

# **Supercritical Fluid Processing of Perfluorinated and Sulfonated Membranes**

by

**Mayra Ocasio Velázquez**

A thesis submitted in partial fulfillment  
of the requirements for the degree of

**Master of Science  
in  
Chemical Engineering**

University of Puerto Rico  
Mayagüez Campus  
**2004**

Approved by:

---

David Suleiman Rosado, Ph.D.  
President, Graduate Committee

---

Date

---

L. Antonio Estévez De Vidts, Ph.D.  
Member, Graduate Committee

---

Date

---

Guillermo Colón Burgos, Ph.D.  
Member, Graduate Committee

---

Date

---

María A. Aponte Huertas, Ph.D.  
Member, Graduate Committee

---

Date

---

Gustavo E. López Quiñones, Ph.D.  
Chairperson of the Department

---

Date

---

Nelson Cardona Martínez, Ph.D.  
Chairperson of the Department

---

Date

# **SUPERCRITICAL FLUID PROCESSING OF PERFLUORINATED SULFONATED MEMBRANES**

Mayra Ocasio Velázquez

Chemical Engineering Department

## **Abstract**

Over the past years, one of the most important challenges facing industry has been the search for environmentally benign and cost effective alternatives to traditional power sources. Many industries invest considerable amount of resources to develop and implement new methods of power production. One of the new technologies under consideration is a proton exchange membrane fuel cell (PEMFC).

Nafion™ is the best-known ionomer membrane used in fuel cell and electrolysis applications due to its excellent chemical and mechanical stability and to its high ionic conductivity. The purpose of this work was to investigate the effects of supercritical fluid processing on the physical properties of Nafion™ and Styrene-ethylene-butylene-styrene (SEBS) ionomer membranes. Various co-solvents, with different solubility parameters, were employed in the search of improving polymer-  $\text{scCO}_2$  interaction. In this study, the properties of Nafion™ and SEBS polymers were investigated by thermal gravimetric analysis. Changes

in the degradation temperature of Nafion™ and SEBS membranes were found as function of co-solvent and processing conditions used.

# **PROCESAMIENTO CON FLUIDO SUPERCRÍTICO DE MEMBRANAS PERFLUORINADAS Y SULFONADAS**

Mayra Ocasio Velázquez

Departamento de Ingeniería Química

## **Resumen**

Durante los últimos años, uno de los desafíos más importantes que ha enfrentado la industria ha sido la búsqueda de alternativas ambientalmente benignas y rentables a las fuentes de energía tradicionales. Muchas industrias invierten una cantidad considerable de recursos para desarrollar y establecer nuevos y mejores métodos para la producción de energía. Una de las nuevas tecnologías bajo consideración es una celda de combustible de membrana del intercambio de protón (PEMFC).

Nafion<sup>MR</sup> es la membrana iónica más conocida utilizada en aplicaciones a celdas de combustible y de electrólisis debido a su excelente estabilidad química y mecánica y a su a una alta conductividad iónica.

El propósito de este trabajo fue investigar los efectos del procesamiento con fluidos supercríticos en las propiedades físicas de las membranas iónicas de Nafion<sup>TM</sup> y de estireno-etileno-butileno-estireno (SEBS). En búsqueda de mejorar la interacción del polímero con el scCO<sub>2</sub> se emplearon diversos co-solventes, con diferente parámetros de solubilidad. En este estudio, se investigaron las

características de los polímeros de Nafion<sup>MR</sup> y SEBS por análisis termogravimétrico. Se encontraron cambios en la temperatura de degradación de las membranas de Nafion<sup>MR</sup> y SEBS como función del co-solvente y de las condiciones del proceso utilizado.

## ACKNOWLEDGEMENTS

First of all, I would like to thank God for giving me the intelligence and strength necessary to fight each day of my life. To my family: Mom, Dad, Uchi, Mabel and Mónica for their support and encouragement, for tolerating my mood swings and panic attacks, but most importantly for always making me feel that no matter what happens, I will always have something to fall back on.

I would also want to thank and to dedicate all my work and my life to my beautiful princess, my daughter, ***Aryangelie***, who makes each day of my life a beautiful one, and who gave me each day a reason to be alive.

I would also like to express my gratitude to my advisor David Suleiman Rosado, without whom this work would never have been possible. Suleiman, thanks for guiding me through the magnificent world of science and for giving me your time to teach me since my first year in this Department, Thanks are also due to my graduate committee for their support and help.

## TABLE OF CONTENTS

|                                                       |    |
|-------------------------------------------------------|----|
| 1. INTRODUCTION .....                                 | 1  |
| 2. JUSTIFICATION .....                                | 3  |
| 3. BACKGROUND .....                                   | 6  |
| 3.1 Polymeric Membranes.....                          | 6  |
| 3.2 Polymer Processing .....                          | 9  |
| 3.3 Polymer Modification .....                        | 17 |
| 4. OBJECTIVES .....                                   | 23 |
| 5. EXPERIMENTAL .....                                 | 24 |
| 5.1 Materials.....                                    | 24 |
| 5.2 Method: SCF Extraction .....                      | 26 |
| 5.3 Method: Thermal Gravimetric Analysis (TGA) .....  | 28 |
| 6. RESULTS .....                                      | 33 |
| 6.1 TGA: SEBS 93%Sulfonated Membranes .....           | 33 |
| 6.2 TGA: Nafion <sup>TM</sup> Membranes .....         | 45 |
| 7. DISCUSSION .....                                   | 72 |
| 7.1 Thermal Degradation of Sulfonated SEBS .....      | 72 |
| 7.2 Thermal Degradation of Nafion <sup>TM</sup> ..... | 77 |
| 8. SUMMARY AND CONCLUSIONS.....                       | 85 |
| 9. FUTURE WORK .....                                  | 87 |
| 10. REFERENCES .....                                  | 88 |

## LIST OF FIGURES

|                                                                                                    |    |
|----------------------------------------------------------------------------------------------------|----|
| Figure 3.2.1 Schematic Phase Diagram for CO <sub>2</sub> , showing the Supercritical Region .....  | 11 |
| Figure 5.1.1 Structure Nafion™ Membrane .....                                                      | 24 |
| Figure 5.1.2 Structure of Sulfonated SEBS Membrane .....                                           | 25 |
| Figure 5.2.1 Supercritical Fluid Extraction Experiment .....                                       | 27 |
| Figure 5.2.2 Supercritical Fluid Extraction Unit .....                                             | 28 |
| Figure 5.3.1 Mettler Toledo TGA/SDTA 851 <sup>e</sup> Equipment.....                               | 30 |
| Figure 5.3.2 TGA of Nafion™ Membrane .....                                                         | 31 |
| Figure 5.3.3 TGA of SEBS Membrane.....                                                             | 32 |
| Figure 6.1.1 TGA of SEBS 93% Sulfonated Unmodified.....                                            | 34 |
| Figure 6.1.3 TGA of SEBS 93% Sulfonated + Isopropyl Alcohol Process in scCO <sub>2</sub><br>.....  | 35 |
| Figure 6.1.4 TGA of SEBS 93% Sulfonated + Tetrahydrofuran Process in scCO <sub>2</sub><br>.....    | 36 |
| Figure 6.1.5 TGA of SEBS 93% Sulfonated + Methylene Chloride Process in<br>scCO <sub>2</sub> ..... | 37 |
| Figure 6.1.6 TGA of SEBS 93% Sulfonated + Cyclohexanone Process in scCO <sub>2</sub><br>.....      | 38 |
| Figure 6.1.7 TGA of SEBS 93% Sulfonated + Acetone Process in scCO <sub>2</sub> .....               | 39 |
| Figure 6.1.8 TGA of SEBS 93% Sulfonated + Acetic Acid Process in scCO <sub>2</sub> .....           | 40 |



|                                                                                                                |    |
|----------------------------------------------------------------------------------------------------------------|----|
| Figure 6.1.9 TGA of SEBS 93% Sulfonated + Acetonitrile Process in scCO <sub>2</sub> .....                      | 41 |
| Figure 6.1.10 TGA of SEBS 93% Sulfonated + Ethanol Process in scCO <sub>2</sub> .....                          | 42 |
| Figure 6.1.11 TGA of SEBS 93% Sulfonated + Methanol Process in scCO <sub>2</sub> .....                         | 43 |
| Figure 6.1.12 TGA of SEBS 93% Sulfonated + Water Process in scCO <sub>2</sub> .....                            | 44 |
| Figure 6.2.1a TGA of Nafion <sup>TM</sup> Unmodified (Trial 1) .....                                           | 47 |
| Figure 6.2.1b TGA of Nafion <sup>TM</sup> Unmodified (Trial 2) .....                                           | 48 |
| Figure 6.2.2a TGA of Nafion <sup>TM</sup> Process in scCO <sub>2</sub> (Trial 1).....                          | 49 |
| Figure 6.2.2b TGA of Nafion <sup>TM</sup> Process in scCO <sub>2</sub> (Trial 2).....                          | 50 |
| Figure 6.2.3a TGA of Nafion <sup>TM</sup> + Isopropyl Alcohol Process in scCO <sub>2</sub> (Trial 1) .         | 52 |
| Figure 6.2.3b TGA of Nafion <sup>TM</sup> + Isopropyl Alcohol Process in scCO <sub>2</sub> (Trial 2) .         | 53 |
| Figure 6.2.4a TGA of Nafion <sup>TM</sup> + Tetrahydrofuran Process in scCO <sub>2</sub> (Trial 1) ...         | 54 |
| Figure 6.2.4b TGA of Nafion <sup>TM</sup> + Tetrahydrofuran Process in scCO <sub>2</sub> (Trial 2) ...         | 55 |
| Figure 6.2.5a TGA of Nafion <sup>TM</sup> + Methylene Chloride Process in scCO <sub>2</sub> (Trial 1)<br>..... | 56 |
| Figure 6.2.5b TGA of Nafion <sup>TM</sup> + Methylene Chloride Process in scCO <sub>2</sub> (Trial 2)<br>..... | 57 |
| Figure 6.2.6a TGA of Nafion <sup>TM</sup> + Cyclohexanone Process in scCO <sub>2</sub> (Trial 1) ....          | 58 |
| Figure 6.2.6b TGA of Nafion <sup>TM</sup> + Cyclohexanone Process in scCO <sub>2</sub> (Trial 2) ....          | 59 |
| Figure 6.2.7b TGA of Nafion <sup>TM</sup> + Acetone Process in scCO <sub>2</sub> (Trial 2).....                | 60 |
| Figure 6.2.8a TGA of Nafion <sup>TM</sup> + Acetic Acid Process in scCO <sub>2</sub> (Trial 1) .....           | 61 |
| Figure 6.2.8b TGA of Nafion <sup>TM</sup> + Acetic Acid Process in scCO <sub>2</sub> (Trial 2) .....           | 62 |
| Figure 6.2.9a TGA of Nafion <sup>TM</sup> + Acetonitrile Process in scCO <sub>2</sub> (Trial 1) .....          | 63 |

|                                                                                                       |    |
|-------------------------------------------------------------------------------------------------------|----|
| Figure 6.2.9b TGA of Nafion <sup>TM</sup> + Acetonitrile Process in scCO <sub>2</sub> (Trial 2) ..... | 64 |
| Figure 6.2.10a TGA of Nafion <sup>TM</sup> + Ethanol Process in scCO <sub>2</sub> (Trial 1).....      | 65 |
| Figure 6.2.10b TGA of Nafion <sup>TM</sup> + Ethanol Process in scCO <sub>2</sub> (Trial 2).....      | 66 |
| Figure 6.2.11a TGA of Nafion <sup>TM</sup> + Methanol Process in scCO <sub>2</sub> (Trial 1) .....    | 67 |
| Figure 6.2.11b TGA of Nafion <sup>TM</sup> + Methanol Process in scCO <sub>2</sub> (Trial 2) .....    | 68 |
| Figure 6.2.12a TGA of Nafion <sup>TM</sup> + Water Process in scCO <sub>2</sub> (Trial 1) .....       | 69 |
| Figure 6.2.12b TGA of Nafion <sup>TM</sup> + Water Process in scCO <sub>2</sub> (Trial 2) .....       | 70 |
| Figure 7.1.1 TGA of SEBS Samples Studies .....                                                        | 71 |
| Figure 7.2.1 Perfluorinated Group on Nafion <sup>TM</sup> membrane.....                               | 76 |

## LIST OF TABLES

|                                                                                          |    |
|------------------------------------------------------------------------------------------|----|
| Table 3.2.1 Comparison of Some Properties of Gases, Liquid, and SCFs .....               | 12 |
| Table 3.2.2 Properties of Some SCF Solvents .....                                        | 16 |
| Table 5.2.2 Properties of Nafion <sup>TM</sup> Membranes .....                           | 24 |
| Table 6.1.1 Decomposition Temperature for SEBS 93% Sulfonated Samples ..                 | 45 |
| Table 6.2.2 Decomposition Temperature for the Nafion <sup>TM</sup> Membranes Studied     | 71 |
| Table 7.1.1 Weight Loss Percent for SEBS Membranes .....                                 | 73 |
| Table 7.1.2 Degradation Temperature of Different Products .....                          | 74 |
| Table 7.2.1 Results of Nafion <sup>TM</sup> TGA Studies .....                            | 77 |
| Table 7.2.2 Average Decomposition Temperature for Nafion <sup>TM</sup> Membranes.....    | 79 |
| Table 7.2.3 Average Weight Loss in the Different Decomposition Temperatures<br>.....     | 81 |
| Table 7.2.4 Standard Bond Energies (Kcal/mol) .....                                      | 83 |
| Table 7.2.5 Water Weight Loss in the Different Nafion <sup>TM</sup> Samples Studied..... | 84 |

## ***1. INTRODUCTION***

Over the past years, one of the most important challenges facing industry has been the search for environmentally benign and cost effective alternatives to traditional power sources. Many industries invest considerable resources to develop and implement new methods of power production. One of the new technologies under consideration is a proton exchange membrane fuel Cell (PEMFC).

A fuel cell is an electrochemical device used to convert the chemical energy of the reaction of a fuel and an oxidant into electrical energy<sup>1</sup>. The main components of a PEMFC are two metal electrodes separated by a polymeric proton exchange membrane (PEM), which is permeable to positively charged molecules. Currently many polymeric membranes are employed as inPEMFCs.

Nafion™ is the best-known ionomer membrane used in fuel cell and electrolysis applications due to its excellent chemical and mechanical stability and to its high ionic conductivity<sup>2</sup>. DuPont first developed perfluorinated membranes in the early 1960's under the trademark Nafion. These ion-exchange membranes are copolymers of tetrafluoroethylene and perfluorinated vinyl ethers containing terminal sulfonyl fluoride groups. Such terminal groups are then treated to produce the proton conducting  $-\text{SO}_3\text{H}$  (or  $-\text{CO}_2\text{H}$ ) groups.

Most of the research performed by the scientific community has concentrated on the design and performance modeling of the PEMFCs. Studies

that have been conducted to mathematically predict long-term performance of the cells,<sup>3-6</sup> have, for the most part, relied on the time-independent, virgin properties of the polymeric materials employed in the PEMFCs. However, PEM properties can significantly change as function of time and exposure to elevated temperatures due to degradation and/or aging. This constitutes the main motivation for the current research.

The current work focuses on the development and optimization of a new chemically-stable, ion-exchange membrane (ionomer membrane) for applications such as PEM fuel cells (PEMFC), chemical protective clothing, drug delivery, etc. The materials chosen for this investigation are the perfluorinated ionomer membrane Nafion<sup>®</sup>, and the styrene-ethylene-butylene-styrene (SEBS) block copolymer. In the search of improving these membranes, they were processed with supercritical fluid (SCF) CO<sub>2</sub> in different chemical environments. The hypothesis of this research is to produce changes in the physical properties and morphology of these membranes during SCF processing.

Our research is focused on the thermal and morphological properties of perfluorinated and sulfonated membranes and aims at having a better understanding of their structure and improving their performance in any of the previously discussed specialty separation applications.

## **2. JUSTIFICATION**

Fluorine compounds are all around us and we use them every day, despite the fact that most people do not know them as such, or at least did not know them until the end of the last century. This is when controversies arose over chlorofluorocarbons (CFCs) and the ozone layer, and over water fluorination. Fluorine is chemically unusual. It is the most reactive halogen, yet its most well known compounds such as CFCs and fluoropolymers (nonstick frying pans, etc.) are best known and used because they are stable and inert.

Fluorine chemicals are important materials, and today have both commercial and political significance. Most of us drink fluorinated water and brush our teeth with fluorinated toothpaste. We drive air-conditioned cars fueled by high-octane unleaded gasoline produced with the assistance of hydrogen fluoride (HF) catalyst. We use Teflon®-coated frying pans and wear Gore-Tex® and other brand name, weather-resistant outdoor clothing.

Other applications of performance fluorine chemicals are not as well known to the average person, but are no less important. This is because they affect chemical and electrical / electronics manufacture, packaging and a number of other important commercial and consumer businesses and markets. This is increasingly important in semiconductor manufacture.

Fluorine chemistry as a separate branch of the chemical industry has been intensively developed since the middle of the last century. This branch of

chemistry has become one of the most important industries providing modern technological progress in all areas of novel techniques such as space, aircraft industry, microelectronics, medicine, etc.

U.S. domestic oil production has been declining since 1970. In 1973, the United States imported about 34% of its oil. Today, this country imports more than 53%, and it is estimated that this could increase to 75% by 21. Most of the world's oil reserves are now in the Middle East. We have witnessed shifts in economic influence through the last three sharp increases in the world's oil prices: the Arab Oil Embargo in 1974, the Iranian Oil Embargo in 1979, and the Persian Gulf War in 1990. It has resulted in periods of negative economic growth and a rising trade deficit. Renewable energy can decrease this dependency on foreign oil imports. Some renewable energy comes either directly or indirectly from water. Hydrogen also can be found in many organic compounds, as well as water. It is the most abundant element on the Earth. But it does not occur naturally as a gas. It is always combined with other elements, such as oxygen as in water. Once separated from another element, hydrogen can be burned as a fuel or converted into electricity.

Interest in fuel cells is high due to their potential as a renewable energy source for cars, homes, commercial buildings, and battery-powered devices like cell phones. Membranes are the heart of PEM fuel cells, serving as the electrolyte to allow ion exchange and create current. The best-known and most widely used membrane material today is Nafion™, a polyperfluorosulfonic acid

product that is cast into films. Since the 1960's, Nafion™ has been the membrane of choice in specialized fuel-cell applications such as spacecraft.

At present, production of fluorine-containing compounds over the world is enumerated in the hundred thousands tons level annually, with continuous expansion. The interest in fluoropolymers is increasing even more because they can meet the requirements of modern, novel applications: they are able to work both at low temperatures ( $-100^{\circ}\text{C}$  or lower), preserving their elasticity, and at high temperatures (up to  $400\text{--}450^{\circ}\text{C}$ ) with no significant change, in their properties. In this connection, fluorinated compounds with functional groups have been of growing interest in recent years, particularly fluorinated surfactants. Much effort has been devoted to the development of technology for manufacturing and using the surfactants based on high-molecular weight perfluorinated acids with a  $\text{R}_f\text{COOH}$  structure, where  $\text{R}_f$  can be  $\text{C}_6\text{F}_{13}$ -,  $\text{C}_7\text{F}_{15}$ -,  $\text{C}_8\text{F}_{17}$ -, or  $\text{CF}_3\text{O}(\text{CF}(\text{CF}_3)-\text{CF}_2)_n$ -.

It is worth to mention also the growing applications of fluorine-containing compounds in medicine. Examples of these are the application of fluorine-containing polymers such as materials for synthetic blood vessels (vasculums), and the manufacture of advanced remedies based on, fluorine-containing antibiotics. Also, the development of ionomer membranes (PEM) suitable for drug delivery has been of great interest.



### **3. BACKGROUND**

#### **3.1 Polymeric Membranes**

A synthetic membrane is a permeable or semi-permeable phase, often a thin polymeric solid, which restricts the motion of certain species. It is a barrier that controls the relative rates of transport of various species diffusing through it and thus, as with all separations, gives one product depleted in certain components and a second product concentrated in these components. Although it is difficult to give an exact definition of a membrane, it could be more generally defined as a selective barrier between two phases<sup>7</sup>.

The performance of a membrane is generally characterized by two simple factors, flux and selectivity. Ideally a membrane with a high selectivity and permeability is required although attempts to maximize one factor are typically compromised by a reduction in the other.

Due to the very different nature of these separations, the types of membranes used, materials, and method of fabrication, differ quite significantly. In recent years membrane material science has been and continues developing rapidly to produce a wide range of materials of different structure and performance.

A membrane can be thick or thin, its structure can be homogeneous or heterogeneous, transport can be active or passive; passive transport can be driven by a pressure, concentration or a temperature difference. Membranes can

be natural or synthetic; membranes can be neutral or charged. They can be classified according to different viewpoints. The first classification is by nature, i.e. biological or synthetic membranes. This is the clearest distinction possible. It is also an essential first distinction since the two types of membranes differ completely in structure and functionality. Another means of classifying membranes is by morphology or structure. This is also a very illustrative route because the membrane structure determines the separation mechanism and hence the application. Two types of synthetic membranes may be distinguished, i.e. symmetric or asymmetric membranes.

The thickness of symmetric membranes (porous or nonporous) range roughly from 1 to 2  $\mu\text{m}$ , the resistances to mass transfer being determined by the total membrane thickness. A decrease in membrane thickness results in an increased permeation rate. A breakthrough to industrial applications was the development of asymmetric membranes. These consist of a very dense top layer or skin with a thickness of 0.1 to 0.5  $\mu\text{m}$  supported by a porous sub-layer with a thickness of about 50 to 150  $\mu\text{m}$ . These membranes combine the high selectivity of a dense membrane with the high permeation rate of a very thin membrane. The resistance to mass transfer is determined largely or completely by the thin top layer. It is also possible to obtain composite membranes, which are, in fact, skinned asymmetric membranes. However, in composite membranes, the top layer and sub-layer originate from different polymeric materials; each layer can be optimized independently. Generally the support layer is already an

asymmetric membrane on which a thin dense layer is deposited. Several methods have been developed to achieve this: dip-coating, interfacial polymerization, in-situ polymerization, and plasma polymerization.

In the case of synthetic polymers, there are several basic features and characteristics that determine the physical and chemical properties, which in turns have a significant bearing on the polymers application as a membrane material. These features include:

- i. The number and molecular weight of repeating units in a polymer.
- ii. Whether the material is a homopolymer, where the repeating unit is the same (e.g.  $\text{CH}_2\text{-CH}_2$  in ethylene), or a copolymer, in which the repeating units are different.
  - a. A block copolymer where the chain is built up by linking blocks of monomers e.g., styrene-isoprene-styrene (SIS).
  - b. Grafted co-polymer, in which polymeric branches are attached to the side of the main chain by chemical means or radiation.
- iii. How the monomers are linked, e.g., as random chains, in synthetic rubbers (nitrile-butadiene, acrylonitrile-butadiene-styrene etc).
- iv. Whether the polymer is linear, branched, or cross-linked. Cross-linked polymers have chains connected by covalent bonding often by chemical reaction or by physical cross-links, e.g., in semi-

crystalline polymers. Cross-linking has the effect of making the polymer insoluble.

- v. Stereoisomerisms. In certain polymers types different side groups are in the repeating units (e.g. vinyl polymers). These side groups can be attached in different ways.
  - a. All lie on the same side of the chain, isotactic
  - b. Arranged randomly on either side of the chain, atactic
  - c. Arranged on alternative sides, syndiotactic

This behavior has a significant effect on the properties of the polymer: a regular structure, i.e., isotactic will produce a crystalline polymer and corresponding atactic polymers are non-crystalline or amorphous. The crystallinity has a major effect on the permeability of a polymer membrane.

### 3.2 Polymer Processing

Chemists and chemical engineers seek new, cleaner methods for polymer synthesis and polymer processing due to their concern over volatile organic solvent emissions and the generation of aqueous waste streams. The use of supercritical carbon dioxide (scCO<sub>2</sub>) has attracted particular attention in both of these areas for the following reasons:

- a. CO<sub>2</sub> is non-toxic, non-flammable, chemically inert, and inexpensive
- b. Supercritical conditions are easily obtained:  $T_c(\text{CO}_2) = 31.1^\circ\text{C}$ ;  $P_c(\text{CO}_2) = 73.8 \text{ bar}$

- c. The solvent may be removed by simple depressurization
- d. The density of the solvent can be 'tuned' by varying the pressure
- e. Many polymers become highly swollen and plasticized in the presence of CO<sub>2</sub>

The use of supercritical fluids requires elevated pressures and relatively specialized equipment. These considerations must be balanced carefully with the perceived advantages for a given application. However, there are many recent examples that suggest that the benefits of using CO<sub>2</sub> as an alternative solvent compensate the additional complexity associated with supercritical-fluid technology, at least for certain applications.

### *Supercritical Fluid Extraction*

A pure supercritical fluid (SCF) is any compound at a temperature and pressure above the critical values (above critical point). Above the critical temperature of a compound the pure, gaseous component cannot be liquefied regardless of the pressure applied. The critical pressure is the vapor pressure of the gas at the critical temperature. In the supercritical environment, only one phase exists. The fluid, as it is termed, is neither a gas nor a liquid and is best described as intermediate to the two extremes. This phase retains solvent power approximating liquids as well as the transport properties common to gases. (see Figure 3.2.1).

The advantage of using supercritical fluids in extraction is the ease of separation of the extracted solute from the supercritical fluid solvent by simple



**Figure 3.2.1 Schematic phase diagram for CO<sub>2</sub>**

expansion. In addition, supercritical fluids have liquid-like densities but superior mass transfer characteristics compared to liquid solvents due to their high diffusion and very low surface tension that enables easy penetration into the porous structure of the solid matrix to release the solute. A comparison of typical values for density, viscosity, and diffusivity of gases, liquids, and SCFs is presented in Table 3.2.1.

**Table 3.2.1 Comparison of some properties of gases, liquids, and SCFs<sup>6</sup>.**

| <b>Property</b> | <b>Density (kg/m<sup>3</sup>)</b> | <b>Viscosity</b> | <b>Diffusivity (mm<sup>2</sup>/s)</b> |
|-----------------|-----------------------------------|------------------|---------------------------------------|
| Gas             | 1                                 | 0.01             | 1-10                                  |
| SCF             | 100-800                           | 0.05-0.1         | 0.01-0.1                              |
| Liquid          | 1000                              | 0.5-1.0          | 0.001                                 |

The shaded area in Figure 3.2.1 indicates the supercritical fluid region. It can be shown that by using a combination of isobaric changes in temperature with isothermal changes in pressure, it is possible to bring a pure component from a liquid state to a gas state (and vice versa) through the supercritical region with no phase change (evaporation or condensation).

The behavior of a fluid in the supercritical state can be described as that of a very mobile liquid. The solubility behavior approaches that of the liquid phase while penetration into a solid matrix occurs readily due to the gas-like transport properties. As a consequence, the rates of extraction and phase separation can be significantly faster than for conventional extraction processes. Furthermore, the extraction conditions can be controlled to effect a selected separation. Supercritical fluid extraction is known to be dependent on the density of the fluid that in turn can be manipulated through control of the system pressure and temperature. The dissolving power of a SCF increases with isothermal increase in density or an isopycnic (i.e. constant density) increase in temperature. In practical terms this means, that SCF can be used to extract a solute from a feed

matrix as in conventional liquid extraction. However, unlike conventional extraction, once the conditions are returned to ambient the quantity of residual solvent in the extracted material is negligible.

The basic principle of SCF extraction is that the solubility of a given compound (solute) in a solvent varies with both temperature and pressure. At ambient conditions (25°C and 1 bar) the solubility of a solute in a gas is usually related directly to the vapor pressure of the solute and is generally negligible. In a SCF, however, solute solubility of up to 10 orders of magnitude greater than those predicted by ideal-gas law has been reported.

The dissolution of solutes in supercritical fluids results from a combination of vapor pressure and solute-solvent interaction effects. The impact of this is that the solubility of a solid solute in a supercritical fluid is not a simple function of pressure. Although the solubility of volatile solids in SCFs is higher than in an ideal gas, it is often desirable to increase the solubility further in order to reduce the solvent requirement for processing. The solubility of components in SCFs can be enhanced by the addition of a substance referred to as a co-solvent. The volatility of this additional component is usually intermediate to that of the SCF and the solute. The addition of a co-solvent provides a further dimension to the range of solvent properties in a given system by influencing the chemical nature of the fluid. Co-solvents also provide a mechanism by which the extraction selectivity can be manipulated. The commercial potential of a particular application of SCF technology can be significantly improved through the use of



co-solvents. A factor that must be taken into consideration when using co-solvents, however, is that even the presence of small amounts of an additional component to a primary SCF can change the critical properties of the resulting mixture considerably.

Supercritical extraction is not widely used yet but, as new technologies come, there are more factors that could justify its use, such as high purity, residual solvent content, and environment protection.

Some of the advantages of SCFs compared to conventional liquid solvents for separations are:

1. Dissolving power of the SCF is controlled by pressure and/or temperature
2. SCF is easily recoverable from the extract due to its volatility
3. Non-toxic solvents leave no harmful residue
4. High boiling-point components are extracted at relatively low temperatures
5. Separations not possible by traditional processes can sometimes be effected
6. Thermally labile compounds can be extracted at low temperatures with minimal damage.

Some of the disadvantages are:

1. Elevated pressure required
2. Compression of solvent requires elaborate recycling measures to reduce energy costs
3. High capital investment for equipment

*Solvents of supercritical fluid extraction*

The choice of the SFE solvent is similar to the regular extraction. Principal considerations are the following:

1. Good solving property
2. Inert to the product
3. Easy separation from the product
4. Inexpensive

Carbon dioxide is the most commonly used SCF, due primarily to its low critical parameters (31.1°C, 73.8 bar), low cost, and non-toxicity. However, several other SCFs have been used in both commercial and development processes. The critical properties of some commonly used SCFs are listed in Table 3.2.2.

Table 3.2.2 Properties of some SCF Solvents<sup>8</sup>

| Fluid                         | Critical Temperature (K) | Critical Pressure (bar) |
|-------------------------------|--------------------------|-------------------------|
| Ethylene                      | 282.4                    | 50.4                    |
| Trifluoromethane (Fluoroform) | 299.3                    | 48.6                    |
| Chlorotrifluoromethane        | 302.0                    | 38.7                    |
| Carbon Dioxide                | 304.1                    | 73.8                    |
| Ethane                        | 305.4                    | 48.8                    |
| Propylene                     | 364.9                    | 46.0                    |
| Propane                       | 369.8                    | 42.5                    |
| Ammonia                       | 405.5                    | 113.5                   |
| n-Pentane                     | 469.7                    | 33.7                    |
| Trichlorofluoromethane        | 471.2                    | 44.1                    |
| Cyclohexane                   | 553.5                    | 40.7                    |
| Toluene                       | 591.8                    | 41.0                    |
| Water                         | 647.3                    | 221.2                   |

A SFE unit working with an organic solvent should be explosion-proof; this fact makes the investment higher. Chlorofluorohydrocarbons (CFCs) are very good solvents in SFE due to their high density, but the industrial use of CFCs is restricted because of their effect on the ozonosphere. CO<sub>2</sub> is the most widely used fluid in SFE.

Besides CO<sub>2</sub>, supercritical water is another increasingly used solvent. One of the unique properties of water is that above its critical point (374°C, 221 bar), it becomes an excellent solvent for organic compounds and a very poor solvent for inorganic salts. Due to this characteristic, the same solvent can be used to extract the inorganic and the organic components.

### 3.3 Polymer Modification

Historically, polymers have mostly been used to make solid plastics where the chains are virtually fixed. However nowadays, people dream of new applications of polymeric liquids where fluctuations and interactions (the sticking together or association of different types of molecules) can play a more important role. Many of the most important research goals involve polymers free to fluctuate about in a small-molecule solvent. An important area of research is the modification of the properties of surfaces by the implementation of sulfonated agents in their structure.

#### 3.3.1 Polymer Fluorination

The aromatic ring in polystyrene is suitable for modification reactions, where an electrophilic aromatic substitution takes place. This electrophilic substitution makes possible the introduction of fluorine atoms or fluorine-containing molecules as well as any sulfonating group into the polymer structure. Fluorinated polymers have shown to be useful materials with remarkable properties that include: low surface energies, low dielectric constants and refractive indexes, high

chemical and thermal stability, enhanced chemical resistance, and high solubility in supercritical CO<sub>2</sub>.

There are two different routes to synthesize fluoropolymers. They can be prepared by the polymerization of fluorine-containing monomers, or they can be prepared by polymer modification reactions, which involve the inclusion of fluorine atoms or fluorine moieties into a non-fluorinated parent polymer.

There are numerous methods to fluorinate polymers, depending on the type of polymer that is investigated. These methods range from reactions that use fluorinated reagents to degrade or crosslink the polymeric substrate, to reactions that add or introduce fluorine atoms in a very selective manner to specific functional groups presented in the parental polymer backbone. An ideal fluorination is one that allows for a selective and controlled introduction of fluorine or fluorine-containing molecules, in the polymer backbone without inducing degradation or crosslinking of the parental polymer chains.

Although there are many ways to carry out a fluorination, only few approaches seem to be useful for the fluorination of polystyrene. Two of these are the direct fluorination and the addition of perfluoroalkyl radicals<sup>9-14</sup>.

Hucul and Hahn report the direct fluorination of polystyrene using F<sub>2</sub> resulting in a bulk modification<sup>9</sup> and a surface modification<sup>10</sup>.

The perfluoroalkylation of polyaromatics compounds has been studied due to the interesting biological and physical properties of the perfluoroalkylated aromatic compounds. In 1985, Shuyama<sup>11</sup> realized the first attempt, reporting

the perfluoroalkylation of poly- $\alpha$ -methyl styrene. Here low perfluoroalkylation extents (up to 36%) were obtained apparently due to chain cleavage reactions in competition with the desired alkylation reaction. Better perfluoroalkylation extents were then obtained by the use of fluorine-containing peroxides<sup>12</sup>. It was shown that fluorinated radicals generated from the decomposition of perfluorobutyryl peroxide ( $n\text{-C}_3\text{F}_7\text{CO}_2$ ) at 4°C led to polystyrene perfluoroalkylation up to 69% conversion, indicating minimal chain cleavage or chain coupling reactions. Modifications to the above procedure were reported<sup>13</sup> giving high yields of fluorinated polystyrene with reaction times as short as 1 h.

Recently, the fluorination of linear polystyrene-polybutadiene-polystyrene triblock copolymers using this chemistry was reported<sup>14</sup>. With molar ratios of the fluorinated peroxide to butadiene repeats units of up to 4, no fluorination of the aromatic rings in styrene was observed. Rather, fluorinated products were obtained in the polybutadiene block, indicating a selective reaction with the olefins in the polybutadiene block.

### 3.3.2 Polymer Sulfonation

Crawford et al,<sup>15</sup> from the Army Research Laboratory (ARL), studied the structure/property relationships in polystyrene-polyisobutylene-polystyrene triblock copolymers (PS-PIB-PS) made by different processes using dynamic mechanical analysis (DMA). The PS-PIB-PS films were composed of approximately 3% polystyrene end-blocks. Techniques such as small angle X-ray scattering (SAXS)

and transmission electron microscopy (TEM) confirmed that a self-assembled, segregated cylindrical morphology forms in the copolymer. Modified PS-PIB-PS copolymers were also characterized and were carried out by conversion of approximately 20% of the polystyrene end-blocks to styrene sulfonic acid. They found out that the modified copolymers exhibited distinctly different thermal characteristics than the unmodified copolymers, which were most notable in the storage modulus and  $\tan \delta$  data and that the presence of the sulfonic acid groups disrupted the morphology and solvent sorption characteristics of the copolymers.

Napadensky and co-workers<sup>16</sup> investigated the morphology, viscoelasticity, and transport properties of the sulfonated PS-PIB-PS block copolymer with respect to sulfonation level and counter-ion substitution. Using the dynamic mechanical analysis (DMA), they examined the dynamic storage modulus  $E'$  and dynamic loss modulus  $E''$ , as they relate to changes in sulfonation levels. Small-angle X-ray scattering (SAXS), were also used to confirmed that at a certain percent of sulfonation, a phase transition occurs from hexagonally packed cylinders to lamellar structure due to swelling of the styrene domains caused by the higher sulfonation levels. Napadensky and co-workers<sup>13</sup> used the transport measurements obtained by a Fourier-Transform Infrared Spectrometer (FTIR) to confirm that the sulfonation level directly dictates the transport rate of small molecules (alcohol and water) through the PS-PIB-PS triblock copolymer membrane. They concluded that faster water transport can be achieved by incorporating more sulfonic acid groups throughout the polymer backbone. In

addition, infrared (IR) data clearly identifies molecular interactions between the solvating alcohol molecules and the PS-PIB-PS triblock copolymer. The observed properties suggest that these ion-containing block copolymers are worthy of further development as barrier membranes to be incorporated into materials such as chemical protective clothing.

The same system was also studied by Storey and Baugh<sup>17</sup>. They focussed their studies on polymer characterization by techniques such as small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). They analyzed solvent-cast films of PS-PIB-PS block copolymers and block ionomers; they investigated four block copolymer samples with center block molecular weights of 52,000 g mol<sup>-1</sup> and PS volume fractions ( $\Phi_{\text{PS}}$ ) ranging from 0.17 to 0.31. They described the morphology of all the samples studied as hexagonally packed cylinders of PS within the PIB matrix, with cylinder spacing ranging from 32 to 36 nm for most samples, and cylinder diameters varying from 14 to 21 nm.

### 3.3.3 Polymer Processing using Supercritical Fluids

The use of SCFs to process polymers has focused primarily in the removal of impurities (*i.e.*, residual solvent, unreacted monomers, etc.), due to the poor solubility of these components in SCF CO<sub>2</sub>. Although this was seen as an advantage by some researchers<sup>18-22</sup> their approach has been limited to a few polymers. The new line of co-solvents has opened a new chemical dimension to



the field of SCFs, which will be aimed in this investigation to polymer processing to pursue specific polymer morphologies.

Although the use of SCFs in industrial processes dates back to several decades ago, the technology has been limited by the poor solubility of both hydrophilic and lipophilic molecules in CO<sub>2</sub>. This has limited significantly the extension of the method to numerous important applications including polymers and biomolecules.

Recent studies have solubilized perfluoroether surfactants into SCF CO<sub>2</sub> to increase their polarity and solvating power<sup>22-25</sup>. This has led to additional approaches to replace environmentally undesirable solvents (*e.g.*, acetonitrile, benzene, methylene chloride, toluene, dimethyl acetamide, dimethyl formamide, N-Methyl Pyrrolidone, etc.) with a new line of SCFs<sup>25-27</sup>. These SCFs can be tuned in polarizability by using common commercial surfactants, as it has been supported by spectroscopic studies<sup>28</sup>.

Although the fine-tuned, surfactant-based SCFs have not been applied to tri-block copolymer ionomers, parallel studies<sup>29</sup> to this investigation have studied solvent effects in sulfonated tri-block copolymer ionomers. That study suggests that a highly sulfonated polymer can be chemically modified beyond normal morphological effects using supercritical fluids. That study focused on one polar aprotic co-solvent with sulfonated ionomers. This investigation will extend that study to per-fluorinated sulfonated membranes and with ten solvents of different polarities.

#### 4. OBJECTIVES

The current work focuses on the development and optimization of a new chemically stable ion-exchange membrane (ionomer membrane) for applications such as PEM fuel cells (PEMFC), chemical protective clothing, drug delivery, etc. The materials chosen for this investigation were the perfluorinated ionomer membrane Nafion<sup>®</sup>, and the styrene-ethylene-butylene-styrene (SEBS) polymer (93% sulfonated and unsulfonated).

Those polymer membranes were exposed to different chemical environments and processed in SCF CO<sub>2</sub> to investigate changes in their physical properties and morphology.

## 5. EXPERIMENTAL

### 5.1 Materials

The chemical structure of the Nafion<sup>TM</sup> membrane used in this study is shown in Figure 5.1.1, while its chemical composition was presented in Chapter 1.

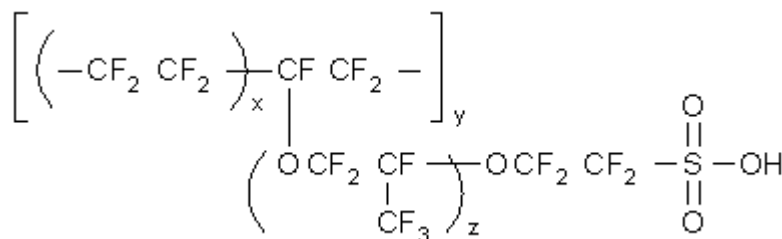


Figure 5.1.1 Structure of Nafion<sup>TM</sup> Membrane

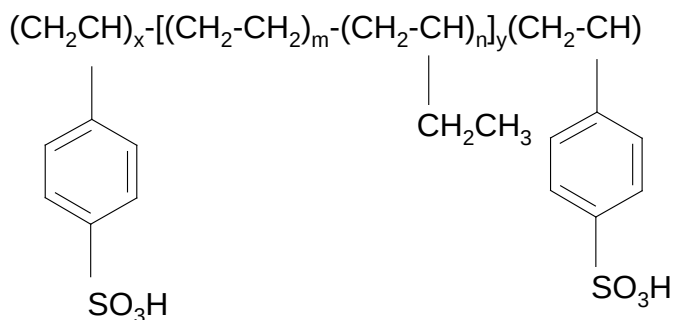
Aldrich Chemicals provided Nafion<sup>TM</sup> membranes. The material was supplied in the form of a film with a thickness of .7 inches. Some relevant properties of the material are listed in Table 5.1.1.

Table 5.1.1 Properties of Nafion<sup>TM</sup> Membranes<sup>30-31</sup>

| <i>Property</i>                  | <i>Typical Value</i>                       |
|----------------------------------|--------------------------------------------|
| IEC (mmol/g)                     | 0.91                                       |
| Density (g/cm <sup>3</sup> )     | 2.27 +/- 0.12                              |
| MeOH permeability                | 1.98 x 10 <sup>-6</sup> cm <sup>2</sup> /s |
| Proton Conductivity              | 0.09 S/cm                                  |
| Activation Energy for Permeation | 10 kJ/mol                                  |

The chemical structure of the SEBS membrane used in this study is shown in

Figure 5.1.2.



**Figure 5.1.2 Structure of Sulfonated SEBS Membrane**

The Army Research Laboratory (ARL) provided sulfonated SEBS membranes. The material was supplied in the form of a film with a sulfonation level of 93%. Kraton™ polymer supplied the unsulfonated SEBS samples. Some relevant properties of the material are listed in Table 5.1.2.

Chemicals to be used were as follows: HPLC grade water (Aldrich), cyclohexanone (Aldrich, ACS grade, Assay 99+%), tetrahydrofuran (Aldrich, ACS grade, Assay 99 +%), isopropyl alcohol (Fisher, HPLC Grade), ethanol (Fisher), acetone (Aldrich, HPLC Grade, 99.9 +%), methanol (Fisher, HPLC Grade), glacial acetic acid (Fisher, Assay 100%), acetonitrile (EM Science, ACS Grade).

## 5.2 Method: SCF Extraction

The basic principle of SCF extraction is that the solubility of a given compound (solute) in a solvent varies with both temperature and pressure. At

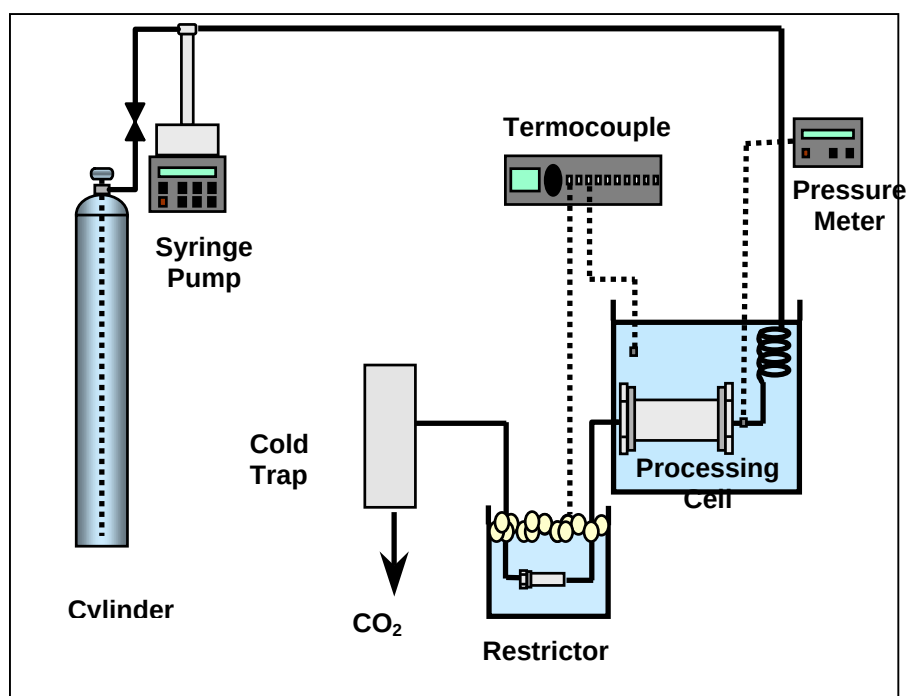
ambient conditions (25°C and 1 bar) the solubility of a solute in a gas is usually related directly to the vapor pressure of the solute and is generally negligible. In a SCF, however, solute solubility's of up to 10 orders of magnitude greater than those predicted by ideal-gas law have been reported.

The dissolution of solutes in supercritical fluids results from a combination of vapor pressure and solute-solvent interaction effects. The impact of this is that the solubility of a solid solute in a supercritical fluid is not a simple function of pressure.

Although the solubility of volatile solids in SCF's is higher than in an ideal gas, it is often desirable to increase the solubility further to reduce the solvent requirement for processing. The solubility of components in SCF's can be enhanced by the addition of a substance referred to as a co-solvent<sup>29</sup>. The volatility of this additional component is usually intermediate to that of the SCF and the solute. The addition of a co-solvent provides a further dimension to the range of solvent properties in a given system by influencing the chemical nature of the fluid.

Co-solvents also provide a mechanism by which the extraction selectivity can be manipulated. The commercial potential of a particular application of SCF technology can be significantly improved through the use of co-solvents. A factor that must be taken into consideration when using co-solvents, however, is that even the presence of small amounts of an additional component to a primary SCF can change the critical properties of the resulting mixture considerably.

Figure 5.2.1 describes the first experiment done. Figure 5.2.2 shows a photograph. In this procedure,  $\text{CO}_2$  is withdrawn from the cylinder into a syringe pump (Isco 260D). The SCF will then go through the extraction unit (Isco SFX-326, Figure 5.2.2), which will be packed with the polymer of choice. Such polymer was exposed to a solvent (e.g., tetrahydrofuran, acetone, methanol, ethanol, acetonitrile, methylene chloride, isopropyl alcohol, glacial acetic acid, cyclohexanone or water). The solvent will then dissolve in the SCF, leaving the solute in the cell in a reverse extraction approach. After the cell, the SCF will be decompressed through a temperature-controlled, coaxially-heated restrictor. At this point, the solvent will condense and will be collected.



**Figure 5.2.1. Supercritical Fluid Extraction Experiment**



**Figure 5.2.2. Supercritical Fluid Extraction Unit**

### 5.3 Method: Thermal Gravimetric Analysis (TGA)

Polymers typically display broad melting endotherms and glass transitions as major analytic features associated with their properties. Both the glass and melting transitions are strongly dependent on processing conditions and dispersion in structural and chemical properties of plastics. Characterization of polymers requires a detailed analysis of these characteristic thermal transitions using either differential scanning calorimeter (DSC) or differential thermal analysis (DTA). Additionally, weight loss with heating is a common phenomenon

for polymers due to degradation and loss of residual solvents and monomers. Weight loss on heating is studied using thermal gravimetric analysis (TGA). This study will be focused on the use of thermal gravimetric analysis.

TGA is a testing procedure in which changes in weight of a specimen are recorded as the specimen is heated in air or in a controlled atmosphere such as nitrogen. Thermogravimetric curves (thermograms) provide information regarding polymerization reactions, the efficiencies of stabilizers and activators, the thermal stability of final materials, and direct analysis. The steps involved during the analysis are:

1. The sample is weighed and a base line established.
2. The temperature of the sample is raised using the heater.
3. Chemical reactions occur that liberate gaseous species or form oxides at various temperatures. As these reactions occur the weight of the sample changes.

The TGA apparatus is a microbalance where the weighing pan can be subjected to a selected temperature or temperature programmed in a selected atmosphere. It is most frequently used for studies of the thermal degradation of polymers but all other chemical reactions resulting in changes of mass can be followed, as well as physical processes such as absorption, adsorption, desorption. Figure 5.3.1 refers to the TGA equipment used in this work.





**Figure 5.3.1 Mettler Toledo TGA/SDTA 851<sup>e</sup> Equipment**

In this work a Mettler Toledo TGA/SDTA 851<sup>e</sup> was used to study thermal degradation behavior of Nafion<sup>TM</sup> and SEBS membranes. Samples were tested using nitrogen atmospheres at a heating rate of 10°C/min. Sample weight varied between 4.0 mg and 5.0 mg. The results were reported as weight percent change vs. temperature and the derivative of weight percent change respect temperature. Characteristic TGA traces of Nafion<sup>TM</sup> and SEBS membranes are shown in Figure 5.3.2 and Figure 5.3.3.

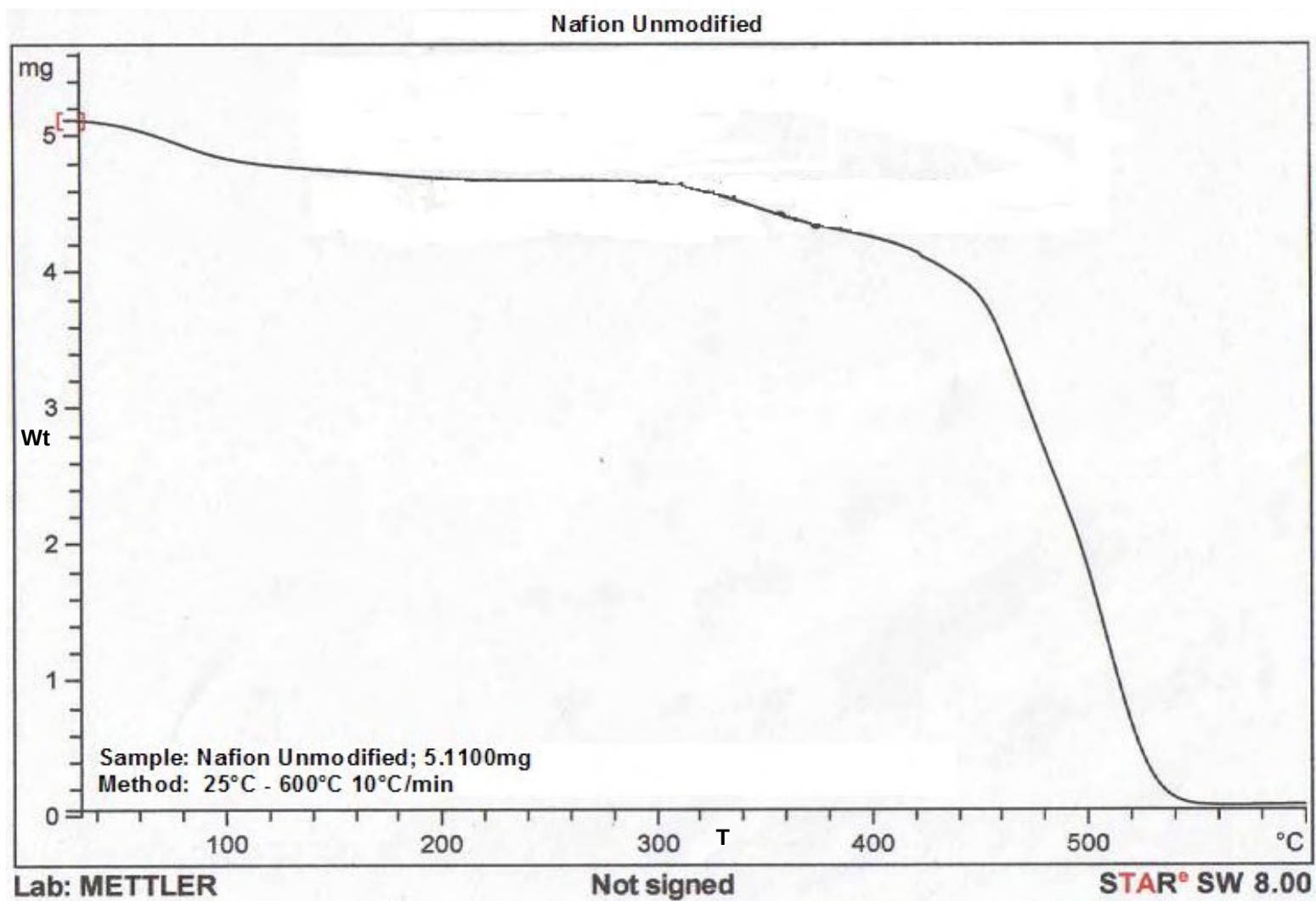


Figure 5.2.2 TGA of Nafion™ in N<sub>2</sub>

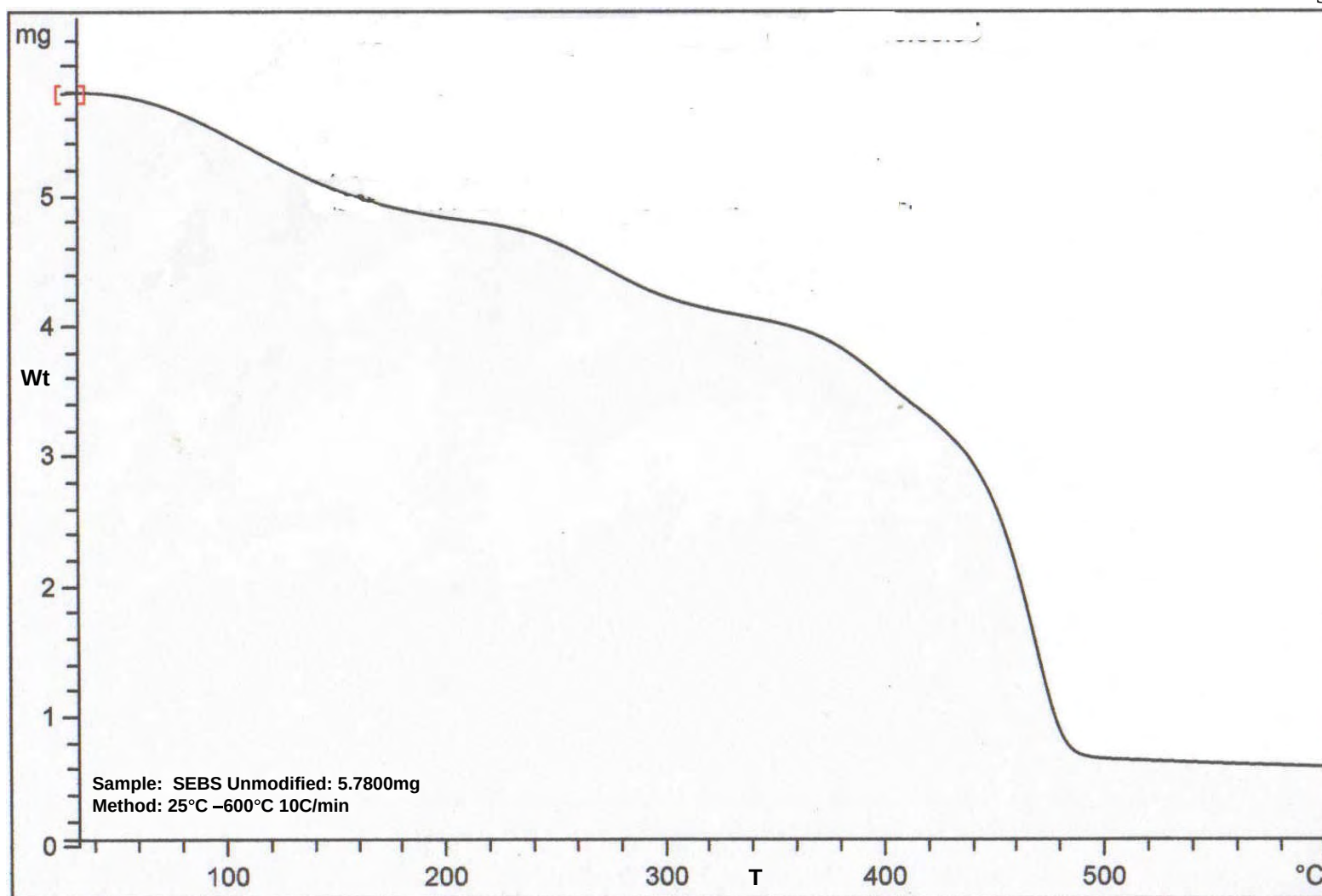


Figure 5.3.3 TGA of SEBS 93% Sulfonation in N<sub>2</sub>

## 6. RESULTS

### 6.1. TGA: SEBS 93 % sulfonated Membranes

The results of TGA scans of sulfonated SEBS membranes under  $N_2$  atmosphere are shown from Figure 6.1.1 to Figure 6.1.12 and summarized in Table 7.1.1.

TGA scan of SEBS 93% sulfonated unmodified (without processing) presents four characteristic peaks. The first peak occurred in a temperature ranges between 40°C and 200°C, second and third peaks corresponded to temperature range from 210°C to 330°C and from 360°C to 410°C. The largest weight derivative peak is observed at 466°C for this sample.

When SEBS samples were processed in different chemical environments with SCF  $CO_2$  some changes the TGA scan were observed. The co-solvents with low solubility parameters ( $\delta < 12.7$ ) show the four peaks presented previously for SEBS unmodified sample. However, changes in the TGA scans were observed for those samples processed in  $scCO_2$  in which co-solvents with high solubility parameter ( $\delta \geq 12.7$ ) were used. Those TGA scans showed only three characteristic peaks as we can note in Figures 6.2.9, 6.2.10 and 6.2.11.

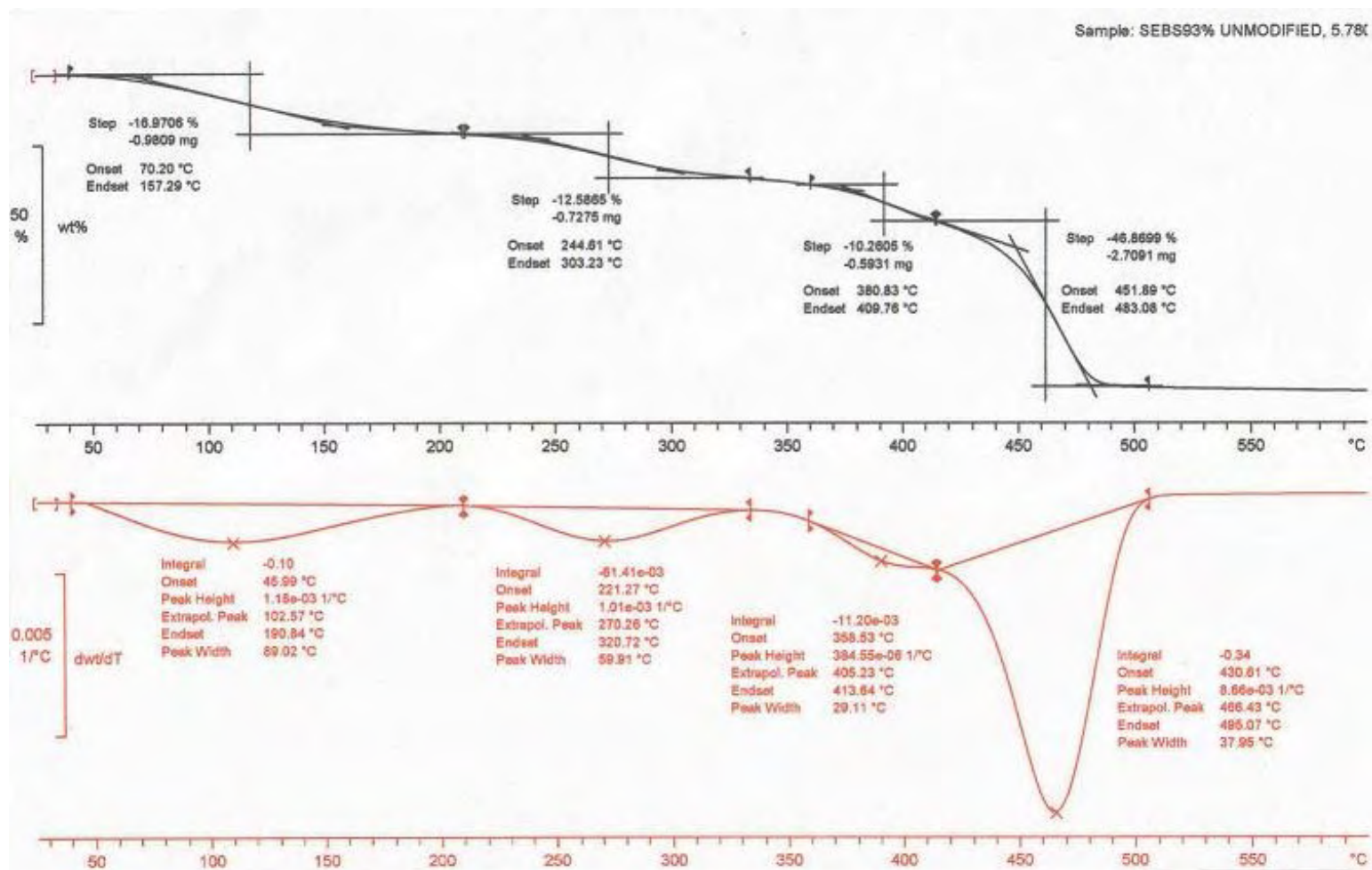


Figure 6.1.1 TGA Scan of SEBS 93% Sulfonated Unmodified

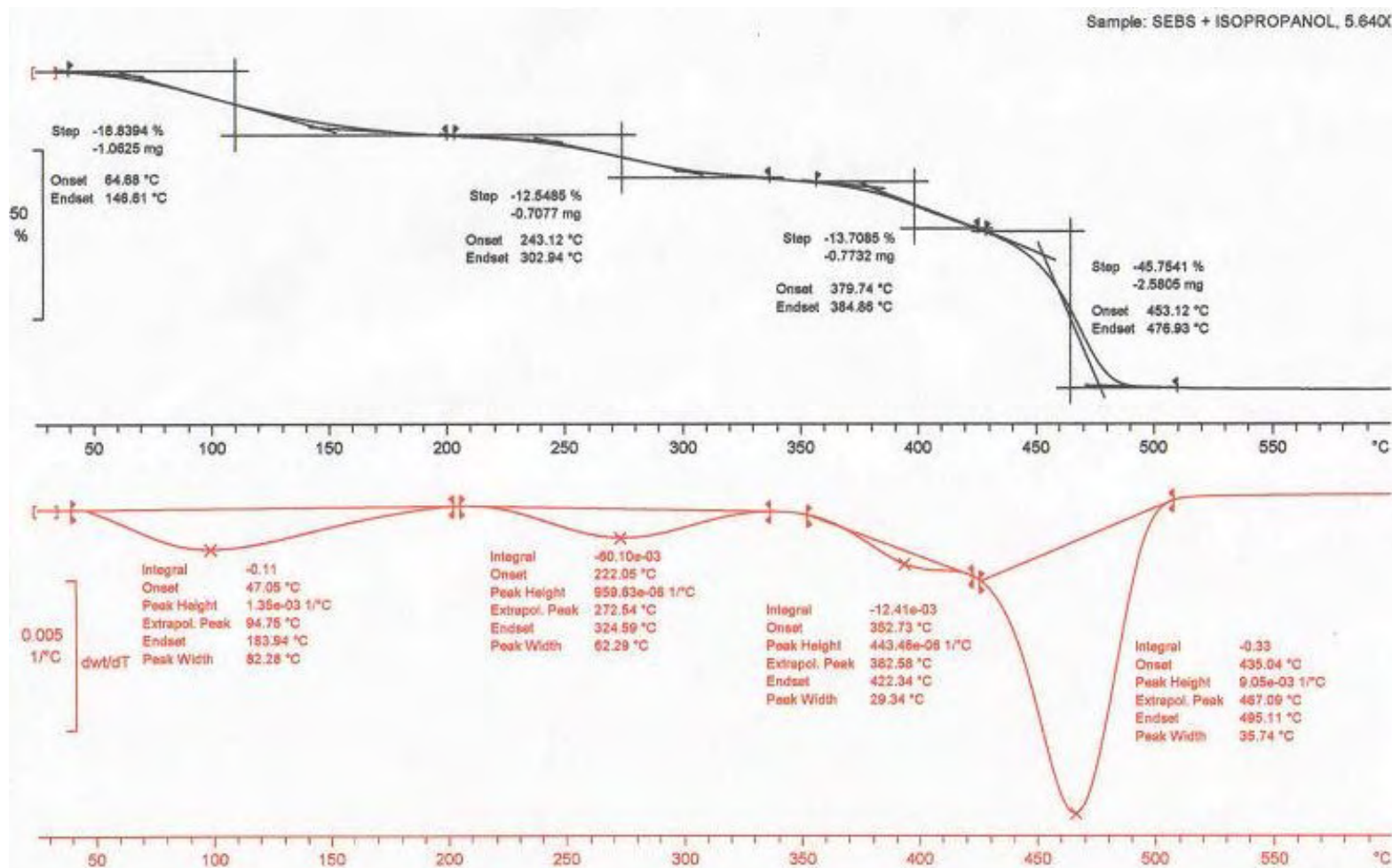


Figure 6.1.2 TGA of SEBS 93% Sulfonated + Isopropyl Alcohol Processed in scCO<sub>2</sub>



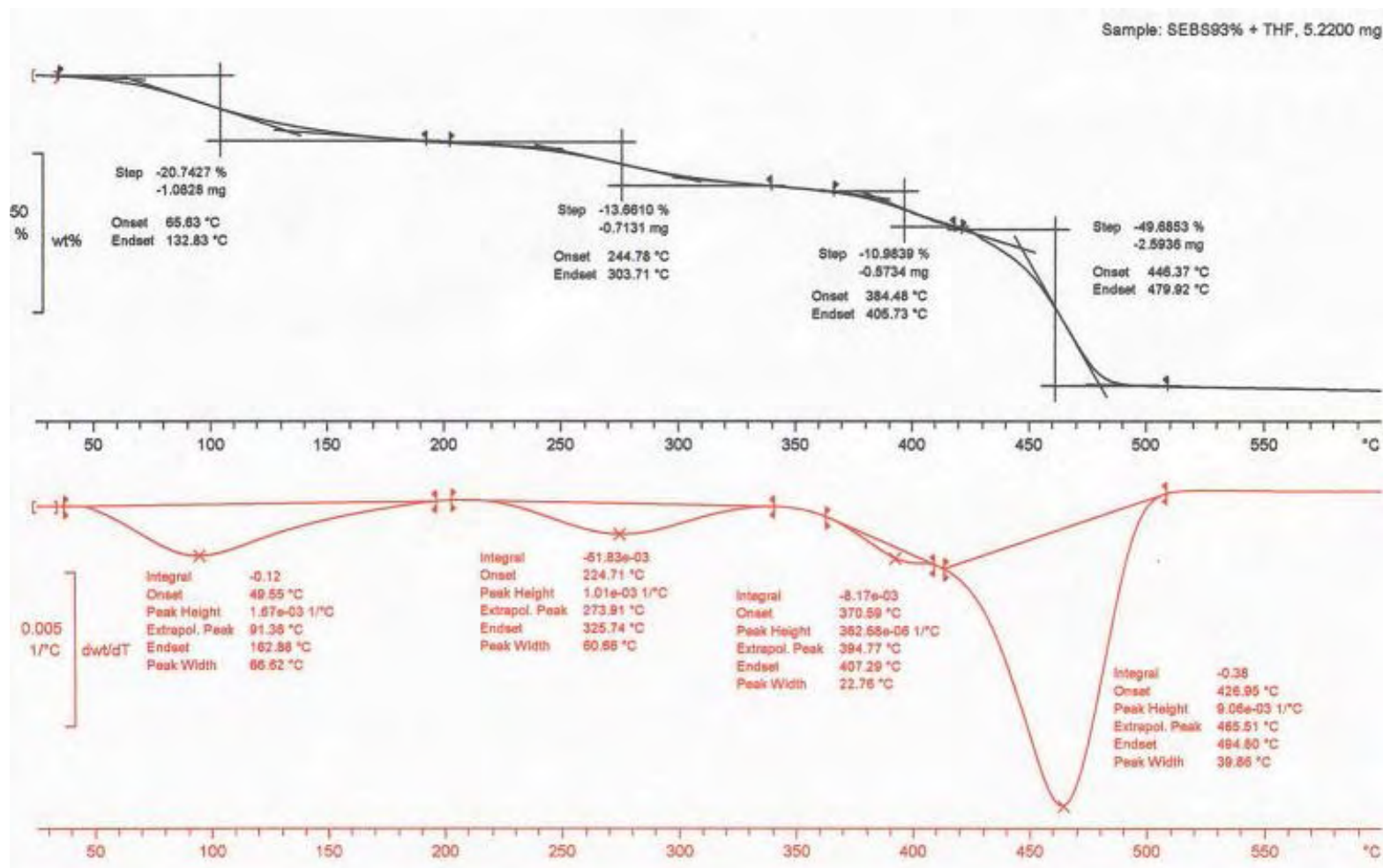


Figure 6.1.3 TGA of SEBS 93% Sulfonated + Tetrahydrofuran Processed in scCO<sub>2</sub>

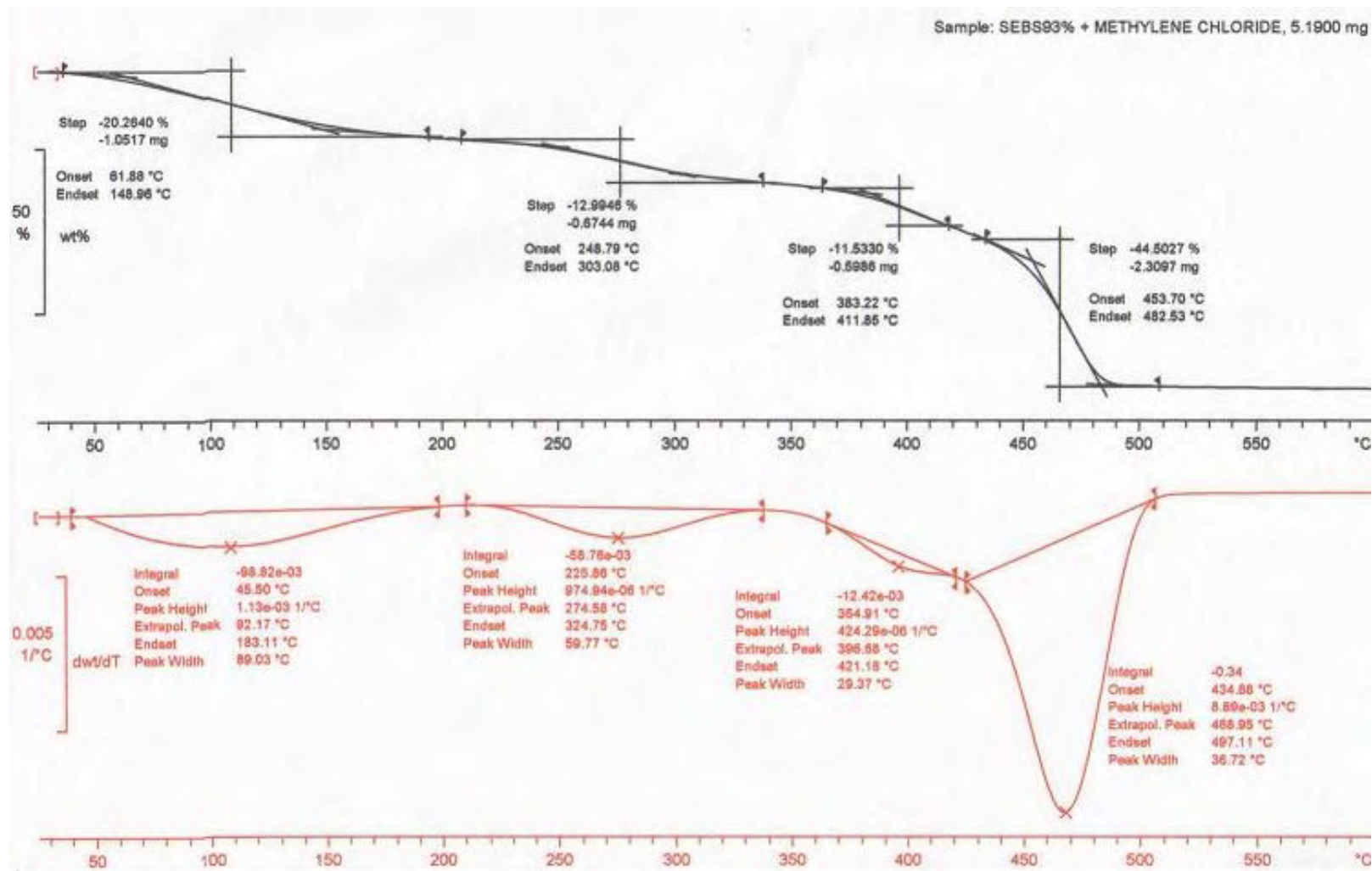


Figure 6.1.4 TGA of SEBS 93% Sulfonated + Methylene Chloride Processed in scCO<sub>2</sub>



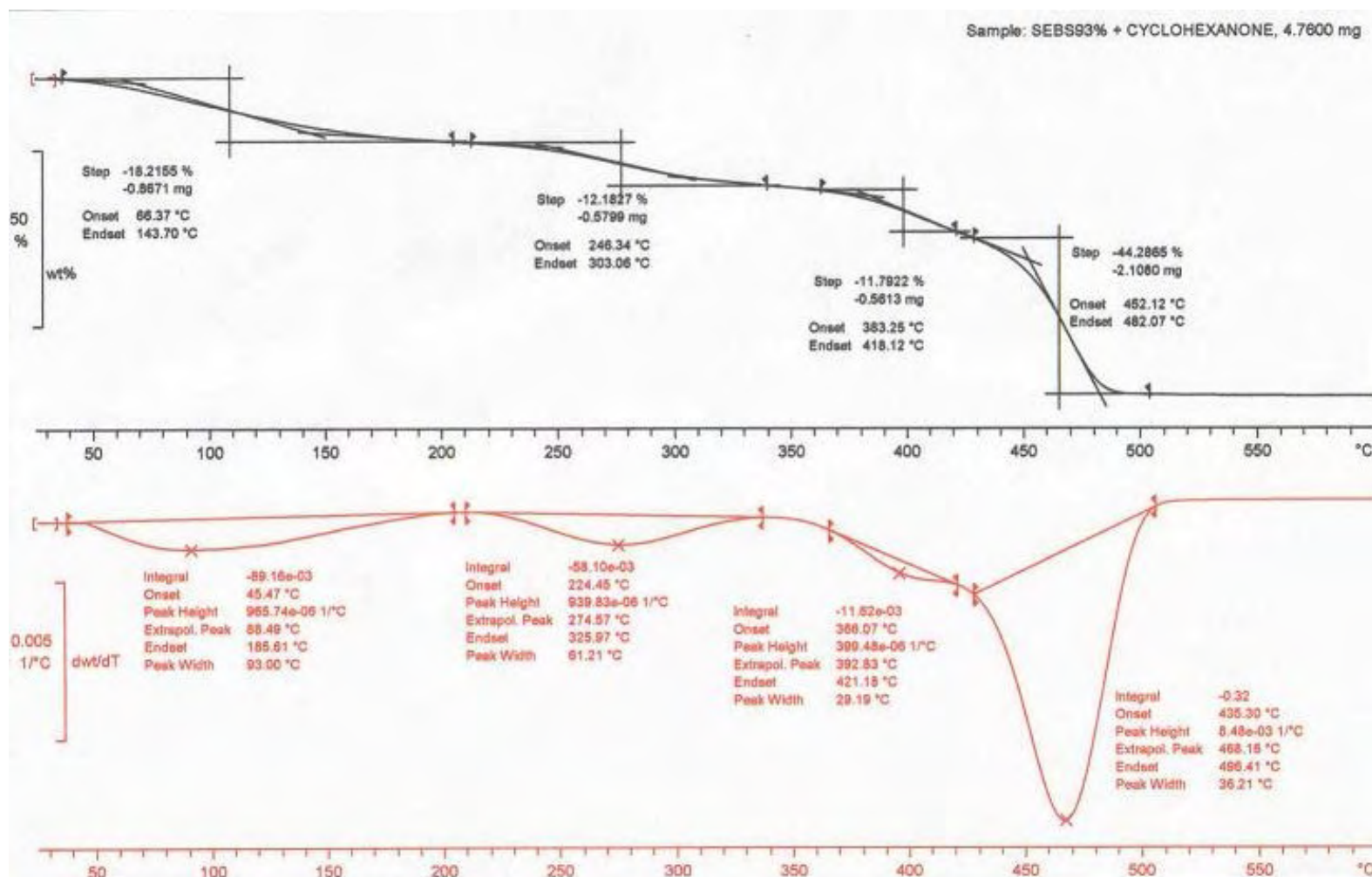


Figure 6.1.5 TGA of SEBS 93% Sulfonated + Cyclohexanone Processed in scCO<sub>2</sub>

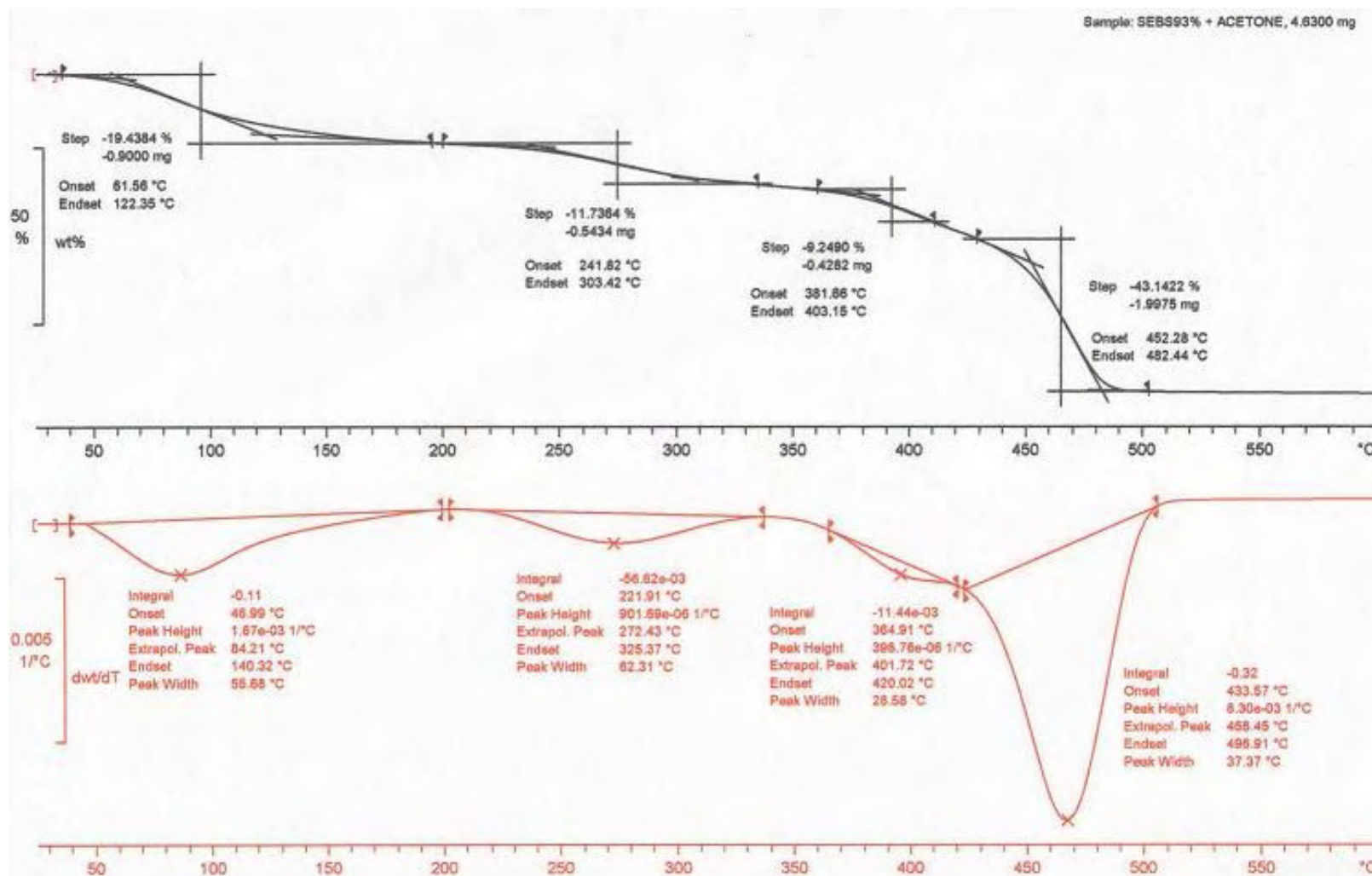


Figure 6.1.6 TGA of SEBS 93% Sulfonated + Acetone Processed in scCO<sub>2</sub>

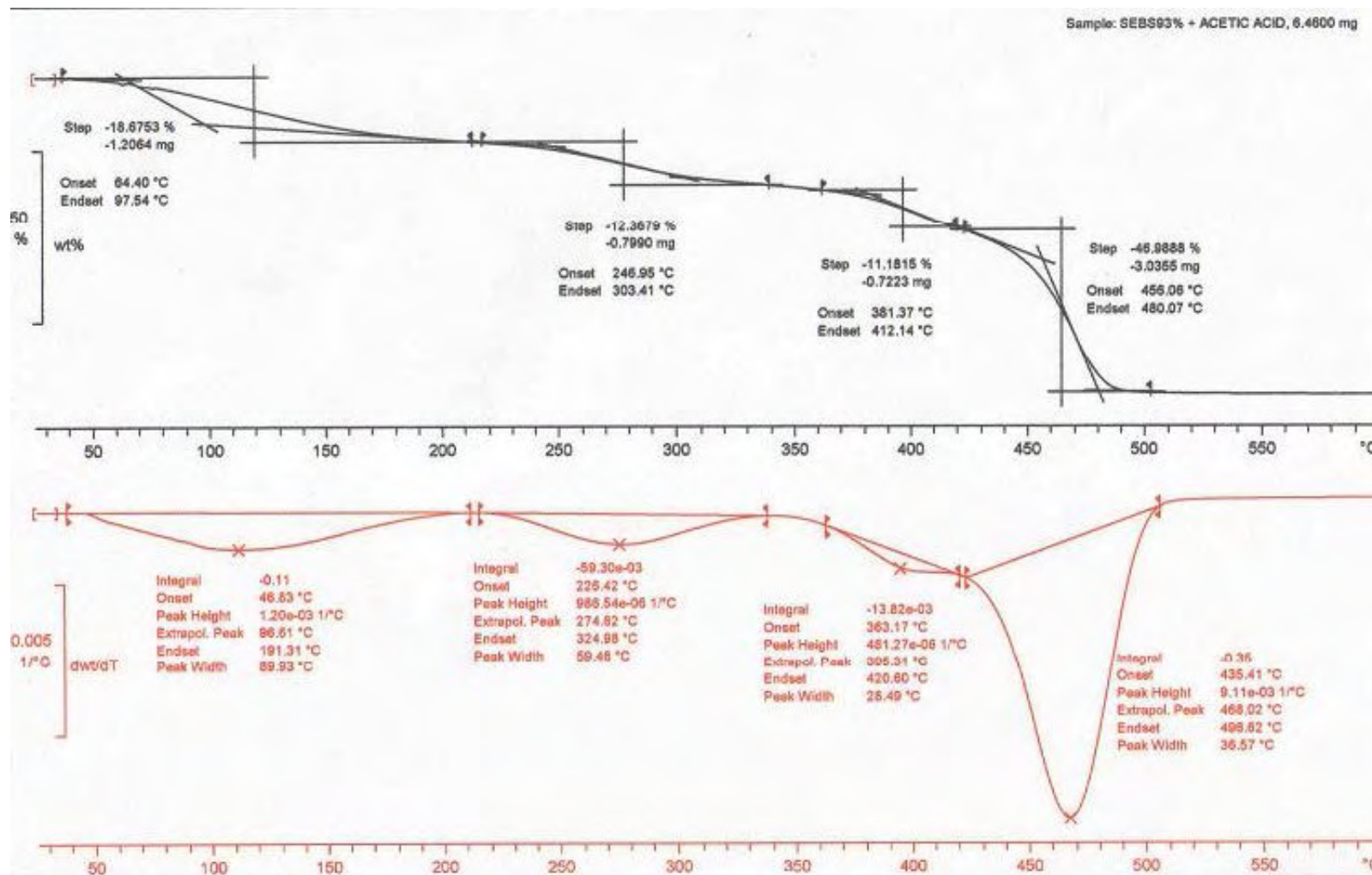


Figure 6.1.7 TGA of SEBS 93% Sulfonated + Acetic Acid Processed in scCO<sub>2</sub>

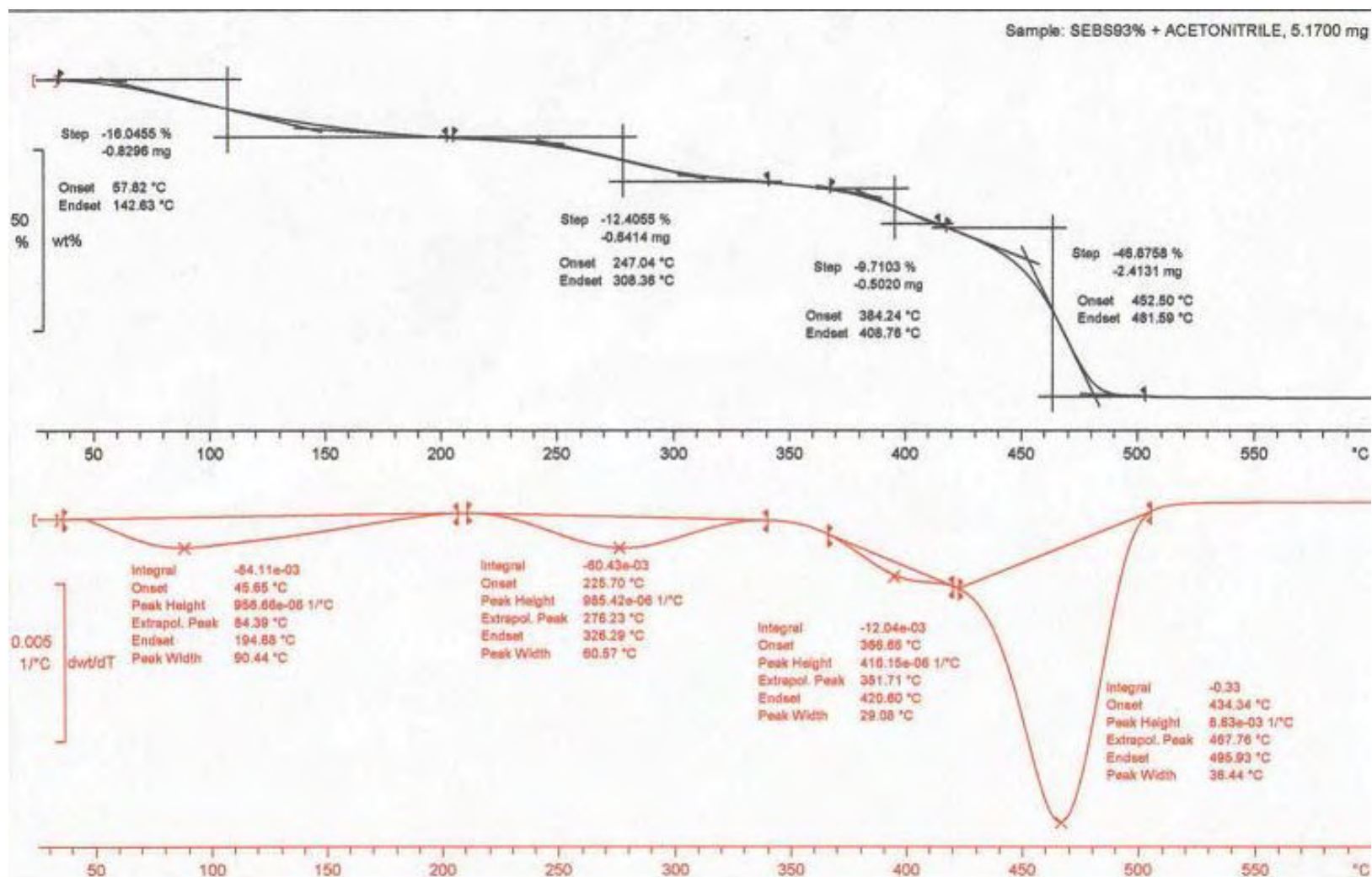


Figure 6.1.8 TGA of SEBS 93% Sulfonated + Acetonitrile Processed in scCO<sub>2</sub>



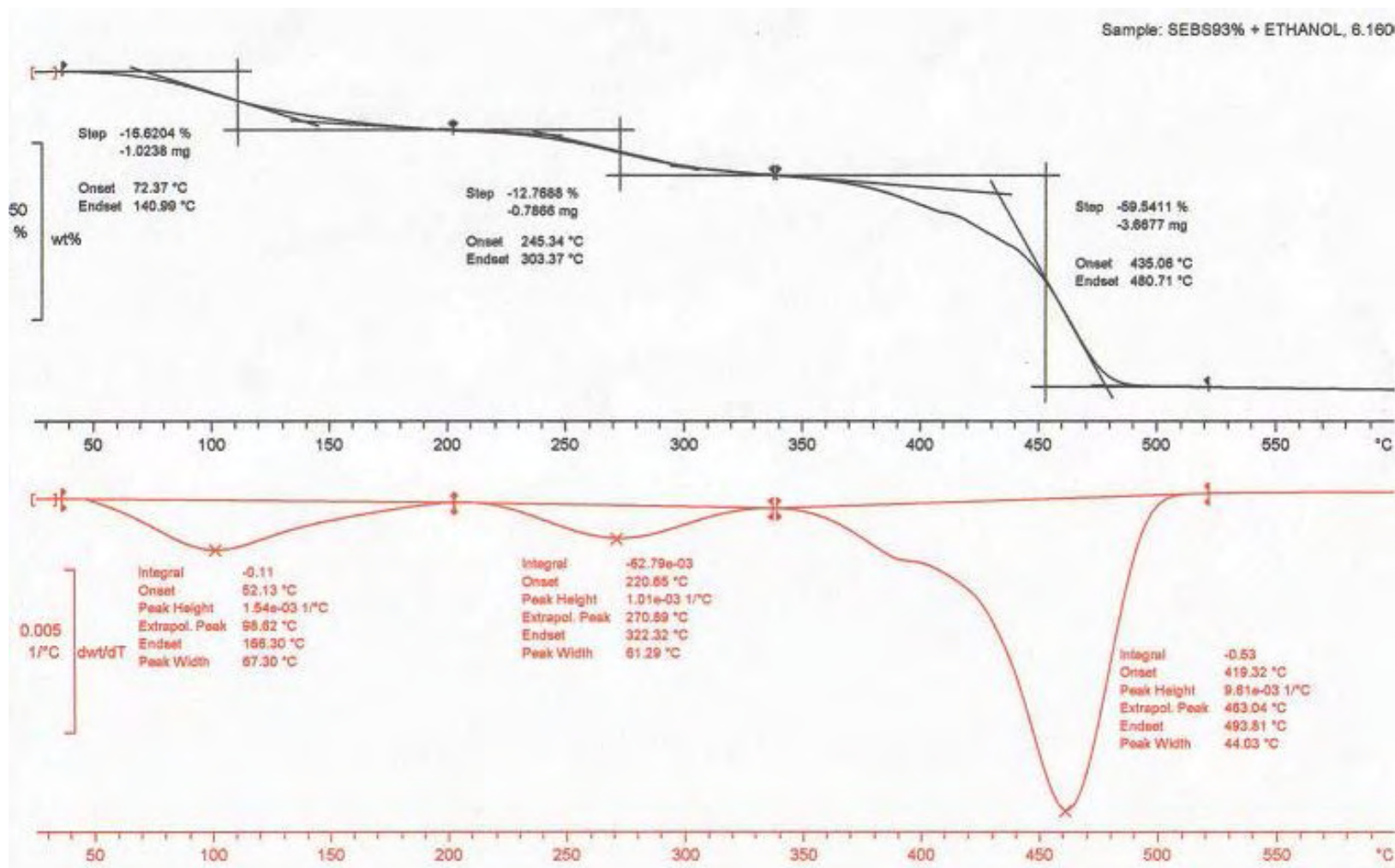


Figure 6.1.9 TGA of SEBS 93% Sulfonated + Ethanol Processed in scCO<sub>2</sub>

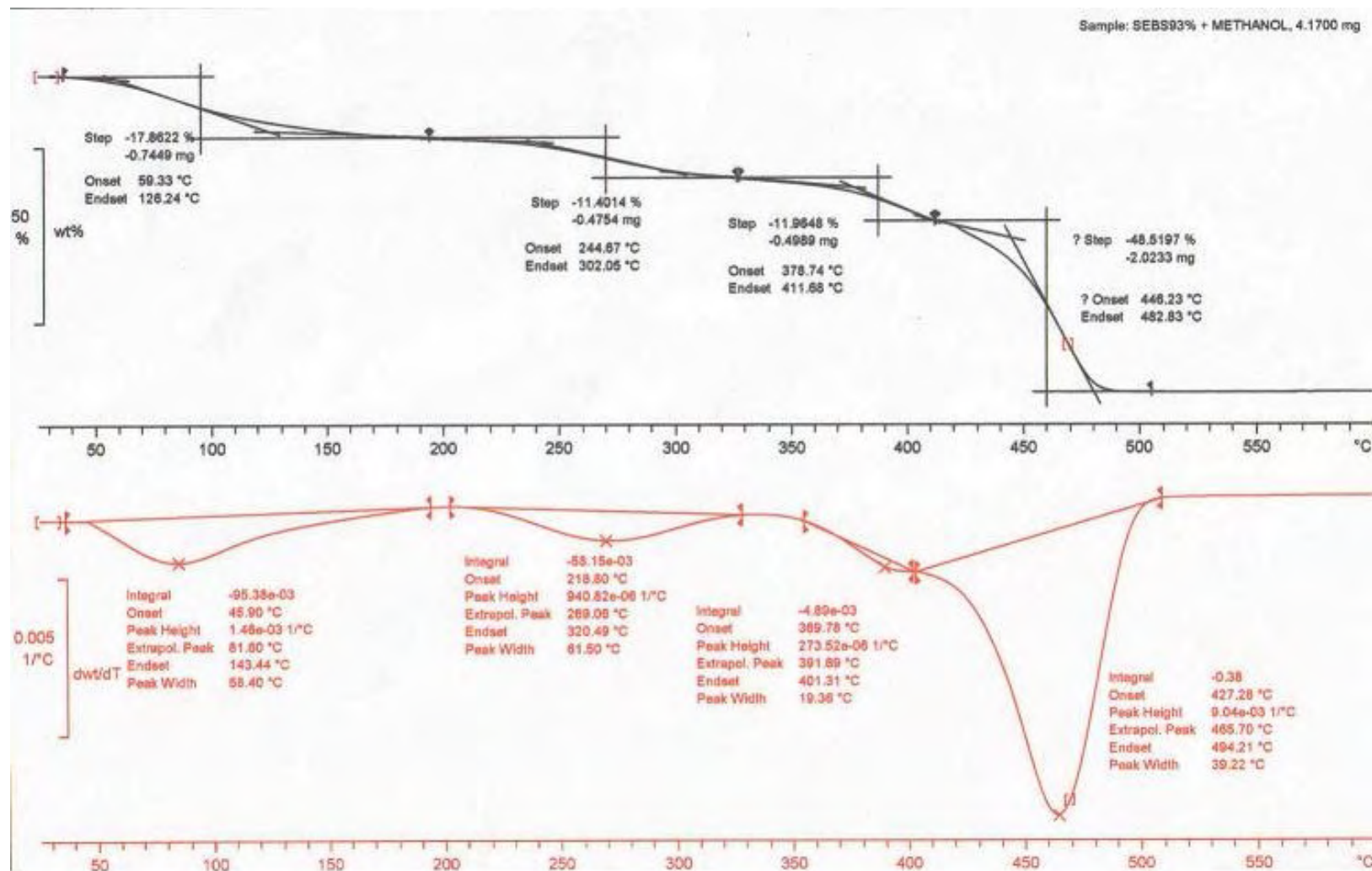


Figure 6.1.10 TGA of SEBS 93% Sulfonated + Methanol Processed in scCO<sub>2</sub>

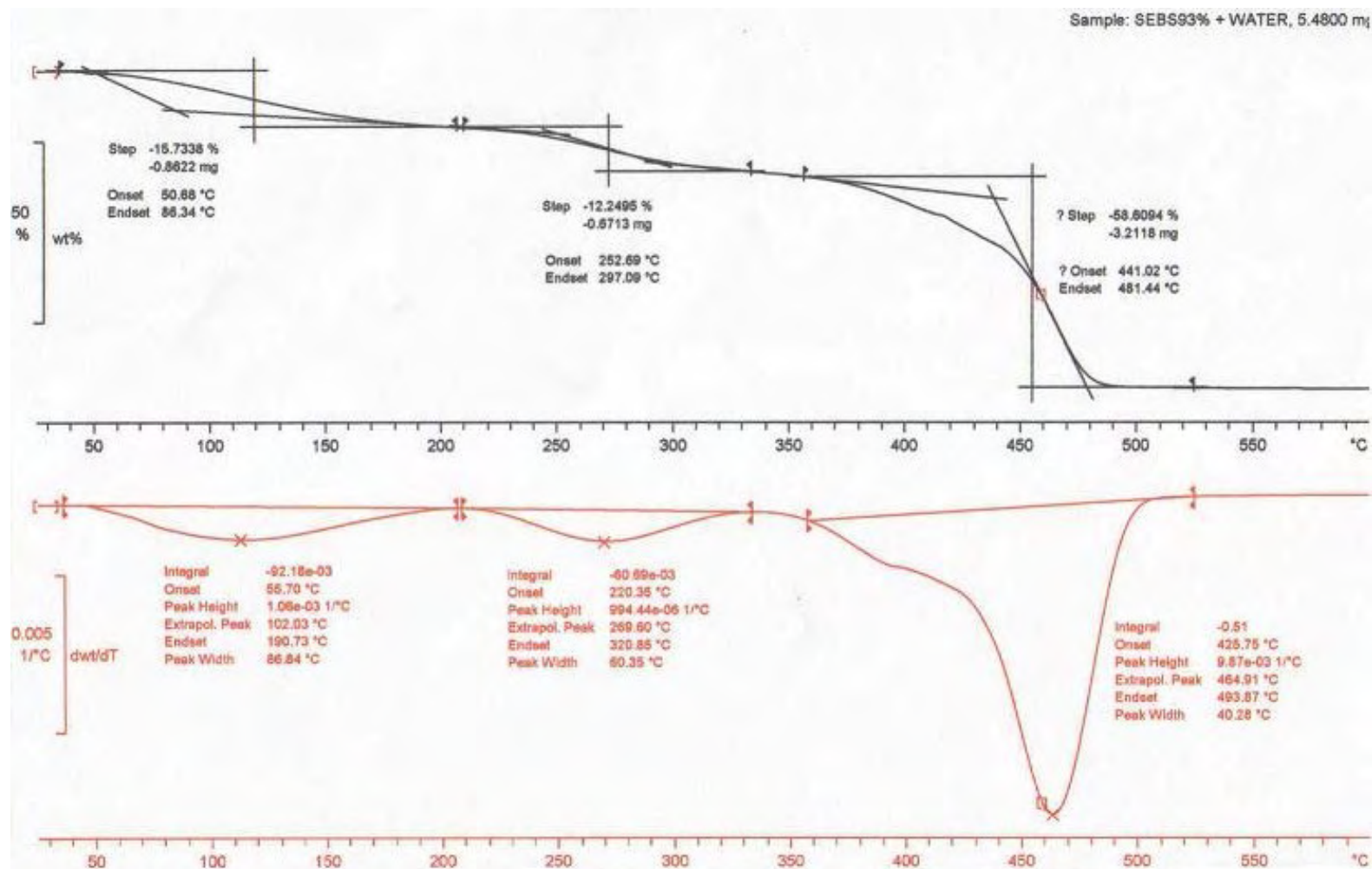


Figure 6.1.11 TGA of SEBS 93% Sulfonated + Water Processed in scCO<sub>2</sub>

Table 7.1.1 Decomposition Temperature for SEBS 93% sulfonated samples

| Sulfonated SEBS Sample           | Decomposition Temperature °C |        |        |        |
|----------------------------------|------------------------------|--------|--------|--------|
|                                  | 102.57                       | 270.26 | 405.23 | 466.43 |
| Unmodified                       | 102.57                       | 270.26 | 405.23 | 466.43 |
| Processed with scCO <sub>2</sub> | 90.14                        | 271.88 | 388.71 | 471.68 |
| Isopropyl Alcohol                | 94.75                        | 272.54 | 382.58 | 467.09 |
| Tetrahydrofuran                  | 91.36                        | 273.91 | 394.77 | 465.51 |
| Methylene Chloride               | 92.17                        | 274.58 | 396.68 | 468.95 |
| Cyclohexanone                    | 88.49                        | 274.57 | 392.83 | 468.16 |
| Acetone                          | 84.21                        | 272.43 | 401.72 | 468.45 |
| Acetic Acid                      | 96.61                        | 274.62 | 395.31 | 468.02 |
| Acetonitrile                     | 84.39                        | 276.23 | 381.71 | 467.76 |
| Ethanol                          | 98.62                        | 270.89 | Absent | 463.04 |
| Methanol                         | 81.60                        | 269.06 | Absent | 465.70 |
| Water                            | 102.03                       | 269.60 | Absent | 464.91 |

## 6.2 TGA: Nafion<sup>TM</sup> Membranes

The result of TGA scans of Nafion<sup>TM</sup> membranes under N<sub>2</sub> atmosphere are shown from Figure 6.2.1 to Figure 6.2.12.

The TGA scan of Nafion<sup>TM</sup> unmodified shows four characteristic peaks in  $74.37 \pm 0.6$ ,  $340.62 \pm 0.6$ ,  $479.22 \pm 5$ ,  $509.83 \pm 2$ , respectively. When Nafion<sup>TM</sup> is



process in  $\text{scCO}_2$ , a difference is presented in the TGA scan in Figure 6.2.2. The difference between the scans is that the small peak on the derivative weight % curve at  $479.22^\circ\text{C}$  present in the Nafion<sup>TM</sup> unmodified membrane is absent in Nafion<sup>TM</sup> processing with  $\text{scCO}_2$ .

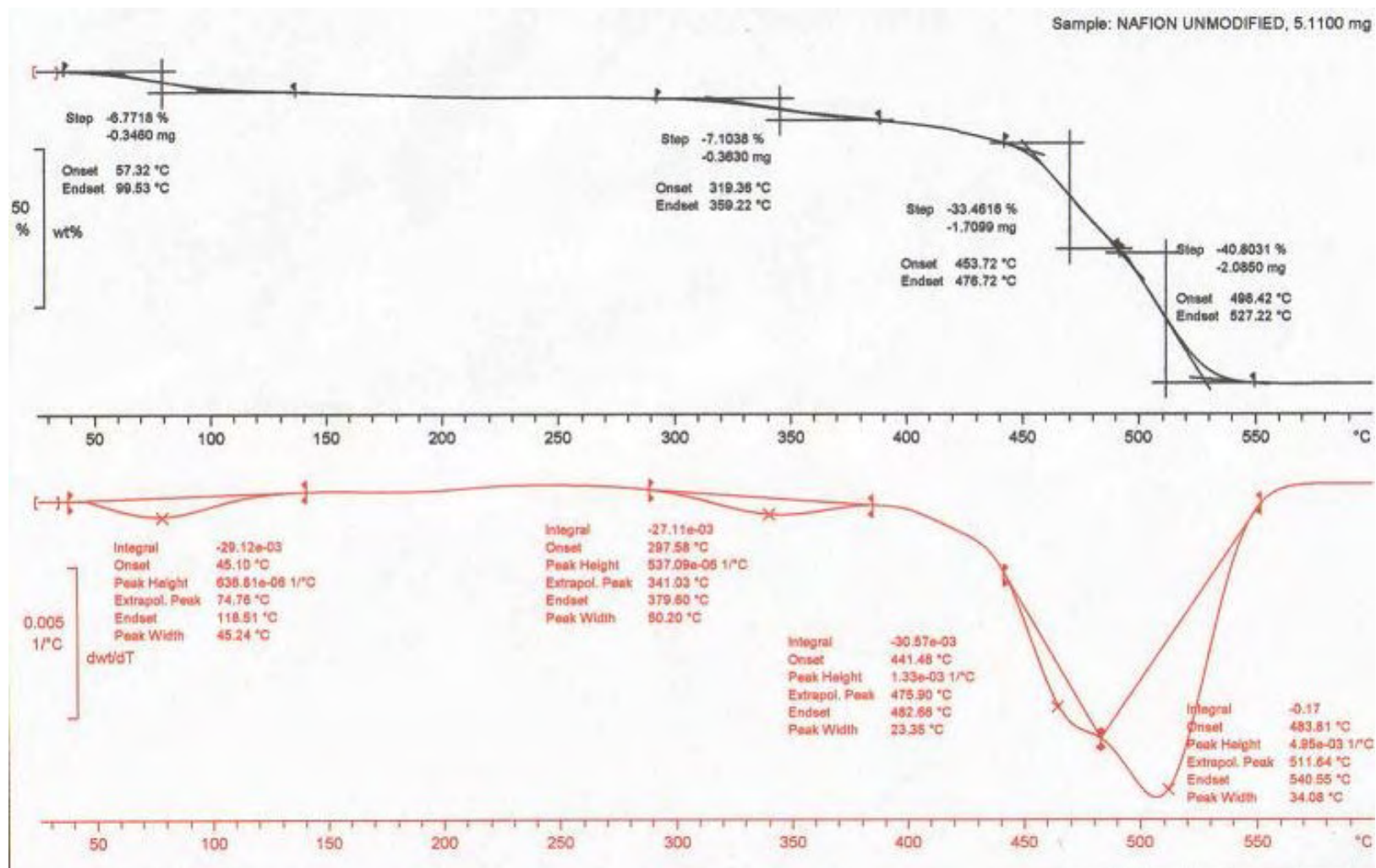


Figure 6.2.1a TGA of Nafion™ Unmodified (Trial 1)

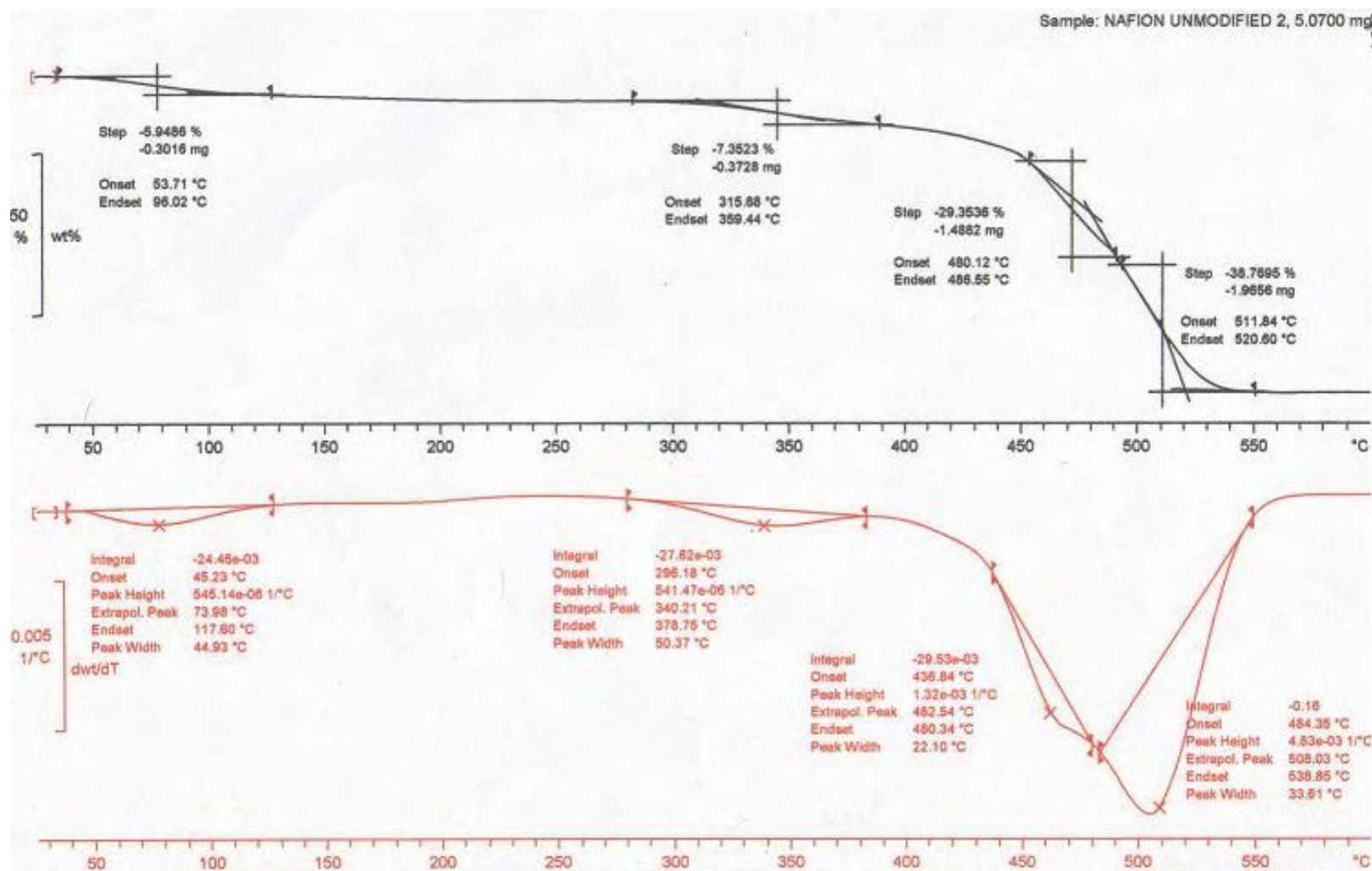


Figure 6.2.1b TGA of Nafion™ Unmodified (Trial 2)

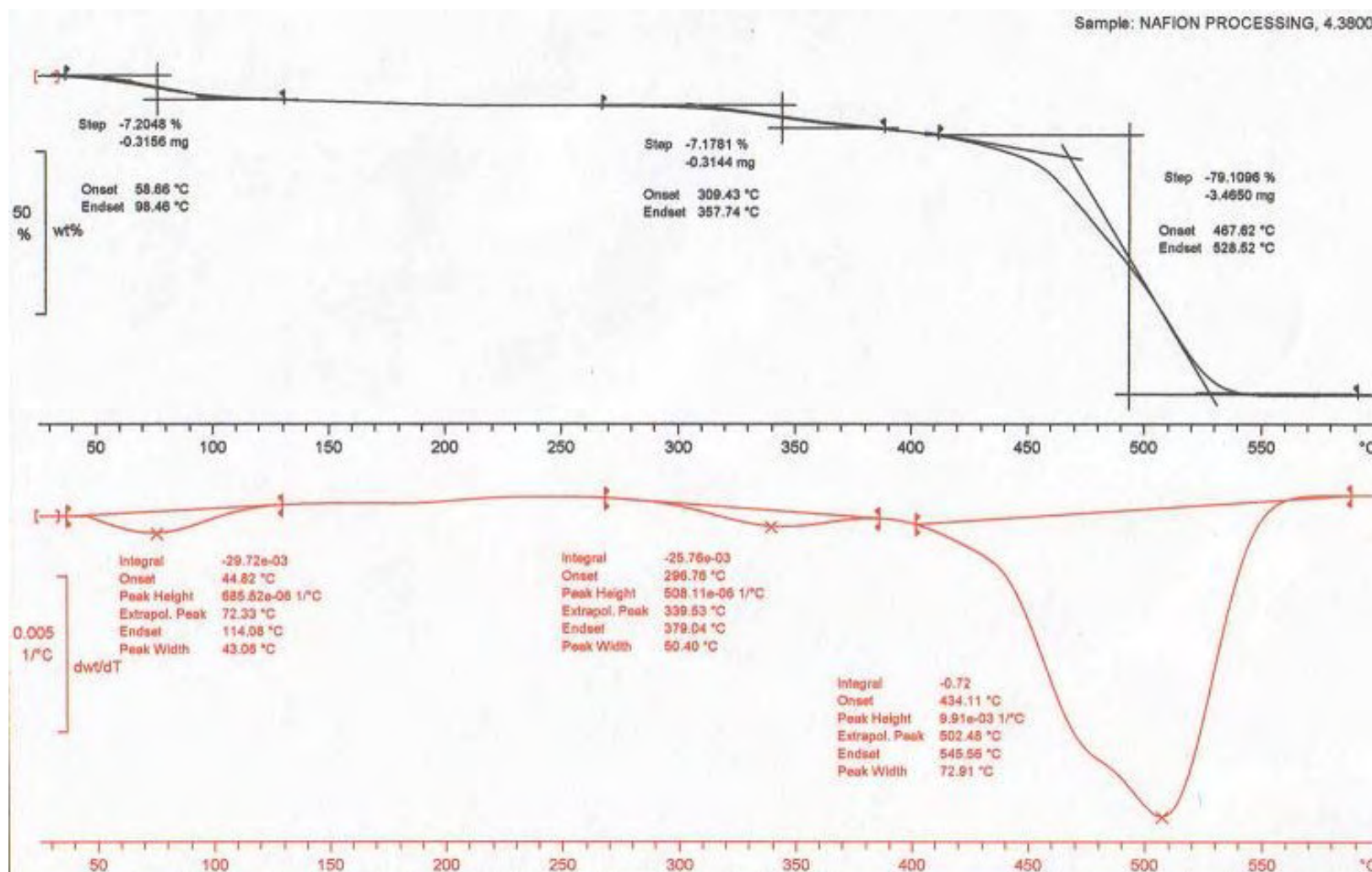


Figure 6.2. 2a TGA of Nafion™ Processed in scCO<sub>2</sub> (Trial 1)

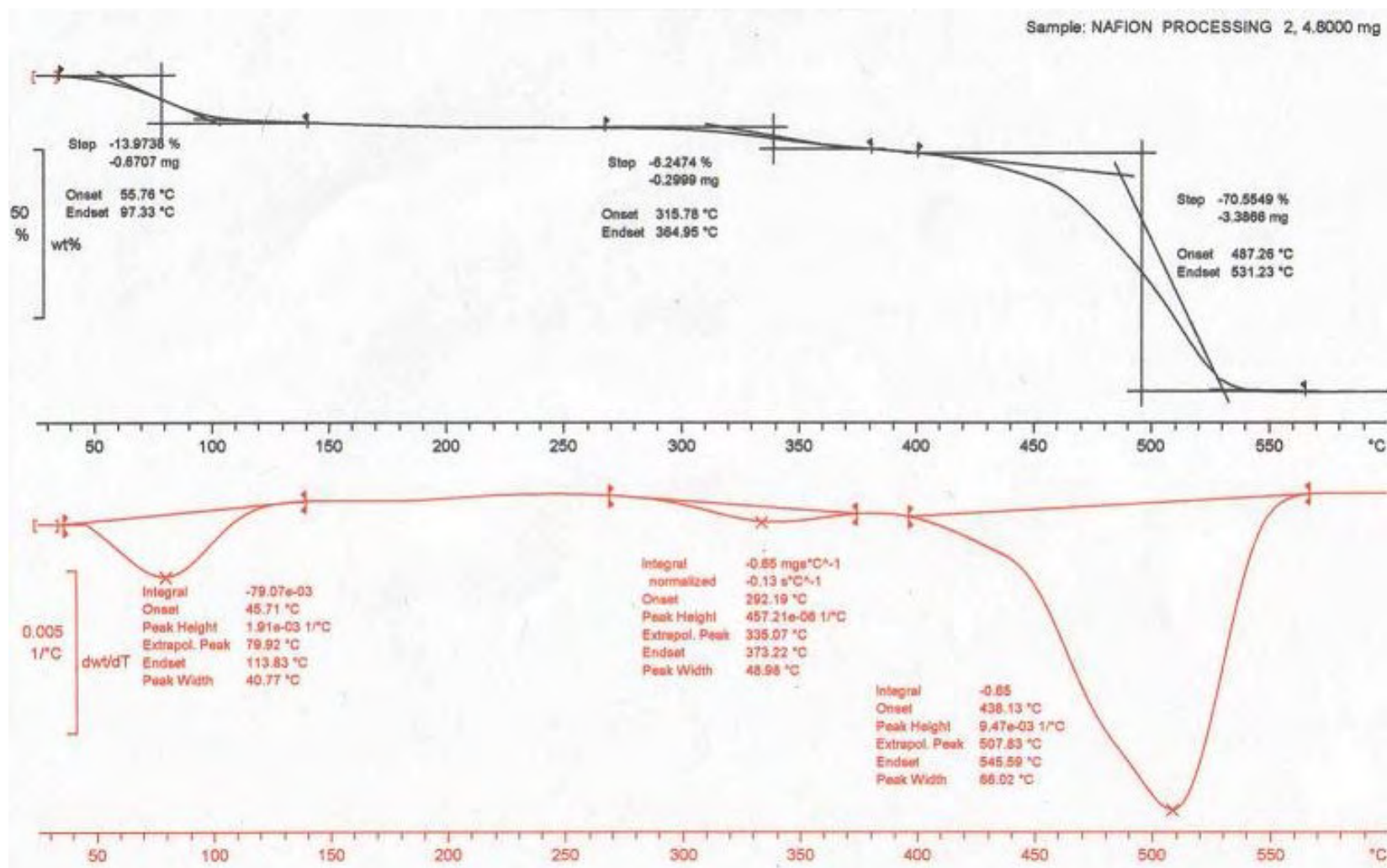


Figure 6.2. 2b TGA of Nafion™ Processed in scCO<sub>2</sub> (Trial 2)

The effect of the co-solvent on the degradation behavior of Nafion<sup>TM</sup> membranes is shown from Figure 6.2.3 to Figure 6.2.12. All traces show two small peaks in the weight derivative curve in the temperature range of 40°C to 375°C. All ten scans possess much of the same characteristic peaks in the derivative weight % curve (Table 6.3.1). Again, the third small peak present in the Nafion<sup>TM</sup> unmodified sample disappears when it is exposed to different polar environments (by the use of different co-solvents) and the position of the large weight loss peak has moved from 508.03°C for unmodified Nafion<sup>TM</sup> to different values ranging from 456.11°C to 510.57°C.



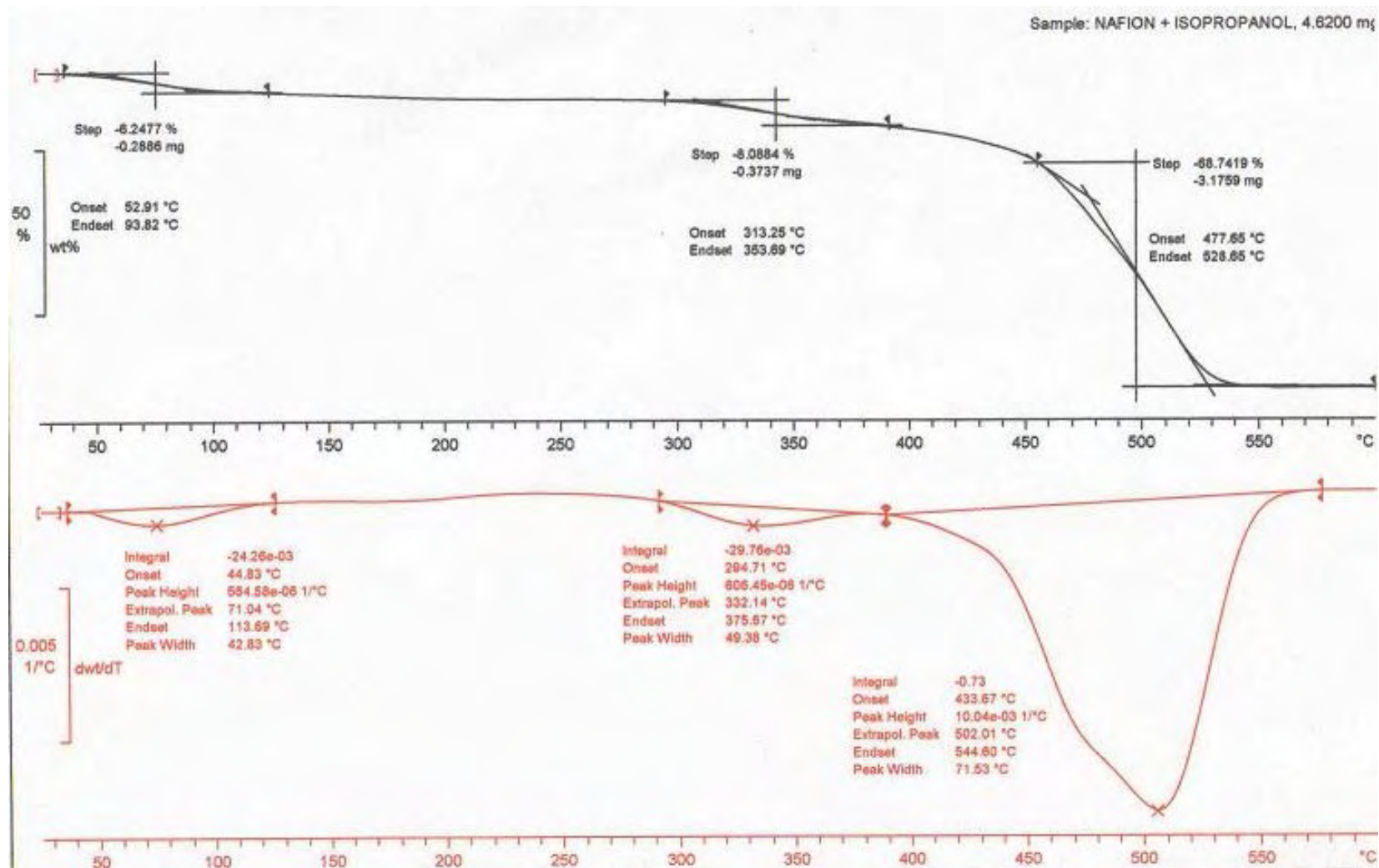


Figure 6.2.3a Nafion™ + Isopropyl Alcohol Processed in scCO<sub>2</sub> (Trial 1)

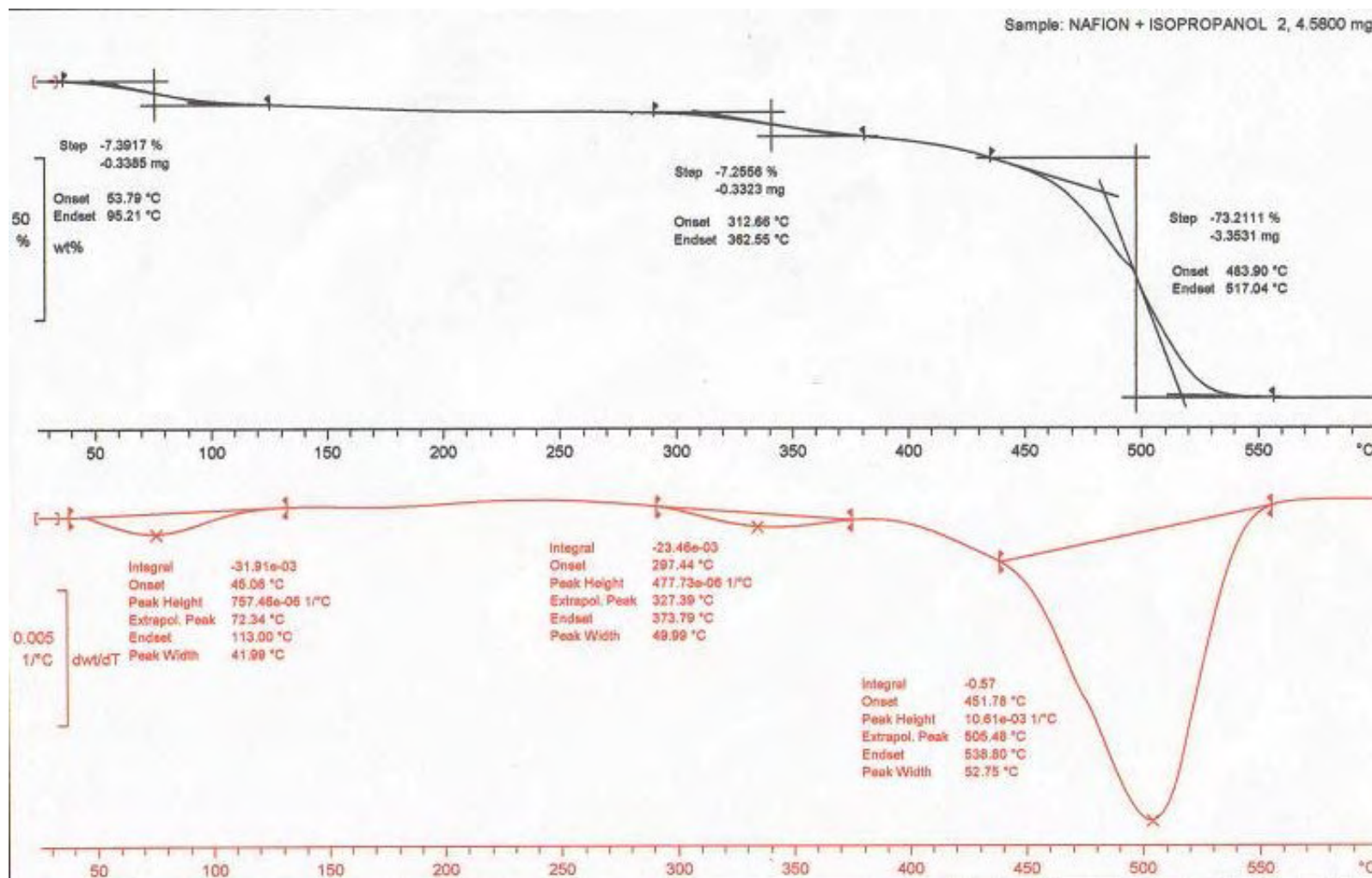


Figure 6.2.3b Nafion™ + Isopropyl Alcohol Processed in scCO<sub>2</sub> (Trial 2)



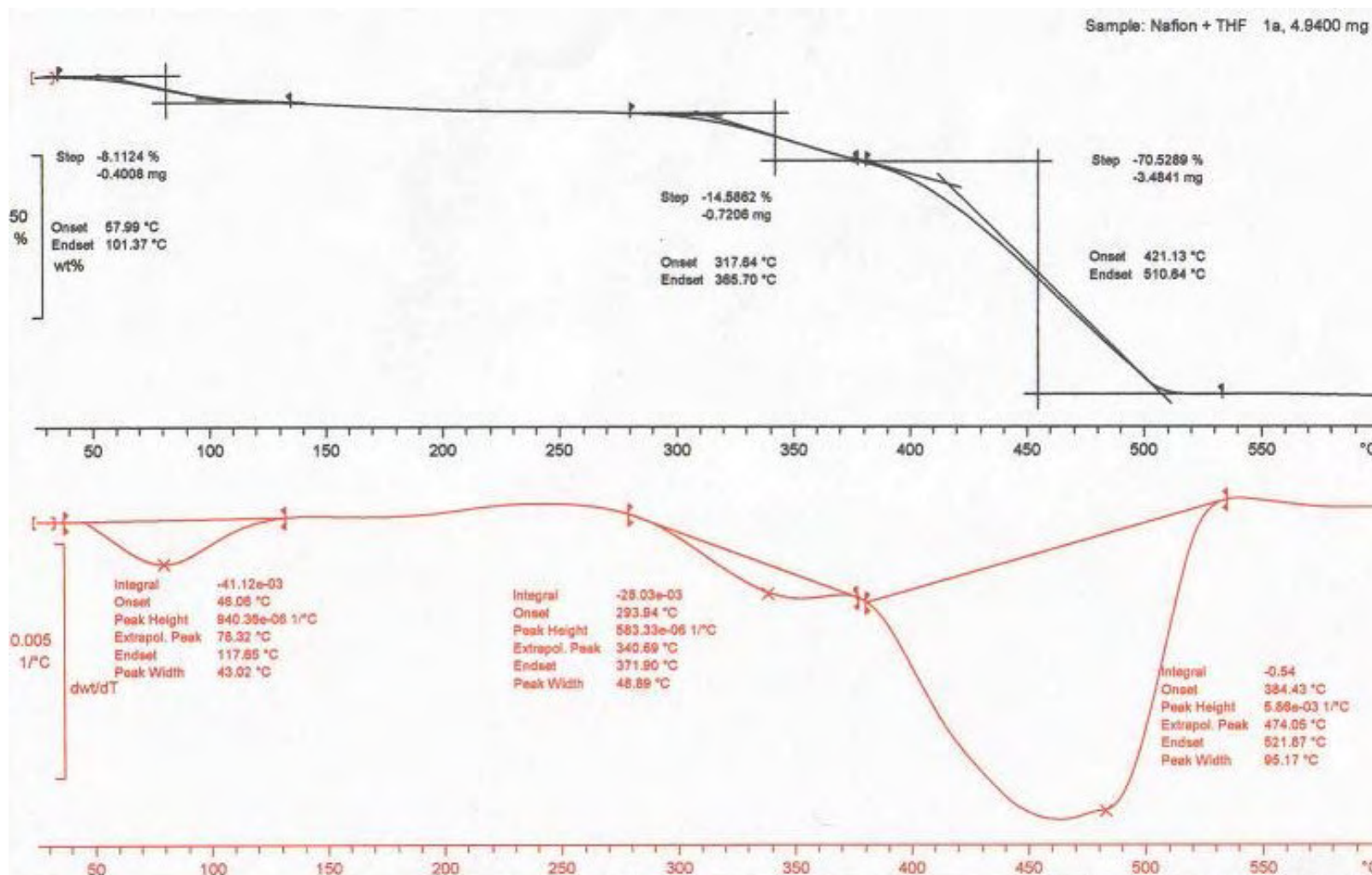


Figure 6.2.4a Nafion™ + Tetrahydrofuran Processed in scCO<sub>2</sub> (Trial 1)

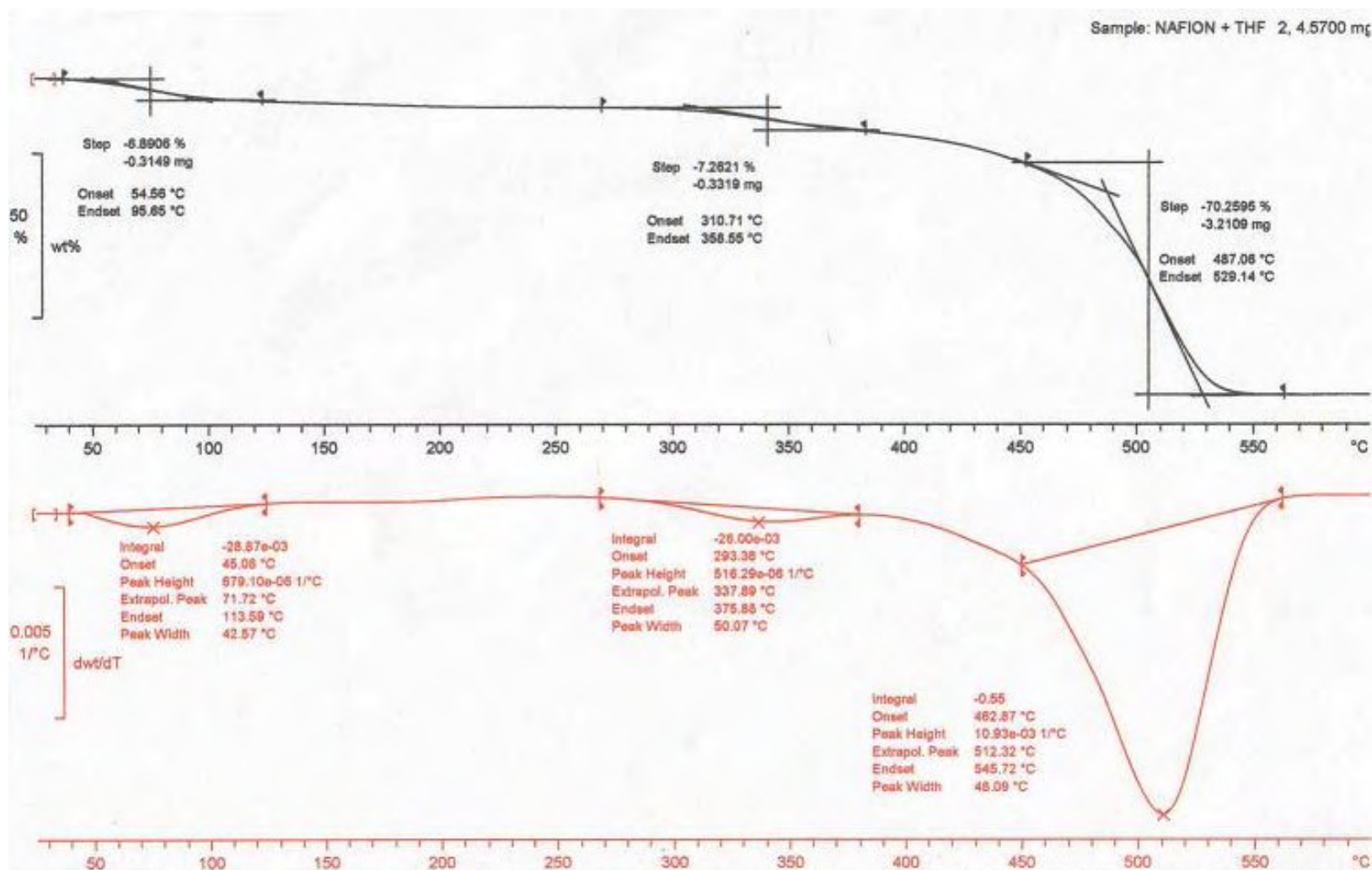


Figure 6.2.4b Nafion™ + Tetrahydrofuran Processed in scCO<sub>2</sub> (Trial 2)

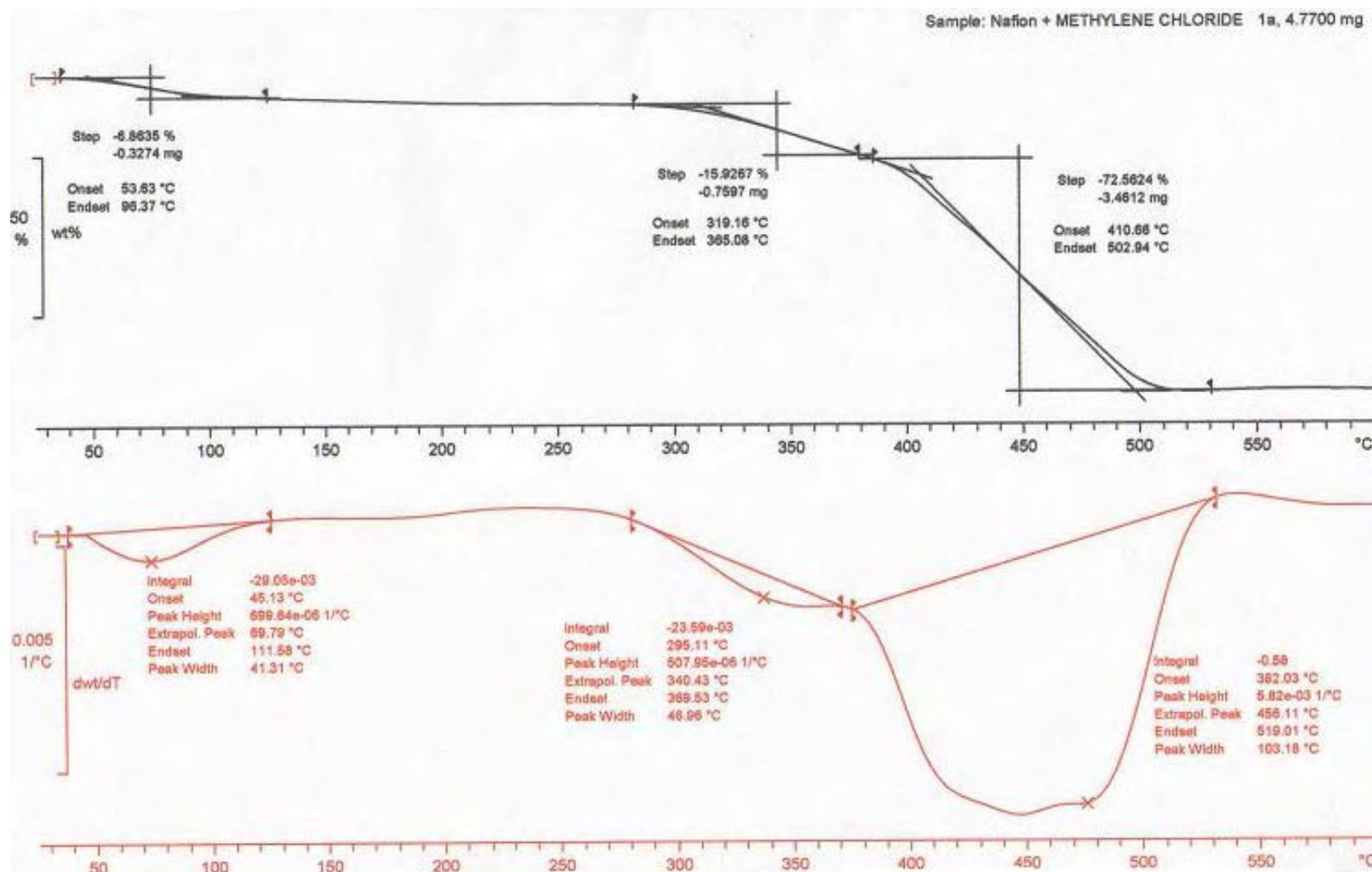


Figure 6.2.5a Nafion™ + Methylene Chloride Processed in scCO<sub>2</sub> (Trial 1)

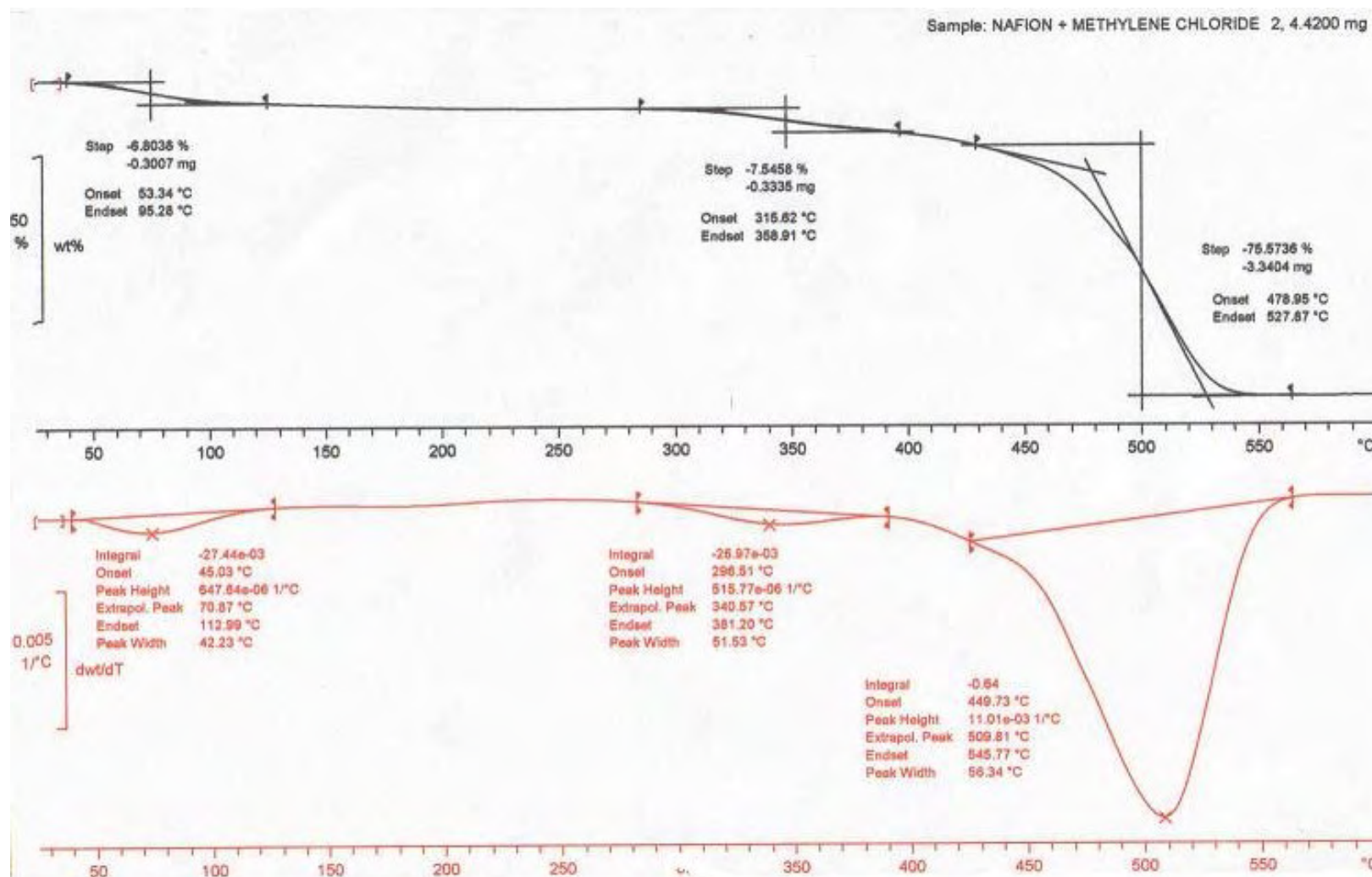


Figure 6.2.5b Nafion™ + Methylene Chloride Processed in scCO<sub>2</sub> (Trial 2)



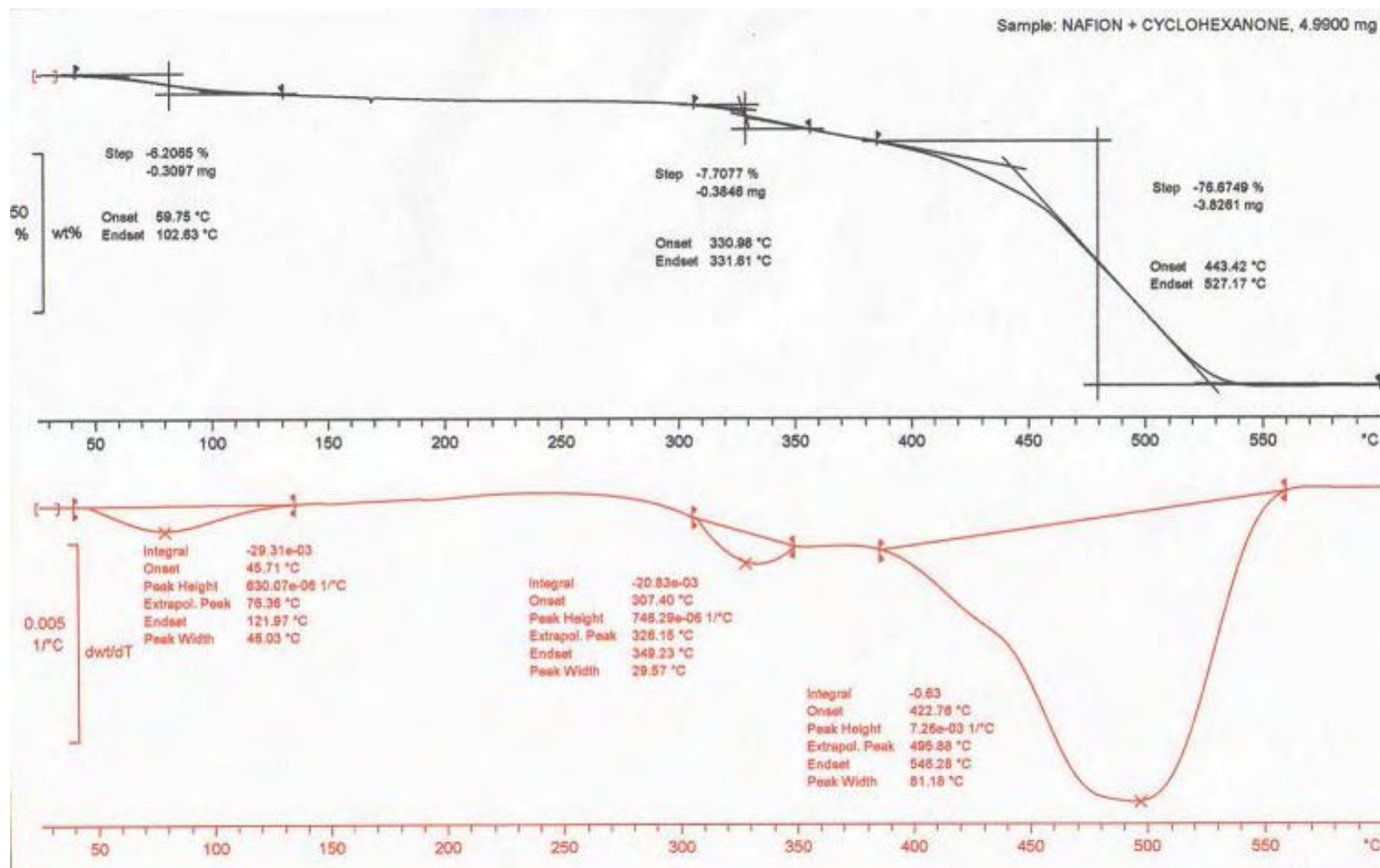


Figure 6.2.6a Nafion™ + Cyclohexanone Processed in scCO<sub>2</sub> (Trial 1)

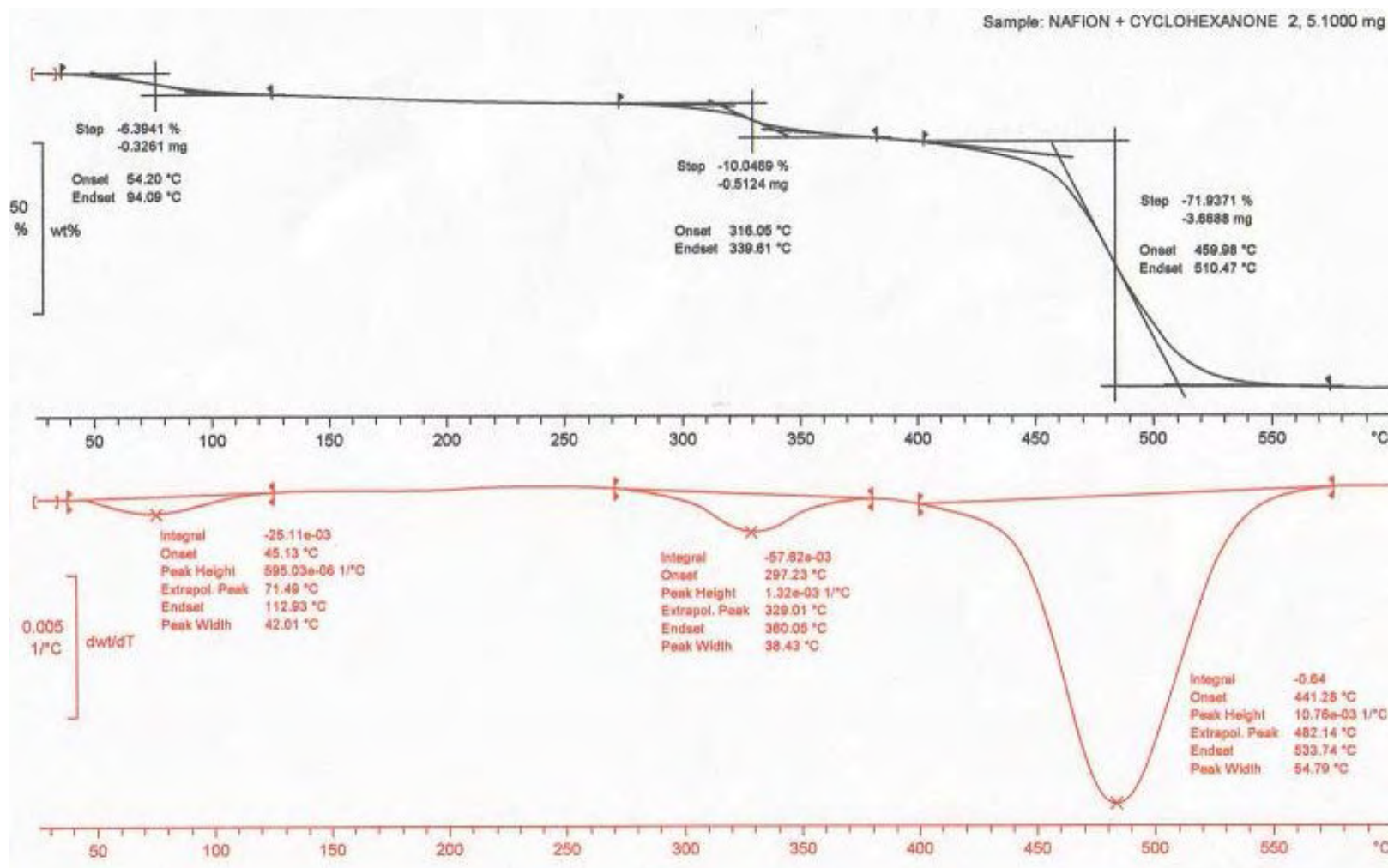


Figure 6.2.6b Nafion™ + Cyclohexanone Processed in scCO<sub>2</sub> (Trial 2)

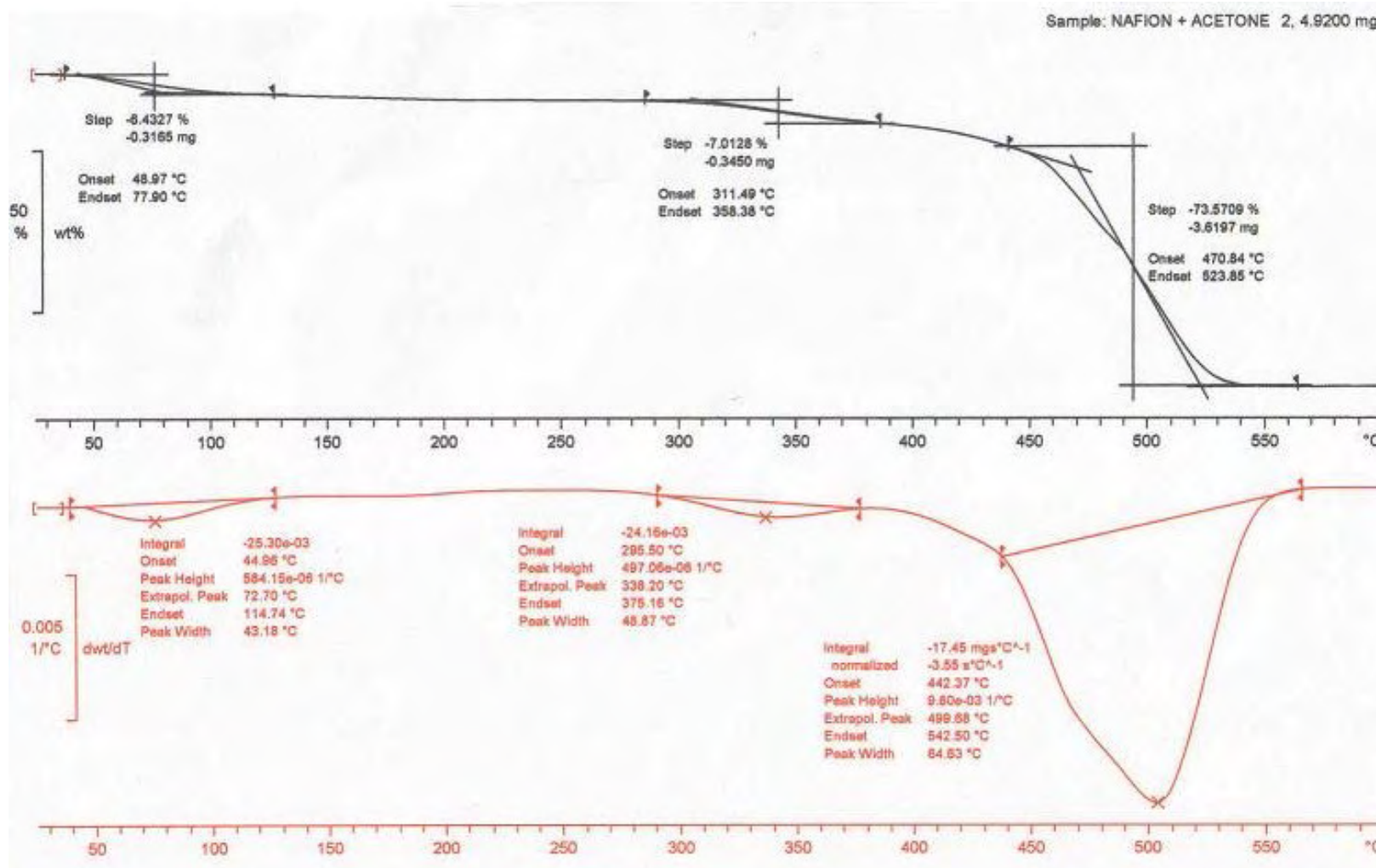


Figure 6.2.7b Nafion™ + Acetone Processed in scCO<sub>2</sub> (Trial 2)

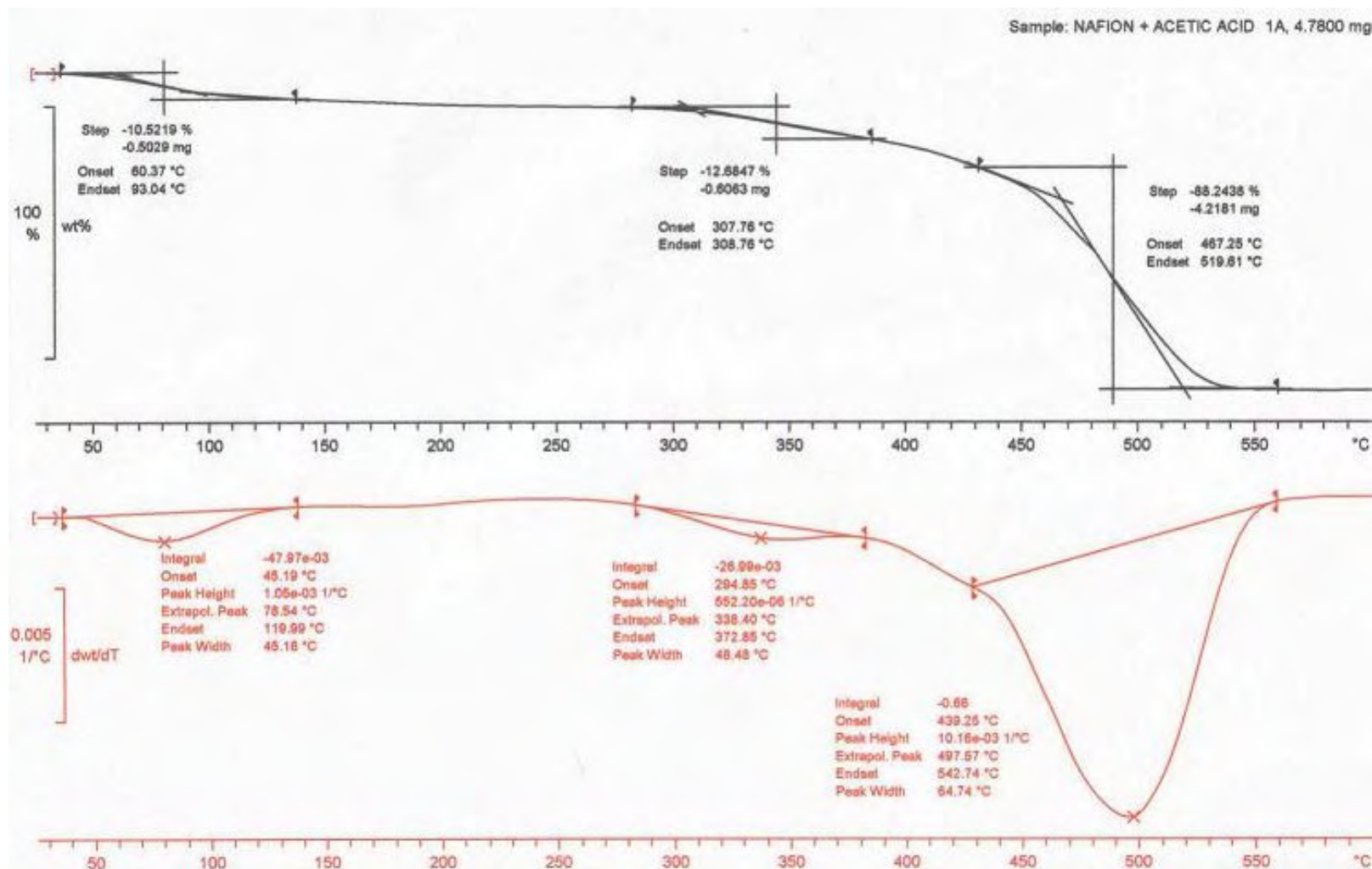


Figure 6.2.8a Nafion™ + Acetic Acid Processed in scCO<sub>2</sub> (Trial 1)



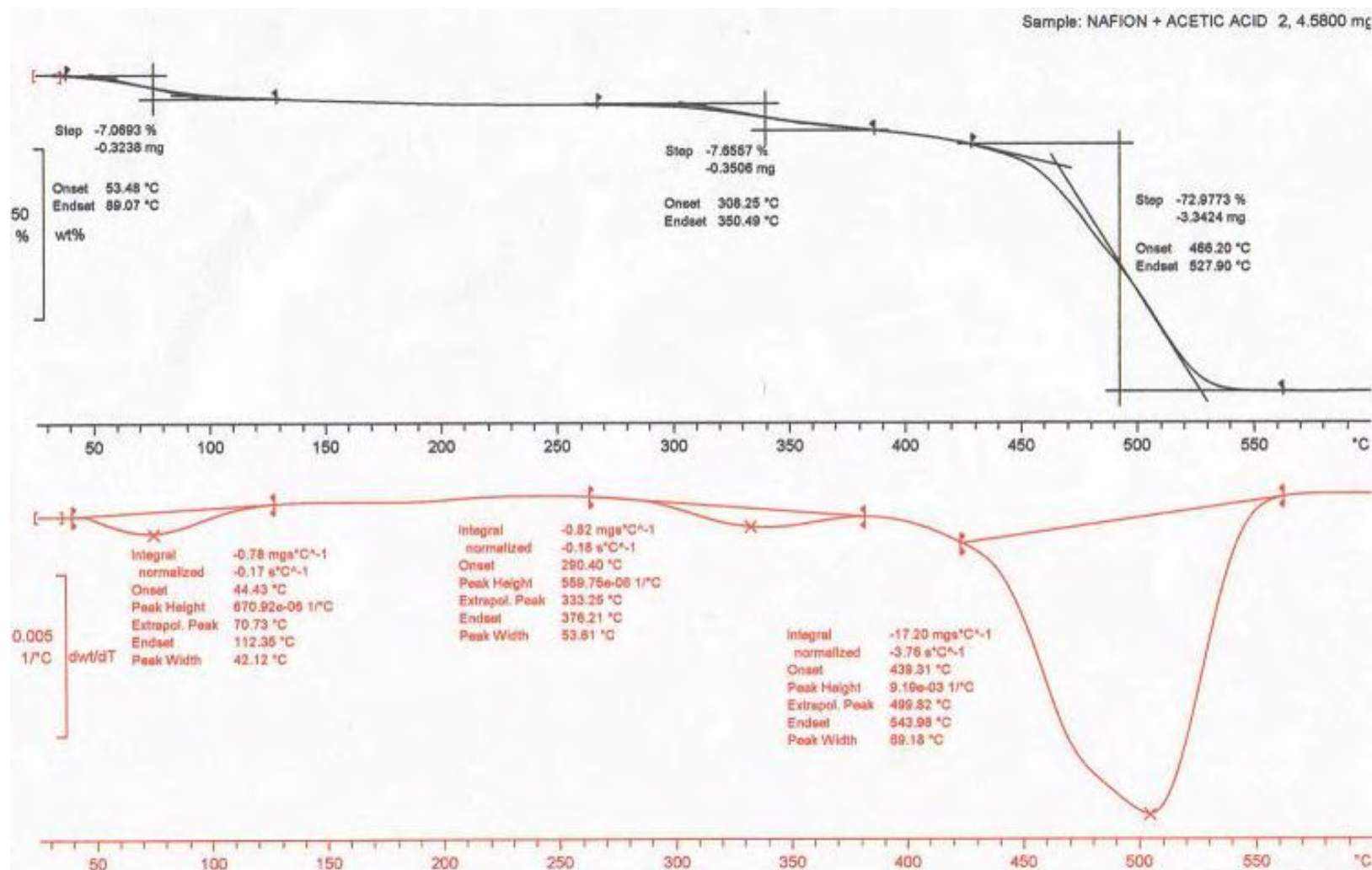


Figure 6.2.8b Nafion™ + Acetic Acid Processed in scCO<sub>2</sub> (Trial 2)

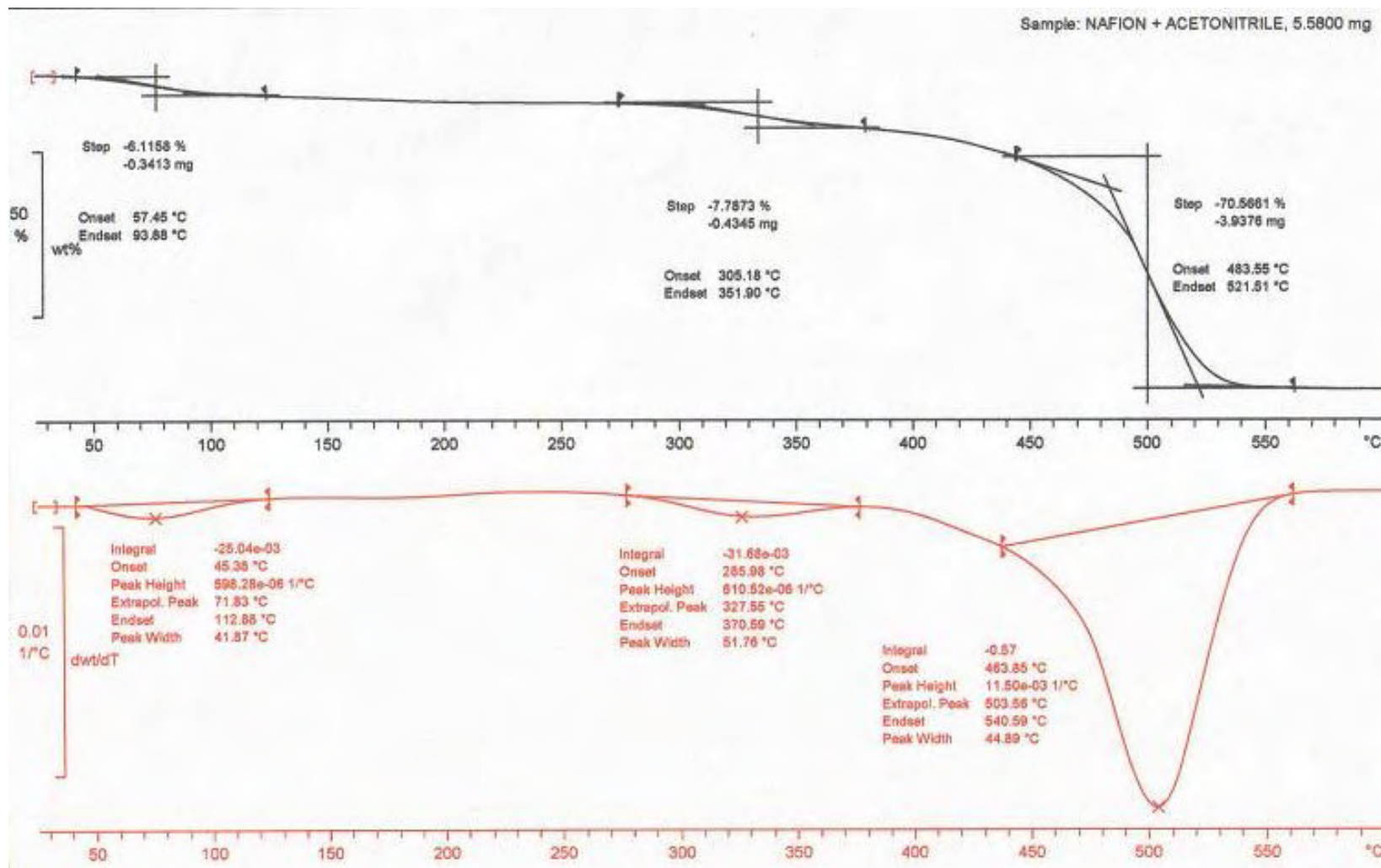


Figure 6.2.9a Nafion™ + Acetonitrile Processed in scCO<sub>2</sub> (Trial 1)

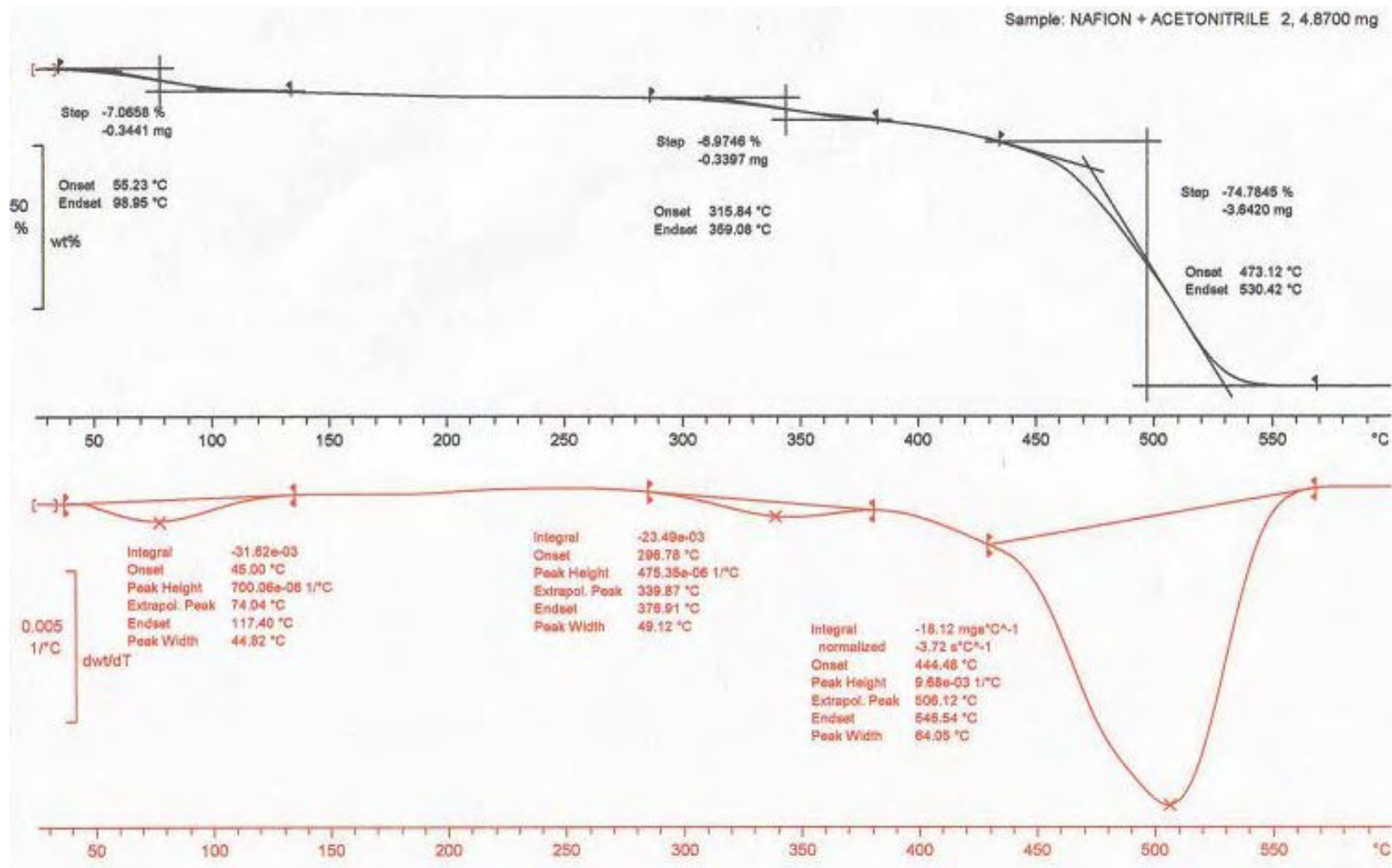


Figure 6.2.9b Nafion™ + Acetonitrile Processed in scCO<sub>2</sub> (Trial 2)

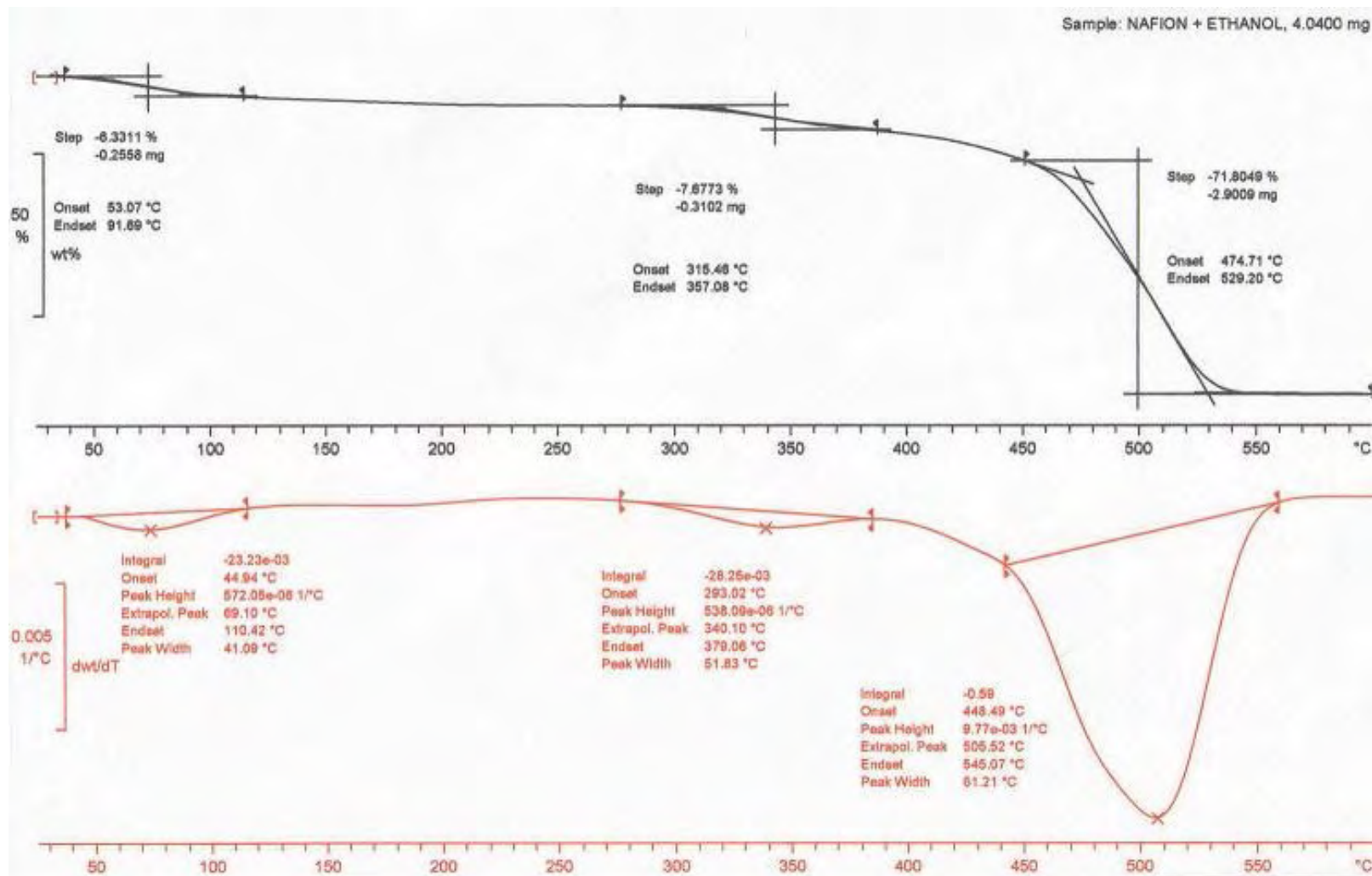


Figure 6.2.10a Nafion™ + Ethanol Processed in scCO<sub>2</sub> (Trial 1)



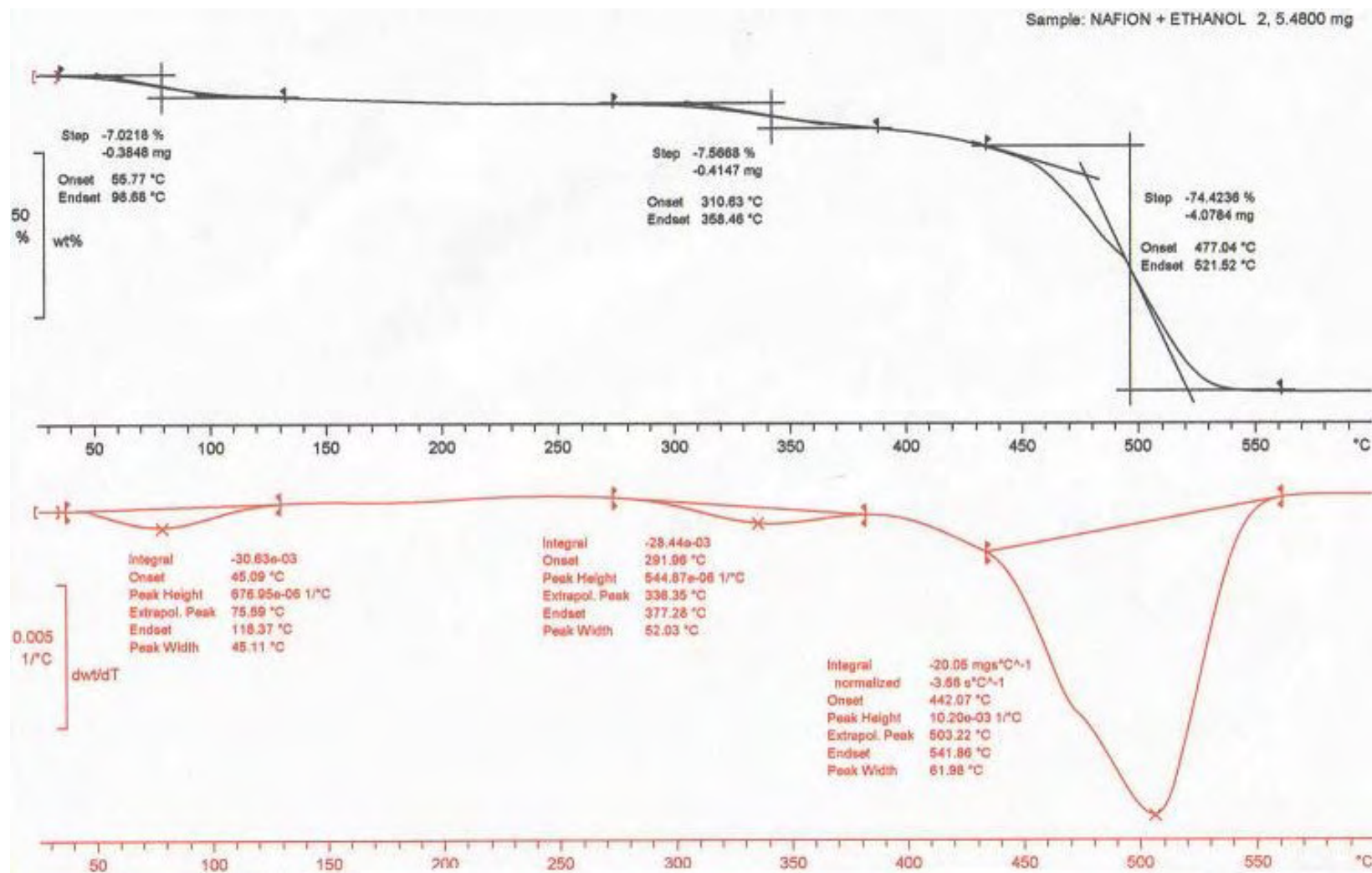


Figure 6.2.10b Nafion™ + Ethanol Processed in scCO<sub>2</sub> (Trial 2)

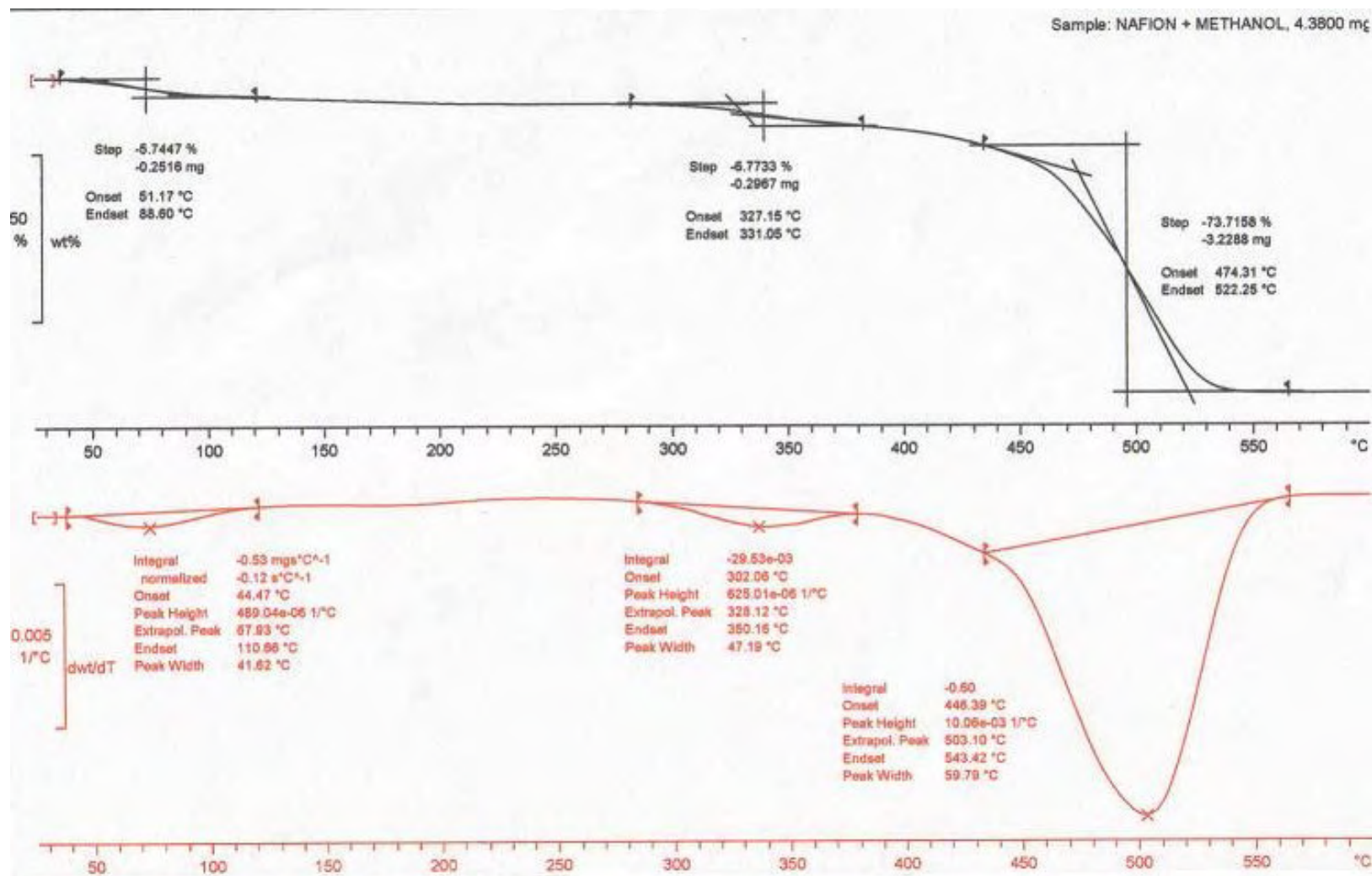


Figure 6.2.11a Nafion™ Methanol Processed in scCO<sub>2</sub> (Trial 1)

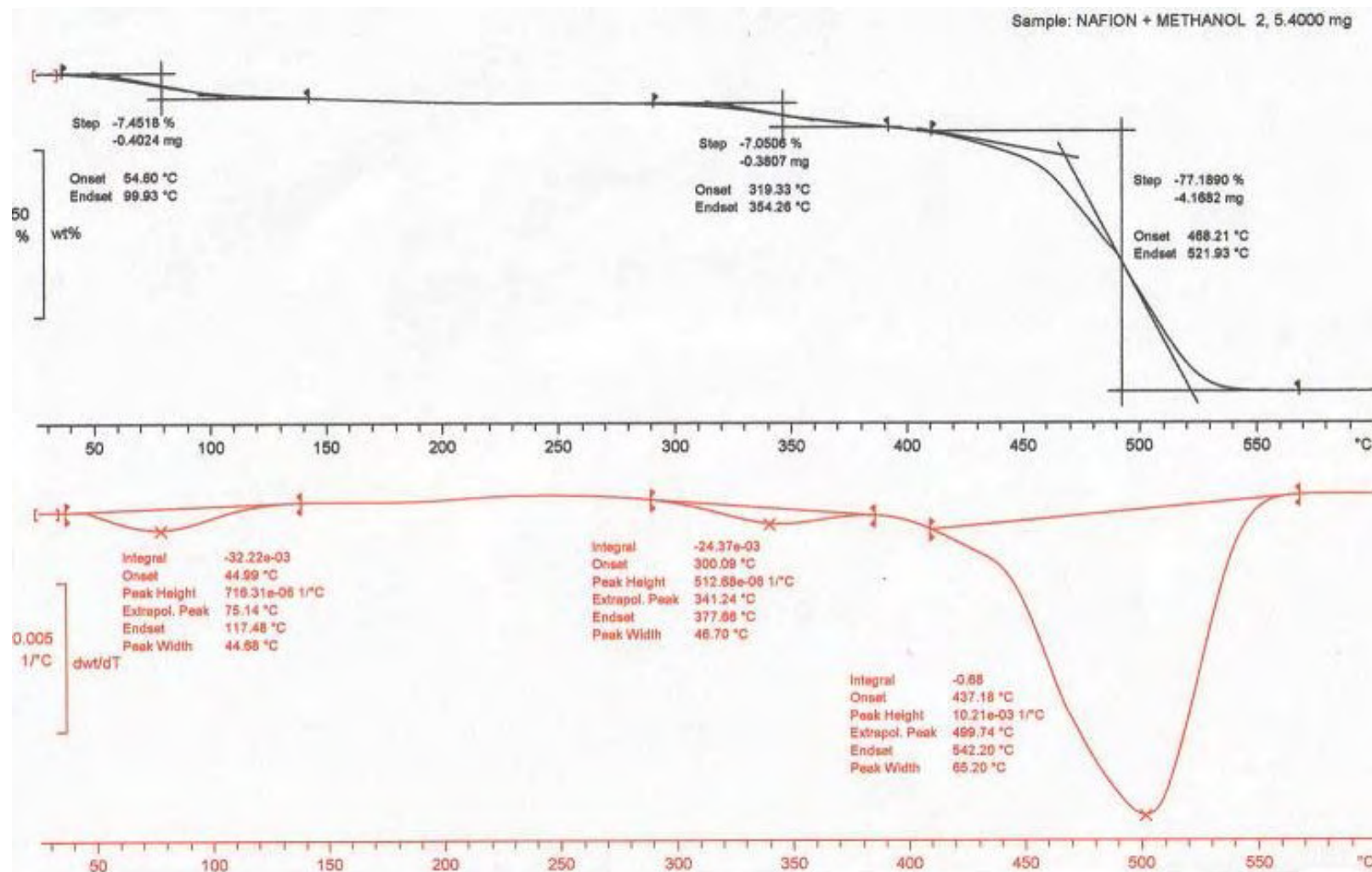


Figure 6.2.11b Nafion™ Methanol Processed in scCO<sub>2</sub> (Trial 2)

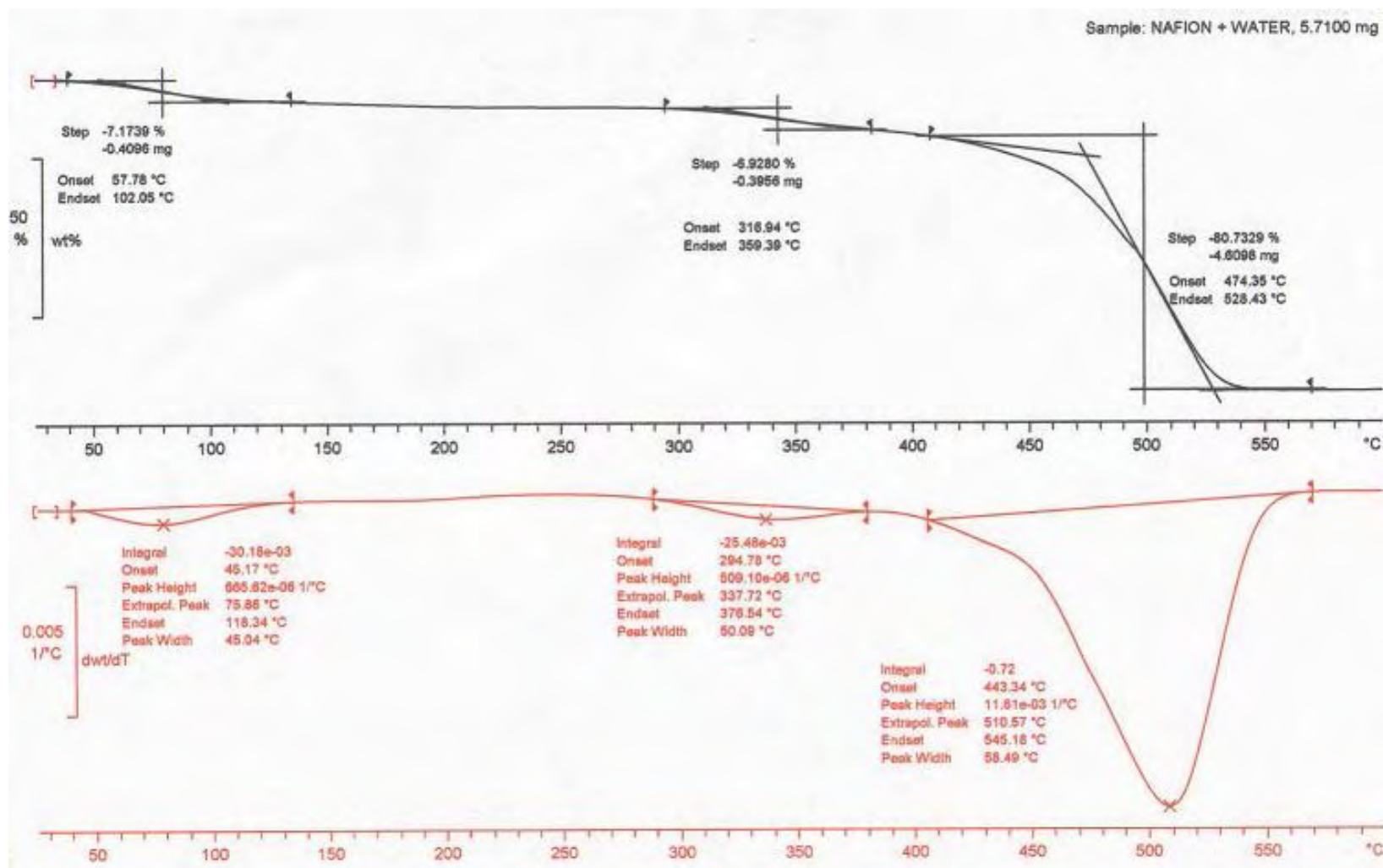


Figure 6.2.12b Nafion™ + Water Processed in scCO<sub>2</sub> (Trial 2)



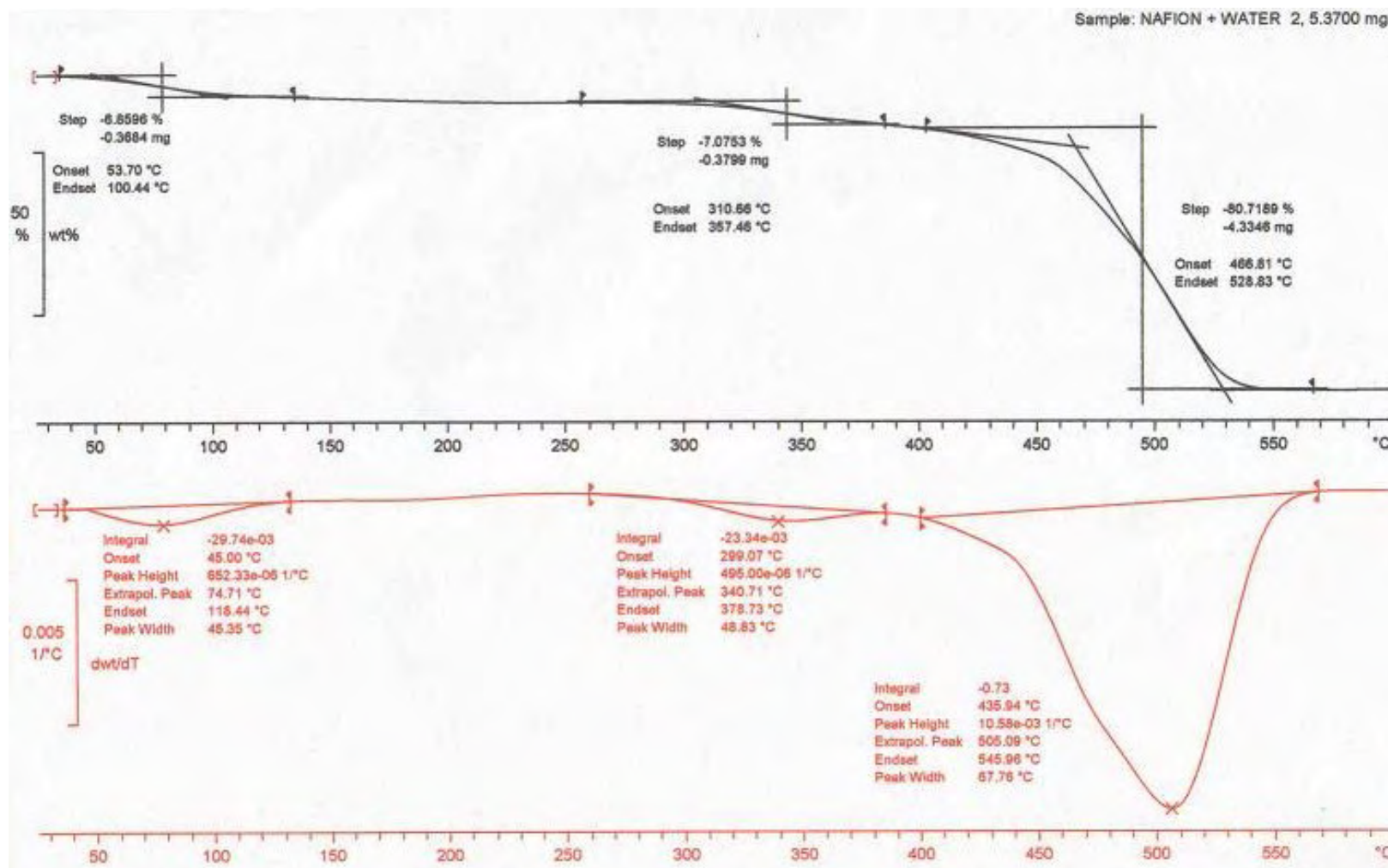


Figure 6.2.12b Nafion™ + Water Processed in scCO<sub>2</sub> (Trial 2)

Table 6.2.2 Decomposition Temperature for the Nafion™ Membranes Studied

| Nafion Sample                  | Decomposition Temperature °C |         |          |         |          |         |          |         |
|--------------------------------|------------------------------|---------|----------|---------|----------|---------|----------|---------|
|                                | Trial #1                     | Trial#2 | Trial #1 | Trial#2 | Trial #1 | Trial#2 | Trial #1 | Trial#2 |
| Unmodified                     | 74.76                        | 73.98   | 341.03   | 340.21  | 475.90   | 482.54  | 511.64   | 508.03  |
| Processed with $\text{scCO}_2$ | 72.33                        | 79.92   | 339.53   | 335.07  | Absent   | Absent  | 502.48   | 507.83  |
| Isopropyl Alcohol              | 71.04                        | 72.34   | 332.14   | 327.39  | Absent   | Absent  | 502.01   | 505.48  |
| Tetrahydrofuran                | 78.32                        | 71.92   | 340.69   | 337.89  | Absent   | Absent  | 474.05   | 512.32  |
| Methylene Chloride             | 69.79                        | 70.87   | 340.43   | 340.57  | Absent   | Absent  | 456.11   | 509.81  |
| Cyclohexanone                  | 76.36                        | 71.49   | 326.15   | 329.01  | Absent   | Absent  | 495.88   | 482.14  |
| Acetone                        | -                            | 72.70   | -        | 338.20  | Absent   | Absent  | -        | 499.68  |
| Acetic Acid                    | 78.54                        | 70.73   | 338.40   | 333.25  | Absent   | Absent  | 497.57   | 499.82  |
| Acetonitrile                   | 71.83                        | 74.04   | 327.55   | 339.87  | Absent   | Absent  | 503.56   | 506.12  |
| Ethanol                        | 69.10                        | 75.59   | 340.10   | 336.35  | Absent   | Absent  | 505.52   | 503.22  |
| Methanol                       | 67.93                        | 75.14   | 328.12   | 341.24  | Absent   | Absent  | 503.10   | 499.74  |
| Water                          | 75.86                        | 74.71   | 337.72   | 340.71  | Absent   | Absent  | 510.57   | 505.96  |

## 7. DISCUSSION

This chapter will focus on the discussion of the results presented in Chapter 4. First, the thermal degradation behavior of SEBS membranes will be discussed, followed by the discussion of the effects of the different polar environments on the properties of this material. Next, the discussion will shift to Nafion<sup>TM</sup> membranes: their thermal behavior followed by the different polar environments effects on their properties.

### 7.1 Thermal Degradation of Sulfonated SEBS

The results of the thermal degradation studies of SEBS membranes in N<sub>2</sub> agree well with the results reported in the literature<sup>32</sup>. Table 7.1.1 shows the weight loss percent data. As presented previously, four peaks in the weight derivative curve were observed for SEBS unmodified sample as well as SEBS samples processed in scCO<sub>2</sub> in which co-solvents with  $\delta < 12.7$  were employed. As expected, there is an initial weight loss of 17-20 wt% below 200°C due to the loss of volatiles, specifically residual water, which is absorbed from the atmosphere at room temperature. The loss of 11-13 wt% in the temperature region between 210°C and 340°C correlates to weight loss due to degradation of the sulfonic groups reported by Weiss et al<sup>32</sup>. A third peak was found for unmodified SEBS and SEBS samples processed in scCO<sub>2</sub> with co-solvents

having  $\delta < 12.7$ . The losses of 9 wt% to 13 wt% between 380°C and 400°C corresponds to the CO<sub>2</sub> decomposition as reported by DuPont Fluoroproducts<sup>33</sup> and presented in Table 7.1.2.

**Table 7.1.1 Weight Loss Percent for SEBS membranes**

| <b>Sulfonated<br/>SEBS Sample</b>   | <b>Weight Loss (%)</b> |                |               |                |
|-------------------------------------|------------------------|----------------|---------------|----------------|
|                                     | <b>Peak #1</b>         | <b>Peak #2</b> | <b>Peak#3</b> | <b>Peak #4</b> |
| Unmodified                          | 16.97                  | 12.59          | 10.26         | 48.87          |
| Processed with<br>scCO <sub>2</sub> | 15.48                  | 11.55          | 9.18          | 41.41          |
| Isopropyl Alcohol                   | 18.84                  | 12.55          | 13.71         | 45.75          |
| Tetrahydrofuran                     | 20.74                  | 13.66          | 10.99         | 49.68          |
| Methylene Chloride                  | 20.26                  | 12.994         | 11.53         | 44.50          |
| Cyclohexanone                       | 18.21                  | 12.182         | 11.79         | 44.29          |
| Acetone                             | 19.44                  | 11.74          | 9.25          | 43.14          |
| Acetic Acid                         | 18.67                  | 12.37          | 11.181        | 46.99          |
| Acetonitrile                        | 16.04                  | 12.40          | 9.71          | 46.68          |
| Ethanol                             | 16.62                  | 12.77          | Absent        | 59.54          |
| Methanol                            | 17.86                  | 11.40          | Absent        | 59.84          |
| Water                               | 15.73                  | 12.245         | Absent        | 58.61          |

**Table 7.1.2 Degradation Temperature of Different Products<sup>33</sup>**

| Compound           | Evolution Temperature (°C) |
|--------------------|----------------------------|
| SO <sub>2</sub>    | 280                        |
| CO <sub>2</sub>    | 300                        |
| HF                 | 400                        |
| CO                 | 400                        |
| R <sub>f</sub> COF | 400                        |
| COF <sub>2</sub>   | 400                        |
| COS                | 400                        |
| R <sub>f</sub> OH  | 400                        |

This peak was not observed in the in SEBS samples processed in sc CO<sub>2</sub> in which ethanol, methanol and water co-solvents were employed. Those co-solvents have high solubility parameters ( $\delta \geq 12.7$ ) and are polar protic solvents. Having a high solubility parameter indicates that they have good affinity with CO<sub>2</sub>, which prevents scCO<sub>2</sub> to forms hydrogen bonding with the acidic proton present in the sulfonic group. Since those co-solvents are polar protic solvents, they have a hydrogen atom to donor that is attracted by CO<sub>2</sub> and extracted during the supercritical fluid extraction.

The highest weight derivative peak is observed at approximately 460°C-470°C. The weight loss of 45-60 wt% corresponded to the backbone decomposition.

As presented in Figure 7.1.1, the chemical environment is not a determining factor in the degradation temperature.

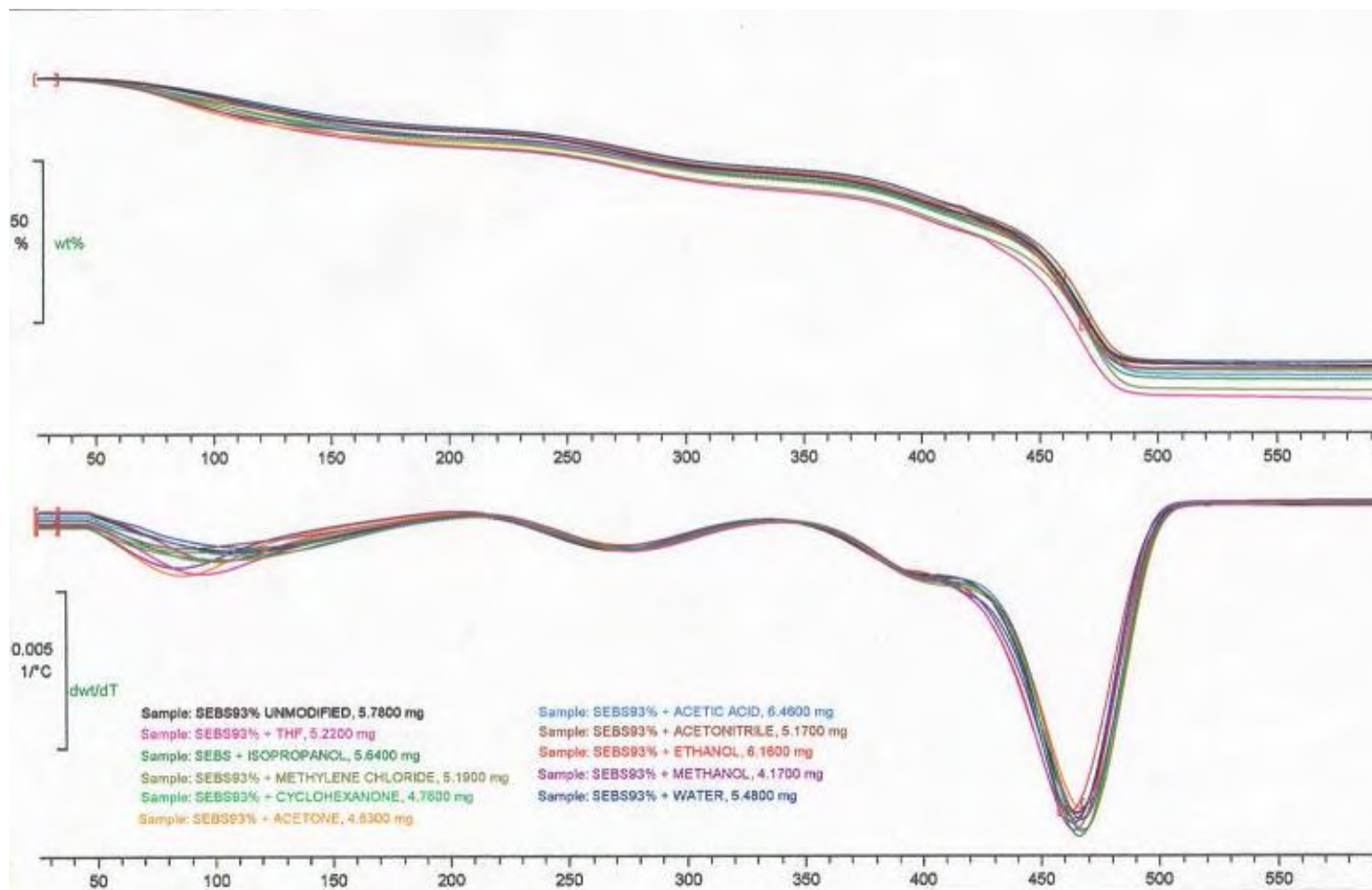


Figure 7.1.1 TGA of SEBS sample studied

## 7.2 Thermal Degradation of Nafion<sup>TM</sup>

Table 7.2.1 shows the results of the thermal degradation studies of Nafion<sup>TM</sup> membranes in N<sub>2</sub> (Figure 6.2.1) agree well with the results reported in the literature.

**Table 7.2.1 Result of Nafion<sup>TM</sup> TGA Studies**

|                                             | Surowiec and Bogoczek <sup>34</sup> | Samms et al. <sup>35</sup>                                          |                                                                                                                    | DeAlmeida and Kawano <sup>36</sup>                            |
|---------------------------------------------|-------------------------------------|---------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------|
| Conditions                                  | Air atmosphere<br>10°C/min          | N <sub>2</sub><br>20°C/min                                          | Air<br>20°C/min                                                                                                    | N <sub>2</sub><br>20°C/min                                    |
| <b>Mass Loss region</b>                     |                                     |                                                                     |                                                                                                                    |                                                               |
| <i>Temperature</i>                          | 50-180°C                            | 75-225°C                                                            | 75-225°C                                                                                                           | 25-290°C                                                      |
| <i>Mass % lost</i>                          | 4%                                  | 5%                                                                  |                                                                                                                    | 6.4%                                                          |
| <i>Groups lost</i>                          | Moisture                            | Moisture                                                            | Moisture                                                                                                           | Moisture                                                      |
| <b>Mass Loss region</b>                     |                                     |                                                                     |                                                                                                                    |                                                               |
| <i>Temperature</i>                          | 310-380°C                           | 275-400°C                                                           | 275-400°C                                                                                                          | 290-400°C                                                     |
| <i>Mass % lost</i>                          | 7.7%                                | 10%                                                                 |                                                                                                                    |                                                               |
| <i>Groups lost / decomposition products</i> | Sulfonic groups                     | Sulfur dioxide                                                      | Sulfur dioxide                                                                                                     | Desulfonation                                                 |
| <b>Mass Loss region</b>                     |                                     |                                                                     |                                                                                                                    |                                                               |
| <i>Temperature</i>                          | 420-590°C                           | 400-600°C                                                           | 400-500°C, 2 peaks                                                                                                 | a) 400-470°C<br>b) 470-560°C                                  |
| <i>Mass % lost</i>                          | 78%                                 | 75%                                                                 |                                                                                                                    |                                                               |
| <i>Groups lost / decomposition products</i> | Perfluorinated matrix               | SOF <sub>2</sub> , COF <sub>2</sub> , C <sub>x</sub> F <sub>y</sub> | SOF <sub>2</sub> , COF <sub>2</sub> , C <sub>x</sub> F <sub>y</sub> , C <sub>x</sub> F <sub>y</sub> O <sub>z</sub> | a) Side-chain decomposition<br>b) PTFE backbone decomposition |

As expected, there is an initial weight loss of approximately of 6% below 200°C due to the loss of the residual water. The loss of 7% in the temperature region between 200°C and 370°C correlates to 7.7% loss due to degradation of



the sulfonic groups reported by Suroweic and Boroczek<sup>34</sup> and 10% loss reported by Samms *et al*<sup>35</sup>. The losses of 71% between 370°C and 600°C are slightly lower than 78% loss reported by Suroweic and Boroczek<sup>34</sup> and 75 wt% loss reported by Samms *et al*<sup>35</sup>; however, both occur in the same temperature region as the ones reported in the literature. The weight loss in this region corresponds to the backbone and side-chain decomposition. The fact that two peaks of the derivative weight percent curve were observed in this region agreed with those results reported by DeAlmeida and Kawano<sup>36</sup>.

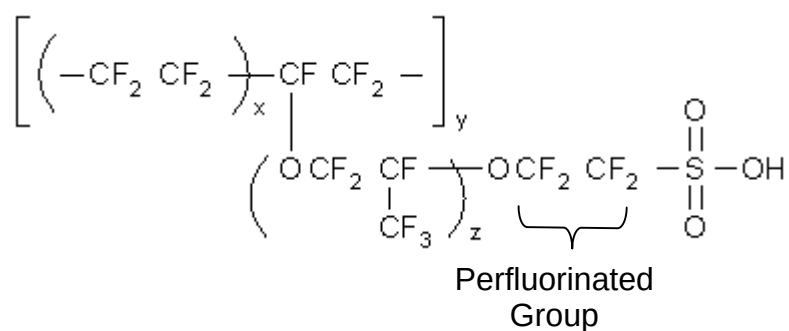
Nafion<sup>TM</sup> membranes were processed in SCF CO<sub>2</sub> and exposed to different chemical environments. The results of the thermal degradation studies of Nafion<sup>TM</sup> membranes process in scCO<sub>2</sub> were showed in Tale 6.3.1 and are summarized in Table 7.2.2.

Table 7.2.1 Average decomposition temperatures for Nafion™ membranes

| Nafion Sample                    | Average Decomposition Temperature °C |              |            |              |
|----------------------------------|--------------------------------------|--------------|------------|--------------|
|                                  |                                      |              |            |              |
| Unmodified                       | 74.37 ± 0.6                          | 340.62 ± 0.6 | 479.22 ± 5 | 509.83 ± 2   |
| Processed with scCO <sub>2</sub> | 76.12 ± 5                            | 337.30 ± 3   | Absent     | 504.95 ± 4   |
| Isopropyl Alcohol                | 71.69 ± 0.9                          | 329.76 ± 3   | Absent     | 503.74 ± 2   |
| Tetrahydrofuran                  | 75.12 ± 4                            | 339.29 ± 2   | Absent     | 493.18 ± 27  |
| Methylene Chloride               | 70.33 ± 0.8                          | 340.50 ± 0.1 | Absent     | 482.96 ± 37  |
| Cyclohexanone                    | 73.92 ± 3                            | 327.58 ± 2   | Absent     | 489.01 ± 9   |
| Acetone                          | 72.70                                | 338.20       | Absent     | 499.82       |
| Acetic Acid                      | 74.63 ± 5                            | 335.82 ± 4   | Absent     | 498.69 ± 2   |
| Acetonitrile                     | 72.93 ± 1                            | 333.71 ± 9   | Absent     | 504.84 ± 2   |
| Ethanol                          | 72.34 ± 4                            | 338.22 ± 3   | Absent     | 504.37 ± 0.5 |
| Methanol                         | 71.53 ± 5                            | 334.68 ± 9   | Absent     | 501.42 ± 2   |
| Water                            | 75.28 ± 0.8                          | 339.21 ± 2   | Absent     | 508.26 ± 3   |

As expected, three regions were found: The first region due to the loss of the residual water. This occurs due to the fact that Nafion™ membrane is a hygroscopic membrane and as a hygroscopic material it readily absorbs water, usually from the atmosphere. As it is showed in Table 7.3.2, this loss of the residual water corresponds to a 6-10 wt% of the material decomposition. The second region was found to occur in an interval of 320°C to 340°C and, as mentioned before, it is due to the degradation of the sulfonic groups and corresponds to a 7 – 10wt% loss. When we analyzed the third region, the first characteristic noted is that those membranes processed in scCO<sub>2</sub> presents just

one peak. The peak presented in a region of 475-480°C for unmodified Nafion<sup>TM</sup> disappeared and just one peak was found and observed in the interval of 480 to 510°C. The disappearing of this peak indicates the cleavage of a bond. According to results reported by Samms *et al*<sup>35</sup>, this peak is due to perfluorinated groups (CF<sub>2</sub> groups). The absence of this peak suggests that a cleavage of the perfluorinated group in Nafion<sup>TM</sup> is occurring. Figure 7.2.1 shows the perfluorinated group that was broken. An analysis of the bond energy of C-O, S-O bonds can lead to the same conclusion.



**Figure 7.2.1 Perfluorinated group in Nafion<sup>TM</sup> membrane**

Table 7.2.3 Average Weight Loss in the Different Decomposition Temperature

| Nafion Sample                  | Average Weight Loss (%) |         |         |         |
|--------------------------------|-------------------------|---------|---------|---------|
|                                | Peak #1                 | Peak #2 | Peak#3  | Peak #4 |
| Unmodified                     | 6.3602                  | 7.2280  | 31.4076 | 39.7863 |
| Processed with $\text{scCO}_2$ | 10.5893                 | 6.7127  | Absent  | 74.8323 |
| Isopropyl Alcohol              | 6.8197                  | 7.6720  | Absent  | 70.9765 |
| Tetrahydrofuran                | 7.5015                  | 10.9242 | Absent  | 70.3942 |
| Methylene Chloride             | 6.8336                  | 11.7363 | Absent  | 74.0680 |
| Cyclohexanone                  | 6.3003                  | 8.8773  | Absent  | 72.7540 |
| Acetone                        | 6.4327                  | 6.8679  | Absent  | 73.5709 |
| Acetic Acid                    | 8.7956                  | 10.1702 | Absent  | 80.6106 |
| Acetonitrile                   | 6.5908                  | 7.3809  | Absent  | 72.6753 |
| Ethanol                        | 6.6764                  | 7.6220  | Absent  | 73.1143 |
| Methanol                       | 6.5982                  | 6.9119  | Absent  | 75.4524 |
| Water                          | 7.0167                  | 7.0016  | Absent  | 80.7259 |

Both the C-O and C-S bonds have low bond energies. The C-O bond has energy of 85.5 kcal/mol, while C-S has bond energy of 65 kcal/mol. Having low bond energies implies that relatively low temperatures are required to break the bond. This fact confirms the idea of the cleavage of the perfluorinated group. The presence of the peak corresponding to the sulfonic group suggests that this

group does not disappear, but a bond was formed between the terminal sulfonic group and the backbone of the polymeric matrix. It also suggests that some kind of morphological changes had occurred. To verify that some morphological change is occurring, swelling studies were done and are summarized in Table 7.2.4. Those studies measure the water uptake of the different Nafion<sup>TM</sup> membranes studied. The membranes were put in contact with water during 24 hours, and then were analyzed by thermal gravimetric analysis. As expected, the results show changes in the water uptake as function of the chemical environment. The chemical environment of Nafion<sup>TM</sup> membranes, which were processed, exerts an effect on the permeability and diffusivity of water in Nafion<sup>TM</sup>. Those polar protic solvents increase the permeability of Nafion<sup>TM</sup> s more than those non-polar or polar aprotic solvents.

Another feature of these TGA scans is the effect of the different chemical environment in the degradation temperature of Nafion<sup>TM</sup>. The used of a co-solvent during the processing shifted the  $dwt/dT$  peaks to lower temperatures. Those co-solvent, which are polar aprotic or non-polar shift the degradation temperature of the backbone and side-chain to temperature as low as 480°C, while polar protic solvent do no make major changes. The weight loss in this region corresponds to 70-80 wt%.

Table 7.2.2 Standard bond energies (kcal/mol)<sup>37-38</sup>

| Single Bonds | $\Delta H^\circ$ | Single Bonds | $\Delta H^\circ$ | Multiple Bonds | $\Delta H^\circ$ |
|--------------|------------------|--------------|------------------|----------------|------------------|
| H-H          | 104.2            | B-F          | 150              | C=C            | 146              |
| C-C          | 83               | B-O          | 125              | N=N            | 109              |
| N-N          | 38.4             | C-N          | 73               | O=O            | 119              |
| O-O          | 35               | N-CO         | 86               | C=N            | 147              |
| F-F          | 36.6             | C-O          | 85.5             | C=O (CO)       | 192              |
| Si-Si        | 52               | O-CO         | 110              | C=O (aldehyde) | 177              |
| P-P          | 50               | C-S          | 65               | C=O (ketone)   | 178              |
| S-S          | 54               | C-F          | 116              | C=O (ester)    | 179              |
| Cl-Cl        | 58               | C-Cl         | 81               | C=O (amide)    | 179              |
| Br-Br        | 46               | C-Br         | 68               | C=O (halide)   | 177              |
| I-I          | 36               | C-I          | 51               | C=S (CS)       | 138              |
| H-C          | 99               | C-B          | 90               | N=O (NO)       | 143              |
| H-N          | 93               | C-Si         | 83               | P=O (PO)       | 110              |
| H-O          | 111              | C-P          | 70               | P=S (PS)       | 70               |
| H-F          | 135              | N-O          | 55               | S=O (SO)       | 128              |
| H-Cl         | 103              | S-O          | 87               | S=O (MSO)      | 93               |
| H-Br         | 87.5             | Si-F         | 135              | P=P            | 84               |
| H-I          | 71               | Si-Cl        | 90               | P=P            | 117              |
| H-B          | 90               | Si-O         | 110              | C=O            | 258              |
| H-S          | 81               | P-Cl         | 79               | C=C            | 200              |
| H-Si         | 75               | P-Br         | 65               | N=N            | 226              |
| H-P          | 77               | P-O          | 90               | C=N            | 213              |

**Table 7.2.4 Water Weight Loss in the Different Nafion™ samples studied**

| <b>Nafion Sample</b>             | <b>Weight Loss (%)</b> |
|----------------------------------|------------------------|
| Unmodified                       | 23.28                  |
| Processed with scCO <sub>2</sub> | 21.66                  |
| Isopropyl Alcohol                | 29.40                  |
| Tetrahydrofuran                  | 6.60                   |
| Methylene Chloride               | 15.46                  |
| Cyclohexanone                    | 14.25                  |
| Acetone                          | 10.77                  |
| Acetic Acid                      | 15.87                  |
| Acetonitrile                     | 17.62                  |
| Ethanol                          | 18.54                  |
| Methanol                         | 20.22                  |
| Water                            | 18.92                  |

## **8. SUMMARY AND CONCLUSIONS**

The purpose of this thesis was the development and optimization of a new chemically stable ion-exchange membrane (ionomer membrane) for the applications such as PEM fuel cells (PEFC), chemical protective clothing, drug delivery etc. In the course of this work, those polymer membranes were exposed to different chemical environments and processed in SCF CO<sub>2</sub> to investigate changes in their physical properties and in morphology. To change the chemical environment in which processing took place, co-solvents with different solubility parameters and polarity were employed. TGA scans were done to identify changes in the degradation temperature as function of the solubility parameter, as well as to have an idea if the processing under these conditions exerts a change in polymer morphology.

The key conclusions of the study are summarized below. In the case of SEBS membranes, we can conclude that the chemical environment does not exert a determining factor in the degradation temperature, but those polar protic solvents with  $\delta \geq 12.7$  have more affinity to SCF CO<sub>2</sub>, which ensure the removing of all CO<sub>2</sub> during the extraction procedure (No CO<sub>2</sub> get trapped in the polymer matrix). On the other hand, the analysis of the TGA traces lead to the conclusion that the processing in SCF CO<sub>2</sub> with and without co-solvents can cause a cleavage of the perfluorinated group presence in the Nafion<sup>TM</sup> membrane and the



shift of the degradation temperature to lower temperatures. Swelling studies confirm the insight of the morphological changes occurring in these samples.

Also we can conclude that Nafion<sup>TM</sup> membrane was stable up to the temperature of 475°C even though sulfonic side-groups are generally considered thermally unstable.

## **9. FUTURE WORK**

This thesis has left many questions unanswered and a range of experiments can be conducted in order to prove unequivocally some of the ideas presented in this work and to clarify others.

Additional experiments could be conducted in order to take a more detailed look into the effect of elevated temperatures on the structure of Nafion<sup>TM</sup> and SEBS membranes. A technique, like FTIR or maybe solid state NMR, that is more sensitive than FTIR to the chemical changes in the polymer molecule, could more precisely explore potential alterations in the molecular structure of these ionomers. A modified thermal degradation study of Nafion<sup>TM</sup> and SEBS material can also answer questions about the thermal stability of the membranes. The weight loss information, obtained by the use of conventional TGA, does not provide an insight into the nature of the chemical groups being broken off. However, if a mass spectrometer is connected to the TGA unit, it can help to determine precisely the onset of the decomposition of sulfonic groups and the boundaries of thermal stability.

## 10. REFERENCES

1. U.S. Fuel Cell Council, *Fuel Cell Glossary*, August 19, **1999**.
2. R.J.Young, *Introduction to Polymers*, Chapman and Hall, New York, p204, **1983**.
3. M.W.Verbrugge, R.F.Hill, *J. Eletrochem. Soc.*, 137, 337, **1990**.
4. T.E.Springer, T.A.Zawodzinski, S.Gottesfeld, *J. Eletrochem. Soc.*, 138, 2334 **1991**.
5. J.C.Amphlett, R.M.Baumert, R.F.Mann, B.A. Peppley, P.R. Roberge, *J. Eletrochem. Soc.*, 142, 1, **1995**.
6. J.C.Amphlett, R.M.Baumert, R.F.Mann, B.A.Peppley, P.R. Roberge, *J. Eletrochem. Soc.*, 142, 9 , **1995**.
7. Supercritical Fluid Extraction: Principles & Practice, McHugh, M. A., Krukonis, V. J. ; *Butterworth-Heinemann*, Boston, 1994.
8. R.J.Young, *Introduction to Polymers*, Chapman and Hall, New York, p204 **1983**.
9. Lagow R.J., Margrave J.L. *Polym. Lett*, 12, 177-184, **1974**.
10. Kharitonov A.P., Moskvina YL, *J. Fluorine Chem.*, 91, 87-93, **1998**.
11. Shuyama H. *J. Fluorine Chem.*, 29, 467-7, **1985**.
12. Shuyama H., Mitani, M., Nakayama, M. Yoshida, M., Kamigata, N. *Polymer*, 31, 63-64, **1990**.

13. Zhou, Z-B., He H-Y., Weng Z-Y., Qu, Y-L, Zhao, C-X. *J Fluorine Chem.*, 79, 1-5, **1996**.
14. Zhou, Z-B., He H-Y., Weng Z-Y., Zhao, C-X., *J Fluorine Chem.*, 14, 285-29, **2000**.
15. Crawford, D.M., Napadensky, E., Beck Tan, N.C., Reuschle, D.A., Mountz, D.A., Mauritz, K.A., Laverdure, K.S., Gido, S.P., Liu, W., Hsiao B. *Thermochimica Acta*, 367-368, 125-134, **2001**.
16. Napadensky, E., Crawford, D., Sloan, J., Beck Tan, Nora, *ARL-TR-2482*, US Army Research Laboratory, Aberdeen Proving Ground, MD, May **2001**.
17. Storey, R.R., Baugh D.W., *Polymer*, 41, 325-3211, **2000**.
18. Storey, R.R., Baugh D.W., *Polymer*, 42, 2321-233, **2001**.
19. Kim, J.H., Paxton, T.E., Tomasko, D.L. *Biotechnology Progress*, 12, 65, **1996**.
20. Alsoy, S., Duda, J.L. *Chemical Engineering & Technology*, 12, 65, **1996**.
21. Elkovitch, M.D., Lee, L.J., Tomasko, D.L. *Polymer Engineering and Science*, 4, 185, **2000**.
22. Kho, Y.W., Kalika, D.S., Knutson, B.L. *Polymer*, 42, 6119, **2001**.
23. Consani, K.A., Smith, R.D. *J. of Supercritical Fluids*, 3, 51-65, **1990**.
24. Laintz, K.E., Wai, C.M., Yonker, C.R., Smith, R.D. *J. of Supercritical Fluids*, 4, 194-198, **1991**.
25. Johnston, K.P., Harrison, K.L., Clarke, M.J., Bright F.V., Carlier, C., Randolph, T.W. *Science*, 271, 624, **1996**.

26. O'Neill, M.L., Yates, M.Z., Johnston, K.P., Smith, C.D., Wilkinson, S.P.  
*Macromolecules*, 31, 2848-2856, **1998**.
27. DeSimone, J. and Policy, J.D. *Proceedings of the 8<sup>th</sup> Meeting on Supercritical Fluids*. Bourdeaux, France, **2002**.
28. Perrut, M. *Proceedings of the 8<sup>th</sup> Meeting on Supercritical Fluids*. Bourdeaux, France, 22.
29. Ramirez, C. **2004** *Structural Tuning of Sulfonated Styrenic Triblock Copolymer with supercritical fluid processing*. Thesis M.S. University of Puerto Rico, Mayagüez, P.R.
30. Shim, J.J., Yates, M.Z., Johnston, K.P. *Ind. & Engr. Chem. Res.*, 4, 536, **2001**.
31. Tricoli et al., *J. Electrochem. Soc.* **2000**.
32. Weiss, R.A., A. Sen, C.L. Willis, L.A. Pottick. *Polymer*, **32**, n 10, 1867, **1991**.
33. DuPont<sup>TM</sup> Technical Information: Safe Handling and Use of Perfluorosulfonic Acid Products.  
<http://www.cem.msu.edu/~reusch/OrgPage/bndenrgy.htm> Activo Feb 2004
34. J. Suroweic, R. Bogoczec, *J. Therm. Analysis*, **33**, 1097 **1988**.
35. S.R. Samms, S. Wasmus, R.F. Savinell, *J. Eletrochem. Soc.*, **143**, n 5, 1498 **1996**.
36. S.H. DeAlmeida, Y. Kawano, *J. Therm. Analysis and Calorimetry*, **58**, 569 **1999**.
37. R.T. Sanderson, *Polar Covalence*, **1983**.

38. R.T. Sanderson, *Chemical Bonds and Bond Energy*, **1976**.

This document was created with Win2PDF available at <http://www.daneprairie.com>.  
The unregistered version of Win2PDF is for evaluation or non-commercial use only.