An e.s.c.a. investigation of the surface oxidation of bisphenol A polycarbonate films induced by reactive oxygen species

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The changes in surface chemistry of bisphenol A polycarbonate films on exposure to various reactive oxygen species have been examined using e.s.c.a. Oxygen uptake, as a result of ozonation involves reactions of both the gem dimethyl and phenyl moieties. Singlet oxygen does not react with polycarbonate. The results presented here indicate that the interpretation of oxidation mechanisms due to singlet oxygen sould be treated with caution when generating this species by the microwave discharge technique.

INTRODUCTION

The natural weathering of polymers is a very complex process. Although photo-oxidation is generally regarded as the predominant cause of degradation, reactions with reactive gaseous molecules (e.g. O_3, SO_2 and NO_2) present as atmospheric pollutants may also have an important role. We have reported in a recent series of papers some theoretical[1,2] and experimental[3-6] aspects of the natural and artificial photoageing of bisphenol A polycarbonate films. In particular we have investigated the role of photo-oxidation in the degradative processes at the solid/gas interface by means of e.s.c.a., and in this paper we complement these studies by an investigation of the surface oxidation of polycarbonate films induced by reactive oxygen species (namely oxygen and ozone) that have received some attention in the literature.

Ozone is produced in the upper atmosphere by the ultra-violet photolysis of oxygen[7]. The result oxygen atoms then combine with oxygen molecules to form ozone. A layer of ozone at an altitude between ~ 12 and 22 miles has been formed with concentrations as high as 500 parts per hundred million (pphm). This layer acts as an efficient filter of the short wavelengths of solar radiation < 290 nm) and protects life at the earth's surface from the harmful effects of ultra-violet light. As a result of winds, ozone which has diffused into the trophosphere is brought down to the earth's surface[8]. Local concentrations vary widely, depending on locality and weather conditions although they are normally higher in coastal regions.

Ozone reacts with virtually all polymers, the rate of attack being strongly dependent on the structure of the material. The reaction with solid polymers occurs mainly at the surface[9-11] and as such a knowledge of the changes in surface chemistry is of prime importance. Thus the first

part of the results and discussion, considers a preliminary investigation of the surface ozonation of polycarbonate with the aid of e.s.c.a.

Since the proposal, by Trozzolo and Winslow[12], that singlet oxygen may play a possible role in the oxidative photo-degradation of polyethylene, the study of singlet oxygen reactions with polymers has been the centre of considerable interest in the literature[13-15]. In the case of polyethylene, singlet oxygen is postulated as arising from the quenching of $n \rightarrow \pi^*$ triplet states of ketone groups by molecular oxygen[12]. However, it should be noted that there is no experimental evidence for this process.

Two out of the various higher states of excited oxygen molecules were considered by Herzberg[16] to consist of singlet oxygen, namely, $^1O_2(^1\Delta_g)$ and $^1O_2(^1\Sigma_g^+)$. These two singlet states have excitation energies with respect to the ground state of ~ 22.5 and ~ 37.5 kcal mole^{-1} respectively. In the gas phase (under low pressure) the $^1\Delta_g$ state is extremely long-lived (ca. 45 min.), whereas the $^1\Sigma_g^+$ state has a much shorter lifetime (ca. 7 s)[13]. Thus, in general, it is the former species which is considered to be involved in the oxidative degradation of the polymers. Levels of singlet oxygen, in the ppm range, have been identified in urban atmospheres[17,18], consequently polymers which are affected by singlet oxygen need to have these reactions taken into account when their ageing in contaminated atmospheres is being studied.

As, in the case of ozonation, singlet oxygen reactions occur predominantly at the surface[19] of a solid polymer although the literature[14] has not considered to any great extent the nature of the reactions at the gas/solid interface. E.s.c.a. has been shown to be of prime importance as a technique for the study of polymer surface degradation[3-6,20-22] and in this chapter it has been utilized to investigate some aspects of the surface oxidation of bisphenol A polycarbonate induced by ozone and singlet oxygen.

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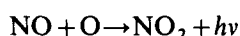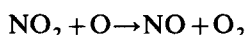
EXPERIMENTAL

Ozonation

Bisphenol A polycarbonate films (30 μm) were exposed to ozone from an ozonator, (Ozone Research and Equipment Corporation) for various periods of time, in a purged pyrex vessel. The ozone concentration, determined by iodometric-thiosulphate titration, was 0.27 mole %[10].

Singlet oxygen

Singlet oxygen was generated by the microwave discharge technique[23]. Oxygen at a pressure of 2 torr was passed through a quartz tube (12.5 mm) encircled by a microwave discharge cavity. The microwave power was supplied by an Electro-Medical Supplies generator (at 60 W and a frequency of 2450 MHz). Singlet oxygen, atomic oxygen and ozone are produced. The concentration of the latter two may be essentially removed by continual distillation of Hg vapour through the discharge region. A ring of mercuric oxide is formed inside the quartz tube downstream of the discharge. The effluent was passed through a dry ice/acetone cold trap ($-78°C$), to remove mercury vapour, and passed to the sample region. The effluent was monitored for atomic oxygen at the sample position, in separate experiments, by the addition of nitric oxide. The fluorescence which arose from the reaction:

$$NO + O \rightarrow NO_2 + h\nu$$
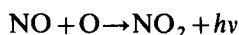
was not observed in the present case. However, a low level of atomic oxygen, estimated to be $\sim 1 \times 10^{-4}$ of the singlet oxygen concentration, has been shown to be present in the effluent from an oxygen discharge even with the presence of mercury vapour[23]. To remove the residual atomic oxygen contamination nitrogen dioxide may be added to the stream beyond the discharge region. This is a very rapid reaction and follows the scheme:

$$NO_2 + O \rightarrow NO + O_2$$
$$NO + O \rightarrow NO_2 + h\nu$$

A bypass system was incorporated to allow the discharge to stabilize before exposing the sample to the effluent. The sample chamber was surrounded by a water jacket enabling this region to be heated to $\sim 80°C$.

The experimental procedure consisted of placing a polymer film mounted on an e.s.c.a. probe tip (using double sided scotch tape) into the reaction chamber and evacuating the whole system to $\sim 10^{-3}$ torr with an Edwards ED50 two-stage rotary pump. After flushing with oxygen at the required pressure for ~ 5 min and ensuring that the flow was directed through the bypass system, the microwave discharge was initiated with an Edwards H. F. Tester and allowed to stabilize for 15 min before passing the effluent over the sample.

As will become apparent from the results and discussion, when mercury vapour is used as the only means of removal of atomic oxygen and ozone; extensive surface oxidation occurs, which may arise from a low level of contamination due to the atomic oxygen and ozone species. To investigate the effect of oxygen atoms on polycarbonate, a flow system based on the design for the singlet oxygen generator described above, was constructed. This essentially consisted of replacing the microwave cavity, with a mercury arc lamp; the dry

ice/acetone cold trap, with liquid nitrogen: and the oxygen by nitrous oxide.

The production of atomic oxygen arose from the mercury sensitized photolysis of nitrous oxide (N_2O) at ~ 254 nm[24]. By passing N_2O through the system at ~ 2 torr with the continual distillation of mercury vapour, a very small level of oxygen atoms was produced. This was supported by the contrast in pressures on either side of the liquid nitrogen cold trap. The pressure in the sample regions was $\sim 10^{-3}$ torr, although an accurate measurement was not possible due to the range of the Edwards Pirani gauge employed.

E.s.c.a. spectra were recorded with an AEI ES200B spectrometer using $MgK\alpha^{1,2}$ radiation. Under the conditions employed the $Au_{4f_{7/2}}$ level at 84.0 eV used for calibration purposes had a full width at half maximum ($FWHM$) of 1.2 eV. Spectra were obtained at electron take-off angles of $\theta = 30°$ and $\theta = 70°$ corresponding to sampling depths of ~ 45 Å and ~ 12 Å respectively. Binding energies were referenced to the $\underline{C}$-H component at 285.0 eV. Line shape analysis of complex spectral envelopes was achieved using a DuPont 310 curve resolver. Area ratios are determined within $\pm 5\%$.

RESULTS AND DISCUSSION

Ozonation

Previous investigations, pertaining to changes in bulk chemistry, of the ozonation of bisphenol A polycarbonate in the solid state[25] and solution phase[9] reveal contrasting degrees of reactivity. It is of interest to compare these data with those obtained for polystyrene[13,19]. The rate of ozonation for polystyrene appears to be greater in the solid state than that in solution whereas the converse situation exists for polycarbonate. An e.s.c.a. study of the surface ozonation of polystyrene films[10] has in fact revealed that extensive oxygen uptake and hence oxidative functionalization occurs. If the trends observed in bulk chemistry are followed then it is to be expected that the changes in the surface chemistry of polycarbonate on ozonation will not be as great as those for polystyrene.

The e.s.c.a. spectra in *Figure 1* reveal the C_{1s} core levels for polycarbonate before and after treatment with ozone. From an initial profile due to peaks arising from $\underline{C}$-H (gem dimethyl and phenyl moieties, $\underset{\underline{C}-O,\ O-\underline{C}-O}{\overset{O}{\underset{\|}{}}}$ and $\pi \rightarrow \pi^*$ shake-up components, additional features due to the $\underset{/}{\overset{\backslash}{}}\underline{C}=O$ and $O-\underline{C}=O$ functionalities appear on exposure to be indicative of oxygen uptake. All the samples revealed a varying degree of surface contamination as supported by the presence of a signal arising from the Si_{2p} core level (~ 102.2 eV). This contamination contributes to the O_{1s} envelope and consequently useful information on oxygen uptake cannot be obtained solely from the O_{1s} levels themselves.

The nature of the changes in the C_{1s} signal are revealed in the component analysis in *Table 1*. The $\underline{C}$-H feature decreases in intensity with concomitant increases in $\underline{C}$-O, $\underset{/}{\overset{\backslash}{}}\underline{C}=O$ and $O-\underline{C}=O$ functionalities. After an initial decrease in the carbonate moiety the level remains relatively constant indicative that this functionality does not play a pre-dominent role in the ozonolysis of poly-

carbonate. The $\pi \rightarrow \pi^*$ shake-up satellite, diagnostic of the aromaticity present, decreases in intensity with increasing ozone exposure such that the level after 32 h is only $\sim 35\%$ of the initial value. These results, therefore suggest that polycarbonate ozonolysis in the surface regions involve both the gem dimethyl groups and aromatic ring systems. It is interesting to note that the extent of reaction of polycarbonate after 32 hours' exposure is not as great as that for polystyrene after two hours under the same degradation conditions. Consequently, the initiation of

oxidative degradation in the natural environment by ozone is of greater importance for the latter system.

Electron spin resonance (e.s.r.) studies of polycarbonate ozonation have revealed radical formation indicating that the formation of peroxy radicals is the predominant reaction over the formation of aromatic ozonides[9]. It is not possible from the data in *Table 1* to delineate the relative predominance of either reaction, however, the decrease in the shake-up satellite intensity suggests that the latter mechanism, in the degradative processes, is of importance in the surface regions.

Ozonated polycarbonate

Figure 1 C_{1s} core levels for ozonated polycarbonate samples

Microwave discharge oxidation of polycarbonate

This section will consider the study of the changes in surface chemistry of polycarbonate films exposed to the effluent of a microwave initiated oxygen discharge; the results from the singlet oxygen reaction studies will be considered later. The reactive oxygen species reaching the sample consists of atomic oxygen, singlet oxygen and ozone. This method has been previously utilized to study the reactions of atomic oxygen with a variety of organic materials[26], including polymers[27], but is generally acknowledged as not being very representative of the reactions involved due to the presence of the other reactive oxygen species.

The e.s.c.a. spectra in *Figure 2* reveals the changes in the C_{1s} and O_{1s} core levels at electron take-off angles of 30° and 70° (of polycarbonate films) after treatment with the effluent of a microwave oxygen discharge (60 W, 2 torr). The increases in complexity of the C_{1s} signal and relative intensity of the O_{1s} envelope provide evidence for intensive oxygen uptake. The spectra for 15 min exposure reveal that the extent of reaction is greater at $\theta = 70°$ and the surface specificity of the oxygen uptake is readily apparent from a comparison of the carbon:oxygen stoichiometries as displayed in *Table 2*. This trend is in essential agreement with that found for the radio-frequency induced plasma oxidation of polymers[20,22].

The nature of the changes in C_{1s} envelope are revealed in the component analysis in *Table 3*. As a take-off angle of 70° after 15 min exposure, carbonyl and carboxylate features are evident contributing 14 and 7% respectively to the total C_{1s} intensity. The carbonate and $\pi \rightarrow \pi^*$ shake-up components have decreased in intensity indicating chain scission at the former and oxidation of the latter. Exposure for a further 15 min results in a decrease in the oxygen content which is reflected by decreases in the contributions of the various oxidized carbon species and an increase in the C–H component at 285.0 eV. This is representative of the ablation of the surface.

On examination of the data for comparable exposures for a take-off angle of 30° the lower degree of reaction is readily apparent. The lesser extent of oxidative
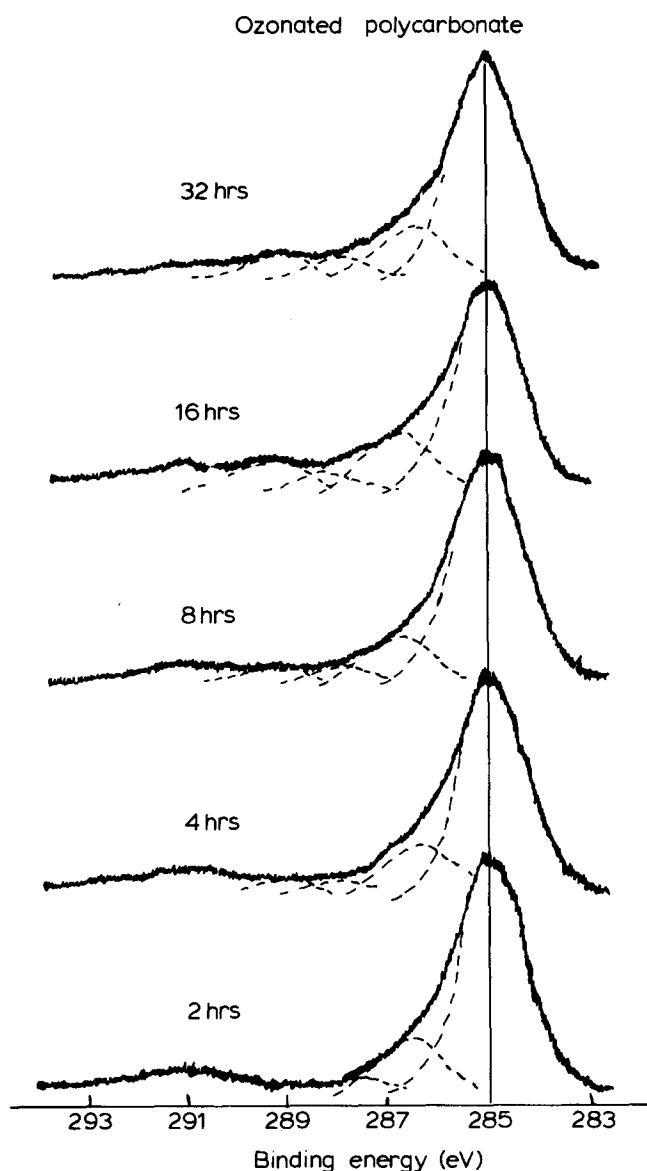
Table 1 Polycarbonate exposed to ozone. Component contributions to the C_{1s} envelope

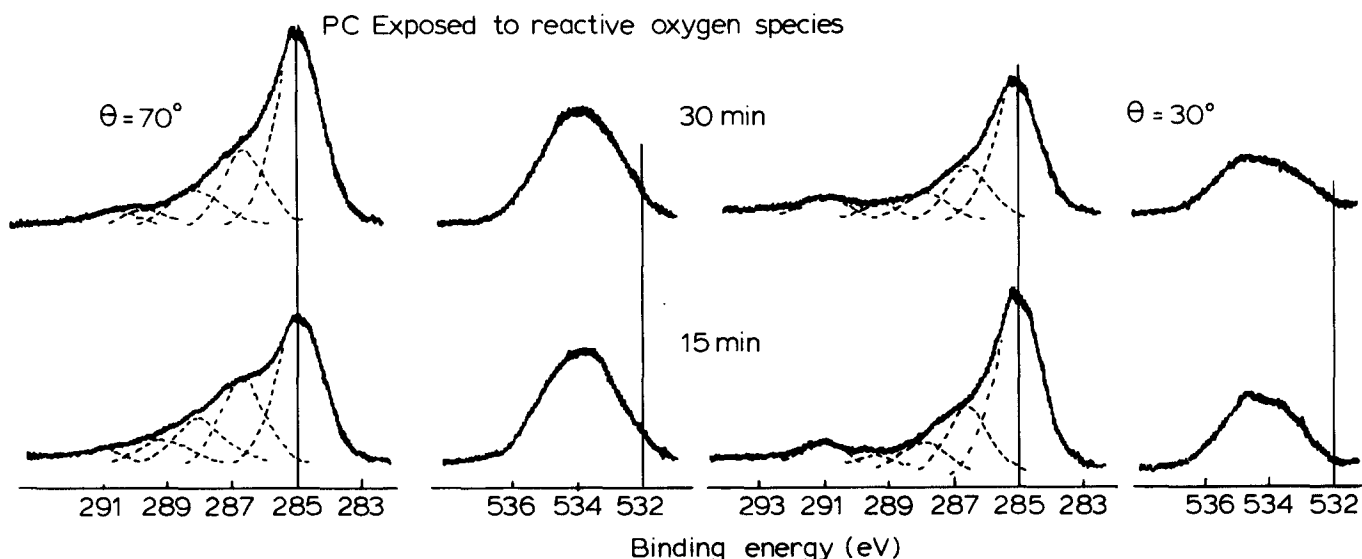| Exposure time (hs)	Total C_{1s}	C–H	C–O	C=O	O–C=O	O–C(=O)–O	Shake-up
0	100	74	15	—	—	7	4
2	100	70	17	4	2	5	2
4	100	69	17	4	3	5	2
8	100	72	15	3	4	5	2
16	100	63	17	6	8	5	1
32	100	64	16	6	7	6	1

Figure 2 C_{1s} and O_{1s} core levels for polycarbonate samples exposed to the effluent of an oxygen microwave discharge

functionalization is highlighted by the higher level of carbonate and shake-up features in comparison to those for $\theta = 70°$.

Singlet oxygen ($^1\Delta O_2$)

The reactions of singlet oxygen ($^1\Delta O_2$) with polymers have been the centre of considerable interest in the literature[14,27,28]. For the study of such reactions with polymers in the solid state, $^1\Delta O_2$ is normally generated by means of a microwave initiated oxygen discharge[23]. To remove the atomic oxygen and ozone before the effluent from the discharge reaches the sample, mercury is continually distilled through the excitation region. The ring of mercuric oxide is formed on the sides of the quartz tube just beyond the microwave cavity. The oxygen atom concentration under these conditions is believed to be less than 10^{-4} of that for the singlet oxygen[23].

The C_{1s} and O_{1s} core levels in *Figure 3* ($\theta = 70°$) reveal the changes in the surface chemistry of polycarbonate films exposed to a stream of singlet oxygen (60 W, 2 torr) for various periods of time. The increase in complexity of the C_{1s} envelope and intensity of the O_{1s} signal reveal extensive oxidation of the surface. The oxygen uptake is more apparent from a consideration of the relative O_{1s}/C_{1s} intensity ratios in *Figure 4*. For comparison the relevant

data for an electron take-off angle of 30° are also included. From these data it is clear that the oxygen uptake is greater for $\theta = 70°$ indicative of the surface specificity of the oxidative processes. It is also interesting to note that the oxygen uptake follows an autocatalytic mechanism
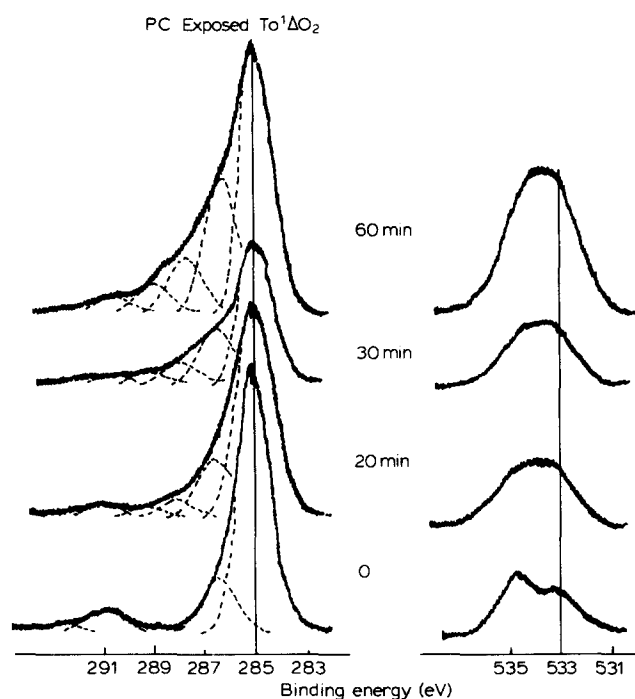

Figure 3 C_{1s} and O_{1s} core levels for polycarbonate films exposed to 'singlet oxygen' for various periods of time (take off angle $\theta = 70°$)

Table 2 C:O stoichiometries for polycarbonate films exposed to the effluent of an oxygen microwave discharge

	C:O stoichiometry	
Time	$\theta = 30°$	$\theta = 70°$
15 min	$C_1:O_{0.31}$	$C_1:O_{0.47}$

Table 3 C_{1s} components for polycarbonate films exposed to the effluent of an oxygen microwave discharge

		Total C_{1s}	C—H	C—O	C=O	O—C=O	CO₃	$\pi \rightarrow \pi^*$
$\theta = 70°$	0	100	76	14	0	0	7	3
	15	100	48	26	14	7	4.5	0.5
	30	100	61	22	10	2.5	4	0.5
$\theta = 30°$	0	100	76	13	0	0	7	4
	15	100	60	20	10	2.0	6	2.0
	30	100	58	20	11	4	5	2

with an induction period of ~ 15 min. A steady state situation is reached after ~ 60 min exposure representative of the balance between oxidation processes and desorption of low molecular weight species.

Examination of the C_{1s} component analysis displayed in *Figure 5* also reveals the autocatalytic nature of the reactions involved. Increases in the C–O, C=O and O–C=O functionalities are evident. The formation of the carbonyl component is a factor of ~ 2 greater than the carboxylate group which contrasts with the results obtained for photo-oxidation[3–5] where the latter is more predominant than the former in a highly oxidized surface.

$$\text{the C-H, O-}\overset{\overset{\text{O}}{\parallel}}{\text{C}}\text{-O and } \pi \rightarrow \pi^* \text{ shake-up components}$$

decrease in intensity autocatalytically. The latter functionality is not evident after ~ 2 h indicative of the loss of aromaticity during the oxidative processes.

It is of interest to compare the nature of the oxidized surface obtained (for similar degrees of oxygen uptake); with polycarbonate films exposed to the effluent of an oxygen microwave discharge, with and without the continuous distillation of mercury through the discharge region. The appropriate data are shown in *Table 4*. There
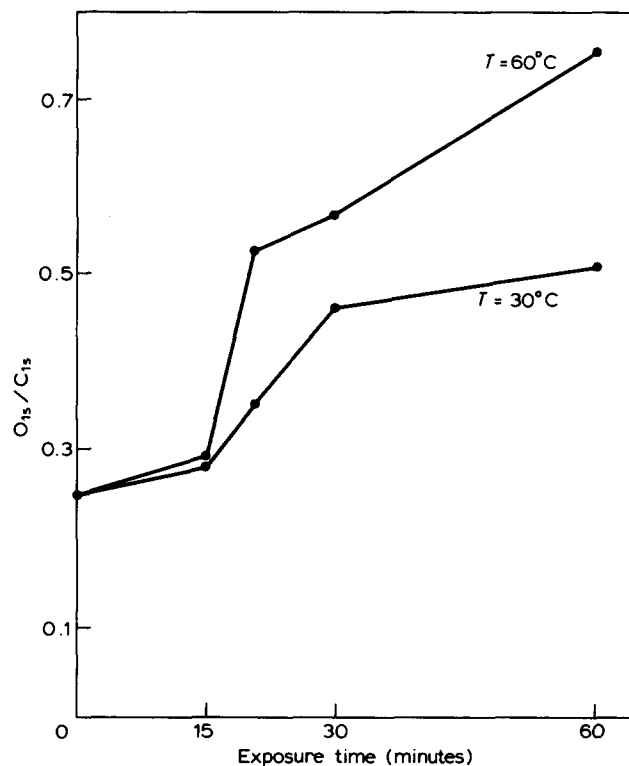

Figure 4 O_{1s}/C_{1s} intensity ratios for polycarbonate films exposed to 'singlet oxygen' as a function of time ($\theta = 70°$ and $30°$)

Figure 5 C_{1s} components for polycarbonate films exposed to 'singlet oxygen' for various periods of time

Figure 6 O_{1s}/C_{1s} intensity ratios for polycarbonate films exposed to 'singlet oxygen' for various periods of time and temperature

are distinct similarities in the distribution of the C_{1s} components for the two surfaces which indicates similar reaction mechanisms. The data in fact suggest that the 'singlet oxygen' reaction is the same as that for the microwave initiated oxygen discharge degradation as described in the previous section but that it occurs at a much slower rate. The extent of oxidation in the subsurface ($\theta = 30°$) is greater for the exposure with continuous mercury distillation.

The 'singlet oxygen' exposures described above were carried out at 20°C. To investigate the effect of temperature on the induction period, polycarbonate films were oxidised at 60°C. The relative oxygen to carbon intensity ratios displayed in *Figure 6* reveals the oxygen uptake for exposures at 20 and 60°C ($\theta = 70°$). It is clear from these data that the induction period is not affected by elevating the temperature. However, when oxidation occurs the rate is dramatically increased and an equilibrium state is reached at a much earlier stage. The contrast in the degree of oxidation at the two temperatures is reflected in *Table 5* where the C:O stoichiometries for polycarbonate films for 60 min exposures are displayed.

As noted above, the nature of the oxidized polycarbonate surfaces for exposures to the microwave discharge effluent (with and without the continuous distillation of mercury vapour), are remarkably similar.
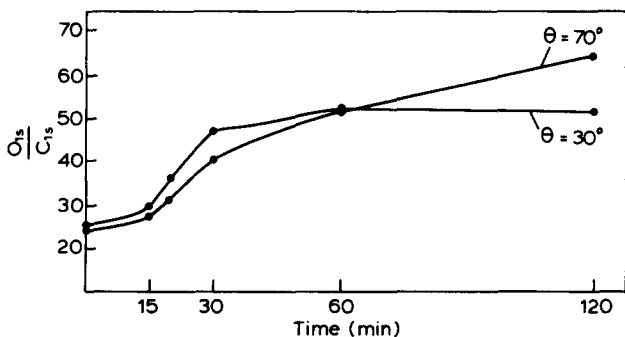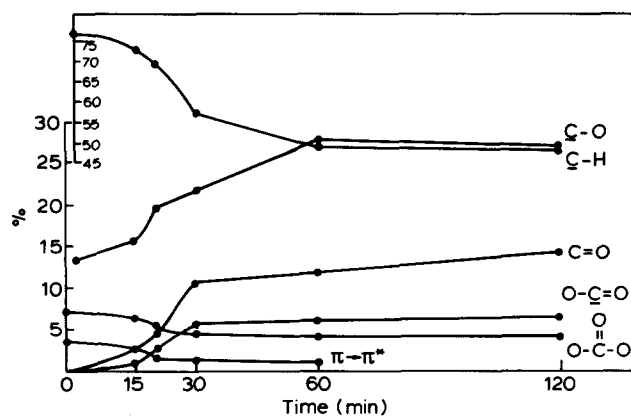
Table 4 Comparison of the C_{1s} components and O_{1s}/C_{1s} intensity ratios for polycarbonate films exposed to the effluent of an oxygen microwave discharge with and without continuous Hg distillation

Time	Total C_{1s}	C–H	C–O	C=O	O–C=O	CO_3	$\pi \rightarrow \pi^*$	O_{1s}/C_{1s}
15 min (without Hg)	100	48	26	14	7	4.5	0.5	0.63
120 min (with Hg)	100	48	27	14	6	5	0	0.65

These data suggest that the mercury vapour does not remove oxygen atoms to a sufficient extent to prevent participation in the degradative processes. It has been reported in the literature that residual traces of atomic oxygen can lead to anomalous results in the quenching of singlet oxygen by hydrocarbons[23]. The results discussed above, therefore, appear to reflect the extremely small level of oxygen atoms reaching the sample. Previously reported studies in the literature[29], where the removal of atomic oxygen relies solely on the reaction with mercury vapour may also suffer from reactions in the surface due to this species.

Residual traces of atomic oxygen may be removed by the continuous titration of nitrogen dioxide (NO_2) into the flow system beyond the discharge region. The reactions, described in the Experimental section, give rise to a weak green glow at the inlet value when viewed in complete darkness. No such glow was observed in the experiments reported here. In the absence of sensitive instrumentation to detect weak chemilumunescent reactions, the amount of NO_2 required can only be obtained on a trial and error basis. Initial runs revealed that an autocatalytic reaction, although to a much lesser extent, was still occurring. This suggested that atomic oxygen was still present but with a greatly reduced concentration.

On increasing the amount of NO_2 added to the system, no change in the C_{1s} and O_{1s} core levels could be detected even after 5 h exposure. The N_{1s} core level was examined to reveal any contamination arising from the NO_2, however no signal arising from this level could be detected. This strongly suggests that singlet oxygen does not react with Bisphenol A polycarbonate under the conditions of these experiments. However, it is possible that the amount of NO_2 titrated may have significantly reduced the singlet oxygen concentration via the following reaction:

$$NO_2 + 3(^1\Delta O_2) \rightarrow NO_2^- {}^* + 3O_2$$
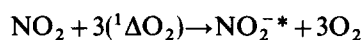
A white glow may be emitted due to a slow energy transfer process[23]. No glow was detected but to ensure that reactive oxygen species (i.e., $^1\Delta O_2$) were reaching the sample, solution cast films of cis-polyisoprene, well known for its reactivity with singlet oxygen[30], were placed downstream of the polycarbonate samples.

Hydroperoxides are believed to be formed in the reaction of singlet oxygen with olefins possessing an allylic hydrogen (the ene reaction) and cis-polyisoprene is thought
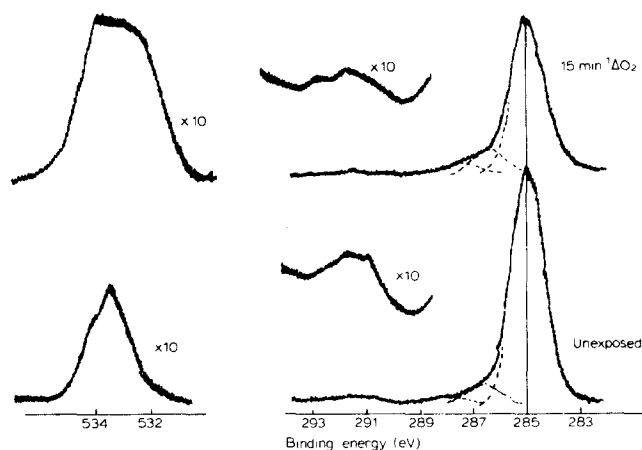

Figure 7 C_{1s} and O_{1s} levels for cis-polyisoprene before and after exposure to singlet oxygen

to react in this manner[30]. The e.s.c.a. spectra in *Figure 7* reveal the C_{1s} and O_{1s} core levels before and after $^1\Delta O_2$ treatment for cis polyisoproprene films placed downstream of the polycarbonate sample position. Although a small degree of surface oxidation is evident from the spectra for the unexposed material, oxygen uptake on $^1\Delta O_2$ treatment is readily apparent. The intensity of the $\pi \rightarrow \pi^*$ shake-up component (diagnostic of the double bonds in the system) as evidenced by the expanded regions of the C_{1s} levels, decreases which is indicative of oxygen occurring at the double bonds of cis-polyisoprene.

The nature of the changes in surface chemistry are vealed in *Table 6*. Decreases in the intensities of the C–O and >C=O functionalities and consequently an increase in the relative O_{1s}/C_{1s} intensity ratio. The presence of $^1\Delta O_2$ reaching the sample region is thus conformed. The data, therefore, suggest that under the present experimental conditions, singlet oxygen does not react with bisphenol A polycarbonate and consequently does not play a role in the oxidative degradation of this polymer, and consequently confirms the results for solution phase studies.

Atomic oxygen

The results discussed in the previous section indicated the dramatic influence on the degradative mechanisms of polycarbonate surfaces when low levels of atomic oxygen are present in the effluent from a microwave oxygen discharge. It is, therefore, of interest to examine the changes in the surface chemistry of polycarbonate films exposed to a low level of pure atomic oxygen in a flow system of similar design to the singlet oxygen generator. This was achieved by the u.v. photolysis of N_2O as described in the Experimental section.

The C_{1s} and O_{1s} core levels in *Figure 8* reveal the changes in the surface on exposure of polycarbonate films to oxygen atoms for various periods of time. These spectra

Table 5 C:O stoichiometries for oxidised polycarbonate films (60 min exposure)

Temperature	C:O stoichiometry
20	$C_1:O_{0.39}$
60	$C_1:O_{0.53}$

Table 6 C_{1s} components and O_{1s}/C_{1s} intensity ratios for cis-polyisoprene and cis-polyisoprene exposed to $^1\Delta O_2$

Time (min)	Total C_{1s}	C–H	C–O	C=O	O–C=O	CO_3	$\pi \rightarrow \pi^*$	O_{1s}/C_{1s}
0	100	91	5	1	0	0	3	0.062
15	100	83	12	4	0	0	1	0.237

correspond to an electron take-off angle of 70°. The characteristic 2:1 doublet of the O_{1s} signal changes on exposure for 60 min to an envelope not as well defined. The nature of the contributions to the C_{1s} envelope are more apparent from the component analysis in *Table 7*. It is clear from these data the the $\underline{C}$-H and $\pi \rightarrow \pi^*$ components are essentially unchanged and only small differences from the initial values for the $\underline{C}$-H, $\underline{C}$-O and

$$\begin{matrix} & O \\ & \| \\ O-\underline{C}-O \end{matrix} \quad \text{functionalities are evident.}$$
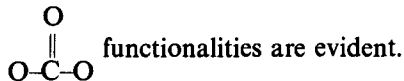
Examination of the corresponding O_{1s}/C_{1s} intensity ratios reveal that the intensity of the oxygen signal decreases with increasing exposure time. Although a component analysis of the O_{1s} core level is difficult, an approximate fit may be obtained by employing two peaks corresponding to O–C and O=C environments and these data and those for the total O_{1s}/C_{1s} ratios are shown in *Figure 9a*. It is evident that after 60 min exposure that the O–C and O=C intensities have decreased and the relative ratio between the two environments is ~1.7:1 (*cf.* the 2:1 ratio for the starting material).

The corresponding spectra for a take-off angle of 30° were recorded immediately after those at 70°. However, the analysis of the O_{1s}/C_{1s} ratios suggested that anomalous results were being obtained (i.e. inconsistent increases and decreases in the intensity of the O_{1s} signal). On re-running the spectra for $\theta = 70°$ after 60 min

exposure (i.e. the spectra were recorded in the sequence $\theta = 70°, 30°, 70°$) it was found that the O_{1s}/C_{1s} intensity ratio had increased relative to the first run. This suggested that the X-ray irradiation of the sample was initiating a reaction in the surface regions, and consequently fresh samples are required for an angular dependence study. The data in *Figure 9b* reveal the changes in the O_{1s}/C_{1s} ratios and the respective contributions arising from O–C and O=C environments. It can be readily seen that there are similar trends for $\theta = 30°$ and $\theta = 70°$.

To investigate the effect of X-rays on the exposed surface the C_{1s} and O_{1s} core levels at $\theta = 70°$ were recorded as a function of X-ray irradiation time for a polycarbonate sample exposed to atomic oxygen for 60 min. The relevant C_{1s} component analysis is shown in *Table 8*. The corresponding changes in the O_{1s} signal are revealed in *Figure 9c*. After ~30 min exposure to the X-rays the proportions of the C_{1s} components are the same as the starting material. The O_{1s}/C_{1s} intensity ratio increases with time and approaches the value for the unexposed polycarbonate. However, the O–C/O=C ratio does not obtain the characteristic 2:1 value.

The data suggest that the X-rays are interacting with a labile species in the surface. It is not possible to determine the nature of this species from the data presented above. It has been reported that the highly oxygenated peroxide link in dibenzoyl peroxide is very unstable to the MgKα radiation employed in the e.s.c.a. experiment[19], and it is possible that a labile peroxide feature is formed in the surface of polycarbonate.

Overall the reaction of polycarbonate with the effluent of an oxygen microwave discharge containing a low level of oxygen atoms is an extremely complex process arising from a combination of singlet oxygen, atomic energy and molecular oxygen interactions.

ACKNOWLEDGEMENTS

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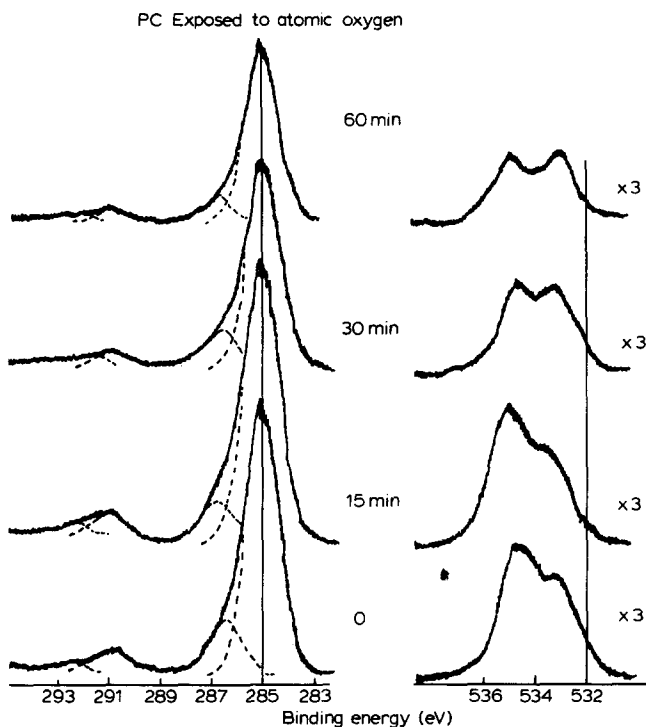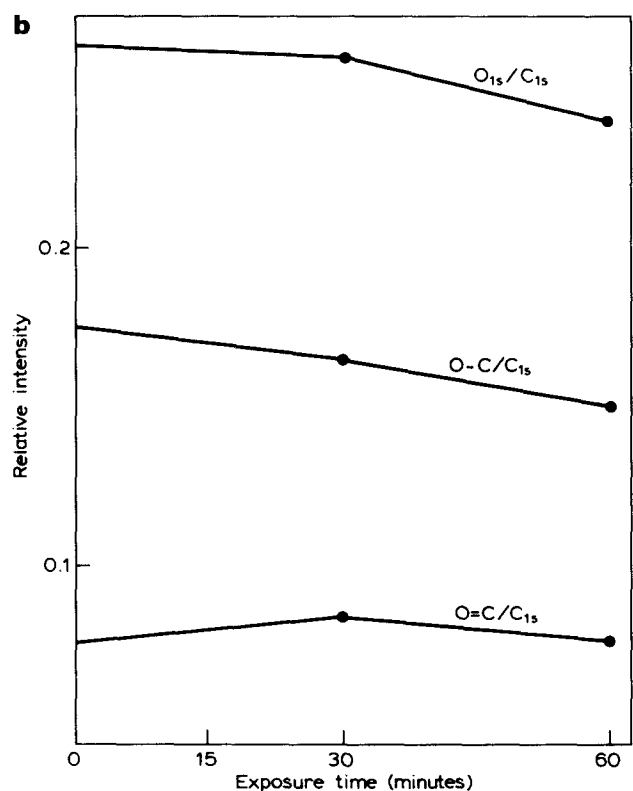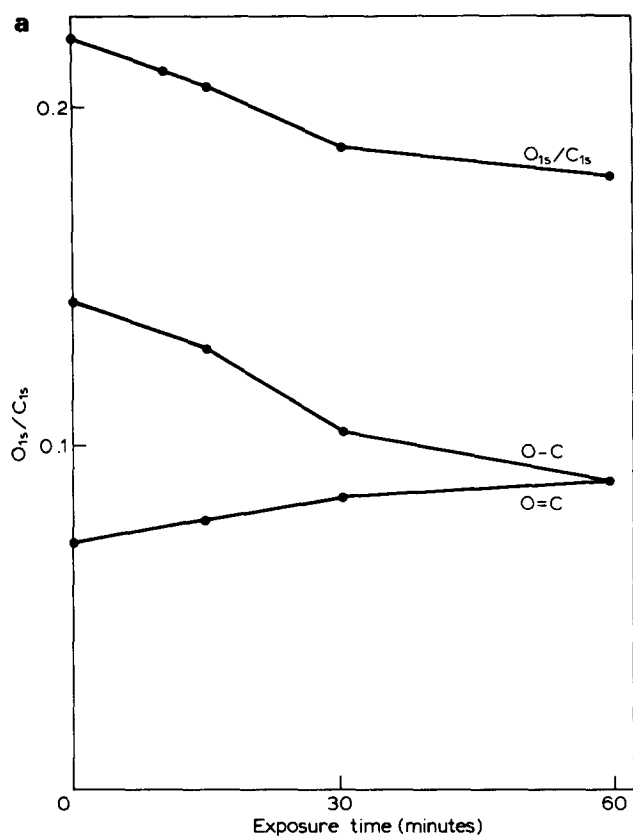
PC Exposed to atomic oxygen

Figure 8 C_{1s} and O_{1s} core levels for polycarbonate films exposed to atomic oxygen as a function of time ($\theta = 70°$)

Table 7 C_{1s} components for polycarbonate films exposed to atomic oxygen

Time	Total C_{1s}	C–H	C–O	C=O	O–C=O	CO_3	$\pi \rightarrow \pi^*$
0	100	79	12	0	0	6	3
15	100	79	13	0	0	5	3
30	100	80	12	0	0	5	3
60	100	81	11	0	0	5	3

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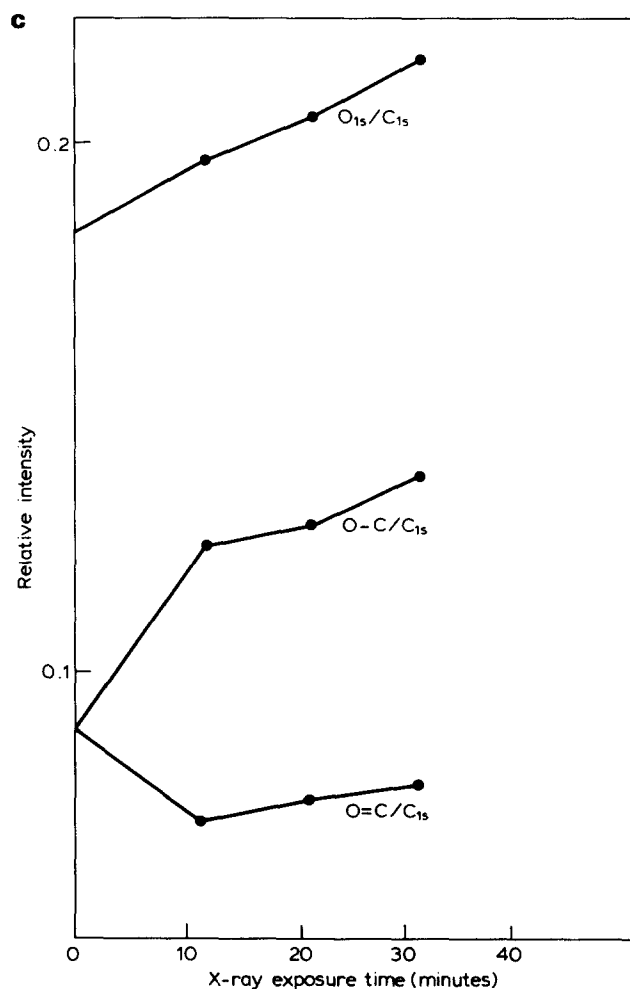19 Dilks, A. *J. Polym. Sci., Polym. Chem. Edn.* 1981, 19, 1319

Figure 9 Changes in the O_{1s}/C_{1s} intensity ratios and the O–C and O=C components of the O_{1s} signal for polycarbonate films exposed to atomic oxygen. (a) $\theta=70°$. (b) $\theta=30°$. (c) Changes in the O_{1s}/C_{1s} intensity ratios and the O–C and O=C components of the O_{1s} signal for a polycarbonate film exposed to atomic oxygen for 1 h, as a function of X-ray irradiation time ($\theta=70°$)

Table 8 C_{1s} components for polycarbonate films exposed to atomic oxygen for 1 h as a function of X-ray irradiation time

X-ray irradiation time (min)	Total C_{1s}	C–H	C–O	C=O	O–C=O	CO_3	$\pi \rightarrow \pi^*$
0	100	81	11	0	0	5	3
12	100	78	13	0	0	6	3
22	100	78	13	0	0	6	3
32	100	79	12	0	0	6	3

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