Solid-State ^{13}C NMR Analysis of Sulfonated Polystyrene

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Abstract: *Atactic polystyrene (PS) has an amorphous structure. Compounds such as H_2SO_4 and SO_3 are commonly used as sulfonating agents for various polymers, including PS. The main purpose of this work is to study chemical structural changes in PS arising from sulfonation through DSC analysis and NMR spectroscopy. An increase in the glass transition temperature (Tg) of sulfonated polystyrene and a decrease of proton relaxation time in the rotating frame ($T_1\rho H$) in relation to pure polystyrene were observed. These findings indicate a reduction in the mobility of chains due to strong interaction between the polymers. The variation of heat capacity (ΔCp) was evaluated to confirm strong interactions with ~SO_3H groups.*

Resumo: *O poliestireno atático apresenta estrutura amorfa. Compostos tais como H_2SO_4 ou SO_3 são comumente usados como agentes de sulfonação para vários polímeros, principalmente para o PS. O objetivo deste trabalho é estudar as mudanças estruturais provocadas no poliestireno (PS) devido à reação de sulfonação, empregando a análise térmica por DSC e a espectroscopia de RMN. Foi observado um aumento na temperatura de transição vítrea do poliestireno sulfonado e uma diminuição no tempo de relaxação do hidrogênio no referencial rotatório ($T_1\rho H$) em relação ao PS puro, indicando a redução da mobilidade das cadeias devido a forte interação entre os polímeros. A variação da capacidade calorífica (ΔCp) foi calculada a fim de confirmar as fortes interações com os grupos ~SO_3H.*

Introduction

The sulfonation of polystyrene with sulfonic acid groups has been demonstrated to be an effective route to compatibilize polystyrene with various nitrogen-containing polymers (for example, polyamides, conducting polymers: polyaniline).[1] Because of their interesting chemical and mechanical properties, these compounds have a number of industrial applications, such as , in the production of compatible blends of non-miscible polymers, ion exchange materials, membranes for reverse osmosis and ultrafiltration.[2] Ever since, sulfonated polystyrene has been growing in various industrial, domestic and medical applications.[3,4] It also has been studied as a membrane for several electrochemical uses, such as fuel cells.[5]

Sulfonation of polystyrene has been studied by a number of researchers[3,4,6]; but data on the relationship between the chemical structure and properties of this polymer are scarce. What is known is that such relationship is based on the

microstructures of each polymer. However, it is important to consider inter and intramolecular phenomena, as well as the microstructures and molecular dynamic motions of these polymers for a better understanding.

Solid-state nuclear magnetic resonance spectroscopy (NMR) is a powerful analytical technique in materials science, especially for the characterization and investigation of the molecular dynamic interaction process of polymers.[7] Heatley[8] investigated in detail the structure of PS in solution, measuring T_1 and T_2. Information about the structure as well as the molecular dynamics can be obtained to establish correlations between the microscopic structure and macroscopic properties.

The main purpose of this work is to study the structural changes in PS, arising from sulfonation, and also to characterize this polymer through differential scanning calorimetry(DSC) and NMR spectroscopy.

Experimental

Polymer preparation

The starting polymer was an atactic PS (Piramidal Termoplásticos) with $\overline{M_n} = 33.000$ g.mol^{-1} and $\overline{M_w}/\overline{M_n} = 4.9$ and was used as received. Sulfuric acid (95-97 %, Merck), acetic anhydride (Synth, p.a.), dichloromethane (Synth, p.a.), 2-propanol (Synth, p.a.), NaOH (Vetec), methanol (Synth, p.a.) and $KHC_8H_4O_4$ (Qeel, p.a.) were used as received without further purification.

Polystyrene was sulfonated in CH_2Cl_2 at 40°C with acetyl sulfate according to our patented procedure.[9] The main steps for sulfonation PS were as follows:

Acetyl sulfate solution preparation

This solution was prepared by mixing a fixed amount of dichloromethane and acetic anhydride under inert atmosphere (N_2). The solution was cooled to 0°C and 95-97% sulfuric acid was carefully added. This reaction mixture (Figure 1a) was stirred until a homogeneous and clear solution was obtained at room temperature. During the preparation, an excess of acetic anhydride was used to scavenge any trace of water, if present. The acetyl sulfate was freshly prepared prior to each sulfonation reaction.

Sulfonation reaction

Different amounts of PS were dissolved in CH_2Cl_2 (different volumes) in a three-neck round-bottomed flask (6 L) equipped with mechanical stirring, thermometer and separator funnel. The flask containing the solution was heated to 40°C in order to obtain total solubilization of PS and purged with N_2 for 30 min. A freshly prepared acetyl sulfate solution was added using the separator funnel. The reaction mixture (Figure 1b) was maintained at 40 ^{o}C under stirring for 2 h. The solution became clear after adding the sulfonation agent. The reaction was interrupted by adding an excess of 2-propanol for 30 min and then cooling to room temperature. Finally, the sulfonated polymer was isolated.
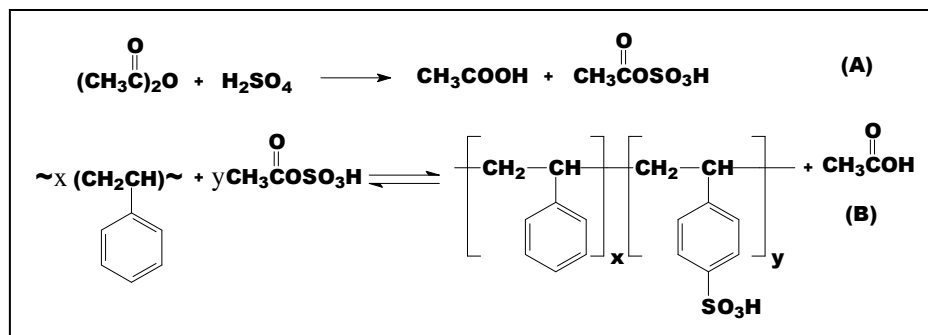
Figure 1. Reaction scheme of homogeneous sulfonation: (A) acetysulfate generation and (B) sulfonation of PS.

PS-SO₃H isolation

The method of isolating PS-SO$_3$H was dependent on the sulfonation level.[4] PS-SO$_3$H was precipitated by dripping the preparation solution into a large volume of boiling water, followed by washing several times with water (to eliminate the solvent and hydrolyze the acetyl sulfate). Afterwards, the product was filtered and dried under vacuum up to constant weight. The PS-SO$_3$H was stored in a desiccator containing CaCl$_2$, because of its extremely hygroscopic nature.

Sulfonation level determination

The sulfonation level of PS-SO$_3$H samples was determined by titration with a standard 0.01 mol L^{-1} NaOH solution in methanol. All titrations were carried out by dissolving 150 mg of PS-SO$_3$H in 15 mL of methanol. The sulfonation degree (x) is expressed as mole percent of the sulfonated styrene repeating units, PS-xSO$_3$H. In this work, the sulfonation degrees used were 12.0, 22.0 and 25.0 mole %.

DSC measurements

DSC measurements were performed in a TA Instruments 2100 analyzer from 30 to 250°C at 10°C min^{-1} under N$_2$ and using approximately 10 mg of sample. All samples were submitted to a first heating stage (30 to 250°C at 10°C min^{-1}) followed by an isotherm for 5 min at 250°C, cooling to 30°C at 10°C min^{-1}, isotherm for 5 min at 30°C and a second heating cycle (30 to 250°C at 10°C min^{-1}), to evaluate irreversible transitions.[10]

NMR measurements

Solid state NMR spectra were obtained on a Varian Unity plus 300 spectrometer operating at 75.4 MHz for ^{13}C. All NMR experiments were carried out at probe room temperature. A zirconium oxide rotor of 5 mm diameter with Kel–F caps was used to acquire NMR spectra and at a spinning speed of 5 kHz. The aromatic signal of hexamethylbenzene was used to determine the Hartmann–Hahn condition for cross-polarization and to calibrate the carbon chemical

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shift scale (methyl group carbons were 17.3 ppm). Cross-polarization with magic angle spinning (CP/MAS) ^{13}C NMR spectra were recorded with 5 s of delay between 90° pulses (6.0 μs). The acquisition time was typically 50 ms; spectral width of 50 kHz; 400 scans were recorded for each spectrum. For proton relaxation time in the rotating frame ($T_1\rho$H) measurements, we used the normal cross-polarization pulse sequence. The magnetization initially builds up to a maximum due to de carbon-proton dipolar interactions, and the signal decays exponentially to equilibrium with time constant $T_1\rho$H [11]. Thus $T_1\rho$H can be obtained from a semilog plot of the intensity as a function of spin-locking time (τ) after the signals have reached their maximum intensity.[12] The spin-lock time was set up from 0.2 to 20 ms (0.2, 1.0, 2.0, 4.0, 8.0, 10.0 and 20.0 ms). NMR analyses were carried out at room temperature and the sample did not undergo any thermal treatment.

Results and Discussion

DSC measurements

DSC curves for PS and PS-SO$_3$H are shown in Figure 2. Both samples of PS-SO$_3$H show an endothermic peak at 130°C in the first heating, which could be assigned to the presence of sulfonated groups in the polymer chains. As expected, they cannot be assigned to crystalline melting because X-ray diffraction analysis indicates that both PS-SO$_3$H samples are amorphous.[4]

This behavior cannot be assigned to the melting of pure PS either, because PS is also amorphous. So, this endothermic peak could be simply due to the relaxation process. These transitions are irreversible, as shown in Figures 2a and 2b for the second heating run. In contrast, the glass transition temperature of PS-SO$_3$H is shifted to higher temperatures, as compared to pure PS (from 100 to 140°C).To elucidate this phenomenon, we evaluated the variation of heat capacity (ΔCp, Table 1). The decrease of ΔCp observed during glass transition for these samples can be considered as an indicator of the increase of structural rigidity of the materials as a function of the increase of the amount of sulfonic groups.[13]

NMR ^{13}C chemical shift

Figure 3 shows the ^{13}C CP/MAS NMR spectrum of commercial PS recorded at room temperature. To correctly assign the signals of PS we used the previously described data in the literature.[14,15] Resonances at 146 and 128 ppm were assigned to non-protonated and protonated aromatic carbons, respectively. Methylene and methine carbon resonances were ascribed to signals at 46 and 41 ppm, respectively.

All observed resonance lines were very broad, as the material is an amorphous polymer. Generally, atactic polyolefins are non-crystalline because of the lack of long regular stereoregularity. In the case of non-crystalline polymer, the chemical shift would be observed at some averaged position between *trans* and *gauche* conformations.[16] Nakoaki *et. al.* have shown that the methylene signal of syndiotactic PS (sPS), atactic PS (aPS), and isotactic PS (iPS) produced distinguished peaks in NMR

spectra at 46.0, 45.6, and 45.0 ppm, respectively. In our measurements, methylene

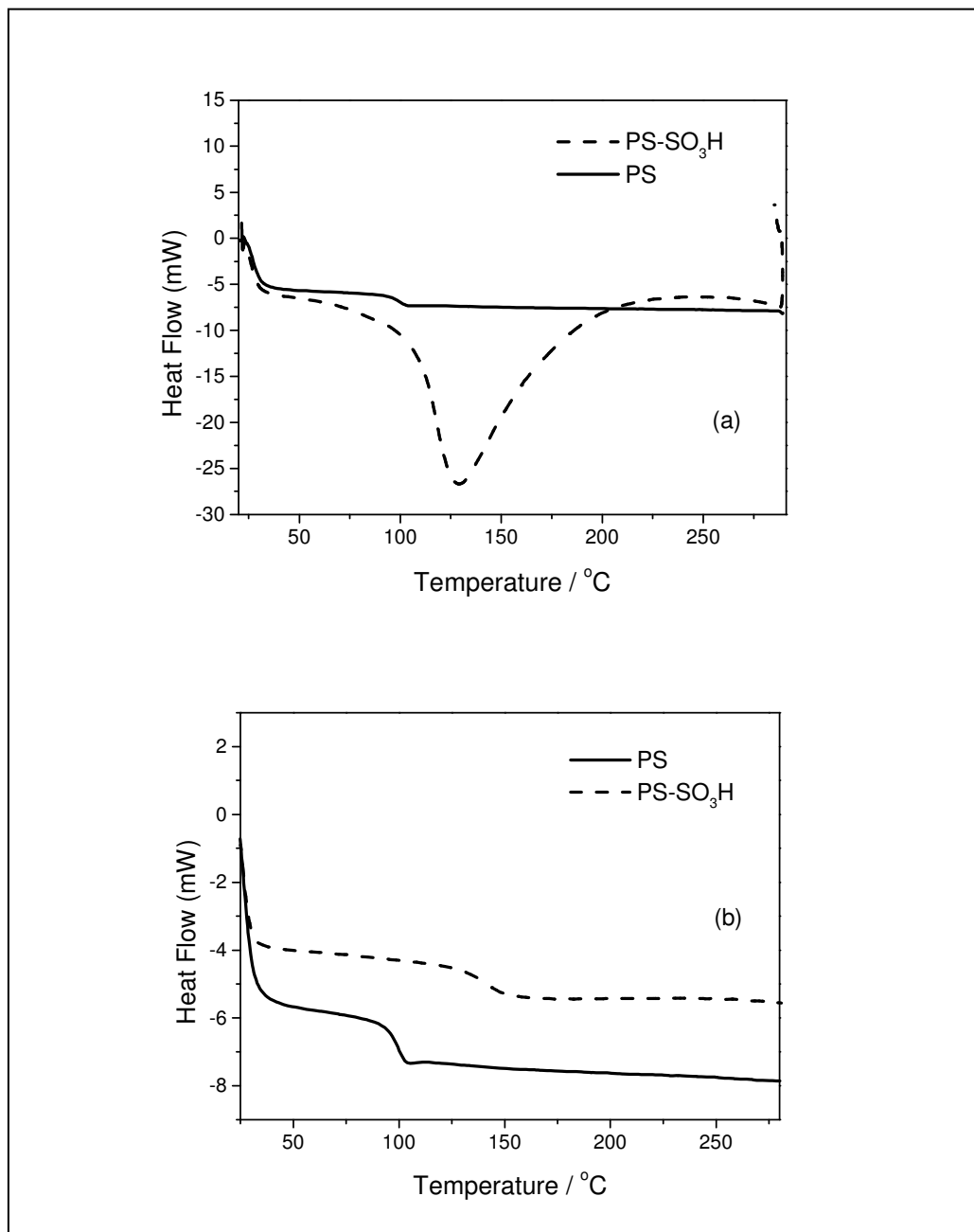signals appeared as a small shoulder at ca. 45 ppm[16], confirming that the polymer is a PS.

Figure 2. DSC curves for PS and PS-22SO$_3$H: (a) first heating run and (b) second heating run.

Table 1. DSC results for PS and PS- 22.0SO$_3$H.

Samples	T_g [a]/ °C	C_p (below[b]) / (J/g °C^{-1})	C_p (after[b]) / (J/g °C^{-1})	ΔC_p [a] / (J/g °C^{-1})
PS	98.44	1.17	1.93	0.33
PS-22.0SO$_3$H	139.70	0.87	1.51	0.28

[a] calculated at second heating run (DSC curve); [b] calculated from heat flow below and after glass transition according to ASTM E 1269-95.
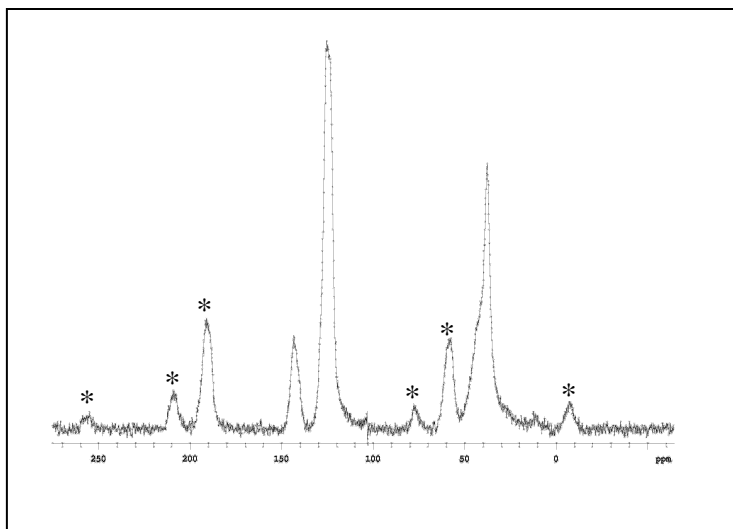
Figure 3. MAS ^{13}C spectrum of PS pure (* spinning side bands).

The NMR ^{13}C spectrum after the sulfonation reaction is shown in Figure 4. This spectrum clearly shows a new signal at 139 ppm. It can be assigned to the chemical shift of the carbon bonding to the SO$_3$ group[17], as expected, to the sulfonated polymer. Methylene, methine and aromatic carbon, except for the carbon substituting the sulfonated group, were not or only slightly influenced by the presence of this group. Signals width did not allow us to make small changes to the electronic density and carbon chemical shift. In this way, the signals in PSS spectra are an average of both polymer PSS and PS.

Measurements of $T_1\rho$H relaxation times

The plots of the $T_1\rho$H measurements of selected carbons in pure PS and PSS are given in Figure 5, and the corresponding $T_1\rho$H values are summarized in Table 2. The relaxation process of $T_1\rho$H follows an exponential function $\ln[M(\tau)/M_0] = -\tau/ T_1\rho$H, where M_0 is the maximum magnetization, M(τ) is the magnetization in τ time and the $T_1\rho$H values can be determined from the slopes in the plots of $\ln[M(\tau)/M_0]$ against τ.[18]
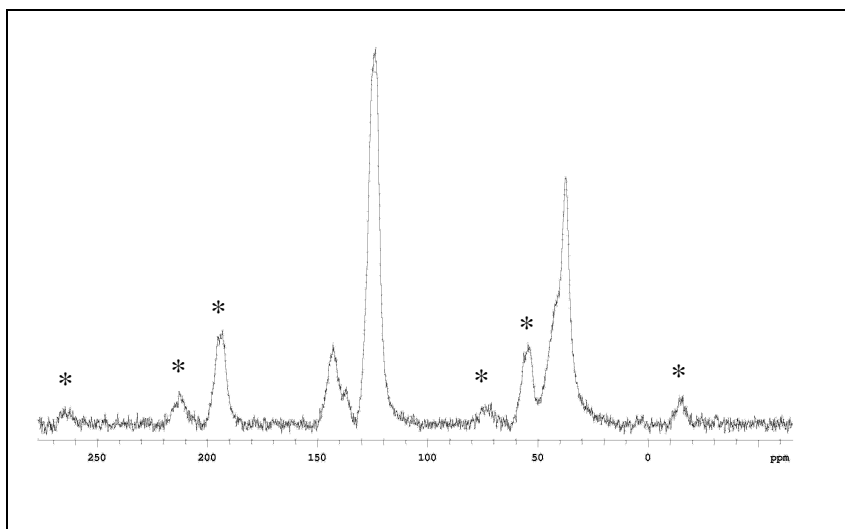
Figure 4. .MAS ^{13}C spectrum of the PS-22SO$_3$H sample.

(a)   (b)
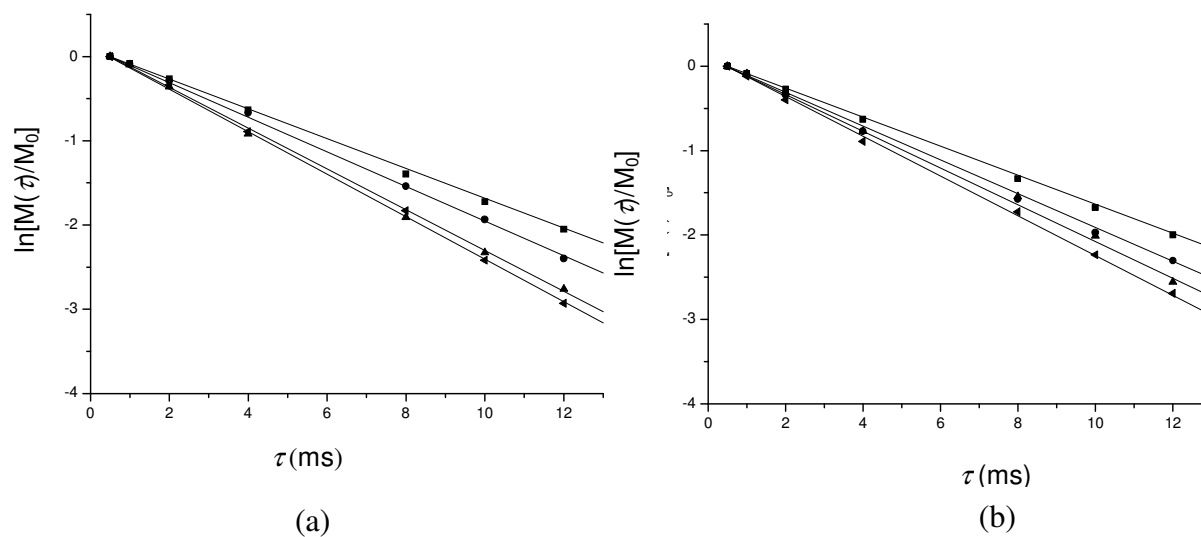
Figure 5. Logarithmic plots of ^{13}C resonance intensities as a function of spin-lock time τ for PS (■), PS-12SO$_3$H (●), PS-22SO$_3$H (▲) and PS-25SO$_3$H (◄) at room temperature; (a) for the signal at 41 ppm and (b) for the signal at128 ppm. The slope yields the proton relaxation time in the rotating frame $T_1\rho$H.

Table 2. Proton relaxation time in the rotating frame values for ^{13}C of PS and PS-xSO$_3$H.

Group	$T_1\rho$H (ms)			
	PS	PS-12SO$_3$H	PS-22SO$_3$H	PS-25SO$_3$H
C methylene-methine	5.6	4.8	4.2	4.0
C protonated aromatic	5.8	5.0	4.8	4.2

estimated error ≤ 5%

Analyzing $T_1\rho$H values through the slopes we observed that the carbons showed different values depending on the sulfonation degree. They can be attributed to the fact that the microstructure has different molecular mobility and consequently belongs to different domains. Comparing $T_1\rho$H values to pure PS with different PS$_x$-SO$_3$H, we find a significant decrease of this parameter. For rigid polymer systems, i.e. below glass transition temperatures (T$_g$), $T_1\rho$H provides information about the level of heterogeneity and mobility. Under the condition of efficient spin diffusion[19], $T_1\rho$H can be directly related to the sizes of molecular domains[20], and the decrease of molecular mobility leads to a reduction of $T_1\rho$H values, due to longer time to magnetization transfer from ^{1}H to ^{13}C. The smaller values of $T_1\rho$H indicated that the presence of the sulfonic group in the PS polymer chain causes an increase of rigidity (Table 2). This result shows that the ~SO$_3$H group acts like a crosslinking agent of PS polymer. The sulfonation reaction could be also accompanied by the sulfone formation by following crosslinking reaction between two sulfonic groups of different PS-SO$_3$H units either by intermacromolecular or intramacromolecular mechanisms.[21] The most probable crosslinking reaction mechanism is shown in Figure 6. The tendency to crosslinking reaction is probably increased with increasing content of sulfonic group and also with increasing concentration of the sulfonating agent in the polymer solution and also with increasing reaction temperature.[21]
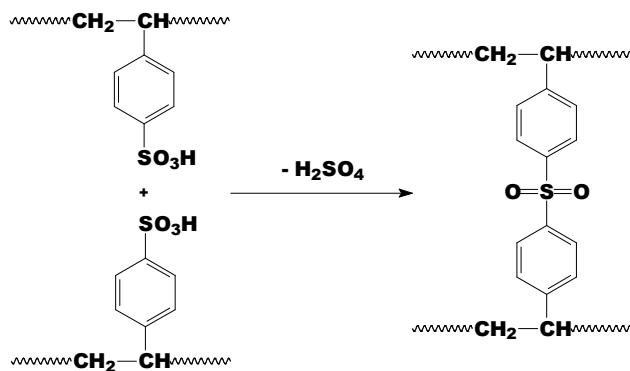
Figure 6. Crosslinking reaction of PS-SO$_3$H.

Previous studies revealed that yields near 30% of sulfone were obtained for reactions at a temperature range from 70 to 80 ^{o}C and the sulfone content increases to ca. 50%, when the reaction was carried out within the interval from 150 to 200 ^{o}C. The sulfone yield was reduced by sulfonation with liquid SO_3 at about -10 ^{o}C, or by addition of acetic acid.[21] This evidence corroborates the results obtained from DSC curve analyses.[4]

4. Conclusion

We studied the structural changes in PS arising from sulfonation and also their characterization through DSC and NMR spectroscopy. The glass transition temperature of sulfonated polystyrene increases in relation to pure PS, and ΔC_p was evaluated in order to confirm strong interactions with $\sim SO_3H$ groups. We measured $T_1\rho H$ of the protonated carbon through solid state CP/MAS, increasing the spin-lock time. The $T_1\rho H$ values obtained for PSS samples were smaller than those for pure PS. These results make it possible to obtain information on the polymer microstructure, showing that the introduction of the sulfonic group led to a decrease of PS molecular mobility.

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