



**Thermogravimetric and Spectroscopic Characterization of
Sulfonated Poly(styrene-isobutylene-styrene) Block
Copolymers: Effects of Processing Conditions**

**by James M. Sloan, David Suleiman, Yossef A. Elabd, Eugene Napadensky,
and Dawn M. Crawford**

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Weapons and Materials Research Directorate, ARL

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14. 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 ~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 desulfonation. These results were confirmed by a reduction in water sorption and 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 vs. heat pressed) and casting solvent (six different solvents).					
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1. Introduction

In the search for selective membranes capable of separating protons from methanol for direct methanol fuel cells (DMFCs) (1–2) or chemical and biological toxins from water in chemical protective clothing (CPC), block copolymer ionomer membranes emerge (3–6). They are highly ordered sequences of both ionic and nonionic blocks, in which the ionic groups are randomly arranged along the polymer chain. This investigation studied one of such block copolymer ionomers, sulfonated poly(styrene-isobutylene-styrene) (S-SIBS). This material has been recently synthesized at unprecedented sulfonation levels (7), and this investigation intends to further characterize them.

This investigation utilizes thermogravimetric analysis (for water solubility and degradation properties) and FTIR-ATR spectroscopy (monitors molecular structure) to characterize these ionic block copolymers. The goal of the investigation is to develop novel materials through the chemistry and morphology, capable of achieving the specialty separations required for the DMFCs and CPC among other applications.

To achieve the desired goal, four different poly(styrene-isobutylene-styrene) tri-block copolymers were studied over a range of processing conditions:

1. Sulfonation level (mole percent sulfonation of available polystyrene: 0%, 29%, 42%, and 82%),
2. Annealing temperature (50, 80, 120, and 180 °C),
3. Film formation (solvent casting vs. heat pressing), and
4. Processing solvent (tetrahydrofuran [THF], benzene, CHCl₃, CH₂Cl₂, cyclohexanone, and cyclohexanol).

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 weight-percent 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: high-performance liquid chromatography (HPLC)-grade water (J.T. Baker), 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 (7). 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 copolymers will be 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.

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

Sample Name ^a	Sulfonation Level (Mole %)	IEC ^b (meq/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

^aS-SIBS = sulfonated poly(styrene-isobutylene-styrene).

^bIEC = ion-exchange capacity.

NA = not applicable.

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 for annealing studies were prepared by solvent casting a 10% (w/v) solution of S-SIBS-29 in methylene chloride at ambient conditions for 3 weeks. Two temperatures were selected for the annealing studies, one sample was annealed under vacuum at 80 °C for 24 hr, while the other sample was annealed under vacuum at 80 °C for 24 hr and then at 180 °C for 48 hr.

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 weight-percent) 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

solvent casting conditions are listed in table 2. The solvents selected cover a range of solubility parameters (i.e., $\delta = 18.6 - 23.3 \text{ MPa}^{1/2}$), polarities, and chemical properties (e.g., polar protic, polar aprotic, nonpolar, etc.).

Table 2. Solvent casting processing conditions of S-SIBS-29 as a function casting solvent.

Casting Solvent	Polymer Concentration (w/v %)	Fume Hood at Room Temperature (Days)	Annealed at 60 °C (Days)	Annealed Under Vacuum at Room Temperature (hr)	Annealed Under Vacuum at 80 °C (hr)
Tetrahydrofuran	10	21	—	24	48
Benzene	6.5	20	—	24	48
Chloroform	6.5	21	—	24	48
Methylene chloride	10	21	—	24	48
Cyclohexanone	6.0	21	50	—	—
Cyclohexanol	4.0	—	21	24	48

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 ~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 hr, 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 3–7 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 attenuated total reflectance (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

3.1 Sulfonation Level

Figure 1 shows the thermal history for both an unsulfonated (S-SIBS-0) and a sulfonated (S-SIBS-42) polymer; the corresponding derivative is also shown by dashed lines. The

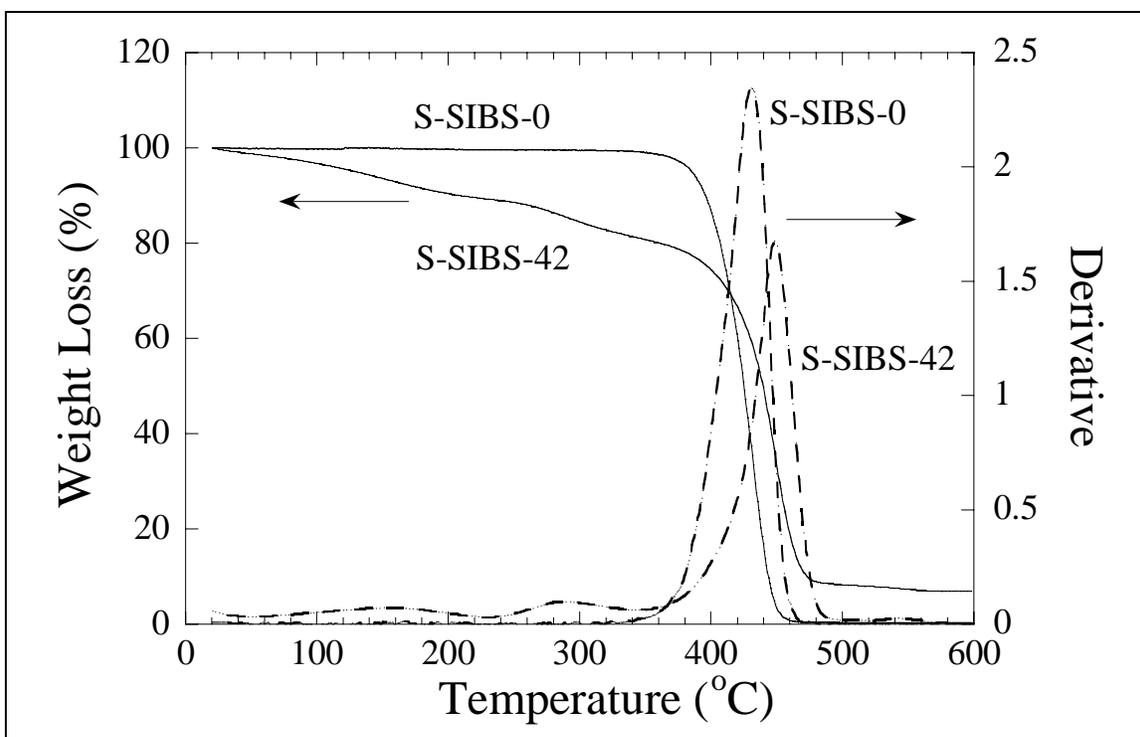


Figure 1. Typical thermogravimetric results of S-SIBS polymers.

unsulfonated polymer has a degradation temperature of 432 °C, determined from the maximum in the derivative. The sulfonated sample reveals two separate degradation temperatures, one at 291 °C and another at 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 3. All the sulfonated polymers show two similar degradation temperatures, with the second one ~17 °C higher than the unsulfonated polymer. Sulfonic acid attached to the backbone of the polymer elevates the degradation temperature; however, there is no 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 (8), where they observed a 14 °C increase in degradation temperature between a sulfonated and unsulfonated styrene-based block copolymer. The additional minor mass loss observed in the sulfonated block copolymers can be attributed to the desulfonation of the polymer. Desulfonation, a cleavage of the aromatic carbon-sulfur bond, has been shown to occur at elevated temperatures (9). Although other investigators (8, 10) have not observed this desulfonation temperature, these studies focused on sulfonated block copolymers neutralized with various salts, where this study only examines the acid form of the sulfonated block copolymers. This suggests that neutralization may stabilize the polymer and prevent desulfonation at higher temperatures.

Table 3. 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 (Weight-Percent) ^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

^aFirst mass loss.

^bSecond mass loss.

^cWeight of water loss/weight of dry polymer.

In addition to thermal stability, the amount of water sorption in preswollen polymer samples were determined by measuring the mass loss of samples that were immersed in deionized water prior to thermogravimetric analysis (TGA) experiments. Figure 2 shows a representation of one of these experiments, where the mass loss versus temperature data is shown for both a dry and a wet sulfonated 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 weight-percent for S-SIBS-82. Increasing the amount of hydrophilic sulfonic acid groups in the backbone of the polymer results in an increase in water weight swelled in the polymer. Water sorption values measured in this study compared well to another study, which used a different gravimetric technique (7).

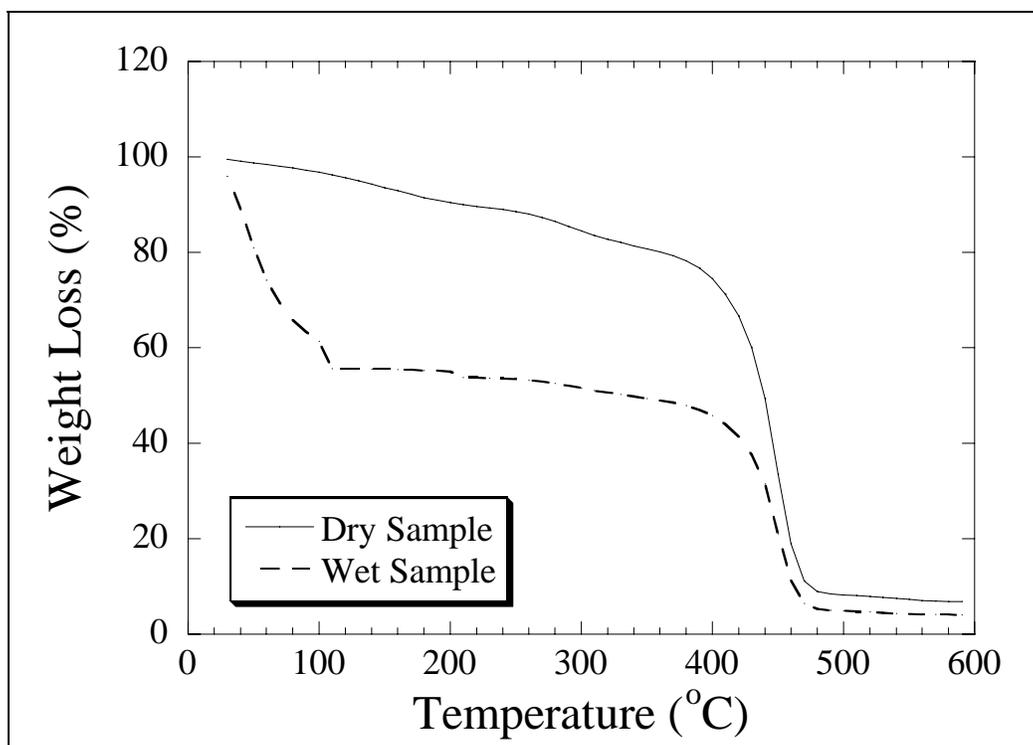


Figure 2. Thermogravimetric results of S-SIBS-42 dry and wet samples.

Figure 3 shows the infrared spectra of S-SIBS at various sulfonation levels (0, 29, 42, and 82 mole %). 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} (*I*). The 1007 and 1127 cm^{-1} vibrational stretching bands represent the in-plane bending vibration of the aromatic ring substituted with the sulfonate 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 sulfonate group, respectively. As shown in figure 3, the intensity of these four bands increases with increasing sulfonation level.

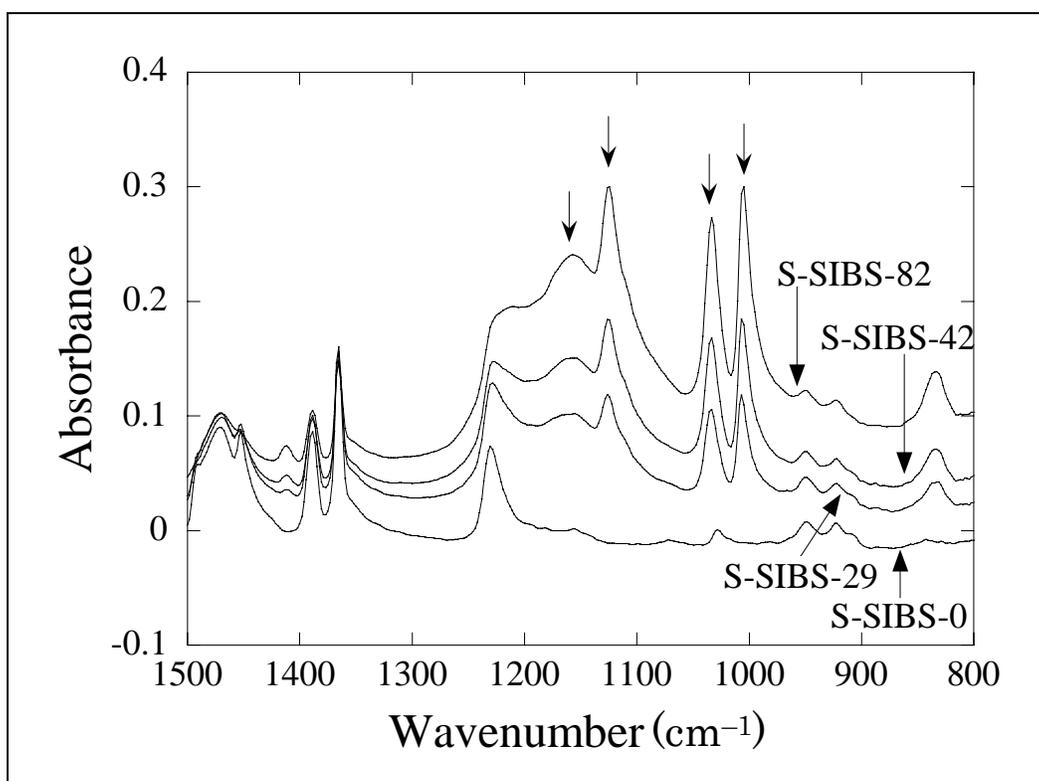


Figure 3. Infrared spectra of various S-SIBS polymers.

3.2 Annealing Temperature

The degradation temperatures were also determined for S-SIBS-29 at two different annealing temperatures: 80 and 180 $^{\circ}\text{C}$, listed in table 4. Both polymers exhibit the same major mass loss at ~ 450 $^{\circ}\text{C}$. However, the sample annealed at 180 $^{\circ}\text{C}$ does not possess the minor mass loss at 290 $^{\circ}\text{C}$, which was observed in the other sulfonated block copolymers. It appears that annealing the sample at 180 $^{\circ}\text{C}$ for an extended period of time (48 hr) results in desulfonation and, therefore, there is no minor mass loss observed at 290 $^{\circ}\text{C}$.

Table 4. 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 (Weight-Percent)
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

^aAnnealing temperature of 80 °C.

^bAnnealing temperature of 180 °C.

^cSolvent cast.

^dHeat pressed.

Infrared spectroscopy supports this conclusion. Figure 4 compares the infrared spectra of S-SIBS-29 annealed at both 80 and 180 °C. The four previously mentioned bands representing sulfonic acid decrease in intensity in the sample annealed at a higher temperature. Table 5 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 gives an indication of the sulfonation level, while the band at 1365 cm⁻¹ represents the symmetric CH₃ deformation in polyisobutylene (a reference band) (7).

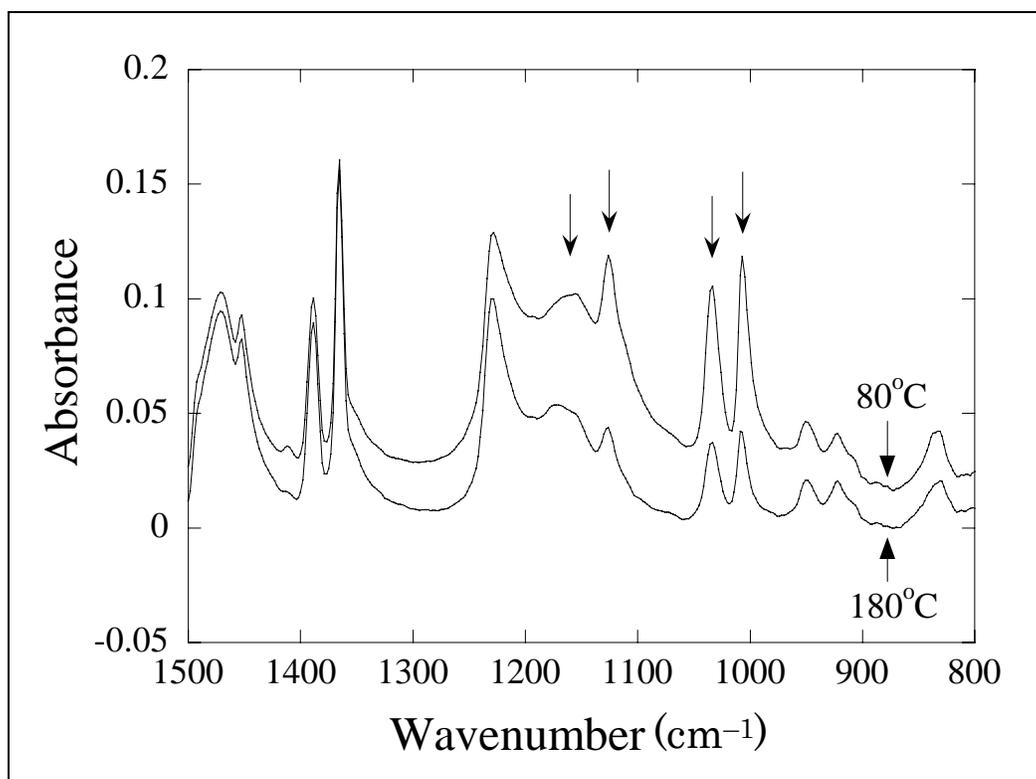


Figure 4. Infrared spectra of S-SIBS-29 annealed at 80 and 180 °C.

Table 5. 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	
S-SIBS-42 ^c	1.17	7
S-SIBS-42 ^d	1.25	

^aAnnealing temperature of 80 °C.

^bAnnealing temperature of 180 °C.

^cSolvent cast.

^dHeat pressed.

This observation is also supported with a reduction in water sorption between S-SIBS-29 annealed at 80 and 180 °C: 21 to 3 weight-percent. Desulfonation results in 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 vs. 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 figure 5 and table 5.

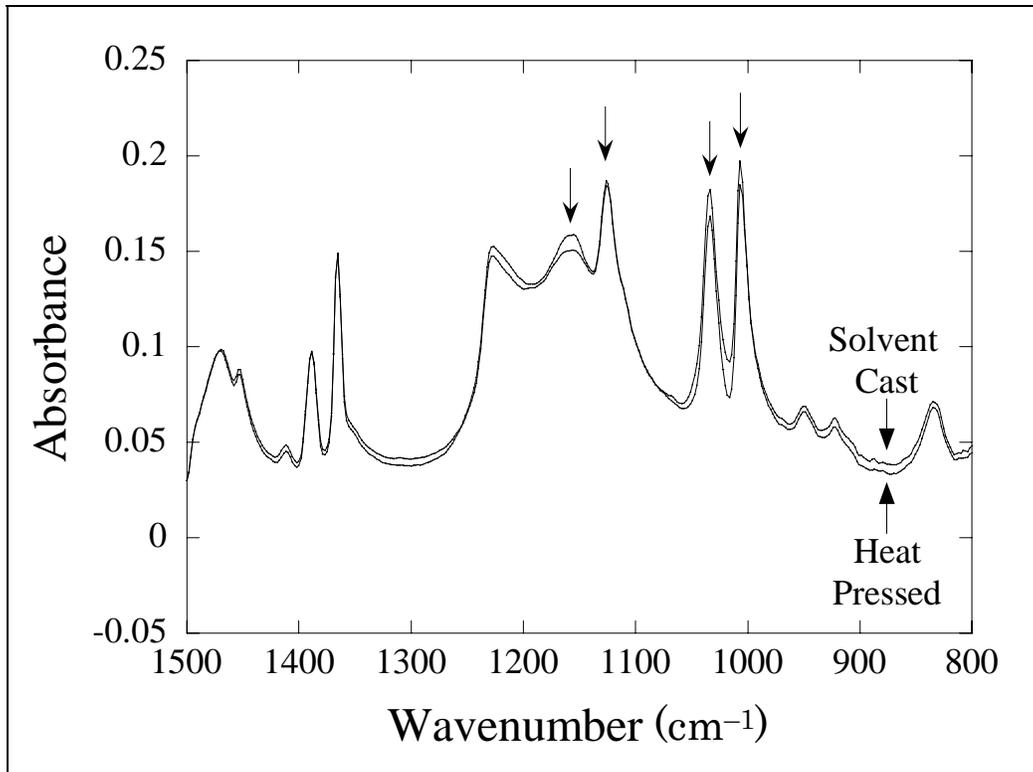


Figure 5. Infrared spectra of S-SIBS-42 heat pressed and solvent cast.

3.4 Casting Solvents

The thermal stability for S-SIBS-29 remains unchanged with different casting solvents (table 6). The water sorption in S-SIBS-29 varies from 9 to 30 weight-percent as a function of different casting solvents (table 6). However, there seems to be no apparent trend between water sorption and casting solvent solubility parameter. A recent study by Kim et al. (11) on sulfonated block copolymers has shown that different casting solvents results in different morphologies. Different morphologies may result in different accessibilities of sulfonic acid groups to water explaining the slight variation in water sorption with different casting solvents.

Table 6. 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 (Weight-Percent)
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

4. Conclusions

A thermogravimetric and spectroscopy characterization of various S-SIBS ionomers was conducted. A thermal degradation of the unsulfonated polymer of 432 ± 1 °C is reported. All sulfonated polymers degraded at 449 ± 4 °C regardless of sulfonation level, annealing temperature, processing method, or solvent used. However, annealing at 180 °C cleaved the sulfonic acid groups as seen by solubility, degradation temperature, and spectroscopic data. Different processing methods (solvent casting vs. heat pressing) did not have a major influence in the solubility, degradation temperature, or IR spectra of the polymers studied. Finally, different processing solvents did not influence the degradation temperature of the polymer, but did influence the water solubilities (9%–30%). Such differences have not been explained in terms of the solvent-polymer interactions, but perhaps different polymer morphologies. Higher sulfonation studies with different solvents should better exaggerate those interactions and perhaps suggest routes to fine-tune these polymers to achieve the desired selectivity of DMFCs or CPC. This will be achieved after coupling the recently developed synthesis method with this and other characterization methodologies including diffusion experiments.

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