

The Sulfonation of Poly(ether ether ketone) as Investigated by Two-Dimensional FTIR Correlation Spectroscopy

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ABSTRACT: Fourier transform infrared and two-dimensional correlation (2D-COS) spectroscopies were used to follow the structural alteration occurring upon sulfonation of poly(ether ether ketone), in concentrated sulfuric acid at room temperature. With the help of high resolution and high sensitivity 2D-COS, it was possible to locate the aromatic ring in which the substitution has taken place. Two new IR bands at 1288 and 1320 cm^{-1} were attributed to substitution occurring on the aromatic ring flanked with two ether groups. Limited oxidation effects of concentrated sulfuric acid manifested itself by the production of new carbonyl species absorbing in the IR at 1720 and 1750 cm^{-1} that were attributed to a fluorenone-type structure and to ester groups. The 2D-COS analysis showed that the band at 1470 cm^{-1} is not only due to the new substitution by sulfone groups and can not be used in the determination of sulfonation degree. Instead, the intensity of the 1490 cm^{-1} band, which can be attributed to skeletal ring vibration, was found to correlate well with the degree of sulfonation calculated from ^1H NMR spectroscopy. The infrared spectroscopy combined with 2D-COS provides a fast and powerful method for qualitative polymer structure verification and help to establish the quantitative analysis.

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INTRODUCTION

Sulfonation is a powerful and versatile route to polymer modification, to convert them into ionomers, which are able to conduct protons and, therefore, can be used to prepare proton exchange membranes, PEM. The extent of sulfonation and the swelling properties of the PEM are extremely important, as they dictate the PEM performance by controlling proton conduction and mechanical properties.^{1,2} The sulfonation of commercially available poly(ether ether ketone) (PEEK; Victrex ICI and Gatone) and crosslinked PEEK using concentrated sulfuric acid have been described in the literature.^{2–10} Most of the interest in sulfonated PEEK is to prepare PEMs that are suitable for the application in low temperature PEM fuel cells. These membranes were found to be both chemically and thermally stable, and possess high proton conductivity, which depends on their degree of sulfonation, DS. The later has been controlled by changing reaction time, temperature, and acid concentration and a DS up to 100% mono-substitution of the repeat unit has been produced.²

Among the various analytical techniques, Fourier transform infrared (FTIR) spectroscopy is an invaluable tool in structure determination and verification. The frequencies at which there

are absorptions of IR radiation can be correlated to specific bonds within the investigated compound. Individual bonds may absorb at more than one IR frequency due to the presence of different modes, for example, stretching and bending, for each inter-atomic bond.^{11–14} This complicates the one-dimensional (1D) spectrum and further analyses using available techniques, for example, difference spectra, derivative, and deconvolution, are required to resolve overlapped molecular events and for proper peak assignments.¹³

Two-dimensional correlation spectroscopy (2D-COS), introduced to vibrational spectroscopy by Noda,¹⁵ has been shown to resolve the overlapping that may be encountered in 1D spectroscopy. It has found applications in wide range of analytical spectroscopies.^{16–18} Another merit of 2D-COS is that it can be used to determine the specific sequential order of spectral intensity changes.^{15,17,19,20}

The objective of this work is to investigate the capability of 2D-COS to obtain structural information related to the side reaction occurring on sulfonation of PEEK, the aromatic ring which is sulfonated and to determine an FTIR band which can be used for the quantitative determination of sulfonation degree. This is important to develop a non-destructive and quantitative

method to analyze sulfonated crosslinked polymers such as SPEEK that are not soluble in any solvents. It is also of interest to investigate any type of side reactions that may occur on sulfonation and result in chemical groups that have negative effects on the stability of the membranes in the final application field.

In this article, the sulfonation of PEEK pellets was carried out in concentrated sulfuric acid and monitored by IR and ^1H NMR spectroscopies. 2D-COS analysis was applied to the IR spectra to evaluate the new structures formed on sulfonation. A correlation of the DS calculated from ^1H NMR with different IR bands intensity was discussed.

EXPERIMENTAL

Materials and Sulfonation Reaction

PEEK in the form of pellets, grades G450 was obtained from Vitrex. Concentrated sulfuric acid (H_2SO_4), Sigma-Aldrich 97.5%, was used as a solvent and sulfonating agent.

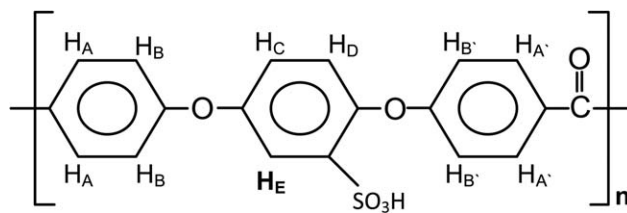
Sulfonation of PEEK was carried out following the procedure outlined elsewhere.⁹ PEEK was reacted at a concentration of 2.4 w/v % of polymer in concentrated H_2SO_4 at 20°C . Approximately 17 g of PEEK was added to 700 cm^3 of concentrated H_2SO_4 and the solution stirred mechanically. In order to study the effect of time on the extent of sulfonation, samples of 100 cm^3 of this solution were precipitated after 24, 48, 72, 96, 120, 144, and 168 h by drop-wise addition of the solution to 500 cm^3 of ice cooled distilled water. The samples were washed until the excess acid was removed, dried in air for 48 h, and finally in an oven at 40°C for 24 h.

^1H NMR Spectroscopy

The ^1H NMR spectra were recorded on a Bruker Biospin spectrometer at a resonance frequency of 400 MHz. For each analysis, a 2–5 wt % polymer solution was prepared in DMSO- d_6 and TMS was used as the internal standard. To perform a quantitative analysis, a full magnetization recovery between pulses must be assured. If a 90° pulse width is used to excite the spins, a total time between pulses longer than five times the longest longitudinal relaxation time (T_1) for the signal of interest is necessary in order to have complete relaxation. If a pulse width less than 90° is used, the total time can be proportionally less.²¹

In this work, the values of T_1 were determined by conducting 1D inversion-recovery T_1 relaxation measurements as described in literature.²¹ The T_1 value for the proton H_E was found to be 3.277 s and the values ranged from 1.877 to 2.530 s for other protons. Thus the acquisition parameters were set to an acquisition time of 4 s, relaxation delay of 1 s and pulse angle of 30° . This is a total time of more than $1.5 \times T_1$ and is longer than the value used in literature¹⁴ which is $0.9 \times T_1$. Thus the setup used in this work ensured that more than 99% of magnetization recovery took place and the ^1H spectra were quantitative.

The DS was calculated by integration of distinct aromatic signals following the procedure outlined elsewhere.¹⁴ In summary, the presence of a sulfonic acid group causes a significant 0.25 ppm down-field shift and intensity variation of the hydrogen H_E compared with H_C and H_D in the hydroquinone ring, as shown in Scheme 1. By evaluating the ratios between the peak



Scheme 1. The aromatic protons labels for SPEEK repeat unit.

area of the signal corresponding to this hydrogen (H_E) and the peak areas of the signals corresponding to the other aromatic hydrogens ($H_{A,A',B,B',C,D}$), taking into account the number x of hydrogen H_E and the number $12-2x$ of residual hydrogens $H_{A,A',B,B',C,D}$ per repeat unit, the value for the DS is obtained. The following expression can be written:

$$\frac{x}{(12-2x)} = \frac{A_{H_E}}{\sum A_{H_{A,A',B,B',C,D}}} \quad (0 \leq x \leq 1) \quad (1)$$

Assuming $z = \frac{A_{H_E}}{\sum A_{H_{A,A',B,B',C,D}}}$ leads to the following equation:

$$x = \frac{12z}{1+2z} \quad (2)$$

where x is the DS (mole %) and the letter A is the integral of the corresponding hydrogen.

FTIR Spectroscopy

A Nicolet Magna-IR 860 FTIR spectrophotometer was used to measure spectra of the sulfonated PEEK samples. An attenuated total reflectance, ATR, attachment was employed using the Golden Gate Accessory and a DTGS detector. All spectra were measured from 600 to 3800 cm^{-1} at a resolution of 2 cm^{-1} and a total of 200 scans and a separate background spectrum was subtracted in each collection.

Data Pretreatment and 2D Correlation Analysis

Prior to 2D calculation, all IR spectra were baseline corrected with the help of OMNIC software package, smoothed with a Savitzky–Golay function of two polynomials and 13 points and normalized to the same height based on the 1600 cm^{-1} band. The 2D correlation analysis was calculated using the 2DShige version 1.3 software (Shigeaki Morita, Kwansai-Gakuin University, 2004–2005) taking the average spectrum over all sulfonation time perturbation as a reference spectrum. The 2D correlation spectra consist of positive (shown in white or red areas) and negative (shown in gray or blue areas) cross-peaks in both synchronous and asynchronous maps.

RESULTS AND DISCUSSION

Changes in the IR Spectrum of PEEK on Sulfonation

Typical IR spectra of PEEK and sulfonated PEEK are shown in Figure 1. The absorption bands are assigned according to the groups in the repeating units shown in Scheme 1. The characteristic spectral features of PEEK in the finger print region include the carbonyl stretching vibration at 1650 cm^{-1} , a number of skeletal ring vibration bands at 1593, 1500, 1485, and 1410 cm^{-1} , the bending motion of the group ($\text{C}-\text{C}(=\text{O})-\text{C}$) at 1305 cm^{-1} , the asymmetric stretching of the diphenyl ether group at 1277 and 1190 cm^{-1} , the aromatic hydrogens in-plane deformation at 1215, 1155, and 1010 cm^{-1} and a number of

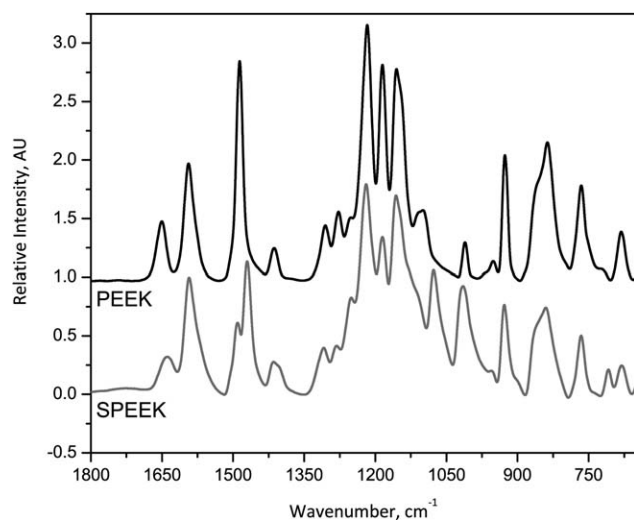


Figure 1. The FTIR spectrum of PEEK and sulfonated PEEK in the fingerprint region.

aromatic hydrogens out of plane bending modes at 925, 860–840 (broad band), and 765 cm^{-1} .^{11,12,22}

Structural changes in PEEK upon sulfonation corresponded with the appearance of new absorption bands consistent with the presence of $-\text{SO}_3\text{H}$ group and the splitting of other bands which confirm the presence of a third substituent on phenyl rings. New absorption bands at 3340, 1250, 1078, 1024, and 709 cm^{-1} have been assigned to the stretching of the O–H in the $-\text{SO}_3\text{H}$ group, the asymmetric and symmetric stretching of the O=S=O group, stretching vibration of the S=O and S–O groups, respectively.^{9,11–13} On the other hand, the aromatic ring absorption bands at 1490 and 1415 cm^{-1} were split on sulfonation and new bands appeared at 1470 and 1402 cm^{-1} , respectively. Moreover, the single broad band between 860 and 840 cm^{-1} was split upon sulfonation into two bands that are characteristic of an isolated hydrogen in a 1,2,4-trisubstituted aromatic ring.^{11,12} It has been reported that the sulfonation reaction can be followed by observing the changes in the intensity ratio of the pairs 1470 and 1490 cm^{-1} as this ratio correlates well with the DS measured by ^1H NMR, elemental analysis, and titration.^{6,9}

Although the 1D FTIR shows that substantial changes in the position, intensity, and breadth of the absorption bands occur with the proceeding of sulfonation reaction, the overlap of some bands makes the assignment of the FTIR spectra difficult and subtle changes could not be observed in the 1D spectra. 2D correlation analysis was applied to follow the sulfonation reaction and confirm that the changes in the observed spectra are due to the substitution of sulfone groups.

2D Correlation Analysis

Two types of spectra are obtained from 2D correlation analyses, namely synchronous and asynchronous. The synchronous spectrum consists of auto-peaks that appear at diagonal and cross-peaks that appear at off-diagonal positions. The auto-peaks are always positive and identify the signals that undergo changes with the external perturbation; reaction time or DS in this

work. The cross-peaks, on the other hand, are positive if the two signals change in the same direction (either increase or decrease) and are negative otherwise.¹⁸ The asynchronous spectrum consists of cross-peaks at off-diagonal positions that appear when two dynamic spectral intensities are out of phase (either accelerated or delayed). A cross-peak with coordinates ν_1 and ν_2 is positive if the spectral intensity change at ν_1 is before that at ν_2 and negative if the opposite is true.¹⁸ It should be mentioned that the direction of change (increase or decrease) is obtained from the 1D-IR spectra or revealed based on the underlying physical and chemical concepts of the studied reaction or process. The knowledge of the relation between a band in the 1D spectra and the external perturbation enables the evaluation of other overlapped bands dependency from their corresponding signs in the 2D maps. The fingerprint region of the IR spectra of PEEK after sulfonation experiments will be discussed in the following sections.

The Region 1800–1350 cm^{-1}

Figure 2(a) shows the changes in the IR spectra in the region 1800–1350 cm^{-1} of PEEK on sulfonation to different time from 0 to 168 h. The band at 1650 cm^{-1} has been assigned to the carbonyl group of diaryl ketones.^{11,12} As shown, it decreases in intensity, broadens progressively and shifts to lower wavenumber with time and proceeding of sulfonation reaction. These could be explained as due to protonation and conjugation of the carbonyl groups by their interaction with newly formed sulfone groups.^{11,12,23} The skeletal vibration, involving carbon–carbon stretching within the ring, bands appear at 1415, 1485, and 1595 cm^{-1} and they depend on the nature of the ring substituents.^{11,12} If the substituent is an electron acceptor group such as $-\text{SO}_3\text{H}$ a new band appears at 1470 cm^{-1} . As shown, the band at 1485 cm^{-1} decreases in intensity while the new bands at 1470 and 1400 cm^{-1} increase with the proceeding of sulfonation reaction.⁹

The 2D analysis of the individual absorption bands shown in Figure 2(a) will be separately analyzed in accordance with their intensity changes as shown in Figure 3(a–f). The corresponding 2D synchronous and asynchronous correlation spectra in the region 1800–1500 cm^{-1} are shown in Figure 3(a,b).

The synchronous spectrum of Figure 3(a) consists of auto peaks at 1565, 1635, and 1650 cm^{-1} , negative cross-peak correlating the band at 1650 cm^{-1} with other bands at 1565, 1635 cm^{-1} and positive cross-peaks correlating the band at 1635 cm^{-1} with the band at 1565 cm^{-1} . This means that the band at 1650 cm^{-1} and the two bands at 1635 and 1565 cm^{-1} changes in the opposite direction with sulfonation. The upper side of the asynchronous spectrum of Figure 3(b) consists of two positive cross-peaks at (1650, 1635) and (1635, 1565) cm^{-1} and one negative cross-peak at (1650, 1565) cm^{-1} . According to Noda's rules,²⁰ the signs of the cross-peaks suggest the earlier occurrence of the weak intensity increase at 1635 cm^{-1} over that at 1565 cm^{-1} and the large intensity decrease at 1650 cm^{-1} before the intensity increase at 1565 cm^{-1} . These changes can be assigned to the increase in conjugation which resulted in the increase of band intensity at 1565 cm^{-1} .^{11,12} The band at 1635 cm^{-1} is due to hydrogen bonded carbonyl stretching

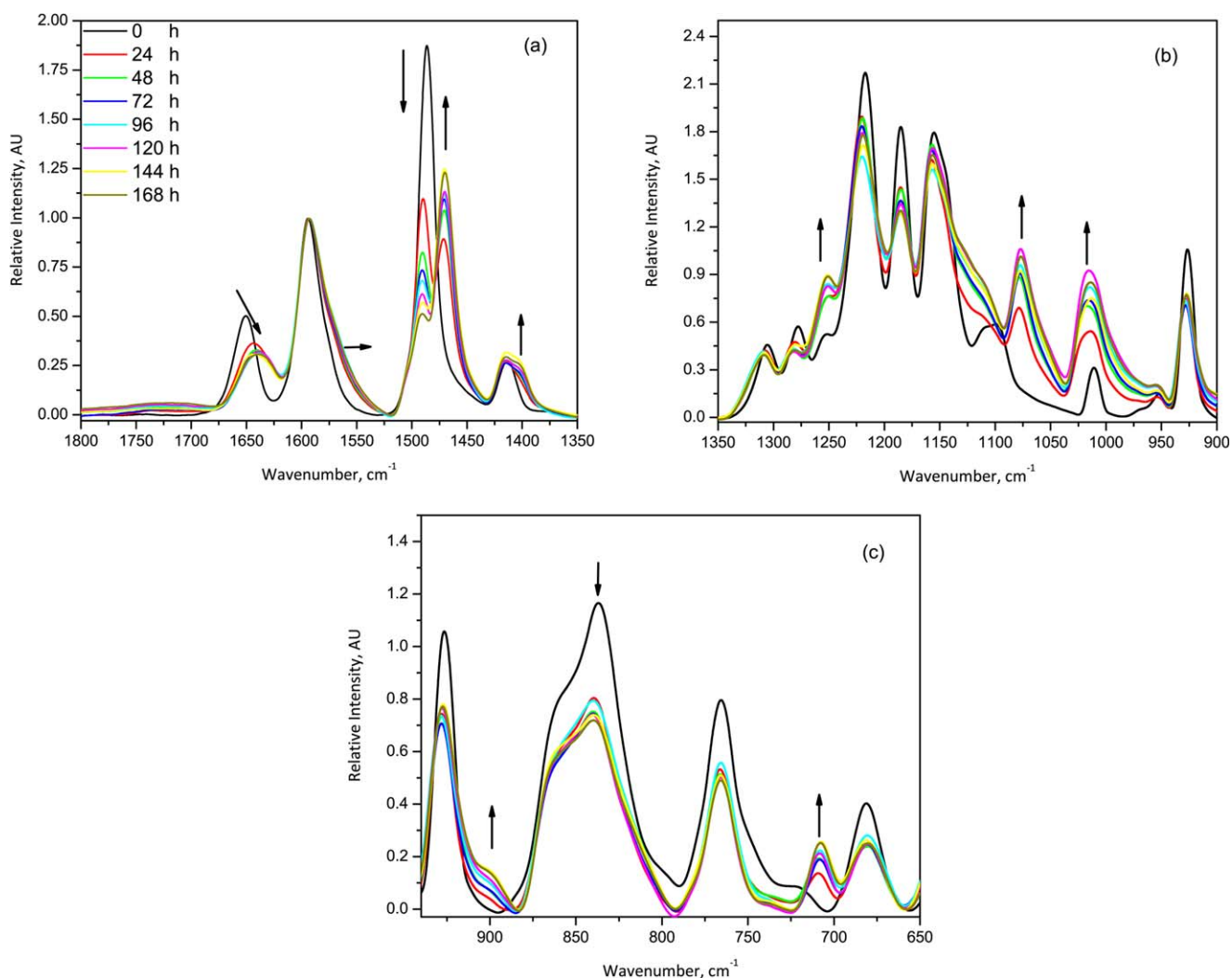


Figure 2. Changes in absorption with sulfonation time. (a) in the region 1800–1350 cm^{-1} , (b) in the region 1350–900 cm^{-1} , and (c) in the region 940–650 cm^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vibration. Note that these changes were not observed in the 1D spectrum.

The 2D-COS maps of Figure 3(a,b) also show new carbonyl species at 1710–1750 cm^{-1} that change in similar direction and at similar rate after the changes in the carbonyl bands. They are believed to arise from a fluorenone-type structure formed by cyclization of a diradical, or due to the keto form with a small amount of enolic unbonded $-\text{OH}$.^{12,13} In addition, the carbonyl peak at 1750 cm^{-1} may arise from ester groups formed by oxidation of the original carbonyl groups.^{11,12,24} These changes indicated that degradation and oxidation of PEEK were taking place during sulfonation reaction. On the other hand, this conclusion does not agree with other literatures^{2,10} in which the sulfonation reaction of PEEK in concentrated sulfuric acid was considered free of degradation or oxidation. The low concentration of the degradation/oxidation products and the empirical methods used to calculate the molecular weight of sulfonated PEEK thought to be the reason for this contradictory results.

The corresponding 2D synchronous and asynchronous correlation spectra in the region 1520–1420 cm^{-1} are shown in Figure 3(c,d). The synchronous spectrum of Figure 3(c) consists of two auto-peaks at 1485 and 1470 cm^{-1} that correlate with each other with negative cross-peaks and the higher wavenumber one of which dominates the intensity contours. These are characteristics of two overlapping bands whose intensities are changing in the opposite direction, the higher wavenumber one decreasing more while the lower one increasing but to a lesser extent.²⁵

The upper side of the asynchronous spectrum of Figure 3(d) consists of four cross-peaks; two of which are positive at (1493, 1470) and (1470, 1460) cm^{-1} and the other are negative at (1493, 1485) and (1482, 1465) cm^{-1} . The characteristic four-leaf-clover pattern in the synchronous correlation spectrum and the butterfly pattern in the asynchronous correlation spectrum is indicative of a band position shift with a small spectral intensity decrease as postulated by Morita et al.²⁶ The band at

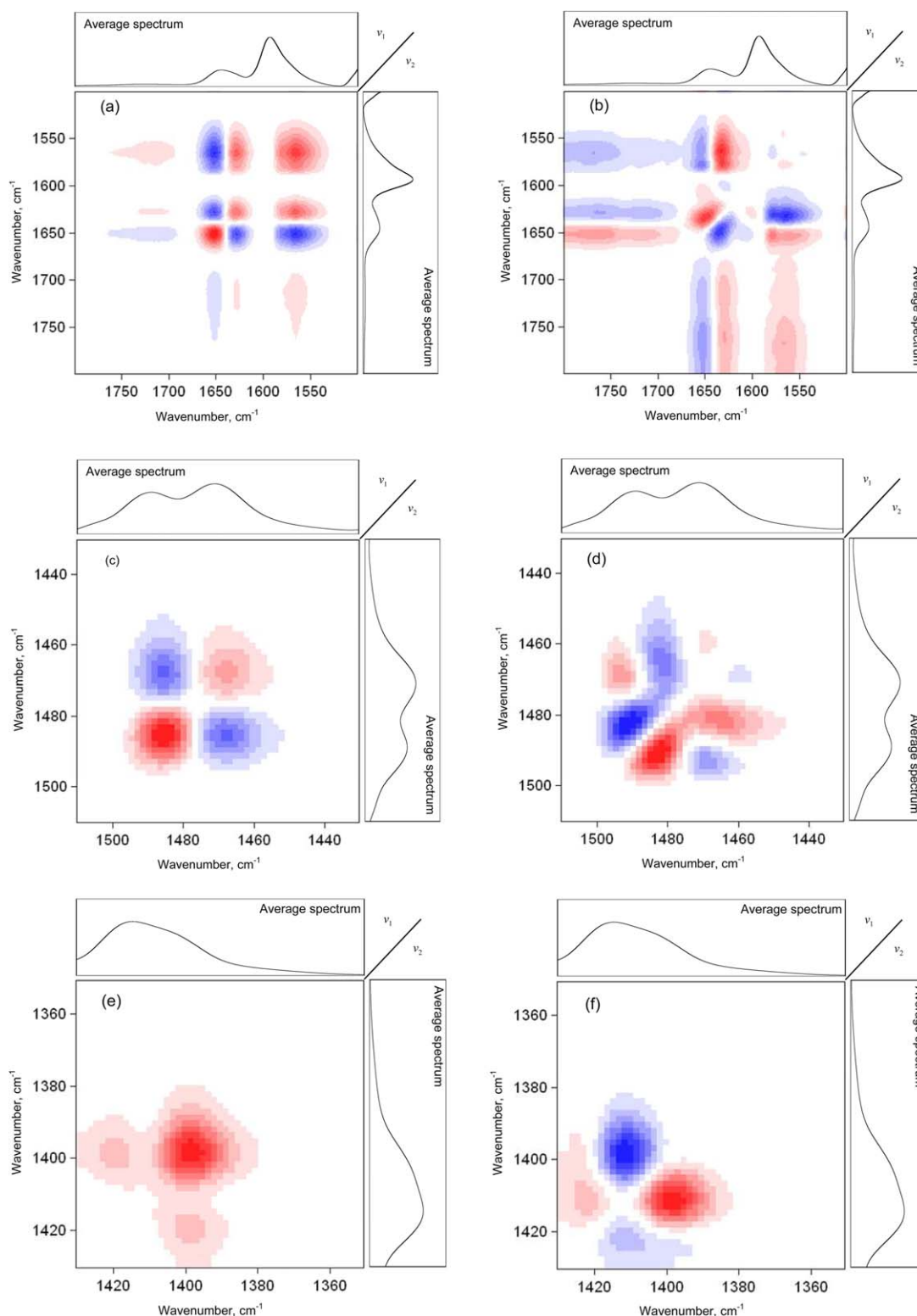


Figure 3. (a), (c), and (e) the synchronous and (b), (d), and (f) the asynchronous 2D correlation maps for sulfonated PEEK. (a) and (b) the region 1800–1500 cm^{-1} , (c) and (d) the region 1520–1420 cm^{-1} , and (e) and (f) the region 1430–1350 cm^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1485 cm^{-1} in the un-sulfonated PEEK shifts to new position at 1492 cm^{-1} and a new band at 1465 cm^{-1} appears which could be related to the $-\text{OH}$ bond.^{12,13}

The corresponding 2D synchronous and asynchronous correlation spectra in the region 1430–1350 cm^{-1} are shown in Figure 3(e,f). The synchronous spectrum of Figure 3(e) consists of one

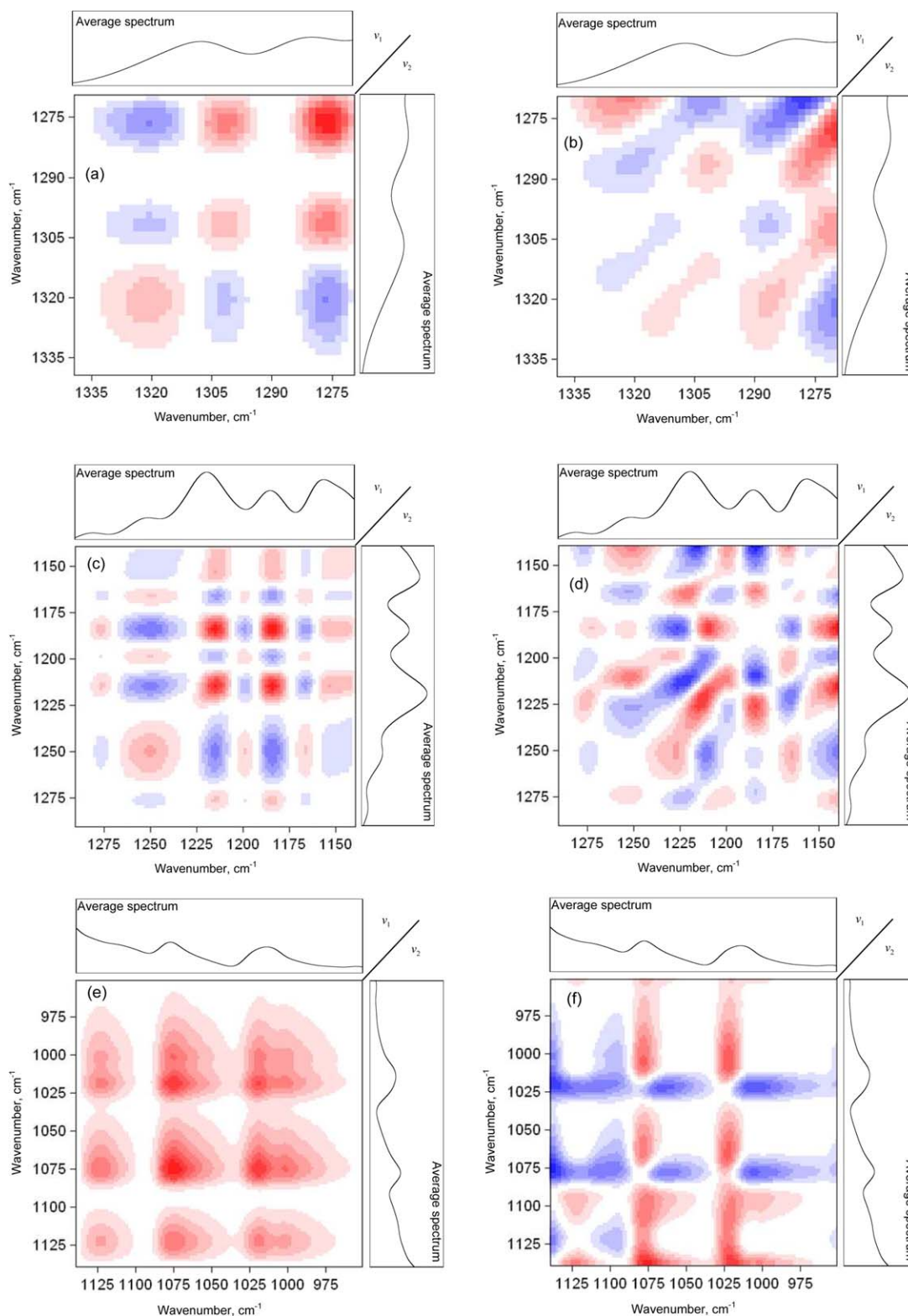


Figure 4. (a), (c), and (e) the synchronous and (b), (d), and (f) the asynchronous 2D correlation maps for sulfonated PEEK. (a) and (b) the region 1340–1270 cm^{-1} , (c) and (d) the region 1290–1140 cm^{-1} , and (e) and (f) the region 1140–950 cm^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

auto peak at 1400 cm^{-1} which correlates to the band at 1420 cm^{-1} with positive cross-peaks. This indicates that the bands at 1400 and 1420 cm^{-1} changes in the same direction,

increasing in intensity with different rate with increasing sulfonation time. The upper side of the asynchronous spectrum of Figure 3(f) shows two cross-peaks one of which is positive at

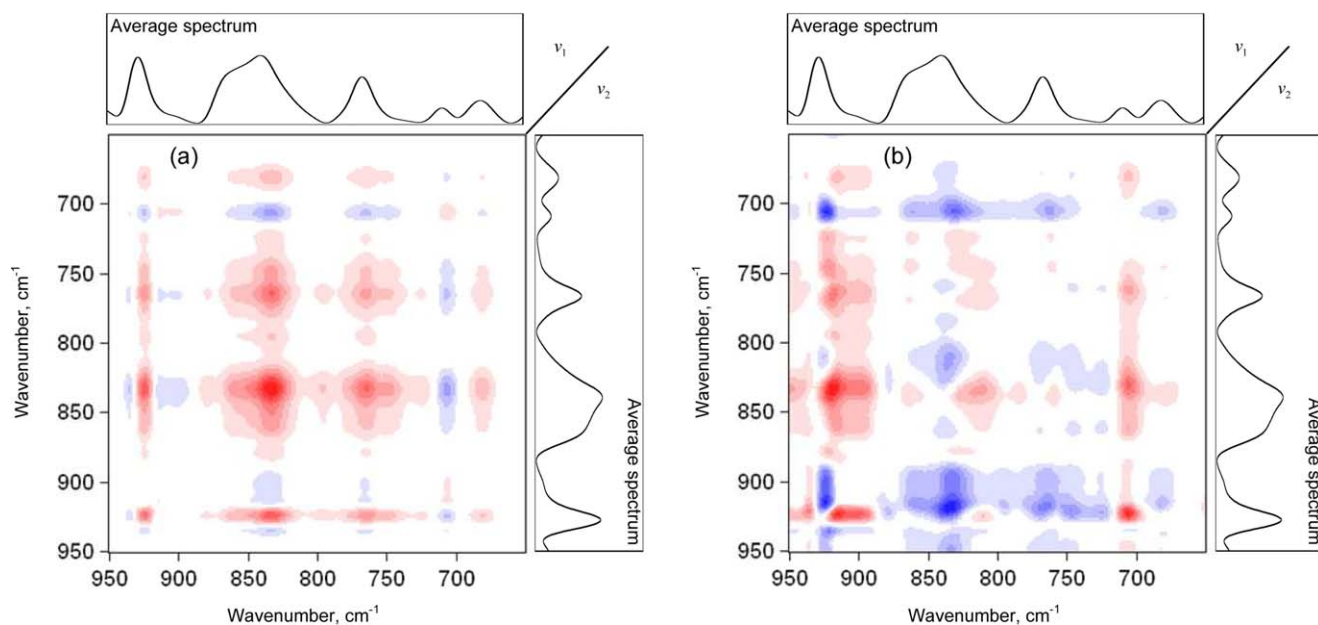


Figure 5. (a) the synchronous and (b) the asynchronous 2D correlation maps for sulfonated PEEK in the region 950–650 cm^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(1420, 1415) cm^{-1} and the other is negative at (1415, 1400) cm^{-1} . The band at 1415 cm^{-1} in the un-sulfonated PEEK shifts to a new position at 1420 cm^{-1} upon sulfonation and split to give a new band at 1400 cm^{-1} which increases in intensity with increasing sulfonation time.

The Region 1350–900 cm^{-1}

Figure 2(b) shows the changes in the IR spectra of PEEK, sulfonated to different time, in the region 1350–900 cm^{-1} . The most important bands in this region are the bending motion of the group (C–C(=O)–C) at 1305 cm^{-1} , the asymmetric stretching of the diphenyl ether group band at 1277 cm^{-1} , the asymmetric and symmetric stretching vibration of the sulfone groups at 1250 and 1080 cm^{-1} , respectively, and the stretching vibration of the group S=O at 1020 cm^{-1} . Moreover, a number of C–H in-plane deformation bands at 1010, 1155, and 1215 cm^{-1} are characteristic for 1,4-disubstituted benzenes.^{11,12,27}

The corresponding 2D synchronous and asynchronous correlation spectra in the region 1270–1340 cm^{-1} are shown in Figure 4(a,b). The synchronous spectrum of Figure 4(a) consists of auto peaks at 1320, 1305, and 1277 cm^{-1} , positive cross-peaks correlate the bands at 1305 and 1277 cm^{-1} and negative cross-peaks correlate the bands at 1305, 1320, and 1277 cm^{-1} . This indicates that the bands at 1305 and 1277 cm^{-1} change in the same direction, decreasing in intensity with increasing sulfonation time. The intensity of the new band at 1320 cm^{-1} is increased with increasing sulfonation time.

The most important features in the asynchronous spectrum of Figure 4(b) correspond to the presence of two positive cross-peaks at (1305, 1288) and (1320, 1275) cm^{-1} and two negative cross-peaks at (1320, 1288) and (1305, 1275) cm^{-1} .

According to Noda's rules,²⁰ the signs of the cross-peaks suggest the earlier occurrence of the intensity decrease at 1277 cm^{-1} before that at 1305 cm^{-1} . These two bands at 1305 and 1277 cm^{-1} are characteristics of amorphous PEEK and have been shown to be sensitive to changes in the molecular structure of PEEK.^{22,27} As shown, these shifted to new position at 1320 and 1288 cm^{-1} upon sulfonation which suggests that there is a significant difference in the structure of the diphenyl ether segments in PEEK before and after sulfonation. The implication of this is that the sulfonation occurs preferably on the phenyl rings flanked with the two ether groups.

The corresponding 2D synchronous and asynchronous correlation spectra in the region 1290–1140 cm^{-1} are shown in Figure 4(c,d). The band at 1250 cm^{-1} is associated with the asymmetric vibration of the O=S=O, and this increase with increasing sulfonation time.⁹

The synchronous spectrum of Figure 4(c) reveals the presence of auto-peaks and cross-peaks at 1277, 1250, 1215, 1200, 1186, 1167, and 1150 cm^{-1} . The positive cross-peaks correlating the 1277 and 1215 cm^{-1} bands with the other two bands at 1186 and 1150 cm^{-1} suggest a similar change in intensity decrease among these four bands. On the other hands, the negative cross-peaks correlating the 1277 and 1250 cm^{-1} bands with the other two bands at 1200 and 1167 cm^{-1} suggest an opposite change in intensity among these four bands.

The corresponding asynchronous spectrum of Figure 4(d) shows the main asynchronous cross-peaks. The signs of the cross-peaks suggest the earlier occurrence of the intensity decrease at 1150 cm^{-1} over those at 1277, 1215, and 1186 cm^{-1} and the intensity increase at 1167 cm^{-1} before those at 1250 and 1200 cm^{-1} .

Table I. Observed Changes in Infrared Spectra of PEEK After Sulfonation Reaction

Wavenumber cm^{-1}	Assignments	change in intensity
Oxidation of carbonyl groups		
1750	Sulfonated PEEK- $\nu(\text{C}=\text{O})$ ester	+ve
1720	Sulfonated PEEK- $\nu(\text{C}=\text{O})$ fluorenone-type structure	+ve
1653	PEEK pellets- $\nu(\text{C}=\text{O})$ diaryl ketone	-ve
1635	Sulfonated PEEK- $\nu(\text{C}=\text{O})$ hydrogen bonded	+ve
Position of new substituent		
1593, 1500, 1490 and 1410	PEEK pellets- $\nu(\text{C}=\text{C})$ skeletal ring vibration of 1,4 di-substituted.	-ve
840-860, 765, 680	PEEK pellets -the aromatic C-H out-of-plane vibrations	-ve
950	Sulfonated PEEK- the aromatic C-H out-of-plane vibrations for molecules containing at least one complete PEEK repeating unit	+ve
750	Sulfonated PEEK -the out of plane bending modes of the aromatic hydrogen.	+ve
1470 and 1400	Sulfonated PEEK- $\nu(\text{C}=\text{C})$ skeletal ring vibration of 1,2, 4 three substituted.	+ve
870,810	The aromatic C-H out-of-plane vibrations of 1,2,4 three substituted	+ve
Sulfonation occurs on the ring flanked with two ether groups		
1320	Sulfonated PEEK - the carbonyl linkage	+ve
1305	PEEK pellets - the carbonyl linkage	-ve
1288	Sulfonated PEEK- the asymmetric stretching of the diphenyl ether	+ve
1277	PEEK pellets -the asymmetric stretching of the diphenyl ether	-ve
Sulfone groups		
1250	Sulfonated PEEK- $\nu(\text{O}=\text{S}=\text{O})$ asymmetric stretching	+ve
1075	Sulfonated PEEK- $\nu(\text{O}=\text{S}=\text{O})$ symmetric stretching	+ve
1020	Sulfonated PEEK- $\nu(\text{S}=\text{O})$ stretching	+ve
705	Sulfonated PEEK- $\nu(\text{S}-\text{O})$ stretching	+ve
Quantitative analysis		
1470	The 1470 cm^{-1} band is overlapped with 1460 and 1465 cm^{-1} bands that were attributed to hydrogen bonding. It can not be used for quantitative analysis.	+ve
1490	The 1490 cm^{-1} band decreased linearly with increasing sulfonation degree.	-ve

+ve and -ve indicate that the intensity increases or decreases after sulfonation.

The corresponding 2D synchronous and asynchronous correlation spectra in the region 1140–950 cm^{-1} are shown in Figure 4(e,f). The synchronous spectrum of Figure 4(e) reveals the presence of auto-peaks and positive cross-peaks at 1125, 1075, 1020, and 1000 cm^{-1} . Positive cross-peaks correlating the 1125 and 1075 cm^{-1} bands with the other two bands at 1020 and 1000 cm^{-1} suggest a similar change in intensity increase among these four bands. The corresponding asynchronous spectrum of

Figure 4(f) shows the main asynchronous cross-peaks. The signs of the cross-peaks suggest the earlier occurrence of the intensity increase at 1020 cm^{-1} over that at 1075 cm^{-1} and of the intensity increase at 1075 cm^{-1} before those at 1125 and 1000 cm^{-1} . This suggests that the two bands at 1075 and 1020 cm^{-1} are arising from the $\text{O}=\text{S}=\text{O}$ symmetric and $\text{S}=\text{O}$ stretching vibration, respectively.

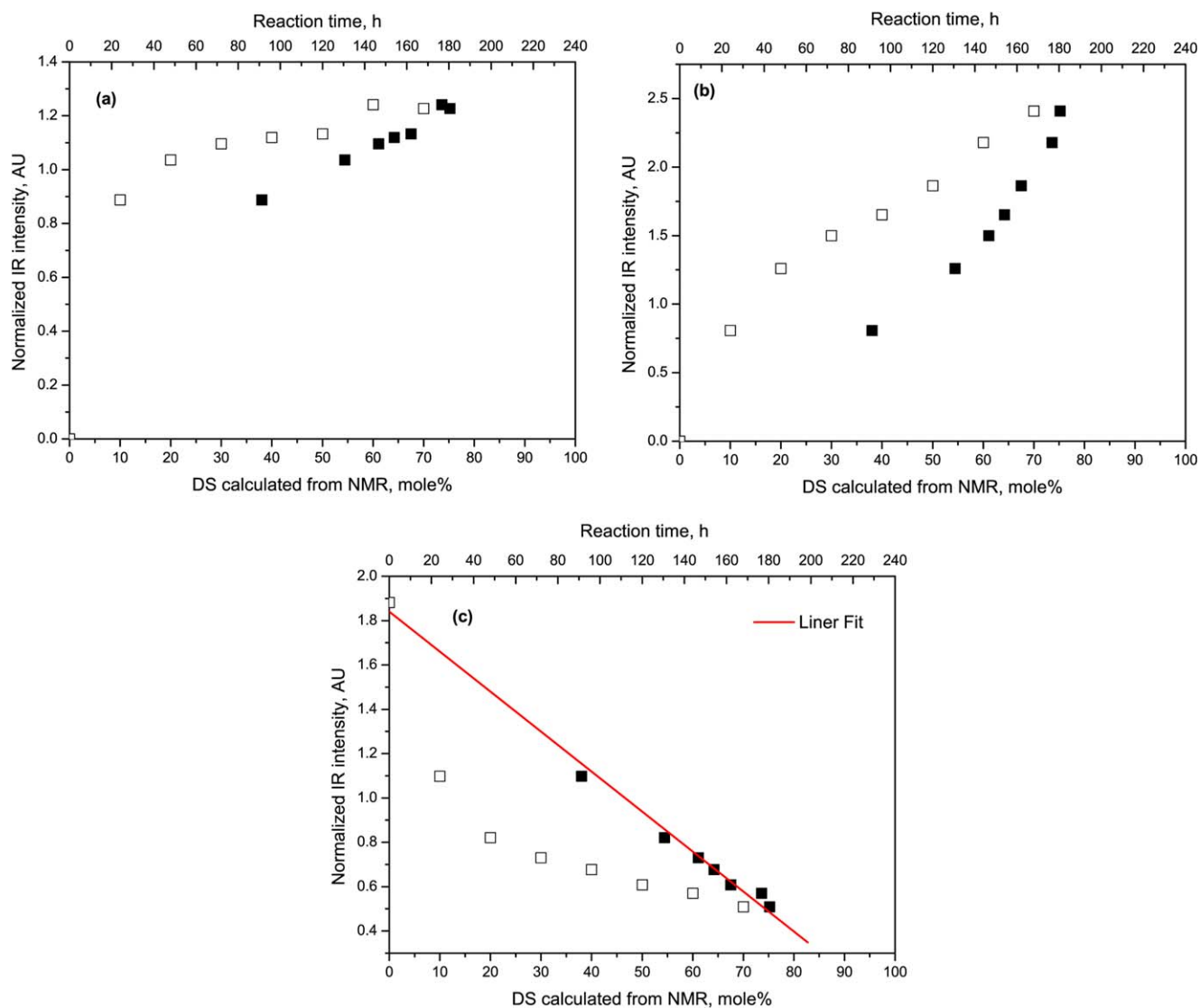


Figure 6. The variation of IR absorbance of the two bands at 1470 and 1490 cm^{-1} with reaction time (open symbols) and correlation of their intensities with the DS calculated from ^1H NMR (solid symbols). (a) the normalized band at 1470 cm^{-1} , (b) the ratio 1470/1490 cm^{-1} , and (c) the normalized band at 1490 cm^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Region 950–650 cm^{-1}

As shown in Figure 2(c), the 1D infrared spectra of PEEK revealed the presence of a broad band in the region 840–860 cm^{-1} which is characteristic of two adjacent hydrogen atoms of 1,4-Disubstituted benzenes. This band was decreased in intensity with sulfonation. Other bands appeared and increased in intensity with sulfonation progress. These were at 940, 900, 870, and 705 cm^{-1} .

The corresponding 2D synchronous and asynchronous correlation spectra in the region 950–650 cm^{-1} are shown in Figure 5(a,b).

The synchronous spectrum of Figure 5(a) reveals the presence of auto-peaks and cross-peaks at 940, 925, 900, 880, 835, 795, 765, 726, 706, and 680 cm^{-1} . Negative cross-peaks correlating the band at 706 cm^{-1} , which is increasing in intensity, with the other bands at 765, 835, 924, and 680 cm^{-1} suggest an opposite

change in intensity among these bands. The later bands correlate to each other with positive cross-peaks supporting the same direction of intensity change with sulfonation. The corresponding asynchronous spectrum of Figure 5(b) shows the main asynchronous cross-peaks. The signs of the cross-peaks suggest the earlier occurrence of the intensity decrease at 924 cm^{-1} over those at 835, 765 and 680 cm^{-1} and the intensity increase at 940 cm^{-1} before those at 706 and 900 cm^{-1} .

These results suggest that the bands at 765, 835, 924 and 680 cm^{-1} are characteristics of two adjacent hydrogens in the rings that had not been sulfonated whereas the other bands at 940, 900, 870 and 795 cm^{-1} are characteristics of isolated hydrogen in the ring that has been sulfonated.

The band at 705 cm^{-1} is attributed to the stretching of S—O groups and this increased in intensity with the proceeding of

sulfonation. The band appears at 765 cm^{-1} is associated with the out of plane bending modes of the aromatic hydrogen. It is reduced in intensity and split to new bands at 795 and 726 cm^{-1} . It has been associated with the crystalline ordered structure of PEEK²⁷ and has been reported to decrease in intensity due to the proceeding of cross linking reaction in the aromatic ring^{22,28} but it is reasonable here to attribute the reduction in this band as due to the increase in substitution levels. The 940 cm^{-1} band has been assigned to the aromatic C—H out of plane vibrations and has been observed only for molecules containing at least one complete PEEK repeating unit.²⁹ The new weak band appears at $900\text{--}910\text{ cm}^{-1}$ increased with sulfonation and may arise from cyclic ether formed by the oxidation effects of concentrated sulfuric acid.^{22,24}

In summary, the most important changes which occur on sulfonation are listed in Table I along with their assignment based on whether the intensity increases (+ve) or decreases (–ve) after sulfonation.

Evaluation of the DS from IR Band Intensity

It was concluded that the band at 1470 cm^{-1} which appears as a single band in the 1D spectra of sulfonated PEEK is not only due to the presence of sulfone group as a third substituent in the aromatic ring. That is why there was a nonlinear relation between the intensity of the band at 1470 cm^{-1} or the ratio $1470/1490$ and the DS calculated from $^1\text{H NMR}$ as depicted in Figure 6(a,b). The analysis of 2D-COS showed that the 1470 cm^{-1} band is overlapped with other bands at 1460 and 1465 cm^{-1} that arise from hydroxyl and hydrogen bonds. This explains the scattered data reported on the literature on correlation the ratio of the bands at 1470 and 1490 cm^{-1} with the DS determined from elemental analysis and $^1\text{H NMR}$ spectroscopy.⁶ On the other hand, Figure 6(c) shows the correlation between the normalized intensity of the 1490 cm^{-1} band and the DS calculated from $^1\text{H NMR}$. A linear relation was obtained with a correlation coefficient of 0.996 . This suggest that the DS can be obtained from the following relation,

$$DS = \frac{(1.84 \pm 0.04) - A_{1490}}{(0.0180 \pm 0.0006)} \times 100 \quad (3)$$

where A_{1490} is the intensity of the band at 1490 cm^{-1} normalized to the 1600 cm^{-1} band. Equation (3) can be used to determine the DS of crosslinked sulfonated PEEK based on their IR spectra.

CONCLUSIONS

ATR-FTIR and 2D-COS were used to identify the structural alteration produced on sulfonation of PEEK with concentrated sulfuric acid. The changes observed in the IR spectra and 2D-COS maps indicate the presence of $-\text{SO}_3\text{H}$ groups and the relative extent of sulfonation (the intensity of the 1490 cm^{-1} band decreased and the intensity of the 1470 cm^{-1} band increased on sulfonation of PEEK). The presence of new carbonyl species absorbing in the IR at 1750 and 1720 cm^{-1} could be considered as one of the reasons that account for the reporting decrease in chemical stability of SPEEK with increasing sulfonation degree.

The appearance of new bands at 1288 and 1320 cm^{-1} indicated that the aromatic ring attached to electron-donating groups such as the two ether groups in the oxy-phenylene-oxy units was sulfonated.

A good correlation between the DS (measured by $^1\text{H NMR}$) and the normalized intensity of the band at 1490 cm^{-1} was found, thereby indicating that FTIR technique can be used for the determination of DS. One important application of this is the determination of DS in cross linked polymers by a simple and non-destructive method. Due to the overlap in molecular events in the IR spectra, it is recommended to perform 2D analysis prior to the use of the intensity of a specific band to perform quantitative analysis.

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