

# Photooxidation of the Surfaces of Polyphenylene Oxide and Polysulfone

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## Synopsis

Changes in the composition and structure of the surfaces of polyphenylene oxide (PPO) and polysulfone caused by UV photooxidation are followed using ESCA. The surface stoichiometry of PPO changes from  $C_8O_1$  to  $C_8O_{4.8}$  on photooxidation, the oxygen being added in the form of carbonyl and especially carboxyl groups. Surface photooxidation is rapid, the ESCA spectra showing substantial changes after a few minutes of irradiation, and no further changes being detected after 10 h of reaction. The surface photooxidation of polysulfone occurs in three stages. In the first 2 h rapid oxidation takes place at carbon atoms, the levels of C—O, carbonyl, and carboxyl groups increasing at comparable rates. This is followed by slower oxygen incorporation up to 15 h of reaction, during which time carbonyl and carboxyl levels increase and oxidation of the sulfone sulfur is observed. Some degradation occurs as groups containing carbon and oxygen are lost from the surface. Further oxidation then produces a decrease in the surface levels of C—O and carbonyl groups, and further degradation. The photooxidized surface has a stoichiometry of  $C_{10}O_6S$ , compared with  $C_{27}O_4S$  in the unreacted polymer.

## INTRODUCTION

As the interaction of a solid polymer with its surroundings occurs at the polymer surface, many properties of a polymer depend upon the surface composition and structure. Changes in the surface regions can affect these properties adversely or favorably. Photooxidation of a solid polymer effects chemical changes throughout the solid, but it is to be expected that the surface is affected to a greater extent than the polymer bulk, as at the surface the oxygen concentration remains uniformly high, not being dependent upon rates of diffusion through the solid, and the photon flux is highest, not being attenuated by absorption in the polymer. Polymer photooxidation has been studied extensively,<sup>1,2</sup> the main emphasis, however, pertaining to bulk effects. ESCA has been shown to be a powerful technique for examining polymer surfaces<sup>3,4</sup> and has recently been used in studies of the surface photooxidation of polystyrene<sup>5</sup> and a number of nonaromatic polymers.<sup>6</sup> In addition to monitoring the extent of oxidation through changes in the overall core electron band intensities, the structures of the oxidized surfaces were determined from the binding energies and relative intensities of the deconvoluted  $C_{1s}$  component peaks. Surface photooxidation of polystyrene occurred considerably more rapidly, and was more extensive, than surface photooxidation of nylon, poly(methyl methacrylate), poly(vinylidene fluoride), or polyethylene. This was attributed to the presence of the aromatic ring as a chromophore providing an efficient means of energy transfer from the ultraviolet radiation to the reactant polymer-oxygen system. These studies have been extended to the aromatic polymers polysulfone and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO).

Both PPO and polysulfone show good thermal and thermal oxidative stability,<sup>7,8</sup> but they are known to be susceptible to ultraviolet photodegradation and oxidation. Indeed, both polymers darken under ultraviolet radiation to such an extent that their darkening has been proposed as a means of monitoring levels of ultraviolet radiation.<sup>9,10</sup> For PPO, the bulk photooxidation processes have been studied by Kelleher et al.<sup>11</sup> and by Jerussi.<sup>12</sup> Photooxidation was shown to result in considerable crosslinking, along with oxygen incorporation and evolution of CO<sub>2</sub> and H<sub>2</sub>. Oxygen incorporation led to the appearance of broad bands in the hydroxyl and carbonyl regions of the infrared spectrum, indicative of a variety of oxidation products. Reaction was believed to occur at the methyl groups. Photooxidation of polysulfone also resulted in the appearance of broad hydroxyl and carbonyl bands in the infrared.<sup>8,13</sup> Decrease in the methyl band intensity indicated especially that the methyl groups were attacked, although it was suggested that all bonds except the C—C and C—H of the aromatic rings underwent scission, the sulfone link being especially susceptible. Identified degradation products included CO, CO<sub>2</sub>, and a highly oxidized low molecular weight sulfonic acid. However, for neither polymer were surface photooxidation effects studied. In this paper the specific surface photooxidation of PPO and polysulfone is described, the course of the oxidation being monitored using ESCA.

## EXPERIMENTAL

The samples studied were films of PPO and polysulfone provided by Dr. A. Davis, MOD ERDE, Waltham Abbey. ESCA analysis of the films as received indicated that in each case the surface stoichiometry was that expected from the molecular formula.

Details of the photooxidation system have been presented.<sup>5</sup> Briefly, for each run a sample of the polymer film was mounted on a probe tip capable of transferring the sample directly from the reaction chamber, where the irradiation was carried out, to the spectrometer sample chamber. Pure oxygen or air was introduced into the reaction chamber at a pressure of ca. 1 atm. The sample was irradiated through a sapphire window using the mercury lamp described previously.<sup>5</sup> The most intense lines of this lamp are at 254, 365, 436, and 546 nm. Irradiations were performed for increasing lengths of time, using a fresh polymer sample each time. Every treatment was followed by evacuation of the reaction chamber, which then functioned as an insertion lock for the spectrometer sample chamber, allowing immediate transfer of the treated film into the spectrometer via a Goddard valve.

ESCA spectra were obtained on an AEI ES200 B spectrometer using Mg-K<sub>α</sub> x-radiation. The base operating pressure in the sample region was ca.  $5 \times 10^{-8}$  torr; any volatile photoproducts would not be retained in the polymer surface at such a pressure. Under the conditions employed in this investigation the Au 4f<sub>7/2</sub> line at 84.0 eV binding energy, used for calibration, had a full width at half maximum of 1.15 eV.

Spectra were deconvoluted and integrated using a DuPont 310 curve resolver. Binding energies were referenced to the hydrogen component peak at 285.0 eV.

Ultraviolet spectra of the polymers in chloroform solution were recorded using a Beckman ACTA MVII spectrophotometer.

## RESULTS

The ESCA spectra of PPO and polysulfone photooxidized in oxygen are shown in Figures 1 and 2 respectively. The increase in the intensity of the  $O_{1s}$  band with the time of photooxidation is evident for each polymer, and is accompanied in each case by the appearance of an envelope of peaks to the high binding energy side of the main  $C_{1s}$  peak. The intensity of this envelope also increases with irradiation time in oxygen. For polysulfone, extensive photooxidation also results in the appearance of high binding energy components in the  $S_{2p}$  region.

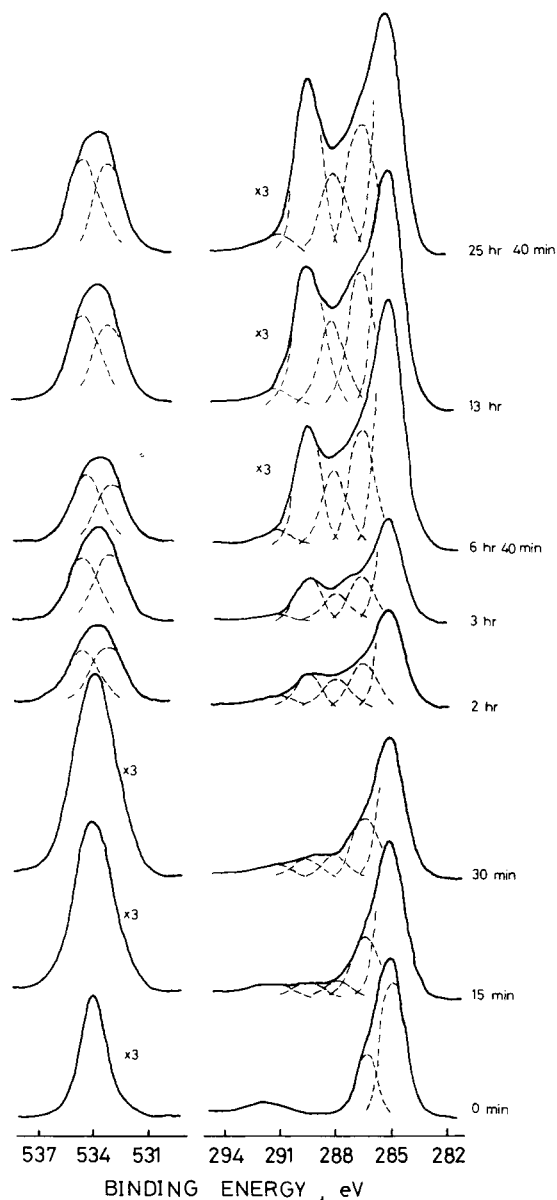


Fig. 1. ESCA spectra of PPO unreacted, and after photooxidation for the indicated lengths of time.

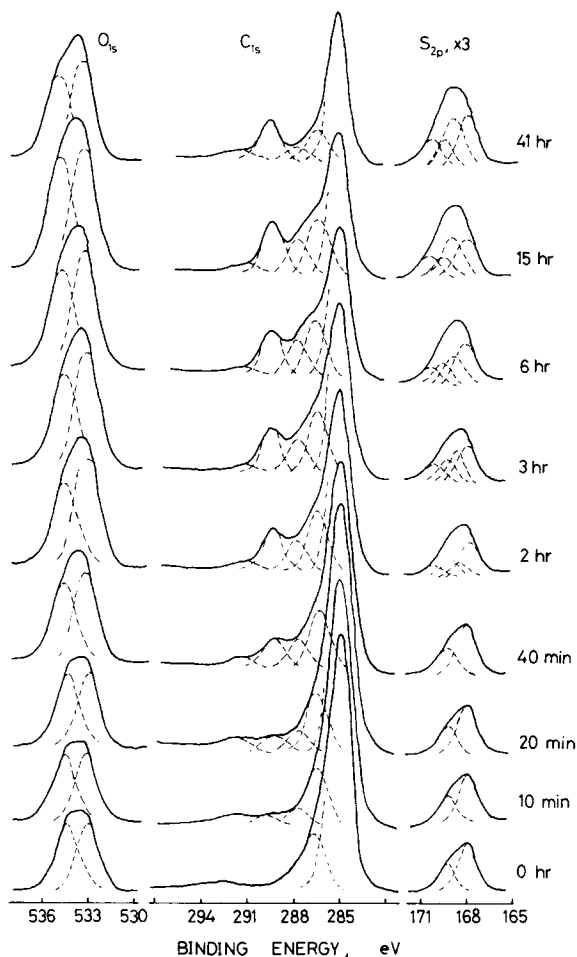


Fig. 2. ESCA spectra of polysulfone unreacted, and after photooxidation for the indicated lengths of time.

Qualitatively, the same changes are observed in the spectra of PPO and polysulfone irradiated in air.

In Figure 3 the increase in the  $O_{1s}$  band intensity is shown quantitatively in plots of the  $C_{1s}/O_{1s}$  intensity ratio as a function of irradiation time in oxygen for PPO and polysulfone, with the data for polystyrene<sup>5</sup> included for comparison. The three polymers behave in a remarkably similar way, all three showing an initial rapid decrease in the  $C_{1s}/O_{1s}$  intensity ratio, leveling off after about 5 h of irradiation. In polysulfone, changes in the intensity of the  $S_{2p}$  relative to the other core level bands provide more insight into the photooxidation of this polymer. Figure 4 shows the  $O_{1s}/S_{2p}$  intensity ratio for polysulfone at first increasing, then gradually decreasing as the extent of photooxidation in oxygen increases. At the same time the  $C_{1s}/S_{2p}$  intensity ratio initially remains constant, and then shows a continuous decrease.

Photooxidation in air rather than oxygen has the same effects on the core level band intensities. The  $C_{1s}/O_{1s}$  intensity ratios decrease less rapidly in the initial stages of reaction, and the limiting values for long reaction time are somewhat

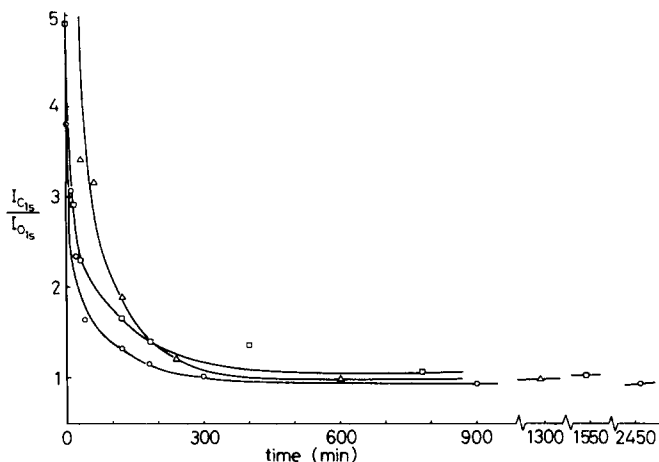


Fig. 3.  $C_{1s}/O_{1s}$  intensity ratios for polystyrene ( $\Delta$ ), PPO ( $\square$ ), and polysulfone ( $\circ$ ), plotted against photooxidation time.

greater than shown in Figure 4, although the trends observed at long reaction times are less pronounced than in the case of photolysis in oxygen.

Deconvolution of the ESCA core level bands is shown in Figures 1 and 2. For the oxidized polymers, the mean values of the binding energies measured from these deconvoluted peaks are given in Table I, with the results for polystyrene<sup>5</sup> included for comparison. The assignment of the  $C_{1s}$  and  $O_{1s}$  components has

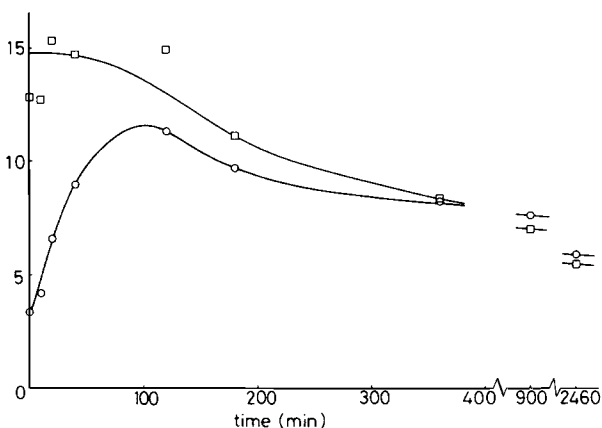


Fig. 4.  $O_{1s}/S_{2p}$  and  $C_{1s}/S_{2p}$  intensity ratios for polysulfone, plotted against photooxidation time. ( $\circ$ )  $I_{O_{1s}}/I_{S_{2p}}$ , ( $\square$ )  $I_{C_{1s}}/I_{S_{2p}}$ .

TABLE I  
Average Binding Energies for Photooxidized Polystyrene, PPO, and Polysulfone

|             | $C_{1s}$ |       |       |       |       | $O_{1s}$ |       | $S_{2p_{3/2}}$ |       |
|-------------|----------|-------|-------|-------|-------|----------|-------|----------------|-------|
| Polystyrene | 285.0    | 286.5 | 287.9 | 289.4 | 291.2 | 533.1    | 534.4 |                |       |
| PPO         | 285.0    | 286.5 | 287.9 | 289.4 | 291.1 | 533.0    | 534.3 |                |       |
| Polysulfone | 285.0    | 286.4 | 287.7 | 289.3 | 291.3 | 532.7    | 534.2 | 169.3          | 170.0 |

been discussed.<sup>5</sup> In summary the  $C_{1s}$  peak at 285.0 eV is due to carbon bonded only to carbon or hydrogen, that at 286.5 eV to carbon having a single bond to oxygen, that at 287.9 eV to carbon with two bonds to oxygen, while the 289.4 eV peak originates in those carbons having three bonds to oxygen. Carbonate-type structures and shake-up peaks due to the aromatic systems<sup>14</sup> together give rise to the component at 291.2 eV. Those carbons with bonds to sulfur in the polysulfone have a binding energy not much different from 285.0 eV,<sup>15</sup> and no attempt has been made to detect this as a separate  $C_{1s}$  component. The  $O_{1s}$  component of higher binding energy can originate in the singly bonded oxygen of acids, esters, carbonates, peroxyacids, or peroxyesters, while the other component is due to acyl oxygens and singly bonded oxygens in alcohols, ethers, and peroxides. Oxygen doubly bonded to sulfur has been shown before<sup>15</sup> to have a significantly lower binding energy than an acyl oxygen. This is consistent with the binding energy of 532.7 eV for the low binding energy component of polysulfone, which contains a contribution from oxygens of the sulfoxide groups, versus 533.1 eV for the analogous peak in polystyrene and PPO. For polysulfone the doublet ( $S_{2p_{3/2}}$  and  $S_{2p_{1/2}}$ ) in the  $S_{2p}$  region at 168.0 and 169.3 eV is due to sulfur as in the unreacted polymer. The appearance of the high binding energy components is indicative of the presence of more highly oxidized sulfur.

The relative intensities of the  $C_{1s}$  component peaks for PPO and polysulfone photooxidized in oxygen are shown in Figures 5 and 6 as the percent each component contributes to the overall  $C_{1s}$  band intensity as a function of irradiation time. Photooxidation in air produces very similar changes in the relative  $C_{1s}$  component intensities.

In the ultraviolet, PPO and polysulfone both begin to absorb strongly just above 300 nm, while the absorption for polystyrene begins around 280 nm. All three polymers absorb strongly at 254 nm, the wavelength of one of the intense lines generated by the lamp used for these experiments.

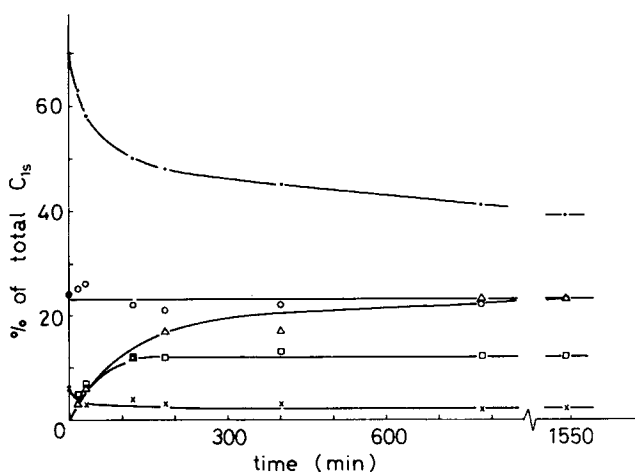


Fig. 5. Intensities of the individual PPO  $C_{1s}$  component peaks, expressed as a percentage of total PPO  $C_{1s}$  band intensity, plotted vs. photooxidation time. (•) 285.0, (○) 286.5, (□) 287.9, (△) 289.4, (x) 291.1.

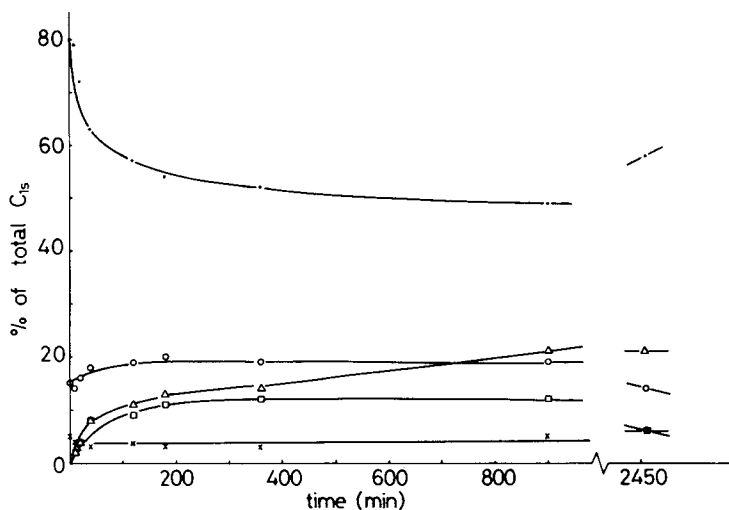


Fig. 6. Intensities of the individual polysulfone  $C_{1s}$  component peaks, expressed as a percentage of total polysulfone  $C_{1s}$  band intensity, plotted vs. photooxidation time. (●) 285.0, (○) 286.4, (□) 287.7, (△) 289.3, (x) 291.0.

## DISCUSSION

### 1. Polyphenylene Oxide

#### a. Composition of the Oxidized Surface

Incorporation of oxygen into the PPO surface on photooxidation in an oxygen atmosphere can be followed via the  $C_{1s}/O_{1s}$  peak intensity ratio (Fig. 3). After ca. 10 h of irradiation this ratio reaches a limiting value of  $\sim 1$ , giving a surface stoichiometry of  $C_8O_{4.8}$  (taking the relative sensitivity of  $C_{1s}/O_{1s}$  as<sup>16</sup> 0.60). Oxygen incorporation into the polymer as a whole has been shown to be very slight, the overall polymer stoichiometry after 500 h of photooxidation corresponding to  $C_8O_{1.09}$ <sup>11</sup> vs.  $C_8O_1$  for pure PPO. Oxidation is thus undoubtedly limited by low access to oxygen in the regions below the surface. The form in which the oxygen is incorporated into the surface can be determined from the  $C_{1s}$  spectral region. In the oxidized PPO, more than half the carbon atoms at the surface are bonded to oxygen (Fig. 5). Of these, roughly 40% have one bond to oxygen (mainly alcohol and/or ether groups, peroxides and hydroperoxides probably being too unstable under extensive uv irradiation to maintain a significant concentration), and an equal number exist in carboxyl groups. Most of the remaining 20% have two bonds to oxygen (probably mainly in carbonyl groups), although a small amount of carbonate-type structural features also appear to be present. The surface of photooxidized PPO differs remarkably in composition and structure from that of the unreacted polymer, and from the bulk of the oxidized polymer. Drastic changes in surface properties can thus be expected for PPO exposed to photooxidative conditions. Furthermore, this modified surface is formed rapidly (Figs. 3 and 5), changes being detected in the ESCA spectrum after 15 min of irradiation. The limiting structure of the surface, at least to the depth sampled by ESCA ( $50 \text{ \AA}$ <sup>17</sup>), is reached after about 10 h.

*b. Mechanism of Surface Oxidation*

Comparison of the progress of photooxidation of the surface to that of the polymer as a whole is informative. Bulk photooxidation of PPO is believed to proceed via hydroperoxides already present in the methyl groups of the polymer.<sup>11</sup> These react to give alcohol and aldehyde groups, which can then be further oxidized to acidic products. These products can undergo further reaction, including decarboxylation. As mentioned above, the total amount of oxygen incorporated into the polymer is small. The observed effects of photooxidation at the surface are not compatible with such a mechanism. For instance, the initial rate of oxygen incorporation into the surface is too high to be accounted for by initiation by low levels of impurities (the ESCA spectrum of unreacted PPO showed no evidence for high levels of any carbonyl or peroxide impurities). The overall similarity to polystyrene photooxidation<sup>5</sup> is noteworthy in this regard. Both PPO and polystyrene absorb strongly at 254 nm, and the similarity in their surface photooxidation characteristics suggests that it is probably absorption of light of this energy by the aromatic groups in the polymers, rather than by some impurity introduced during processing or polymerization, that is responsible for initiating the extensive surface photooxidation of these polymers.

Furthermore, the ESCA data cannot be reconciled with reaction only at the methyl groups, as more than half the carbon atoms at the surface have formed some bond with oxygen (Fig. 5) in the oxidized polymer. Direct evidence for oxidation of the aromatic rings is the decrease in the intensity of the  $C_{1s}$  shake-up satellites, which are known to be characteristics of the aromatic rings.<sup>14</sup>

As photooxidation results in an initially rapid increase in the oxygen content at the surface, the rate decreasing considerably after about 5 h of irradiation, it would appear that after this length of time the surface groups most susceptible to oxidation have reacted. The amount of carbon not bonded to oxygen (giving the  $C_{1s}$  peak at 285.0 eV) decreases steadily, while the proportion of carbon with one bond to oxygen (286.5 eV) remains constant. This implies then that the formation of any surface hydroxyl groups must be accompanied by a cleavage of the backbone ether linkage to about the same extent. The amount of carbon having two bonds to oxygen (287.9 eV, mostly in carbonyl groups) at first increases, then levels off after about 2 h of reaction, so that the proportion of carbon of this type does not exceed 12% of all the carbon atoms at the surface. Apparently the carbonyl groups undergo further oxidation to carboxylic products. Thus the  $C_{1s}$  peak at 289.4 eV, due to carboxylic groups, increases less rapidly than the carbonyl peak, but after 2 h of photooxidation more carbon is present in the more highly oxidized groups, and about 23% of the surface carbon is in this form after 13 h.

As photooxidation proceeds, the trend is towards an increase in the proportion of more highly oxidized functional groups at the surface. This can be seen clearly in Figure 7, where the  $C_{1s}/O_{1s}$  ratio for only those carbons to which oxygen is bonded is plotted vs. oxidation time. In the unreacted polymer this gives a stoichiometry of  $C_2O$ , corresponding to the carbons in the ether linkage, while in the limiting oxidized surface this composition is  $C_1O_1$ .

Since the limiting composition and structure is reached after 10 h of irradiation, beyond which no further changes in the ESCA spectrum are observed (Figs. 3 and 5), further reaction must be limited to the bulk of the polymer beyond the ESCA sampling depth (ca. 50 Å<sup>17</sup>), or alternately it must involve loss of volatile



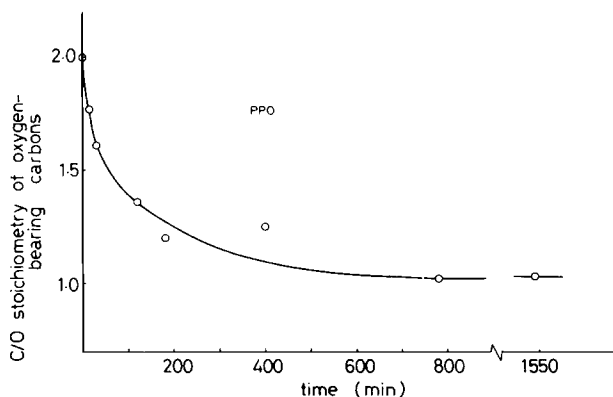


Fig. 7.  $C_{1s}/O_{1s}$  intensity ratio for the oxidized carbons in PPO, plotted vs. photooxidation time.

oxidized groups (e.g., CO or CO<sub>2</sub>) accompanied by oxidation of the remaining polymer in a steady-state situation at the surface. CO<sub>2</sub> has been detected as a photooxidative degradation product from PPO,<sup>11</sup> suggesting that the latter process does occur. Evolution of CO<sub>2</sub> from such a highly oxidized surface (e.g., by decarboxylation of carboxylic acid groups) is considerably more likely than evolution from the polymer bulk, which remains relatively unchanged in composition.

Photooxidation in air produces changes in the ESCA spectra of PPO very similar to those observed for irradiation in oxygen. There is no evidence that the reaction at the surface proceeds at a significantly different rate or by a different mechanism when carried out in air.

## 2. Polysulfone

### a. Composition of Photooxidized Surface

Photooxidation of polysulfone in an oxygen atmosphere results in the formation of an oxidized surface whose composition after 15 h of reaction corresponds to C<sub>13</sub>O<sub>8</sub>S, calculated from the relative ESCA peak intensities and the core level sensitivity ratios.<sup>15</sup> Unlike the case of PPO and polystyrene, however, the surface does not attain an unchanging composition within this time of reaction, further reaction resulting in nonuniform degradation of the polymer. Thus after 41 h the surface has the stoichiometry C<sub>10</sub>O<sub>6</sub>S. The mechanistic aspects of these features are discussed in more detail below. As expected, the surface of the reacted polymer is considerably enriched in oxygen, but in addition the relative amount of sulfur at the surface has increased markedly (the stoichiometry of the starting polymer being C<sub>27</sub>O<sub>4</sub>S). Indeed, the changes in the surface composition occurring after the first 10 h of reaction involve only an apparent increase in the sulfur level, the C/O ratio remaining unchanged.

The oxygen in the oxidized surface is incorporated into both oxidized carbon and oxidized sulfur groups. After 15 h of oxidation half the carbon atoms are bonded to oxygen. 40% of these have one bond to oxygen, 25% have two bonds, and about 30% are in carboxyl groups. The remainder of the oxidized carbon is present in carbonate groups. The appearance of a highly binding energy component in the S<sub>2p</sub> spectral region is evidence for further oxidation of the

sulfone sulfur.<sup>15,18</sup> About half the sulfur in the surface region of the polymer has undergone this further oxidation after 15 h, and the proportion does not appear to have changed upon photooxidation for up to 41 h. Such extensive photooxidation does, however, change the distribution of oxidized carbon groups in the surface. After 41 h 35% of the oxidized carbon has one bond to oxygen, while the amount of carbon with two bonds to oxygen has decreased to 10%, about the same as the proportion present in carbonate groups. About 45% of the carbon atoms which are bonded to oxygen are in carboxyl groups.

Photooxidation of polysulfone in air produces very similar changes in surface composition and structure to those observed for photooxidation in oxygen.

For polysulfone, as was the case for polystyrene and PPO, the considerable changes induced in the surface composition and structure undoubtedly have an effect on the surface properties of the polymer. Again, changes in the surface are detected after a very short time of exposure (ca. 10 min) to ultraviolet light and oxygen.

### *b. Mechanism of the Surface Photooxidation*

The initial photooxidation reaction results in oxidation at carbon atoms in the polymer. Specifically, this gives rise to an increase in the surface C—O content, and to the appearance of carbonyl and carboxyl groups. These all increase in concentration at the surface at approximately equal rates. There is no evidence for oxidation of the sulfur groups in the first 2 h of irradiation. In these early stages of photooxidation the  $C_{1s}/O_{1s}$  ratio decreases sharply (Fig. 3), the  $O_{1s}/S_{2p}$  ratio increases, and the  $C_{1s}/S_{2p}$  ratio remains constant (Fig. 4), as the primary effect on the surface is oxidation at carbon sites.

Between 2 and 15 h of reaction the content of surface C—O groups remains unchanged, while the proportion of carbonyl and carboxyl groups increases, but at a rate considerably slower than that observed during the first 2 h of reaction. The carboxyl content increases at a slightly faster rate than the carbonyl content, continuing the trend noted for PPO and polystyrene to an enhancement in the proportion of the more highly oxidized groups at the surface. Only after 2 h of irradiation does a high binding energy component in the  $S_{2p}$  region become evident, indicating the onset of oxidation at the sulfone groups. The proportion of the more highly oxidized sulfur increases with oxidation time, accounting for half the sulfur at the surface after 15 h. Oxidation of the sulfur therefore occurs at a rate considerably slower than oxidation of the carbon sites, in polysulfone. During this stage of the polymer oxidation the  $C_{1s}/O_{1s}$  intensity ratio decreases much more gradually than in the first 2 h of reaction. Both the  $O_{1s}/S_{2p}$  and  $C_{1s}/S_{2p}$  intensity ratios now decrease. This suggests that degradation of the polymer is occurring, involving the loss of volatile compounds composed of carbon and oxygen from the surface. The observed oxidation of the sulfone groups does not give rise to volatile products which are lost from the polymer, as does oxidation of the carbon sites. The result is a marked increase in the relative sulfur content at the polysulfone surface. Furthermore, since the  $O_{1s}/S_{2p}$  ratio decreases, the rate at which oxygen is lost from the surface through evolution of oxidized carbon groups apparently exceeds the rate at which oxygen is incorporated into the surface via oxidation of the remaining polymer.

Photooxidation beyond 15 h and up to 41 h continues these trends. Reaction

during this time results in a decrease in the level of C–O and carbonyl groups at the surface, so that the more highly oxidized carboxyl and carbonate groups predominate. The proportion of sulfur that has undergone further oxidation remains at about 50% of the total surface sulfur. Further degradation of the surface via loss of oxidized carbon species occurs, as the  $O_{1s}/S_{2p}$  and  $C_{1s}/S_{2p}$  intensity ratios continue to decrease while the  $C_{1s}/O_{1s}$  ratio remains constant.

Overall, then, the photooxidation of the surface of polysulfone can be summarized as relatively rapid oxidation at carbon sites in the polymer, giving rise to an increasingly higher proportion of more highly oxidized carbon groups as the reaction proceeds. This is accompanied by a slower oxidation of the sulfone sulfur. Photooxidative degradation occurs as highly oxidized carbon compounds evolve from the surface. Any evolution of oxidized sulfur groups occurs at a slower rate. This generally conforms with the observations made on the bulk photooxidation of polysulfone.<sup>8,13</sup> Thus it was found that most of the oxygen consumed appears as CO and CO<sub>2</sub> photodegradation products, very little sulfur being evolved in any form (e.g., SO<sub>2</sub>, CS<sub>2</sub>, COS). The sulfone sulfur was found to be further oxidized producing highly oxidized oligomeric sulfonic acids. As discussed above, analysis of the photooxidized polymer showed only a small amount of oxygen incorporation. The ESCA data suggest that this is almost exclusively at the surface. The initiation of the photooxidation has been attributed to uv absorption by the sulfone group<sup>19</sup> rather than impurities in the polymer, and the initial rapid rate of oxygen incorporation agrees with this. Polysulfone, like PPO and polystyrene, absorbs strongly at 254 nm, and in the present experimental conditions this absorption probably initiates the reaction. However, the fact that over half the carbons are oxidized in the surface of the polymer, coupled with the disappearance of the C<sub>1s</sub> shake-up peaks, in the photooxidized polysulfone indicates that the aromatic rings do not remain intact as is apparently the case in the polymer bulk.<sup>8,13</sup>

Finally, photooxidation carried out in air rather than oxygen produces almost identical changes in the polymer surface.

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