Sulfonation Distribution in Sulfonated Polystyrene Ionomers Measured by MALDI-ToF MS

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S *Supporting Information*

ABSTRACT: Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF MS) was used to quantify the sulfonation level and sulfonation distribution of sulfonated polystyrene ionomers prepared by homogeneous solution sulfonation. The sulfonation levels obtained by MALDI-ToF MS and acid−base titration were compared, and the sulfonate distributions determined by MALDI-ToF MS were compared with theoretical random distributions. The results indicate that the sulfonation reaction used produces a sample with a random sulfonate distribution.
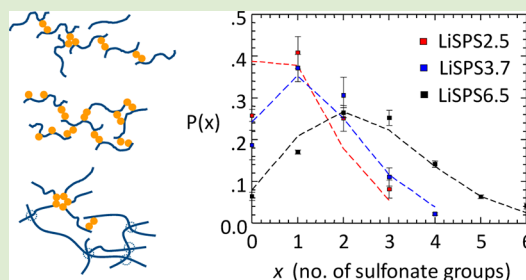
Ionomers are predominantly hydrophobic polymers containing a small fraction of chemically bonded ionic groups, usually <15 mol %.[1] Over the past few decades, lightly sulfonated polystyrene (SPS) has served as a model ionomer system for the study of melt rheology,[2] solution behavior,[3] morphology,[4−6] dynamics,[7−10] and wetting behavior[11,12] of ionomers. In addition to its use as a model ionomer system, SPS has been used in applications such as adhesives,[13] drilling fluid,[14] compatibilizing agents for polymer blends,[15] golf balls,[16] fluid viscosification,[17] organogels,[18] and propellants.[19]

SPS ionomers are most commonly synthesized following the procedure developed by Makowski et al.,[20] which involves a homogeneous solution sulfonation using acetyl sulfate as the sulfonating agent. The sulfonation level, which is usually defined in terms of mol % sulfonation (i.e., the average number of sulfonate groups in 100 styrene units) can be conveniently determined by elemental analysis, acid−base titration or ^{1}H NMR.[21]

The Makowski sulfonation method is considered to proceed randomly along the chain, primarily at the para-position of the phenyl ring, and one would expect that there is a inhomogeneous, but random distribution of sulfonate groups on the polystyrene chains.[22] That distribution has been estimated with a binomial distribution function:[2,11,22]

$$P(x) = \frac{N!}{(N-x)!x!}p^x(1-p)^{(N-x)}$$

(1)

where $P(x)$ is the probability that for an average sulfonation level p, a chain with N repeat units has x sulfonate groups. However, no experimental studies have confirmed this sulfonation distribution for solution SPS. An extensive solid state NMR investigation by VanderHart et al.[22] of a low molecular weight SPS, $N = 38$ and $p = 0.025$, where eq 1 predicts that ∼40% of the chains should be unsulfonated, failed to detect phase separation of unsulfonated chains.

The quantification of the ion distribution in SPS ionomers remains an open question in the field of ionomers, and a rather important one given the large number of research groups that use that material in their research. One problem with SPS as a model ionomer system is the inhomogeneous ion distribution at low sulfonation levels. The interesting properties of SPS evolve from intermolecular association of the sulfonate groups, which provides a network structure dominated by the formation of ionic nanodomains. The influence of the ion distribution on the microstructure is unknown, but may be important. For example, at low sulfonation levels, there may be a significant fraction of chains that are completely unsulfonated or have only one or two sulfonate groups. Unsulfonated and monosubstituted chains are ineffective for carrying load in a physically cross-linked ionomer network (see Figure 1). At best, multiple associations of monosubstituted chains will produce a micelle-like structure or dangling branches from a multiply sulfonated chain. Disubstituted chains can produce chain-extension by simple associations or ionic bonding between sulfonate groups. If multiple associations occur, such as when the sulfonate groups are incorporated into nanodomain aggregates (ionic clusters), they can produce a network structure. Even chains with only two sulfonate groups can participate in such a network if both are incorporated into different clusters. Chains containing three or more sulfonate groups can easily form network structures by simple association.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF MS)[23−25] provides an opportunity to reveal the ion heterogeneity in SPS. MALDI-ToF MS can yield quantitative information on individual chains, which makes it useful in characterizing mixtures of polymer systems
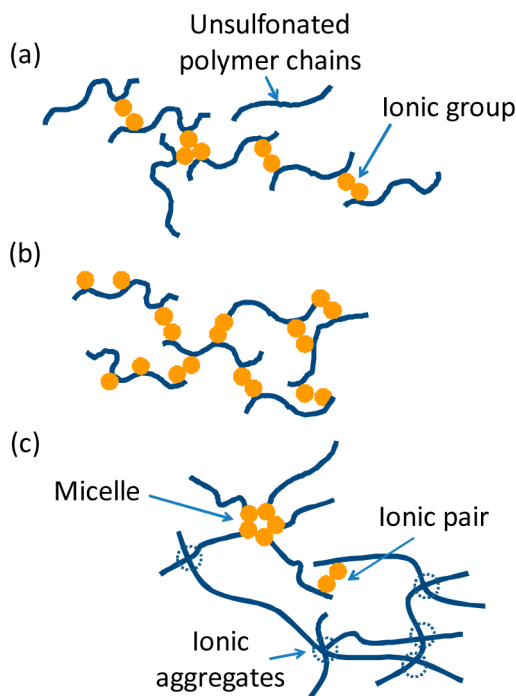
Figure 1. Schematics of chain structures with associative ionic groups. (a) Chains with one or two sulfonate groups can result in chain extension. Chains without ionic functionality are inactive. (b) Chains with three or more sulfonate groups may form a network structure. Chains with two sulfonate groups can participate in a network if both sulfonate groups are incorporated into different ionic clusters. (c) Multiple associations of monofunctional chains will form a micelle-like structure or dangling branches from a multiple sulfonated chain.

with complex chemical structures.[26,27] For example, MALDI-ToF MS has been successfully applied, without the use of calibrants, for the quantitation of polystyrene end groups introduced by reacting poly(styryl) lithium with ethylene oxide;[28] the degree of ethylene oxide oligomerization determined by MALDI-ToF MS was in excellent agreement with NMR results.[28] In the present work, the sulfonation level and the sulfonation distribution of SPS ionomers were measured by MALDI-ToF MS. The sulfonation levels obtained by MALDI-ToF MS were compared to the values deduced by conventional acid−base titration, which normally shows very good agreement with elemental analysis.[7,29] The measured sulfonate distributions were also compared to the predictions of eq 1. To our knowledge, this is the first report of experimentally measuring the sulfonation distribution of randomly sulfonated SPS.

Due to the random nature of the sulfonation reaction, SPS is essentially a mixture of chains with varying sulfonate functionality, including unsulfonated polystyrene. Therefore, differences in ionization efficiencies between all the components in the mixture need to be accounted for and the MALDI-ToF MS experimental conditions need to be optimized. Three SPS polymers were prepared from a narrow molecular weight distribution polystyrene (Pressure Chemical Co.; M_w = 4000 Da, polydispersity index = 1.06) by sulfonation according to the procedure of Makowski et al.[20] The sulfonation levels (p) were 2.5, 3.7, and 6.5 mol % (by titration). The neutralized samples are denoted as MSPSp, where M is the metal cation and p is the average sulfonation level.

Three MALDI matrices, namely, 1,8-dihydroxy-9,10-dihydroanthracen-9-one (dithranol, DIT), trans-2-(3-(4-*tert*-butylphenyl)-2-methyl-2-propenyliedene)malononitrile (DCTB), and 2,5-dihydroxybenzoic acid (DHB), and five different monovalent metal cations (Li, Na, K, Rb, and Ag) were examined in order to obtain the most effective experimental conditions for MALDI-ToF MS analysis. When DCTB or DIT was used, the spectra were severely biased toward monosulfonated chains, while using DHB overcame this issue. When alkali cations other than lithium were used, either the ion peaks overlapped or the unsulfonated chains were not detected by MALDI-ToF MS. AgSPS failed to provide good quality mass spectra. No extra cationizing agent was added because the one tested, lithium trifluoroacetate (LiTFA), was found to severely deteriorate the spectra, most likely due to high excess salt concentration that results in poor signal-to-noise ratio.

Optimization studies (see details in Supporting Information) indicated that LiSPS and DHB without a cationizing agent, using the dry-droplet sample preparation method,[30] provided the best quality MALDI-ToF MS spectra for analysis of the sulfonation distribution. A representative MALDI-ToF MS spectrum of LiSPS2.5 is shown in Figure 2a. The spectra for LiSPS3.7 and LiSPS6.5 were qualitatively similar to the LiSPS2.5 spectrum (Figures S2 and S3). The expanded mass spectra of these three samples, Figure 2b, demonstrate the variation in the sulfonation distribution for the three polymers. The major peaks labeled as "Sx" indicate polystyrene chains
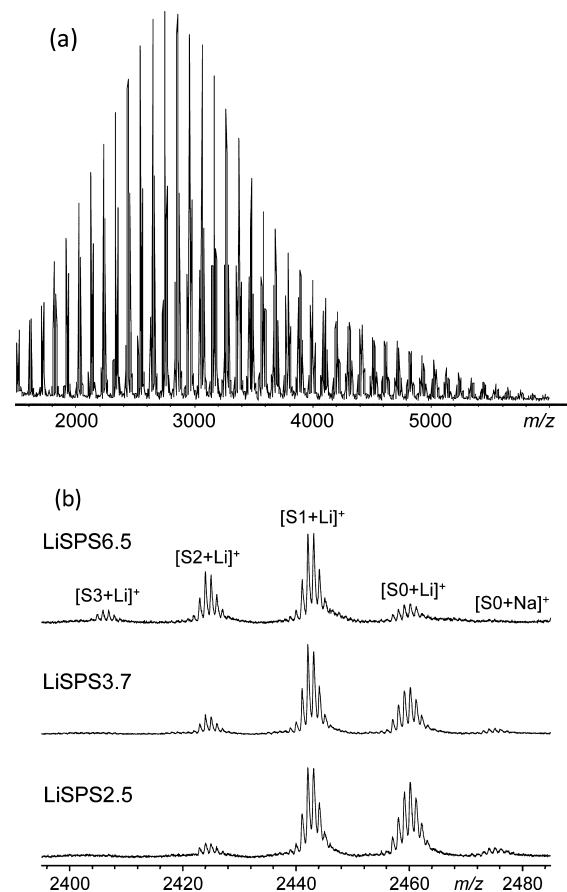

Figure 2. (a) MALDI-ToF MS spectrum of LiSPS2.5; (b) expanded view of mass spectra of LiSPS2.5, LiSPS3.7, and LiSPS6.5. "Sx" refers to polystyrene chains with x sulfonate groups. Note that the degree of polymerization of S3, S2, S1, and S0 is 20, 21, 22, and 23, respectively.

with x sulfonate groups. It should be noted that all ionic peaks detected are Li$^+$ adduct peaks, except for the minor component peak labeled as $[S0 + Na]^+$, which is the sodium adduct of unsulfonated chains. Peaks from sodium ions appear due to the trace sodium ions present as impurities in the sample holder and glassware used.[23,31] As the sulfonation level increased, the distribution shifts toward higher sulfonation levels.

The average sulfonation levels of the three ionomers were calculated from the mass spectra, and the results are compared with the titration results in Table 1. The sulfonation levels

Table 1. Sulfonation Level Determined by MALDI-ToF MS (mol %)

sample	MALDI-ToF MS	titration
LiSPS2.5	3.12 ± 0.20	2.47 ± 0.11
LiSPS3.7	3.74 ± 0.31	3.70 ± 0.10
LiSPS6.5	6.82 ± 0.06	6.57 ± 0.12

determined by MALDI-ToF MS for LiSPS3.7 and LiSPS6.5 are in good agreement with the respective titration values, though the MALDI-ToF MS value for LiSPS6.5 is about 4% higher than the titration value. The sulfonation level of LiSPS2.5 given by MALDI-ToF MS is ∼25% higher than the titration value. With the MALDI-ToF MS experimental conditions applied, two effects are likely to exist. First, the sulfonated species have significantly higher ionization efficiency than the unsulfonated species. Second, the ionization efficiency continues to increase as the sulfonate functionality increases, albeit at a significantly smaller extent compared to moving from the unsulfonated to monosulfonated polystyrene.

The disparity in the sulfonation level by the two techniques for LiSPS2.5 is attributed to the first effect. As will be discussed later in this paper, the molar ratios of the unsulfonated species calculated by MALDI-ToF MS for LiSPS2.5, LiSPS3.7, and LiSPS6.5 were about 33, 25, and 9 mol %, respectively. These values agree reasonably well with the binomial distribution values calculated from eq 1 at 38, 24, and 8 mol %, respectively. The first effect becomes prominent since the molar ratio of unsulfonated species is much higher in LiSPS2.5. Consequently, MALDI-ToF MS tends to underestimate the amount of unsulfonated species, so that the MALDI-ToF MS sulfonation level for LiSPS2.5 is overestimated. For LiSPS6.5, the MALDI-ToF MS value is slightly higher than the titration value due to the second effect.

The above-mentioned arguments can be further supported by the variation of MALDI-ToF MS sulfonation levels with degree of polymerization, N, as shown in Figure 3. Because MALDI-ToF MS provides quantitative information on individual chains, it is possible to determine the effect of chain length on the sulfonation distribution. For LiSPS2.5 and LiSPS3.7, the sulfonation level slightly decreases and eventually plateaus with increasing molecular weight of the chains, giving rise to average sulfonation levels of 3.1 and 3.7 mol %, respectively. The independence of sulfonation level on chain length confirms that the sulfonation process is random.

For chains with a lower degree of polymerization, there is a higher probability for completely unsulfonated chains. The considerable ionization efficiency difference between the unsulfonated and sulfonated species will therefore overpredict the degree of sulfonation at low molecular weight. For LiSPS6.5, on the other hand, except for the lowest molecular weight chains, which also had the largest experimental error, the
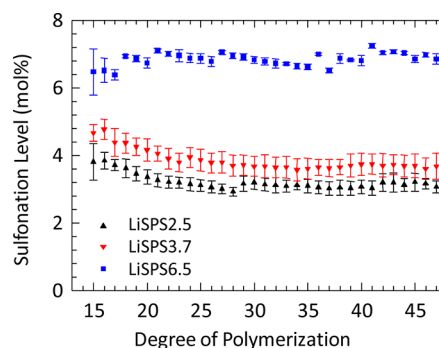

Figure 3. Sulfonation level versus degree of polymerization for $N = 15-47$.

sulfonation level was reasonably constant with molecular weight and near the average value of ∼6.8 mol %. The errors in the MALDI-ToF MS measurements for LiSPS6.5 were relatively small (<1%) compared with the two lower sulfonation levels where the error for the average sulfonation level was ∼6−8% (see Table 1). This is consistent with the conclusion that the larger fractions of unsulfonated chains for the lower average sulfonation levels result in an overestimation of the sulfonation level. The fraction of unsulfonated chains in LiSPS6.5 predicted by eq 1 is about 30% of that for LiSPS3.7 and 20% of that for LiSPS2.5.

The sulfonation distributions for the three ionomers calculated from the MALDI-ToF MS data are compared with the predictions from eq 1 in Figure 4. For each ionomer, the concentration of monofunctional species ($x = 1$) is overestimated and the multifunctional species ($x \geq 2$) are generally underestimated. This is most likely due to mass discrimination effects in the MALDI-ToF MS data, that is, the low molecular
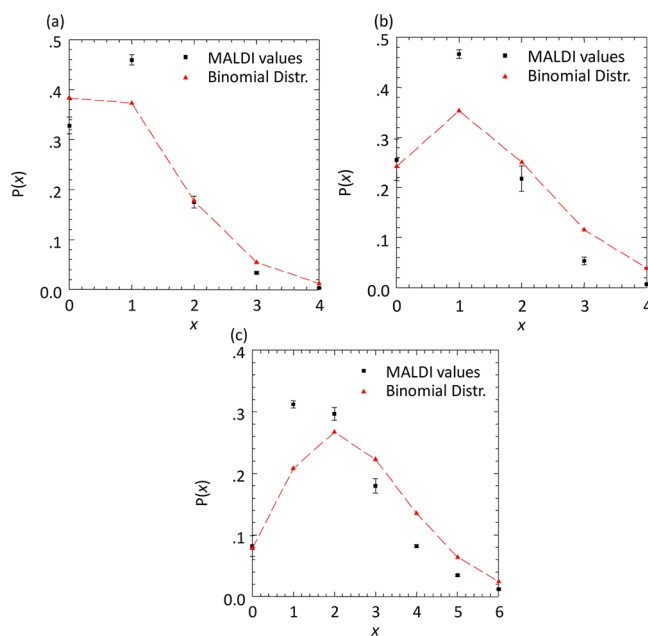

Figure 4. Sulfonation distribution measured by MALDI-TOF MS and binomial distribution predictions (eq 1) for (a) LiSPS2.5, (b) LiSPS3.7, and (c) LiSPS6.5. The dashed lines have no physical significance. They are only included to make it clear that the points denoting the predictions of the binomial distribution, eq 1, are discrete values (the points connected by the lines).

weight species have stronger desorption/ionization efficiency than the higher molecular weight species (with the same degree of sulfonation).[32] Multisulfonated species mainly appear in the high molecular weight region where the signals are partially suppressed due to mass discrimination. However, because of the relatively low polydispersity of the parent polystyrene (M_w = 4150 Da; polydispersity index = 1.08 from MALDI-ToF MS, and M_w = 4000 Da; PDI = 1.07 from GPC), the mass discrimination effects were not that severe. The overestimation of the monofunctional species can be explained in a similar way. For unsulfonated species, both mass discrimination and ionization discrimination occur and offset each other, resulting in better agreement with the theoretical prediction for random sulfonation.

Equation 1 ignores any effect that the molecular weight distribution may have on the sulfonation level, which based on the discussion above can be significant for a low molecular weight sample, especially for the low molecular weight fraction of a low average molecular weight sample. That may also increase the disparity between the experimental and theoretical sulfonation distributions. For the parent polystyrene used (M_w = 4000 g/mol), the number average degree of polymerization is N = 38. The MALDI-ToF MS data for N = 38 were isolated and analyzed to determine their sulfonation distributions. Such an analysis removes the effect of mass discrimination on the spectra because only a single N is considered. Figure 5 shows
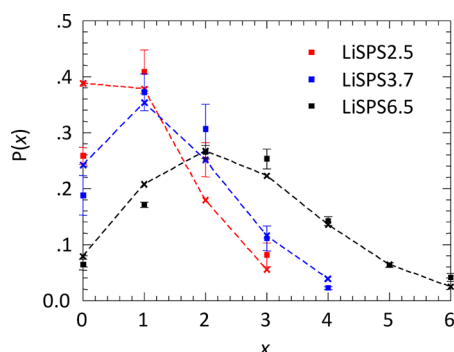

Figure 5. Sulfonation distribution from the N = 38 fraction of LiSPS2.5, LiSPS3.7, and LiSPS6.5. The dashed lines have no physical significance. They are only included to make it clear that the points denoting the predictions of the binomial distribution (marked by ×), eq 1, are discrete values (the points connected by the lines).

the results for each of the three ionomers, and in this case, with the exception of the datum point for the unsulfonated fraction of LiSPS2.5, the MALDI-ToF MS and theoretical predictions are in good agreement. This result again supports the random nature of the sulfonation reaction. The unsulfonated fraction in the LiSPS2.5 is expected to be the most problematic one to measure correctly by MALDI-ToF MS, because of the ionization discrimination toward unsulfonated species, as explained earlier.

In summary, the sulfonation distribution of an SPS ionomer was, for the first time, measured experimentally by MALDI-ToF MS. Deviation of the MALDI-ToF MS results from a random sulfonation prediction decreased for ionomer fractions with increasing molecular weight and with increasing sulfonation level for the low molecular weight ionomers discussed herein. The results from the MALDI-ToF MS analysis deviated from a theoretical random distribution due to errors associated with mass discrimination effects from the

molecular weight distribution and ionization discrimination for chains without sulfonation. The experimental and theoretical distributions for the number average molecular weight fraction (N = 38) of the low molecular weight ionomers were in good agreement. That result, as well as the independence of the sulfonation level on the chain length, indicates that the solution sulfonation procedure described by Makowski et al.[20] is indeed random, which implies the validity of using a binomial distribution to describe the sulfonation distribution. Most work on SPS ionomers has involved polymers with much higher molecular weights, where it is unlikely that the mass and ionization discrimination effects described in this paper will be as noticeable as seen herein for a low molecular weight ionomer. Thus, a binomial distribution appears to be reasonable for describing random ionomers, especially when the polymers are not readily or quantitatively analyzable by MALDI-ToF MS.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental details and additional MALDI mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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