ADVANCES IN ESCA APPLIED TO POLYMER CHARACTERIZATION

David T. Clark

Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE, England.

Abstract – Many of the important chemical, physical, electrical and mechanical properties of polymers depend on surface structure. In the past decade ESCA has been developed as the single most important tool for surface structure determinations and the article details three recent areas of application which illustrates the important dimension in surface characterization of polymeric systems provided by the technique.

INTRODUCTION

The range of properties which can now be built into a polymer system is enormous and this coupled with the techniques which are available for the chemical, physical, electrical and mechanical modification of surface and bulk properties provides almost unlimited scope for tailor making materials for particular applications. The emphasis therefore, over the past 15 years or so in polymer science has shifted from the chemistry of polymerization processes to the processing of polymers. Since many of the important features in this respect are determined by the structure, bonding and reactivity of the outermost few tens of angstroms, the motivation for applying the methods of surface science to polymers is not difficult to understand.

In addition to the self evident technologically (and industrially) important areas of the surface science of polymers such as those involved in lamination, printing, weathering and segregation of additives, the development of organic based thin film device technology in the past few years has been materially aided by the detailed insights provided by the shots in the surface scientists' locker.

Since the predominant emphasis is on organic based polymers we consider here some recent developments in the surface science of such systems by means of ESCA which has proven to be the single most powerful tool for the non-destructive elaboration of details of structure, bonding and reactivity on the 10's of angstrom scale.

Before considering these developments however, it is of interest in a symposium such as this (where the predominant emphasis is on the bulk characterization of polymers) to consider the distinctive features which set the investigation of polymer surfaces in a category of their own. The first point to note is that organic based polymers represent extremes in terms of both complexity of structure and sensitivity to interrogation and the single most powerful tool which has emerged for these investigations has proved to be ESCA (Ref. 1). Polymers in the state of their end use are not normally pure materials. In many cases there are added substances which alter the engineering and/or chemical, physical, electrical properties of the polymer in a useful way (Ref. 2). For this reason and indeed in the very processing of the polymer the surface may well be different than the bulk and complete characterization therefore mandates both surface and bulk studies.

In recent reviews (Ref. 1) we have considered the unique features of polymers which make the development of their surface science such a challenge. The unique attributes of ESCA for such studies has also been considered in detail and are well documented (Ref. 3). For the sake of completeness we merely summarise in the next section the important information levels available from the ESCA experiment.

ESCA AS A PROBE FOR SURFACE STRUCTURE

The data levels and experimental parameters in ESCA are listed in Table 1.

The primary sources of information provided by the ESCA experiment may be summarised as follows:-

TABLE 1. Schematic of data levels and variable experimental parameters in
a typical application of ESCA to the study of polymers

Experimental parameter	Data level					
	Absolute binding energy	Shake up energies and intensities	Auger parameters (Ref. 4)	Relative intensities of levels	Charging phenomena	Valence bands
Photon source (energy)	Core levels					

Photon source (energy)

Commonly employed are
$Mg_{K\alpha_{1,2}}$ 1253.7 ev;

$Al_{K\alpha_{1,2}}$ 1486.6 ev;

$Ti_{K\alpha_{1,2}}$ 4510 ev.

Angular dependence
(Take off angle θ
wrt sample surface)

Biasing experiments
and use of flood
gun

Core levels

Corresponding sampling depths in the range typically
10-200Å depending on kinetic energy, structure and
bonding and changes therein in the surface, sub-
surface and bulk. Sample inhomogeneities (lateral,
vertical etc.).

(i) Absolute binding energies, relative peak intensities and shifts in binding energy
The predominant emphasis is in studying core levels (viz. C_{1s}, O_{1s} etc.) for which the
photoionization cross-sections are substantial. The study of these features provide a means
of element mapping, of analytical depth profiling if sensitivity factors and electron mean
free paths have been quantified and also allow the identification of structural features (Ref.
1).

(ii) Angular dependent studies
For solids with a fixed arrangement between the analyser and X-ray source the variation in
take off angle between the sample and analyser provides a means of differentiating between
surface, sub-surface and bulk effects. Such studies can only be carried out on continuous
samples (films not powders) and provide a complementary means of gaining information on
sample homogeneities (in a vertical sense) to studies using different photon sources (Ref. 1).

(iii) Shake-up-shake-off satellites
The observation of monopole excited states and their energy separations with respect to the
direct photoionization peaks and their relative intensities, allow information to be derived
primarily on the nature of unsaturated features in the polymer.

(iv) Auger parameters (Ref. 4) and charging shifts (Ref. 5)
Since most polymers of their very nature are insulators under the conditions of the ESCA
experiment energy referencing requires a knowledge of sample charging. Detailed studies have
shown (Ref. 5) that under a given set of instrumental conditions the shift in energy scale
associated with charging phenomena is characteristic of the surface structure and therefore
constitutes a useful information level.

For a limited number of substituted polymeric systems containing 2nd and 3rd row atoms (e.g.
Cl, Br etc.) the observation of intense direct photoionisation and Auger peaks allows the
determination of a charge independent Auger parameter (Ref. 4). Two dimensional chemical
state plots involving the core level shift and Auger parameter can in such circumstances
provide an exceptionally fine technique for chemical speciation.

(v) Valence bands
Although cross-sections for photoionisation of valence levels are typically small compared
with core levels, nonetheless the soft X-ray excited valence band spectra of polymers are
often useful finger-prints for a given polymer structure (Refs. 1 and 6).

With this outline of the information available from ESCA on polymer surface structure we now
consider some recent developments which encompass three distinct themes namely:

(a) Surface structure of multicomponent systems.

(b) Environmental modification of polymers.

(c) Polymer synthesis by means of plasma techniques.

SURFACE STRUCTURE OF MULTICOMPONENT SYSTEMS

A potentially complex surface structure might well be anticipated for multicomponent systems and as a particularly interesting example of this genre we consider here the two component propellant system represented by nitrocellulose (NC)-nitroglycerin (NG) pastes of differing compositions (Refs. 7 and 8).

We outline here the surface structure of two component propellants encompassing the bulk composition range from $\sim$ 60:40 to $\sim$ 40:60 mole % in the two components. An added complication is the incorporation of low levels (1-2%) of stabilizer (diethyl diphenyl urea, DEDPU) to the bulk formulation. The core level spectra for nitrocellulose itself or indeed of cotton linters shows evidence for a component in the C_{1s} levels in addition to that expected on a statistical basis for the $\underline{C}{\stackrel{\nearrow O}{\searrow}}_O$ and $\underline{C}$-O functionalities (Ref. 8) for a given βD-gluco-pyranose (or nitrate ester thereof) residue. Experiments with harder X-ray sources (e.g. $Ti_{K\alpha}$) show that such a signal centred $\sim$ 285 ev arises from a patched overlayer of hydro-carbon which is intrinsic in the samples. The core level spectra shown for the 35/65 NG/NC have been determined for paste samples studied with a $Mg_{K\alpha_{1,2}}$ photon source at a temperature of -100°C. The C_{1s} levels (Figure 1) show 3 components assigned in decreasing binding energy to $\underline{C}{\stackrel{\nearrow O}{\searrow}}_O$, $\underline{C}$-O and $\underline{C}$-H functionalities whilst the O_{1s} and N_{1s} components are essentially single components appropriate to $-O-NO_2$ functionalities.* The nitrogen corresponding to the urea
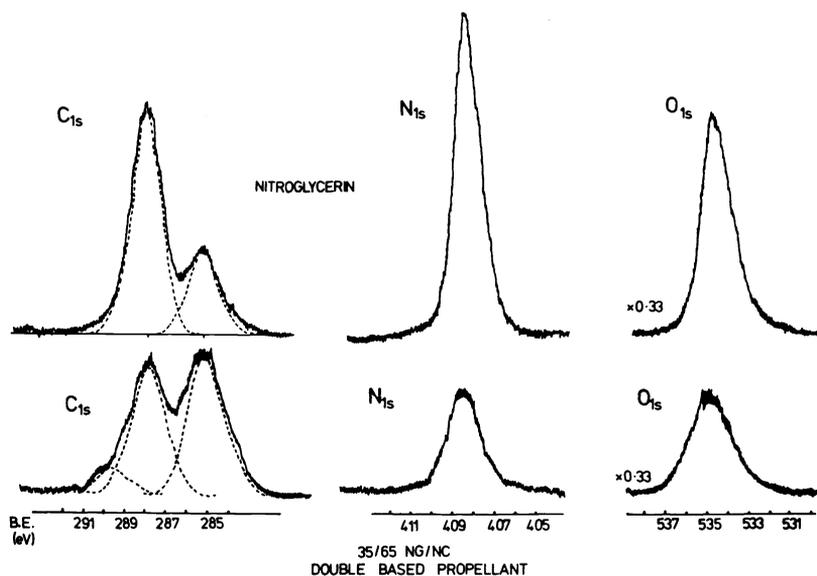

Figure 1. Core level spectra for 35/65 nitroglycerin/nitrocellulose and for nitroglycerin film as an overlayer on an NG/NC paste.

functionality occurs at much lower binding energy ($\sim$ 400 ev) and is (except where noted below) generally obscured by the $Mg_{K\alpha_{3,4}}$ satellites of the high binding energy peak. Once due allowance has been made for the extraneous hydrocarbon peak and differences in instrumental sensitivity and cross-section factors, the measurement of 3 core level spectra for a given sample provides two independent measurable parameters, namely the C/N and C/O stoichiometries,

---

* A small contribution to the O_{1s} signal arises from the unsubstituted sites in given βD-glucopyranose residues for the nitrocellulose for which the average degree of substitution (no. of nitrate ester groups per glucose residue was $\sim$ 2.8).

on the ESCA depth sampling scale. For a series of NG/NC samples the surface composition is determined by two parameters namely the two independent ratios of three components (NG, NC and DEDPU). The ESCA data therefore allows a straightforward determination of surface stoichiometry and this is shown in Figure 2.
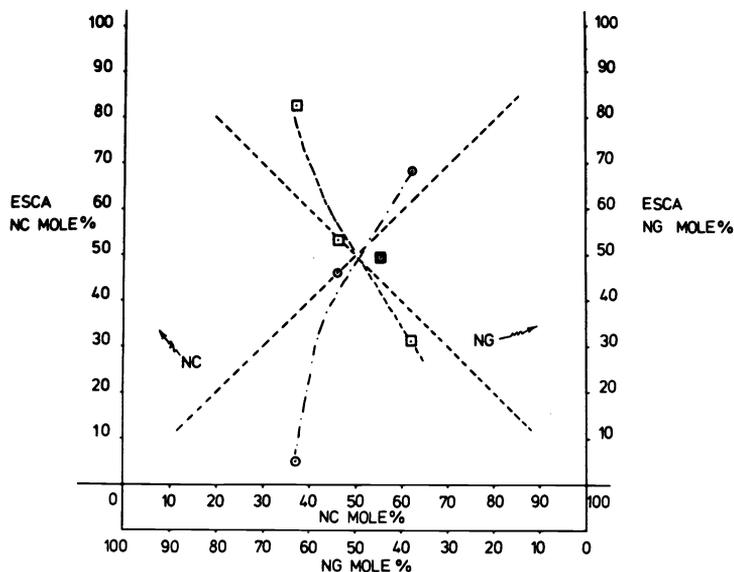

Figure 2.   ESCA versus bulk mole percentage composition for NG/NC pastes.

These data show that for compositions close to 50:50 mole % (e.g. 45:55 and 55:45) the surface stoichiometry is very close to that of the bulk. For lower NG compositions (e.g. 60:40 NC/NG) the surface is slightly poorer in NG compared to the bulk. However for higher NG compositions two features emerge. Firstly the surface is enriched in NG and in consequence the DEDPU also segregates to the surface. Hence for the 36:65 NC/NG bulk composition the surface composition corresponds in mole % to 83:5:12 NG:NC:DEDPU.* Since many of the important properties of a propellant paste dependent on surface composition (initial burn rate and environmental stability to name but two) ESCA provides important information not currently available by other techniques. The segregation of NG to the surface in higher composition pastes allows the direct measurement for the first time of the core level spectra of nitroglycerin. Thus by allowing samples to warm to room temperature and then rapidly cooling the probe tip (after the pressure in the vacuum chamber of the spectrometer had risen by an order of magnitude indicating rapid desorption of NG from the surface) it has proven possible to obtain the core level spectra for NG itself. Since this is a thin overlayer now on the NC which itself has a patched overlayer of hydrocarbon the C_{1s} spectra show a low binding energy shoulder due to the CH components at 285 ev and this is evident in Figure 1.

ENVIRONMENTAL MODIFICATION OF POLYMERS

(a)   Introduction
In a series of papers we have shown how ESCA may be used to study the surface aspects of environmental modification of polymers (Refs. 9-11). We describe here recent experiments on Bisphenol A based polycarbonates which illustrate the striking difference between bulk and surface degradative reactions (Refs. 12 and 13).

Since all solids communicate with the rest of the world primarily by means of their surfaces, the surface is of prime importance in environmental modification. Thus it should be evident from the schematic outline in Figure 3 that the partial pressure of oxygen and

---

* The DEDPU composition may be independently determined in this case since the N_{1s} levels associated with the urea functionality is clearly distinguishable at such high levels from the N_{1s} satellite structure from the nitrate functionality.

other reactive gases which might be present in the atmosphere is highest at the surface as is the incident photon flux and any precipitation. In view of this it would be somewhat
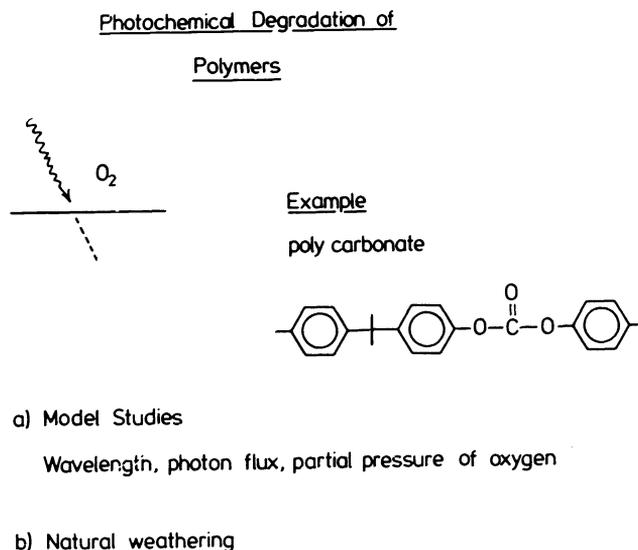
Photochemical Degradation of

Polymers

Example

poly carbonate

a) Model Studies

Wavelength, photon flux, partial pressure of oxygen

b) Natural weathering

Figure 3. Photochemical degradation of polymers; the importance of surfaces.

surprising if the reactions at the surface were entirely representative of those in the bulk. It is conceivable however, that with rapid surface reactions leading to low molecular wt. molecules which can readily desorb from the surface that the surface reactions could dominate the overall degradation of the sample particularly if this had a high surface area to volume ratio (e.g. a film).

There is a considerable literature on the photochemical degradation of polycarbonates ranging from fundamental photophysics studies (Ref. 14) to investigations of molecular weight changes during irradiation (Ref. 15). The majority of investigations have involved solution phase studies at wavelengths < 290 nm and are not thus strictly relevant to the solid state photodegradation of polycarbonate in sunlight. The main features of the main routes for photochemical degradation which have been described in the literature together with a summary of the available data on the nature of the excited state involved is set out in Figure 4. Evidence has been presented for the dominant role of photo Fries rearrange-

FIRST SINGLET STATE
QUENCHING STUDIES
LOW QUANTUM YIELD OF FLUORESCENCE (<0.05)
LONG RADIATIVE LIFE TIME ($>10^{-5}$s)
LOW INTERSYSTEM CROSSING RATE
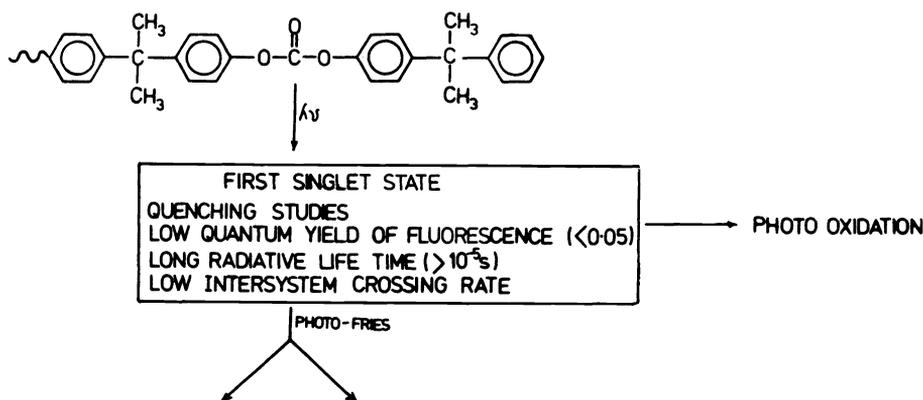
PHOTO OXIDATION

PHOTO-FRIES

Figure 4. Data on the nature of the excited state involved in the photo-degradation of Bisphenol A polycarbonate.

ments by both inter- and intra-molecular processes and the classic text by Raby and Ranbek also emphasize the importance of photo Fries rearrangements (Ref. 13). However the detailed studies recently reported by Factor and Chu (Ref. 12) suggest that photo-oxidative pathways involving the gemdimethyl and phenyl groups are of greater importance in photodegradation of polycarbonate in the solid state in oxygen rich atmospheres and at wavelengths corresponding somewhat more closely to sunlight than in previous studies. In this somewhat confused situation it is clear that a detailed investigation of the surface aspects of the photo-degradation would be particularly apposite at this time. We therefore report here in preliminary form the main conclusions to be drawn from detailed ESCA studies of the photo-degradation of Bisphenol A polycarbonate (Ref. 11).

(b) Theoretical aspects

Before considering the experimental data we may briefly consider some recent theoretical computations (Ref. 11) which shed new light on the nature of the excited states involved in photodegradation of polycarbonates. The most complete studies relating to samples studied in the solid state per se arise from the work of Moacanin and co-workers (Ref. 14). On the basis of the low quantum yield of fluorescence, on the long radiative lifetime and the lack of triplet quenching it has been inferred that the excited state involved is probably $n \rightarrow \pi^*$ singlet in character. There have been no detailed studies of the conformational energy preferences for either the ground or excited states of Bisphenol A polycarbonate and most discussions have therefore centred on the early suggestions of Flory and Williams (Ref. 16) which suggested an energetically preferred trans-trans configuration with a strong possibility of an orthogonal arrangement of the phenyl groups with respect to the carbonate group in the ground state. A knowledge of the electronic configuration of simple carbonyl, carboxyl and carbonate esters would suggest that a $n \rightarrow \pi^*$ designation for the excited state involved in polycarbonate photodegradation is unlikely (Ref. 17). Thus if the ground state does indeed involve an orthogonal configuration then the electronic effects of the phenyl groups as far as the carbonyl groups (of the carbonate) are concerned are equivalent to alkyl groups. It is well known that the effect of replacing an alkyl group by an oxygen functionality in going across the series ketone, carboxy ester, carbonate ester is that whereas the n orbital remains roughly constant in energy the π orbital increases in energy (Ref. 17). Indeed UPS valence band studies reveal this trend in a graphic manner (Ref. 18). One manifestation of this is that the $n \rightarrow \pi^*$ states move to progressively higher energy across the series and the lowest excited states of carbonate esters are therefore normally different from those for simple carbonyl compounds. UPS data also reveals that the n orbital of a simple carbonyl group is at a higher ionization potential than the ring π orbitals of a phenyl ring (Ref. 19). This all adds up to considerable uncertainty in the assignment and nature of the excited states of Bisphenol A polycarbonate.

To shed some light on this we have recently completed (Ref. 11) a detailed MNDO SCF MO study of aspects of the energy hypersurface for diphenyl carbonate as a model for the chromophore system of Bisphenol A polycarbonate. We report here the main outline of this work.

The relative energies of various orthogonal and planar configurations of diphenyl carbonate are shown in Figure 5.
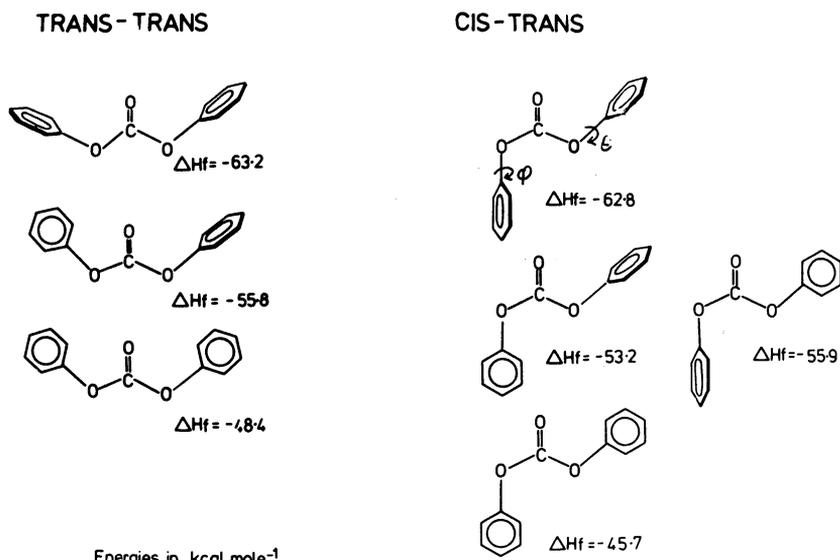

Energies in kcal mole^{-1}

Figure 5.   MNDO SCF MO computed relative heats of formation for various conformers of diphenyl carbonate as a model for the poly-carbonate chromophore.

It is clear from this that the orthogonal trans-trans and cis-trans configurations are of similar energy, substantially below the corresponding planar configurations.

There is a small energetic preference for the trans-trans configuration and the cross-section (Figure 6) through the PE surface relating this to the cis-trans configuration shows that this is a low energy process. Inspection of the relevant eigenvalues reveals
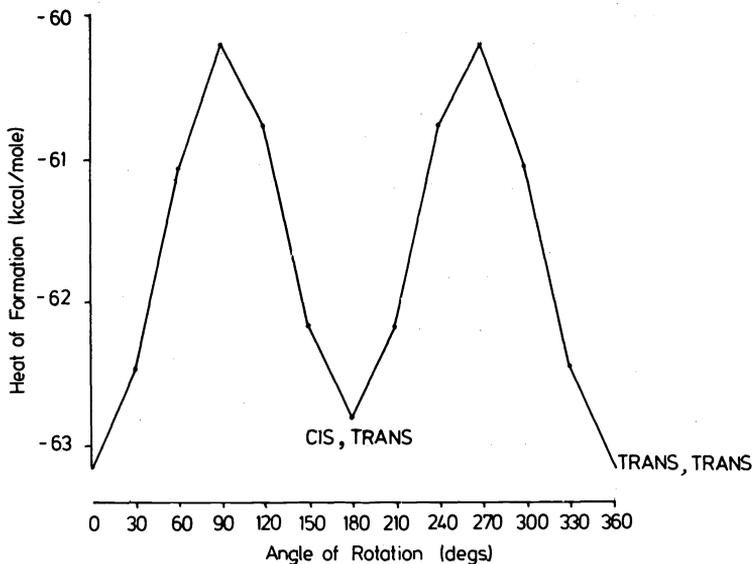
Figure 6. Cross section through the potential surface relating the ortho-gonal configurations of the cis-trans and trans-trans conformers of diphenyl carbonate.

that the lowest excited state is $\pi \rightarrow \pi^*$ in character with considerable phenoxy character. Whilst the ground state involves orthogonal arrangement of phenyl and carbonate groups the excited state probably involves an equilibrium geometry closer to a planar arrangement. This is outlined schematically in Figure 7. The identification of the $\pi \rightarrow \pi^*$ singlet nature of the excited state and the change in PE surface is entirely consistent with the experi-mental data and also falls into a consistent picture with the extensive background information on substituted benzenes and simple carbonyl, carboxyl and carbonate chromophores.
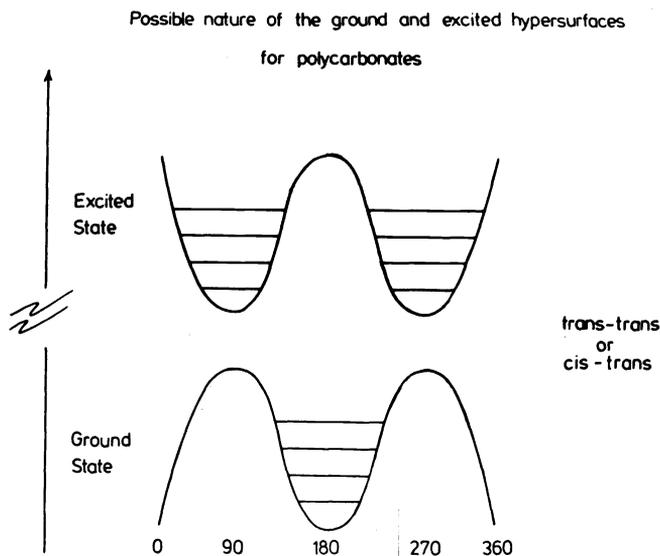
Figure 7. Possible nature of cross sections through potential energy surfaces for the ground and excited states of the diphenyl carbonate chromophore showing the energetic preference for orthogonal configurations for the former and planar for the latter state.

(c) Model photochemical studies

The main emphasis of this work has been to investigate reactions at the gas solid interface
at wavelengths > 290 nm. To facilitate such studies a special reactor has been constructed
which enables samples to be irradiated in a controlled atmosphere whilst mounted on an
ESCA probe so that samples may be directly studied after irradiation (Figure 8). The dosage
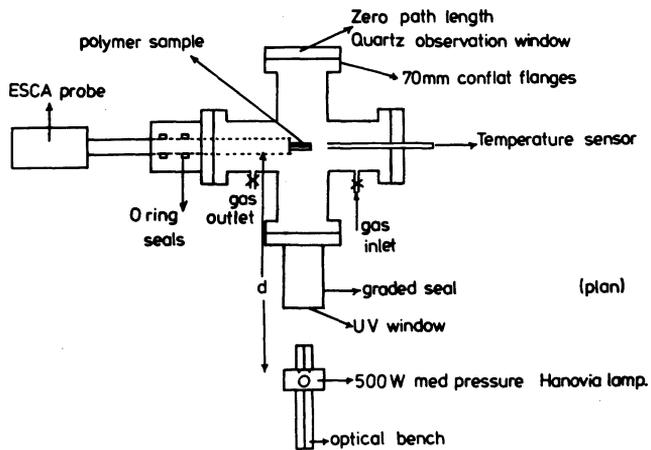
REACTION CHAMBER FOR MODEL PHOTO OXIDATION

STUDIES

Figure 8. Schematic of reaction chamber used for model photo-
            oxidation studies of polycarbonate.

under a given set of conditions may readily be monitored by the following absorption
changes at 330 nm. in polysulphone films exposed under identical conditions as described by
Davis (Ref. 20). For comparison purposes the dosages using a 500 watt medium pressure
lamp at distances of 18 cms. or 50 cms. from the sample position produce the dosages shown
in Figure 9. 15 minutes irradiation at 50 cms. corresponds roughly to 1½ hrs. exposure at

Lamp intensities > 290 nm

(monitored at 330 nm by polysulphone)

		whm^{-2}h^{-1}	Equivalent times
Hanovia	50cms	5·7	15mins ≅ 90mins PERME, 54mins JTTRE
500 Med pressure Lamp	18cms	52·5	
		whm^{-2} d^{-1}	
PERME (June)		9	
			15mins at 18cms gave same change at
JTTRE (Australia) (October)		15	330nm as 2days in Dhahram, Saudi Arabia (September)

Figure 9. Photon flux data for lamp configurations employed in the
            model photo-oxidation studies. For comparison purposes photon
            fluxes for natural weathering are also included.

mid-day on a sunny day in Southern England. Changes produced by such a short exposure are
not apparent from conventional multiple attenuated total internal reflectance IR studies but
are readily detected by ESCA as will become apparent.

As a starting point for the investigation of changes in surface chemistry we consider the irradiation of polycarbonate films in an oxygen atmosphere for varying periods at a dosage of 5.7 $whm^{-2}h^{-1}$. The ESCA data shown in Figure 10 are distinctive and reveal the extensive changes in surface chemistry under these experimental conditions. Starting from a C_{1s}
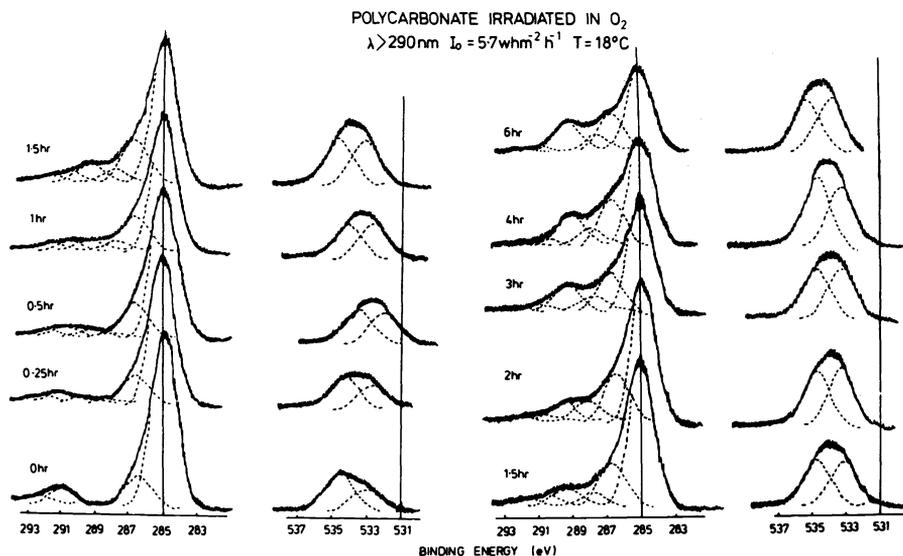
POLYCARBONATE IRRADIATED IN O_2

$\lambda > 290nm$ $I_o = 5.7 whm^2 h^1$ $T = 18°C$

BINDING ENERGY (eV)

Figure 10. C_{1s} and O_{1s} core level spectra ($Mg_{K\alpha_{1,2}}$) for polycarbonate samples irradiated in an oxygen atmosphere.

profile showing four components corresponding in increasing energy to $\underline{C}H$, $\underline{C}-O$, $O\underset{O}{>}\underline{C}=O$, and $\pi \rightarrow \pi^*$ shake-up components the C_{1s} profile rapidly increases in complexity with extra components originating from $>\underline{C}=O$ and $O-\underline{C}=O$ functionalities appear. The O_{1s} signal starting from a 2:1 doublet corresponding to the two types of oxygen environment increases in relative intensity and after a period of 6 hrs. irradiation the two components are of comparable intensity. The data illustrate the great surface sensitivity of ESCA and reveal that extensive oxidative functionalisation has occurred. This is more readily apparent from a comparison of the O_{1s} and C_{1s} intensity ratios and from a consideration of the relative proportion of the C_{1s} signal arising from carbons representing oxidation functionalities and this is shown in Figure 11. It is clear from this that the photo Fries rearrangement cannot represent the main contribution to the photodegradative process. At an electron take off
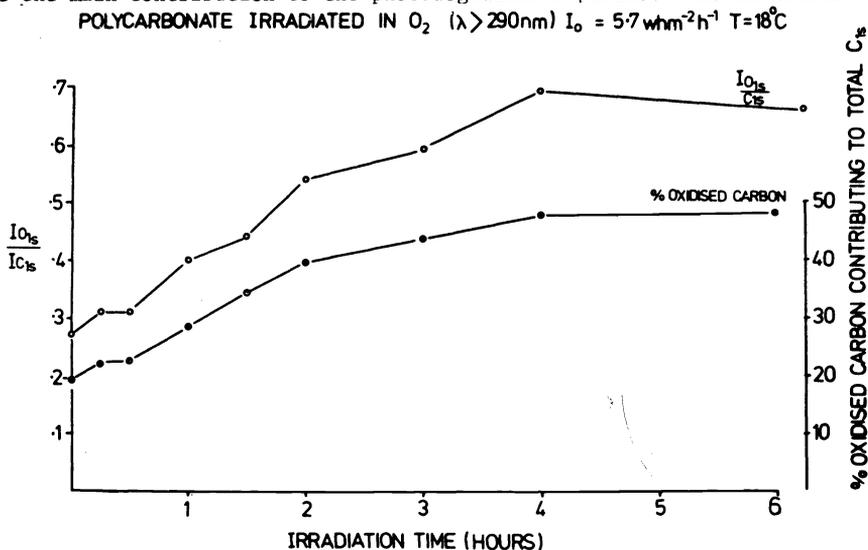
POLYCARBONATE IRRADIATED IN O_2 $(\lambda > 290nm)$ $I_o = 5.7 whm^{-2}h^{-1}$ $T = 18°C$

IRRADIATION TIME (HOURS)

Figure 11. C_{1s}/O_{1s} intensity ratios and percentage of oxygenated features defined from the C_{1s} levels for photo-oxidized polycarbonate samples.

angle of 30° 95% of the C_{1s} signal intensity displayed in Figure 10 originates from the
outermost $\sim 40\text{Å}$. By employing a variable take off angle and more particularly by going to
a harder X-ray source (e.g. $Ti_{K\alpha_{1,2}}$) sampling depth $\sim 100\text{Å}$ it may be shown that the

oxidative reaction extends well into the sub-surface. This is apparent from the substantial
changes in O_{1s} and C_{1s} core level spectra taken with a $Ti_{K\alpha}$ X-ray source as is evident from
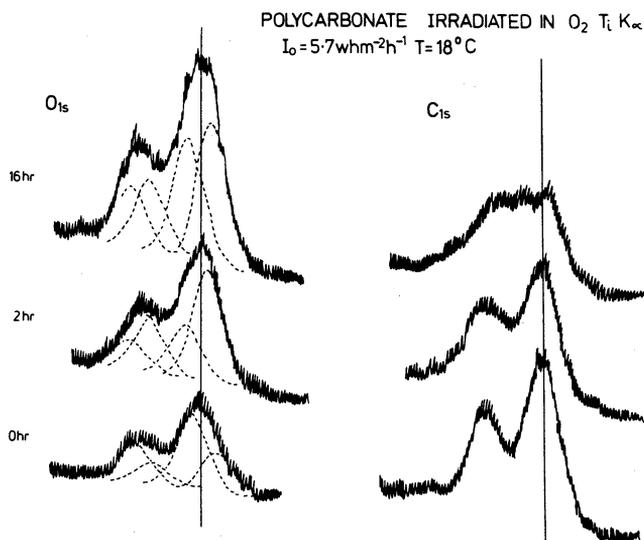Figure 12.

POLYCARBONATE IRRADIATED IN O_2 Ti K_α
$I_o = 5\cdot7\,whm^{-2}h^{-1}$ $T = 18^\circ C$

Figure 12. C_{1s} and O_{1s} core level spectra for photo-oxidized poly-
carbonate obtained with $Ti_{K\alpha_{1,2}}$ photon source.

The nature of the oxidative functionalisation becomes clear from the component analysis for
the spectra in Figure 10 displayed in Figure 13. The CH component (phenyl group other than
carbon directly attached to oxygen and gem-dimethyl group) decreases in intensity as a
function of the irradiation whilst the C-O, >C=O and O-C=O functionalities increase in
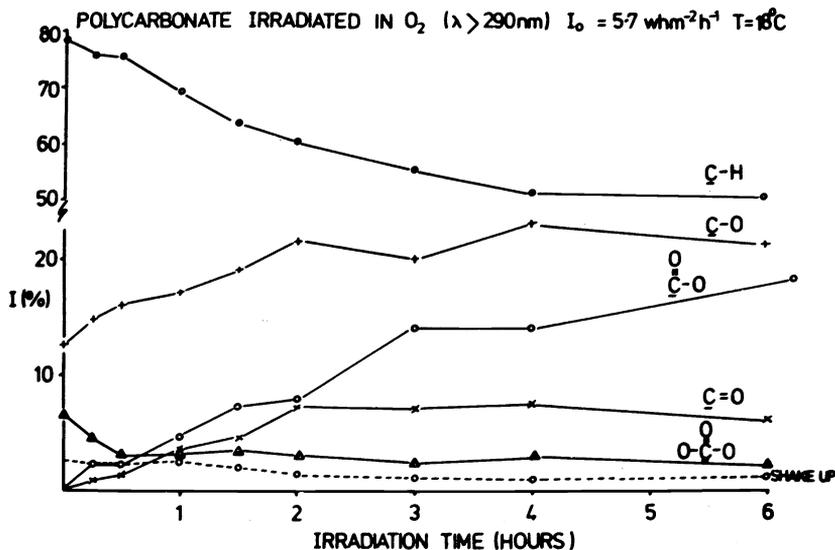intensity. The $\pi \rightarrow \pi^*$ component decreases in intensity and this is consistent with loss of

POLYCARBONATE IRRADIATED IN O_2 $(\lambda > 290nm)$ $I_o = 5\cdot7\,whm^{-2}h^{-1}$ $T = 18^\circ C$

Figure 13. Component contributions to C_{1s} line profile for the core
level spectra displayed in Figure 10 for photo-oxidized
polycarbonate.

aromaticity. The data therefore suggest oxidation of both the aromatic ring system and the gem-dimethyl moiety. The carbonate structural feature decreases in intensity but stabilizes at a low percentage contribution to the overall structure. This in fact appears to be a general feature of the photo-oxidation and indeed plasma oxidation of aromatic polymers.

It is not possible from the C_{1s} and O_{1s} line profiles alone to delineate the importance of hydroperoxide (-O-O-H) structural features and we have accomplished this by allowing the irradiated films to be exposed to a stream of SO_2 to convert the hydroperoxide to $-SO_4H$ functionalities (Figure 14). With a knowledge of instrumentally dependent response factors

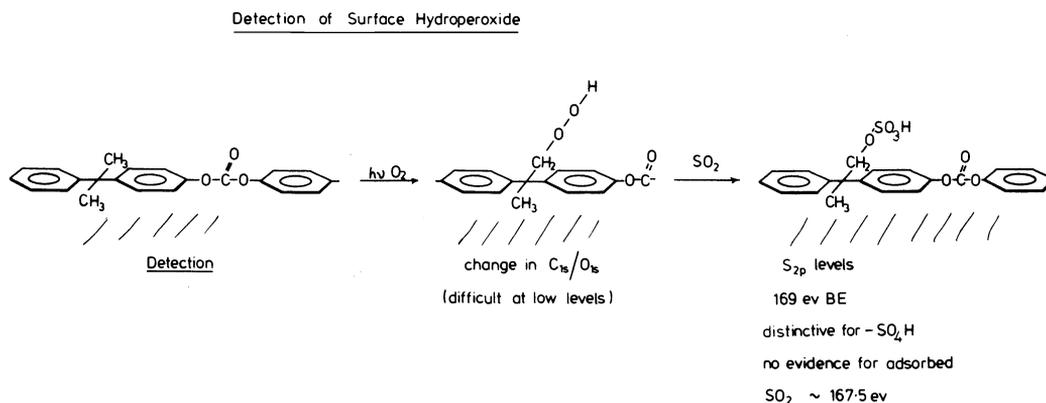Detection of Surface Hydroperoxide

Figure 14. Scheme for the detection of surface hydroperoxide functionalities by conversion to sulphonic acid groups.

and the distinctive binding energy for the sulphonic acid group in the S_{2p} core level photoemission it is possible to follow the role played by hydroperoxide in the photodegradative process and this is shown in Figure 15. The hydroperoxide and carbonyl functionalities
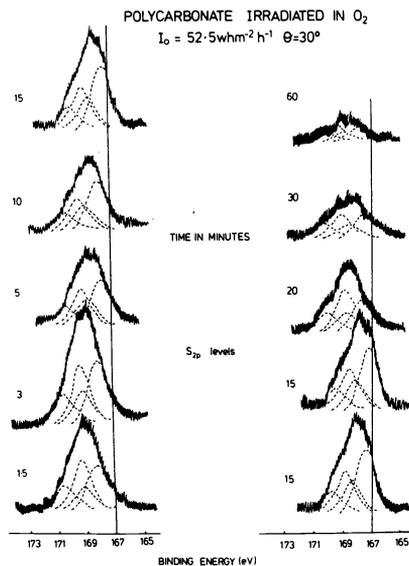

Figure 15. S_{2p} levels for photo-oxidized polycarbonate films exposed to SO_2.

build up to a maximum and then decrease slowly as is apparent from the component analysis in Figure 16. The induction period is not apparent from studies at higher lamp intensities since the hydroperoxide builds up much more rapidly initially and this is well illustrated by comparison of the data in Figures 16 and 17. The increased rate of oxidative
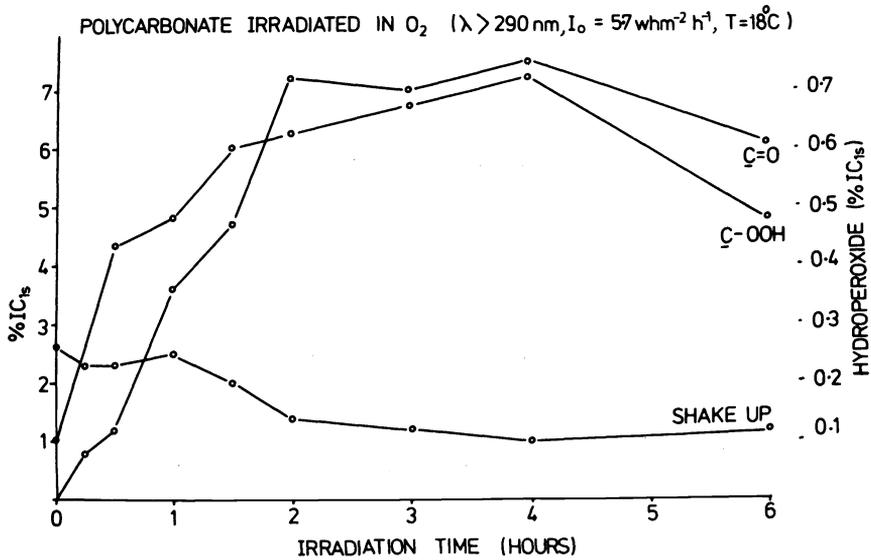
POLYCARBONATE IRRADIATED IN O_2 ($\lambda > 290\,nm$, $I_o = 57\,whm^{-2}\,h^{-1}$, $T=18°C$)

Figure 16. $\rangle C=O$, $-COOH$, and $\pi \rightarrow \pi^*$ shake-up components for photo-oxidized polycarbonate films.

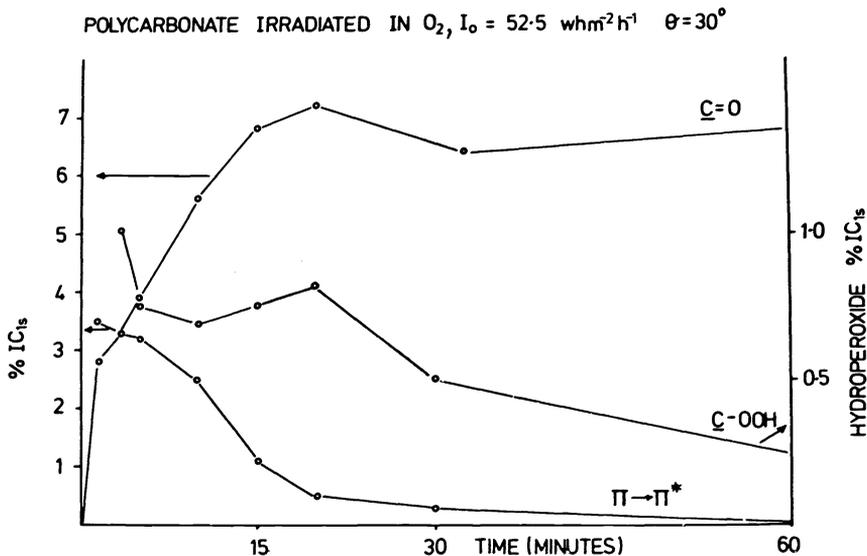POLYCARBONATE IRRADIATED IN O_2, $I_o = 52.5\ whm^{-2}\,h^{-1}$ $\theta = 30°$

Figure 17. Components as for Figure 16 with higher photon flux.

functionalisation with increased UV dosage is illustrated by the data in Figure 18. At higher dosages there is a tendency for the sample temperature to increase somewhat so that superimposed on the expected increase in rate as a function of dosage is the increased sample temperature and this is indicated in Figure 19.

As a comparison we have carried out similar studies for polycarbonate samples irradiated in nitrogen atmospheres. The C_{1s} and O_{1s} core level spectra for samples irradiated at an intermediate dosage in a nitrogen atmosphere are displayed in Figure 20. It is clear from this that there is a small oxygen uptake and the component analysis (Figure 21) shows
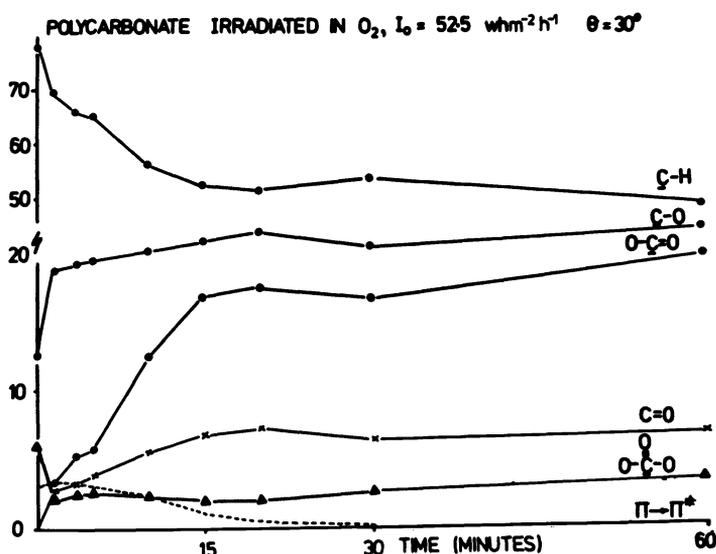
POLYCARBONATE IRRADIATED IN O₂, I₀ = 52·5 whm⁻²h⁻¹ θ = 30°

Figure 18.   Components of C_{1s} levels ($Mg_{K\alpha_{1,2}}$) for photo-oxidized poly-carbonate films at higher photon flux.

POLYCARBONATE IRRADIATED IN O₂ FOR 15 MINUTES
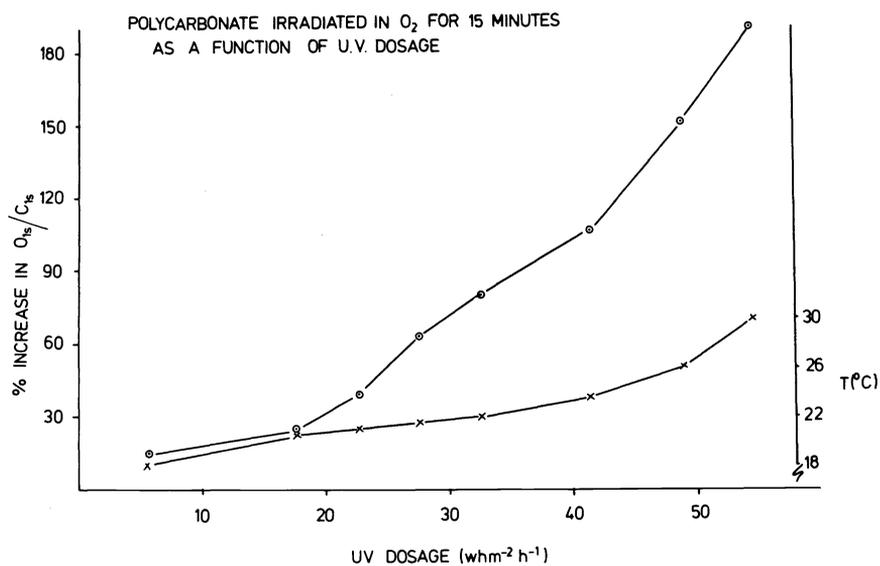AS A FUNCTION OF U.V. DOSAGE

Figure 19.   % increase in O_{1s}/C_{1s} intensity ratios for polycarbonate samples
irradiated in oxygen as a function of UV dosage. (Also shown is
the sample temperature as a function of UV dosage.)

striking differences with respect to samples irradiated at lower dosage in an oxygen
atmosphere. The π → π* shake-up satellite remains roughly constant showing that the
aromatic residues remain intact. The carbonate structural feature decreases whilst the
carboxylate intensity increases and this is most readily accommodated by a photo Fries re-
arrangement mechanism. There is a small contribution from >C=O structural features
suggesting a low level of oxidation of gem-dimethyl groups presumably arising from the low
level of dissolved oxygen in the polymer film. This provides a solid state analogue of the
solution phase photochemistry studies which have received so much attention in the
literature and which also involves a photo Fries rearrangement since the level of dissolved
oxygen is also low. The low degree of oxygen uptake for the samples irradiated in nitrogen
is also shown by comparison of the relative intensities of the O_{1s} and C_{1s} levels and this
is shown in Figure 21. The level of oxygen incorporation for the samples irradiated in a
nitrogen atmosphere is somewhat below that for samples irradiated at much lower dosage in
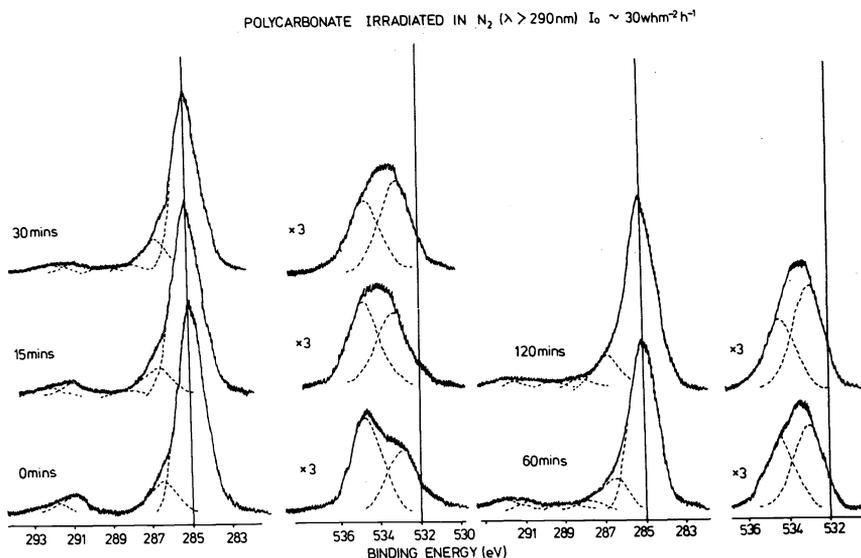
POLYCARBONATE IRRADIATED IN N_2 ($\lambda > 290$nm) $I_0 \sim 30$whm^{-2}h^{-1}

Figure 20. C_{1s} and O_{1s} levels ($Mg_{K\alpha_{1,2}}$) as a function of irradiation time
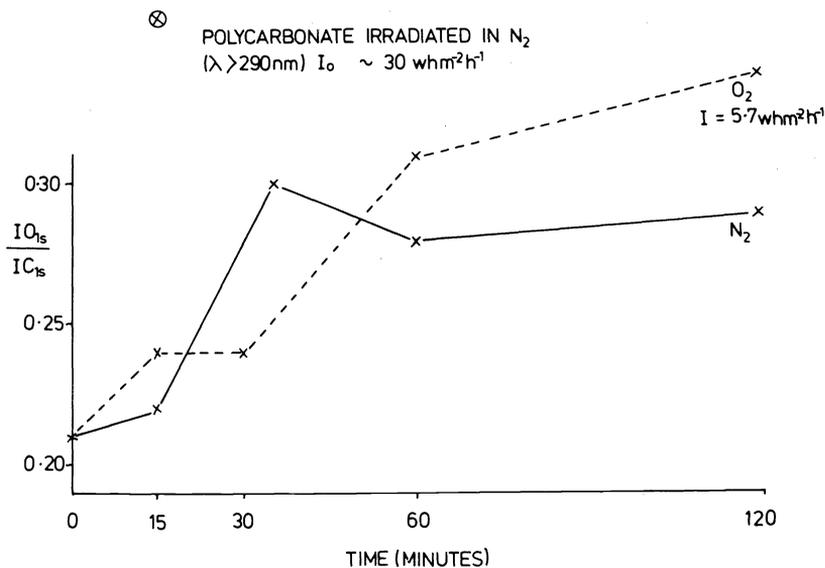for polycarbonate samples irradiated in a nitrogen atmosphere.

Figure 21. O_{1s}/C_{1s} intensity ratio as a function of irradiation time for
polycarbonate in a nitrogen atmosphere. Also shown are
corresponding ratios for irradiation in oxygen.

oxygen. This difference is highlighted by comparison of oxygen uptake at identical u.v.
dosages for 15 minutes. The point to the top lefthand corner of Figure 21 shows the
oxygen uptake for a sample irradiated in oxygen. Whereas the sample irradiated in a
nitrogen atmosphere shows little oxygen uptake that in oxygen shows $\sim$ 100% increase.

These data show that the surface reaction of polycarbonate is rapid and is dominated by
photo-oxidation. Photo Fries rearrangements form a relatively minor role in these surface
reactions of samples irradiated in oxygen and by inference air and this is outlined
schematically in Figure 23. The particular virtue of ESCA is that these reactions can be
monitored at a very early stage. These studies provide strong confirmatory evidence for
the scheme outlined by Factor (Ref. 12) who by contrast studied the bulk phase after
extended irradiation periods at elevated temperatures. The results presented here show that
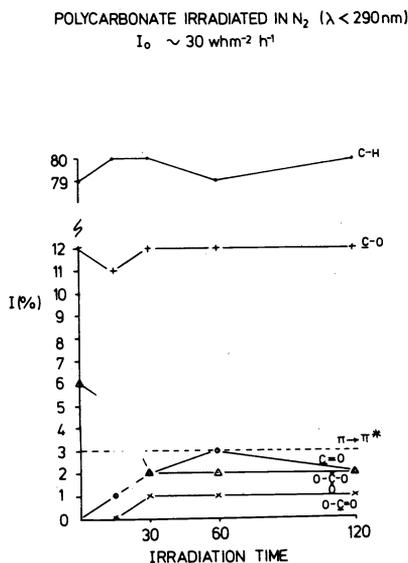
POLYCARBONATE IRRADIATED IN N_2 ($\lambda < 290$ nm)

$I_0 \sim 30$ whm^{-2} h^{-1}

Figure 22.   Components of the C_{1s} levels for polycarbonate irradiated in a nitrogen atmosphere.
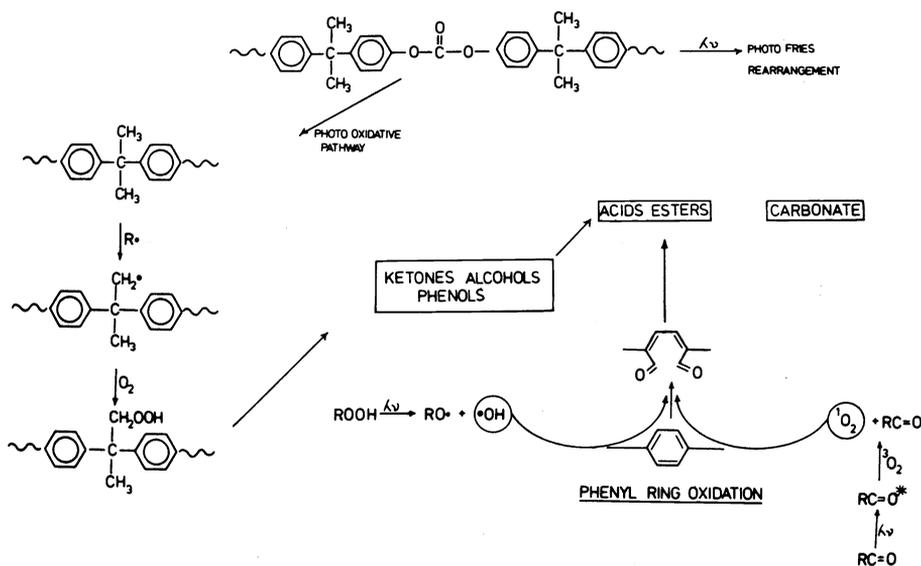

Figure 23.   Summary of main photo-degradative pathways for polycarbonate.

such reactions occur in the surface regions at ambient temperatures and at relatively low u.v. dosages. Information on the characterization of polymers exposed to environmental degradation has not previously been amenable, prior to the development of ESCA as a powerful spectroscopic tool for such surface studies.

POLYMER SYNTHESIS BY MEANS OF PLASMA TECHNIQUES

Introduction

The past few years have witnessed a growing awareness of the great potential of the field which might loosely be defined by the term 'Plasma Chemistry' in areas of polymer chemistry and physics (Refs. 21-23). The wide ranging capability in respect of both *in situ* polymer synthesis and in the surface modification and selective functionalization of polymers is

already apparent.

Although there are excellent well established routes from functional monomers to polymers the range of materials which can be synthesized is greatly expanded by the addition of plasma techniques to the synthetic chemists' armoury. The particular virtues of plasma techniques with the capability under appropriate conditions of polymerizing any monomer and of producing pore free, uniform films of unusual physical, chemical, electrical and mechanical properties at first sight make it difficult to understand why the field has been so slow to develop. It is now more than a century ago since Crookes prophesied (Ref. 24) that the investigation of the 4th state of matter (subsequently denoted as the plasma state) (Ref. 25) would be one of the most exciting growth points in chemistry and physics. Progress in the intervening period has been slow, however, considerable advances have been made in the past few years and this can be traced directly to the possibility of direct interrogation of polymer structure by means of ESCA. The characterization of plasma polymer films which are generally of a highly cross-linked nature and are therefore insoluble presents particular difficulties. Since the interest is also in the deposition of ultrathin films < 1μ the development of the field has had to await the arrival of a technique capable of allowing direct investigation of such films *in situ* on the substrates on which the films are deposited. In a series of papers we have recently shown (Ref. 26) how ESCA may be used to study the fundamental aspects of plasma polymerization of simple fluorinated alkenes (Ref. 27), aromatics (Refs. 28 and 29), alicyclics (Ref. 28) and heterocyclics (Ref. 30) and we present here a brief survey of some of the most recent developments.

Although plasmas may be excited under a variety of conditions, in studying the main features relating 'monomer' structure to that of the plasma polymer the most convenient instrumentation involves low power inductively coupled plasmas excited in flow systems. In such an experiment an important parameter which must be considered is the total power dissipated in the plasma per unit weight of material. Thus if W is the total power input to the plasma, F is the flow rate and M is the molecular weight of the 'monomer' in which the plasma is excited then W/FM is a convenient definable parameter in the investigation of synthetic routes (Ref. 23). The dynamic processes obtaining in a plasma experiment are indicated schematically in Figure 24, where we propose the use of the symbol to denote a plasma ⟶
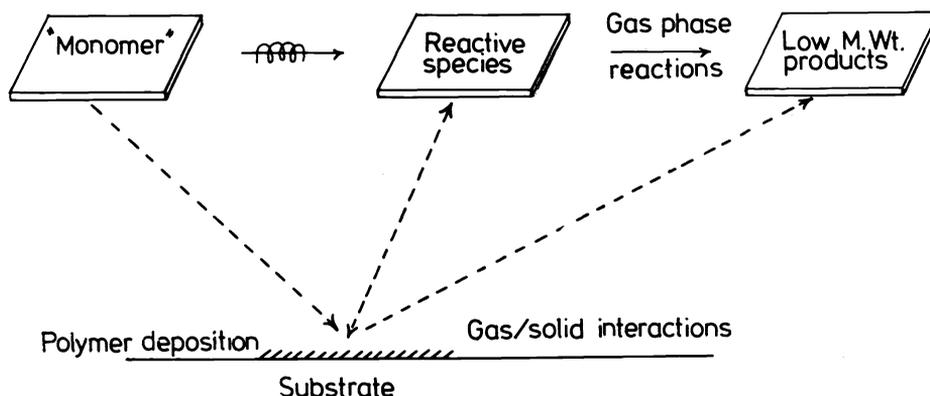

Figure 24. Dynamic processes in plasma polymerization. Competitive ablation and polymerization (CAP) mechanism.

reaction. Excitation of the plasma creates a pool of reactive species including ions, radicals and excited states and these can undergo gas phase reactions to produce gas phase products. Indeed under appropriate conditions gas phase homogeneous reactions can be the dominant process and there is considerable potential for effecting cost effective cyclizations, isomerizations and eliminations in one step using electrical power as opposed to multi-step reactions requiring skilled synthetic chemists (Ref. 31).

The particular interest as far as this symposium is concerned, however, is the investigation of polymers produced by reactions at the gas/solid interface. A competitive process of stepwise build-up of polymer from reaction of 'monomer' and reactive species in the plasma and of ablation of the polymer also by reactive species in the plasma implies that under certain conditions ablation will dominate so that no polymer is deposited whilst under

other conditions polymerization may be extremely rapid. A schematic of the typical
behaviour of the deposition rate for polymer versus the W/FM parameter is shown in Figure
25. At low power inputs and high flow rates it may be difficult to sustain a plasma and the

Plasma polymerization

(SCHEMATICS)

Figure 25. Plasma polymerization schematic of rate of deposition as a
function of W/FM.

deposition rate may therefore be negligible. At high power inputs and low flow rates the
power dissipated per unit mass of 'monomer' may be sufficiently high to lead to ablation of
the surface and the deposition rate therefore again drops to zero. There are therefore
optimum conditions for polymer deposition. Under certain conditions nucleation can occur in
the gas phase to give rise to powdery products whilst under other conditions lower molecular
weight oily materials can be obtained. The work described here corresponds to the
deposition of clear films in the region close to the maximum in rate of deposition for a
given monomer.

We may draw a distinction in basic mechanism of formation of polymers and this is indicated
schematically in Figure 26. For functionalised monomers, e.g. an alkene,it is possible

Figure 26. Plasma polymerization classification of plasma induced
polymerization (PIP) and CAP mechanisms.

under certain conditions to produce linear polymers. These arise from conventional cationic or radical addition mechanism, the plasma then acting as a source of reactive intermediates to initiate the process. This is termed plasma initiated polymerization (PIP). It is invariably the case, however, that in the region of maximum glow where the density of reactive species is highest polymerization occurs in a stepwise manner by a competitive process of polymerization and ablation (CAP process) even for functionalised monomers. By contrast for such systems PIP may well be of importance in other regions of the plasma.

The main point of interest in the work to-date has been plasma polymers produced from fluorocarbon precursors. One reason for the interest in fluoropolymer systems is the ease of study by means of ESCA. Thus, Figure 27 shows the distinctive nature of the C_{1s} core

Typical C_{1s} binding energies

Fluoropolymers
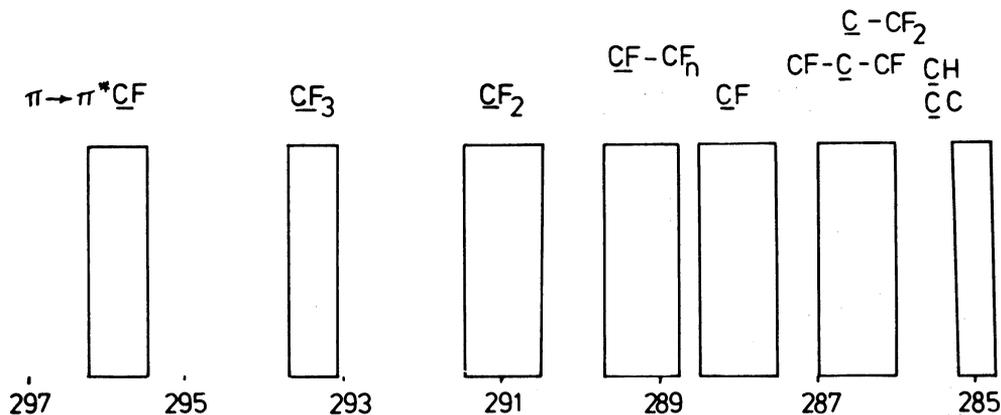
Figure 27. Distinctive nature of C_{1s} levels for typical structural features in fluoro-polymers.

level spectra for various structural features which might arise in a polymer. In the following section we provide a cross-section of some of the recent work which amply demonstrates the substantial role ESCA has played in the characterization of these interesting materials.

Fluoropolymer synthesis
The number of reactive species likely to be present in a plasma excited in even a simple monomer such as a difluoroethylene is considerable and the general impression in much of the early literature is that plasma polymerization is a rather unspecific process. At high power densities this may well be so but with W/FM parameters in the range $10^6 - 10^8$ joules Kg^{-1} encompassing low power (0-20 watt) plasmas at pressures of 50-200μ the routes to plasma polymers may be complex but they can also be rather specific. As a particular example, Figure 28 shows the C_{1s} and F_{1s} levels for plasma polymers synthesized from the isomeric difluoroethylenes. The C_{1s} line profiles in each case show evidence for extensive molecular rearrangements with components arising for $\underline{CF}_3$, CF_2 and $\underline{C}F$ structural features as well as carbons which do not have primary fluorine substituents (Refs. 26 and 27). Analysis of the overall C_{1s}/F_{1s} area ratios and the components of the C_{1s} levels reveals that the stoichiometries for the plasma polymers prepared from the isomeric difluoroethylenes are C:F 1:0.5 compared with 1:1 for the initial monomer. These C_{1s} line profiles reveal that whilst the structural features for the isomeric 1,2-difluoroethylenes are the same those for the 1,1-difluoroethylene are distinctively different. Thus the gem-difluoro isomer shows a significantly higher proportion of $\underline{CF}_3$ groups in the plasma polymer compared to the geometric isomers, whilst the latter show a higher proportion of $\underline{CF}_2$ groups.

Also shown in Figure 28 are the Au_{4f} levels for gold substrates on which the polymer films were deposited under identical conditions of W/FM. The attenuation of the substrate signal provides a means of monitoring the rate of deposition of polymer film and the order cis 1,2 > trans 1,2 > 1,1-difluoro taken with the component analyses mentioned above reveals the rather specific nature of the polymerization process. The order of rate of
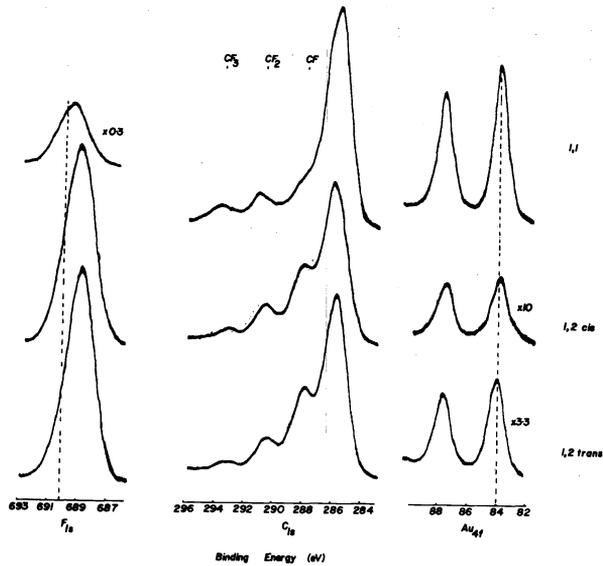
Figure 28. F_{1s}, C_{1s} and Au_{4f} levels for plasma polymers from 1,1-difluoro
and the isomeric 1,2-difluoroethylenes deposited onto gold
substrates under identical conditions of W/FM.

deposition (reactivity of monomers) of the plasma polymers follows the rate of gas phase
elimination from the difluoroethylenes suggesting a route based on fluoroacetylene radical
cation as a reactive intermediate.

Figure 29 shows C_{1s} and F_{1s} levels for the plasma polymers from perfluorobenzene and
perfluorocyclohexane (Ref. 28).
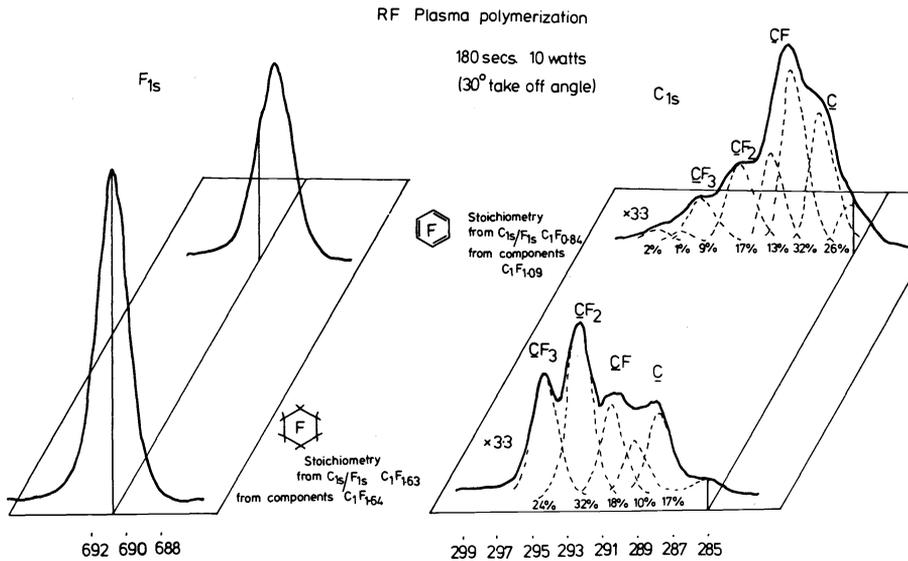
Figure 29. C_{1s} and F_{1s} spectra for fluoropolymers produced from perfluoro-
benzene and perfluorocyclohexane.

These provide interesting examples illustrating the range of monomers from which polymers
may be produced. Thus, benzenes are not conventionally thought of as starting materials
for polymers, whilst perfluorocyclohexane has very little conventional chemistry anyway.
Analysis of the core level data reveals that for the benzene the C:F stoichiometry of the
polymer is essentially the same as that of the monomer whilst for perfluorocyclohexane the
plasma polymer C:F stoichiometry of 1:1.6 is substantially below that of the monomer (1:2).
The data reveal evidence of substantial rearrangement accompanying core ionization and this
has been investigated in the series from the aromatic to the alicyclic via the isomeric

dienenes and perfluorocyclohexene. The component analysis, Figure 30, shows how the structural features present in the polymer varies with the monomer. Thus the $\underline{CF}_3$ component
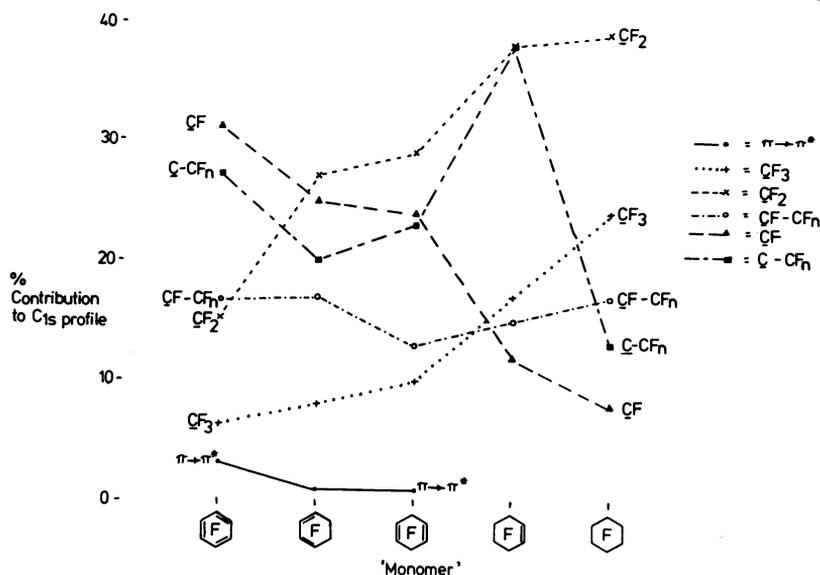

Figure 30.   Components structural features of plasma polymers from the
             perfluorinated series from benzene to cyclohexane.

contribution increases across the series whilst the $\underline{CF}$ component decreases. Such data was not available prior to the development of ESCA. The stoichiometries of the fluoropolymers are compared with those of the monomers in Figure 31 and it is evident from this that as the
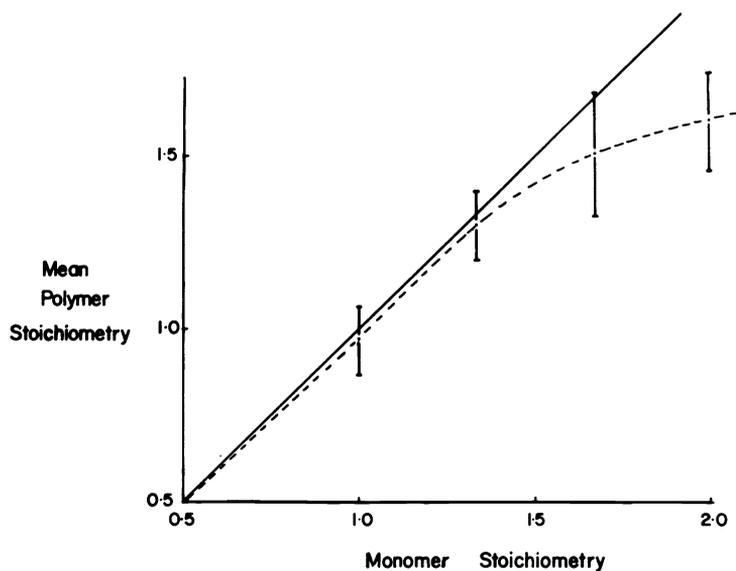

Figure 31.   Mean polymer C:F stoichiometry versus mean polymer stoichiometry
             for the perfluorinated series from benzene to cyclohexane.

degree of unsaturation decreases polymerization involves elimination of fluorine. Comparison of deposition rates reveals that there is a considerable decrease in rate across the series with perfluorobenzene depositing polymer film substantially faster than for perfluoro-cyclohexane.

As we have previously noted the very short mean free path for electrons in polymers provides an excellent means of measuring directly the initial rate of deposition of plasma polymers. Figure 32 shows for example the F_{1s}, C_{1s} and Au_{4f} levels for plasma polymer films deposited from pentafluorobenzene. The attenuation of the Au_{4f} levels attests to the rapid rate of
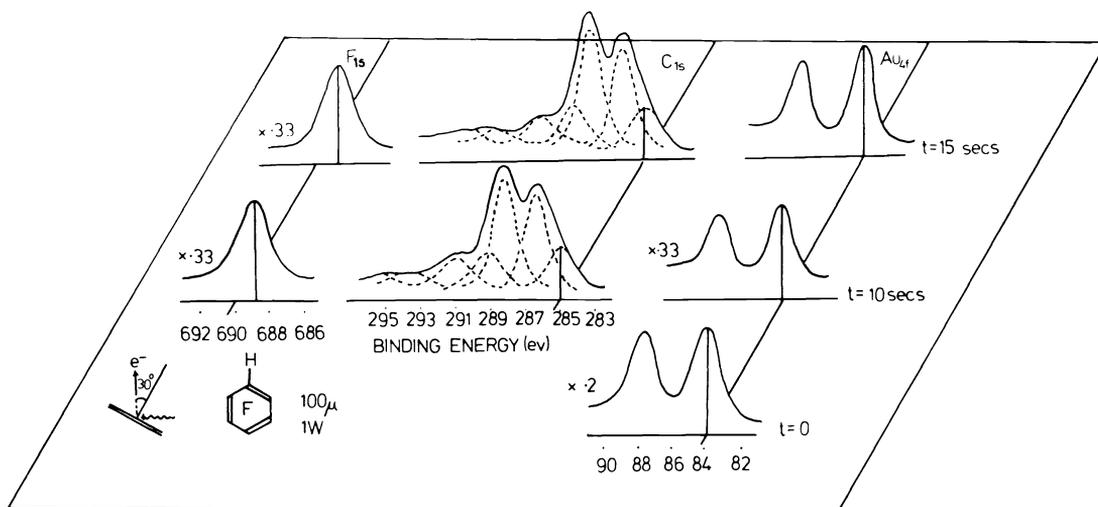
Figure 32. F_{1s}, C_{1s} and Au_{4f} levels for plasma polymer deposited onto
gold substrates from pentafluorobenzene.

polymer deposition and the strong dependence on operating parameters and this is more
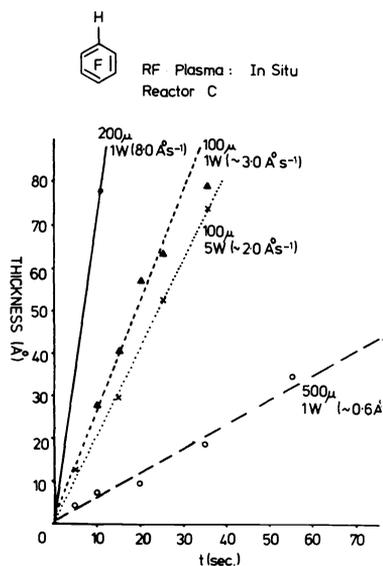readily apparent from the data displayed in Figure 33. The strong dependence of rate of

Figure 33. Initial rates of deposition of pentafluorobenzene plasma
polymer as a function of operating parameters.

deposition on W/FM is clear from this as is the exceptional degree of control which may be
exercised in the deposition process.

The results presented here show the considerable detail that ESCA supplies in the
characterization of these interesting materials. For the fluorinated aromatics the data
suggests extensive molecular rearrangement with $\underline{CF_3}$, $\underline{CF_2}$, $\underline{CF}$ and $\underline{C}$ structural components.

One manifestation of this is that the measured critical surface tensions reflect the
differences in surface chemistry. Figure 34 shows typical data for plasma polymers prepared
from the series of fluorobenzenes. As the fluorine content of the polymer decreases the
critical surface tension increases. For the polymer produced from perfluorobenzene it is
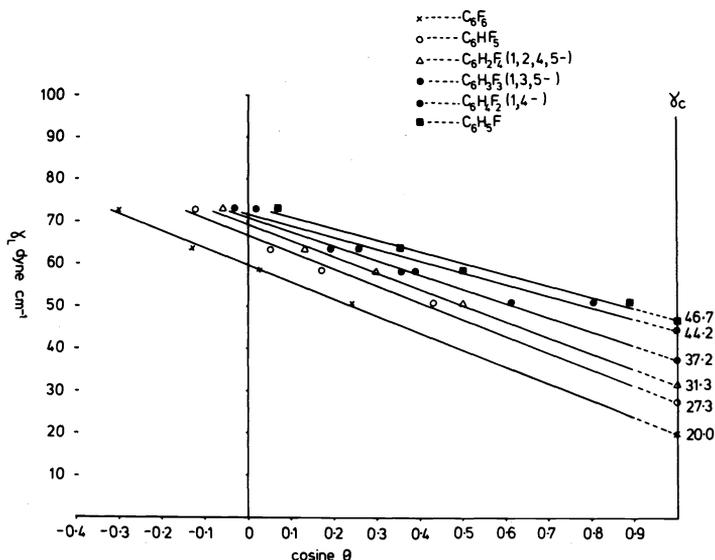
Figure 34. Critical surface tensions for plasma polymers prepared from the series of fluorobenzenes.

interesting to note that the critical surface tension of ~ 20 dynes is significantly below that of polyvinylidene fluoride (~ 27 dynes) for the same C:F stoichiometry.

The investigations described to this stage pertain to polymer films deposited in the glow region at the centre of the coil region in inductively coupled plasmas. It is generally the case that the structure of the polymer film and its rate of deposition remain essentially constant in the region of maximum glow. ESCA does allow, however, a detailed investigation to be made of structure and composition of plasma polymers as a function of site of deposition covering both glow and non-glow regions (Ref. 29).

As a particular example, Figure 35 shows a reactor configuration in which a number of deposition sites may be studied. Typical stoichiometric data are shown in Figure 36.
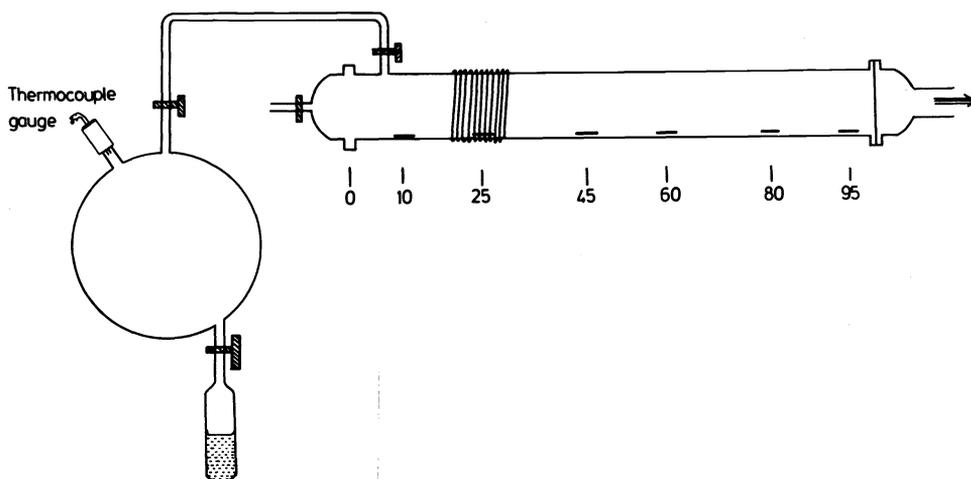

Figure 35. Reactor configuration for the investigation of dependence of structure on site of deposition in plasma polymerization.
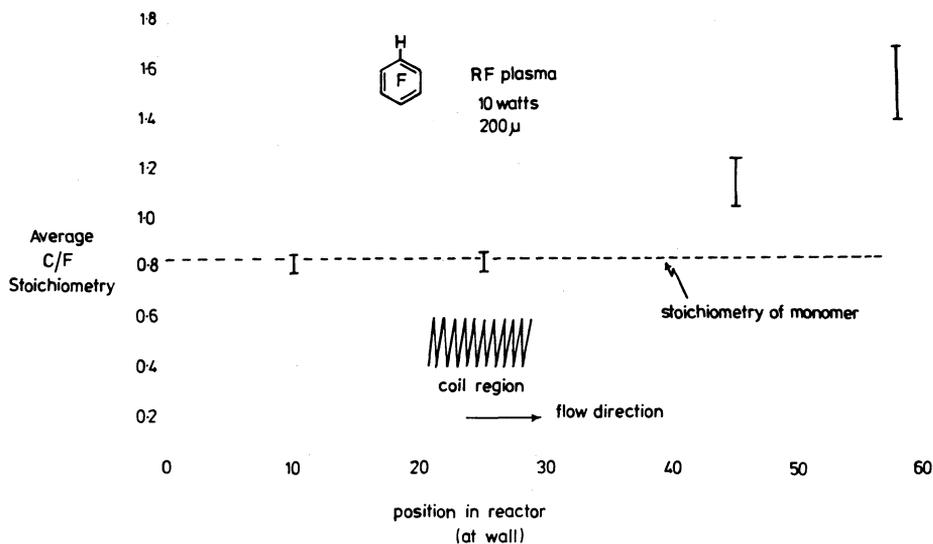
Figure 36. C:F stoichiometry versus site of deposition for plasma
polymers deposited from pentafluorobenzene.

The stoichiometry of the polymer is essentially that of the monomer in the region of
maximum glow, however, downstream the fluorine content of the polymer films increases
considerably. The rate of deposition also decreases outside of the glow region and the
spectra reveal a greater contribution from CF_2 structural features. It therefore seems
likely from these studies that less reactive species (e.g. difluorocarbene and species
derived therefrom) are involved in the polymerization process in the non-glow regions.

CONCLUSION

The three examples cited here exemplify the role ESCA is playing in the developing
interest in the surface characterization of polymers. Such studies complement those
available in the bulk, and allow a direct comparison of structural features. The importance
of this comparison particularly in evaluating heterogeneous reactions at the gas/solid and
liquid/solid interface cannot be over-emphasized.

ACKNOWLEDGEMENTS

REFERENCES

1. (a) D.T. Clark in Advances in Polymer Science, H.J. Cantow (Ed.), Springer Verlag,
         Berlin, 24, 125 (1977).
    (b) D.T. Clark in Photon, Electron and Ion Probes of Polymer Structure and Properties,
         D.W. Dwight, T.J. Fabish and H.R. Thomas (Eds.), A.C.S. Symposium Series, 162,
         Washington, D.C., Chap. 17 (1981).
2. A.D. Jenkin (Ed.), Polymer Science, North-Holland Pub. Co., Amsterdam, 2 (1972).
3. (a) D.T. Clark in Chemistry and Physics of Solid Surfaces, R. Vanselow (Ed.),
         CRC Press, Boca Raton, Florida, Vol. II (1977).
    (b) D.T. Clark in Polymer Surfaces, D.T. Clark and W.J. Feast (Eds.), Wiley, London,
         Chap. 7 (1978).
4. C.D. Wagner in Photon, Electron and Ion Probes of Polymer Structure and Properties,
    D.W. Dwight, T.J. Fabish and H.R. Thomas (Eds.), A.C.S. Symposium Series, 162,
    Washington, D.C., Chap. 14 (1981).
5. (a) D.T. Clark, A. Dilks and H.R. Thomas, J. Polym. Sci., Polym. Chem. Ed., 16, 1461
         (1978).
    (b) D.T. Clark, A. Dilks, H.R. Thomas and D. Shuttleworth, J. Polym. Sci., Polym. Chem.
         Ed., 17, 627 (1979).

6.   J.J. Pireaux, J. Riga, R. Caudano and J. Verbist in Photon, Electron and Ion Probes of Polymer Structure and Properties, D.W. Dwight, T.J. Fabish and H.R. Thomas (Eds.), A.C.S. Symposium Series, 162, Washington, D.C., Chap. 13 (1981).
7.   (a) D.T. Clark and P.J. Stephenson, Proceedings of Conference on Nitrocelluloses, Waltham Abbey, T.J. Lewis (Ed.), Plenum Press (1980).
     (b) D.T. Clark, P.J. Stephenson and F. Heatley, Polymer, 22, 1110 (1981).
8.   D.T. Clark and P.J. Stephenson, Polymer, 22, 1303 (1981).
9.   J. Peeling and D.T. Clark, Polym. Degrad. and Stab., 3, 97 (1981); Polym. Degrad. and Stab., 3(3), 177 (1981).
10. A. Dilks and D.T. Clark, J. Polym. Sci. (Chem. Edn.), 1981, in press.
11. D.T. Clark and H.S. Munro, Polym. Degrad. and Stab., 1981, in press.
12. A. Factor and M.L. Chu, Polym. Degrad. and Stab., 2(3), 203 (1980).
13. B. Ranby and J.F. Rabek, Photodegradation, Photo-oxidation and Photostabilization of Polymers, John Wiley & Sons, London (1975).
14. (a) A. Gupta, A. Rembaun and J. Moacanin, Macromolecules, 11, 1285 (1978).
     (b) A. Gupta, R. Liang, J. Moacanin, R. Goldbeck and D. Kliger, Macromolecules, 13, 262 (1980).
15. E. Ong and H.E. Bair, Polymer Preprints, 20, 945 (1979).
16. A.D. Williams and P.J. Florey, J. Polym. Sci., A-2, 6, 1945 (1968).
17. (a) J.N. Murrel, The Theory of Electronic Spectra of Organic Molecules, Methuen & Co. Ltd., London (1963).
     (b) M.M. Jaffe and H. Orchin, Theory and Application of Ultraviolet Spectroscopy, Wiley, New York (1962).
18. J.F. Meeks, J.F. Arnett, D. Larson and S.P. McGlynn, Chem. Phys. Lett., 30, 190 (1975).
19. D.W. Turner, Molecular Photoelectron Spectroscopy, Wiley Interscience, Chichester (1970).
20. A. Davis, G.H.W. Deane and K.J. Ledbury, Weathering Plast. Rubbers, Int. Symp., B1.1-B9.9 (1976).
21. J.R. Hollahan and A.T. Bell (Eds.), Techniques and Applications of Plasma Chemistry, Wiley, N.Y. (1974).
22. D.T. Clark and W.J. Feast (Eds.), Polymer Surfaces, Wiley, London (1978).
23. H. Yasuda and T. Hirotsu, J. Polym. Sci., Polym. Chem. Ed., 16, 743 (1978).
24. W. Crookes, Phil. Trans., Pt. I, 152 (1879).
25. K.T. Crompton and I. Langmuir, Electrical Discharges in Gases, I, Rev. Modern Physics, 2, 123 (1930).
26. D.T. Clark and D. Shuttleworth, Euro. Polym. J., 15, 265 (1978).
27. (a) D.T. Clark and D. Shuttleworth, J. Polym. Sci., Polym. Chem. Ed., 16, 1093 (1978).
     (b) D.T. Clark and D. Shuttleworth, J. Polym. Sci., Polym. Chem. Ed., 17, 1317 (1979).
28. (a) D.T. Clark and D. Shuttleworth, J. Polym. Sci., Polym. Chem. Ed., 18, 27 (1980).
     (b) D.T. Clark and D. Shuttleworth, J. Polym. Sci., Polym. Chem. Ed., 18, 407 (1980).
29. D.T. Clark and M.Z. AbRahman, J. Polym. Sci., Polym. Chem. Ed., in press.
30. D.T. Clark and M.Z. AbRahman, J. Polym. Sci., Polym. Chem. Ed., in press.
31. H. Suhr in Techniques and Applications of Plasma Chemistry, J.R. Hollahan and A.T. Bell (Eds.), Wiley, N.Y., Chap. 2 (1974).