the sulfonic groups (S=O=S stretch).

In Fig.3.2 (b) the intensity of the band at 1670 cm^{-1} is increased after the addition of AcFe which is due to the C=O strecthing of monoacetylferrocene. The band at 1250 cm^{-1} is due to the strecthing vibration of one cyclopentadienyl ring. In addition, the peaks appeared at 1160 and 1115 cm^{-1} belong to the vibration of skelatal ketone (monoacetylferrocene).

Although it is known that transition metal cation ionomers show different effects in the FTIR spectrum because of the strong interaction between the d-electrons and the $–SO^{3-}$ anions, in the spectrum of AcFe/SPS, this affect is not visible.

Altering the sulfonation degree did not change the characteristic peak positions, but increased the peak intensities with increasing the degrees of sulfonation. Therefore, the FTIR spectra of all the polymers (0.845% SPS-0.845% AcFe/SPS, 2.21% SPS-2.21% AcFe/SPS) are given in the Appendix A Figure A.2 and A.3. In order to determine the peaks clearly, the FTIR spectra of all the polymers (0.845% SPS-0.845% AcFe/SPS, 2.21% SPS-2.21% AcFe/SPS, 3.66% SPS-3.66% AcFe/SPS) are given in the Appendix A Figure A.4 to A.6.

3.2. Sulfonation Degree Determination

Sulfonation degree determination is carried out by two different methods; first method is the conventional sodium hydroxide titration method and the second method is the calorific value determination by adiabatic bomb calorimeter, which will be discussed separately.

3.2.1. Titration Method

The results of the titration of sulfonated polystyrene samples with toluene/methanol (1/9 v/v) mixing solution are shown in Table 3.3;

Table 3.3. Titration results of SPS samples

Theoretical Sulfonation Degree %	**Normality of NaOH**	**Volume of NaOH used in titration (mL)**	**Experimental Degree of Sulfonation %**
1	0.045	0.4	0.85
2.5	0.045	0.7	2.21
4	0.045	0.8	3.66
2.5	0.01885	1.1	1.84
4	0.01885	3.0	3.93
1	0.01054	1.0	0.95
3	0.01054	1.8	1.87
5	0.01054	2.9	3.98

Even though the degree of sulfonation of PS can be within any desirable range, it was observed that the SPS sample containing 6.51 % AcFe showed phase separation. So the sulfonation degree of PS samples and the amount of AcFe addition kept below 5%.

As is observed from Table 3.3 there are some sulfonations and monoactylferrocene derivatives which have very close percentages. This is due to insufficient amount of the substances which were regenerated to complete all the remaining tests. No matter how hard we tried, it was not possible to achieve the identical percentages of sulfonation or monoacetylferrocene amount with the depleted samples. That is why some characterization experiments do not have identical amount with others

3.3. Adiabatic Bomb Calorimeter Measurements

The heat of combustion values would give an idea about how strongly the atoms are held to each other; by means of calorific value, which represent the bond energies.

It is expected that stronger and larger the number of bonds, larger will be the energy of atomization and smaller will be the calorific value.

The heat of combustion values for each sample i.e. PS, SPSs and SPS with different percentages of AcFe determined experimentally are represented in Figure 3.3. It is clearly obvious that there existed a nearly linear trend between the $\Delta H_{combustion}$ values with varying both sulfonation degree and corresponding monoacetylferrocene added SPS (% AcFe/SPS).

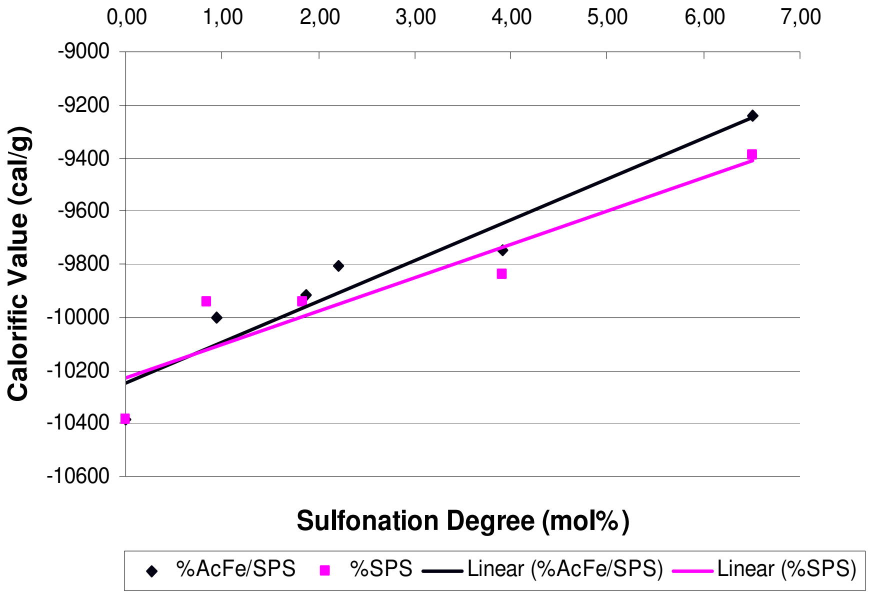


Figure 3.3. Calorific values vs % SPS and %AcFe/SPS graphs

These results are consistent with the previous study [59] and showed an increase in the calorific value with increasing degree of sulfonation and AcFe addition.

3.4. Differential Scanning Calorimeter Results

Table 3.4. shows the Tg values for PS, SPS with varying percentages of sulfonation and their corresponding AcFe/SPS samples.

Table 3.4. Tg values of PS, SPS and SPS/AcFe samples obtained from DSC analysis.

Sample	Tg (^{o}C)
PS	94.76
0.95% SPS	94.17
0.95% SPS/AcFe	94.72
1.87% SPS	94.86
1.87% SPS/AcFe	90.23
2.21% SPS	94.00
2.21% SPS/AcFe	86.40
3.98% SPS	93.86
3.98% SPS/AcFe	73.78

All samples displayed a single glass transition temperature (Table 3.4.), suggesting no phase separation, that is PS, SPS and AcFe/SPS are completely miscible.

Effect of sulfonation is not too profound when the sulfonation degree is less than 5%, therefore in the above samples no direct correlation between percentage sulfonation and Tg is observed [60].

However, the SPS samples after the addition of AcFe displayed lower values of T_g. In the case of metal neutralized SPS samples, there is an increase in Tg values for the ionomers with increasing ion content, due to the formation of ion-ion dipoles, multiplets, clusters or even aggregates. AcFe showed an opposite effect on the Tg values and as seen from Table 3.4 Tg values decreased with increasing AcFe amount.

This is a very interesting and a novel observation and the softness of the samples could also be noticed by hand.

DSC thermograms for all the samples are given at the Appendix B in Figures B.1 to B.9.

3.5. Limiting Oxygen Index Value Determination Results

Due to catalytic combustion effects of ferrocene and its derivatives, it was thought that sulfonated polystyrene samples could gain flammibility after addition the of AcFe.

The effect of addition of AcFe on the flammibility of the SPS samples was investigated using LOI method. The determined LOI values of pure PS, SPS samples with various degrees of sulfonation and AcFe added SPS samples are given in Table 3.5.

Table 3.5. LOI values of the polymers

SAMPLE	**LOI VALUE**
PS	18
0.95 % SPS	17
0.95 % SPS/AcFe	17
1.87 % SPS	17
1.87 % SPS/AcFe	17
3.98 % SPS	17
3.98 % SPS/AcFe	17

It was found that the flame retardancy of pure polystyrene decreased one unit with sulfonation, it is assumed that the incorporation of oxygen atoms favoured the burning process. However, increasing sulfonation degree and addition of AcFe to SPS samples did not affect their flame retardancy.

3.6. Mechanical Analysis Results

The modulus of elasticity values of PS, SPS samples and AcFe added SPS samples obtained by Lloyd 30K Universal Testing Machine is given in Table 3.6. The effect of sulfonation degrees and amount of added AcFe is summarized in this table.

Table 3.6. Modulus of elasticity values

MODULUS OF ELASTICITY (MPa)				
	0 %	1.84 %	2.21 %	3.93 %
SPS	1810	1389	1368	1481
AcFe/SPS	1810	1204	1278	1326

It is apparent from Table 3.6 that lower values of modulus of elasticity were obtained after both sulfonation of PS and incorporation of AcFe to SPS samples.So the highest value of the modulus of elasticity was determined for pure polystyrene (1810 MPa). It was thought that polystyrene being a very brittle material could gain some mechanical properties after sulfonation and insertion of AcFe. For this purpose the modulus of elasticity of SPS and AcFe/SPS samples were also determined.

When the modulus values for SPS and AcFe/SPS are compared, it was observed that the incorporation of AcFe to the SPS samples caused the modulus of elasticity values to decrease as can be seen from Table 3.6.

Fig.3.4 shows the modulus of elasticity vs. Degrees of sulfonation and Fig.3.5 represents the same plot for AcFe added SPS samples.

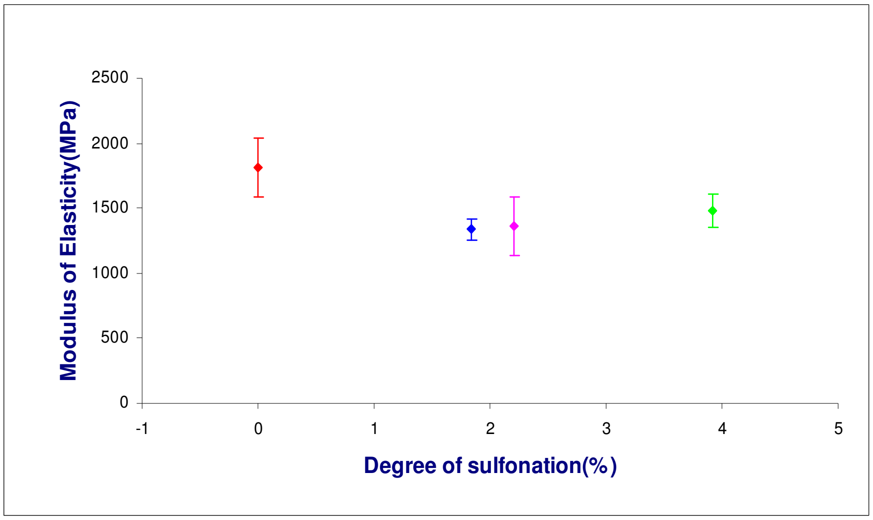


Figure 3.4. Modulus of elasticity vs. Sulfonation degree

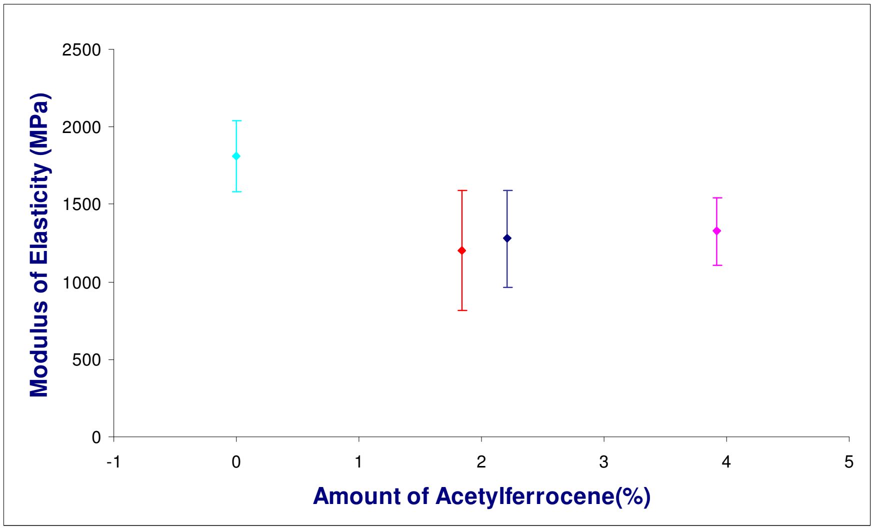


Figure 3.5. Modulus of elasticity vs. % Amount of AcFe

According to Figure 3.4. as the sulfonation degree increased the values of modulus of elasticity increased. The same effect was also observed for the samples AcFe/SPS as can be seen from Figure 3.5.

The mechanical property data other than Modulus of Elasticity (Stress at Break, Extension at Break) for the SPS samples and their corresponding monoacetylferrocene added derivatives are given in Appendix C in Table C.1.

3.7. Scanning Electron Microscopy Results

The SEM photographs for SPS with various degrees of sulfonation and their corresponding AcFe added samples are given in Figures 3.6 to 3.11. No phase seperation was observed in any of the samples as supported by Tg values in Section 3.3.

The results of energy dispersed microanalysis where the hard copy is not available, showed an increase in the intensity of the iron (II) peaks as expected due to the increasing amount of AcFe. These results also confirm the successful incorporation of monoacetylferrocene to the sulfonated polystyrene samples.

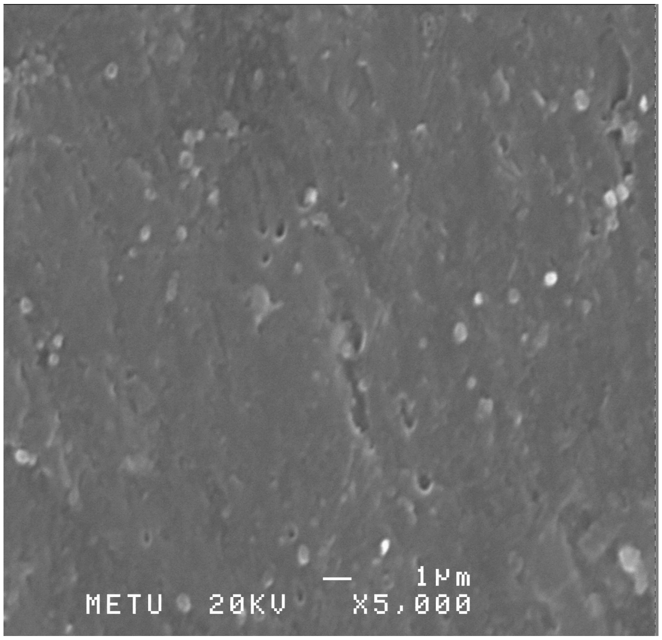


Figure 3.6. SEM photograph of 0.845 % SPS

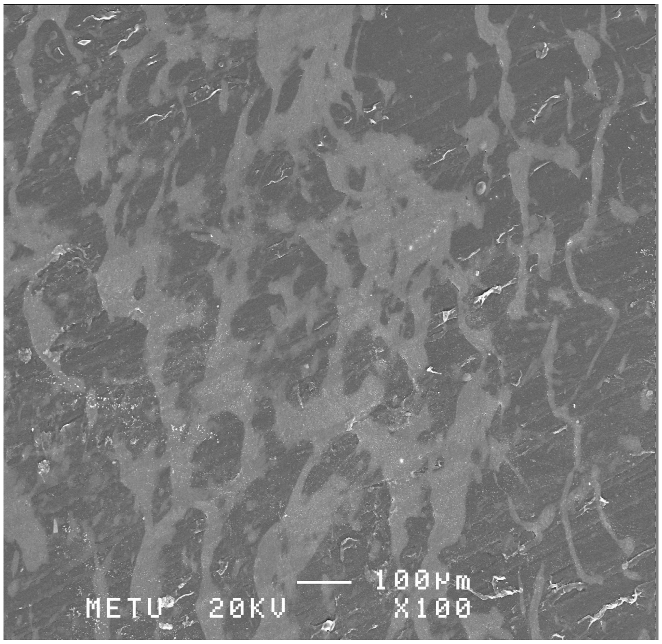


Figure 3.7. SEM photograph of 0.845 % SPS/AcFe

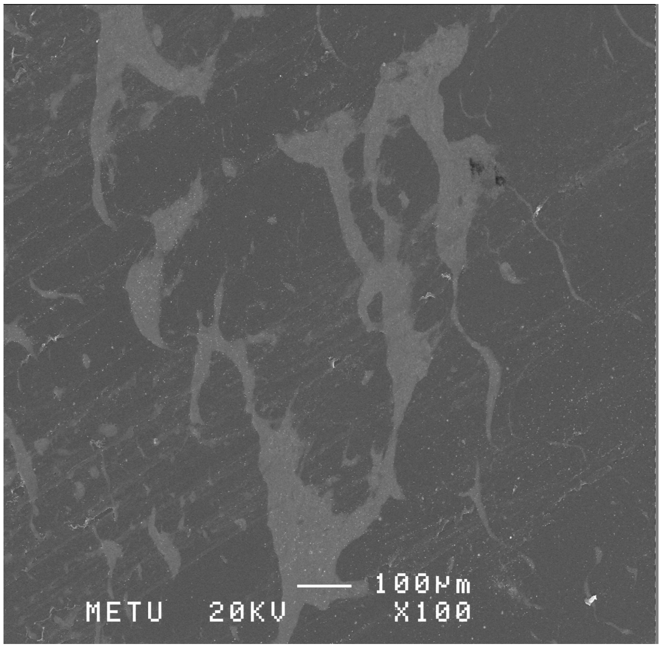


Figure 3.8. SEM photograph of 2.21 % SPS

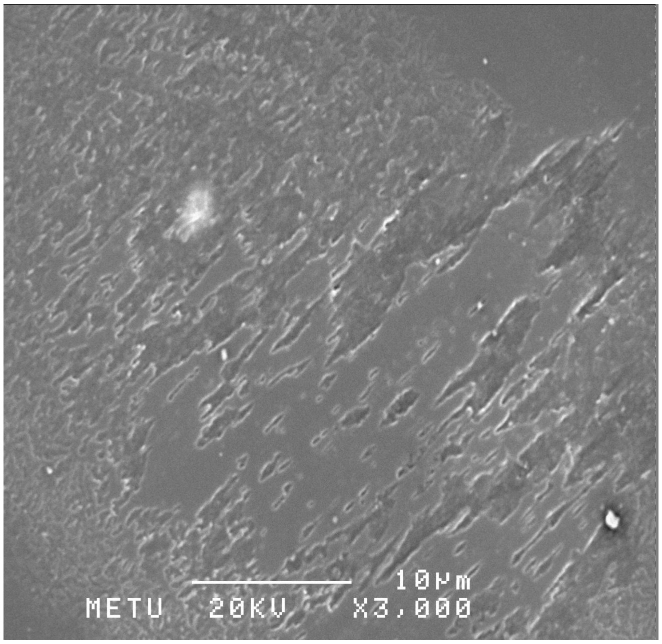


Figure 3.9. SEM photograph of 2.21 % SPS/AcFe

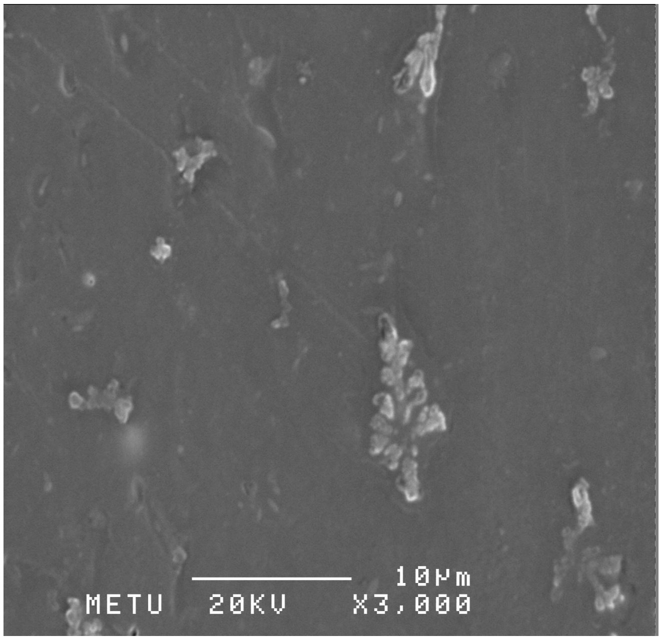


Figure 3.10. SEM photograph of 3.66 % SPS

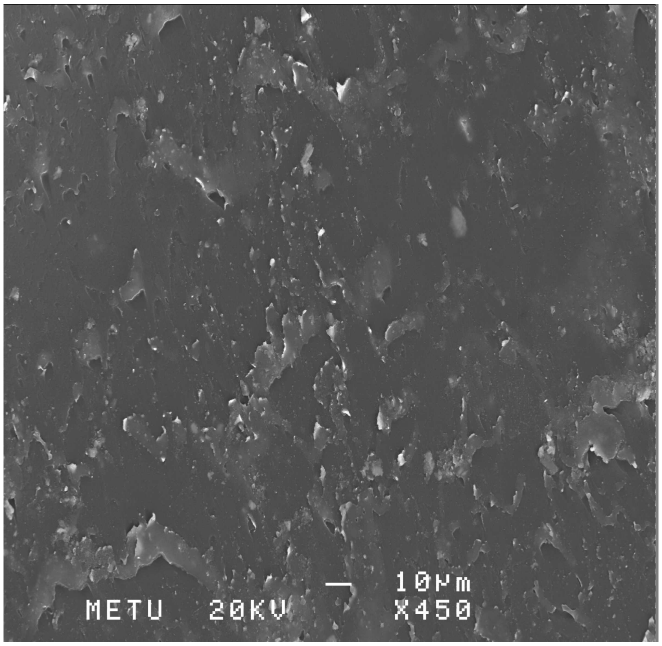


Figure 3.11. SEM photograph of 3.66 % SPS/AcFe

CHAPTER 4

CONCLUSIONS

In this study a novel method which is based on the simple ionomer preparation procedure to incorporate monoacetylferrocene to the sulfonated polystyrene samples is presented.

However there had been some doubts about the structure of the resultant polymer. The characterization methods showed that the most probable structure of the resultant polymer could be the ionomer form. Moreover, to determine whether any properties have altered or not after incorporation of AcFe, some characterization methods were performed.

According to the results of these analysis, the following conclusions are obtained:

1) FTIR spectroscopy is the informative experimental technique to support the successful incorporation of AcFe to the SPS samples. The defined vibration bands revealed the successful addition of AcFe.

2) The heat of Combustion values would give an idea about how strongly the atoms are held to each other; by means of calorific value.

3) It is clearly obvious that there exists a nearly linear trend between the $\Delta H_{combustion}$ values with varying both sulfonation degree and corresponding monoacetylferrocene added SPS (% AcFe/SPS) derivative.

4) All samples display a single glass transition temperature.

5) Effect of sulfonation on T_g is not too profound when the sulfonation degree is less than 5%.

6) SPS samples after addition of AcFe display lower values of T_g.

7) LOI value of polystyrene decreases one unit with sulfonation. However, increasing sulfonation degree and addition of AcFe to SPS samples do not affect their flame retardancy.

8) The highest value of the modulus of elasticity is obtained for pure polystyrene.

9) Incorporation of AcFe to the SPS samples decreases the value of modulus of elasticity.

10) No phase separation is observed from the SEM photographs of the SPS samples after incorporation of AcFe.

As a result the most probable structure that we can propose for the AcFe added SPS is given in the following figure (Fig.4.1). the size and the density of the aggregate depends on the degree of sulfonation that is later monoacetylferrocene incorporated product.

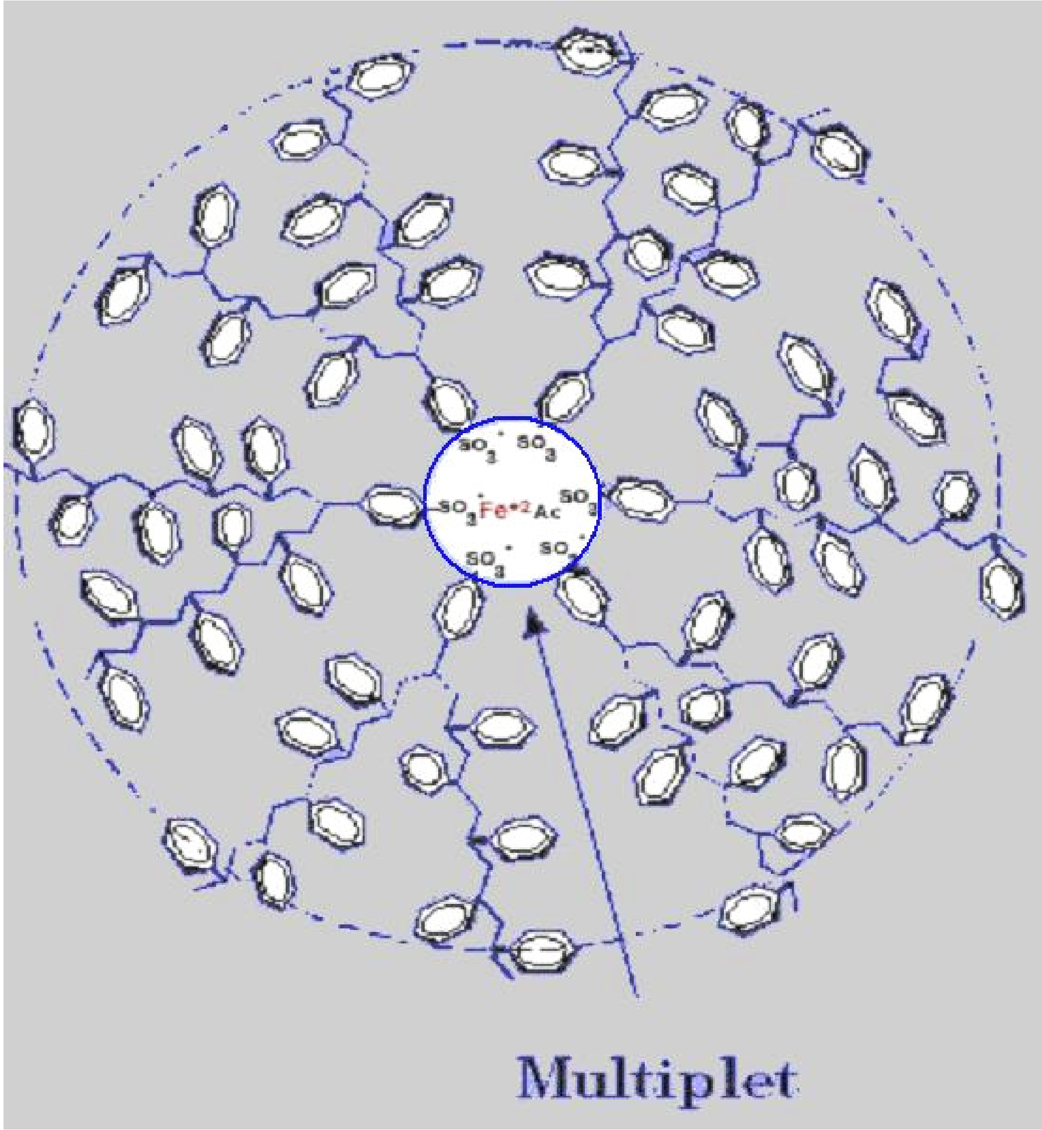


Figure 4.1. The most probable structure of the resultant polymer.

REFERENCES

1. Eisenberg A., *Adv. Polym. Sc*i., 5, 59, 1967.

2. Leadley S. R., Davies M. C., Vert M., Braud C., Paul A. J., Shard A. G., Watts J. F., *Macromolecules*, 30, 6920, 1997.

3. Eisenberg A., *Ion-Containing Polymer*s, Journal of Polymer Science, Polymer Symposium 45.

4. Eisenberg A., *Ion-Containing Polymer*s, Wiley, New York, 974. Advances in Chemistry 187, American Chemical Society, Washington DC, 1982.

5. Eisenberg A., Yeager H.L., *Perfluorinated Ionomer Membrane*s, ACS Symposium Series 180, American Chemical Society, Washington DC, 1982.

6. Eisenberg A., Bailey F.E., *Coulombic Interactions in Macromolecular System*s, ACS Symposium Series 302, American Chemical Society, Washington DC, 1986.

7. Utracki L. A., Weiss R. A., *Multiphase Polymers: Blends and Ionomer*s, ACS Symposium Series 395, American Chemical Society, Washington DC, 1989.

8. Salmen, L.; Htun, M., *Properties of Ionic Polymer*s, Natural & Synthetic, STFI Meddelande, Stockholm, 1991.

9. Otocka E. P. J., *Macromol. Sci. Rev. Macromol. Chem.*, C5, 275-294, 1971.

10. Longworth R., Plast. Rubber Mater. Appl., 75-86, 1978..

11. Bazuin C. G., Eisenberg A., *Ind. Eng. Chem. Prod. Res. Dev.,* 20, 271-286, 1981.

12. MacKnight W. J., Earnest T. R. Jr., *J. Polym. Sci. Macromol. Re*v. , 16, 41-122, 1981.

13. Bazuin C. G., In *Polymeric Materials Encyclopedi*a, Salamone, J. C., Ed., CRC, Boca Raton, FL, 3454-3460, 1996.

14. Holliday, L., *Ionic Polymer*s, Ed., Applied Science, London, 1975.

15. Wilson A. D., Prosser H. J., *Developments in Ionic Polymers* Eds, Elsevier, London, 1986.

16. Xiao H. X., Frisch K. C., *Advances in Urethane Ionomer*s, Eds., Technomic, Lancaster, PA, 1995.

17. Schlick S., *Ionomers: Characterizations, Theory, and Application*s, Ed., CRC, Boca Raton, FL 1996.

18. Tant M. R., Mauritz K. A., Wilkes G. L., *Ionomers: Synthesis, Structure, Properties, and Application*s, Eds., Chapman & Hall, New York, 1997.

19. Tant M. R., Mauritz K. A., Wilkes G. L., *Ionomers: Synthesis, Structure, Properties, and Application*s, Eds., Chapman & Hall, New York, 1997.

20. Eisenberg A., King M., *Ion-Containing polymers, Physical Properties and Structure*, Academic, New York, 1977.

21. Schlick S., *Ionomers: Characterization, Theory, and Application*s, CRC Press, Inc., Florida, 1996.

22. MacKnight W.J., McKenna L.W., Read B.E., J. *Appl. Phy*s., 38, 4208, 1967.

23. Ward T. C., Tobolsky A. V., J. *Appl. Polym. Sc*i., 11, 2403, 1967.

24. Tobolsky A. V., Lyons P.F., Hata N., Macromolecules, 1, 515, 1968.

25. Eisenberg A., Hird B., Moore R. B., Macromolecules, 23, 4098, 1990.

26. Eisenberg A., King M., *Ion-Containing polymers, Physical Properties and Structure*, Academic, New York, 1977.

27. Eisenberg A., Adv. *Poly. Sc*i., 5, 59-112, 1967.

28. Rees R.W., U.S. Patent, 3, 322, 734, 1996, to E.I. du Pont de Nemours & Co.

29. Weiss R.A., Lundberg R.D., Werner A., *J. Poly. Sci.: Poly. Chem. Ed.,* 18, 3427, 1980.

30. Weiss R.A., Turner S.R., Lundberg R.D., Werner A., *J. Poly. Sci.: Poly. Chem. Ed.,* 23, 525, 1985.

31. Turner S.R., Weiss R.A., Lundberg A., *J. Poly. Sci.: Poly. Chem. Ed.,* 23, 535, 1985.

32. Weiss R.A., Turner S.R., Lundberg R.D., Werner A., *J. Poly. Sci.: Poly. Chem. Ed.,* 23, 549, 1985.

33. Allen R.D., Yilgor I., McGrath J.E., *Coulombic Interactions in Macromolecular Systems,* Eisenberg A., Bailey F.E., Eds., ACS Semposium Series, 302, 79, *Am.Chem.Soc*., 1896.

34. Makowski H.S., Lundberg R.D., Singhal G.H., U.S. Patent, 3, 870, 841, 1975.

35. Makowski H.S., Lundberg R.D., Westerman L., Bock J., *Ions in Polymers,* Eisenberg A. Ed., Adv. Chem. Ser., 187, 3, Amer. Chem.Soci. Washington DC, 1980.

36. Bishop M.T., Karasz F.E., Russo P.S., Langley K.H., *Macromolecules,* 18, 86, 1985.

37. Jin K., Bishop M.T., Ellis T.S., Karasz F.E., *Br. Poly. J.,* 17, 4, 1985.

38. Kucera F., Jancar J., *Homogeneous and Heterogeneous Sulfonation of Polymers, Polymer Engineering and Science,* 38 (5), 783-792, May 1996.

39. Kucera F., PhD Thesis, Brno University of Technology, Faculty of Chemistry, Chemistry of Materials, 2001.

40. Wilkinson G., Stone F. G. A., Abel E., *Comprehensive Organometallic Chemistry II,* Eds, Pergamon Press, Oxford, England, 1-9, 1995.

41. Bruce D.W., O'Hare D., *Inorganic Materials,* Eds., John Wiley & Sons, Chichester, U.K., 1992.

42. Kealy T.J., Pauson P.L., *Nature,* 168, 1039, 1961.

43. Miller S.A., Tebboth J.A., Tremaine J.F., *J. Chem. Soc.,* 632, 1952.

44. Rosenblum M., *Chemistry of the Iron Group Metallocenes,* Part I., Wiley-Interscience, New York, 1965.

45. The Royal Society of Chemistry, web page (www.rsc.org).

46. The Royal Society of Chemistry Analystical Div. Thermal Methods group web page (www.thermalmethodsgroup.org).

47. Ward I.M. and Hadley D.W., *An Introduction to the Mechanical Properties of Solid Polymers,* Wiley, Chichester, 1993.

48. Godovsky Y.K., *Thermophysical Properties of Polymers,* Springer-Verlag, Berlin, 1992.

49. Parr Instrument Co.Calorimeter Selection Guide.

50. Schwenker R.F., Whitwell J.C., *Analytical Calorimetry,* 1, 249-259, 1968.

51. Westrum F.E., *Analytical Calorimetry,* 1, 231-238, 1968.

52. Chang S.S., *Thermal Analysis in Polym.Charac.,* The Eastren Analytical Symp., 1980.

53. IKA 4000 Calorimeter Manual.

54. Bauzin C.G. and Eisenberg A.J., *J.Chem.Educ.,* 58, 938, 1981.

55. Piccioni F., Giorgi I., Passaglia E., Ruggeri G., Aglietto M., *Polm. Int.,* 50, 714-721, 2001.
56. ASTM D 2863, *Annual Book of Standards,* Philadelphia, USA, 1991.

57. Cheikh R.B., Askeland P.A., Schalek R.L., Drzal L.T., *J.Adhesion Sci.Technol.,* 16, 12, 1651-1668, 2002.

58. Rao C.N.R., *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York and London, 1963.

59. Dumanlı A.G., M.Sci., Middle East Technical University, 2003.

60. Picchioni F., Giorgi I., Passaglia E., Ruggeri G., Aglietto M., *Polym. Int.*, 50, 714-721, 2001.

APPENDIX A

FOURIER TRANSFORM INFRARED (FTIR) SPECTRA FOR POLYMERS

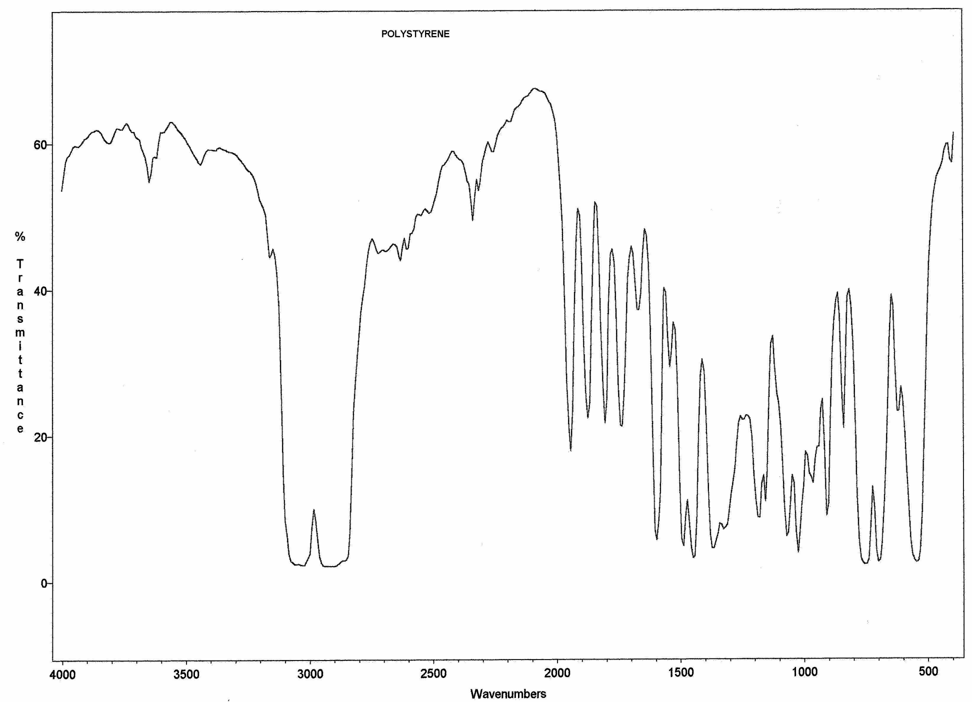


Figure A.1. FTIR Spectrum of PS

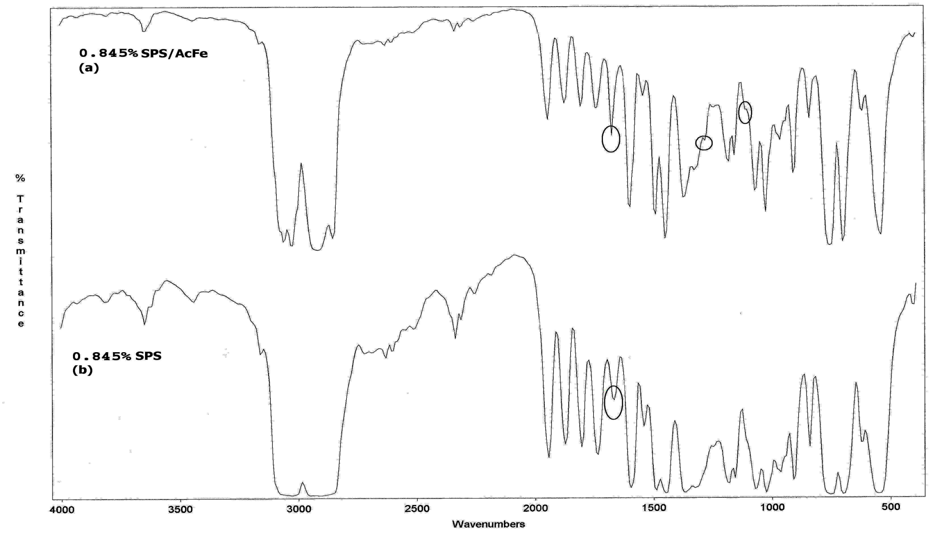


Figure A.2. FTIR Spectrum for (a) 0.845 % AcFe/SPS

(b) 0.845 % SPS

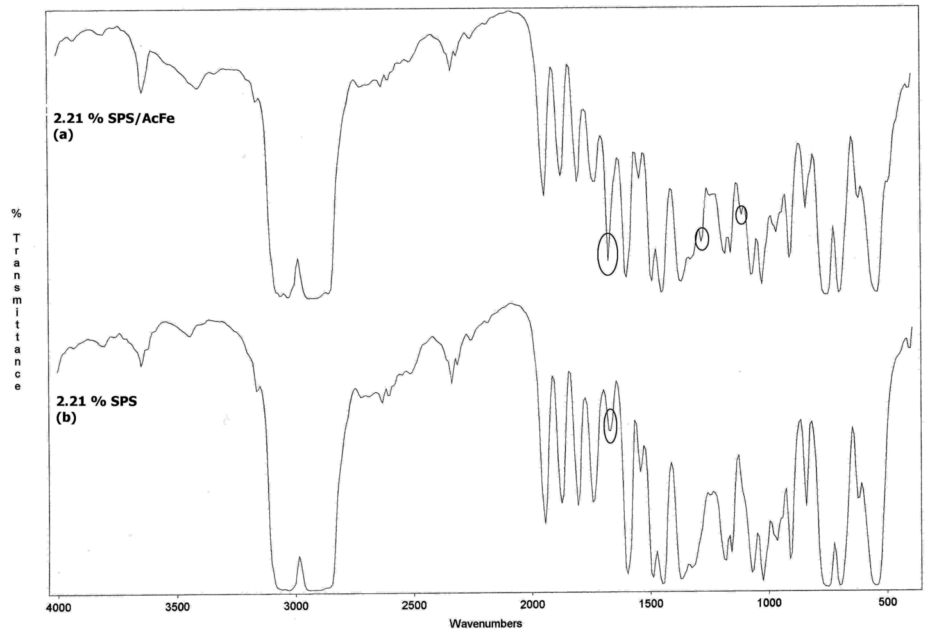


Figure A.3. FTIR Spectrum of (a) 2.21 % SPS/AcFe

(b) 2.21 % SPS

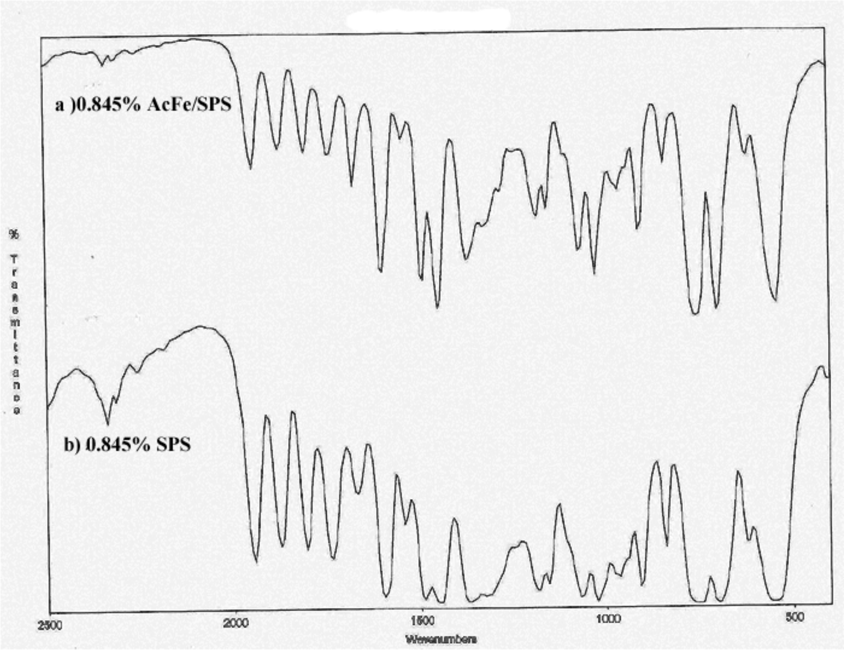


Figure A.4. FTIR Spectrum for (a) 0.845 % AcFe/SPS

(b) 0.845 % SPS

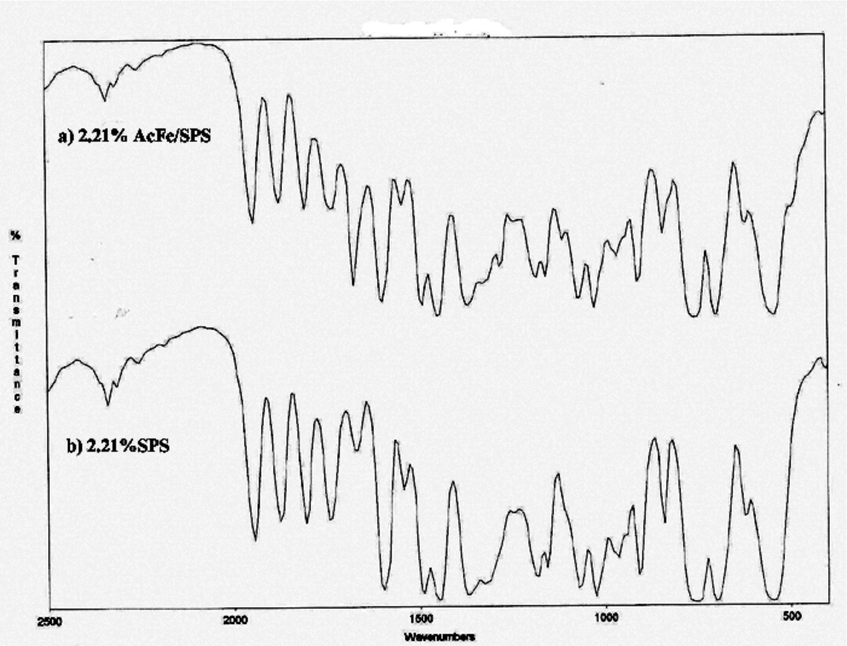


Figure A.5. FTIR Spectrum of (a) 2.21 % SPS/AcFe

(b) 2.21 % SPS

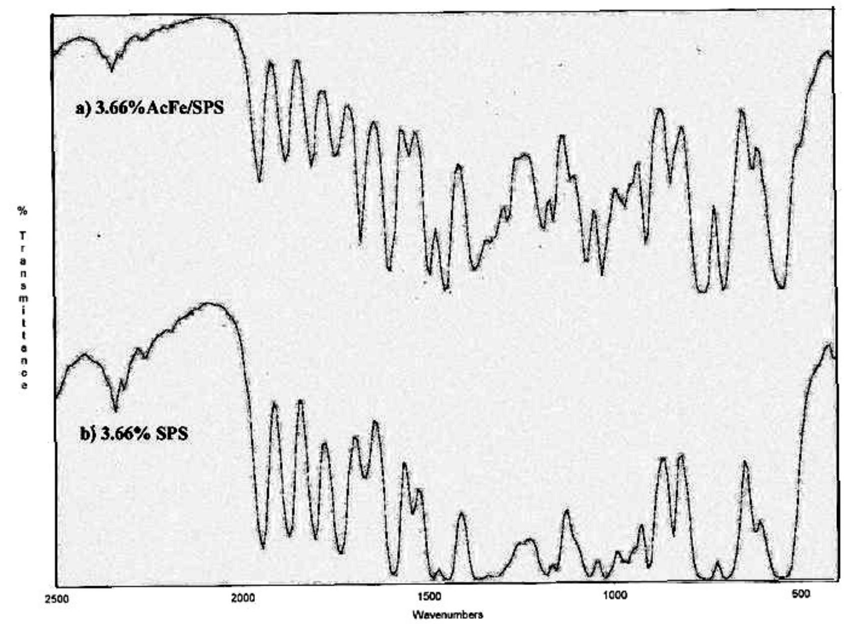


Figure A.6. FTIR Spectrum of (a) 3.66 % SPS/AcFe
(b) 3.66 % SPS

APPENDIX B

DIFFERENTIAL SCANNING CALORIMETRY (DSC) THERMOGRAMS FOR THE POLYMERS

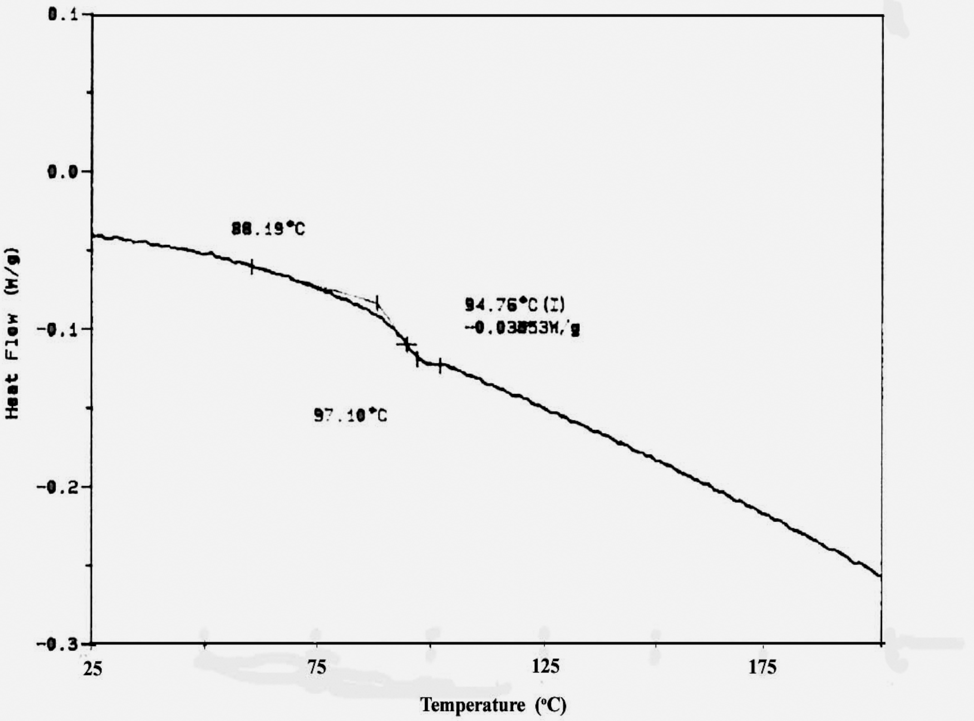


Figure B.1. DSC Thermogram of PS

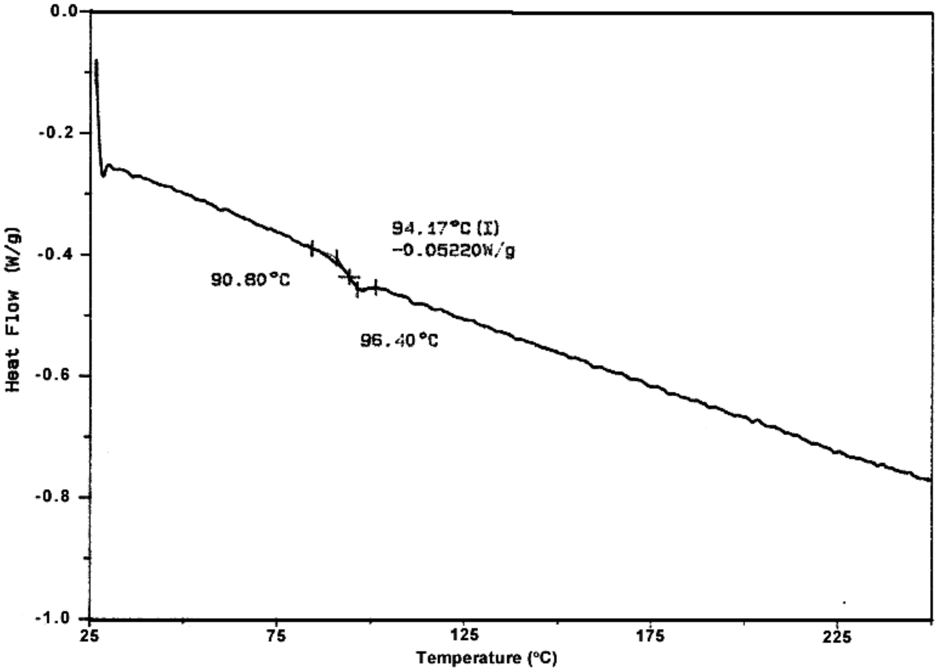


Figure B.2. DSC Thermogram of 0.95 % SPS

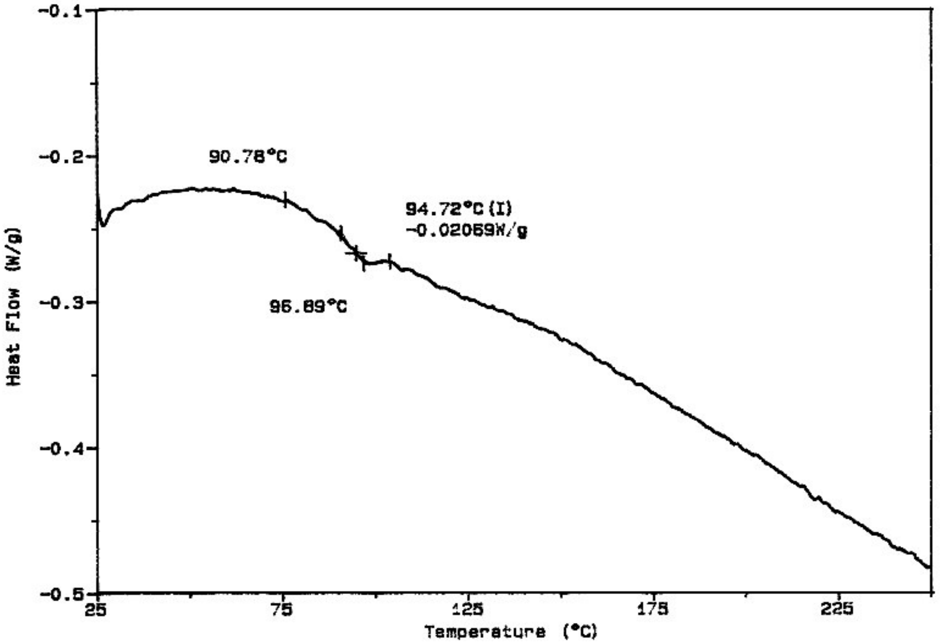


Figure B.3. DSC Thermogram of 0.95 % AcFe/SPS

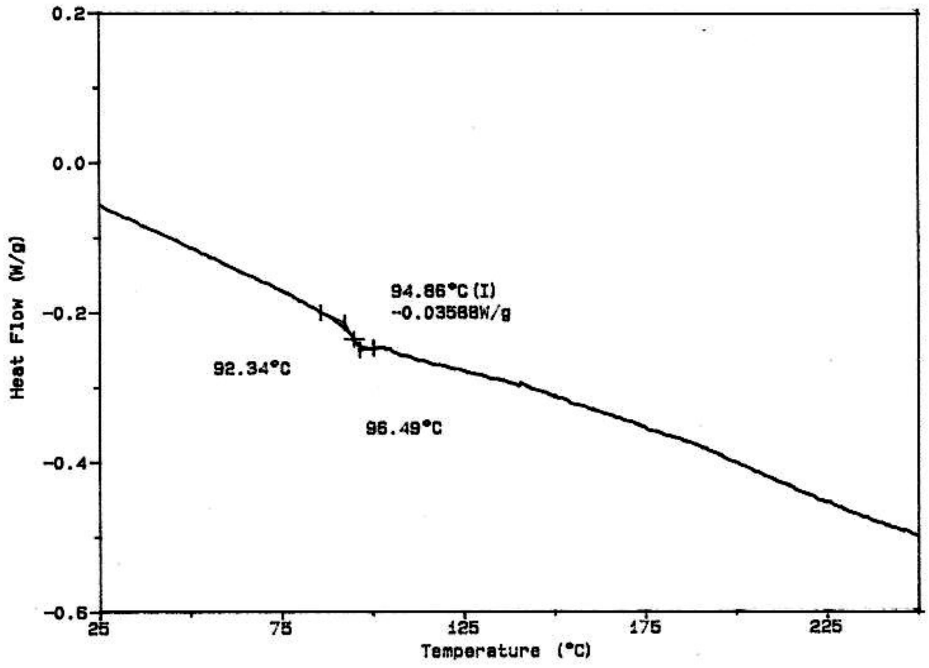


Figure B.4. DSC Thermogram of 1.87 % SPS

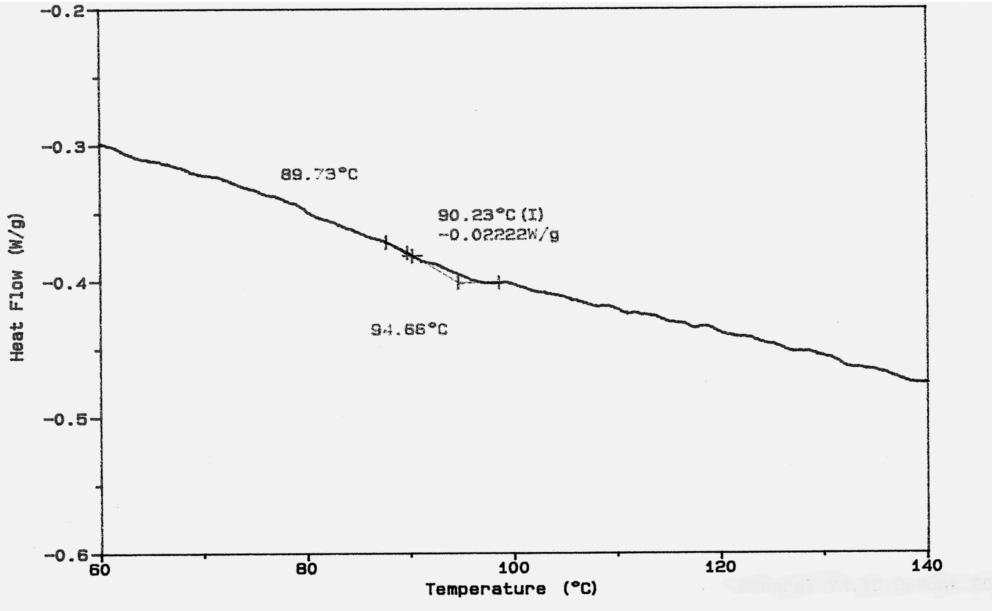


Figure B.5. DSC Thermogram of 1.87 % AcFe/SPS

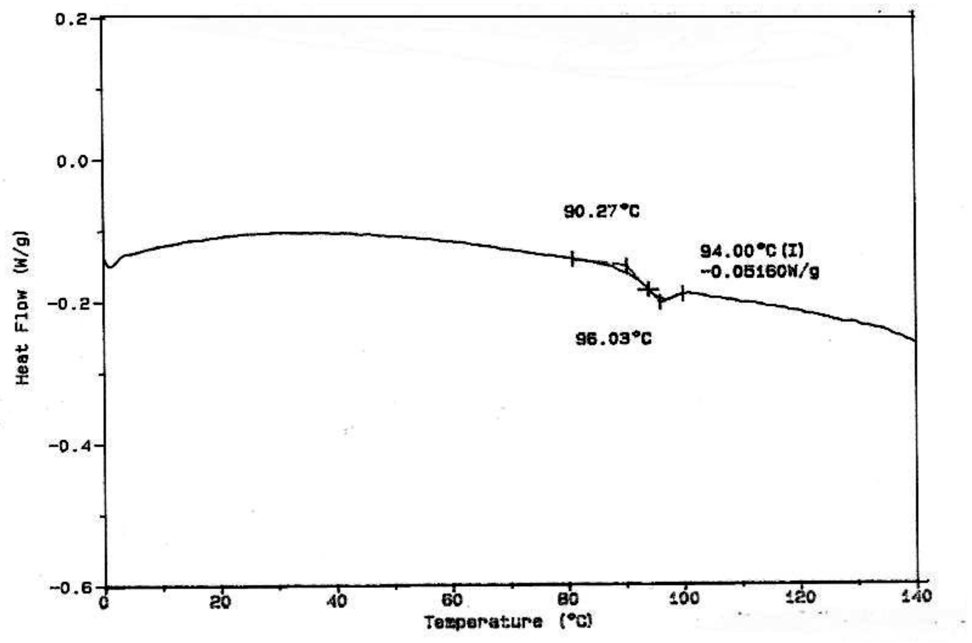


Figure B.6. DSC Thermogram of 2.21 % SPS

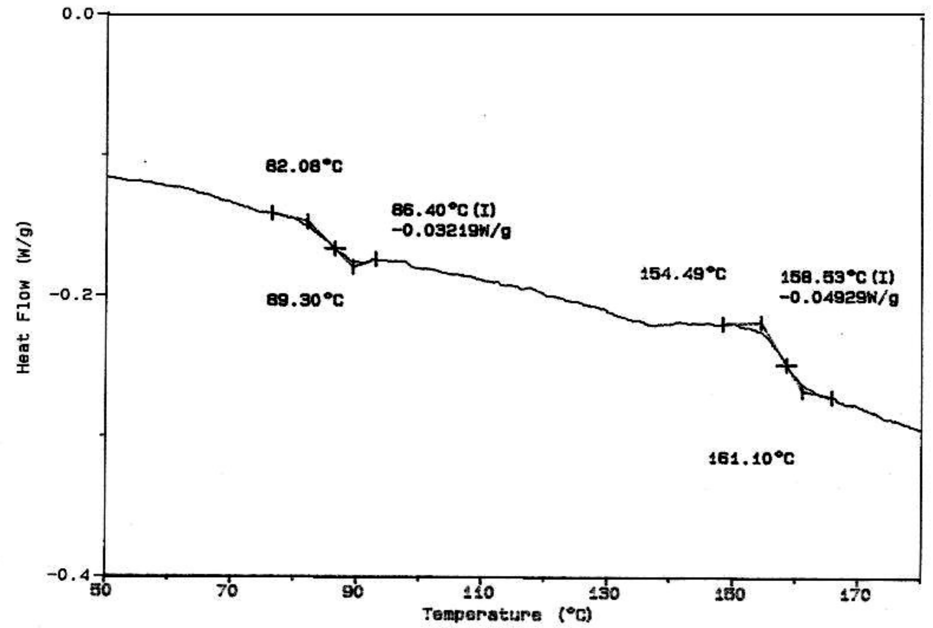


Figure B.7. DSC Thermogram of 2.21 % AcFe/SPS

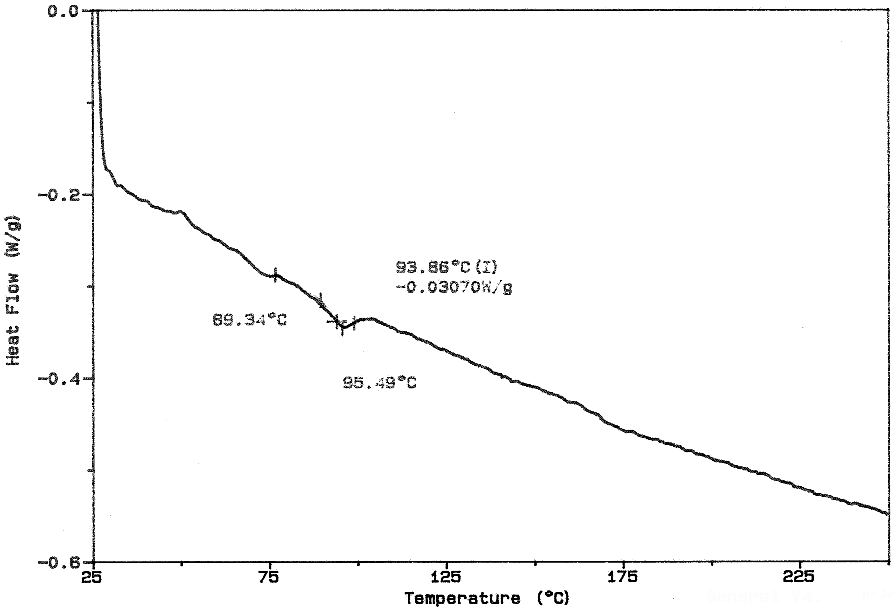


Figure B.8. DSC Thermogram of 3.98 % SPS

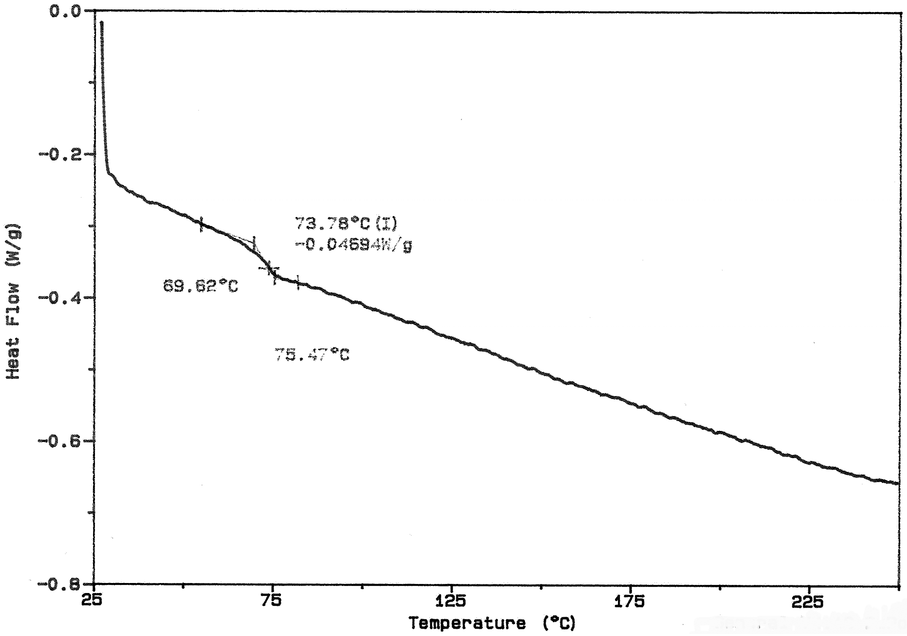


Figure B.9. DSC Thermogram of 3.98 % AcFe/SPS

APPENDIX C

MECHANICAL ANALYSIS

Table C.1. Mechanical Property data for SPS samples and their corresponding monoacetylferrocene added derivatives.

SAMPLE	STRESS AT BREAK (N/mm^2)	STRAIN AT BREAK
1.84% SPS	8.41 ± 1.99	0.014 ± 0.003
1.84% AcFe/SPS	14.32 ± 3.43	0.015 ± 0.0034
2.21% SPS	7.97 ± 1.51	0.027 ± 0.034
2.21% AcFe/SPS	12.21 ± 3.26	0.011 ± 0.0016
3.93% SPS	16.11 ± 2.63	0.017 ± 0.011
3.93% AcFe/SPS	12.80 ± 2.03	0.015 ± 0.002