Macromolecules 1989, *22*, 1201-1207 **1201**

the movement of bound water protons is restricted, it must be less effective in averaging the dipolar interactions. The relaxation time decreased with increasing concentration of agarose gels. This is quite consistent because bound water content increases with increasing concentration of agarose gels as shown in DSC analysis. The fact that the observed relaxation time is unique, although the movements of protons in bound water and free water are different, may be understood in terms of the rapid exchange model proposed by Zimmerman and Brittin,[16] as was discussed by Ablett et al. in the case of agarose gel[17] and by Maquet et al. in the case of gelatin gels.[18]

Structure of Agarose Gels. X-ray diffraction diagrams of 15% and 30% agarose gels are shown in Figure 9. Only a halo, characteristic of amorphous materials, was observed in X-ray diffraction patterns from gels whose concentration was less than 25%, but beyond this concentration a sharp peak characteristic of crystalline materials was observed at 20°. These peaks became more prominent with increasing concentration of gels. Note that the scales of the ordinates of parts A and B of Figure 9 are different. The helical chain segments are forced to aggregate to make a bundle and give rise to junction zones. This process is promoted by the increase of concentration of polymers. This situation is similar to the formation of liquid crystals of, e.g., poly(γ-benzyl L-glutamate); the rigid-rod molecules are obliged to orientate at higher concentrations.

Figure 10 shows the scanning electron micrographs of a 30% agarose gel. Dense networks are observed in these photographs and these, are quite different from the porous structures observed in dilute gels, although they are not shown here. The densely packed regions are thought to be junction zones which consist of a bundle of double-helical chain segments.

Registry No. Agarose, 9012-36-6.

References and Notes

(1) Rees, D. A. *Pure Appl. Chem.* **1981**, *53*, 1.
(2) Indovina, P. L.; Tettamanti, E.; Micciancio-Giammarinaro, M. S.; Palma, M. U. *J. Chem. Phys.* **1979**, *70*, 2841.
(3) Tokita, M.; Hikichi, K. *Phys. Rev. A* **1987**, *35*, 4329.
(4) Hayashi, A.; Kanzaki, T. *Food Hydrocolloids* **1987**, *1*, 317.
(5) Watase, W.; Nishinari, K. *Makromol. Chem.* **1987**, *188*, 1177.
(6) Watase, M.; Nishinari, K. *Rheol. Acta* **1983**, *22*, 580.
(7) Watase, M.; Nishinari, K. *Nippon Shokuhin Kogyo Gakkaishi* **1983**, *30*, 368.
(8) Nishinari, K.; Koide, S.; Ogino, K. *J. Phys. (Paris)* **1985**, *46*, 793.
(9) Treloar, L. R. G. *The Physics of Rubber Elasticity*; Clarendon Press: Oxford, 1975.
(10) Clark, A. H.; Ross-Murphy, S. B. *Br. Polym. J.* **1985**, *17*, 164.
(11) Clark, A. H. In *Food Structure and Behaviour*; Blanshard, J. M. V., Lillford, P. J., Eds.; Academic Press: New York, 1987; Vol. 1, pp 13-34.
(12) Gordon, M.; Ross-Murphy, S. B. *Pure Appl. Chem.* **1975**, *43*, 1.
(13) Oakenfull, D. *J. Food Sci.* **1984**, *49*, 1103.
(14) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1980; Vol. 3, Crystal Melting.
(15) Watase, M.; Nishinari, K. In *Gums and Stabilisers for the Food Industry* 3; Phillips, G. O., Wedlock, D. J., Williams, P. A., Eds.; Elsevier Applied Science Publishers: London, 1985; pp 185-194.
(16) Zimmerman, J. R.; Brittin, W. E. *J. Phys. Chem.* **1957**, *61*, 1328.
(17) Ablett, S.; Lillford, P. J.; Baghdadi, S. M. A.; Derbyshire, W. *J. Colloid Interface Sci.* **1978**, *67*, 355.
(18) Maquet, J.; Thèveneau, H.; Djabourov, M.; Lebrond, J.; Papon, P. *Polymer* **1986**, *27*, 1103.

Electron Spectroscopy for Chemical Analysis Study of the Surface Oxidation of Poly(phenylene sulfide) Powder by Heterogeneous Reactions[†]

Amarjeev Kaul* and Kishore Udipi

Monsanto Chemical Company, Springfield, Massachusetts 01151. Received June 20, 1988

ABSTRACT: The oxidation of poly(phenylene sulfide) (PPS) powder investigated by electron spectroscopy for chemical analysis (ESCA), in terms of the extent of reaction, suggests that a random terpolymer type of a surface layer is generated consisting of sulfide, sulfoxide, and sulfone groups. Slurry conditions, in two reaction schemes, were employed since a good solvent is not available for PPS. It was expected that the surface of the polymer particle would be oxidized. Reaction A was carried out at 60 °C in toluene with a mixture of formic acid and hydrogen peroxide as the oxidizing agent while reaction B was carried out in a methylene chloride medium at 25 °C with 3-chloroperoxybenzoic acid. ESCA results indicate that up to 75% of the sulfide (—S—) sulfur is oxidized to sulfoxide (—[S═O]—) and sulfone (—[O═S═O]—) in the surface region. The phenyl ring is unaffected. Depth profiling with Ar$^+$ ion sputtering (~100 Å) indicates that the reactions have also occurred in the subsurface region, but to a lesser extent.

Introduction

The primary objective of this study is to evaluate the extent and nature of the oxidation of poly(phenylene sulfide) (PPS) by a wet chemical process. Since the polymer does not have a good solvent, the reaction was carried out under slurry conditions.

The heterogeneous reactions have been found to generate sulfoxide and sulfonyl groups on the surface by the oxidation of the sulfide group. The resulting polymer powder is studied by electron spectroscopy for chemical analysis (ESCA) in order to gain insights into surface-enhanced slurry reactions. For example, Clark and Stephenson[1] used ESCA to study the nitration of cellulose fibers. Zadorecki and Ronnhult[2] have also used this technique to characterize cellulose fibers in the form of paper sheets chemically modified with trichloro-*s*-triazine. Millard[3] has studied corona-treated wool fibers while Carr et al.[4,5] have characterized chemically treated wool fibers by ESCA.

The crystal structure of PPS has been determined by Tabor et al.[6] by X-ray diffraction and IR. The electronic structure has been studied by Riga et al.[7] using ESCA.

[†] Published partially in *Polymer Preprints*. ACS National Meeting, Denver, CO, 1987.

0024-9297/89/2222-1201$01.50/0

Table I
Experimental Conditions for Oxidation of Poly(phenylene sulfide)

reactn	oxidizing agent	S(sulfide)/ O(peracid) molar ratio	solvent	temp, °C
A	performic acid[a]	1:1	toluene	60
B	3-chloroperoxybenzoic acid	1:0.5	methylene chloride	25

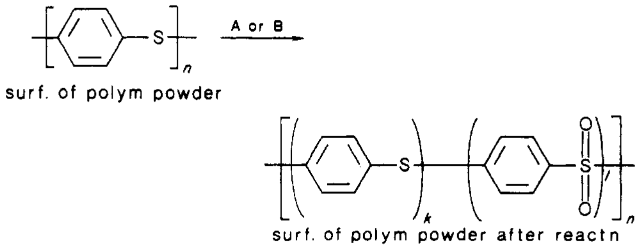
[a] Generated in situ with formic acid and hydrogen peroxide.

Joshi and Radhakrishnan,[8] Rubner et al.,[9] and Zeng et al.[10] have used PPS in coatings, for circuit board fabrication, and in carbon fiber composites, respectively. Additionally, doped poly(phenylene sulfide) is an interesting conductive polymer.[11-15] Various mechanisms have been proposed for the origin of this conductivity. The role of the double-bond character of the C–S bond in doped PPS systems has been investigated by Kispert et al.[16] using electron paramagnetic resonance and by Tsukamoto and Matsumura[17] using ESCA, IR, and carbon-13 NMR. Surface conductivity of doped unoxidized and oxidized PPS may potentially provide a method of evaluating the role of the sulfur heteroatom in the main chain of the PPS polymer. An understanding of surface-enhanced reactions can, thus, be useful in such an investigation.

The physical properties[6,18,19] of PPS have also been studied extensively. On the basis of the repeat unit structure, properties[20-22] of the polymer (sulfide linkage) can be chemically modified. Organic sulfides can be oxidized to sulfoxides by a number of oxidizing agents.[23] For example, oxidation of PPS has been patented by Vives and Brady.[24] The effect of oxidation on its crystallization behavior[18] is known. Some information related to surface[25] and bulk[26] characterization of unoxidized and oxidized poly(phenylene sulfide) has been reported by the authors.

Experimental Section

The oxidation of PPS powder (RYTON P-4, unfilled grade, Phillips Chemical Co.) was carried out in two heterogeneous reaction schemes designated as A and B. Reaction A was performed in toluene at about 60 °C with a mixture of formic acid (H[C=O]OH) and hydrogen peroxide (H_2O_2). Thus, performic acid is generated in situ in this case. Reaction B was carried out in a methylene chloride medium at about 25 °C with 3-chloroperoxybenzoic acid ($ClC_6H_4[C{=}O]OOH$). The above two solvents were chosen as the slurry media since oxidation with peracids proceeds better in aromatic and chlorinated solvents than in aliphatic solvents.[27] The reaction time for both reactions is about 3 h. The reactive group in both cases is the acid group similar to performic acid (—[C=O]OOH) and the expected overall reaction is



The experimental conditions are given in Table I. The amount of peracid required for the oxidation was determined on the basis of the polymer molecular weight[28] (M_n) of 30 000. The reaction mechanism is described in Figure 1.

For ESCA studies, the control PPS polymer powder was extracted with methanol to remove additives. For oxidation reactions, the polymer was used as received. Oxidized PPS is referred to as PPS/A and PPS/B after reactions A and B, respectively. Both PPS/A and PPS/B were washed with methanol after reaction and vacuum dried overnight at 60 °C under nitrogen flow. ESCA studies were performed on VG Scientific ESCALAB MKI using a soft Mg $K\alpha_{1,2}$ X-ray source. The samples were mounted as powder on two-sided tape. The source excitation energy was 1253.6 eV and the pressure in the analysis chamber was maintained below 10^{-8} Torr. High-resolution multiregion scans were obtained with a pass energy of 10 eV and a step size of 0.05 eV. The emission was maintained at 200 W (10 kV and 20 mA). Sensitivity factors were used to obtain atom percent or elemental composition. Curve resolution of individual peak signals was performed by using Gaussian peaks. Further, the depth of information is believed to be within 50 Å. The sulfur $S_{2p_{1/2}}$ contribution to the sulfur S_{2p} signal has been subtracted so that the atom percent values are only based on the $S_{2p_{3/2}}$ component. During curve fitting the $S_{2p_{1/2}}$ and $S_{2p_{3/2}}$ doublet was not resolved, rather a combined S_{2p} peak was assumed. The $^1/_2$ component, in pure sulfur, will have an intensity equal to about half that of the 3/2 component and will be shifted about 1.1 eV from the latter. Peak binding energies are normalized with respect to the hydrocarbon carbon (C—C, C=C) C_{1s} peak at 285 eV. Depth profiling was performed using Ar^+ ions at an input energy of 5 keV, a chamber pressure of 10^{-5} Torr, a 2.54-cm defocused ion beam, and a target current of about 300 μA.

Table II
ESCA Atom Percent of Control and Oxidized Poly(phenylene sulfide) Powders

surface	atom % C	O	S
PPS[a]	85.0	3.6	10.5
PPS/A[b]	77.9	13.9	8.2
PPS/B[b]	79.6	13.1	7.3
PS[c]	86.4	11.0	2.6

[a] PPS, poly(phenylene sulfide). [b] PPS/A, oxidized PPS, reaction with $H[C{=}O]OH/H_2O_2$; PPS/B, oxidized PPS, reaction with $ClC_6H_4[C{=}O]OOH$. [c] PS, polysulfone, used as a reference material.

Table III
ESCA Atom Percent of Resolved Peaks in the Sulfur (S_{2p}) Signal of Control and Oxidized Poly(phenylene sulfide) Powders

surface	$S_{2p_{3/2}}$, atom % sulfide	sulfoxide	sulfone
PPS	10.2	0.3	0.0
PPS/A	1.5	1.1	5.6
PPS/B	1.6	1.0	4.7
PS	0.2	0.0	2.4

Results and Discussions

Surface Studies. The sulfur to carbon atom ratio in the PPS repeat unit is ideally 0.17. Table II gives the total atom percent of all the elements on the surface. The data on polysulfone is provided for reference purposes. ESCA S/C atom ratios for PPS, PPS/A, and PPS/B are 0.12, 0.11, and 0.09, respectively. A constant ratio is expected, and the differences are not significant, since there should be no change in the total number of C or S atoms. About 3.6% oxygen is detected on PPS. The oxygen content of the surface increases with oxidation to 13.9% and 13.1% for PPS/A and PPS/B, respectively. Increase in the total oxygen content by over 9.5%, compared to control PPS, is an indication of a successful slurry reaction. Table III provides the atom percent of component sulfur S_{2p} peaks. Figure 2 shows the changes induced in the S_{2p} signal due to the reactions which result in a higher oxidation state compared to the sulfide in PPS. A new major peak appears at a higher binding energy. About 0.3% of the total sulfur is assigned to a sulfoxide (—[S=O]—). Thus, PPS has very small amounts of sulfoxide groups randomly distributed, to begin with. This, however, does not account

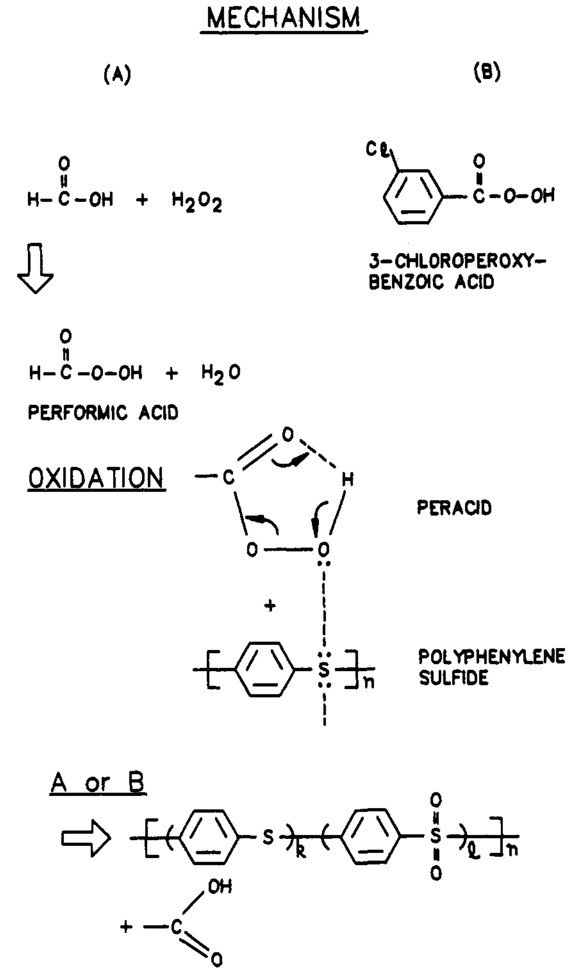


Figure 1. Expected oxidation of poly(phenylene sulfide) powder with peracids using reaction routes A and B.

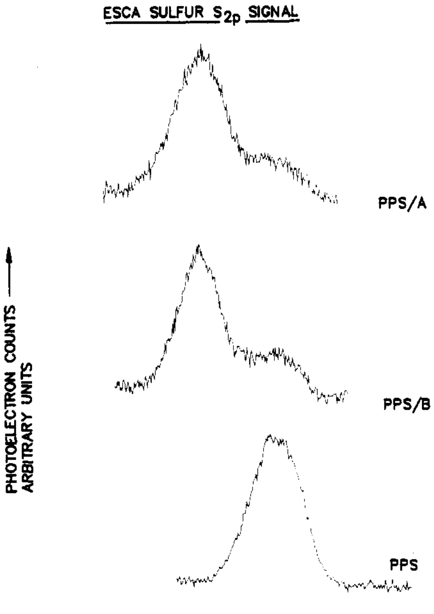


Figure 2. ESCA sulfur S_{2p} signals of control unoxidized poly(phenylene sulfide) (PPS) and oxidized PPS, referred to as PPS/A and PPS/B, powder surfaces.

for all the oxygen detected on the control PPS surface and shall be discussed later.

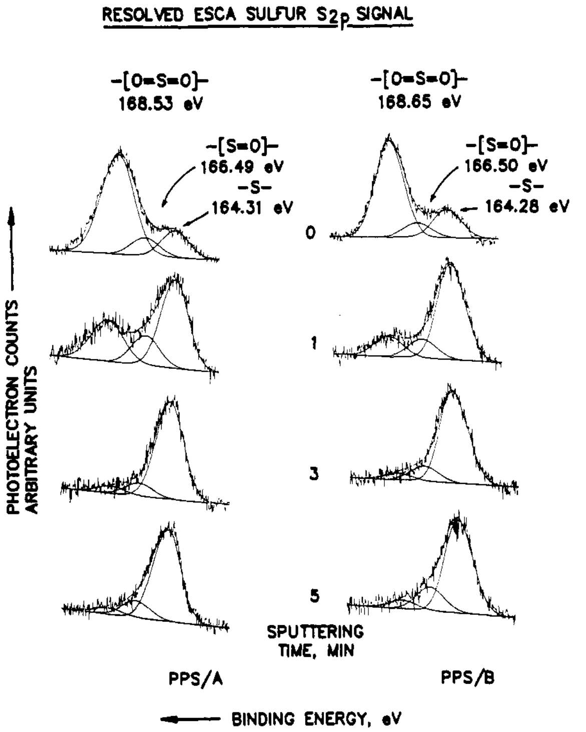


Figure 3. Resolved ESCA sulfur S_{2p} component peaks of oxidized poly(phenylene sulfide), referred to as PPS/A and PPS/B, powder surfaces before and after Ar^+ ion sputtering. Binding energies indicated are average values.

Table IV
ESCA Binding Energies of Resolved Peaks in the Sulfur (S_{2p}) Signal of Control and Oxidized Poly(phenylene sulfide) Powders

	binding energy,[a] eV, $S_{2p_{3/2}}$		
surface	sulfide	sulfoxide	sulfone
PPS	134.30 (2.4)[c]	166.40 (2.4)	[b]
PPS/A	164.55 (2.4)	166.75 (2.4)	168.85 (2.8)
PPS/B	164.45 (2.4)	166.65 (2.4)	168.65 (2.4)
PS	164.35 (2.2)	[b]	168.55 (2.2)

[a] Normalized with (C—C, C=C) at 285 eV. [b] Peak does not exist. [c] Full width at half-maximum (FWHM), eV.

Table V
ESCA Atom Percent of Resolved Peaks in the Carbon (C_{1s}) Signal of Control and Oxidized Poly(phenylene sulfide) Powders

	C_{1s}, atom %	
surface	C—C, C=C	C—O, C—S
PPS	83.8	2.1
PPS/A	63.6	14.3
PPS/B	73.3	6.3
PS	71.4	15.0

The sulfur S_{2p} signal in both PPS/A and PPS/B has three components to it as seen in Figure 3 (zero sputtering time). The sulfide (—S—), sulfoxide (—[S=O]—), and sulfone (—[O=S=O]—) atom percents (Table III) are 1.5, 1.1, and 5.6 in the case of PPS/A and 1.6, 1.0, and 4.7 for PPS/B, respectively. Since the phenyl ring is an electron donor the shift in binding energy (BE) of the sulfide from elemental sulfur is small while the sulfonyl groups show a higher BE shift. The shift for the sulfone is the greatest. Binding energies associated with the various chemical groups related to the sulfur atom are presented in Table IV. The full width of each peak at half-maximum (FWHM) is basically 2.4 eV. The splitting of the S_{2p} signal into a $S_{2p_{1/2}}$ and $S_{2p_{3/2}}$ doublet about 1.1 eV apart, due to spin–orbit coupling effects, is not resolved on any of the surfaces. A FWHM of 2.8 eV for the sulfone group on PPS/A may indicate a small amount of sulfur species with a higher oxidation state but is not confirmed. The BE

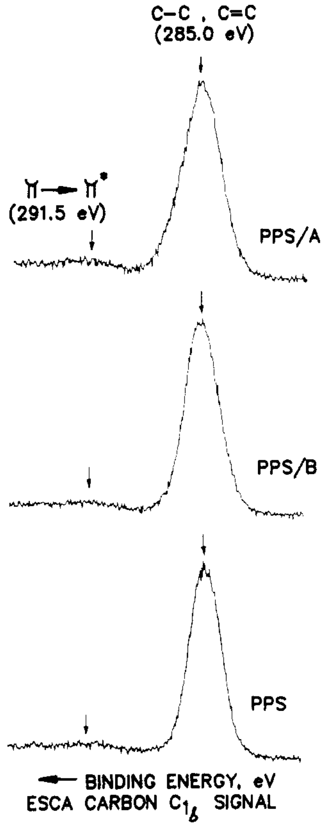


Figure 4. ESCA carbon C_{1s} signal of control unoxidized poly(phenylene sulfide) (PPS) and oxidized PPS, referred to as PPS/A and PPS/B, powder surfaces showing the hydrocarbon carbon (C—C, C=C) and the $\pi \rightarrow \pi^*$ phenyl ring (C=C) transition peaks.

assignments[7,16] can be confirmed, further, through references of Siegbahn et al.[29] and Pfluger and Street.[30] It can be seen in Table IV that the average BE shifts with respect to the sulfide (—S—) sulfur are about 2.17 and 4.25 eV for the sulfoxide (—[S=O]—) and the sulfone (—[O=S=O]—), respectively. Thus, the BE shift for the sulfone is about two times that for the sulfoxide and is directly related to the number of oxygen atoms reacted with the sulfur. This further confirms the similarity in the oxygen environment with respect to the sulfur atom in the two cases; i.e., both the sulfoxide and the sulfone have sulfonyl (doubly bonded oxygen) type of oxygen bonding. There is no evidence for cross-linking of two chains via a S-O-S type of bond.

Compared to the inherent sulfoxide in control PPS the number of sulfoxide groups have increased more than three times after oxidation. The sulfone/sulfide ratios for PPS/A and PPS/B are 3.73 and 2.93, respectively, revealing a high degree of conversion to sulfone. Thus, there is a significant number of sulfone groups randomly distributed after the oxidation reactions. Therefore, both PPS/A and PPS/B will tend to show surface properties predominately similar to that of polysulfone in comparison to that of poly(phenylene sulfide). The above ratios are only true in the surface region since the core of the PPS polymer particle has just the original sulfide and sulfoxide groups, as is suggested by sputtering studies presented later in the section on depth profiling.

Since two oxygen atoms are associated with a sulfone and one with a sulfoxide, the calculated amount of O associated with S is 0.3%, 12.3%, and 10.4% for PPS, PPS/A, and PPS/B (from Table III), respectively. The total amount of oxygen detected, compared to the calculated value, in each case is greater by 3.3%, 1.6%, and 2.7%, respectively. This is believed to be due to oxygen containing carbonaceous material associated with the surface as well as the bulk and possibly explains why the ideal S/C ratio of 0.17 is not observed in either of the cases. The $\pi \rightarrow \pi^*$ shakeup transition due to the phenyl ring is clearly observed in the carbon signal for all three surfaces, Figure 4. The carbon peak can be resolved into two peaks, hydrocarbon carbon (C—C, C=C) and carbon due to C—O. The ether group may have C—S associated with it. The ideal C—S/(C—C, C=C) ratio in PPS based on the number of atoms is 0.2. The measured (C—O, C—S)/(C—C, C=C) ratio is only 0.03. The ratio of total oxygen to the (C—C, C=C) signal on control PPS, however, is about 0.04. Thus, the C—S shift in PPS is greatly suppressed due to the electron-donating character of the phenyl ring. However, the (C—O, C—S)/(C—C, C=C) and O/(C—C, C=C) ratios are 0.22 and 0.22 for PPS/A after reaction A and 0.09 and 0.18 for PPS/B after reaction B, respectively. This increase suggests that oxidizing the sulfur atom essentially makes the S atom more electronegative. Thus, the C—S bond shift is no longer suppressed which results in a higher (C—O, C—S)/(C—C, C=C) ratio, than the ideal C—S/(C—C, C=C) ratio in PPS. This, then, is evidence of the double-bond character of the C—S bond in poly(phenylene sulfide) and is an important factor in the conductivity properties of this polymer. ESCA and other evidence[7,16,17] of this double-bond character exists in the literature.

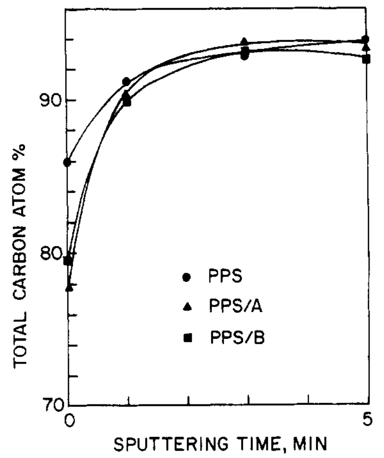


Figure 5. Carbon C_{1s} depth profiles (using Ar^+ ion sputtering) of control unoxidized poly(phenylene sulfide) (PPS) and oxidized PPS, referred to as PPS/A and PPS/B, powder surfaces.

Depth Profiling. Since the samples investigated were powders, depth profiling by sputtering was performed in order to evaluate whether the reactions had progressed within the pores or the subsurface region of the polymer particles. The sputtering times employed were 1, 3, and 5 min and correspond to depths of 20, 60, and 100 Å, respectively. These depth values reported are highly approximate and may be in error by up to 25%. In all three cases, viz., PPS, PPS/A, and PPS/B, the same surface is subjected to the sputtering conditions. It is assumed that there is no contribution from the tape used to mount the powders. The effect of sputtering on the S_{2p} signal is observed in Figure 3 for the case of PPS/A. Similar effects are observed for PPS/B. Figure 5 is a plot of total carbon versus sputtering time for the three cases. The initial value of the carbon content (atom percent) for PPS is much higher, as expected, than for both PPS/A and PPS/B and increases with depth. The total amount of carbon in the case of PPS/A and PPS/B levels off at about the same value as that for unsputtered PPS with increasing sputtering time. For example, after 5 min of sputtering the carbon values in the three cases are 93.7% (PPS), 93.4%

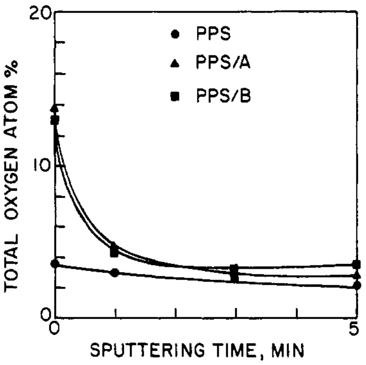


Figure 6. Oxygen O_{1s} depth profiles (using Ar^+ ion sputtering) of control unoxidized poly(phenylene sulfide) (PPS) and oxidized PPS, referred to as PPS/A and PPS/B, powder surfaces.

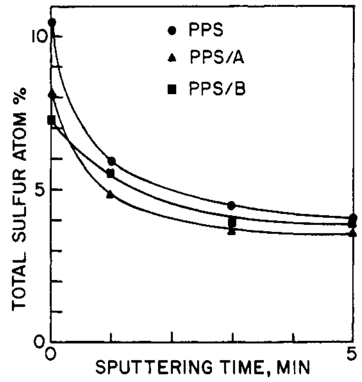


Figure 7. Sulfur S_{2p} depth profiles based on $S_{2p_{3/2}}$ component signal (using Ar^+ ion sputtering) of control unoxidized poly(phenylene sulfide) (PPS) and oxidized PPS, referred to as PPS/A and PPS/B, powder surfaces.

(PPS/A), and 92.5% (PPS/B), respectively. The $\pi \rightarrow \pi^*$ shakeup transition of the phenyl ring is suppressed on sputtering in each of the three cases. Figure 6 is a similar plot of total oxygen but the trend is opposite to that of carbon. The oxygen percent for PPS, however, does not change appreciably with depth. For PPS/A and PPS/B they decrease and level off to similar values as that for PPS. Thus, O is retained even after 5 min of sputtering and is not just a surface contaminant, a small fraction of which is due to the sulfoxide (—[S=O]—) group in every case. Trace amounts of sulfoxide are present in control PPS. Figure 7 is a plot of total sulfur. For PPS, sulfur decreases with depth and levels off at about 38% of the initial concentration. If the PPS, for example, can be assumed to be a uniform polymer particle, then the total S or S/C ratio should remain relatively constant with depth. The results in Figure 7 suggest that Ar^+ ion sputtering results in preferential fragmentation with respect to the S atom in the polymer main chain. Figure 8 is a plot of the various forms of sulfur versus sputtering time. The sulfide group decreases with depth to about 30% of its original signal while the sulfoxide signal increases slightly for PPS. The sulfide fraction for PPS/A and PPS/B, on the other hand, increases and levels off at the level of the sputtered PPS surface. Further, the sulfoxide does not change significantly while the sulfone decreases and levels off at 0.1%, after 3 min of sputtering. These results are consistent with the fact that the core of the polymer particle remains unchanged after reaction.

Carbon Signal. Atom percents from the resolved carbon C_{1s} peaks are given in Table VI. It can be seen in Table VI and in Figure 9 (example of the control PPS surface) that after sputtering carbonyl (C=O) and carboxylate ([C=O]O) groups are detected. This may be due

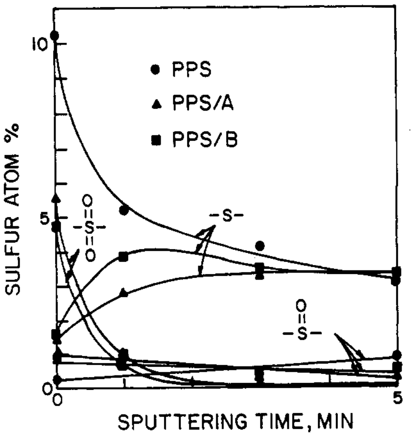


Figure 8. Sulfide (—S—), sulfoxide (—[S=O]—), and sulfone (—[O=S=O]—) group depth profiles based on the sulfur $S_{2p_{3/2}}$ component signal (using Ar^+ ion sputtering) of control unoxidized poly(phenylene sulfide) (PPS) and oxidized PPS, referred to as PPS/A and PPS/B, powder surfaces.

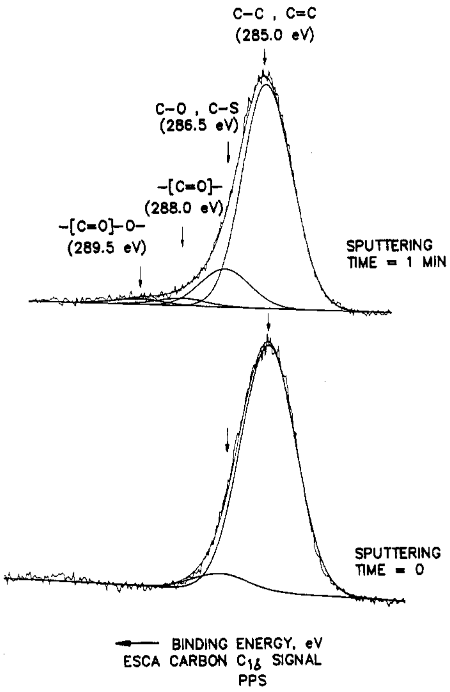


Figure 9. Carbon C_{1s} signals of the control unoxidized poly(phenylene sulfide) (PPS) surface, before Ar^+ ion sputtering and after sputtering for 1 min, showing component peaks.

Table VI
ESCA Atom Percent of Resolved Peaks in the Carbon (C_{1s}) Signal of Sputtered Surfaces

sputtering time, min	C—C, C=C	C—O, C—S	C=O	[C=O]O
		PPS		
0	83.8	2.1	0.0	0.0
1	79.3	10.6	0.6	0.6
3	79.1	10.1	2.5	1.2
5	74.9	14.3	2.9	1.8
		PPS/A		
0	63.6	14.3	0.0	0.0
1	70.2	19.1	1.2	0.0
3	81.0	9.7	2.2	0.8
5	77.7	12.4	2.0	1.3
		PPS/B		
0	73.3	6.3	0.0	0.0
1	74.5	14.1	0.7	0.7
3	78.3	13.3	0.7	0.7
5	71.2	18.5	2.1	0.7

Table VII
Total Oxygen Calculations Based on All Forms of Oxidized Carbon and Sulfur

sputtering time, min	oxygen source from chem groups,[a] atom % (CO)-([C=O]O)	C=O	2([C=O]O)	S=O	2(O=S=O)
		PPS			
0	2.1	0.0	0.0	0.3	0.0
1	10.0	0.6	1.2	0.7	0.0
3	8.9	2.5	2.4	0.4	0.0
5	12.5	2.9	3.6	0.9	0.6
		PPS/A			
0	14.3	0.0	0.0	1.1	11.2
1	19.1	1.2	0.0	1.0	2.0
3	8.9	2.2	1.6	0.3	0.2
5	11.1	2.0	2.6	0.4	0.2
		PPS/B			
0	6.3	0.0	0.0	1.0	9.4
1	13.4	0.7	1.4	1.0	1.4
3	12.6	0.7	1.4	0.4	0.2
5	17.8	2.1	1.4	0.6	0.2

[a] COC and [C=O]OH groups considered to be negligible.

Table VIII
Estimated Values of the C—S Group Based on Total Oxygen Detected and the Total Oxygen Calculated from Table VII

sputtering time, min	total oxygen calcd (A)	detected (B)	total C—S calcd (A − B)	C—S/(C—C, C=C) calcd
		PPS		
0	2.4	3.6	[a]	[a]
1	12.5	3.0	9.5	0.12
3	14.2	2.6	11.6	0.15
5	20.5	2.1	18.4	0.25
		PPS/A		
0	26.6	13.9	12.7	0.20
1	23.3	4.7	18.6	0.26
3	13.2	2.7	10.5	0.13
5	16.3	2.9	13.4	0.17
		PPS/B		
0	16.7	13.1	3.6	0.05
1	17.9	4.4	13.5	0.18
3	15.3	3.1	12.2	0.1
5	22.1	3.6	18.5	0.26

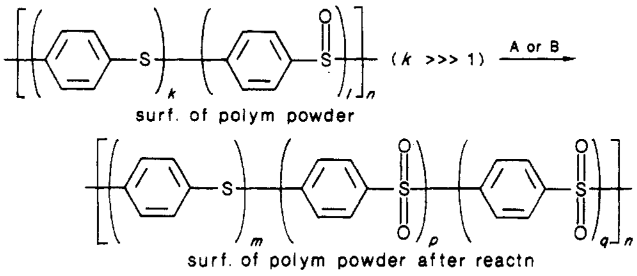
[a] Negative number.

to several factors: viz., the source of argon may have oxygen or the argon gas line may have air trapped in it, there may be a contribution from the two-sided tape to the carbon signal, sputtering may reincorporate oxygen into the surface region, and there may be chemisorbed methanol, used to wash the polymer after reaction, retained by the polymer powder. The C=O/[C=O]O ratio is not constant and not always equal to one, and only C=O is detected after 1 min of sputtering in the case of PPS/A, for example. It is, thus, not possible to identify any one particular source.

Oxidized PPS has a higher level of ether (C—O, C—S) type carbon. Unsputtered PPS has a much lower level. Since the sulfide sulfur is bonded to a carbon atom which is part of a phenyl ring, it appears that a shift due to the C—S bond does not appear in the carbon spectrum. This shift would be less than 1.5 eV as is the case for C—O, due to the higher electronegativity of oxygen. However, when a C—S shift occurs along with C—O a combined peak would be observed since it would not be possible to resolve the two types of carbon bonds. For the control PPS surface, sputtering increases the (C—O, C—S) peak component dramatically. The source of oxygen from chemical groups has been calculated in Table VII. A carboxylate group has two oxygen atoms associated with it and one C—O group, assuming that it is not an acid group. Thus, in terms of atom percent, one oxygen is subtracted from the C—O group in the first column in Table VII. Similarly, the two oxygens in the carboxylate group are represented by the third column. The fifth column also has two oxygens for every sulfone chemical group. The total oxygen calculated in Table VIII can now be compared to the total oxygen detected on the surfaces given in Table II. Except for unsputtered PPS and PPS/B none of the values are comparable. It is possible that the excess oxygen apparently calculated mainly on sputtered surfaces is due to C—S contribution to the C—O group, since this increase is not reflected in the total oxygen signal detected. The actual C—S atom percent can be calculated, Table VIII, from this data. The calculated C—S/(C—C, C=C) ratio given in Table VIII randomly varies in comparison to the ideal ratio of 0.2 in unoxidized PPS. The conclusion of this analysis is that some loss of the phenyl ring or phenyl ring opening may be occurring during sputtering in order for the C—S shift to be observed, as shown by calculations. This can also account for the suppression of the phenyl ring transition ($\pi \rightarrow \pi^*$) observed in the carbon signal. As already mentioned, other possibilities like air contamination of the argon gas and the amount of C—O due to chemisorbed methanol are difficult to evaluate.

Summary

ESCA studies indicate that surface oxidation of poly(phenylene sulfide) powder in a heterogenous reaction is feasible. Sulfonyl groups are generated on the surface with an excess of sulfone groups compared to sulfoxide groups. About 75% of the sulfide groups are oxidized in the surface region and the sulfone/sulfide ratios are 3.73 (PPS/A) and 2.93 (PPS/B) for two reaction schemes. The depth profiling study suggests that the oxidation of PPS has occurred within the pores of the polymer particle or below the subsurface region under slurry conditions, up to a depth of at least 100 Å. Ar^+ ion sputtering results in preferential secondary ions or mass fragments with respect to the S atom and possible opening up of the phenyl ring. The phenyl ring $\pi \rightarrow \pi^*$ transition is suppressed on all sputtered surfaces. ESCA analyses also suggest that a random terpolymer type of surface layer is created and that the actual chemical reaction can be depicted as



Oxidation does not affect the phenyl ring since both unoxidized and oxidized PPS surfaces show the $\pi \rightarrow \pi^*$ transition associated with the unsaturation in the phenyl ring. There is some evidence for the double-bond character of the C—S bond in poly(phenylene sulfide).

Conclusions

Several conclusions can be drawn from the ESCA study of the oxidation of poly(phenylene sulfide) (PPS) in a heterogeneous reaction scheme.

The total oxygen content of oxidized PPS increases by over 9.5%. PPS is reacted with formic acid–hydrogen peroxide to give polymer PPS/A and with 3-chloroperoxybenzoic acid to give polymer PPS/B.

PPS has about 0.3% sulfoxide (—[S=O]—) sulfur. Oxygen incorporation results in the generation of additional sulfoxide and also sulfone (—[O=S=O]—) groups monitored by the component peaks in the sulfur S_{2p} signal. The sulfone to sulfide ratios for PPS/A and PPS/B are 3.73 and 2.93, respectively. The sulfoxide to sulfide ratios are 0.73 and 0.63, respectively.

The binding energy shift between the sulfone (—[O=S=O]—) and the sulfide (—S—) sulfur is about two times that between the sulfoxide (—[S=O]—) and the sulfide, confirming the peak assignments, which seems to be directly related to the number of oxygen atoms reacted with the sulfur atom.

The extent of conversion of the sulfide group to a sulfonyl group is comparable for both of the oxidizing agents under the specific reaction conditions employed. The reaction condition may be controlled to give a specific sulfone/sulfide or (sulfone + sulfoxide)/sulfide ratio.

Oxidation does not affect the phenyl ring since both unoxidized and oxidized PPS surfaces show the $\pi \rightarrow \pi^*$ transition associated with unsaturation in the phenyl ring. The results, further, support the double-bond character of the C—S bond suggested in the literature.

Excess oxygen associated with the carbon C_{1s} signal detected may be due to oxygen-containing carbonaceous material associated with the surface as well as the bulk, for example, methanol retained after washing. Apparent contribution to the ether or alcohol group (C—O) from the C—S link in sputtered surfaces is also possible.

Ar^+ ion sputtering of the PPS, PPS/A, and PPS/B surfaces increases the carbon and decreases the oxygen signal down to bulk values present in unsputtered PPS. Depth profiling of oxidized surfaces shows an increase in the sulfide and a decrease in the sulfone concentration, the former approaching the bulk concentration of 2.8 atom % in sputtered PPS and the latter tending to zero.

The complex phenomenon occurring during ion sputtering is revealed in this study. The $\pi \rightarrow \pi^*$ shakeup transition of the phenyl ring is suppressed. Preferential fragmentation of the sulfur atom seems to occur. Sputtered PPS shows a 70% decrease in the resolved sulfide signal compared to unsputtered PPS. The total sulfur content (sulfide + sulfoxide + sulfone) also decreases by about 62%. The sulfoxide group on the other hand is retained. Both splitting of the phenyl ring and reincorporation of oxygen are evident.

Depth profiling results, further, suggest that the core of the PPS polymer particle remains unchanged after oxidation and that the overall effect of the reaction is the creation of a surface and subsurface region equivalent to a random terpolymer consisting of sulfide, sulfoxide, and sulfone groups bonded to the phenyl ring in the main chain.

Acknowledgment. We thank the Monsanto Chemical Co. for allowing the publication of this work.

Registry No. PPS (homopolymer), 9016-75-5; PPS (SRU), 33411-63-1; performic acid, 107-32-4; 3-chloroperoxybenzoic acid, 937-14-4.

References and Notes

(1) Clark, D. T.; Stephenson, P. J. *Polymer* **1982**, *23*, 103A.
(2) Zadorecki, P.; Ronnhult, T. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 737.
(3) Millard, M. M. *Anal. Chem.* **1972**, *44*, 828.
(4) Carr, C. M.; Leaver, I. H.; Hughes, A. E. *Text. Res. J.* **1986**, *56*(3), 216.
(5) Carr, C. M.; Leaver, I. H.; Hughes, A. E. *Text. Res. J.* **1986**, *56*(7), 457.
(6) Tabor, B. J.; Magre, E. P.; Boon, J. *Eur. Polym. J.* **1971**, *7*, 1127.
(7) Riga, J.; Boutique, J. P.; Pireaux, J. J.; Verbist, J. J. In *Physicochemical Aspects of Polymer Surfaces*; Mitlal, K. L., Ed.; Plenum Press: New York, 1981; Vol. 1, p 45.
(8) Joshi, S. G.; Radhakrishnan, S. *Thin Solid Films* **1986**, *142*, 213.
(9) Rubner, M. F.; Morris, P.; Cukor, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25*(2), 280.
(10) Zeng, H.; Guoren, H.; Yang, G. *Angew. Makromol. Chem.* **1986**, *142*, 25.
(11) Shimizu, H.; Tanabe, Y.; Kanetsuna, H. *Polym. J.* **1986**, *18*(4), 367.
(12) Czerwinski, W. *Angew. Makromol. Chem.* **1986**, *144*, 101.
(13) Rabolt, J. F.; Clarke, T. C.; Kanazawa, K. K.; et al. *J. Chem. Soc., Chem. Commun.* **1980**, 347.
(14) Chance, R. R.; Shaacklette, L. W.; Miller, G. G.; et al. *J. Chem. Soc., Chem. Commun.* **1980**, 348.
(15) Schoch, K. F., Jr.; Bartko, J. *Annu. Tech. Conf.—Soc. Plast. Eng.* **1986**, 273.
(16) Kispert, L. D.; Files, L. A.; Frommer, J. E.; et al. *J. Chem. Phys.* **1983**, *78*(8), 4858.
(17) Tsukamoto, J.; Matsumura, K. *Jpn. J. Appl.* Phys. **1985**, *24*(8), 974.
(18) Brady, D. G. *J. Appl. Polym. Sci.* **1976**, *20*, 2541.
(19) Hawkins, R. T. *Macromolecules* **1976**, *9*, 189.
(20) Hill, H. W., Jr.; Brady, D. G. *Polym. Eng. Sci.* **1976**, *16*, 832.
(21) Short, J. N.; Hill, H. W., Jr. *Chem. Technol.* **1972**, *2*, 481.
(22) Brady, D. G. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1981**, *No. 36*, 231.
(23) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; p 1089.
(24) Vives, V. C.; Brady, D. G. U.S. Patent 4,377,660.
(25) Kaul, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 1,229.
(26) Udipi, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 217.
(27) Swern, D. In *Encyclopedia of Polymer Technology*; Mark, F., Gaylord, N. G., Eds.; Interscience: New York, 1965; p 85.
(28) Stacy, C. J. *J. Appl. Polym. Sci.* **1986**, *32*, 3959.
(29) Siegbahn, K.; Nordling, C.; Fahlman, A.; et al. *Electron Spectroscopy for Chemical Analysis*; Technical Report No. AFML-TR-68-189, NTIS; U.S. Department of Commerce: Washington, DC, 1968; p 112.
(30) Pfluger, P.; Street, G. B. *J. Chem. Phys.* **1984**, *80*(1), 544.