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NMR and FT-IR studies of sulfonated styrene-based homopolymers and copolymers

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Abstract

A series of sodium poly(styrene sulfonate)-*block*-poly(4-*tert*-butylstyrene) (NaPSS-*b*-P*t*BS) copolymers and related homopolymers were characterized by Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy. The homopolymers included polystyrene (PS), poly(4-*tert*-butylstyrene) (P*t*BS), sodium poly(4-styrene sulfonate) (NaP4SS), sodium poly(styrene sulfonate) (NaPSS) with various sulfonation levels, and partially sulfonated P*t*BS (P*t*BSS). The structures of NaPSS and P*t*BSS were elucidated, and the effect of sulfonation level on the NaPSS FT-IR spectrum was studied. The characteristic peaks for NaPSS and P*t*BSS in FT-IR and NMR spectra were identified.

Keywords: Sodium poly(styrene sulfonated); Poly(4-*tert*-butylstyrene); Nuclear magnetic resonance

1. Introduction

Asymmetric neutral/ionic block copolymers, sodium poly(styrene sulfonate)-*block*-poly(4-*tert*-butylstyrene) (NaPSS-*b*-P*t*BS), with long hydrophilic NaPSS blocks and short hydrophobic P*t*BS blocks, form micelles in aqueous solutions [1] and ordered structures at interfaces (air/liquid or liquid/solid interfaces) [2,3]. These self-organized structures are frequent subjects for theoretical [4–6] and experimental studies [7–9]. The first synthesis of this material was reported by Valint and Bock [10], in which NaPSS-*b*-P*t*BS was prepared by selective sulfonation of polystyrene (PS) blocks in PS-*b*-P*t*BS block copolymers, followed by neutralization to yield NaPSS-*b*-P*t*BS. Since many properties of this amphiphilic block copolymer are related to its molecular characteristics, the preparation and thorough molecular characterization of these polymer samples are critical.

Synthesis of model NaPSS-*b*-P*t*BS block copolymers involves two steps [10–12]. The first step is anionic polymerization to create a neutral block copolymer PS-*b*-P*t*BS. The second step is selective sulfonation and neutralization of the PS block to form a NaPSS block. Characterization of the neutral PS-*b*-P*t*BS block copolymer may provide parameters such as degree of polymerization and composition, which can also be used to describe the NaPSS-*b*-P*t*BS products if the sulfonation reaction does not alter the polymer backbone. Many techniques such as size exclusion chromatography (SEC), light scattering (LS), osmometry, and viscometry can be used in the characterization of neutral PS-*b*-P*t*BS. However, they have limitations in the characterization of neutral/ionic block copolymers due to the micellization of these amphiphilic copolymers. Neutral/ionic block copolymers normally have extremely low critical micelle concentrations (cmc), which are lower than the working concentrations for the previously mentioned techniques. Data obtained from such measurements do not directly yield the characteristics of the individual molecules.

Recently, the matrix-assisted laser desorption ionization/time-of-flight/mass spectrometry (MALDI/TOF/MS) technique has been applied to the characterization of such polymers in our laboratory [12,13]. It has been shown that this technique is an effective method for the measurement of molecular weight (MW), molecular weight distribution (MWD) and sulfonation degree of NaPSS-*b*-P*t*BS block copolymers.

Nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopy are traditional techniques used in structural analysis, and they may be used to

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characterize polymer chemical structures after the sulfonation reactions. NMR is extensively used in polymer microstructure characterization [14]; however, NMR studies of sulfonated PS (sPS) are rare [15,16]. The ^{1}H NMR of polystyrene-*co*-poly(styrene sulfonic acid) (PS-*co*-PSSA) in dimethyl sulfoxide (DMSO) solution was reported in a study of ionomers [16]. An NMR investigation on the sulfonation blockness of partially sulfonated PS has recently been published [15]. A weak peak in two-dimensional NMR (2D NMR) spectrum was suggested as a diagnostic marker for sulfonated styrene blocks. Isotactic P*t*BS was also studied by long-range heteronuclear spin locking (HSL) 2D NMR spectroscopy, and the assignment of resonance in ^{1}H and ^{13}C NMR spectra of P*t*BS was given [17].

The FT-IR technique has also been applied in the characterization of sPS [18–20]. A comprehensive survey of IR studies on poly(styrene sulfonic acid) (including its metal salt forms) appeared in 1969 [20]. The IR spectra of PS, poly(styrene sulfonic acid), and the salt form of poly(styrene sulfonic acid) were studied and a complete adsorption bands assignment (4000–600 cm^{-1}) was summarized. The IR spectra of lightly sulfonated PS and syndiotactic PS was reported by Su et al. [19]. In their report, the bands at 1600 and 1582 cm^{-1} were used to normalize spectra due to variations in sample layer thickness. These two extremely localized bands are assigned to the benzene ring stretching vibrations and are insensitive to structural changes associated with sulfonation along the chain [21]. The observation of intensity changes for the band at about 840 cm^{-1} after sulfonation, assignable to CH out-of-plane vibrations for *para*-disubstituted benzene [21], suggests that the SO_3^- group must be predominantly at the *para*-position [19]. Orler et al. [18] used FT-IR to characterize the sulfonation of syndiotactic PS. The appearance of a band at 1175 cm^{-1} was used to confirm sulfonation of PS [19]. Further evidence of sulfonation could be seen, according to their paper, by observing the peaks at 1097 and 1128 cm^{-1}. These bands have been attributed to the in-plane skeletal vibrations of the disubstituted benzene rings. Rigdahl and Eisenberg [22] used bands at about 1200 cm^{-1} (stretching vibration of SO_2 of the sodium salt of sPS) [20] and 700 cm^{-1} (out-of-plane CH deformation on unsubstituted PS) to measure sulfonation levels.

This paper reports the results of FT-IR and NMR experiments on a series of NaPSS-*b*-P*t*BS copolymers and related model homopolymers. By comparison of data on block copolymers with data on model materials, structural information on these NaPSS-*b*-P*t*BS block copolymers was obtained.

2. Experimental section

2.1. Materials

Styrene (S, Fisher, 99%), and 4-*tert*-butylstyrene (*t*BS, Scientific Polymer Products, 95%) were purified by vacuum distillation over calcium hydride (CaH_2, Aldrich, 95%) and dibutylmagnesium (Aldrich, 1.0 M heptane solution) sequentially, according to the literature [23]. The purified monomers were kept in vacuum in glass ampoules with break seals at about − 18 °C. 4-Styrene sulfonic acid sodium salt (Aldrich) was purified by recrystallization twice from a water/acetone solvent mixture. The anionic polymerization initiator *sec*-butyllithium was prepared from *sec*-butylchloride (Aldrich, 99%) and lithium metal powder (Aldrich, 99%). Sulfur trioxide (SO_3, Aldrich, 99%), triethylphosphate (TEP, Aldrich, 99%), sodium sulfite (Fisher, A.C.S. certified), potassium persulfate (Fisher, A.C.S. certified), sodium methoxide (Aldrich, 95%), and solvents (methanol (Fisher, 99.8%), pentane (Fisher, certified), 1,2-dichloroethane (DCE, Aldrich, 99%), tetrahydrofuran (THF, Fisher, certified), deuterated chloroform ($CDCl_3$, Aldrich, 99.8 at.% D), and deuterated DMSO (DMSO-d_6, 99.9 at.% D, Cambridge Isotope Lab., Inc. Andover, MA)) were used as received. Dialysis tubing with MW cutoff 3500 g/mol was purchased from Spectrum Lab (Laguna, CA).

2.2. Polymer synthesis

The precursor PS-*b*-P*t*BS block copolymers were synthesized by anionic polymerization as described previously [10,12]. For convenience a brief description of the polymerization procedure for sample DB307/10 is given as follows. First, the block copolymers were prepared by sequential addition of S (18.3 ml) and *t*BS (0.95 ml) monomers into an evacuated reactor, in which *sec*-butyllithium (0.5 mmol in 2.8 ml hexanes) was used as initiator and purified benzene (250 ml) was used as solvent. The living diblock copolymers were terminated using degassed methanol and were precipitated in methanol. The polymers were dried in a vacuum oven at 70–80 °C overnight (isolated yield about 95%). Triblocks of S and *t*BS were synthesized by the addition of S, *t*BS, and S sequentially. Since S and *t*BS have similar reactivities in anionic polymerization, their living anions can initiate each other rapidly and completely [12]. Radical polymerization of sodium 4-styrene sulfonate (monomer) was conducted in distilled water under reduced pressure by using a redox initiator. Monomer (7.8 g) was dissolved in 48 ml distilled water, then sodium sulfite (0.44 g) and potassium persulfate (0.21 g) were added into the reactor. The reaction solution was degassed twice via the freeze–thaw method on the vacuum line. It was then kept at 20 °C with stirring for 5 min to ensure complete dissolution of reagents before its temperature was raised to 45 °C and was maintained at 45–50 °C for 2 h. The final product was precipitated in 250 ml acetone, and was dried in vacuum at room temperature for overnight (92% isolated yield).

2.3. Sulfonation

Conversion of the precursors to water-soluble polymers was done via selective sulfonation of the S block of the polymers [10]. The general procedure was to place 0.2 equivalent of TEP (dissolved in DCE, 2 g of TEP/100 ml of DCE), into a dry reactor fitted with a mechanical stirrer and two dropping funnels. The solution was cooled to below 0 °C, and 1.0 equivalent of polymer (relative to PS block) dissolved in DCE (5 g of polymer/100 ml of DCE) was placed in one dropping funnel, and 1.1 equivalents of SO_3 (relative to PS block) in DCE was placed in the other dropping funnel. The SO_3 solution was added first at about 1–2 drops per second. Polymer solution was added a few seconds later at the same rate while maintaining strong stirring. A salt water-ice bath was used to keep the temperature below 0 °C during the whole reaction period. The sulfonated polymer precipitated from solution and was washed with pentane. The polymer was dissolved in water (sometimes water and methanol mixtures) and neutralized with sodium methoxide to a pH of approximately 7. The organic solvents (DCE, pentane, and methanol) were removed by rotary evaporation. Polymers were purified by dialysis and freeze-dried. Polymer samples and their characteristics are listed in Table 1.

2.4. Characterization

Polymer MWs were measured by SEC and LS as previously reported [12]. Elemental analysis (EA) was conducted by Atlanta Microlab (Norcross, GA).

NMR characterization. NMR experiments were carried out on Bruker DRX-400 and ARX-300 spectrometers. Precursor (PS-*b*-P*t*BS) block copolymers were dissolved in $CDCl_3$. Water-soluble polymers were dissolved in DMSO-d_6. Mixtures of DMSO-d_6 and $CDCl_3$ up to 8:2 volume ratio were used if necessary to dissolve the polymers. Samples in $CDCl_3$ were analyzed at room temperature, while samples in DMSO-d_6 or mixtures were measured at 358 K. The ^1H and ^{13}C spectra were acquired with recycle times of 5 and 3 s, respectively. Spectra were referenced to residual solvent peaks; the probe temperature was calibrated using neat ethylene glycol.

2D heteronuclear multiquantum coherence (HMQC) data were acquired with a bilinear rotational decoupling (BIRD) pulse sequence in a phase-sensitive mode (tppi) with ^{13}C decoupling during spin–spin relaxation time t_2. 2D heteronuclear multibond connectivity (HMBC) data were acquired in magnitude mode with $^1J_{CH}$ filtering and without ^{13}C decoupling. Both data sets were collected as a 400 (t_1) real and 2048 (t_2) complex points. The t_1 dimension was linearly predicted to 800 points. The data were apodized with various sine functions, and zero-filled to 2k prior to Fourier transformation.

FT-IR characterization. FT-IR spectra of polymer samples were obtained with a Bruker Vector 22 spectrometer. Dilute polymer solutions (5 mg/ml solvent) were prepared in solvent (THF or water) and were deposited on Germanium IR window. They formed thin films upon evaporation of solvent using a tungsten lamp. Further removal of solvent was conducted in a vacuum oven at room temperature overnight. All FT-IR spectra represent an

Table 1
Molecular characteristics of polymer samples

Samples[a]	Structure	$\bar{M}_n$[b] ($\times 10^{-4}$)	PDI[c]	P*t*BS[d] (wt%)	Sulfonation degree[e]
PS	PS	0.4	N.A.	0	0
NaPSS-S	NaPSS	1.29 (M_w)	1.20	0	105
NaP4SS	NaPSS	N.A.	N.A.	0	100
NaPSS100	NaPSS	5.0	1.06	0	100
NaPSS64	NaPSS	1.8	1.07	0	64
NaPSS50	NaPSS	0.96	1.05	0	50
P*t*BS	P*t*BS	0.4	1.07	100	0
P*t*BSS	Sulfonated P*t*BS	0.4	1.07	100	27
DB307/10	NaPSS/P*t*BS	3.4[f]	1.03	4.8	85
TB653/26/233	NaPSS/P*t*BS/NaPSS	11.0	1.05	4.4	97
TB778/23/194	NaPSS/P*t*BS/NaPSS	10.4	1.05	3.4	101
SB10/307b	Star-P*t*BS/NaPSS	64[f]	1.12	4.8	92
TB427/23/204	NaPSS/P*t*BS/NaPSS	7.1[f]	1.02	5.4	100
DB114/4	NaPSS/P*t*BS	1.25	1.07	5.0	97
DB678/38	NaPSS/P*t*BS	8.4[f]	1.09	8.0	86

[a] Homopolymers were named after their structures, combined with sulfonation degree for some NaPSS samples with various sulfonation levels. Block copolymer samples were named after their structures and degree of polymerizations of each block. DB, TB, and SB represent diblock, triblock, and star-block, respectively. The degrees of polymerization of blocks are given in the order of NaPSS and P*t*BS (and NaPSS again in case of triblock copolymer samples).

[b] Values obtained from SEC measurements prior to sulfonation.

[c] Molecular weight PDI values obtained in SEC.

[d] Calculated from monomer feeding.

[e] Calculated from EA.

[f] Values obtained from LS results prior to sulfonation.

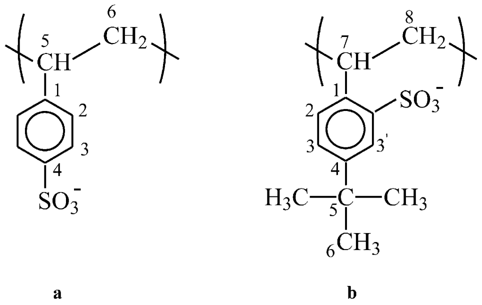
average of 256 scans with a frequency resolution of 2 cm^{-1} and frequency range of 4000–600 cm^{-1}.

3. Results and discussion

3.1. FT-IR measurements

Comparison of FT-IR spectra of PS, NaP4SS, and NaPSS100. NaP4SS was synthesized by radical polymerization using sodium 4-styrene sulfonate monomer. Therefore this homopolymer has sulfonate groups at *para* sites on each repeat unit (Scheme 1). A comparison of PS and NaP4SS FT-IR spectra are shown in Fig. 1. Complete absorption band assignments for both samples can be found in the literature [20]. The OH stretching vibration of H_2O in frequency region 3700–3000 cm^{-1} and H_2O scissor vibration in 1700–1570 cm^{-1} were obvious in NaP4SS FT-IR spectra. The four weak bands in the 2000–1700 cm^{-1} region of PS FT-IR spectrum were absent in NaP4SS FT-IR spectrum. In the frequency range of 1500–600 cm^{-1}, NaP4SS samples yielded very different spectra than PS. The characteristic peaks of NaP4SS samples were found at about 1185, 1130, 1042, 1011, 668, and 639 cm^{-1}, as shown in Fig. 1. The SO_3^- group antisymmetric and symmetric vibrational adsorption peaks can be assigned to the peaks at 1184 and 1042 cm^{-1}, respectively, [20]. Peaks at 1130 and 1011 cm^{-1} can be assigned to the in-plane skeleton vibration of benzene ring and in-plane bending vibration of benzene ring [20]. Orler et al. [18] used peaks at 1175, 1097, and 1128 cm^{-1} to confirm the sulfonation of syndiotactic PS. There was no absorption peak found at about 1097 cm^{-1} in the spectrum of NaP4SS sample. This may be due to the fact that PSSA was used in Orler's study instead of NaPSS, because PSSA showed a peak at 1097 cm^{-1} [23]. The peak at 1175 cm^{-1} was also not observed in our NaP4SS FT-IR spectrum, instead a peak at 1185 cm^{-1} was found.

The FT-IR spectrum of NaPSS100 is also shown in Fig. 1. NaPSS100 was prepared by complete sulfonation of PS homopolymer (EA results showed that its sulfonation degree was 100%). It was observed that NaPSS100 and NaP4SS yielded essentially the same spectrum except for some slight differences in intensities of some bands. This observation suggests that NaP4SS and NaPSS100 have the same structures. In other words, polymers made by polymerization of pure sodium 4-styrene sulfonate and by sulfonation of PS have very similar structures. The SO_3 groups are predominantly attached on the *para*-position of the benzene rings in these samples. This finding is in agreement with NMR results as discussed below.



Scheme 1. Illustration of structures for (a) sodium poly(4-styrene sulfonate), and (b) sulfonated poly(4-*tert*-butylstyrene).

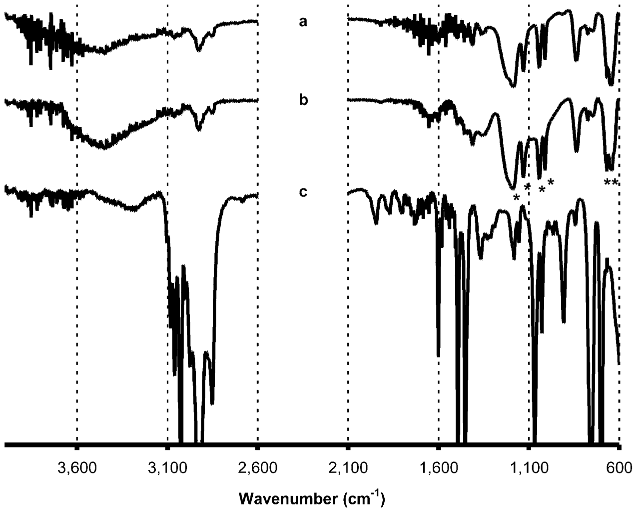


Fig. 1. FT-IR spectra of polymer samples (a) NaPSS100, (b) NaP4SS, and (c) PS. The characteristic peaks of NaP4PSS are indicated by the symbol *.

Effect of sulfonation degree on the NaPSS FT-IR spectrum. In the case of incomplete sulfonation, NaPSS samples made by sulfonation of PS showed a slightly different FT-IR spectrum. Fig. 2 shows FT-IR spectra (1350–600 cm^{-1} region) of NaPSS type polymers at various sulfonation degrees (50, 64, and 100%) as calculated from EA results. Basically these FT-IR spectra are the same except for two bands: one is at 699 cm^{-1}, and the other is at 759 cm^{-1}. These two bands are characteristic bands of PS sample's out-of-plane skeleton bending vibrations of benzene ring and out-of-plane bending vibration of the five –CH– groups in the benzene ring characteristic of the monosubstituted benzene ring (see PS FT-IR spectrum in Fig. 1) [20]. Thus these two bands, especially the band at 699 cm^{-1}, provide a way to check the completion of PS block sulfonation of NaPSS type polymers. It also seems that the intensity of these two peaks, especially for the peak at 699 cm^{-1}, is correlated to sulfonation degree. The lower the sulfonation degree, the greater the intensities of these bands.

In Fig. 2, it is also seen that all samples show peaks at 836 cm^{-1}, which are assignable to CH out-of-plane vibration for *para*-disubstituted benzene [19,20]. This observation supports the idea that sulfonation occurs at the *para*-position on the benzene ring. The relative intensities of these peaks are found to be basically the same for three samples that have sulfonation degrees between 50 and 100%. Another interesting observation is

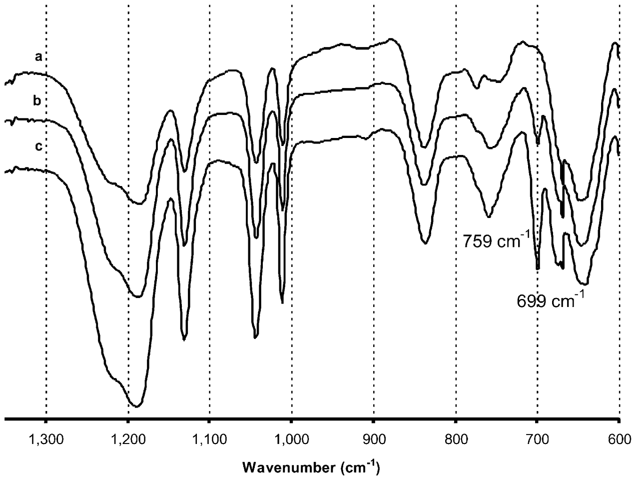


Fig. 2. The effect of sulfonation degree on FT-IR spectra of (a) NaPSS100, 100% sulfonation degree; (b) NaPSS64, 64% sulfonation degree; and (c) NaPSS50, 50% sulfonation degree.

that the FT-IR spectrum for the sample with 50% sulfonation degree is very similar to the spectrum of the sample with 100% sulfonation degree except for the two peaks at 699 and 759 cm^{-1} mentioned earlier. This is surprising because one would expect that, for a sample with 50% sulfonation degree, the FT-IR spectrum would be intermediate to those for NaPSS and PS.

Comparison of PtBSS and PtBS. During NaPSS-*b*-P*t*BS block copolymer sample preparation, it is assumed that P*t*BS is not sulfonated under the employed sulfonation conditions, because the preferred position for sulfonation (*para*-position) is occupied, and PS is available for SO_3 to react with. However, the possibility of P*t*BS being sulfonated cannot be ruled out.[1] To investigate the sulfonation of P*t*BS, P*t*BS homopolymer was sulfonated in a similar manner to that used with PS, and the effect of sulfonation on P*t*BS FT-IR spectrum was studied. Here we believe that the P*t*BS sulfonation level will be greatly enhanced as compared to that of P*t*BS during PS-*b*-P*t*BS block copolymer sulfonation because with P*t*BS homopolymer there is no PS available for SO_3 to attack.

The FT-IR spectra of P*t*BS and P*t*BSS are shown in Fig. 3. The dramatic change in the FT-IR spectra and the presence of characteristic SO_3^- peaks at about 1185 cm^{-1} indicate that P*t*BS was sulfonated. The FT-IR spectra of P*t*BSS in 900–1300 cm^{-1} regions are very similar to the FT-IR spectra of *o*-toluenesulfonic acid found in the literature [23]. This similarity seems to support the NMR finding that the SO_3^- groups are attached to the *ortho*-position on the benzene rings. From EA results, P*t*BSS was found to be partially sulfonated (~27% sulfonation degree based on sulfur content). Quite interestingly, the sulfonated sample is insoluble in both water and chloroform. By comparing the FT-IR spectra of PS,

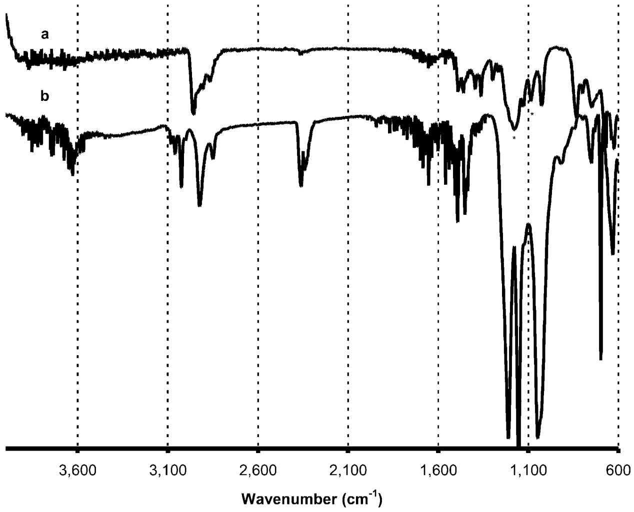


Fig. 3. FT-IR spectra of (a) P*t*BSS and (b) P*t*BS.

P*t*BS, and NaP4SS, the 1085 cm^{-1} peak in the P*t*BSS spectrum was identified as its characteristic peak because no adsorption band was found at this frequency position for PS, P*t*BS, or NaP4SS.

Comparison of NaPSS-b-PtBS samples. Based on the information gained so far, a number of NaPSS-*b*-P*t*BS block copolymer samples were analyzed, and their FT-IR spectra in the 1350–600 cm^{-1} range are shown in Fig. 4. A few interesting observations can be made.

First of all, the sulfonation degree of each sample can be estimated from their FT-IR spectra at about 699 cm^{-1}. These samples except DB678/38 contain similar amounts of P*t*BS block (from 3.4 to 5.4 wt%), but their FT-IR spectra at about 699 cm^{-1} are different. Samples DB307/10 and DB114/4 show small peaks, which that indicate their sulfonation degrees are lower than others. From EA results, it was confirmed that these two samples have lower

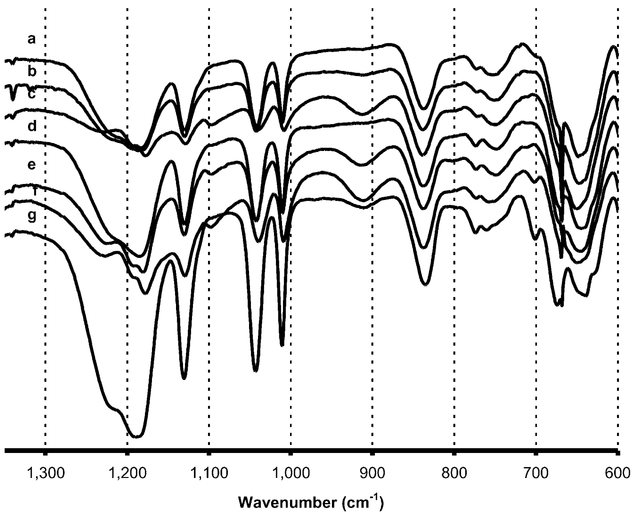


Fig. 4. FT-IR spectra of NaPSS-*b*-P*t*BS block copolymer samples. (a) DB307/10, (b) TB653/26/233, (c) TB778/23/194, (d) SB10/307b, (e) TB427/23/204, (f) DB114/4, and (g) DB678/38.

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[1] Rose et al. [24] report up to 75% sulfonation of P*t*BS homopolymer using sulfonation conditions similar to those employed in this work.

sulfonation degrees than the others (except for SB10/307b, which has a similar sulfonation degree as DB114/4). Sample DB678/38 has a relatively large peak at about 699 cm^{-1} as compared to other samples. Its lower sulfonation degree suggests that this peak is due to incomplete sulfonation; however, the contribution from the strong P*t*BS peak at 697 cm^{-1} (Fig. 3) cannot be ruled out since DB678/38 contains a relatively large amount of P*t*BS (8.0 wt% P*t*BS prior to its sulfonation).

Two more differences among these samples' FT-IR spectra are found at about 1090 and 907 cm^{-1}. These two peaks are strongest in samples TB778/23/194, TB-368/20/173, and DB114/4. Also, for these samples the bands in the 1080–1250 cm^{-1} region look more like triplets than doublets, which is more or less similar to the *o*-toluenesulfonic acid and P*t*BSS FT-IR spectra in the same frequency region. Thus, it is suggested that the occurrence of peaks at 1090 and 907 cm^{-1}, along with the triplet band shape in the 1080–1250 cm^{-1} region, is related to either the sulfonation of the PS block at *ortho*-position or the sulfonation of P*t*BS block. Nevertheless, it is obvious that, for different samples with essentially complete sulfonation of PS blocks (near 100% sulfonation degree), their FT-IR spectra show some differences in their fine band shapes. These differences reflect subtle structural differences. Thus, FT-IR spectroscopy can be used as a valuable diagnostic method in sample preparation and characterization.

3.2. NMR Measurements

The ^{1}H NMR spectra of sulfonated PS samples were obtained (Fig. 5). These samples include NaP4SS, NaPSS100, and a commercial NaPSS standard (NaPSS-S). NaP4SS is used as a reference sample because it was prepared from radical polymerization of sodium 4-styrene sulfonate. Sample NaPSS100 was prepared in our lab by sulfonating homopolymer PS under the same conditions as PS-*b*-P*t*BS diblock copolymers. NaPSS-S was purchased from Polymer Standards Service (Mainz, Germany). It has, according to the supplier, a weight-average molecular weight ($\bar{M}_w$) of 12,900 and polydispersity index (PDI) of 1.20 (Table 1).

In Fig. 5, the huge sharp peaks at 3.0 or 3.3 ppm are due to H_2O, which is difficult to exclude from NaPSS type samples since they are hygroscopic. Other solvent peaks, such as DMSO, $CDCl_3$, and $CHCl_3$, are marked in the spectra. For all the three samples, spectra are essentially identical to each other, which indicate that these samples have very similar structures. In other words, samples NaPSS100 and NaPSS-S have their SO_3^- groups connected at *para*-positions on the phenyl rings, identical to the structure of sample NaP4SS. This confirms the FT-IR findings. One interesting observation is that the peak area of H3 at 7.4 ppm is always slightly larger than that of the peak at 6.4 ppm (about 5% higher) for NaP4SS and NaPSS100. The reason for this is not clear. One possible origin might come from disubstitution of aromatic protons by SO_3Na. However, the aromatic proton of a disubstituted phenyl ring should give a peak in the further downfield region with corresponding intensity, which is not observed. The ratio of peak area of aliphatic protons (H5 and H6) to aromatic proton H2 and H3 of samples NaP4SS and NaPSS100 are 0.75 and 0.74, respectively. These values are very close to 0.75, which is the ratio of aliphatic protons to aromatic protons. The sulfonation degree could be calculated from the peak areas of aliphatic and aromatic protons in the ^{1}H NMR spectrum.

Valint and Bock [10] assumed that the P*t*BS blocks in the NaPSS-*b*-P*t*BS block copolymers were not affected by the sulfonation reaction. However, the chance of sulfonation of P*t*BS cannot be ruled out.[1] An attempt to study the possible sulfonation of P*t*BS has been conducted. Fig. 6 shows the ^{1}H NMR spectrum of P*t*BSS. This P*t*BSS was prepared by sulfonating homopolymer P*t*BS under the same conditions as for NaPSS-*b*-P*t*BS. EA results showed that it was partially sulfonated (about 27% sulfonation degree). In Fig. 6, the peak at about 7.8 ppm is assigned to aromatic proton next to the SO_3^- group, and the peaks at about 7.1 and

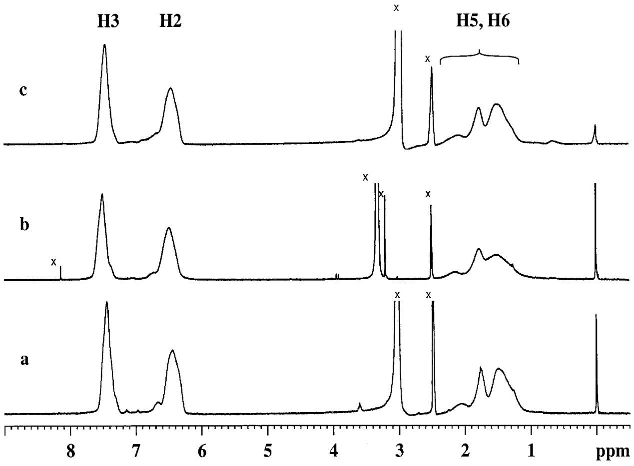

Fig. 5. Proton NMR spectra of sample (a) NaP4SS, (b) NaPSS100, and (c) NaPSS-S. Solvents peaks are marked by the symbol ×.

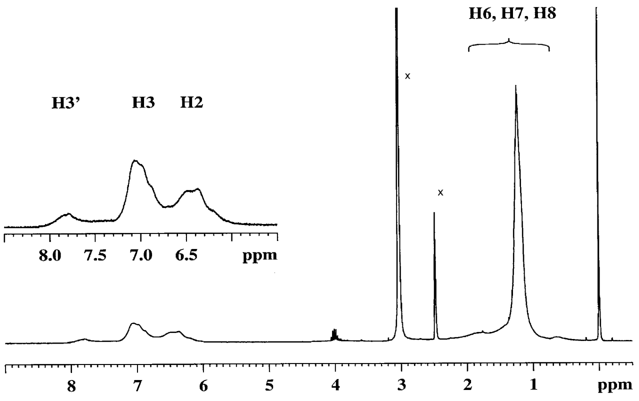

Fig. 6. Proton NMR spectrum of sample P*t*BSS in DMSO-d_6.

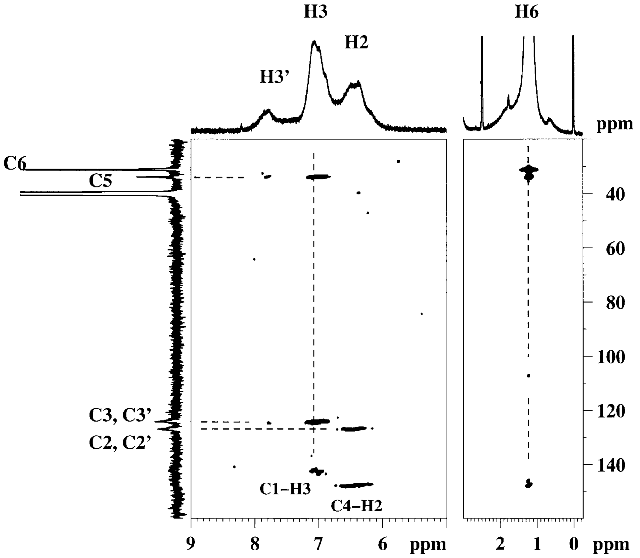

Fig. 7. HMBC 2D NMR spectra of P*t*BSS in DMSO-d_6.

6.4 ppm are due to other aromatic protons on both sulfonated and unsulfonated phenyl rings. Since there is no peak at 7.8 ppm in the ^{1}H NMR spectrum for the NaPSS sample, the peak at 7.8 ppm in the ^{1}H NMR of sulfonated P*t*BS could be used as a potential diagnostic marker for sulfonation of the P*t*BS block in NaPSS-*b*-P*t*BS sample.

2D NMR spectra (HMQC and HMBC) of P*t*BSS were also measured (Figs. 7 and 8). Peak assignments of P*t*BSS were made based on these HMBC and HMQC 2D NMR spectra. It was found that the SO_3Na group is mainly attached at the C2 position (Scheme 1). The FT-IR spectrum of this material also shows evidence to support this assignment.

The ^{13}C NMR spectra of NaP4SS and NaPSS-S are very similar except for the fine structure of the C1 peak (Fig. 9).

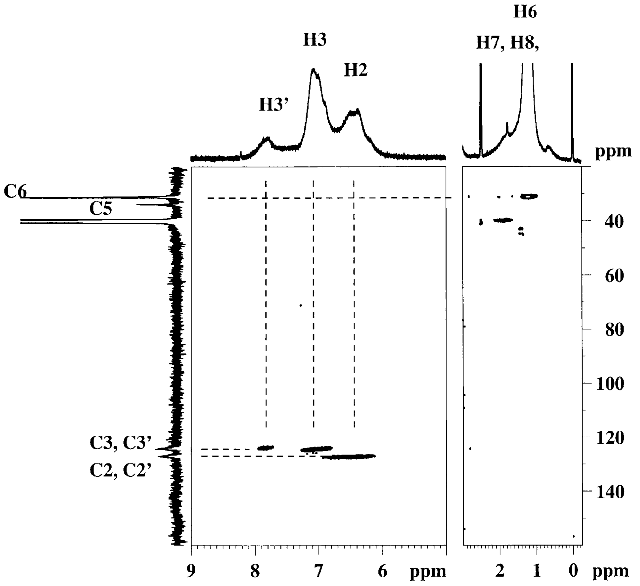

Fig. 8. HMQC 2D NMR spectra of P*t*BSS in DMSO-d_6.

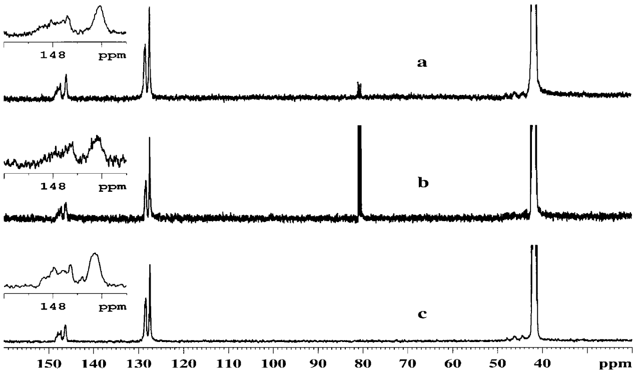

Fig. 9. ^{13}C NMR spectra of (a) NaPSS100, (b) NaPSS-S, and (c) NaP4SS in DMSO-d_6.

Since for PS the C1 peak in ^{13}C NMR is affected by the tacticity, it is believed that the difference in C1 peaks in Fig. 9 is also related to polymer tacticity. Further investigation is needed because the SO_3^- effect on the C1 peak in the ^{13}C NMR spectrum is not clear. The assignments of peaks in NaP4SS ^{13}C NMR were confirmed by their 2D NMR spectra (not shown).

A typical ^{1}H NMR spectrum for a NaPSS-*b*-P*t*BS block copolymer sample (in this case, DB114/4) is shown in Fig. 10. The peak at about 7.4 ppm confirms the sulfonation of the PS block. The peak at about 7.0 ppm is due to aromatic protons H3, H4 in either P*t*BS blocks, or unsulfonated PS units. No evidence for sulfonation of the P*t*BS blocks (no peak at about 7.8 ppm) was found for any of the NaPSS-*b*-P*t*BS block copolymers.

4. Conclusions

The FT-IR spectra of model polymers PS, P*t*BS, NaPSS, P*t*BSS, and a number of NaPSS-*b*-P*t*BS block copolymers were obtained. From FT-IR analysis, it was found that the sulfonation reaction converts PS to NaPSS, in which SO_3^- groups are predominantly attached at *para* sites on the benzene rings. Incomplete sulfonation caused two bands to appear at 699 and 758 cm^{-1} for NaPSS homopolymers. The

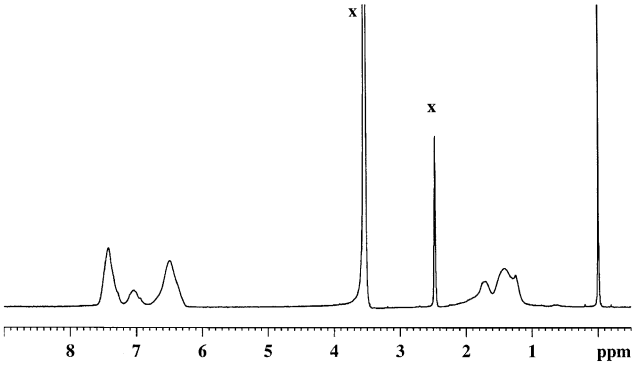

Fig. 10. ^{1}H NMR spectrum of DB114/4 in DMSO-d_6. Solvent and water peaks are marked by the symbol ×.

more efficiently the polymer was sulfonated, the lower the intensities of these two bands. For 100% sulfonation, there was no 699 cm^{-1} peak and no small peak at 758 cm^{-1}. These bands also can be used to estimate the sulfonation degree for NaPSS-*b*-P*t*BS block copolymers with similar P*t*BS contents. For sulfonated NaPSS-*b*-P*t*BS copolymers, some variations in their FT-IR spectra were observed at about 907, 1090 cm^{-1} wavelength as well as in the 1180–1250 cm^{-1} region. It is suggested that these variations are due to structural deviations from perfect model NaPSS-*b*-P*t*BS, and thus FT-IR can be used as a quality control method in sample preparation and characterization.

^{1}H, ^{13}C, and 2D NMR spectra of NaPSS, P*t*BSS, and block copolymer samples were obtained. By comparing the spectra of NaP4SS made from polymerizing 4-styrene sulfonate sodium salt with NaPSS100 made by sulfonation of PS followed by neutralization with sodium methoxide, it was found that they have essentially the same structure. The SO_3^- group is, within the limits of detection, exclusively attached at the *para*-position on the phenyl rings. P*t*BSS was found to be partially sulfonated (27%). This reveals that it is more difficult to sulfonate P*t*BS than to sulfonate PS. The P*t*BSS had the SO_3^- group attached at the *ortho*-position. The aromatic proton H3′ was seen at about 7.8 ppm, which could be used as a diagnostic peak for P*t*BSS. C1 peaks in ^{13}C NMR of NaP4SS and NaPSS-S showed different patterns. Finally, ^{1}H NMR spectra of block copolymers were recorded. No evidence was observed to suggest sulfonation of the P*t*BS block in these copolymers.

Acknowledgments

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