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Thermo Stability of Highly Sulfonated Poly(styrene-isobutylene-styrene) Block Copolymers: Effects of Sulfonation and Counter-Ion Substitution

by James M. Sloan, David Suleiman, Eugene Napadensky, and Dawn M. Crawford

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14. ABSTRACT

In this study, poly(styrene-isobutylene-styrene) (SIBS) block copolymers were characterized by thermogravimetry as a function of sulfonation level (53% to 97%) and counter-ion substitution (Mg^{+2}, Ca^{+2}, Ba^{+2}). Sulfonated samples showed an additional minor loss of mass at ~290 ± 2ºC, which was not observed in the unsulfonated polymer. At this temperature, desulfonation or a cleavage reaction of the aromatic carbon-sulfur bond occurs. The counter-ion substituted membranes did not show the degradation temperature at 290 °C, but additional unique degradation temperatures above 500 °C, which suggests improved thermal stability for the ionically cross-linked polymer with cations. Some cations (Mg^{+2}, Ca^{+2}, Ba^{+2}) showed multiple high temperature degradations, which suggest that different cross-linked structures occur throughout the phase-segregated morphology.

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1. Introduction

Phase-segregated polymers exhibit unique chemical and physical properties that can be useful in numerous diverse applications. This is attributable, in part, to the distinct phases that can be optimized to meet desired properties such as mechanical strength and permeation behavior resulting in a superior multifunction material (*1*). In addition, these materials can be chemically modified to engineer the material to the desired properties.

Sulfonated block co-polymers are an example of phase-segregated polymers that are particularly attractive because of their potential as proton exchange membranes (PEMs) for hydrogen and methanol fuel cells. This application calls for the membrane to conduct protons across the ion-rich domains of the polymer, while blocking the hydrogen and methanol fuel sources. For these membranes to be considered as PEMs, they must meet three requirements: (1) have high water transport properties, (2) possess low methanol permeation, and (3) exhibit excellent thermal stability at elevated temperatures. In this report, we address the thermal stability concern since it is not unusual for fuel cells to operate at 120 °C or higher. Thermogravimetric analysis (TGA) offers a simple and effective method for characterizing the degradation properties of these polymer membranes.

One promising class of such polymers is block co-polymers, such as poly(styrene-isobutylene-styrene) (SIBS) tri-block co-polymer (*2*, *3*). The major component of the tri-block co-polymer is polyisobutylene (PIB), which comprises 70% by weight of the base polymer. The PIB gives the material low temperature flexibility as well as excellent barrier properties. The polystyrene (PS) comprises 30% by weight of the material and forms a glassy region that imparts mechanical strength to the polymer film. In the solid state, the thermodynamic immiscibility of the two components results in a micro-phase separation where domains of PS are formed in the rubbery PIB matrix (*4*). The fraction of PS controls the resultant morphology, which can be for example cylinders, lamellae, spheres, or a complex mixture.

Sulfonated di-block (AB) and tri-block (ABA) co-polymers have been widely researched in recent years. These include sulfonated polyether ether ketone (*5*, *6*), sulfonated poly (phenylene oxide) (*7*), sulfonated polyphosphazene (*8*), sulfonated polybenzomidazole (*9*), and a variety of styrene-based block co-polymers (*10–13*).

In addition to their use as fuel cell membranes, we are also interested in designing materials that can be useful as a breathable chemical protective barrier. To accomplish this, we chemically modify the PS units with sulfonic acid groups to form ionic domains creating ion-containing polymers, also called ionomers. These ionic phases are interconnected and allow for high water transport (*14*, *15*), while acting as a chemical barrier to organic toxins.

In previous work, we have used multi-scale modeling to examine the effect of the molecular structure of these tri-block co-polymers on the transport properties and have found that all the water transport is localized in the ionic regions (*16*). Simulations clearly identify a phase separation occurring between the ionic phase (SO_3^-, H_3O^+, H_2O) and the non-ionic region consisting of polyisobutylene and unsulfonated polystyrene groups resulting in a lamellar type structure of water molecules linked to the sulfonate groups (*17*).

In this work, we evaluate the effect of using inorganic counter ions to neutralize the sulfonic acid groups. Our reasoning for this was to minimize the amount of swelling that the acid polymers exhibit. We have selected to study +2 cation-exchanged S-SIBS (Mg^{+2}, Ca^{+2}, Ba^{+2}) to create highly cross-linked membranes. In this report, we examine the thermal stability of these ionomeric polymers before and after neutralization with +2 cations.

2. Experimental

2.1 Materials

The poly(styrene-isobutylene-styrene) tri-block co-polymer was provided by Kuraray Co., Ltd., Tsukuba Research Laboratories with the reported properties: 30.84 weight-percent styrene, 0.95 specific gravity, M_w = 71,920 g/mole, M_n = 48,850 g/mole, and poly dispersity index = 1.47. Other chemicals used were as follow: tetrahydrofuran (THF) (Burdick & Jackson, high pressure liquid chromatography (HPLC) grade, Assay 99.9%), hexanol (J.T. Baker, Assay 99%), toluene (VWR,* HPLC grade), and methylene chloride (Electromagnetic Science, HPLC grade).

2.2 Processing Conditions

The sulfonation of poly(styrene-isobutylene-styrene) was performed previously with acetyl sulfate as the sulfonating agent and is described in more detail elsewhere (*14*). Figure 1 shows the chemical structure for membranes prepared for this study. The mole percent of styrene sulfonated in each polymer was controlled by the amount of acetyl sulfate used in each reaction, and its exact amount was determined by elemental analysis (EA). EA was conducted by Atlantic Microlab, Inc., in Norcross, GA, and the results are listed in table 1. Hereafter, the sulfonated block co-polymers are referred to as S-SIBS-#, where S-SIBS represents sulfonated poly(styrene-isobutylene-styrene) and the succeeding number, #, refers to the mole percent of styrene sulfonated.

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*VWR is not an acronym.

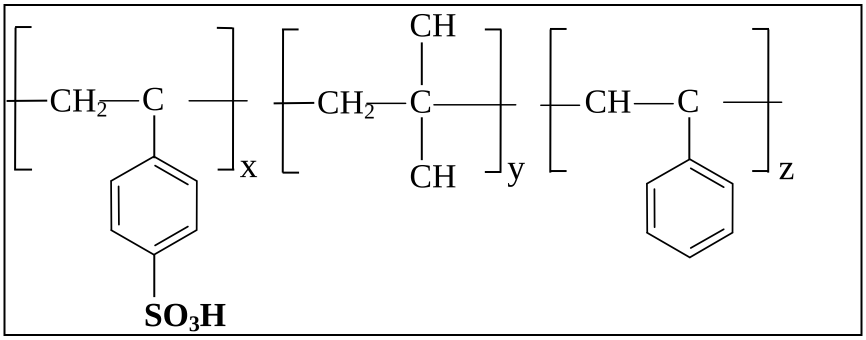

Figure 1. Chemical structure of SIBS tri-block co-polymer.

Table 1. Relationship between sulfonation level and ion-exchange capacity.

Sample Name[a]	**Sulfonation Level (mol%)**	**IEC**[b] **(meq/g)**
S-SIBS-0	NA	NA
S-SIBS-53	53.1	1.28
S-SIBS-64	63.8	1.62
S-SIBS-97	97.3	2.28

[a] S-SIBS = sulfonated poly(styrene-isobutylene-styrene).
[b] IEC = ion exchange capacity.
Note: NA = not applicable.

After sulfonation, the S-SIBS samples were solvent casted in a toluene/hexanol (85/15 weight-percent) solution in an open Teflon* Petri dish for several days at ambient conditions. For S-SIBS-0, pure toluene was used to cast the membranes. The films were then annealed under vacuum at 50 °C for an additional 2 weeks to remove any residual solvent.

The cations selected for cross-linking the membranes were Mg^{+2}, Ca^{+2}, and Ba^{+2}. They were selected to allow ionic interactions to occur between two individual sulfonic acid groups. The sulfonated polymers were irreversibly cross-linked by immersion for several hours in a 1.0-M solution of magnesium perchlorate $Mg(ClO_4)_2$, calcium chloride $CaCl_2$, or barium chloride $BaCl_2$, depending on the desired cation. The cross-linked solutions were washed with de-ionized water and left to dry for at least 24 hr in a vacuum oven at 50 °C.

2.3 TGA

The thermal history and water loss (sorption) of the S-SIBS block co-polymers were determined with a high resolution TGA 2950 thermogravimetric analyzer (TA Instruments). In each experiment, a polymer sample weighing ~5–10 mg was used. We determined degradation temperatures by heating the polymer samples in a nitrogen environment to 650 °C at 10 °C/min and observing regions of significant weight loss. We determined the degradation temperatures measured in this study by measuring each sample at least twice; the values reported correspond to the averages and standard deviations of those measurements.

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*Teflon is a registered trademark of E.I. DuPont de Nemours & Co.

2.4 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra of all polymer samples were collected with an FTIR spectrometer (Nicolet Magna 560 Series) equipped with a Thunderdome (Spectra-Tech) accessory with a single-reflection attenuated total reflectance crystal (ZnSe, refractive index = 2.4). This accessory contains a pressure mechanism for excellent sample-to-crystal contact. All infrared spectra were collected with 128 scans and 4 cm^{-1} resolution.

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3. Results and Discussion

3.1 Degradation Temperatures

Figure 2 shows the TGA spectra for three highly sulfonated functionalized S-SIBS membranes, 53, 64, and 97 mole percent. Generally, all three curves appear similar in shape. Three weight loss stages can be clearly identified for the acid form. These occur at 50–200, 250–400, and 390–475 °C. The weight loss in the 50–200 °C range can be confidently attributed to the release of atmospheric moisture that occurs as a result of the hydroscopic nature of the S-SIBS. The unusually high ionic charge of the sulfonic acid groups causes a strong ionic interaction to occur with the absorbed water molecules, resulting in the release of the water molecules over an extended temperature range. This effect can be more clearly seen if we use the derivative TGA (DTGA) curves presented in figure 3. From the TGA curve, one can obtain an estimate of the amount of atmospheric moisture that the acid form of the S-SIBS absorbs. S-SIBS-53 picks up 9% by weight atmospheric moisture, while S-SIBS-64 picks up 10% and the S-SIBS-97 picks up 15% water. This agrees with the highly hydroscopic nature of these systems.

The weight loss occurring in the 250–400 °C range is attributable to the breakdown of the sulfonate group attached to the styrene rings. This assignment agrees with data published by Smitha et al. (*18*) for sulfonated polystyrene. From the TGA curves in figure 2, we can also estimate the amount of sulfonate groups present in the functionalized SIBS. To do this, it is first necessary to subtract the moisture content from the TGA spectra and then calculate for sulfonate groups. The general formula is $S_nIB_mS_n$, where S stands for a monomer of styrene and IB is a monomer of isobutylene. Since the monomer weights are about 104 and 56 g/mole for styrene and isobutylene, respectively, one can calculate that the corresponding molecular formula should be approximately $S_{73}IB_{602}S_{73}$. For the sulfonated forms, SO_3H (MW = 81) is added in proportional amounts to determine an estimate of weights. Table 2 shows a comparison of calculated and experimentally determined sulfonate levels. Generally, good agreement is observed between the calculated and experimentally determined sulfonation levels; however, a slight deviation is seen at the higher sulfonate levels.

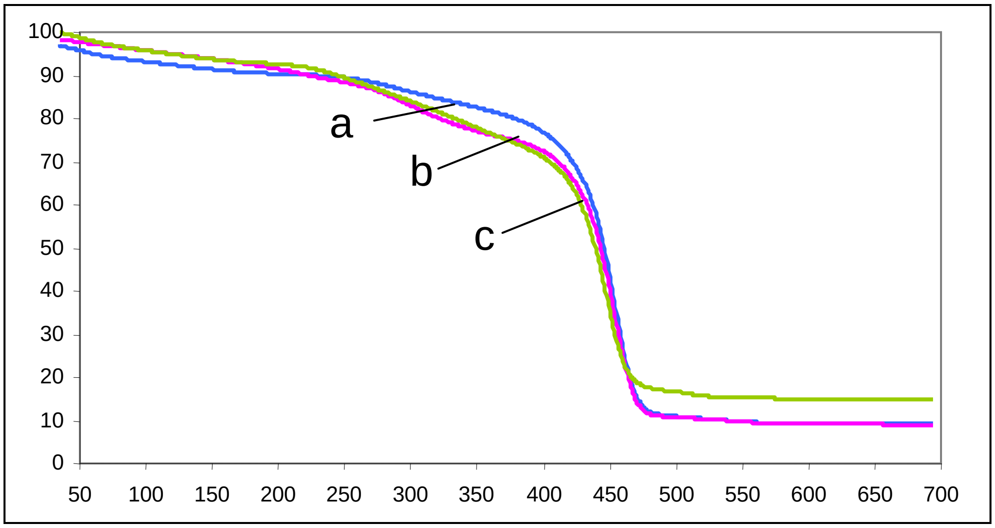

Figure 2. TGA data for three sulfonated SIBS block co-polymers: a – 54%, b – 64%, and c – 97%.

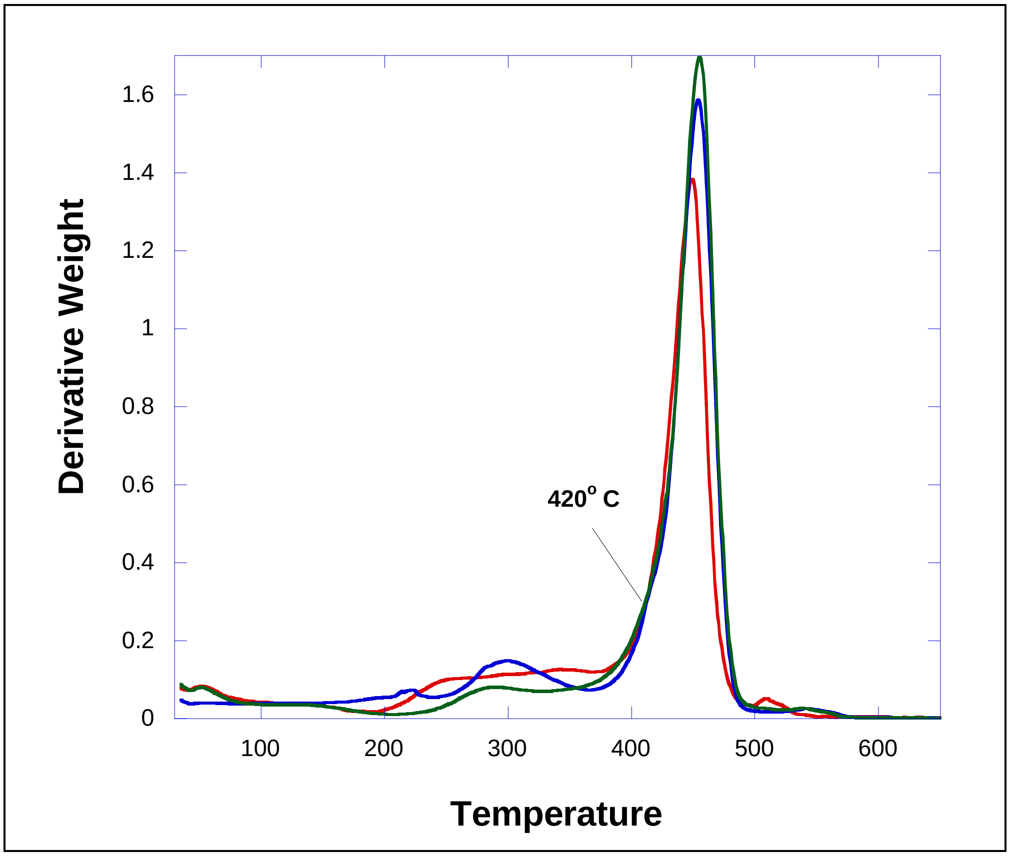

Figure 3. DTGA spectra for acid forms (53%, 64%, and 97%) of SIBS.

Table 2. Comparision of sulfonation levels for S-SIBS polymers from TGA and elemental analysis.

Sample Name	Sulfonation Level (Weight-Percent) Calculated	Sulfonation Level (Weight-Percent) Experiment
S-SIBS-0	NA	NA
S-SIBS-53	11.1	12.0
S-SIBS-64	12.9	15.1
S-SIBS-97	18.4	21.3

Note: NA = not applicable.

The last weight loss region occurring at 390–475 °C is attributable to the decomposition of the polystyrene and polyisobutylene segments. A close examination of figure 3 reveals that this broad peak centered at ~455 °C has two components, one small peak at ~420 °C and one centered at 455 °C. The small peak at ~420 °C is attributable to the polystyrene block decomposition. Other authors have reported similar maxima for sulfonated polystyrene (*18*). The weight loss at 455 °C is attributable to the polyisobutylene block decomposition. In many of the TGA spectra, these two bands overlap and are nearly indistinguishable from each other.

We now turn our attention to the cation neutralized polymer membranes. The membranes were neutralized in an attempt to dimensionally stabilize the polymer by introducing cross-links into the structure to reduce the water swelling (figure 4). For example, the S-SIBS-64 membrane could take more than 300% by weight of water (*14*). In figure 5, four different films are shown: the acid form of S-SIBS-53 and three ionically exchanged films with Mg^{+2}, Ca^{+2}, and Ba^{+2}. The DTGA of the cation exchanged films in figure 5 shows three weight loss stages as well. These occur at 50–200, 425–475, and 475–600 °C. The first two weight loss stages are identical to the acid form ionomer, loss of atmospheric moisture and decomposition of polyisobutylene backbone. The weight loss at 300 °C is noticeably absent in these curves; however, a new weight loss region is now observed around 475–600 °C. Other investigators (*18*) have postulated that this weight loss may be attributable to chain splitting or residual solvent. In our experiments, we have observed that this weight loss has been observed for all cation exchanged samples, while no high temperature loss has been observed in any of the acid forms. Additionally, the lack of sulfonate decomposition at 250–400 °C seems to suggest that this loss is attributable to the decomposition of the styrenic groups that are ionically associated to the individual cations. These clusters have the ability to thermally stabilize the entire polymer membrane by shifting the degradation temperature to 450 °C.

Figure 6 presents the DTGA data comparing the three sulfonation levels and corresponding cation neutralized forms. The higher temperature weight loss region can be clearly seen in figure 6. We note that multiple peaks are evident above 500 °C for the Mg^{+2} and Ca^{+2} forms, which suggests that different cross-linked structures occur throughout the phase-segregated morphology. These structures appear to vary in thermal stability. The case of the Ba^{+2} neutralized forms is slightly different in that only one detectable peak is evident and this peak is shifted to a lower temperature at around 500 °C . Again, this position is driven by the strength of the localized environment.

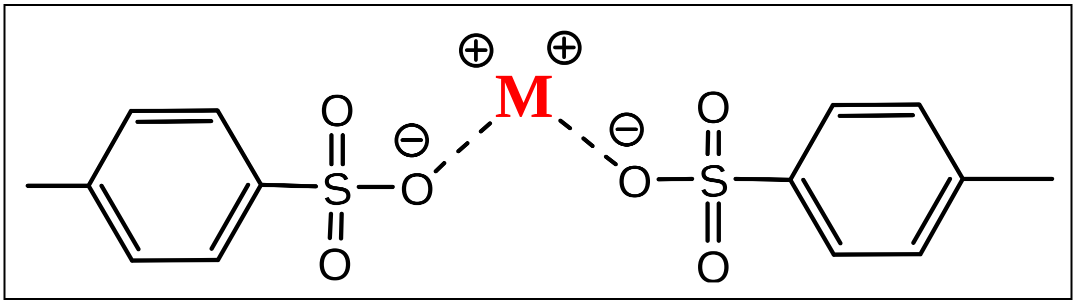

Figure 4. Structure of SIBS-metal ion complex.

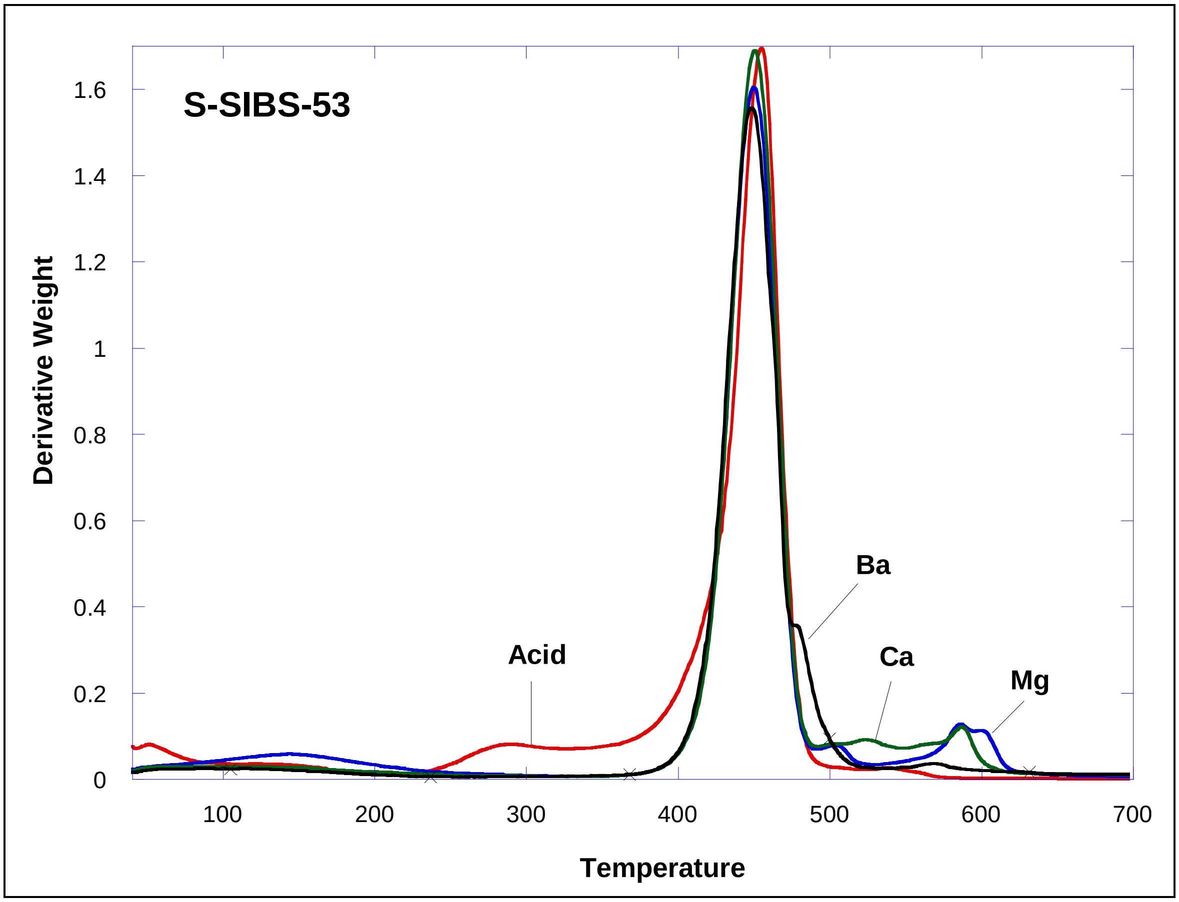

Figure 5. DTGA of acid form and cation exchanged S-SIBS-53.

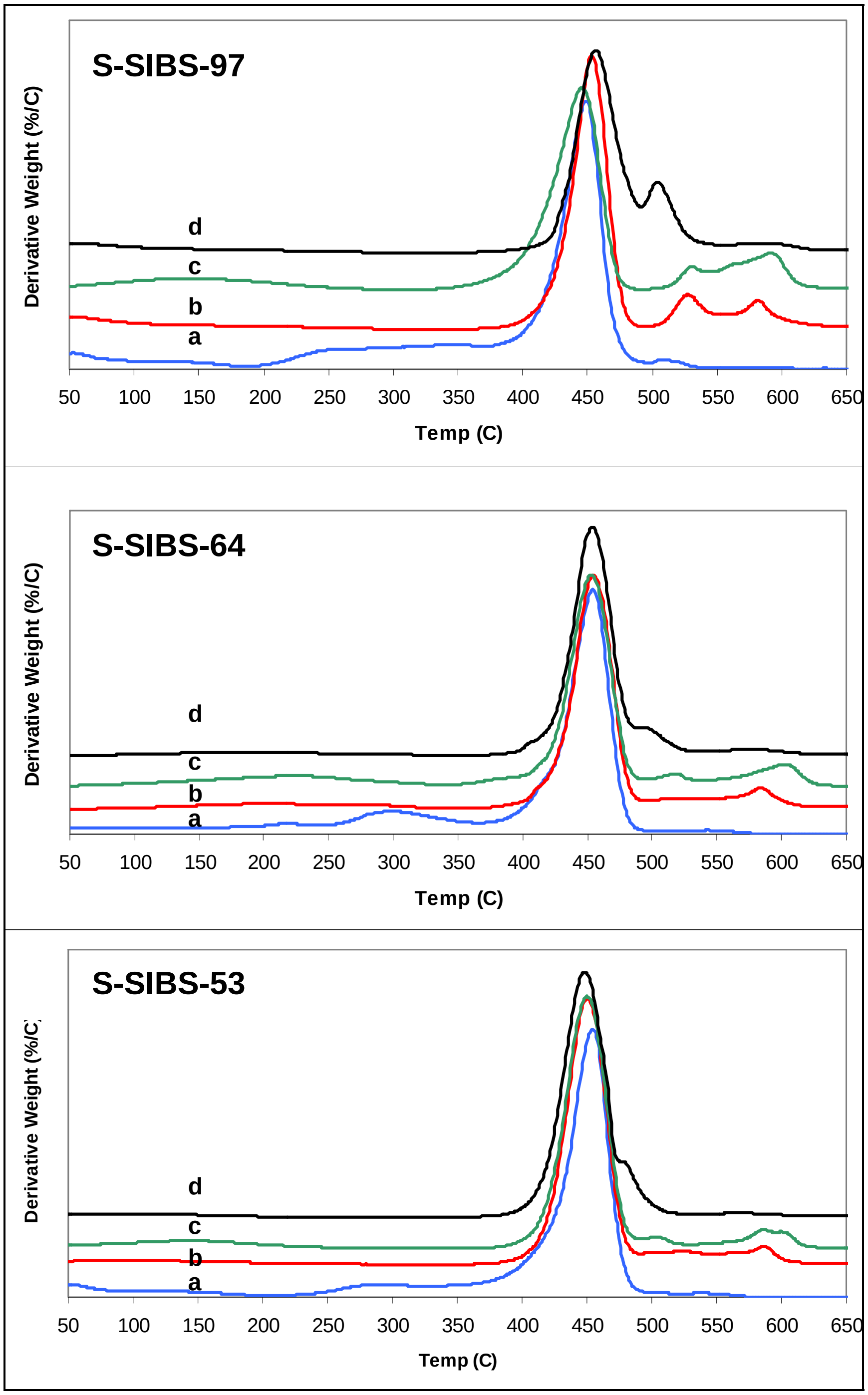

Figure 6. DTGA data for S-SIBS-53, S-SIBS-64, and S-SIBS-97. (Curves designated with a are in acid form, b is neutralized with Mg^{+2}, c is neutralized with Ca^{+2}, and d represents neutralization with Ba^{+2}.)

Figure 6 also shows an increase in the size of the weight loss in the high temperature region with increasing sulfonation levels, thus yielding further evidence that these weight loss maxima are directly related to the ionic complexes formed as a result of the cation-sulfonate group interactions.

A summary of the degradation temperatures for all the membranes studied is presented in table 3, excluding the hydroscopic region. As in our previous communication (*19*), the sulfonated un-neutralized samples reveal two separate degradation temperatures, one at ~290 ± 5 °C, attributable to sulfonic acid loss and another at ~453 ± 3 °C, attributable to polymer backbone. The location of the 290 and 453 °C are identical, regardless of sulfonation level. All neutralized sulfonated polymers show two degradation temperatures, one occurring at 453 ± 3 °C, attributable to polymer backbone and another in the 500–600 °C range, attributable to the counterion-sulfonic acid complex. The locations of the peak maxima at 453 °C and the transitions above 500 °C are identical, regardless of sulfonations level or counterion type.

Table 3. TGA degradation temperatures for cation-exchanged SIBS of different sulfonation levels.

Sample Name	**First Degradation Temperature (°C)**	**Second Degradation Temperature (°C)**	**Third Degradation Temperature (°C)**	**Fourth Degradation Temperature (°C)**	**Fifth Degradation Temperature (°C)**
S-SIBS-53-H	290 ± 5	454 ± 2	—	—	—
S-SIBS-53-Mg	—	451 ± 2	507 ± 2	604 ± 2	—
S-SIBS-53-Ca	—	453 ± 1	592 ± 2	—	—
S-SIBS-53-Ba	—	450 ± 1	481 ± 2	—	—
S-SIBS-64-H	290 ± 5	455 ± 2	—	—	—
S-SIBS-64-Mg	—	453 ± 2	521 ± 3	606 ± 3	—
S-SIBS-64-Ca	—	456 ± 2	517 ± 2	586 ± 2	—
S-SIBS-64-Ba	—	455 ± 1	502 ± 2	582 ± 3	—
S-SIBS-97-H	290 ± 5	449 ± 2	—	—	—
S-SIBS-97-Mg	—	454 ± 2	536 ± 3	570 ± 4	594 ± 2
S-SIBS-97-Ca	—	454 ± 1	532 ± 2	585 ± 3	—
S-SIBS-97-Ba	—	457 ± 1	505 ± 2	—	—

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

In order to confirm the identification of the higher temperature thermal weight loss transitions, FTIR was used to identify the chemical structures remaining in the polymer membrane. Figure 7 shows the S-SIBS-53 membrane before and after annealing at 350 °C for 15 min. The bands associated with the SO_3 group (1007, 1034, and 1125 cm^{-1}) are identified with asterisks and can clearly be observed decreasing when the membrane is annealed at 350 °C.

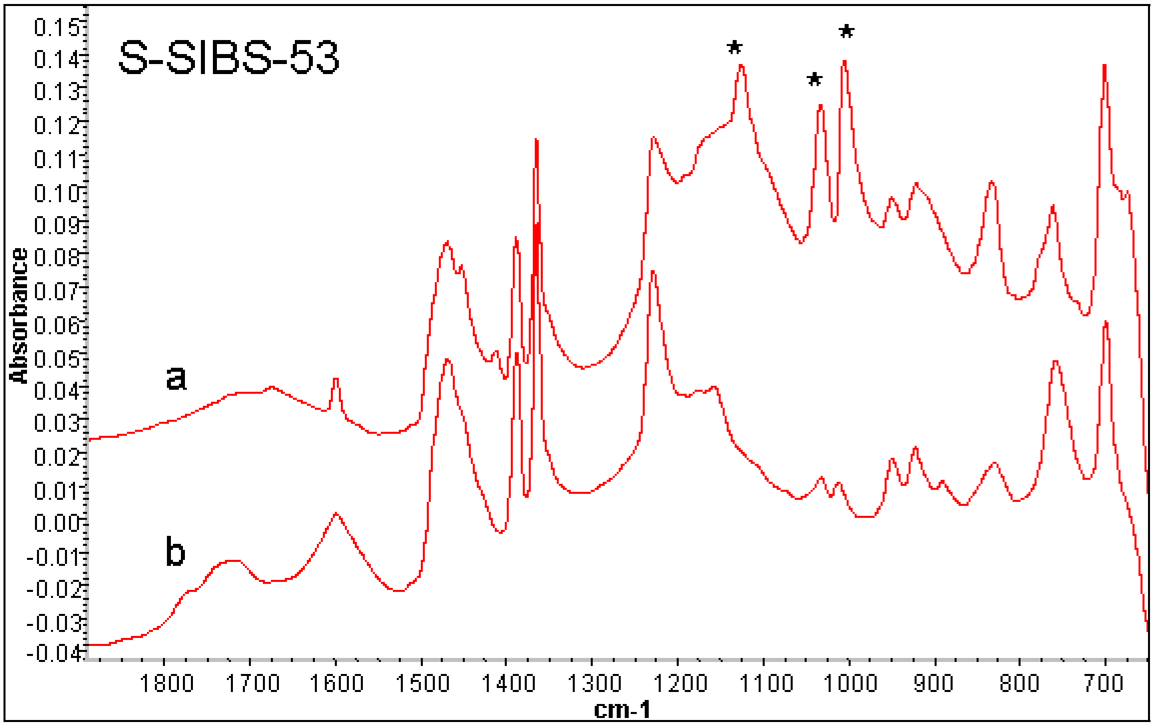

Figure 7. FTIR spectra for S-SIBS-53 membrane. (The top spectrum (a) is for S-SIBS-53-in acid form. The bottom spectrum (b) is for S-SIBS-53 annealed at 350 °C for 15 min. The IR peaks marked with asterisks are attributable to the SO_3 stretching.)

In contrast to this effect, figure 8 shows the corresponding spectra for the S-SIBS-53-Ca membrane. In this case, the three bands associated with the SO_3 group do not disappear; in fact, they remain unchanged. This indicates that the new ionic cross-link structures are thermally more stable than their acidic counterpart.

4. Conclusions

We have studied the degradation of highly sulfonated S-SIBS block co-polymers and three cation neutralized forms, Mg^{+2}, Ca^{+2}, and Ba^{+2}. The acid forms show low temperature degradation because of the release of the sulfonate groups. This amount of the weight loss increases with increasing sulfonation levels, but the position remains unchanged. All counter-ion neutralized polymers show a shift of this degradation of almost 300 °C. This is because of a unique and robust complex formed between the sulfonate groups and metal cations. We have used FTIR to verify that the sulfonate linkages degrade at ~300 °C. However, in the counter-ion neutralized forms, this degradation is shifted to ~550 °C, while the polymer backbone still degrades at 450 °C.

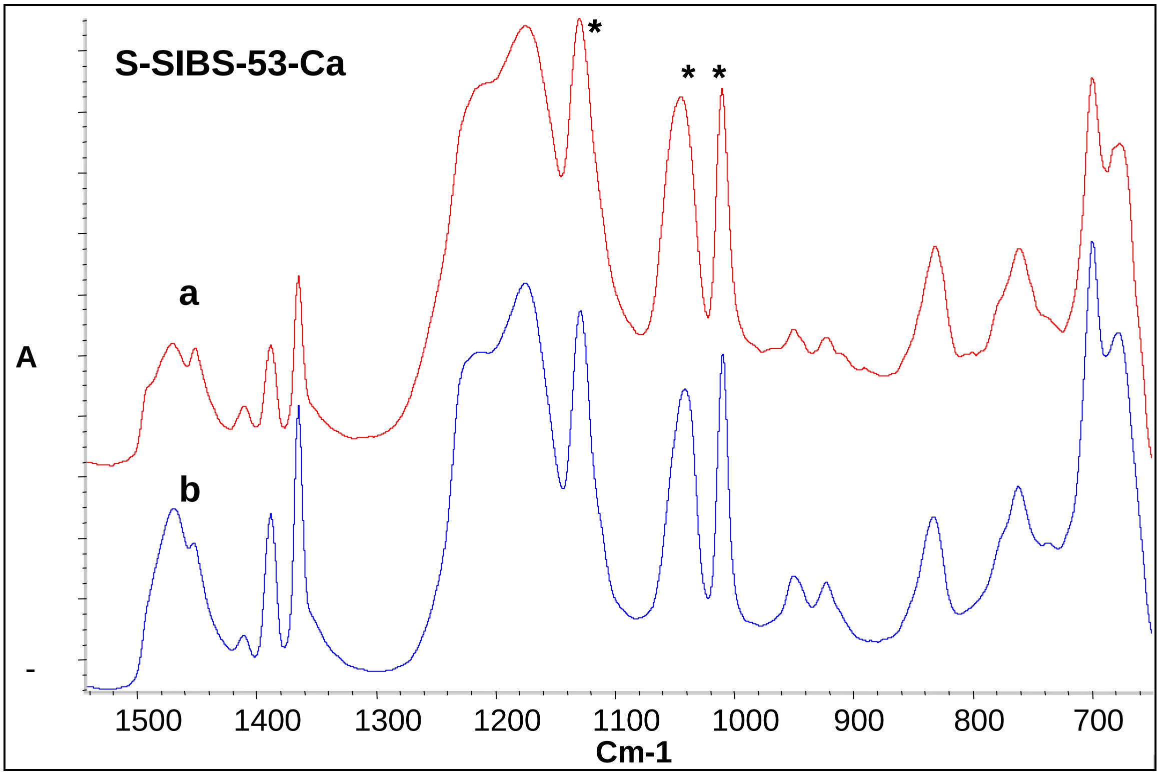

Figure 8. FTIR spectra for S-SIBS-53-Ca. (The bottom spectrum (b) is for S-SIBS-53-Ca before annealing at 350 °C for 15 min. The top spectrum (a) is for S-SIBS-53-Ca after annealing at 350 °C for 15 min. The IR peaks marked with asterisks are attributable to the SO_3 stretching.)

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