THERMOGRAVIMETRIC CHARACTERIZATION OF POLYSTYRENE-BASED, TRIBLOCK COPOLYMERS: EFFECTS OF SULFONATION, COUNTER-ION SUBSTITUTION, NUMBER AVERAGE MOLECULAR WEIGHT, AND POLYSTYRENE WEIGHT FRACTION

by

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Abstract

In this study, poly (styrene-isobutylene-styrene) (SIBS) was characterized using thermogravimetric analysis. The thermal behavior of three types of SIBS, with different average number molecular weight, $\overline{M_n}$, and polystyrene weight percent, are discussed as a function of sulfonation level and substitution with different ions (Ba^{+2}, Ca^{+2}, and Mg^{+2}). For unsulfonated samples, a decrease in the degradation temperature was observed with an increase in $\overline{M_n}$, for 30 % polystyrene by weight. Also, a decrease in the degradation temperature was observed with an increase in percent polystyrene with $\overline{M_n}$ of 100,000 g/mol. At high sulfonation levels, the backbone degradation temperature of the studied polymers increased up to a constant value, suggesting morphological similarities. The weight loss stage corresponding to the degradation of sulfonic groups was not observed in sulfonated polymers cross-linked with cations; however, two new weight loss stages are observed, which are attributed to the loss of cations and sulfonic groups. They are lost in two stages due to different coordination of the cations. SIBS with 15 % polystyrene by weight and $\overline{M_n}$ of 100,000 g/mol has a higher polymer backbone degradation temperature when compared to the other two studied SIBS, thus it can be considered more thermally stable.

Resumen

En este estudio se caracterizó poli (estireno-isobutileno-estireno) (SIBS) utilizando análisis termogravimétrico. El comportamiento térmico de tres tipos de SIBS, con diferente peso molecular promedio en número, $\overline{M_n}$, y porcentaje en peso de poliestireno, se evaluó en función del nivel de sulfonación y sustitución con diferentes iones (Ba^{+2}, Ca^{+2} y Mg^{+2}). En SIBS sin sulfonar se observó una disminución en la temperatura de degradación con un aumento en $\overline{M_n}$, con 30 % en peso de poliestireno. Además, para $\overline{M_n}$ de 100,000 g/mol, se observó una disminución en la temperatura de degradación al aumentar el porcentaje de poliestireno. Para altos niveles de sulfonación, se observó que la temperatura de degradación de la columna vertebral del polímero aumentó hasta un valor constante, sugiriendo así similitudes morfológicas. La pérdida en peso correspondiente a la degradación de grupos sulfónicos no se observó en polímeros sulfonados cuando éstos se interconectaron con cationes. Sin embargo, se observaron dos nuevas etapas de pérdida en peso, que corresponden a la pérdida de grupos sulfónicos y cationes. Éstos se pierden en dos etapas debido a diferencias en la coordinación de los iones. SIBS con 15 % en peso de poliestireno y $\overline{M_n}$ de 100,000 g/mol tiene una temperatura de degradación más alta que los otros dos SIBS estudiados, por lo que puede considerarse térmicamente más estable.

Remember to always believe in yourself…

To…

… Mom, Dad, Fred, You and Myself

Acknowledgments

It has been a long path, but at the end it was all worth it. The end of this project represents the beginning of a new stage where I will reap the rewards of my years of dedication. This work would have not been possible without the support of key persons. I would like to thank Dr. L. Antonio Estévez, Dr. Guillermo Colón, Yahaira Soto, Ariangelis Ortiz, and Noelia Lasanta for their collaboration, and especially my advisor, Dr. David Suleiman for his trust and guidance. I would also like to thank all my friends, especially to Ana, thanks for being there! I am also really grateful to that superior force that allows me to be alive and enjoy every day of my life. Finally, a very special thanks to the most important persons in my life, my beautiful parents, Freddy and Felisa and my special brother Fred, thanks for your love and support, I love you with all my heart!

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AFC	Alkaline fuel cell
PAFC	Phosphoric acid fuel cell
PEMFC	Proton exchange membrane fuel cell
MCFC	Molten carbonate fuel cell
PEMFC	Proton exchange membrane fuel cell
SOFC	Solid oxide fuel cell
SIBS	Styrene-Isobutylene-Styrene
TGA	Thermogravimetric Analysis
$\overline{M_n}$	Number average molecular weight
IEC	Ion exchange capacity
Co Ltd.	Company Limited
EA	Elemental Analysis
M	Molarity
TG	Thermogravimetric
DTG	Derivative thermogravimetric

I. INTRODUCTION

Our society, which is strongly dependant on petroleum as an energy source, is in special need for new energy alternatives that are efficient, cost effective, and environmentally friendly. Fuel cells, which produce clean electricity when hydrogen and oxygen are converted into water, are an attractive power-generation technology because of their high-efficiency and zero pollution (with hydrogen as fuel cell). It is common that fuel cells are classified based on the nature of the electrolyte used in the fuel cell. Therefore, based on this classification, fuel cells include the following different types: (1) alkaline fuel cells (AFC), (2) phosphoric acid fuel cells (PAFC), (3) solid proton exchange membrane (PEMFC), (4) molten carbonate fuel cells (MCFC), and (5) solid oxide fuel cells (SOFC). Table 1 summarizes the operating and applicable properties.[1] The proton exchange membrane fuel cell is one of the most promising fuel cell technologies[2-6]. This type of fuel cell will probably end up powering cars, and probably even our houses.

Table 1: Operating and applicable properties of five main types of fuel cells.[1]

Type of Fuel Cell	Operating Temp. (°C)	Power density (mW/cm^2)	Fuel Efficiency (Chem. To Elec.)	Lifetime (hr)	Capital Cost ($/kW)	Area of application
AFC	60-90	100-200	40-60	>10,000	>200	Space, Mobile
PAFC	160-220	200	55	>40,000	3000	Distributed power
PEMFC	50-80	350	45-60	>40,000	>200	Portable,Mobile,Stationary
MCFC	600-700	100	60-65	>40,000	1000	Distributed power generation
SOFC	800-1000	240	55-65	>40,000	1500	Baseload power generation

In order for membranes to be considered a suitable proton exchange membrane (PEM), they must have high water-transport properties, possess low methanol permeation and exhibit excellent thermal stability at operating temperatures[7]. Ion-exchange polymers containing sulfonic acid are frequently used as PEM. Nafion®, a perfluoroether sulfonic acid polymer, which has been frequently used as a membrane in fuel cells, has reported several disadvantages including its high cost and very high rate of methanol permeation[8-11].

Poly (styrene-isobutylene-styrene) (SIBS), which is inexpensive and commercially available, has been studied as an alternative PEM[7, 12-15]. Sulfonation of SIBS can cause considerable changes in its overall thermal stability[16]. Thermal analysis is of special concern since fuel cells largely depend on its thermal stability. In the past, thermogravimetric analysis (TGA) has been perfomed on sulfonated SIBS block copolymer with 30.84 % polystyrene by weight and number average molecular weight ($\overline{M_n}$) of 48,850 g/mol as a function of sulfonation level, annealing temperature, film formation, casting solvent and counter-ion substitution (Ba^{+2}, Ca^{+2}, and Mg^{+2})[7, 15]. In this study, the thermal behavior of three types of SIBS, with different $\overline{M_n}$ and polystyrene weight percent, which have not been reported before, are discussed as a function of high sulfonation level and counter-ion substitution (Ba^{+2}, Ca^{+2}, and Mg^{+2}).

II. LITERATURE REVIEW

Several alternative PEMs have been recently investigated for fuel cell applications[2, 4-6, 13, 14, 17, 18]. Phase segregated polymers, which may be used as PEMs, exhibit unique properties and can be modified chemically to obtain the desired properties. SIBS, composed of polyisobutylene and polystyrene, which impart excellent barrier properties and mechanical strength, respectively, has been studied as an alternative PEM[7]. Unique properties such as increased strength and proton conductivity arise via sulfonation of these polymers[12]. To achieve water transport and block the organic groups, the polystyrene units are chemically modified with sulfonic acid groups creating ion containing domains. Suleiman and co-workers have used multiscale modeling to study the effect of molecular structure on the transport properties, and found that all water transport is localized in the ionic regions[7].

As already mentioned, for membranes to be considered PEMs, they must have high water-transport properties, possess low methanol permeation, and exhibit excellent thermal stability at operating temperatures. Thermal stability is of special concern since it is common for fuel cells to operate at 120˚C or higher[7].

SIBS, with 30.84 % polystyrene by weight and $\overline{M_n}$ of 48,850 g/mol has been characterized by TGA as a function of: sulfonation level, annealing temperature, film formation, and casting solvent. Sulfonated samples showed an increase in degradation temperature, regardless of the sulfonation level or other processing conditions[15].

SIBS with 30.84 % polystyrene by weight and $\overline{M_n}$ of 48,850 g/mol has also been characterized by TGA as a function of sulfonation level (53 % to 97 %) and counter-ion substitution. Sulfonated samples showed additional temperature loss at lower temperature from that observed in the unsulfonated samples. Counter-ion substitutions of the membranes shifted the degradation temperatures to approximately 300°C, which is attributed to unique and robust complex formed between the sulfonated groups and metal cations. The study concluded that sulfonation and counter-ion substitution increased the thermal stability of the cross-linked polymer with cation[7].

III. THERMOGRAVIMETRIC ANALYSIS

In thermogravimetric analysis, measurement of the change in sample mass with temperature are made using a thermogravimetric balance. This is a combination of an electronic microbalance with a furnace and associated temperature programmer. The balance should be in a suitable enclosed system so that the atmosphere can be controlled[19]. TGA is especially useful for the study of polymeric materials including: thermoplastics, thermosets, elastomers, composites, films, fibers, coatings and paints. TG measurements provide valuable information that can be used to select materials, predict product performance and improve product quality.

Actual TG curves may be classified into various types as illustrated in Figure 3 [20]. Possible interpretations are as follows:

Type I: The sample undergoes no decomposition with loss of volatile products over the range shown.

Type II: The rapid initial mass loss observed is characteristic of desorption or drying.

Type III: These represent decomposition of the sample in a single stage.

Type IV: This indicates multi-stage decomposition with relatively stable intermediates.

Type V: These also represent multi-stage decomposition, but in this example stable intermediates are not formed and little information on all but the stoichiometry of the overall reaction can be obtained.

Type VI: These shows a gain in mass as a result of reaction of the sample with the surrounding atmosphere. The typical example would be the oxidation of a metal sample.

Type VII: These are not often encountered. The product of an oxidation reaction decomposes again at higher temperatures.

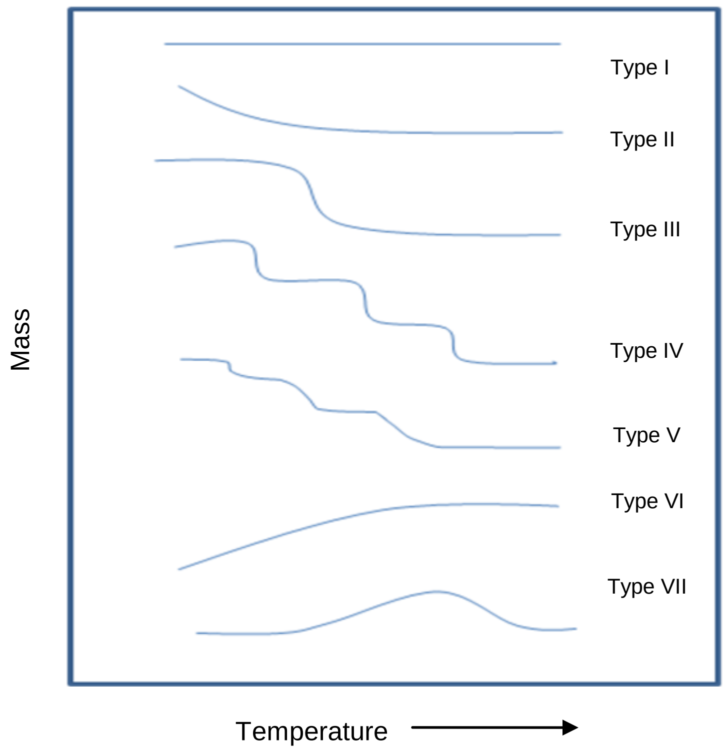

Figure 1: Main types of TG curves[19, 20].

Resolution of stages for TG curves can be improved by recording derivative TG (DTG) curves (Figure 4). Such curves may also be produced from digital TG data by numerical differentiation.

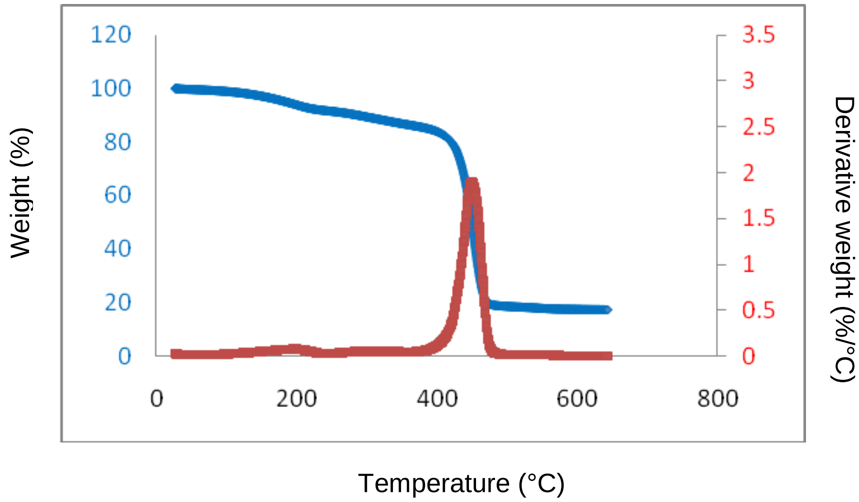

Figure 2: Comparison of TG and DTG curves.

IV. METHODOLOGY

The polymer used in this work is SIBS. SIBS (Figure 1) was supplied by Kuraray Co. Ltd (Pasadena, TX). The sulfonation of SIBS (Figure 2) was performed using acetyl sulfate as the sulfonating agent and is described in more details elsewhere[12]. The ion exchange capacity of membranes was determined by elemental analysis. In elemental analysis, the amount of sulfuric acid relative to the moles of polystyrene dictates the resulting sulfonation level of the polymer. Elemental Analysis tests were conducted by Atlantic Microlab, Inc. in Georgia. Hereinafter, the sulfonated block copolymers will be referred to as S-SIBS-wt%-$\overline{M_n}$ - #-XX, where S-SIBS represents sulfonated poly(styrene-isobutylene-styrene), wt%, refers to the polystyrene weight percent, $\overline{M_n}$, refers to the number average molecular weight, #, refers to the mol percent of polystyrene sulfonated and XX refers to the cation used for crosslinking the membranes. For example, sulfonated SIBS with 30 % polystyrene by weight, number average molecular weight of 100,000 g/mol, 76 mol percent of polystyrene sulfonated, and crosslinked with Ca^{+2} will be referred as S-SIBS-30-100K-76-Ca.

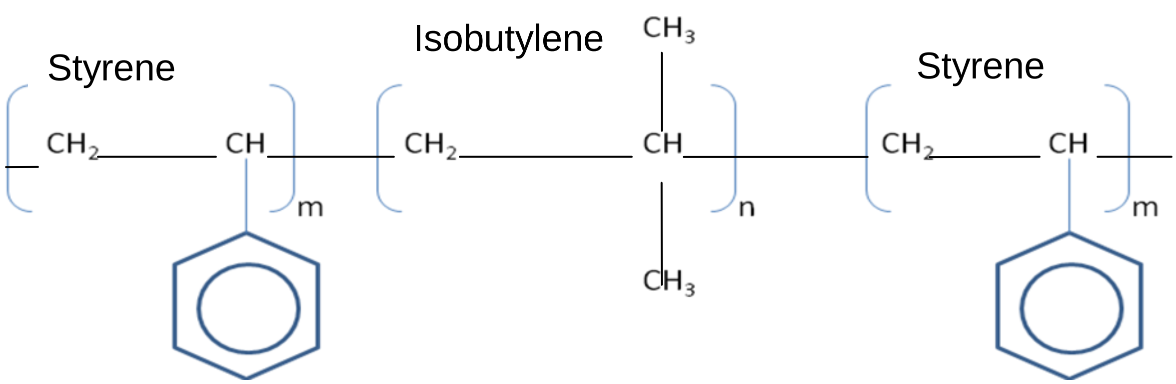

Figure 3: SIBS chemical structure

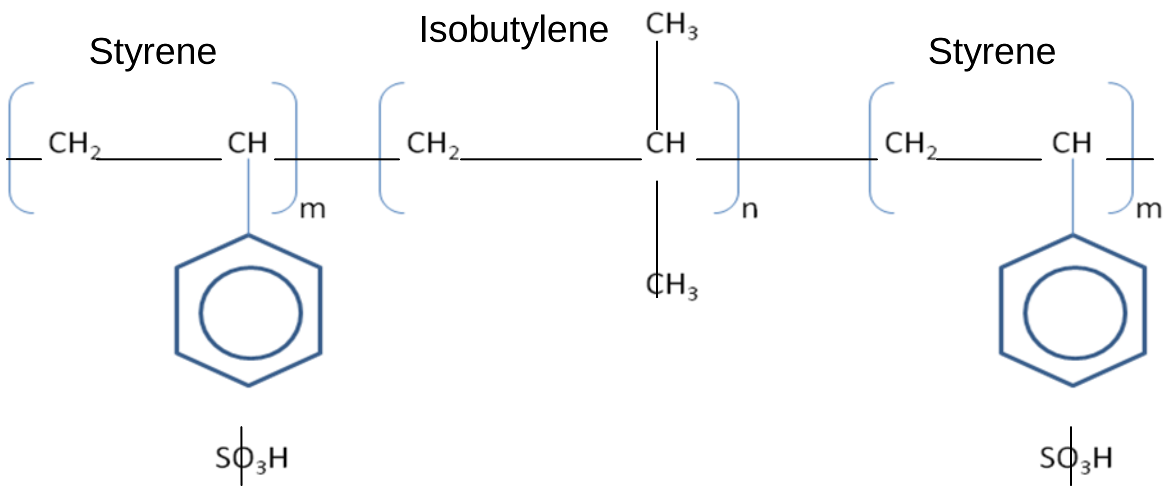

Figure 4: SIBS chemical structure with sulfonic groups. The styrene block is randomly sulfonated in the para-position of the aromatic rings.

To allow ionic interaction to occur between two individual sulfonic acid groups and to enhance selectivity, sulfonated SIBS membranes are crosslinked with Ba^{+2}, Ca^{+2}, or Mg^{+2}. The sulfonated polymers were irreversibly cross-linked by immersing them for several hours in a 1.0 M solution of magnesium chloride $MgCl_2$ (Acros Organics (Bridgewater, NJ), pure, molecular weight = 95.21 *g/mol*), barium chloride $BaCl_2$ (Fisher Scientific (Fair Lawn, NJ), pure, molecular weight = 208.23 *g/mol*) a calcium chloride $CaCl_2$ (Acros Organics, 96 %, molecular weight = 110.99 *g/mol*) depending on the desired cation. The cross-linked solutions were washed with de-ionized water and left to dry for at least 24 hours in an oven at 50°C. [7]

Instrument TGA/STDA851^e of Mettler Toledo (Columbus, OH) was used for characterization. Degradation temperatures were determined by heating the polymer samples in a nitrogen environment to 650°C at 10°C/min and observing regions of significant weight loss. In each experiment, a polymer sample weighing approximately 4.5 mg to 6 mg was used. Fifteen different samples were characterized, in triplicates. The complete data sets are listed in Appendix A. The studied samples, have different number average molecular weight and polystyrene weight percent, and are evaluated as a function of sulfonation level and counter-ion substitution (Ba^{+2}, Ca^{+2}, and Mg^{+2}).

Table 2: Characteristics of the membranes used for Thermogravimetric Analysis

Name	Polystyrene, wt %	Number Average Molecular wt, $\overline{M}_n$	Sulfonation Level %
SIBS-22.5-65K	22.5	65,000	84.24
SIBS-15-100K	15	100,000	81.67
SIBS-30-100K	30	100,000	76.03

V. RESULTS AND DISCUSSION

The average degradation temperature results for unsulfonated SIBS are listed in Table 3. Figures 5 and 6 show the TG and DTG spectra respectively, for unsulfonated SIBS-22.5-65K (22.5 % polystyrene by weight and $\overline{M_n}$ of 65,000). One weight loss stage can be identified; this occurs at 339°C - 432°C. Figures 7 and 8 show the TG and DTG spectra respectively, for unsulfonated SIBS-15-100K (15 % polystyrene by weight and $\overline{M_n}$ of 100,000). One weight loss stage can be identified; this occurs at 348°C - 448°C. Figures 9 and 10 show the TG and DTG spectra respectively, for unsulfonated SIBS-30-100K (30 % polystyrene by weight and $\overline{M_n}$ of 100,000). One weight loss stage can be identified; this occurs at 350°C - 440°C. The weight loss stage is attributed to the polymer backbone degradation. It was previously reported that the degradation temperature for SIBS with 30 % polystyrene by weight and $\overline{M_n}$ of 48,850 is 432±1°C. The weight loss stage for SIBS-30-48,850 was reported to be 360°C - 460°C.[15]

A decrease of 26°C was observed with an increase in $\overline{M_n}$ at 30 % polystyrene by weight, this is attributed to an increase in isobutylene in the polymer. A decrease of 10°C was observed with an increase in percent polystyrene by weight with $\overline{M_n}$ of 100,000 g/mol, suggesting that morphological effects predominate.

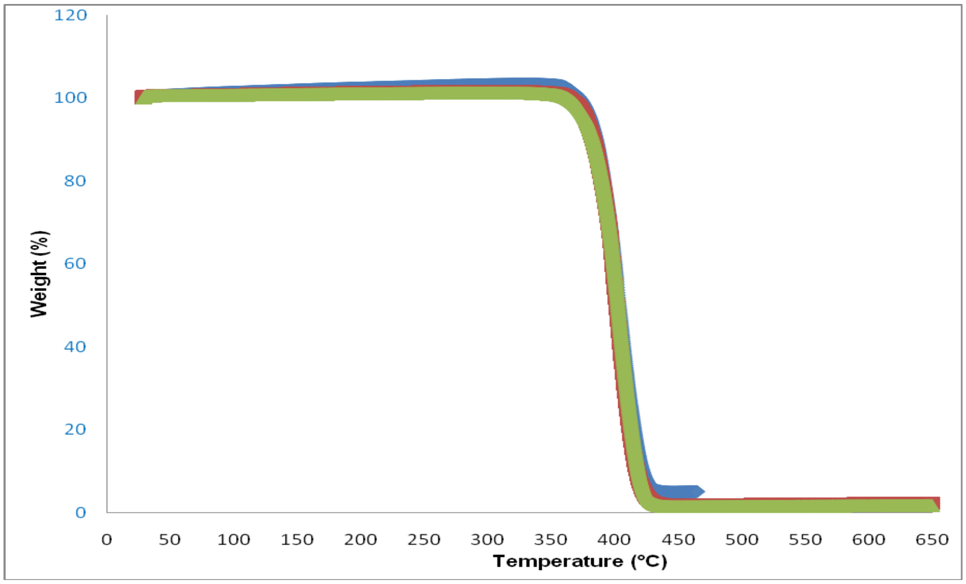

Figure 5: TG data for SIBS-22.5-65K.

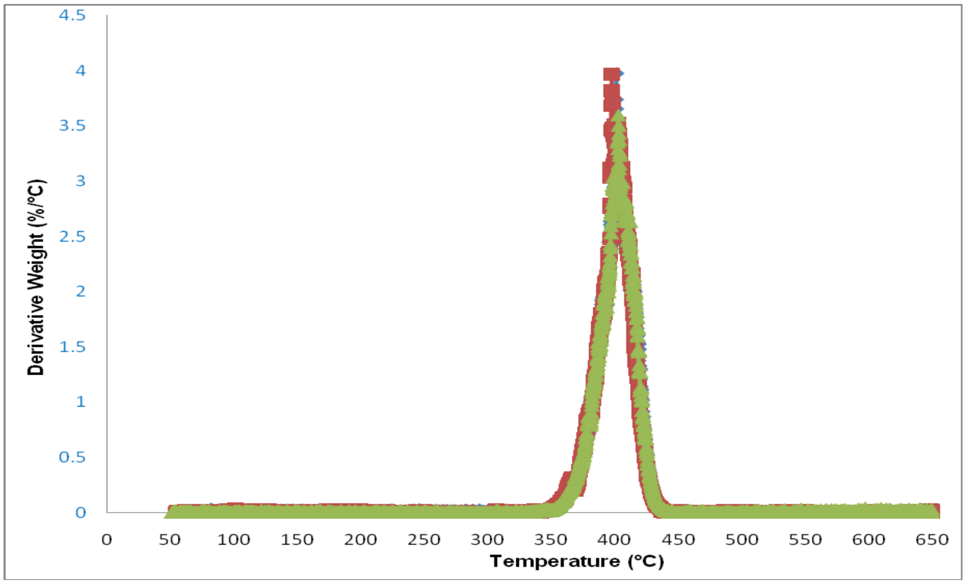

Figure 6: DTG data of SIBS-22.5-65K.

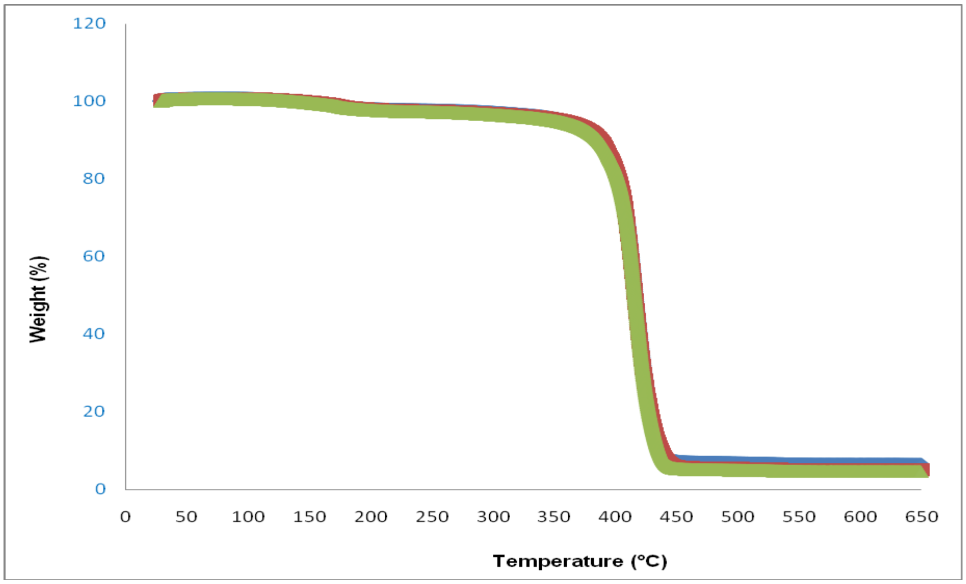

Figure 7: TG data for SIBS-15-100K.

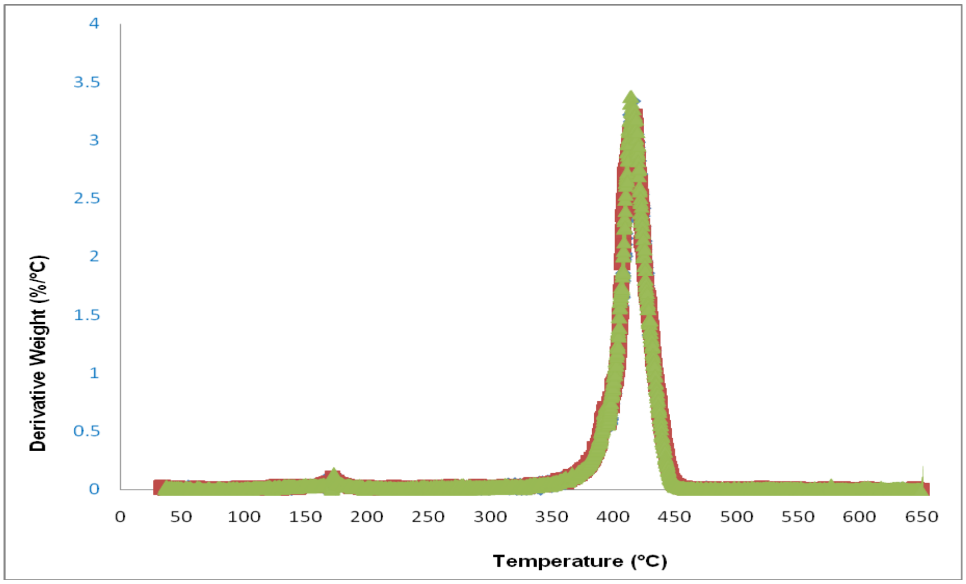

Figure 8: DTG data of SIBS-15-100K.

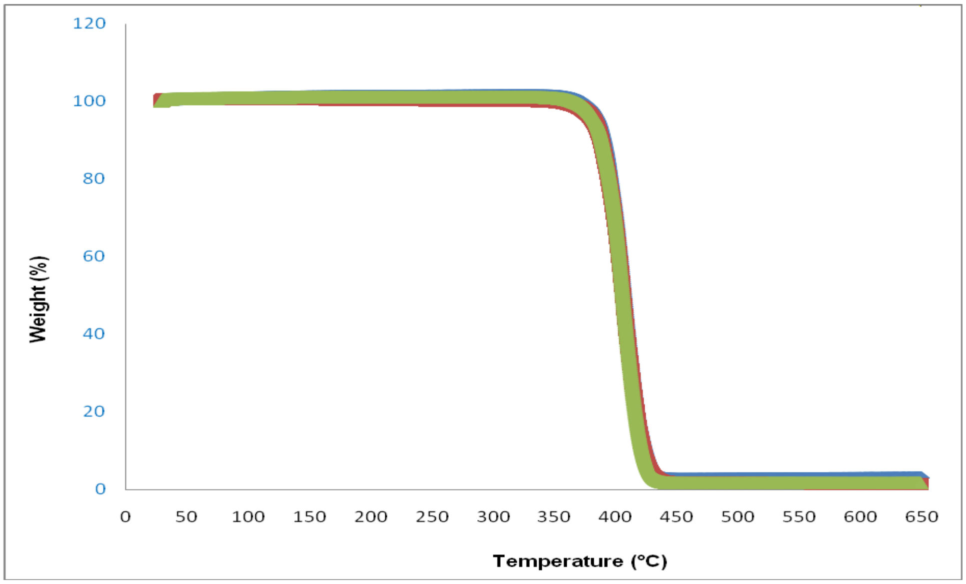

Figure 9: TG data for SIBS-30-100K.

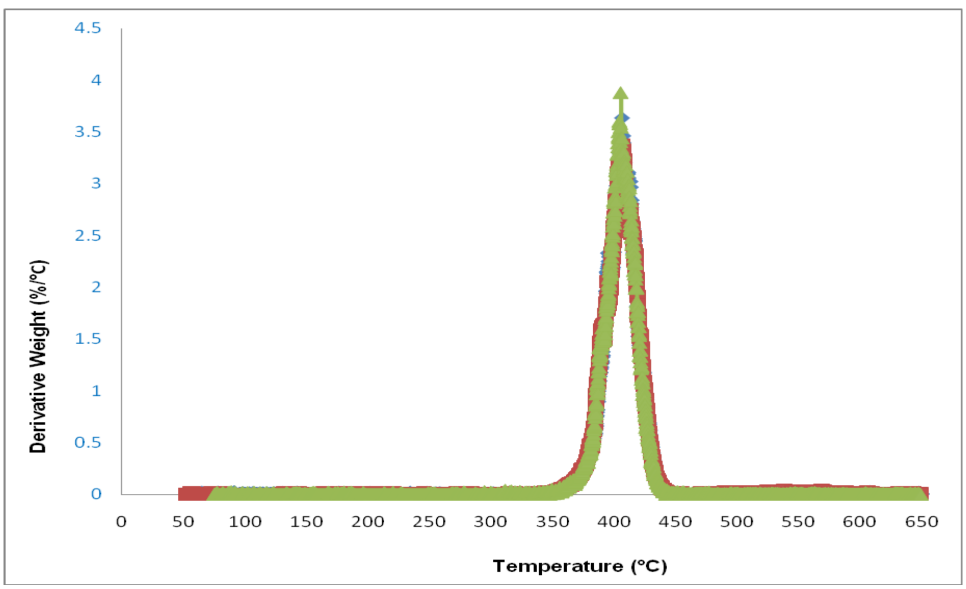

Figure 10: DTG data of SIBS-30-100K.

Table 3: TGA degradation temperatures for unsulfonated SIBS.

Sample Name	First degradation Temperature (°C) Sulfonic Groups	Second degradation temperature (°C) Polymer Backbone	Third Degradation temperature (°C) Cation and Sulfonic Groups	Fourth Degradation temperature (°C) Cation and Sulfonic Groups
SIBS-22.5-65K	Not observed	400.8±2.6	Not observed	Not observed
SIBS-15-100K	Not observed	416.1±1.0	Not observed	Not observed
SIBS-30-100K	Not observed	406.4±0.6	Not observed	Not observed

The average degradation temperature results for sulfonated SIBS to high IEC are listed in Table 4. Figures 11 and 12 show the TG and DTG spectra respectively, for S-SIBS-22.5-65K-84. Two weight loss stages can be identified; these occur at 203°C - 318°C and 345°C - 453°C. Figures 13 and 14 show the TG and DTG spectra respectively, for S-SIBS-15-100K-82. Two weight loss stages can be identified; these occur at 241°C - 311°C and 350°C - 455°C. Figures 15 and 16 show the TG and DTG spectra respectively, for S-SIBS-30-100K-76. Two weight loss stages can be identified; these occur at 205°C - 340°C and 350°C - 454°C. The first weight loss stage can be attributed to the sulfonic groups, and the second weight loss stage to the polymer backbone degradation.[15]

Sulfonation increases the polymer backbone degradation temperature to a consistent value of approximately 423°C for all studied samples due to the lamellar structure formed at high sulfonation levels regardless the polystyrene weight percent or $\overline{M_n}$. Combining polyisobutylene with sulfonated polystyrene decreases sulfonated polystyrene weight loss stage temperature, since sulfonated polystyrene alone has a weight loss stage from 465-510 °C. [2]

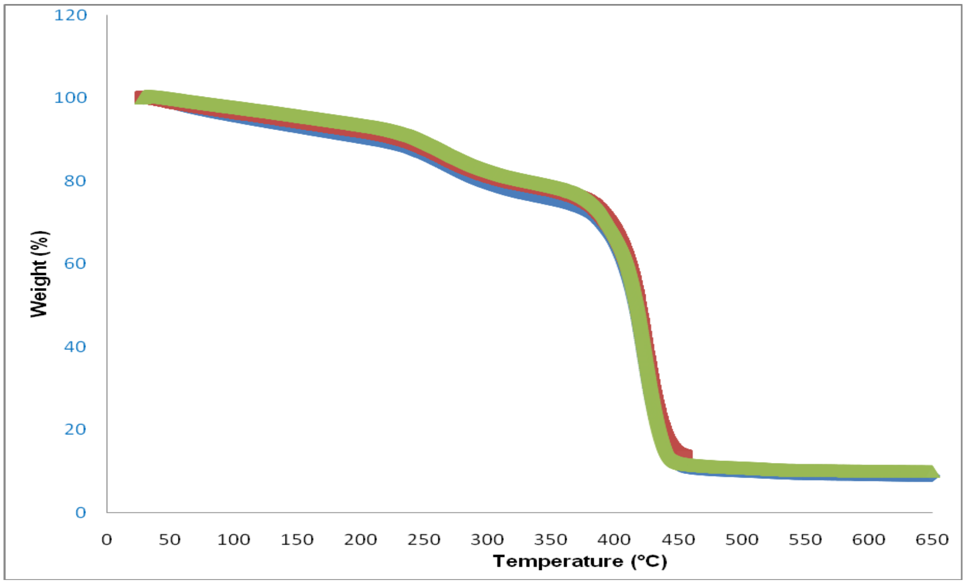

Figure 11: TG data for S-SIBS-22.5-65K-84.

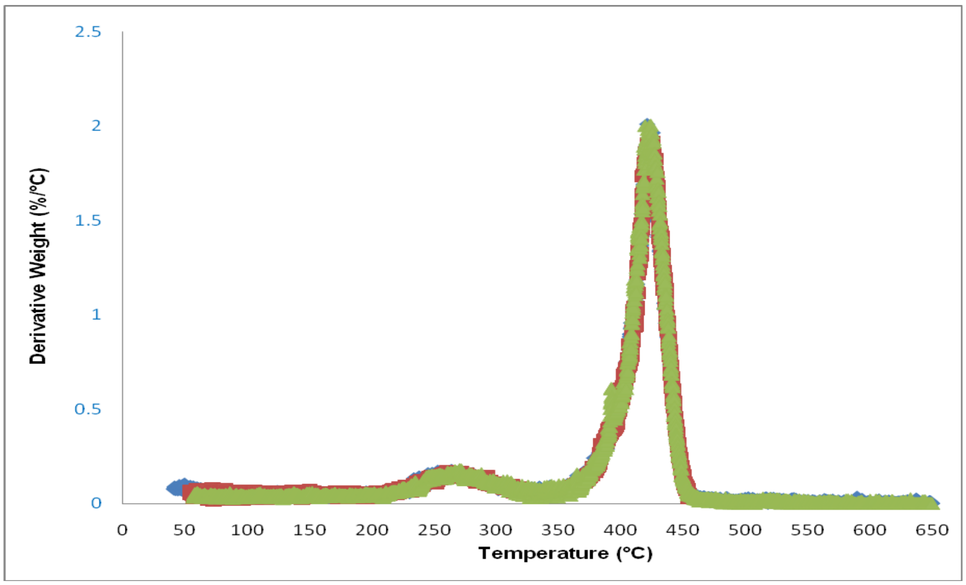

Figure 12: DTG for S-SIBS-22.5-65K-84.

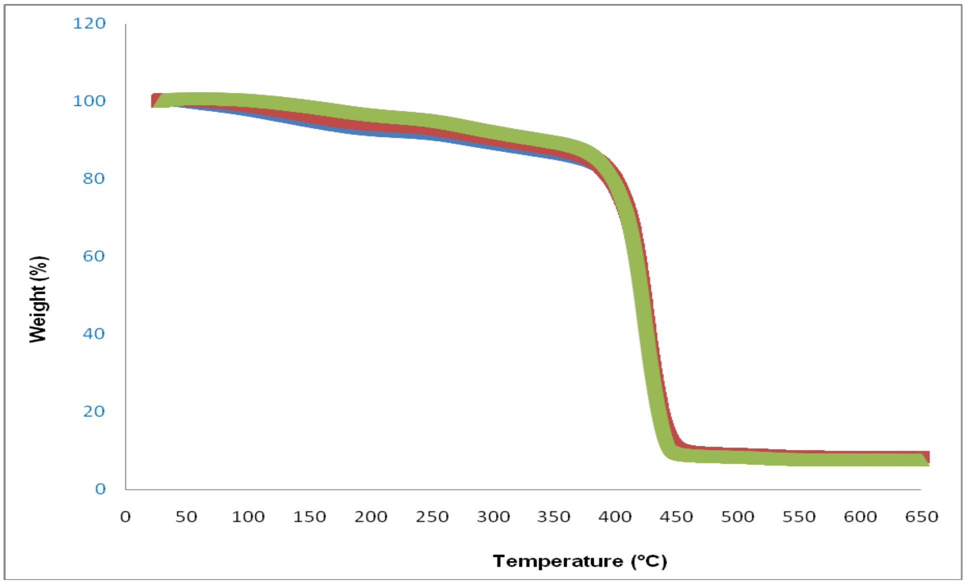

Figure 13: TG data for S-SIBS-15-100K- 82.

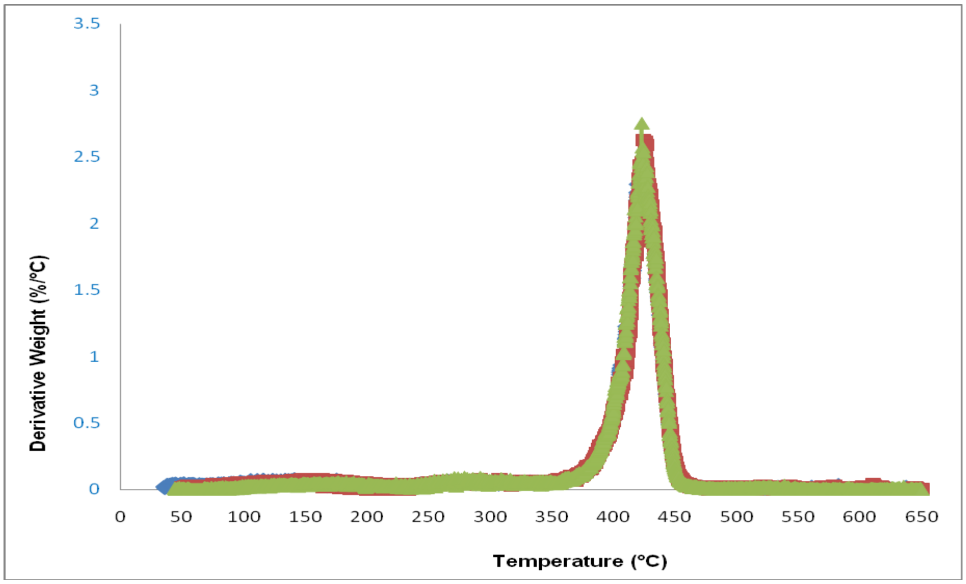

Figure 14: DTG data for S-SIBS-15-100K-82.

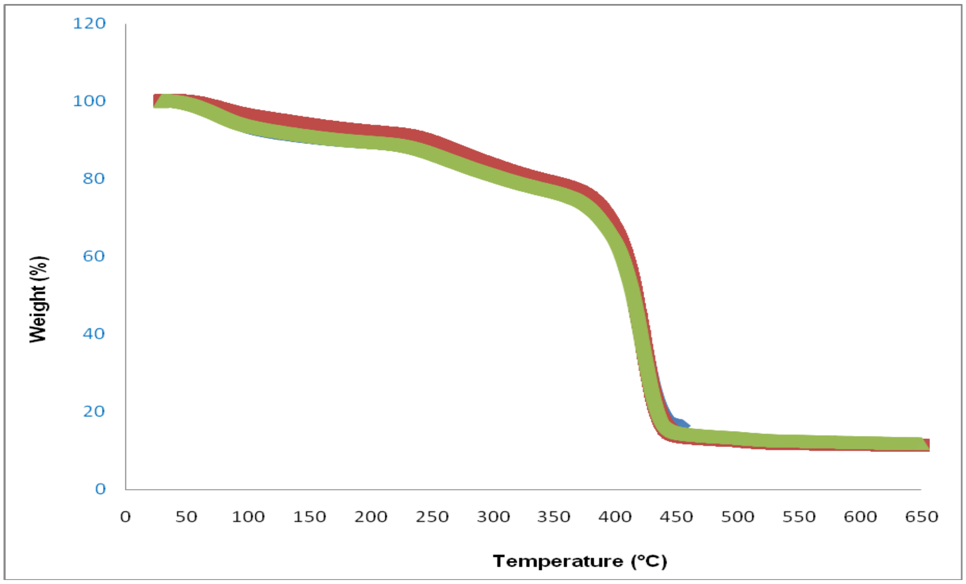

Figure 15: TG data for S-SIBS-30-100K-76.

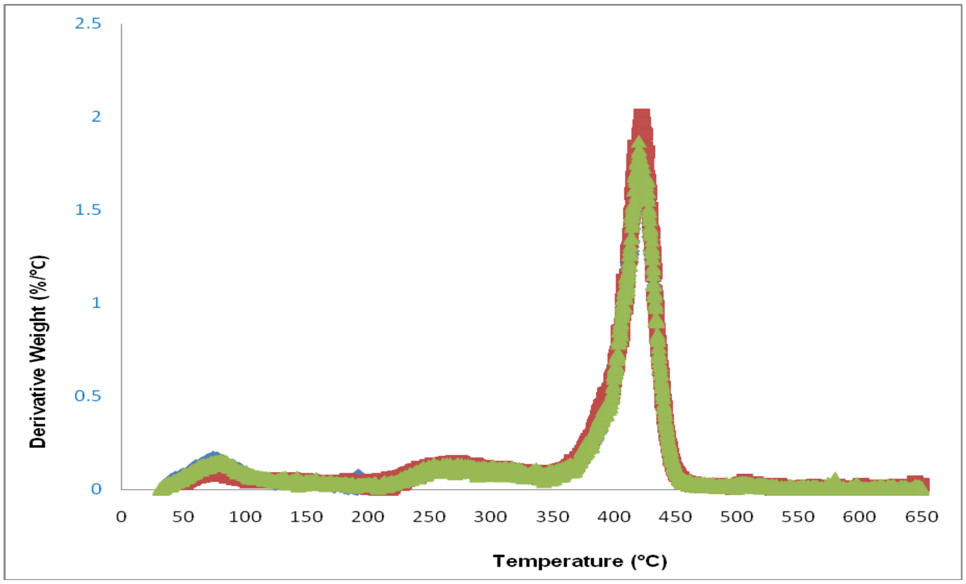

Figure 16: DTG data of S-SIBS-30-100K-76.

Table 4: TGA degradation temperatures for sulfonated SIBS.

Sample Name	First degradation Temperature (°C) Sulfonic Groups	Second degradation temperature (°C) Polymer Backbone	Third Degradation temperature (°C) Cation and Sulfonic Groups	Fourth Degradation temperature (°C) Cation and Sulfonic Groups
S-SIBS-22.5-65K-84	265.3±4.8	423.6±2.3	Not observed	Not observed
S-SIBS-15-100K-82	278.4±6.6	424.7±1.5	Not observed	Not observed
S-SIBS-30-100K-76	261.5±8.0	422.2±1.9	Not observed	Not observed

The average degradation temperature results for sulfonated SIBS cross-linked with cation, Ba^{+2} are listed in Table 5. Figures 17 and 18 show the TG and DTG spectra respectively, for S-SIBS-22.5-65K-84-Ba. Three weight loss stages can be identified; these occur at 355°C - 448°C, 463°C - 515°C, and 526°C - 581°C. Figures 19 and 20 show the TG and DTG spectra respectively, for S-SIBS-15-100K-82-Ba. Three weight loss stages can be identified; these occur at 356°C - 451°C, 463°C - 508°C, and 510°C - 581°C. Figures 21 and 22 show the TG and DTG spectra respectively, for S-SIBS-30-100K-76-Ba. Three weight loss stages can be identified; these occur at 354°C - 447°C, 449°C - 500°C, and 522°C - 585°C. The weight loss stage observed in sulfonated SIBS-22.5-65K and SIBS-30-100K on the region from 200°C - 340°C is absent in sulfonated polymers cross-linked with Ba^{+2}; however, two new weight loss stages in the region of 449°C - 515°C and 510°C - 585°C are observed. These two stages can be attributed to the loss of cations and sulfonic groups. They are lost in two regions due to different coordination of the cations.

For S-SIBS with Ba^{+2} it is observed that the second degradation temperature attributed to the polymer backbone degradation has a reduction of approximately 11°C in comparison with S-SIBS without cation.

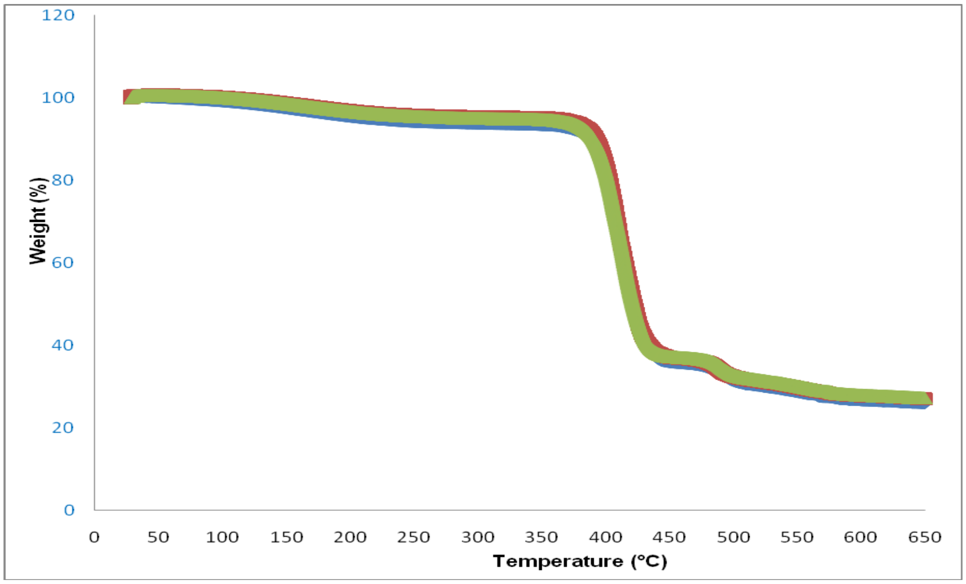

Figure 17: TG data for S-SIBS-22.5-65K-84-Ba.

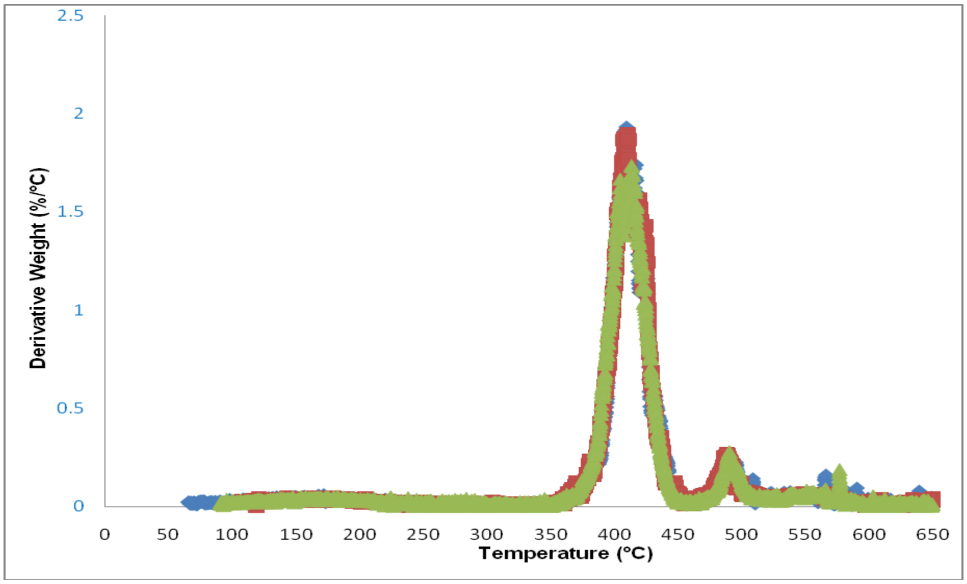

Figure 18: DTG data for S-SIBS-22.5-65K-84-Ba.

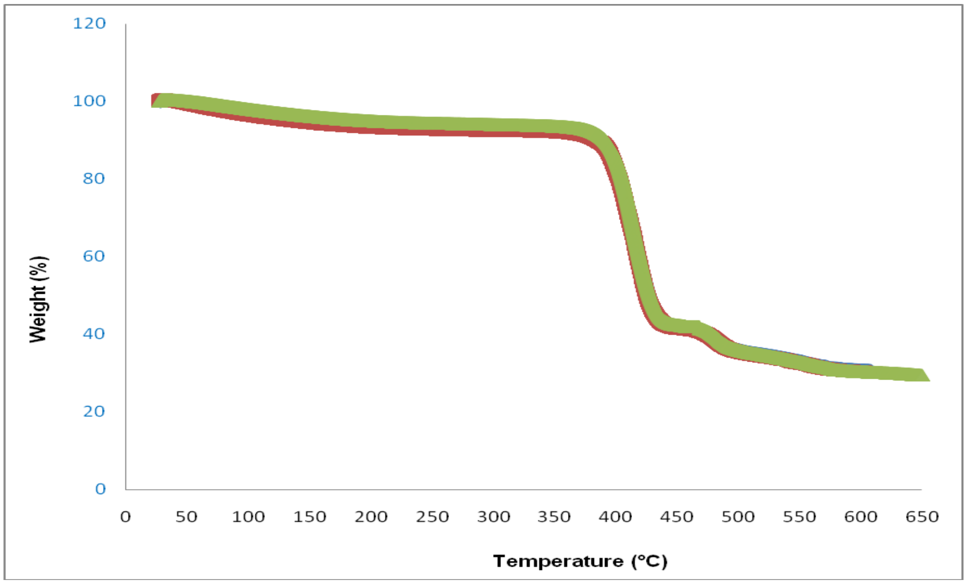

Figure 19: TG data for S-SIBS-15-100K-82-Ba.

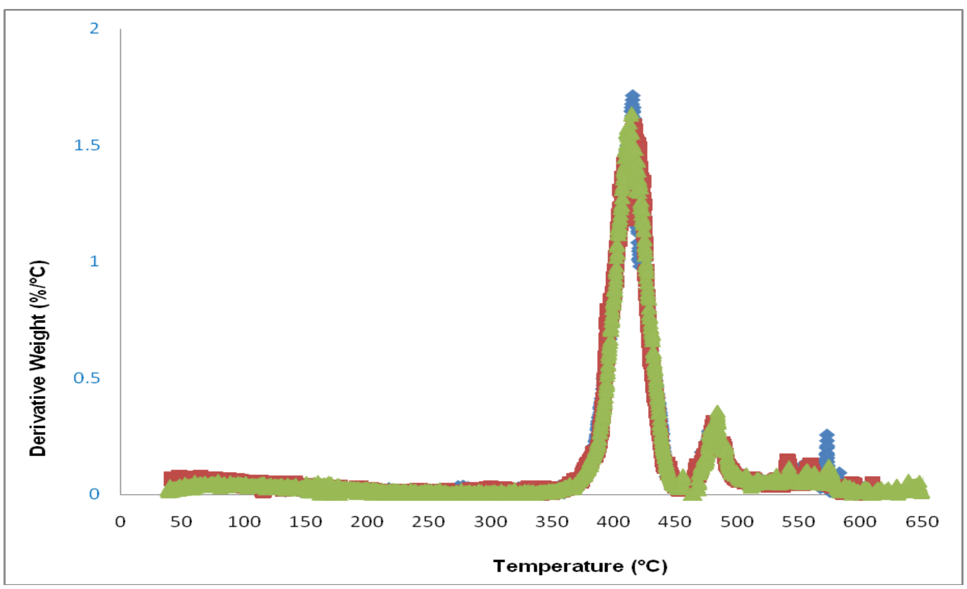

Figure 20: DTG data for S-SIBS-15-100K-82-Ba.

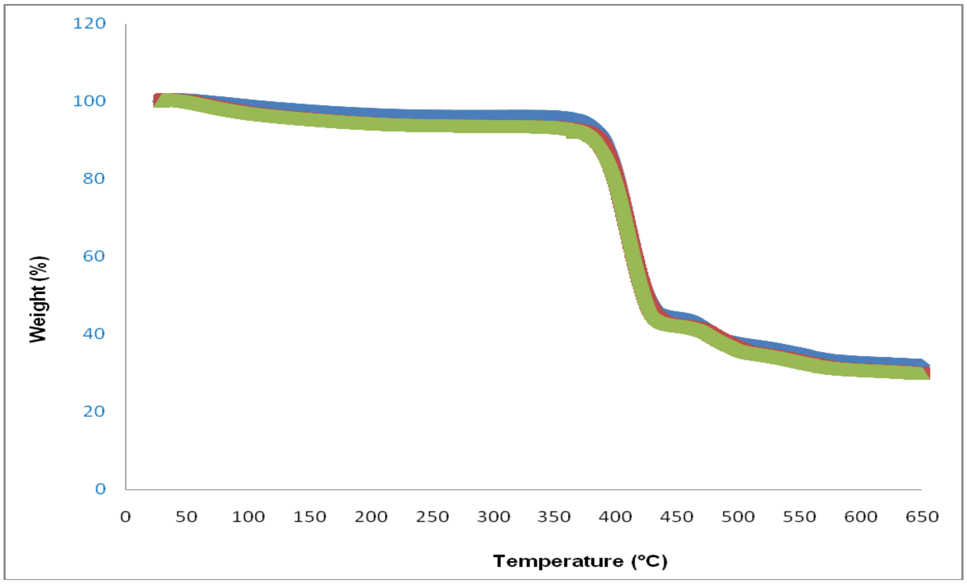

Figure 21: TG data for S-SIBS-30-100K-76-Ba.

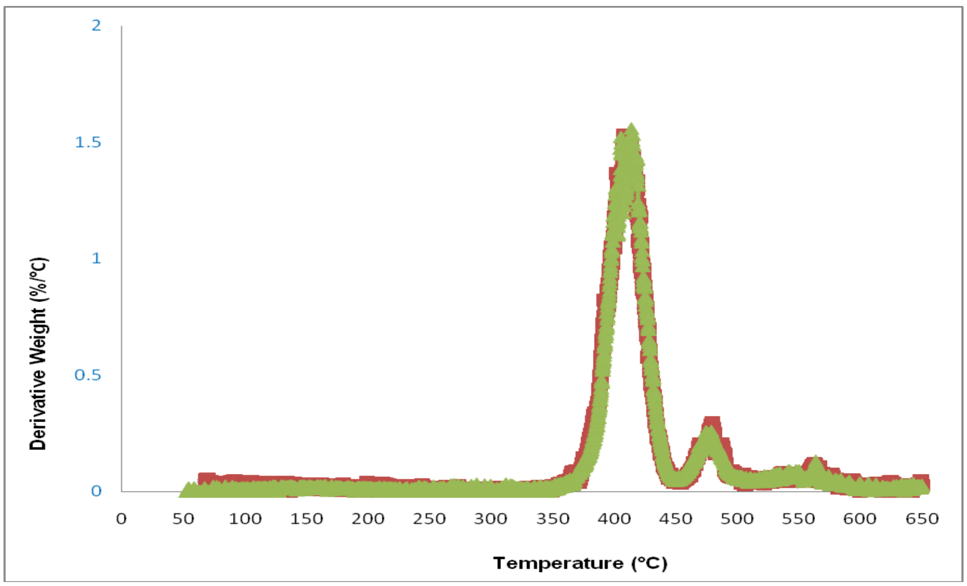

Figure 22: DTG data for S-SIBS-30-100K-76-Ba.

Table 5: TGA degradation temperatures for sulfonated SIBS with cation (Ba^{+2}).

Sample Name	First degradation Temperature (°C) Sulfonic Groups	Second degradation temperature (°C) Polymer Backbone	Third Degradation temperature (°C) Cation and Sulfonic Groups	Fourth Degradation temperature (°C) Cation and Sulfonic Groups
S-SIBS-22.5-65K-84-Ba	Not observed	411.3±2.0	491.5±3.7	572.4±5.5
S-SIBS-15-100K-82-Ba	Not observed	415.5±0.9	481.6±2.1	562.9±19.0
S-SIBS-30-100K-76-Ba	Not observed	410.1±3.2	478.7±1.1	564.0±2.5

The average degradation temperature results for sulfonated SIBS cross-linked with cation, Ca^{+2} are listed in Table 6. Figures 23 and 24 show the TG and DTG spectra respectively, for S-SIBS-22.5-65K-84-Ca. Three weight loss stages can be identified; these occur at 350°C - 446°C, 476°C - 518°C, and 531°C - 565°C. Figures 25 and 26 show the TG and DTG spectra respectively, for S-SIBS-15-100K-82-Ca. Three weight loss stages can be identified; these occur at 350°C - 449°C, 461°C - 525°C, and 530°C - 573°C. Figures 27 and 28 show the TG and DTG spectra respectively, for S-SIBS-30-100K-76-Ca. Three weight loss stages can be identified; these occur at 345°C - 445°C, 456°C - 516°C, and 517°C - 575°C. The weight loss stage observed in sulfonated SIBS-22.5-65K and SIBS-30-100K on the region from 200°C - 340°C is absent in sulfonated polymers cross-linked with Ca^{+2}; however, two new weight loss stages in the region of 456°C - 525°C and 517°C - 575°C are observed. These two stages can be attributed to the loss of cations and sulfonic groups. They are lost in two regions due to different coordination of the cations.

For S-SIBS with Ca^{+2} it is observed that the polymer backbone degradation temperature decreases slightly with an increase in percent polystyrene by weight with $\overline{M_n}$ of 100,000 g/mol.

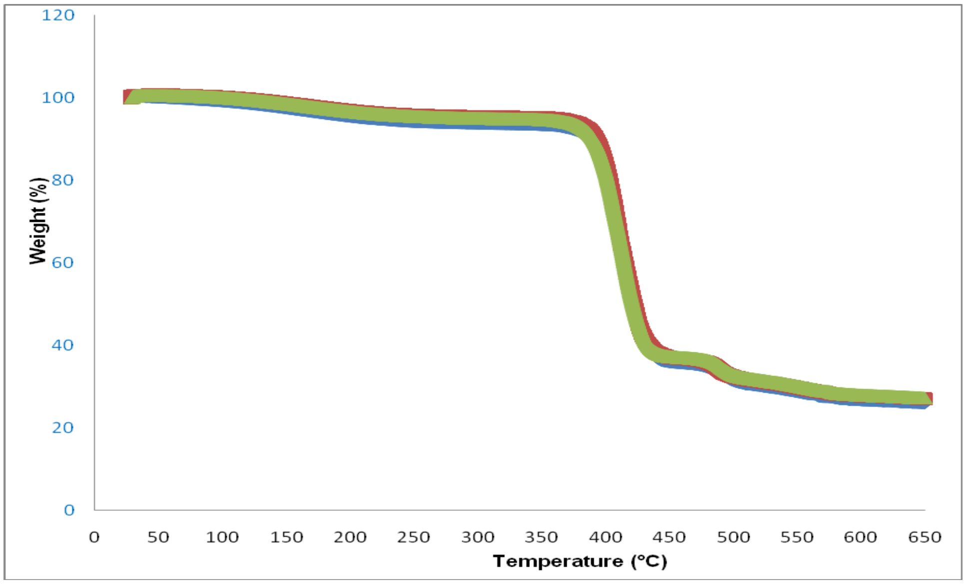

Figure 23: TG data for S-SIBS-22.5-65K-84-Ca.

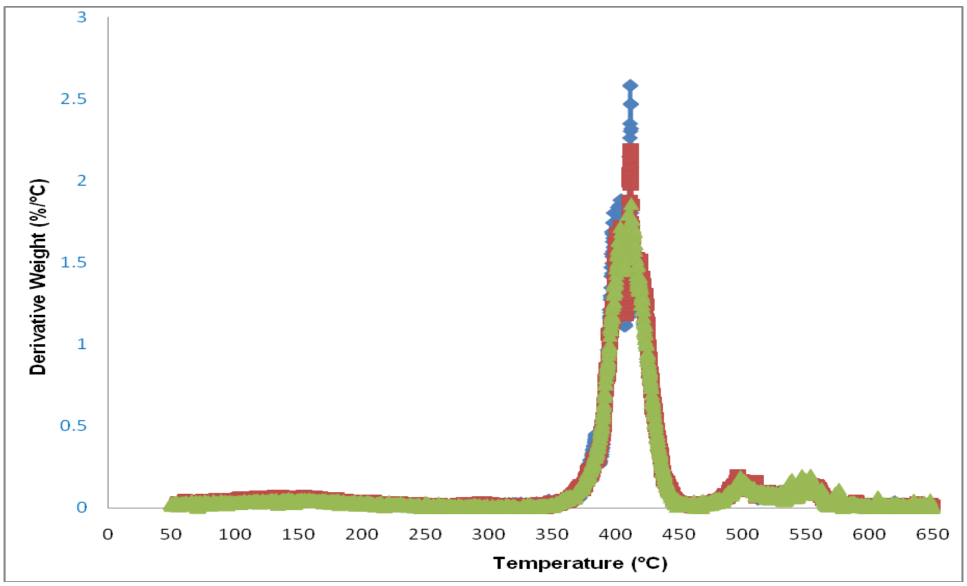

Figure 24: DTG data for S-SIBS-22.5-65K-84-Ca.

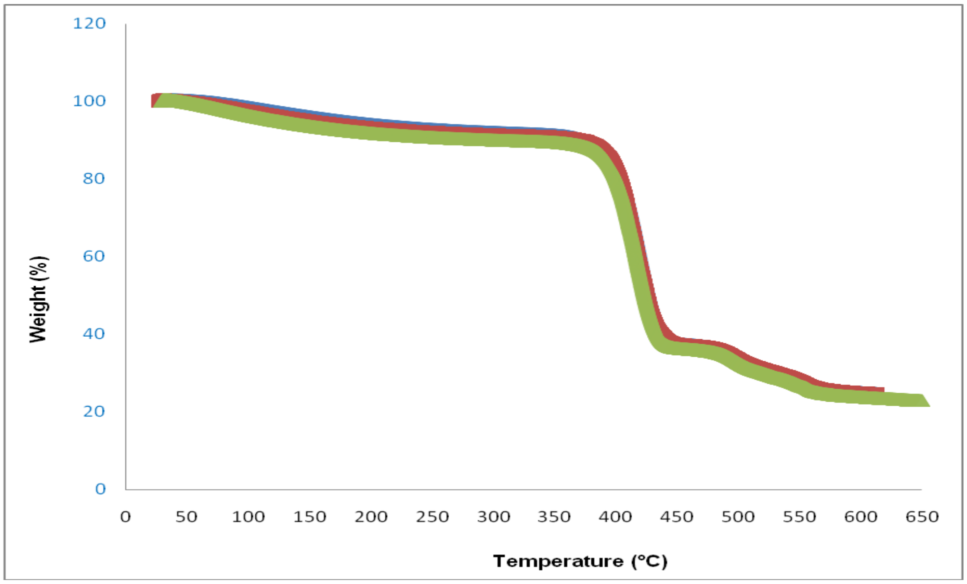

Figure 25: TG data for S-SIBS-15-100K-82-Ca.

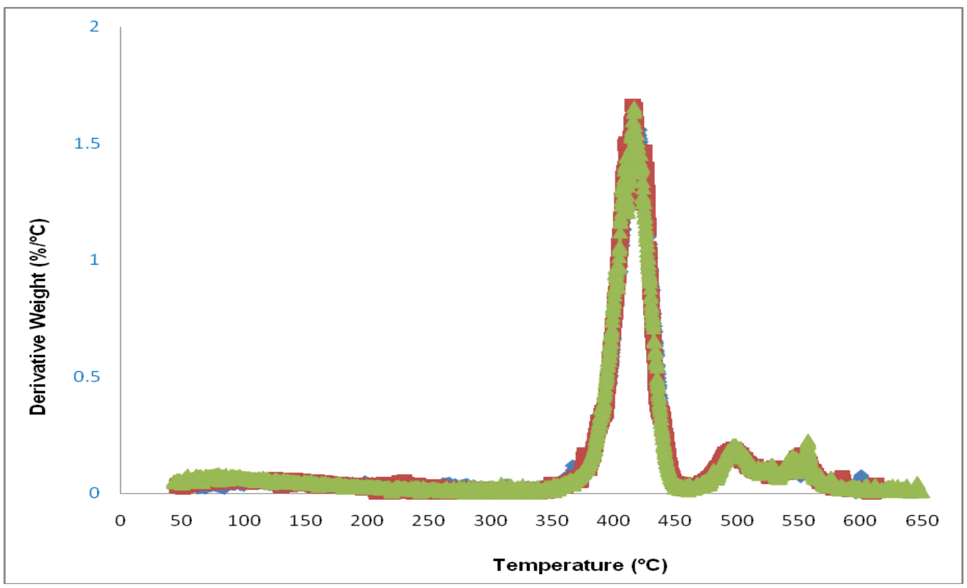

Figure 26: DTG data of S-SIBS-15-100K-82-Ca.

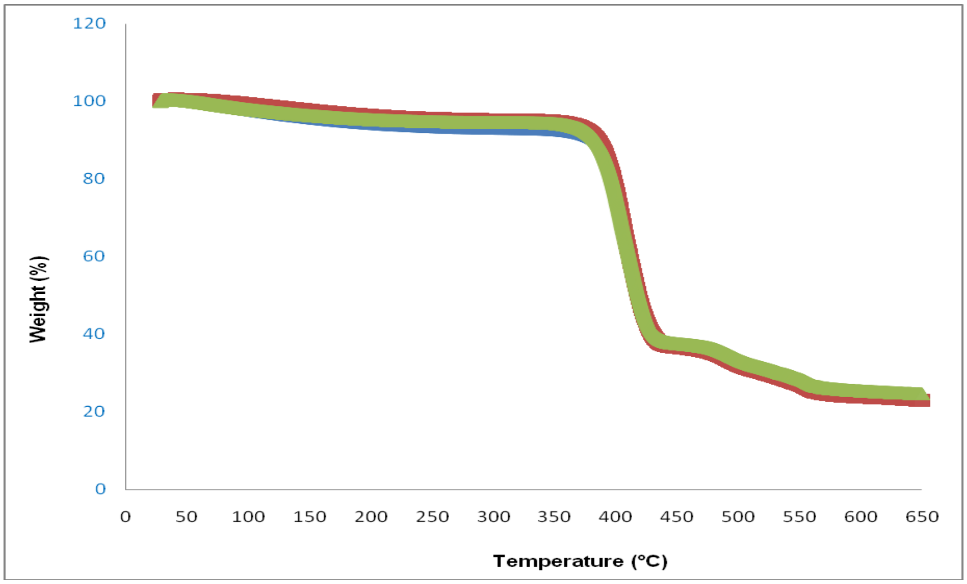

Figure 27: TG data for S-SIBS-30-100K-76-Ca.

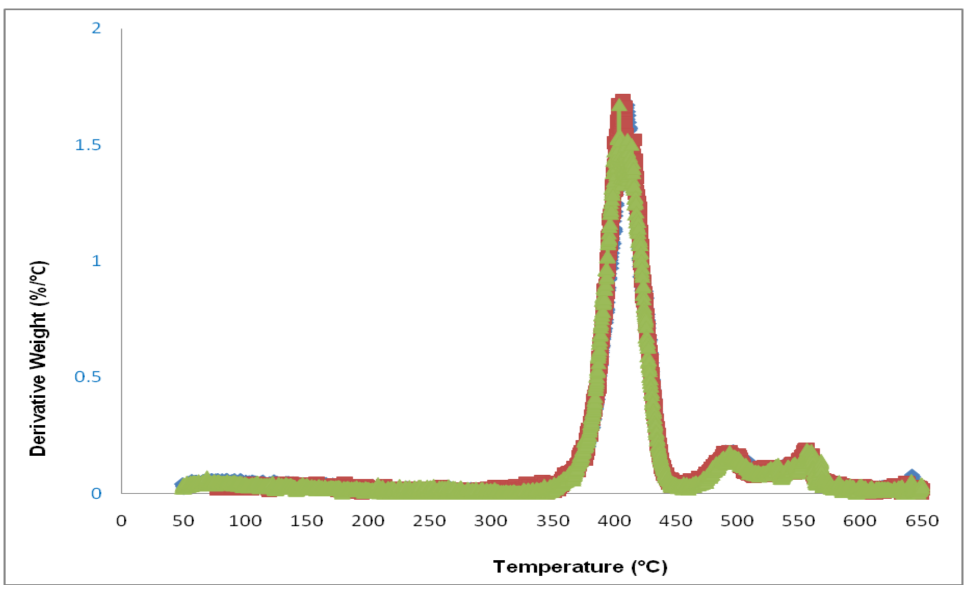

Figure 28: DTG for S-SIBS-30-100K-76-Ca.

Table 6: TGA degradation temperatures for sulfonated SIBS with cation (Ca^{+2}).

Sample Name	First degradation Temperature (°C) Sulfonic Groups	Second degradation temperature (°C) Polymer Backbone	Third Degradation temperature (°C) Cation and Sulfonic Groups	Fourth Degradation temperature (°C) Cation and Sulfonic Groups
S-SIBS-22.5-65K-84-Ca	Not observed	412.1±0.4	498.8±2.5	555.6±2.0
S-SIBS-15-100K-82-Ca	Not observed	416.0±0.4	498.5±0.9	555.7±2.8
S-SIBS-30-100K-76-Ca	Not observed	406.5±2.2	494.6±1.6	555.0±2.2

The average degradation temperature results for sulfonated SIBS cross-linked with cation, Mg^{+2} are listed in Table 7. Figures 29 and 30 show the TG and DTG spectra respectively, for S-SIBS-22.5-65K-84-Mg. Three weight loss stages can be identified; these occur at 353°C - 448°C, 477°C - 515°C, and 516°C - 578°C. Figures 31 and 32 show the TG and DTG spectra respectively, for S-SIBS-15-100K-82-Mg. Three weight loss stages can be identified; these occur at 353°C - 449°C, 468°C - 514°C, and 515°C - 579°C. Figures 33 and 34 show the TG and DTG spectra respectively, for S-SIBS-30-100K-76-Mg. Three weight loss stages can be identified; these occur at 338°C - 447°C, 474°C - 510°C, and 511°C - 586°C. The weight loss stage observed in sulfonated SIBS-22.5-65K and SIBS-30-100K on the region from 200°C - 340°C is absent in sulfonated polymers cross-linked with Mg^{+2}; however, two new weight loss stages in the region of 468°C - 525°C and 511°C - 586°C are observed. These two stages can be attributed to the loss of cations and sulfonic groups. They are lost in two regions due to different coordination of the cations.

For S-SIBS with Mg^{+2} it is observed that the polymer backbone degradation temperature is the same regardless the percent polystyrene by weight and $\overline{M_n}$.

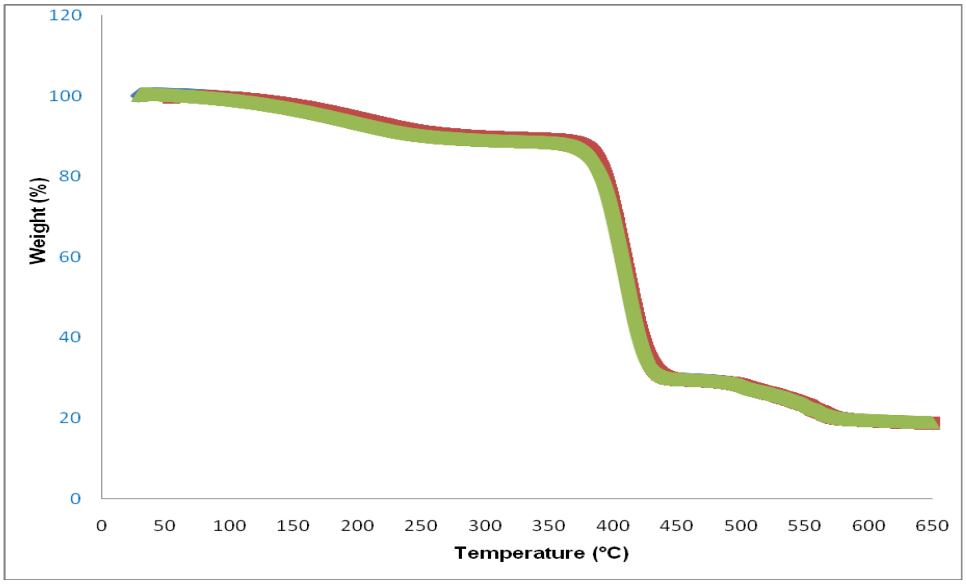

Figure 29: TG data of S-SIBS-22.5-65K-84-Mg.

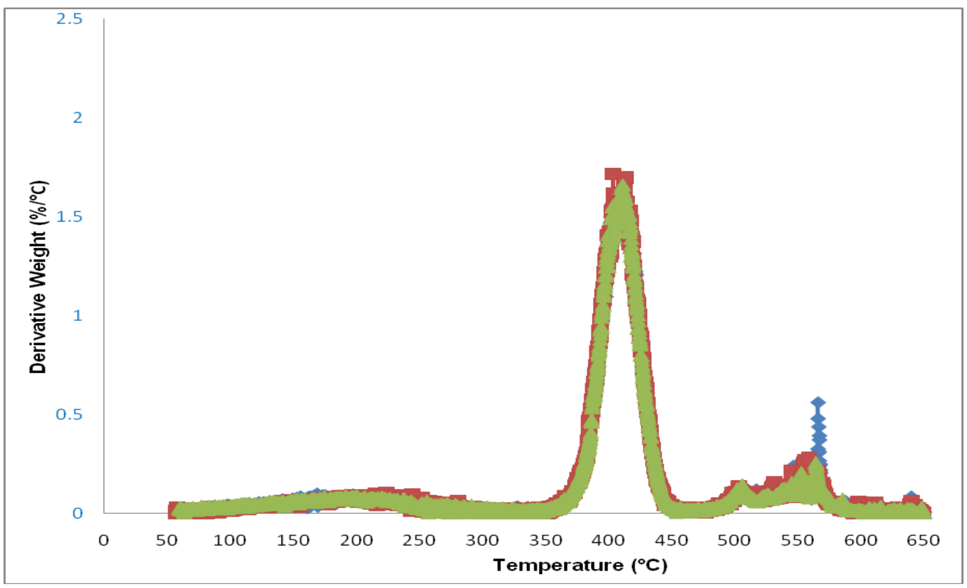

Figure 30: DTG data for S-SIBS-22.5-65K-84-Mg.

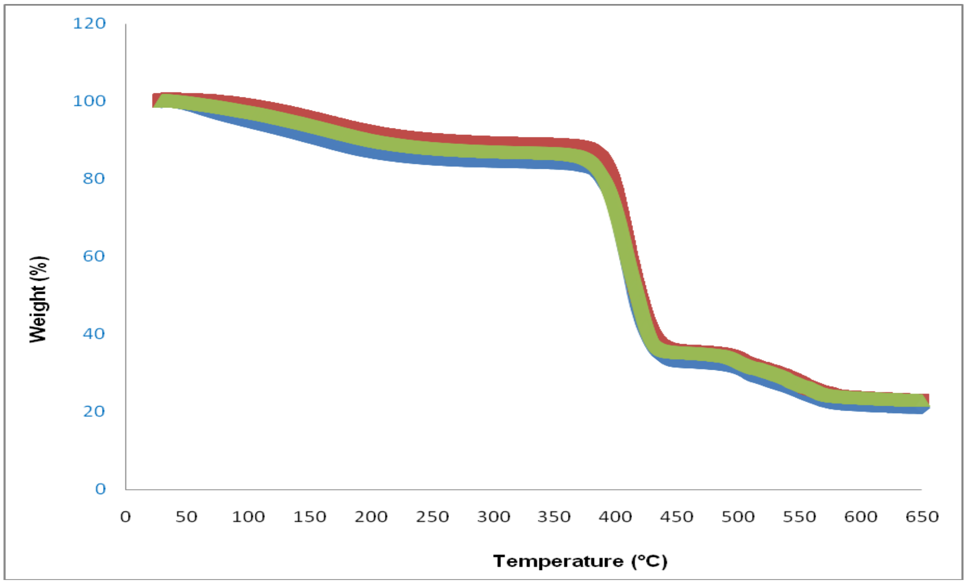

Figure 31: TG data of S-SIBS-15-100K-82-Mg.

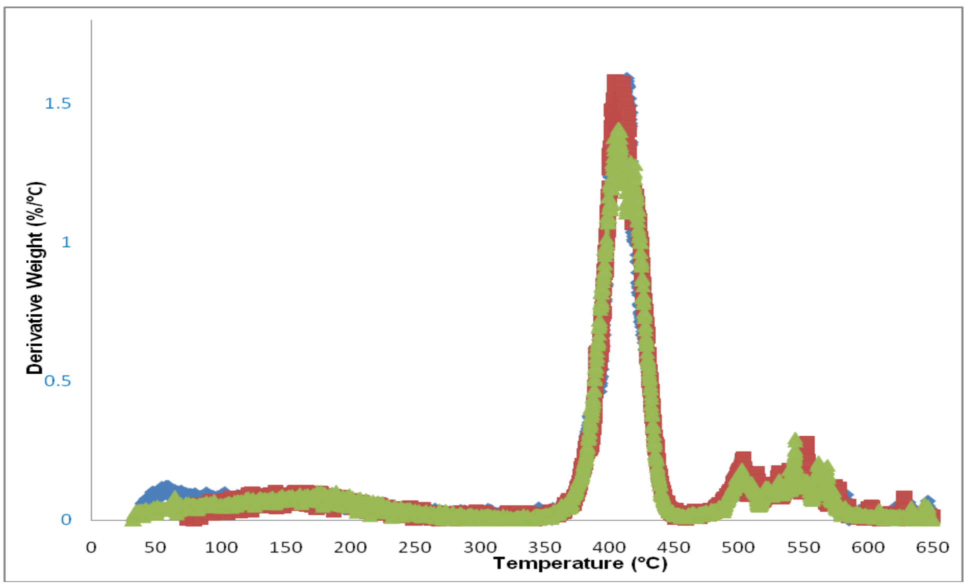

Figure 32: DTG data for S-SIBS-15-100K-82-Mg.

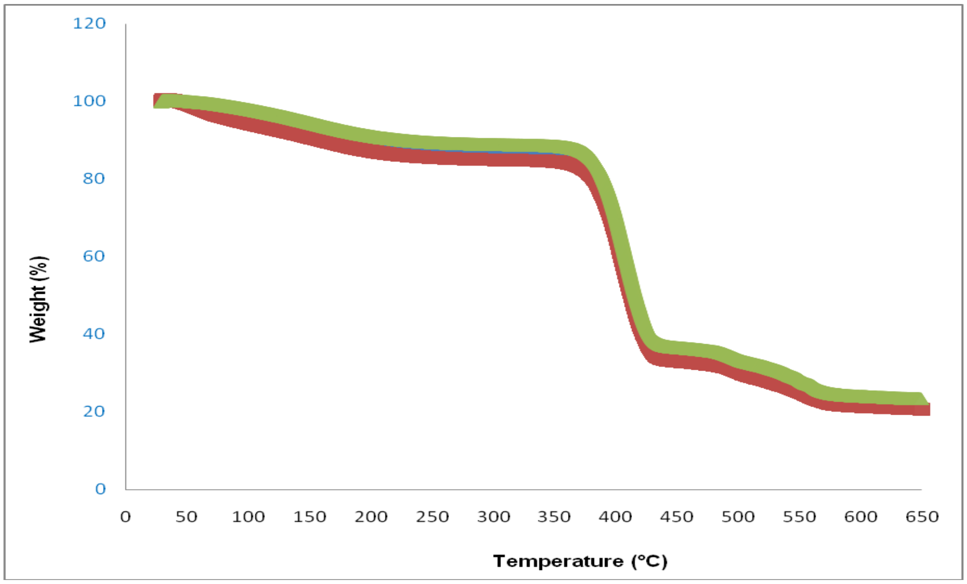

Figure 33: TG data for S-SIBS-30-100K-76-Mg.

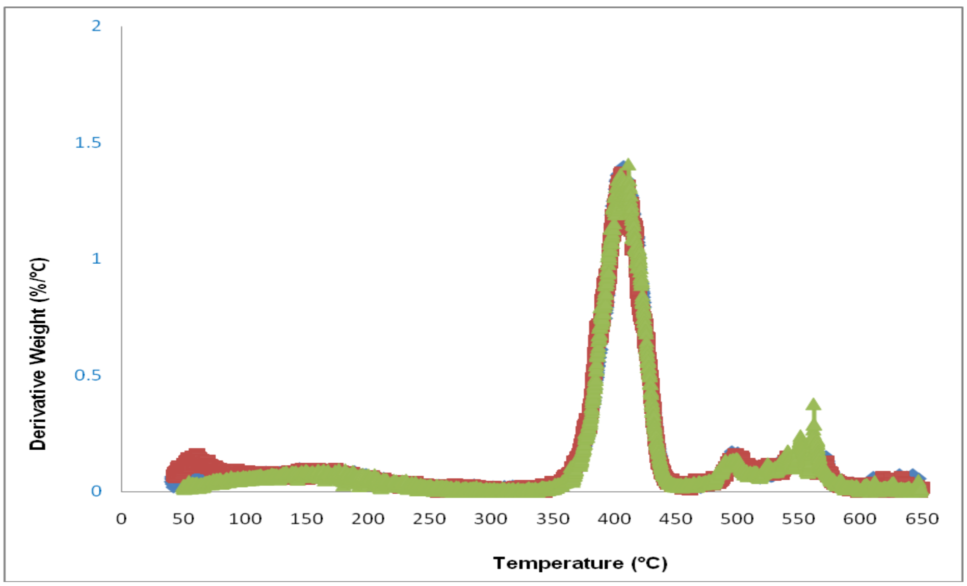

Figure 34: DTG data for S-SIBS-30-100K-76-Mg.

Table 7: TGA degradation temperatures for sulfonated SIBS with cation (Mg^{+2}).

Sample Name	First degradation Temperature (°C) Sulfonic Groups	Second degradation temperature (°C) Polymer Backbone	Third Degradation temperature (°C) Cation and Sulfonic Groups	Fourth Degradation temperature (°C) Cation and Sulfonic Groups
S-SIBS-22.5-65K-84-Ca	Not observed	408.0±3.8	504.7±0.9	563.1±3.5
S-SIBS-15-100K-82-Ca	Not observed	408.3±4.8	503.0±0.7	551.3±6.8
S-SIBS-30-100K-76-Ca	Not observed	408.6±2.7	497.9±2.3	559.2±3.3

VI. CONCLUSIONS

The thermal behavior of unsulfonated and highly sulfonated SIBS (counter-ion substituted) with different $\overline{M_n}$ and polystyrene weight percent, has been studied. For unsulfonated samples, a decrease in the polymer backbone degradation temperature was observed with an increase in $\overline{M_n}$, with 30 % polystyrene by weight, which is attributed to an increase in isobutylene in the polymer. Also a decrease in the polymer backbone degradation temperature was observed with an increase in percent polystyrene by weight, with $\overline{M_n}$ of 100,000 g/mol suggesting that in this case morphological effects predominate. Sulfonation increases the polymer backbone degradation temperature to a consistent value of approximately 423°C for all studied samples due to the lamellar structure formed at high sulfonation levels. The weight loss stage corresponding to the degradation of sulfonic groups was not observed in sulfonated polymers cross-linked with cations; however two new weight loss stages are observed, which are attributed to the loss of cations and sulfonic groups. They are lost in two stages, due to different coordination of the cations. Membrane attained superior thermal stability when exchanged with cation with a larger ionic radius. SIBS with 15 % polystyrene by weight and $\overline{M_n}$ of 100,000 g/mol has a higher polymer backbone degradation temperature than SIBS with 22.5 % polystyrene by weight and $\overline{M_n}$ of 65,000 g/mol and SIBS with 30 % polystyrene by weight and $\overline{M_n}$ of 100,000 g/mol, thus it can be considered more thermally stable.

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APPENDIX A - TGA Degradation temperatures

Appendix A-1: TGA degradation temperatures for SIBS-22.5-65K.

Sample Name	First degradation Temperature (°C) Sulfonic Groups	Second degradation temperature (°C) Polymer Backbone	Third Degradation temperature (°C) Cation and Sulfonic Groups	Fourth Degradation temperature (°C) Cation and Sulfonic Groups
SIBS-22.5-65K	Not observed	401.7	Not observed	Not observed
	Not observed	397.9	Not observed	Not observed
	Not observed	402.8	Not observed	Not observed
S-SIBS-22.5-65K-84	Not observed	264.1	Not observed	Not observed
	Not observed	261.2	Not observed	Not observed
	Not observed	270.6	Not observed	Not observed
S-SIBS-22.5-65K-84-Ba	Not observed	409.7	Not observed	Not observed
	Not observed	410.8	Not observed	Not observed
	Not observed	413.5	Not observed	Not observed
S-SIBS-22.5-65K-84-Ca	Not observed	411.8	Not observed	Not observed
	Not observed	411.9	Not observed	Not observed
	Not observed	412.6	Not observed	Not observed
S-SIBS-22.5-65K-84-Mg	Not observed	408.8	Not observed	Not observed
	Not observed	404.0	Not observed	Not observed
	Not observed	411.3	Not observed	Not observed

Appendix A-2: TGA degradation temperatures for SIBS-15-100K.

Sample Name	First degradation Temperature (°C) Sulfonic Groups	Second degradation temperature (°C) Polymer Backbone	Third Degradation temperature (°C) Cation and Sulfonic Groups	Fourth Degradation temperature (°C) Cation and Sulfonic Groups
SIBS-15-100K	Not observed	415.9	Not observed	Not observed
	Not observed	417.4	Not observed	Not observed
	Not observed	415.0	Not observed	Not observed
S-SIBS-15-100K-82	271.6	426.5	Not observed	Not observed
	284.8	424.6	Not observed	Not observed
	278.8	422.8	Not observed	Not observed
S-SIBS-15-100K-82-Ba	Not observed	415.6	479.7	573.3
	Not observed	416.4	481.2	541.0
	Not observed	414.6	483.8	574.3
S-SIBS-15-100K-82-Ca	Not observed	415.8	499.3	557.2
	Not observed	415.6	497.6	552.5
	Not observed	416.5	498.5	557.5
S-SIBS-15-100K-82-Mg	Not observed	413.6	502.6	557.2
	Not observed	404.4	503.8	552.8
	Not observed	406.9	502.7	543.9

Appendix A-3: TGA degradation temperatures for SIBS-30-100K.

Sample Name	First degradation Temperature (°C) Sulfonic Groups	Second degradation temperature (°C) Polymer Backbone	Third Degradation temperature (°C) Cation and Sulfonic Groups	Fourth Degradation temperature (°C) Cation and Sulfonic Groups
SIBS-30-100K	Not observed	406.6	Not observed	Not observed
	Not observed	406.9	Not observed	Not observed
	Not observed	405.8	Not observed	Not observed
S-SIBS-30-100K-76	261.7	423.6	Not observed	Not observed
	269.3	422.9	Not observed	Not observed
	253.4	419.9	Not observed	Not observed
S-SIBS-30-100K-76-Ba	Not observed	407.8	479.8	561.7
	Not observed	408.9	477.7	566.7
	Not observed	413.7	478.7	563.5
S-SIBS-30-100K-76-Ca	Not observed	408.3	496.4	552.5
	Not observed	407.2	493.8	556.2
	Not observed	404.0	493.7	556.4
S-SIBS-30-100K-76-Mg	Not observed	407.2	495.2	559.3
	Not observed	406.8	498.8	556.2
	Not observed	411.6	499.6	562.2