Notes

NMR Characterization of Sulfonation Blockiness in Copoly(styrene−sulfonated styrene)

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Ionomers containing styrene and sulfonated styrene have a variety of uses, including proton exchange membranes for fuel cells,[1] viscosifiers,[2] gels,[2] and compatabilizers for polymer blends.[3] The introduction of a sulfonate species into a styrenic polymer may be accomplished either by copolymerization of styrene with a sulfonated styrene monomer[4,5] or, more commonly, by sulfonation of a preformed styrene homopolymer or copolymer with another unreactive monomer.[6] In the latter approach, relatively low amounts of sulfonation are achieved using acetyl sulfate as the sulfonating agent,[7] while higher sulfonate concentrations are usually accomplished with a complex of triethyl phosphate and sulfur trioxide.[8] The mechanism of the sulfonation reaction as well as that of alternative procedures of sulfonation was recently reviewed by Kuchera and Jancar.[9]

The proton conductivity function of polymers in membranes, specifically in sulfonated, hydrogenated styrene−butadiene copolymers, needs to be understood in terms of polymeric microstructure; thus, questions arise about the blockiness of the sulfonation in various preparations. Blockiness is especially uncertain in the case of preparations which use strongly reacting sulfur trioxide-based reactants. Ordinarily, blockiness would be an easy property to assess by common NMR techniques which have given so detailed a picture of the microstructure of polystytrene itself to the octad level.[10] However, in the case of sulfonation the solubility of the ionomer changes rapidly with increased sulfonation, owing to the immense polarity and association of sulfonate groups even in the case of free acid derivatives. As the sulfonate level reaches even a few percent, the solubility drops sharply even in good solvents for polystyrene homopolymer. This militates against obtaining NMR data for the necessary range of copolymers to assign the various compositional and microstructural peaks. While this study failed in its initial goal to discern the microstructure of the 55−60% sulfonated Kratons used in fuel cells, this note reports some of our observations which will be useful for others needing to characterize blockiness in sulfonated or other post-polymerization modified polystyrenes.

The usual NMR characterization of polystyrene microstructure involves simple proton decoupled carbon-13 spectra run at high temperatures to maximize resolution with tacticity information being reflected in the configurational chemical shifts of resonances for the backbone CH (41−42 ppm), CH_2 (43−47.5 ppm), and C1 aromatic (145−146 ppm) regions.[10] With partially sulfonated polystyrenes the resolution and assignment of the additional compositional and tacticity sequences are complicated by the overlapping of resonances from sulfonated and unsulfonated sequences. This overlap is especially true for the methylene carbons which are those most sensitive to tacticity. For this reason we extended our study beyond simple ^{13}C NMR spectra to the take advantage of the markedly increased resolution in two-dimensional NMR. Also, we were restricted to concentrations below 15% of the sulfonated moiety because of solubility, so sensitivity was a serious concern. Sensitivity can be increased over simple ^{13}C NMR by as much as a factor of 32 per scan if proton-observe indirect NMR methods are employed as was the case here. $^{1}H-^{13}C$ correlation NMR showed that even in the 2D NMR there was severe overlap in the CH_2 and CH domains for the sulfonated and unsulfonated resonances. The cleanest reflection of microstructure in this case would be the C1 aromatic carbon which of course does not show up in a simple $^{13}C-^{1}H$ correlation as there is no directly bonded proton. However, an indirect 2D NMR method which correlates a given proton with carbons that are one to several bonds away from the carbon to which the proton in question is bonded (HMBC: heteronuclear multiple bond correlation)[11] can be used to great advantage.

The samples chosen for our study were the following: RST/12sST, random sulfonated polystyrene synthesized by sulfonation of polystyrene in solution with acetyl sulfonate to a 12% sulfonation level;[7] BST/3sST, a copolymer of 97% polystyrene with a single block of sulfonated polystyrene on each end amounting to 3 mol % sulfonation, polymerized by emulsion polymerization.[5,6] This sample is believed to have blocky segments of the sulfonated species.[4] A similar sample with 5% single block of polystyrene was also studied with similar results to the 3%, but the signal-to-noise in the NMR spectra, perhaps due to solubility/aggregation limitations, was somewhat poorer and is thus not shown in this report. Rco-ST/45sST-HB (Dais-Analytic Corp., Ballston Spa, NY) is a random copolymer of butadiene and styrene (45 mol % styrene with butadiene units hydrogenated, obtained from Goodyear), sulfonated to a level of 60 mol % of the styrene units. All samples

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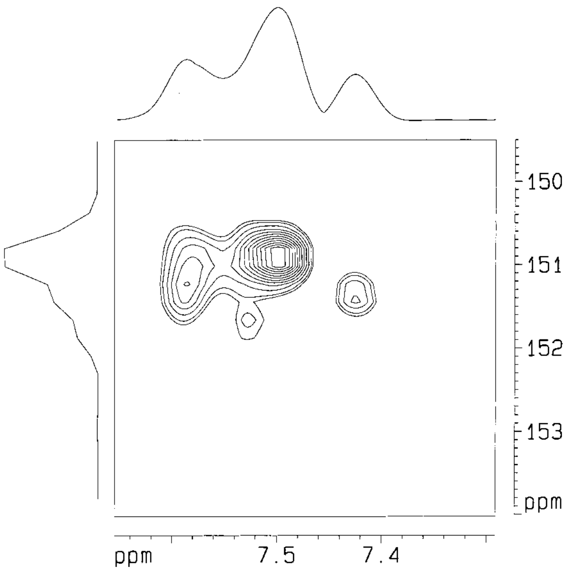

Figure 1. $^1H-^{13}C$ HMBC of RST/12sST, a random 12% sulfonated polystyrene, showing the region of correlation between the H2 proton and C1 carbon of the sulfonated aromatic ring.

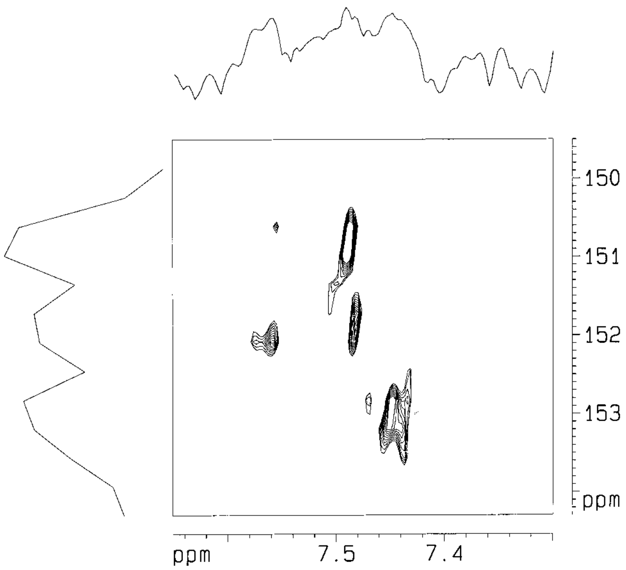

Figure 2. $^1H-^{13}C$ HMBC of BST/3sST, a sulfonated polystyrene with terminal blocks of sulfonated polystyrene amounting to 3 mol %, showing the region of correlation between the H2 proton and C1 carbon of the sulfonated aromatic ring.

were converted to free acid, i.e., protonated, sulfonate groups by twice treating the THF solution with excess HCl and extensive reprecipitation in methanol.

The proton exchange membrane material, BcoSt/45sST-HB, a sulfonated block copolymer (Dais-Analytic Corp., 45 mol % sulfonation) obtained by sulfonation of Kraton G1650 (Shell), 29% styrene did not yield resolved styrenic NMR signals even in its swelled state to be analyzed. For some of the assignment analysis a sample of atactic polystyrene (Pressure Chemicals, M_w 100 000) was used.

To eliminate uncertainties of assignment resulting from solvent changes, we chose to work exclusively in d_8-tetrahydrofuran although a series of solvents were attempted for the copolymers as will be described. Generally sample solutions were stored for 24 h under nitrogen gas, fresh nitrogen was flushed through, the sample frozen, and the top sealed with a torch. NMR spectra were all run at 58 °C on a Bruker AMX-II-500 spectrometer fitted with a 5 mm indirect triple nucleus probe and *z*-axis gradient coil. The HMBC spectra were obtained with 0.227 s proton acquisitions of 2048 points, each covering 5.2 ppm with 256 t_1 values in the 220 ppm carbon dimension. The recycle delay time was 1.5 s. The 5:3:4 pulsed field gradients were used to select the ^1H coherence which had been coupled to ^{13}C. The data were processed with sinebell windows and magnitude mode display as a 2048 × 1024 matrix. Generally 24 h runs were sufficient, but the BST/3sST sample required 4.7 days with 920 scans per slice.

An extensive unsuccessful search for improved solubility was made with DMF at high temperatures, HFIB, and a range of DMF/THF mixed solvents.

We show in Figure 1 a section of $^1H-^{13}C$ HMBC for the random 12% sulfonated sample. The region plotted shows the correlation between the aromatic H2 proton and C1 carbon of the *sulfonated* styrenic ring. The RST/12sST sample shows three main peaks resolved mostly via the proton chemical shift. As the probability of adjacent sST monomers can be calculated to be only 5% in this sample, the observed peaks reflect the conformational shift of the sST due to the adjacent ST moieties, i.e., mm, rr, and mr/rm in the usual triad sense. A reasonable assignment of the three peaks can be made on the basis of comparison to the detailed assignments for pure polystyrene (ref 10, Figure 1): the accuracy of this comparison is encouraged by the observation that the intensity pattern of the peaks in the carbon projection follows the same trend of sharp decrease with increasing carbon chemical shift as for polystyrene.[10] This would make the low field peak at 152 ppm the mm triad and rr the high field peak, but overlap is too severe to resolve mr and rm sequences.

The case of the block sulfonated polystyrene copolymer is more complicated and the quality of the spectrum is poorer because of the very low concentration of sulfonated groups. However, in Figure 2 a section of the HMBC spectrum for the 3% block sulfonated polystyrene shows peaks in the same sulfonated styrene monomer (H2, C1) aromatic region. The peaks seem to be basically in three regions as also reflected in the three peaks in both the proton and carbon local projections. Given the poor signal-to-noise, detailed interpretation of any apparent fine structure would be unwise, but the projections indicate the overall reliability of the major displayed contours. In comparison to Figure 1, these peak positions reflect chemical shift changes with change of the adjacent monomers from styrene to sulfonated styrene in the block segments, as well as the conformational shifts discussed above. Thus, it is not reliable to transfer assignments from the pure styrene case. Without appropriate model compounds and/or a series of polymers with a range of concentrations, it is not possible to make further assignments. However, as a practical empirical matter, the strongest peak at the coordinates of 7.45, 153 ppm could be used as a diagnostic marker for sulfonated styrene blocks.

The HMBC of the same region as in Figures 1 and 2 for Rco-ST/45sST-HB sample (not shown) reveals one major strong peak at 7.75, 150.5 ppm with a weaker peak at 7.64, 149.9 ppm. These peaks show no shoulders or indication of structure in either the proton or carbon direction. A simple probability calculation shows that the majority of the styrenes will be flanked by one hydrogenated butadiene and a smaller number by two butadienes. These are respectively the assignments we make to these two observed peaks. The absence of adjacent styrene groups greatly changes both the carbon and proton chemical shifts of the isolated aromatic units so that there is only compositional information in the chemical shift and of course no conformation information on the styrenes.

This is as far as we are prepared to develop this work as a great deal of solvent searching would be required. Our result is that there is a diagnostic set of peaks illustrated in Figure 2 for block sulfonated polystyrene. The applicability of HMBC to this sort of problem should be generalizable and of use to those concerned with sulfonated polystyrene in particular, or polymer blockiness in modified polystyrenes in general, especially if solubility problems are less acute.

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