Dynamics of Sulfonated Ionomers in the Solid State: Inelastic Neutron Scattering Studies

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ABSTRACT: An inelastic neutron scattering study was performed on atactic and isotactic polystyrene (PS) and sodium sulfonated polystyrene. Vibrational modes due to the ring and chain moieties were identified by the process of selective deuteration. It was found that the process of sulfonation has a very similar effect upon the spectrum of isotactic PS as that observed in atactic PS. A new mode appearing at 500 cm^{-1} upon sulfonation was detected. This is interpreted as a mixed mode of a benzene ring vibration and a phonon wing. The results indicate that the process of sulfonation results in releasing a low-frequency "breathing mode" between the chains. These results are consistent with our structural investigations using spin-polarized neutrons and shed new light on the process of microphase separation in ionomers.

1. Introduction

Ion-containing polymers (ionomers) possess physical properties very different from those of their "parent" (neutral) polymers. Changes occur at a relatively low level (<10 mol%) of ionic group content and are attributed to both intra- and intermolecular Coulombic interactions. The vast body of data accumulated in recent years on these systems was interpreted as showing the effect of ion pair aggregation and clustering.[1,2] Such multiplets give the polymer properties similar to those observed in a cross-linked system. These property modifications are, however, due to physical interactions rather than chemical bonding. It is thought that they tend to form larger aggregates with increasing ionic content. Although a general picture of ionic aggregation is accepted, the details are still a subject of dispute, especially about whether the ionic species form a separate microphase.[3] The ultimate aim of fundamental studies carried out on an ionomer system is to find a link between macroscopically observable properties, (e.g., elasticity and viscosity) and chain microstructure.

As a first step in this direction it is easier to begin with an investigation of selected properties on a microscopic level. Inelastic neutron scattering (INS) affords an insight into the dynamics via the scattering law $S(Q,\omega)$, which is related to the density of states and the mean square displacement of the scattering atom in its normal mode ω. Because of the high incoherent scattering cross-section of the hydrogen compared to those of the other atoms (80 barns for H compared to 0.001 barn for C), actually the vibrational spectrum of hydrogen was measured. This type of measurement is usually carried out at low temperatures, since with increasing temperature the higher levels are populated according to the Boltzmann distribution. This results in a smearing out of the spectra and the corresponding difficulties in their assignment.

Despite the appearance of a number of commercially important ionomers, sulfonated polystyrene (SPS) neutralized with different metal cations is often selected as a model system. We have chosen to study the dynamics of sodium sulfonated polystyrene (Na-SPS) in comparison with the dynamics of polystyrene (PS) using an indirect geometry time-of-flight spectrometer. To this end, we have compared spectra as a function of polymer conformation, selective deuteration of the chain and the ring, and the degree of sulfonation.

2. Experimental Section

(a) Sample Preparation. Typically, the various deuterated polystyrenes were obtained through emulsion polymerization of the deuterated styrene monomer using potassium persulfate as the initiator and sodium lauryl sulfate as the surfactant. Precautions were taken to obtain high molecular weight products.

For example, a mixture of 90.0 mL of distilled water, 10.0 g of styrene-α,α,β-d_3, 1.0 g of sodium lauryl sulfate, and 0.1 g of potassium persulfate was introduced into a 500-mL- four-neck flask, vigorously agitated, degassed with argon gas, and heated to 50 °C for 24 h. The whole polymerization process took place in the argon atmosphere and is known to produce atactic polymer. Appropriate care was taken to eliminate any minor amount of residue surfactant. Subsequently the polymer was isolated from the emulsion by a large excess of acetone and dried in a vacuum oven at 65 °C for 48 h. Sulfur analysis showed negligible surfactant concentration. This polymer is labeled DH in Table I, where other samples used in this experiment are listed. All materials were characterized with gel permeation chromatography, with their corresponding weight-average molecular weights M_W and polydispersity M_w/M_n also listed in Table I.

These selectively deuterated materials were then sulfonated. For example, the polymer denoted DH74—a sodium poly(styrene-α,α,β-d_3) ionomer Na-SPS—was obtained by dissolving 2.7 g of poly(styrene-α,α,β-d_3) DH in 50.0 mL of 1,2-dichloroethane (1,2-DCE) at 25 °C. The resulting polymer concentration is 5.4 g/dL. After this solution was heated to 50 °C, 0.3 mL of acetic anhydride and 0.17 mL of concentrated sulfuric acid were added. The solution was continuously stirred for 1 h at 50 °C.

The reaction was terminated by adding 0.45 g of sodium acetate dissolved in a mixture of 4.5 mL of methanol and 0.3 mL of water, which also neutralized all free acids. The filtered and neutralized ionomer was isolated by the steam stripping procedure for 1 h. The ionomer was dried in a vacuum oven at 100 °C for 48 h. To calculte the sulfonation level, Dietert sulfur analysis was used to measure the sulfonation level. For this polymer, the sulfonate content was 7.4 mol % (2.06 wt % sulfur).

The isotactic polystyrene was prepared according to the procedure of Natta.[4] The resulting polymer is regular but still contains a few percent atactic component. The crystallinity was eliminated through a process of quenching from the melt phase (260 °C). The quenched polymer was subsequently dissolved in boiling toluene and then filtered and precipitated into vigorously stirred methanol. The atactic polystyrene component was eliminated via Soxhlet extraction for 96 h with methyl ethyl ketone. The remaining polymer was then dried in a vacuum

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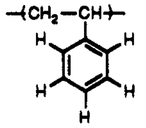
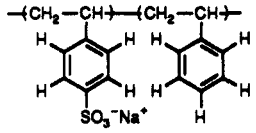
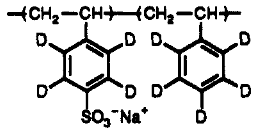
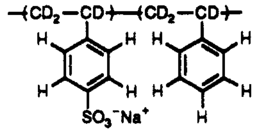
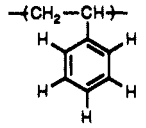
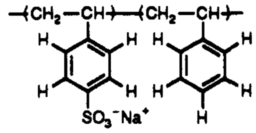
Table I[a]

sample	code	mol wt (M_w/M_n)	structure of monomer	av mol wt per monomer	σ_{inc} [b] weight/g
neutral PS (C_8H_8), fully hydrogenous	S_1, HH	600 000 (1.06)		104	639.28 50.87 b/sr 0.48
3.9 mol % sulfonated, fully hydrogenous	S_2, HH	600 000 (1.06)		107.98	636.23 50.63 b/sr 0.32
6.3 mol % sulfonated, ring deuterated	S_3, HD	1.171×10^6 (6.6)		110.68	249.95 19.89 b/sr 0.32
7.4 mol % sulfonated, chain deuterated (α,α,β-d_3)	S_4, DH74	2.107×10^6 (2.4)		117.77	399.91 31.82 b/sr 0.32
isotactic PS, neutral		2.6×10^6 (3.6)			639.28 50.87 b/sr 0.17
1.2, 8.8, and 10.5 mol % sulfonated isotactic PS					similar to S_2, HH

[a] b/sr = barn/steradian where 1 b = 10^{-28} m^2.

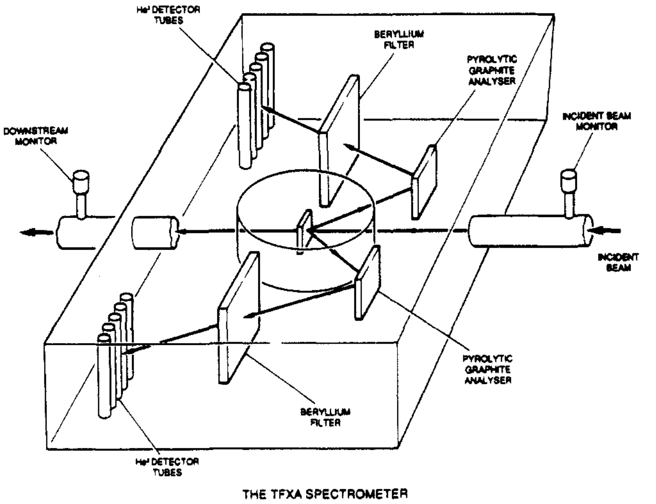


Figure 1. Schematic drawing of the TFXA spectrometer.

Table II
Assignment of Vibrational Frequencies (cm^{-1}) from INS Data

isotactic PS	atactic PS	vibration type
184		?
	200	ring
224		?
248		?
	264	chain
272		?
320	320	chain & ring
403	403	ring
496		?
560	560	chain & ring
608	608	chain & ring
696	696	ring
752	752	ring
840	840	ring
912	912	ring
976	976	ring
1030	1030	ring
1070	1070	ring
1180	1180	ring
1340	1340	chain
1460	1460	chain
1500		?

oven at 60 °C for 24 h. This procedure produces an ultrahigh isotacticity (99.9%).

The characteristics of other ionomers used in this study are listed in Table I.

(b) Neutron Scattering Measurement. Measurements were carried out on the time-focused crystal analyzer TFXA, an indirect geometry time-of-flight inelastic scattering spectrometer[5] (Figure 1) at the spallation source ISIS, Rutherford Appleton Laboratory. To achieve good count rates and good energy transfer resolution, this instrument uses a time-focused pyrolytic graphite analyzer. In TFXA the sample and detector arrays are in the same plane, with the analyzing crystal set parallel to this plane. All detected neutrons have the same time-of-flight after scattering in this inverse geometry. In addition to time focusing, the Marx principle is used to provide energy focusing, which reduces the positional uncertainty in analyzing energy E_2. The energy transfer range covered in these experiments was 2–500 meV (corresponding to 16–4000 cm^{-1}). The energy of the analyzer is 32 cm^{-1}, and above this energy, the scattering vector of detected neutrons is practically independent of the scattering angle. Below 32 cm^{-1}, there is a mixture of diffraction and inelastic lines, since one cannot assume that the energy of the detected neutrons is small compared to the incident energy.

We have investigated both atactic and isotactic polystyrene samples in the powder form, denoted as a-PS and iso-PS, respectively. The atactic ionomers (denoted a-SPS) were in-

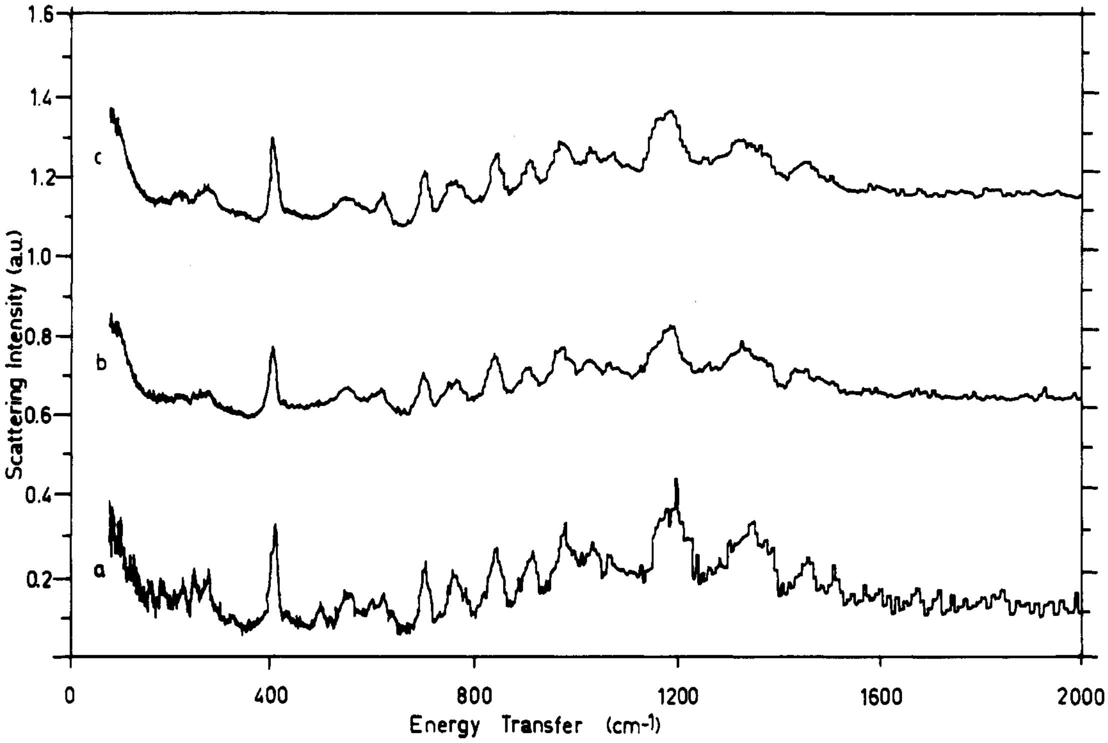


Figure 2. INS spectra measured on TFXA. Energy transfer for (a) isotactic polystyrene, (b) 10.5 mol % sulfonated isotactic PS, and (c) atactic PS.

vestigated in the fully hydrogenous form and also in their chain- and ring-deuterated forms. The isotactic, fully hydrogenous polystyrene ionomers (denoted iso-SPS) were studied as a function of the degree of sulfonation.

(c) Data Analysis. Spectra were corrected for background scattering, normalized to the monitor counts, and transformed to $S(Q,\omega)$ in the standard way. Further normalization to the benzene ν_{16} out-of-plane vibration at 400 cm^{-1} was carried out to allow for a direct comparison of the intensities of the obtained spectra. Spectra were also compared with the spectrum of benzene to confirm the assignment of frequencies to the benzene ring. This was done under the assumption that the integrated area of the peak is proportional to the number of benzene rings in the sample and therefore to the number of scattering centers. Peaks were identified only when the spectra were statistically different, i.e., 3 standard deviations outside the experimental error. They were also compared with the spectrum of ice to eliminate the possibility of contamination of the spectra by water. No traces of water were found. The spectrum of 94.8 mol % Na-SPS ionomer was heavily contaminated by water; therefore, we could not analyze the data in a meaningful manner.

The instrumental resolution is 2%, and the precision of the measurement is ±2 cm^{-1}. The scattering law $S(Q,\omega)$ was obtained with the constant scattering angle, as described in the Experimental Section. Since the experiment was performed at low temperatures (below 20 K), $S(Q,\omega)$ is proportional to the density of the state function $g(\omega)$ and the mean square displacement of the normal mode ω, as discussed in ref 6.

3. Results and Discussion

The spectra measured provide information about the molecular vibrations in polystyrene and sulfonated polystyrene in the energy domain 32–4000 cm^{-1}. In Table II the normal mode vibrations obtained from the spectra of different samples are listed.

Differences Due to Configuration. In Figure 2 the spectra of isotactic PS, 10.5 mol % sulfonated isotactic PS, and atactic PS are shown, denoted a, b, and c, respectively. Two major effects are observed in these spectra: broadening of the spectrum of atactic PS and sulfonated isotactic PS as compared to unfunctionalized isotactic PS and the appearance of new peaks in the iso-PS spectrum.

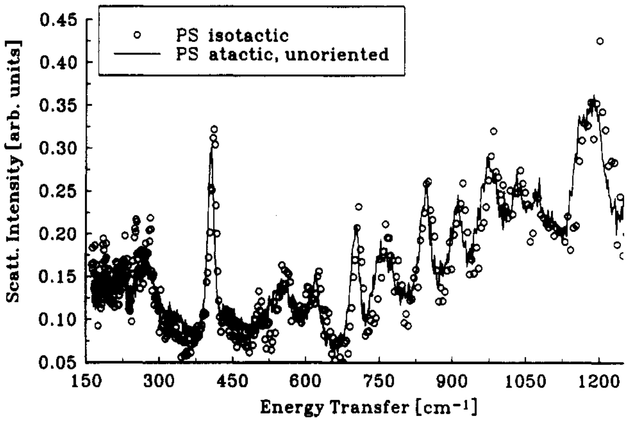


Figure 3. Comparison of INS spectra of isotactic PS (○) and atactic PS (continuous line).

The first effect is particularly clear for the low frequencies (below 400 cm^{-1}). Two groups of well-defined frequencies between 248–272 and 184–224 cm^{-1} appearing in the iso-PS spectrum are broadened to peaks centered at 200 and 264 cm^{-1}. Such a broadening is associated with the free volume accessible to the system.[7] This can be caused by a loss of either intra- or intermolecular ordering, a change from the regular configuration of iso-PS to a more random structure as exemplified in atactic PS. A loss of crystallinity present in the isotactic PS implies that the free volume can be increased in atactic PS.

The second effect is an appearance of a peak at 500 cm^{-1} in the iso-PS spectrum which is absent in the spectrum of atactic PS. This is interpreted as a mixed mode, where the ν_{16} mode of the benzene ring is overlaid with a 97-cm^{-1} mode from the phonon wing. This low-frequency transition suggests an appearance of a "breathing" mode between two chains, which originates from the increased distance between chains. This effect can be seen in Figure 3, where the normalized spectra of the isotactic and atactic

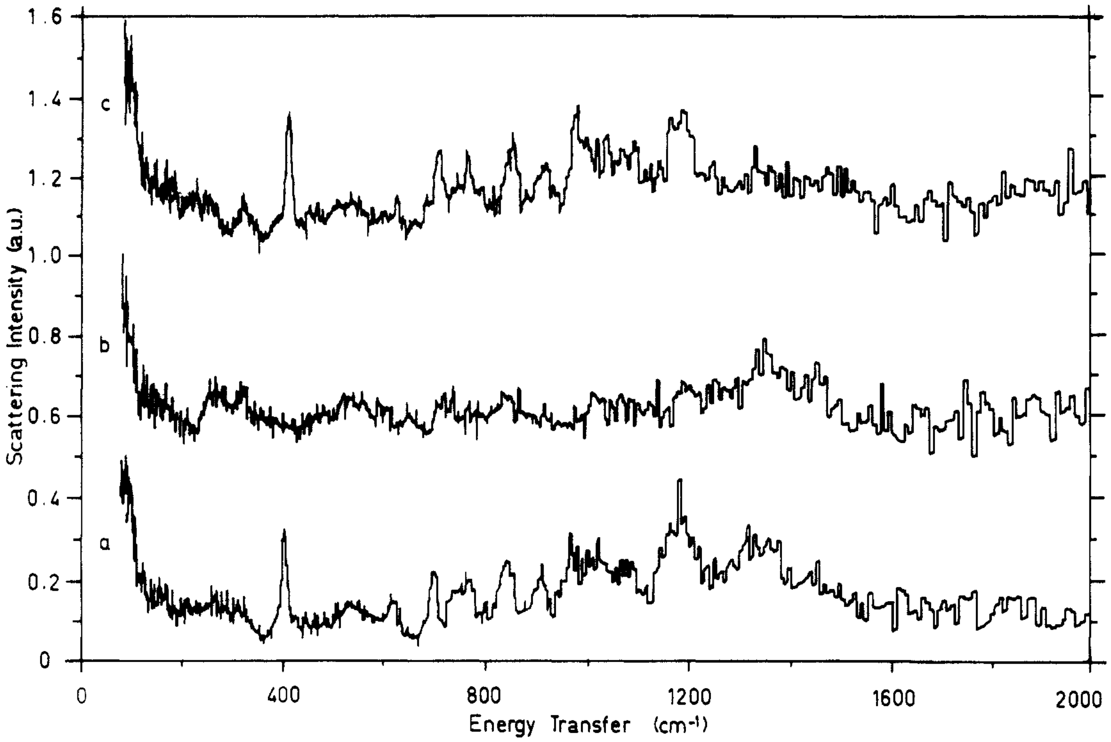


Figure 4. INS spectra for atactic PS: (a) 3.9 mol % sulfonated, fully hydrogenous structure; (b) 6.3 mol % sulfonated, ring-deuterated structure; (c) 7.4 mol % sulfonated, chain-deuterated structure.

PS are compared. We have previously found a destruction of the short-range order upon sulfonation using spin-polarized neutrons with spin-polarization analysis.[8] Moreover, this energy region is known to be sensitive to the changes in the polymer chain configuration.[9]

Differences Due to Deuteration of the Chain. The spectra of sulfonated atactic Na-SPS are shown in Figure 4. Spectrum a is measured on a fully hydrogenous sample, while spectra b and c are measured on the sample with a deuterated ring and the completely deuterated chain, respectively. This gives essentially the vibrational spectra of the backbone (Figure 4b) and the benzene ring (Figure 4c) since the deuterated moieties have an incoherent cross-section that is small compared to that of hydrogen (2 and 80 barns, respectively). Hence the assignment of the vibrational modes appearing in the fully hydrogenous spectrum a is facilitated.

It can be seen in Figure 4 that upon deuteration of the benzene ring a sharp peak appearing at 403 cm^{-1} disappears, proving that this is indeed the benzene ring vibration. It confirms the infrared assignment of this peak[10] and justifies the choice of this peak for normalization of the spectra after background subtraction. Interestingly, several other peaks disappear as well. The results are summarized in Table II.

Differences Due to Functionalization of the Chain. We have investigated the influence of sulfonation in the range spanning from 0 to 10.5 mol % on the spectra of isotactic polystyrene. As noted previously, the samples are listed in Table I.

Sulfonation of iso-PS has a marked effect on the spectral features. The result is shown in Figure 2 (spectrum b compared to that of the iso-PS is similar to the spectrum of the atactic material). Furthermore, the peak at 500 cm^{-1} disappears upon sulfonation, an effect already observable at low degrees of sulfonation (not shown). In Figure 5, the normalized spectra of isotactic PS and the 10.5 mol % sulfonated isotactic PS are displayed. The most striking changes occur at low energies. For example, the peaks at 186, 226, 250, and 274 cm^{-1} present in the iso-PS are broadened into two distinct peaks, which appear at 202 and 266 cm^{-1} in sulfonated iso-PS. Another visible change occurs in the energy region between 403 and 565 cm^{-1} in sulfonated PS, where the spectrum of vibrations fills the gap between 403 and 500 cm^{-1} that exists in iso-PS. Therefore it is concluded that sulfonation either destroys the configuration order within the chain or causes loss of crystallinity and ordering in the polymer.

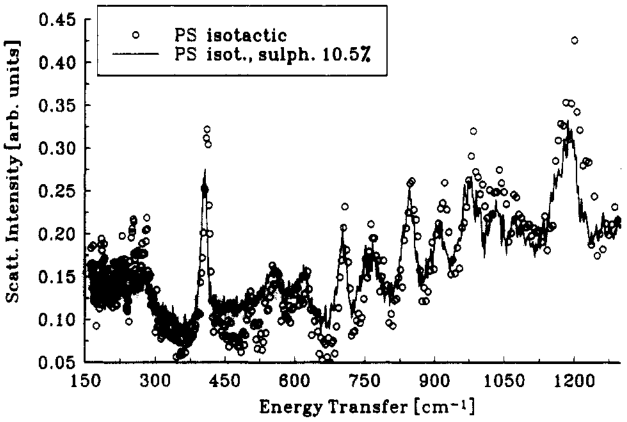


Figure 5. Comparison of the INS spectra of the isotactic (○) and 10.5 mol % sulfonated isotactic PS.

4. Conclusions

It is necessary to recall that the frequency domain where INS operates is high compared to that commonly encountered in studies of relaxation in polymers, (i.e., dynamical mechanical relaxation and related measurements). Therefore only very short-range motions are accessed directly by INS. Although some predictions can be made about the even slower, long-range motions of the whole chains, they are bound to be speculative at this stage.

The results presented in this paper corroborate the structural findings obtained using spin-polarized neutrons with spin polarization analysis.[8,11] INS measurements

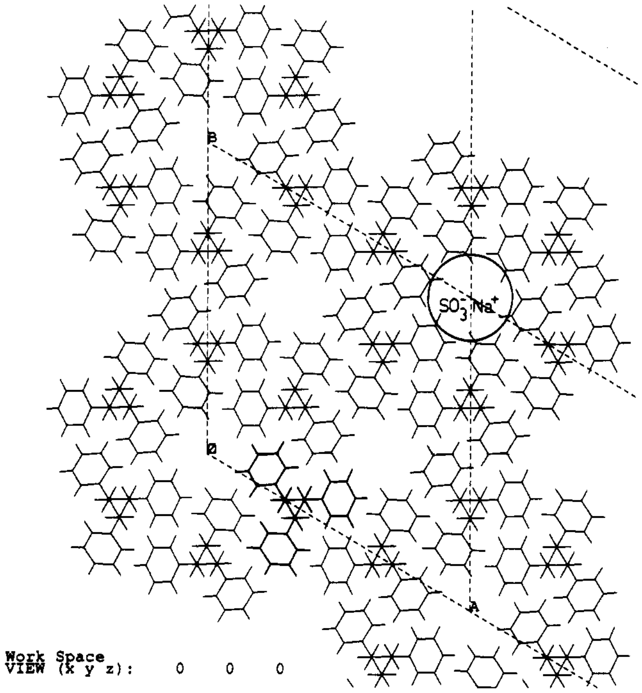


Figure 6. A cell of isotactic PS, symmetry $R\bar{3}$, with inserted sulfonated group.

confirm that the process of sulfonation destroys the short-range order present in both isotactic and atactic PS, which in turn leads to an increased local disorder in sulfonated PS. This process is schematically presented in Figure 6, where a single sodium sulfonate group is inserted in a unit cell of iso-PS. The addition of the sulfonate group clearly enhances the local chain mobility. At present there is no quantitative microscopic theory about the modification of the normal vibrations in styrene upon sulfonation. There is an early work by Painter et al.[12] where the normal vibrations for iso-PS were calculated. The individual ionic groups are usually assumed to form microphase-separated regions. Presently, however, there are only qualitative predictions by Eisenberg et al.[2] about the influence of ionic clusters on the overall chain dynamics. It is anticipated that the sulfonation process would result in restricted "mobility" of the chains surrounding the ionic microphase-separated regions. It is not clear what the effect would be on the local dynamics. These studies are presently being undertaken. It should be noted that to directly compare the data obtained from INS and measurements gathered from viscoelastic measurements, the experiments should be carried out under identical conditions. At present this is not easy since at temperatures where polymers flow, the density of state functions would be overly smeared out by the Boltzmann distribution. As a result the neutron spectrum would be meaningless without being based on an acceptable theoretical model. Then powerful techniques for data analysis, such as the maximum entropy method, can be used. At present we are pursuing related measurements to investigate the effect of ion pairing and clustering on the dynamics of ionomer chains.

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