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FOURIER TRANSFORM INFRARED ANALYSIS OF DEUTERATED POLYSTYRENE

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Abstract: To understand the changes occurring in the structure upon deuteration, a series of hydrogenous atactic polystyrene with different selectively deuterated variants was analyzed by Fourier Transform Infrared (FTIR) Spectroscopy. It was observed that the spectra were sensitive to a modification by deuteration of adjacent functional groups. These results also clearly show that the vibrational bands depend on the strength of the bonds and the masses of the atoms involved in the particular vibrational mode. Also using the selectively deuterated functional groups allowed to uniquely assigning peaks, which were not assigned previously to chain or ring vibration.

Keywords: Deuterium, FTIR spectroscopy, functional groups, hydrogenous atactic polystyrene, vibrational bands.

INTRODUCTION

The *infrared spectroscopy* is a technique of spectroscopic measurements in the infrared region of electromagnetic spectrum. It involves vibrational energy levels of molecules but often provides only part of the complete vibrational spectrum. It is probably one of the most widely used analytical techniques in the field of the identification and analysis of organic compounds. It is an extremely versatile technique, enabling sample evaluation in liquid, solid or gaseous state relatively simply. Its main application in the area of fingerprinting or obtaining functional group information enables unknown materials to be correlated with known standard spectra. The technique can also be used to determine the concentration of individual components in a mixture of known compounds. However, Fourier transform infrared (FTIR) spectroscopy provides interesting information on the interactions at the molecular level of the components.

The aim of the present study is to investigate changes due to deuteration in the vibrational spectra of polystyrene. Therefore, we have studied the vibrational spectrum of hydrogenous atactic polystyrene with different selectively deuterated variants of atactic polystyrene. This analysis will enable us to assign peaks to chain or ring vibration. This information is vital for employing FTIR for the study of the chain conformation (e.g. clusters). It was hoped, moreover, to gain some insight into the changes occurring in the structure upon deuteration. This type of information could help with understanding of process occurring in polymer blends [Bhutto 1999].

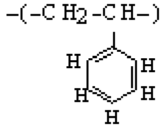
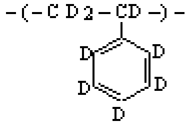
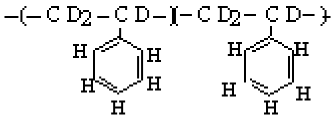
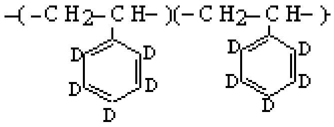
MATERIALS AND METHODS

SAMPLE PREPARATION

The deuterated polystyrene samples were prepared at Exxon Research and Engineering Co. by Dr. D.G. Peiffer, and the procedures adopted are described below. The chemical structures are shown in Table 1.

All the deuterated polystyrene samples used in this study were obtained through emulsion polymerization of the deuterated styrene monomer using potassium persulfate as initiator and sodium lauryl sulphate as the surfactant. The whole polymerization process was conducted under argon atmosphere and is known to produce an atactic polymer. 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 sulphate, and 0.1 g of potassium persulfate were stored into a 500 ml four-neck flask, vigorously agitated, degassed with argon gas and heated at 50ºC for 24 hours. 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 65ºC for 48 hours.

Table 1: List of the samples of atactic polystyrene with different selectively deuterated variants.

Sample	Structure of monomers
Fully hydrogenous	
Fully deuterated	
Chain deuterated	
Ring deuterated	

MEASUREMENTS

Infrared spectra of these specimens were recorded on a FTIR spectrometer *Nicolet 60 SXB* of the Materials Engineering Department, Brunel University London. Spectra were recorded with resolution of 2 cm^{-1} and were averaged from 100 scans, within the wavelength range 400 – 4000 wave-numbers (cm^{-1}). All infrared spectra were obtained at room temperature. The measurements were carried out either on thin pressed films at 160°C or by solid thin solvent-cast films in toluene.

RESULTS AND DISCUSSION

The measured infrared spectra of polystyrene in fully hydrogenous form and in their chain, ring and also fully - deuterated forms were analyzed. Upon careful inspection of these figures, it is apparent that important changes in the recorded spectra are observed, as discussed below. In Table 2, the observed vibrational frequencies and their assignments of fully hydrogenous polystyrene are listed. The characteristic bands of selectively deuterated samples are presented in Table 3.

Table 2: Infrared absorption assignments for fully hydrogenous polystyrene.

Wave numbers (cm^{-1})	Assignments
3001 – 3103	C - H aromatic stretching vibration
2925	C - H asymmetrical stretching vibration of CH_2
2850	C - H symmetrical stretching vibration of CH_2
1601	C - C stretching frequency of ring in plane
1583	C - C stretching frequency of ring in plane
1493	C - H stretching frequency of ring in plane
1452	C - H bending vibration due to CH_2.
1069	C - H bending vibration ring in plane
1029	C - H bending frequency ring in plane
1003	C = bending vibration out-of-plane
840	C - H out-of-plane bending vibration
757	C - H out-of-plane bending vibration
699	C - H out-of-plane bending vibration

Fig. 1 shows the infrared spectra of hydrogenous polystyrene, chain deuterated, ring deuterated and fully deuterated polystyrene in the high frequency region from 2700 to 3300 cm^{-1}. The high frequency spectrum of fully hydrogenous polystyrene consists of two bands at 2850 and 2925 cm^{-1} of CH_2 symmetrical and asymmetrical stretching vibration associated with chain hydrogenous form near the calculated [Englewood and Prentice-Hall 1965] values 2926 and 2853 cm^{-1}, with series of C-H aromatic stretching bands around 3000 cm^{-1} (i.e. 3001, 3026, 3060, 3082 and 3103 cm^{-1}). The high frequency spectrum (denoted by “b” in Fig. 1) of chain deuterated polystyrene exhibits the same bands as those appearing in the spectrum of hydrogenous PS mentioned above (around 3000 cm^{-1}). However, two sharp peaks appearing at 2850 cm^{-1} and 2925 cm^{-1} of C-H stretching vibration of CH_2 and CH group nearly disappeared, yet still small shoulders are present in chain deuterated and fully deuterated spectrum (“d” in Fig. 1). The appearance of these shoulders implies that chain and “fully deuterated” samples are not fully chain deuterated. However in ring deuterated spectrum (“c” in Fig. 1) only two bands of symmetrical and asymmetrical stretching modes of CH_2 groups are present at 2924 and 2851cm^{-1}, but the series of C-H aromatic stretching bands around 3000 cm^{-1} and a sharp peak of benzene ring vibration at 403 cm^{-1} have completely disappeared [Gabrys *et al.*1993]. Also several other peaks disappear upon deuteration of benzene ring, as demonstrated later in this paper. The assignment of vibrational modes appearing in the fully hydrogenous spectrum (“a” in Fig. 1) is facilitated by companion with the INS spectrum, since the deuterated moieties have an incoherent cross-section that is small compared to that of hydrogen (2 and 80 barns (1 barn=10^{-24} cm^{2}, respectively [Gabrys *et al.* 1993]).

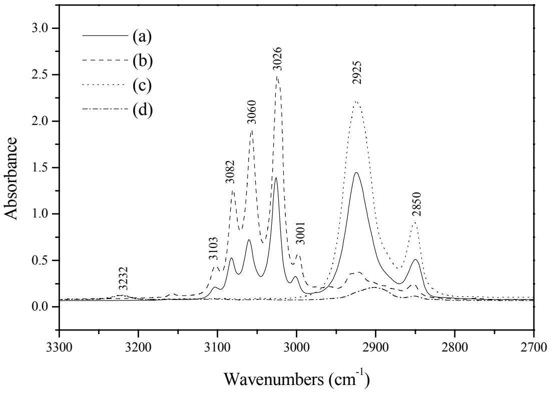


Fig. 1: Infrared spectra of polystyrene in the high frequency region (i.e. 3300 to 2700 cm^{-1}) (a) Fully hydrogenous (b) Chain deuterated (c) Ring deuterated (d) Fully deuterated polystyrene.

The spectra of 2350 to 1650 cm^{-1} regions are shown in Fig. 2. Traces A and B of Fig. 2 illustrate the spectra of ring deuterated and fully deuterated, while traces C and D represent chain deuterated and fully hydrogenous polystyrene spectra, respectively. It can be seen that upon deuteration of the benzene ring a sharp peak appears in the ring deuterated and fully deuterated spectra due to stretching vibration of C – D group of the benzene ring. The chain deuterated and fully deuterated spectra exhibit two absorption features at 2100 and 2194 cm^{-1} which correspond to symmetrical and asymmetrical stretching vibration of the C – D modes for the deuterated analogues on the polystyrene chain. But in chain deuterated polystyrene the 2100 cm^{-1} peak shifts by four wave-numbers to lower frequencies at 2096 cm^{-1}. This indicates that deuterated analogues in chain deuterated PS affect the hydrogenous vibration of the ring. The above observation correlates with the double mass of D atom compared to that of H atom, as expected. The frequency position of the maximum absorbance of an IR band depends on the strength of the bonds and the masses of the atoms involved in the particular vibrational mode [Englewood and Prentice-Hall 1965] as well as charge of cation [Kujawski *et al.* 1992]. Thus, these frequencies shift due to the mass variation (i.e. the substitution of deuterium atom for hydrogen). On the other hand the electron diffraction measurements of C_2H_6 and C_2D_6 showed a C – H bond distance of 1.1122 ± 0.0012 Å and C – D distance of 1.1071 ± 0.0012 Å [Bartell 1965] respectively, which shows that the interatomic bond is shorter for C – D bond.

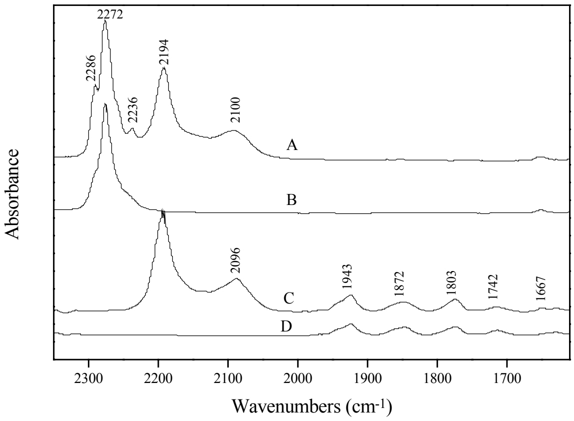


Fig. 2: Infrared spectra of C – D stretching region. Trace (A) ring deuterated, (B) fully deuterated, (C) chain deuterated and (D) fully hydrogenous polystyrene.

In the range of 2000 – 1650 cm^{-1} (Fig. 2), weak bands or combination bands are present in all fully hydrogenous and chain deuterated spectra. The pattern of these weak bands is characteristic of the substitution pattern of the ring. Because they are weak, these bands are most readily observed in spectra obtained from thick samples. The position of substitution on benzene rings can often be determined by the number of bands [Englewood and Prentice-Hall 1965]. This procedure is limited by the weak absorption of such overtone (or combination) bands. If there is a strong absorption in that region (such as a carbonyl stretch) the weak overtone bands are obliterated. These bands map out the vibrations of the ring pattern, which completely disappears in polystyrene spectra with deuterated ring and in the spectra of fully deuterated polystyrene. The ring-deuterated spectrum shows one band at 2272 cm^{-1} corresponding to C – D stretching mode of a deuterated ring. But the same band is detectable in fully deuterated spectra with two additional small shoulders at 2286 and 2236 cm^{-1}. These bands are difficult to assign without unjustified speculation.

Table 3: IR absorption assignments for deuterated polystyrene.

Wave numbers (cm^{-1})			Assignments
Chain Deuterated	Ring Deuterated	Fully Deuterated	
3001 - 3103	-	-	C – H aromatic stretching vibration (H-ring)
-	2924	-	C – H asymmetrical stretching vibration (H – chain)
-	2851	-	C – H symmetrical stretching vibration (H – chain)
2194	-	2194	C – D asymmetrical stretching vibration (D – chain)
2096	-	2100	C – D symmetrical stretching vibration (D – chain)
-	2272	2272	C – D stretching ring vibration (D- ring)
1602	1607	1607	C – C stretching vibration of ring in plane
1580	1569	1569	C – C stretching vibration of ring in plane
1492	-	-	C – H stretching vibration of ring in plane (H-ring)
1446	1447	1441	C – C stretching vibration of ring in plane
-	838	841	C – D out-of-plane bending vibration (D- ring)
-	823	822	C – D out-of-plane bending vibration (D- ring)
759	-	-	C – H out-of-plane bending vibration (H- ring)
699	-	-	C – H out-of-plane bending vibration (H- ring)
-	551	548	C – D out-of-plane bending vibration (D- ring)
-	487	465	C – D out-of-plane bending vibration (D- ring)

Figs. 3 and 4 show 1400 cm^{-1} to 1650 cm^{-1} region spectra for all samples. In this spectral range the four bands can be assigned to the benzene ring vibrations. These vibrations mainly involve C = C stretching of ring bonds but there is little interaction with CH in plane bending vibration. The two bands are observed at almost constant wave numbers of 1493 and 1452 cm^{-1} respectively [Liang and Krimm 1958, Randy and Painter 1981], and the intensity of these absorption bands is almost the same in fully hydrogenous and chain-deuterated polystyrene. But in chain deuterated polystyrene the 1452 cm^{-1} peak shifts down by six wave numbers to a lower frequency of 1446 cm^{-1}. However, the vibration at 1492 cm^{-1} remains the same as in the fully hydrogenous polystyrene spectrum. These results suggest that in deuterated analogues of polystyrene (either ring – deuterated or chain – deuterated) the C = C vibration of the benzene ring is affected. Furthermore, two bands appearing in fully hydrogenous and chain deuterated polystyrene spectra (at 1583 and 1601 cm^{-1}) are also assigned to the benzene ring C = C stretching vibration. The position and intensity of these vibrations are also different for hydrogenous and deuterated samples. The spectrum of ring-deuterated polystyrene shows a small peak at 1607 cm^{-1} with two extra peaks showing at 1569 and 1447 cm^{-1}, respectively. But the C – C bending vibration at 1493 cm^{-1} has completely disappeared in both fully deuterated and deuterated ring polystyrene spectra. Fully deuterated polystyrene spectrum exhibits only two peaks at 1607 and 1569 cm^{-1} with a very small peak at 1441 cm^{-1}, as shown in Fig. 4. This is difficult to explain without independent structural information, but it clearly shows the strong influence the deuteration has on the benzene ring vibration.

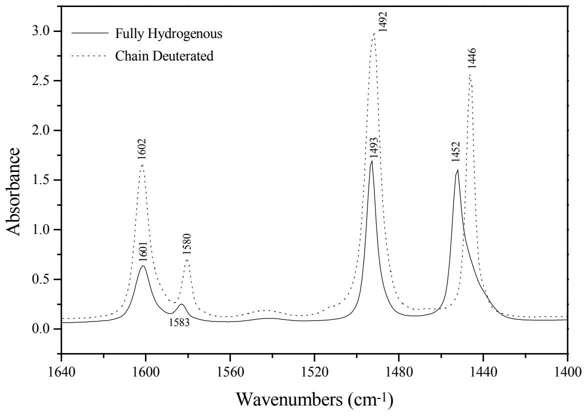


Fig. 3: Infrared spectra of Fully Hydrogenous and Chain deuterated polystyrene in the 1650 to 1400 cm^{-1} region.

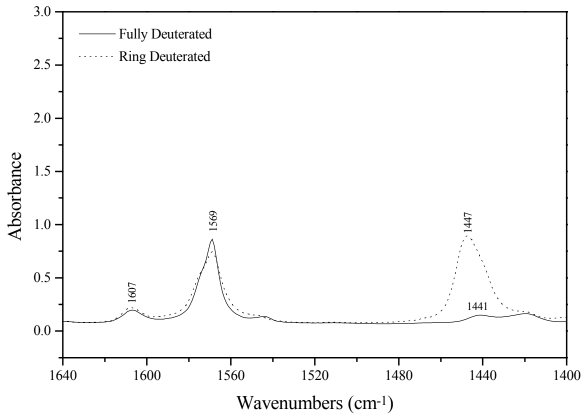


Fig. 4: Infrared spectra of Fully deuterated and Ring deuterated polystyrene in the 1650 to 1400 cm^{-1} region.

Figs. 5 and 6 show the asymmetric –SO_3– stretching vibration region [Lu and Weiss 1996] in fully hydrogenous and fully deuterated SPS ionomers respectively. The band appears in the 1181 to 1250 cm^{-1} region for fully hydrogenous and for fully deuterated. It appears as very broad feature from 1150 to 1260 cm^{-1}, comprising two bands, which become more distinct with increasing deuterium concentration, and its asymmetric stretching vibration is doubly degenerated. The splitting of this band and the position of the peak are sensitive to the effect of the increasing deuteration. The broad background in deuterated samples could possibly be due to the strong composite absorption of the S = O and D – O systems. These results may also indicate the possibility of a formation of a stronger ionic field with the increasing deuterium concentration. The whole change in the spectral feature is believed to be due to the effect of increasing deuterium concentration; deuterium participate in cluster formation together with the sulfonate ions or local environment of $–SO_3–$ group.

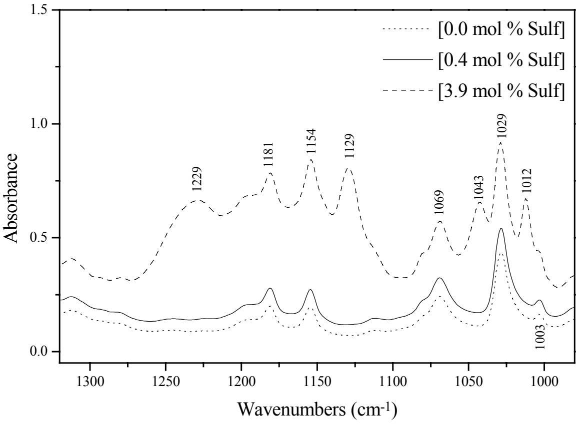


Fig. 5: Infrared spectra of the S – O stretching region for fully hydrogenous polystyrene.

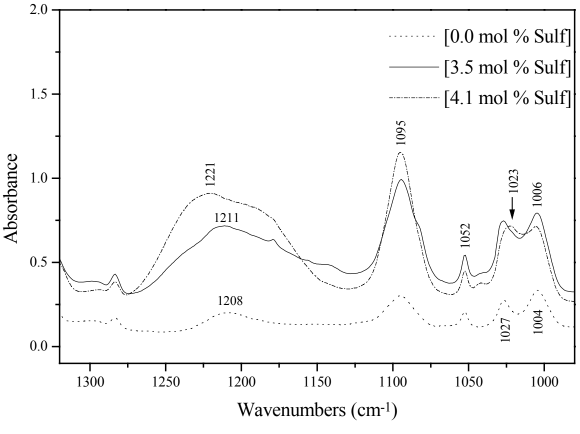


Fig. 6: Infrared spectra of the S – O stretching region for fully deuterated polystyrene.

This analysis has shown that the effects the deuteration has on the vibrational spectrum of the benzene rings (the peak shift of C – H vibration to C – D vibration and the C = C stretching vibration intensity and position) are also different for hydrogenous and deuterated polymers.

CONCLUSIONS

In this study we have found that the FTIR spectra of the chain deuterated and fully deuterated polystyrene revealed the presence of residual hydrogen on the chain. Selectively deuterated functional groups allowed us to uniquely assign peaks, which were not assigned previously to chain or ring vibration. It is also shown that the spectra are sensitive to a modification by deuteration or by sulfonation of adjacent functional groups (e.g. C – H vibration of the chain).

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