

Thermogravimetric characterization of highly sulfonated poly(styrene–isobutylene–styrene) block copolymers: Effects of sulfonation and counter-ion substitution

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Received 8 March 2007; received in revised form 1 May 2007; accepted 7 May 2007

Available online 18 May 2007

Abstract

In this study, poly(styrene–isobutylene–styrene) (SIBS) block copolymers were characterized by thermogravimetry as a function of sulfonation level (53–97%) and counter-ion substitution (Mg^{2+} , Ca^{2+} , Ba^{2+}). Sulfonated samples showed an additional minor loss of mass at approximately 290 ± 2 °C, 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, suggesting 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 are formed throughout the phase segregated morphology.

Published by Elsevier B.V.

Keywords: Poly(styrene–isobutylene–styrene) block copolymers; Ion-exchange membranes; Cross-linked membranes; Thermogravimetric properties

1. Introduction

Phase segregated polymers exhibit unique chemical and physical properties which can be useful in numerous diverse applications. This is due, 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 copolymers are an example of phase-segregated polymers that are particularly attractive because of their potential as proton exchange membranes (PEM) for both 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 paper, we address the thermal stability concern as it is not unusual for fuel cells to operate at 120 °C or higher. TGA offers a simple and effective method for characterizing the degradation properties of these polymer membranes.

One promising class of materials are block copolymers, such as poly(styrene–isobutylene–styrene) (SIBS) triblock copolymer [2,3]. The major component of the triblock copolymer 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) makes up 30% by weight of the material and forms a glassy region which imparts mechanical strength to the polymer film. In the solid state, the thermodynamic immiscibility of the two components results in a microphase 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 diblock (AB) and triblock (ABA) copolymers have been widely researched in recent years. These include sulfonated polyether ether ketone [5,6], sulfonated poly(phenylene

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oxide) [7], sulfonated polyphosphazene [8], sulfonated polybenzimidazole [9], and a variety of styrene based block copolymers [10–13].

In addition to their use as fuel cell membranes, we are also interested in designing materials that can be useful as 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 multiscale modeling to examine the effect of the molecular structure of these triblock copolymers on the transport properties and have found out that all of 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 utilizing 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 paper, 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) triblock copolymer was provided by Kuraray Co., Ltd., Tsukuba research laboratories with the reported properties: 30.84 wt% styrene, 0.95 specific gravity, $M_w = 71,920$ g/mol, $M_n = 48,850$ g/mol, and $\text{PDI} = 1.47$. Other chemicals used were as follows: tetrahydrofuran (THF) (Burdick & Jackson, HPLC grade, Assay 99.9%), hexanol (J.T. Baker, Assay 99%), toluene (VWR, HPLC Grade), and methylene chloride (EM Science, HPLC Grade).

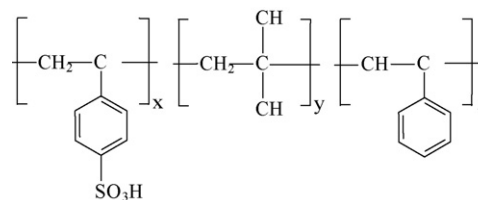


Fig. 1. Chemical structure of SIBS triblock copolymer.

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]. Fig. 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, Georgia and the results are listed in Table 1. Hereafter, the sulfonated block copolymers will be referred to as S-SIBS-#, where S-SIBS represents sulfonated poly(styrene–isobutylene–styrene) and the succeeding number, #, refers to the mol% of styrene sulfonated.

After sulfonation, the S-SIBS samples were solvent casted in a toluene/hexanol (85/15 wt%) 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 immersing them for several hours in a 1.0 M solution of magnesium perchlorate $\text{Mg}(\text{ClO}_4)_2$, 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 h in a vacuum oven at 50°C .

2.3. Thermogravimetric analysis (TGA)

The thermal history and water loss (sorption) of the S-SIBS block copolymers were determined using a Hi-Res TGA 2950

Table 1
S-SIBS block copolymers as a function of sulfonation level

Sample name ^a	Sulfonation level ^b (mol%) (%) of available styrene units	IEC ^c (mequiv./g)	Sulfonation level (mol%), calculated	Sulfonation level (mol%), experimental
S-SIBS-0	NA	NA	NA	NA
S-SIBS-53	53.1	1.28	11.1	12.0
S-SIBS-64	63.8	1.62	12.9	15.1
S-SIBS-97	97.3	2.28	18.4	21.3

NA = not applicable.

^a S-SIBS: sulfonated poly(styrene–isobutylene–styrene).

^b Obtained from elemental analysis.

^c IEC: ion-exchange capacity.

Thermogravimetric Analyzer (TA Instruments). In each experiment, a polymer sample weighing approximately 5–10 mg was used. 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. The degradation temperatures measured in this study were determined by measuring each sample at least twice; the values reported correspond to the averages and standard deviations of those measurements.

2.4. Fourier transform infrared spectroscopy (FT-IR)

Infrared spectra of all polymer samples were collected using a FT-IR spectrometer (Nicolet Magna 560 Series) equipped with a Thunderdome™ (Spectra-Tech) accessory with a single-reflection ATR crystal (ZnSe, refractive index = 2.4). This accessory contains a pressure mechanism for excellent sample-to-crystal contact. All infrared spectra were collected using 128 scans and 4 cm⁻¹ resolution.

3. Results and discussion

3.1. Degradation temperatures

Fig. 2 shows the thermogravimetric analysis spectra for three highly sulfonated functionalized S-SIBS membranes, 53 mol%, 64 mol% and 97 mol%. 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 °C, 250–400 °C 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 to occur over an extended temperature range. This effect can be more clearly seen by using the derivative TGA (DTGA) curves presented in Fig. 3. From the TGA curve, one can obtain an estimate on the amount of atmospheric moisture the acid form of the S-SIBS picks up. 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 is all in-line with the highly hydroscopic nature of these systems.

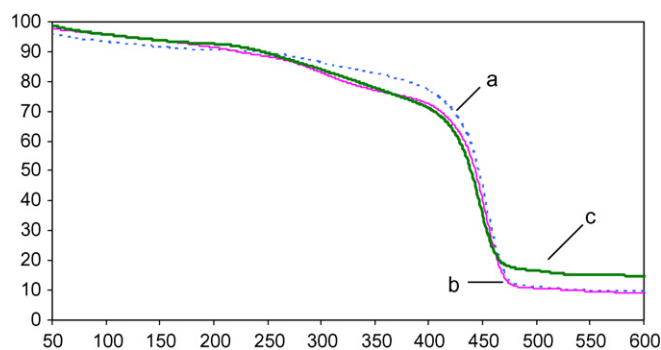


Fig. 2. TGA data for three sulfonated SIBS block copolymers: (a) 53%, (b) 64% and (c) 97%.

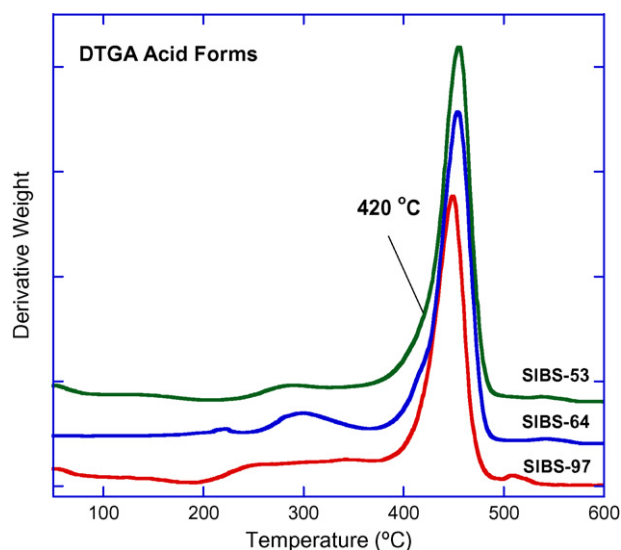


Fig. 3. DTGA spectra for acid forms (53%, 64% and 97%) of SIBS.

The weight loss occurring in the 250–400 °C range is due 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 Fig. 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 g/mol and 56 g/mol 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 ($M_w = 81$) is added in proportional amounts to determine an estimate of weights. Table 1 shows a comparison of calculated and experimentally determined sulfonate levels. Generally, good agreement is observed between the calculated and experimentally determined; however, a slight deviation is seen at the higher sulfonate levels.

The last weight loss region occurs at 390–475 °C is due to the decomposition of the polystyrene and polyisobutylene segments. A close examination of Fig. 3 reveals that this broad peak centered at approximately 455 °C has two components, one small peak located at approximately 420 °C and one centered at 455 °C. The small peak at approximately 420 °C is due to the polystyrene block decomposition. Other authors have reported similar maxima for sulfonated polystyrene [18]. The weight loss at 455 °C is due 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 crosslinks into the structure to reduce the water swelling (Fig. 4). For example, the S-SIBS-64 membrane could take up over 300% by weight of water [14]. In Fig. 5, four different films are shown; the acid form of S-SIBS-53 and three ionically exchanged films



Fig. 4. Structure of SIBS-metal ion complex.

with Mg^{2+} , Ca^{2+} , and Ba^{2+} . The DTGA of the cation exchanged films in Fig. 5 show three weight loss stages as well. These occur at 50–200 °C, 425–475 °C 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 located at 300 °C is noticeable 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 due to chain splitting or residual solvent. In our experiments, we have observed that this weight loss occurs in all cation exchanged samples, while no high temperature loss have 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 due to the decomposition of the styrenic groups that are ionically associated to the individual cations. These clusters have the ability to ther-

mally stabilize the entire polymer membrane by shifting the degradation temperature to 450 °C.

Fig. 6 presents the DTGA data comparing the three sulfonation levels and corresponding cation neutralized forms.

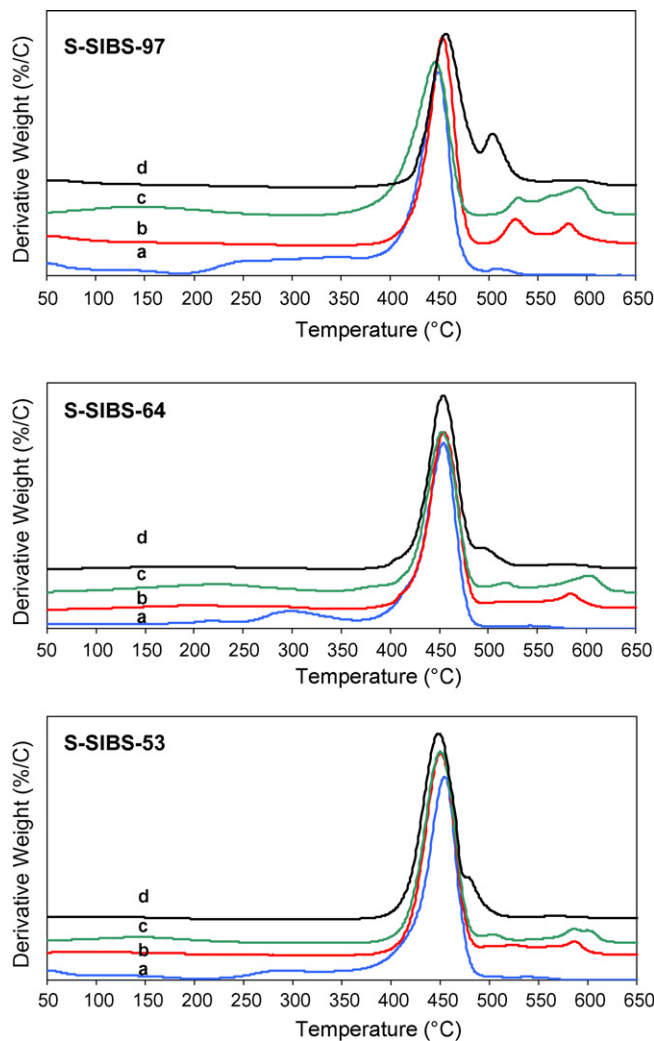


Fig. 6. DTGA data for S-SIBS-53, S-SIBS-64 and S-SIBS-97. Curves designated with a is in acid form, b is neutralized with Mg^{2+} , c is neutralized with Ca^{2+} and d represents neutralization with Ba^{2+} .

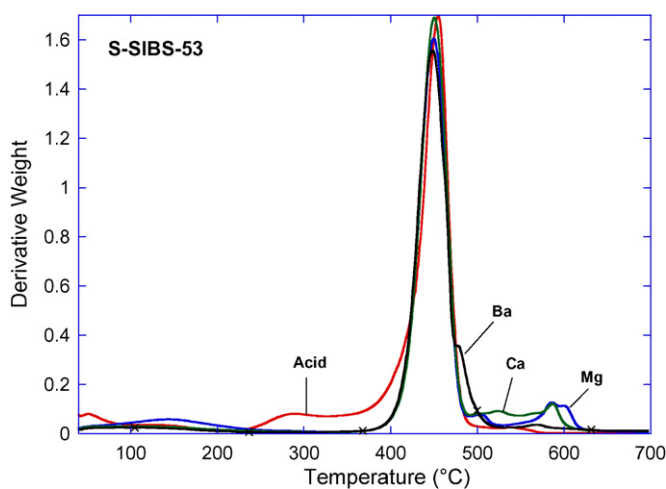


Fig. 5. DTGA of acid form and cation exchanged S-SIBS-53.

Table 2
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	–	–

The higher temperature weight loss region can be clearly seen in Fig. 6. We note that multiple peaks are evident above 500 °C for the Mg^{2+} and Ca^{2+} forms, suggesting 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.

Fig. 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 are presented in Table 2, excluding the hydroscopic region. As in our previous communication [19], the sulfonated un-neutralized samples reveal two separate degradation temperatures, one at approximately 290 ± 5 °C, attributed to sulfonic acid loss and another at approximately 453 ± 3 °C, due to polymer backbone. The location of the 290 °C and 453 °C are identical regardless of sulfonation level. All neutralized sulfonated polymers show two degradation temperatures, one occurring at 453 ± 3 °C, due to polymer backbone and another in the 500–600 °C range, due to the counter-ion–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 counter-ion type.

3.2. Fourier transform infrared spectroscopy (FT-IR)

In order to confirm the identification of the higher temperature thermal weight loss transitions, FT-IR was used to identify the chemical structures remaining in the polymer membrane. Fig. 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 cm^{-1} , 1034 cm^{-1} and 1125 cm^{-1}) are identified

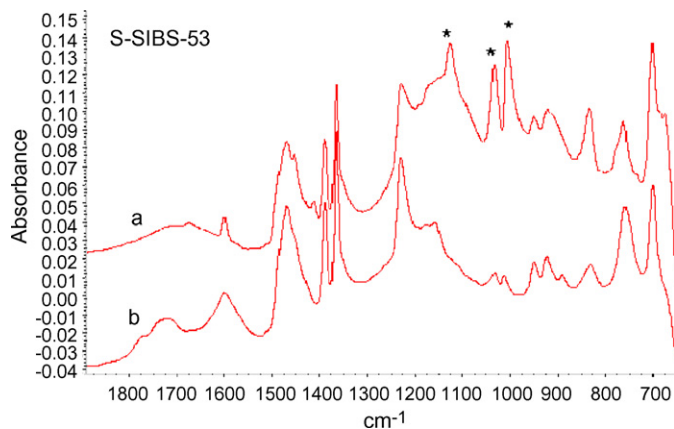


Fig. 7. FT-IR spectra for S-SIBS-53 membrane. The top spectrum a is for S-SIBS-53 in acid form. The bottom spectrum b is for S-SIBS-53 annealed at 350 °C for 15 min. The IR peaks marked with asterisks are due to the SO_3 stretching.

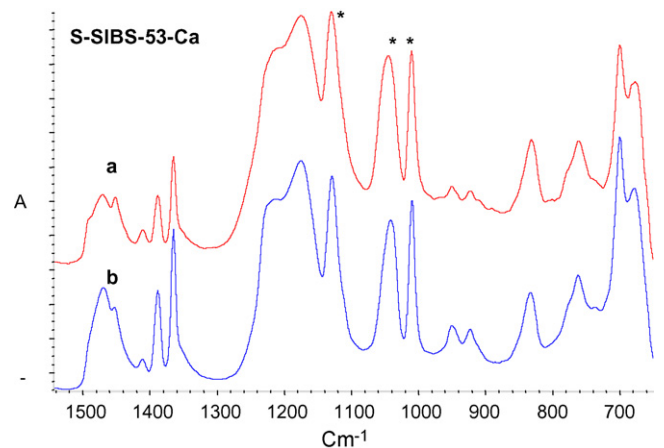


Fig. 8. FT-IR spectra for S-SIBS-53-Ca. The bottom spectrum b is for S-SIBS-53-Ca before annealing at 350 °C for 15 min. The top spectrum a is for S-SIBS-53-Ca after annealing at 350 °C for 15 min. The IR peaks marked with asterisks are due to the SO_3 stretching.

with asterisks and can clearly be observed decreasing when the membrane is annealed at 350 °C.

In contrast to this effect, Fig. 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 poly(styrene–isobutylene–styrene) (S-SIBS) block copolymers and three cation neutralized forms, Mg^{2+} , Ca^{2+} and Ba^{2+} . The acid forms show low temperature degradation due to 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 due to a unique and robust complex formed between the sulfonate groups and metal cations. We have used FT-IR to verify that the sulfonate linkages degrade at approximately 300 °C. However, in the counter-ion neutralized forms this degradation is shifted to approximately 550 °C, while the polymer backbone still degrades at 450 °C.

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