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Thermochimica Acta 430 (2005) 149–154
thermochimica acta
www.elsevier.com/locate/tca

Thermogravimetric characterization of sulfonated poly(styrene-isobutylene-styrene) block copolymers: effects of processing conditions

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Received 3 September 2004; received in revised form 13 January 2005; accepted 18 January 2005
Available online 15 February 2005

Abstract

In this study, sulfonated poly(styrene-isobutylene-styrene) (S-SIBS) block copolymers were characterized by thermogravimetry as a function of four different processing conditions: sulfonation level, annealing temperature, film formation, and casting solvent. Sulfonated samples showed an increase in degradation temperature from 432 to 450 °C compared to the unsulfonated polymer, regardless of sulfonation level or other processing condition. Sulfonated samples also showed an additional minor loss of mass at approximately 290 °C, which was not observed in the unsulfonated polymer. At this temperature, desulfonation or a cleavage reaction of the aromatic carbon–sulfur bond occurs. In addition, annealing the sulfonated block copolymer at a higher temperature (180 °C) for an extended period of time also results in a partial desulfonation. These results were confirmed by a reduction in water sorption and in intensity of the infrared bands associated with sulfonic acid. There was no change in thermal stability in S-SIBS block copolymers as a function of film formation (solvent cast versus heat pressed) and casting solvent (six different solvents).
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Keywords: Block copolymer; Ionomer; Sulfonic acid; Ion-exchange membrane; Fuel cell

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1. Introduction

Ion-exchange polymers are used in a number of applications, including sensors, electrolyzers, electrodialysis, fuel cells, water purification, and selective membranes. More specifically, ion-exchange polymers containing sulfonic acid (e.g., Nafion®) have frequently been used as proton-exchange membranes (PEMs) in fuel cells. A variety of sulfonic acid (or sulfonated) polymers have been synthesized and explored for their application to fuel cells, such as sulfonated polyphosphazene [1], sulfonated polyphenylene oxide [2], sulfonated polyarylene ether sulfone [3], sulfonated polyether ether ketone [4], and sulfonated poly(styrene-isobutylene-styrene) [5]. Recently, sulfonated block copolymers have generated interest, particularly as it applies their unique relationships between morphology and transport properties [6–14]. These structure–transport property relationships have been explored in relation to the optimization of fuel cell performance [14].

In addition to transport properties, the performance of sulfonated polymers as it applies to operating temperatures of fuel cells and other applications largely depends on its thermal stability. Sulfonation of a polymer can cause considerable changes in the overall thermal stability of a polymer [15,16]. In this study, the thermal behavior of a sulfonated block

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0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.01.030

copolymer, sulfonated poly(styrene-isobutylene-styrene) (S-SIBS), was investigated with thermogravimetry in combination with infrared spectroscopy. In addition to the effect of sulfonation on the block copolymer, the thermal behavior was explored as a function of several membrane processing conditions: annealing temperature, film formation (solvent cast versus heat pressed), and processing solvent.

2. Experimental

2.1. Materials

The poly(styrene-isobutylene-styrene) block 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 PDI = 1.47. Other chemicals used were as follows: HPLC grade water (J.T. Baker), tetrahydrofuran (THF) (Burdick & Jackson, HPLC grade, Assay 99.9%), chloroform (Burdick & Jackson, HPLC Grade), benzene (EM Science, HPLC Grade), cyclohexanol (EM Science, HPLC Grade), hexanol (J.T. Baker, Assay 99%), toluene (VWR, HPLC Grade), and methylene chloride (EM 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 [5]. The mol 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 and evaluation, the S-SIBS samples were processed by a variety of methods. The unsulfonated sample (S-SIBS-0) was prepared by solvent casting a 5% (w/v) solution in toluene in an open Teflon Petri dish for several days at ambient conditions. The film was then annealed under vacuum at 50 °C for an additional two weeks to remove any residual solvent. Samples as a function of annealing temperature were prepared by solvent casting a 10% (w/v) solution of S-SIBS-29 in methylene chloride at ambient conditions for 3 weeks. Then samples at two different annealing temperatures were prepared. One sample was annealed under vacuum at 80 °C for 24 h, while the other sample was annealed under vacuum at 80 °C for 24 h and then at 180 °C for 48 h. S-SIBS-42 was prepared by two different film formation techniques: solvent casting and heat pressing. For solvent casting, a 10% (w/v) S-SIBS-42 solution in THF was solvent cast similar to S-SIBS-0. For heat pressing, S-SIBS-42 was cryogenically ground to a powder and then heat pressed at 125 psi and 120 °C. A 2.5% (w/v) solution of S-SIBS-82 in a mixture of toluene/hexanol (85/15 wt.%) was solvent cast for 25 days at ambient conditions and then annealed under vacuum for 13 days at 50 °C.

In addition to the preparation of S-SIBS at different sulfonation levels, annealing temperatures, and film formation techniques, S-SIBS-29 was solvent cast from six different solvents. The solvents selected covered a range of solubility parameters (i.e., δ = 18.6–23.3 MPa$^{1/2}$), polarities, and chemical properties (e.g., polar protic, polar aprotic, non-polar, etc.). Each solvent used a specific polymer concentration and annealing history. For THF, a 10% (w/v) S-SIBS-29 sample was dissolved and kept in a fume hood at room temperature for 21 days. It was then annealed under vacuum at room temperature for 24 h followed by a second annealing process under vacuum at 80 °C for 48 h. The same procedure was used with benzene, chloroform, and methylene chloride, but using different polymer concentrations, 6.5, 6.5 and 10% (w/v), respectively. When benzene was used as the casting solvent, samples were left in the fume hood for 20 instead of 21 days. For cyclohexanone, a 6% (w/v) S-SIBS-29 sample was dissolved and kept in a fume hood at room temperature for 21 days. The sample was then annealed at 60 °C for 50 days. For cyclohexanol, a 4% (w/v) sample was first annealed at 60 °C for 21 days. This procedure was followed by a second annealing step under vacuum at room temperature for 24 h and a third one under vacuum at 80 °C for another 48 h.

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

Sample name[a]	Sulfonation level (mol%)	IEC[b] (mequiv./g)
S-SIBS-0	NA	NA
S-SIBS-29	29.23	0.81
S-SIBS-42	41.95	1.13
S-SIBS-82	82.41	2.04

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

2.3. Thermogravimetric analysis

The thermal history and water loss (sorption) of the S-SIBS block copolymers were determined using a Hi-Res TGA 2950 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 to 600 °C at 5 °C/min under nitrogen and observing regions of significant weight loss. For water sorption measurements, samples were pre-saturated in HPLC grade water for at least 48 h, excess water was carefully removed before the samples were placed in the TGA, and the weight loss of water was measured from the mass loss that occurs below 100 °C. The degradation temperatures and water sorption values measured in this study were determined by measuring each sample three to seven times, and the values reported correspond to the averages and standard deviations of those measurements.

2.4. *Infrared spectroscopy*

Infrared spectra of all the polymer samples were collected using a Nicolet Nexus 870 Spectrometer equipped with a diamond ATR objective (Spectra-Tech Infinity Series). The diamond ATR objective (refractive index = 2.73) is a nondestructive technique that provides intimate contact with the polymer sample. Infrared spectra were collected using 500 scans and 4 cm^{-1} resolution.

3. Results and discussion

3.1. *Sulfonation level*

Fig. 1 shows the thermal history for both an unsulfonated (S-SIBS-0) and a sulfonated (S-SIBS-42) polymer; the corresponding derivative is shown by dashed lines. The unsulfonated polymer has an approximate degradation temperature of 432 °C, shown more clearly from the maximum in the derivative. The sulfonated sample reveals two separate degradation temperatures, one at approximately 291 °C and another at approximately 450 °C. The first one is a minor loss in mass and the second is a major loss in mass similar to the unsulfonated polymer. The degradation temperature results for all sulfonation levels are listed in Table 2. All the sulfonated polymers show two similar degradation temperatures, with the second one approximately 16 °C higher than the unsulfonated polymer. Sulfonic acid attached to the backbone of the polymer elevates the degradation temperature; however, there is no significant difference in degradation temperature at different sulfonation levels. The increase in degradation temperature in the sulfonated block copolymers was also observed in another study on sulfonated block copolymers [9], where they observed a 14 °C increase in degradation temperature between a sulfonated and unsulfonated styrene-based block copolymer. This difference could be related to a chemical change that occurs to the polymer due to the substitution of sulfonic acid to the backbone of the polymer. However, further studies are required to confirm this hypothesis. The additional minor mass loss observed in the sulfonated block copolymers can be attributed to the desulfonation of the polymer [17–18]. Several investigators have shown that desulfonation, a cleavage of the aromatic carbon–sulfur bond, has been shown to occur at elevated temperatures in sulfonated polymers with desulfonation temperatures ranging from 200 to 350 °C [15–16].

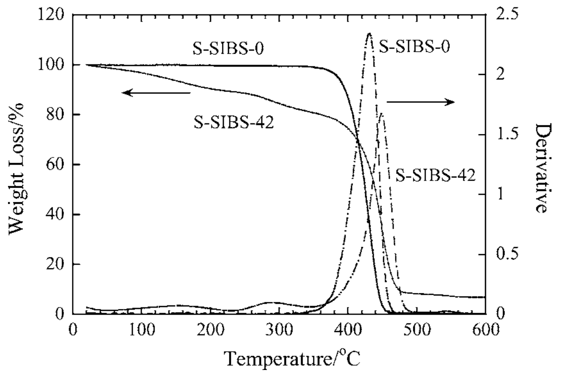

Fig. 1. Thermogravimetric results (solid lines) for an unsulfonated (S-SIBS-0) and sulfonated (S-SIBS-42) block copolymer. The maximum of the derivative (dashed lines) highlights the degradation temperatures or regions of significant mass loss.

Table 2
Thermogravimetric characterization of S-SIBS as a function of sulfonation level

Sample name	First degradation temperature (°C)[a]	Second degradation temperature (°C)[b]	Water sorption (wt.%)[c]
S-SIBS-0	–	432 ± 1	1 ± 0
S-SIBS-29	290 ± 2	448 ± 1	21 ± 1
S-SIBS-42	291 ± 4	450 ± 2	89 ± 1
S-SIBS-82	291 ± 4	445 ± 1	341 ± 4

Three to seven replicas per sample.

[a] First mass loss.

[b] Second mass loss.

[c] Weight of water loss/weight of dry polymer.

In addition to desulfonation and degradation, the sulfonated block copolymer in Fig. 1 reveals another small loss of mass from room temperature up to 200 °C with a maximum in the derivative at approximately 150 °C. This has also been documented by other investigators [15,16] in sulfonated polymers and is regarded as a three-step degradation pattern for sulfonated polymers: dehydration, desulfonation, and degradation.

Dehydration is more clearly illustrated in Fig. 2, where the water sorption of wet polymer samples was determined by measuring the mass loss of samples that were immersed in deionized water prior to TGA experiments. Fig. 2 shows a representation of one of these experiments, where the mass loss versus temperature data is shown for both a dry

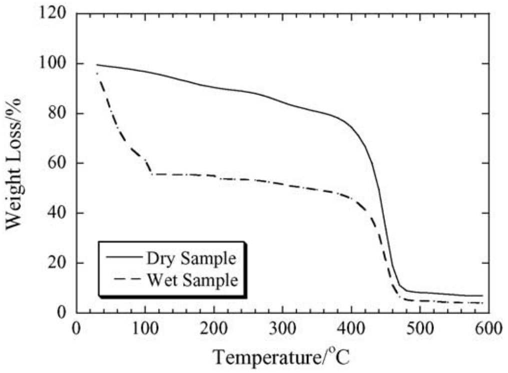

Fig. 2. Thermogravimetric results for a dry (solid line) and wet/pre-hydrated (dashed line) sulfonated block copolymer (S-SIBS-42). The mass loss <100 °C for the wet sample was used to determine water sorption.

Table 3
Thermogravimetric characterization of S-SIBS as a function of annealing temperature and film formation

Sample name	First degradation temperature (°C)	Second degradation temperature (°C)	Water sorption (wt.%)
S-SIBS-29[a]	290 ± 2	448 ± 1	21 ± 1
S-SIBS-29[b]	–	449 ± 1	3 ± 0
S-SIBS-42[c]	291 ± 4	450 ± 2	89 ± 1
S-SIBS-42[d]	283 ± 4	447 ± 1	88 ± 3

Three to seven replicas per sample.

[a] 80 °C annealing temperature.

[b] 180 °C annealing temperature.

[c] Solvent cast.

[d] Heat pressed.

and a wet sample (S-SIBS-42). There is a major loss in mass <100 °C for the wet sample. Table 3 lists the water sorption measured at each sulfonation level. As sulfonation level increases, the water sorption increases, as high as 341 wt.% for S-SIBS-82. An increase in the amount of hydrophilic sulfonic acid groups in the backbone of the polymer results in an increase in water sorption. Water sorption values measured in this study compared well to another study, which used a different gravimetric technique [5].

Fig. 3 shows the infrared spectra of S-SIBS at various sulfonation levels (0, 29, 42, and 82 mol%). There are a number of vibrational stretching bands that appear between 1000 and 1200 cm^{-1} in the sulfonated polymers that do not appear in the unsulfonated polymer. In particular, four distinct bands associated with sulfonic acid were identified in the sulfonated polymers at 1155, 1125, 1034, and 1007 cm^{-1} [5,6,19–21]. The 1007 and 1127 cm^{-1} vibrational stretching bands represent the in-plane bending vibration of the aromatic ring substituted with the sulfonated group in the *para*-position and the sulfonated anion attached to the aromatic ring, respectively. The bands at 1034 and 1155 cm^{-1} represent the symmetric and asymmetric stretching vibration of the sulfonated group, respectively. As shown in Fig. 3, the intensity of these four bands increases with increasing sulfonation level.

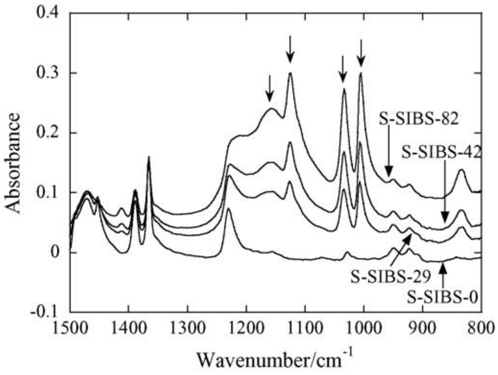

Fig. 3. Infrared spectra of S-SIBS at various sulfonation levels (0, 29, 42, and 82 mol%). Infrared bands representing the stretching vibrations associated with sulfonation are indicated by the arrows.

Table 4
Infrared characterization of S-SIBS as a function of annealing temperature and film formation

Sample name	A_{1007}/A_{1365}	Difference (%)
S-SIBS-29[a]	0.67	83
S-SIBS-29[b]	0.28	83
S-SIBS-42[c]	1.17	7
S-SIBS-42[d]	1.25	7

[a] 80 °C annealing temperature.

[b] 180 °C annealing temperature.

[c] Solvent cast

[d] Heat pressed.

3.2. Annealing temperature

The degradation temperatures were also determined for S-SIBS-29 at two different annealing temperatures: 80 and 180 °C, listed in Table 4. Both polymers exhibit the same major mass loss at approximately 450 °C. However, the sample annealed at 180 °C does not posses the minor mass loss at 290 °C, which was observed in the other sulfonated block copolymers. It appears that annealing the sample at 180 °C for an extended period of time (48 h) results in a partial desulfonation, and therefore there is no minor mass loss observed at 290 °C.

Infrared spectroscopy supports this conclusion. Fig. 4 compares the infrared spectra of S-SIBS-29 annealed at both

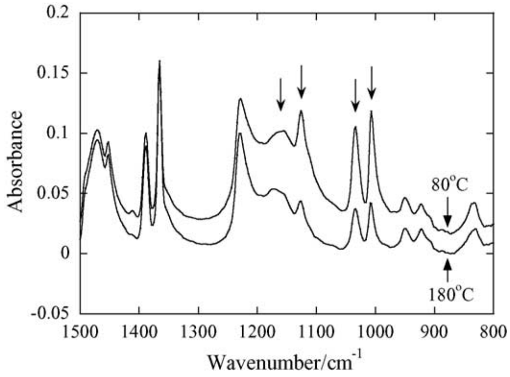

Fig. 4. Infrared spectra of S-SIBS-29 annealed at 80 and 180 °C.

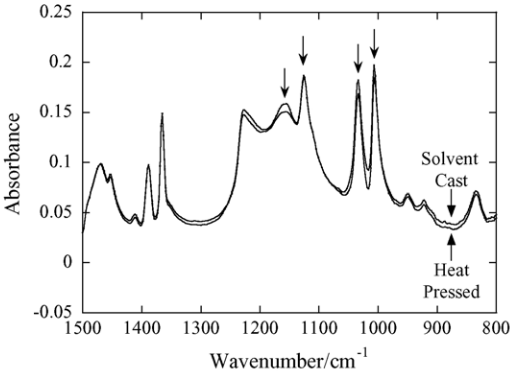

Fig. 5. Infrared spectra of S-SIBS-42 for two different processing techniques: heat pressed and solvent cast.

Table 5
Thermogravimetric characterization of S-SIBS as a function of casting solvent

Sample name	Casting solvent	Solubility parameter ($MPa^{1/2}$)	First degradation temperature (°C)	Second degradation temperature (°C)	Water sorption (wt.%)
S-SIBS-29	Tetrahydrofuran	18.6	287 ± 2	444 ± 2	18 ± 4
S-SIBS-29	Benzene	18.8	286 ± 3	444 ± 2	12 ± 2
S-SIBS-29	Chloroform	19.0	293 ± 2	444 ± 2	25 ± 2
S-SIBS-29	Methylene chloride	19.8	290 ± 2	448 ± 1	21 ± 1
S-SIBS-29	Cyclohexanone	20.3	286 ± 2	446 ± 2	30 ± 3
S-SIBS-29	Cyclohexanol	23.3	290 ± 2	444 ± 2	9 ± 2

Two to three replicas per sample.

80 and 180 °C. The four previously mentioned bands representing sulfonic acid decrease in intensity in the sample annealed at a higher temperature. Table 4 quantitatively shows a significant reduction in intensity due to annealing at higher temperatures: an 83% difference. This intensity decrease was quantified by calculating the peak height of 1007 cm^{-1} and normalizing it with the peak height at 1365 cm^{-1}. The band at 1007 cm^{-1} is associated with sulfonation, while the band at 1365 cm^{-1} represents the symmetric CH_3 deformation in polyisobutylene (a reference band) [5]. This observation is also supported with a reduction in water sorption between S-SIBS-29 annealed at 80 and 180 °C: 21–3 wt.% (Table 4). Partial desulfonation leads to less hydrophilic sulfonic acid groups in the backbone of the polymer, and therefore lowers the water sorption.

3.3. Film formation

The properties of S-SIBS-42 were examined as a function of film formation technique: solvent cast versus heat pressed. There was no difference in thermal stability or water sorption between the two samples (Table 4). In addition, there is approximately no difference in the infrared spectra between the solvent cast and heat pressed sample as shown in Fig. 5 and Table 5.

3.4. Casting solvents

The thermal stability for S-SIBS-29 remains unchanged with different casting solvents (Table 5). The water sorption in S-SIBS-29 varies slightly from 9 to 30 wt.% as a function of different casting solvents (Table 5). However, there seems to be no apparent trend between water sorption and casting solvent solubility parameter.

According to a recent study by Kim et al. [22] on sulfonated block copolymers, different casting solvents result in different morphologies. Therefore, different morphologies may result in different accessibilities of sulfonic acid groups to water, explaining the slight variation in water sorption with different casting solvents. These morphological changes, although significant to influence water sorption, appear to be small enough not to change the degradation temperature of the sulfonic group or the remaining backbone.

4. Conclusions

Understanding thermal behavior in sulfonated polymers is critical for membrane stability as it applies to specific applications, such as fuel cells. In this study, sulfonated poly(styrene-isobutylene-styrene) revealed a degradation temperature at approximately 450 °C regardless of sulfonation level, which was approximately 16 °C higher than the unsulfonated polymer. More importantly, the sulfonated version of the block copolymer desulfonates at approximately 290 °C. In addition, annealing the sulfonated block copolymer for extended times at 180 °C also results in partial desulfonation. These thermal properties are important to note, in particular, as it applies to possible high temperature applications. Other processing conditions appear to not have any significant effect on thermal behavior.

Acknowledgements

The authors wish to acknowledge the financial support of the Hispanic Alliance for Colleges and Universities (HACU) and the Army Research Laboratory (ARL). This work was performed while D. Suleiman held a HACU Summer Faculty Award and Y.A. Elabd held a National Research Council Associateship Award at the US Army Research Laboratory.

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