

Modification of polymer surfaces by far-ultraviolet radiation of low and high (laser) intensities

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Far-ultraviolet radiation (e.g. 185 nm from a mercury resonance lamp or 193 nm from a pulsed excimer laser) is highly effective in modifying the surfaces of a variety of polymers because of its short penetration depth ($<3000\text{\AA}$) and its high (>0.1) quantum yield for bond breaking. With continuous low-level irradiation at 185 nm in the presence of specific gases functional groups can be introduced on the surface while etching is kept at a low rate. In contrast, the pulsed laser radiation at 193 nm causes ablative photodecomposition leading to a surface showing negligible reaction with the surrounding atmosphere. This process can be conveniently used in controlled etching of polymers.

(Keywords: laser etching; photoablation; photoetching; polymer surface; polyester, polyimide)

INTRODUCTION

The section of the electromagnetic spectrum which extends from 200 to 150 nm is formally defined as far-ultraviolet radiation. The narrow band which lies between 200 and 180 nm is a practical and highly effective region for the photochemical modification of polymers for several reasons. An Einstein of photons at 184.9 nm which is the wavelength of a readily available mercury line is equivalent to 155 kcal of energy which exceeds the strength of most of the bonds in a typical organic polymer. It is therefore quite efficient in bringing about photochemical reactions. Nearly all organic compounds (with the exception of saturated aliphatic hydrocarbons and fluorocarbons) absorb intensely at this wavelength ($\epsilon \approx 0.5\text{--}1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). As a result, this radiation penetrates organic polymers to only $\approx 300 \text{ nm}$ before 95% of its intensity is absorbed. The quantum yields for many organic compounds for photochemical transformations at 185 nm in the condensed phase have been measured¹. These values range from 0.1 to 1.0 which are an order of magnitude larger than the values that are encountered in the mid- and near-ultraviolet regions. From a practical point of view, the 180–200 nm region of the far-ultraviolet is a convenient one since fused silica freely transmits these wavelengths, water vapour has hardly any absorption while the oxygen in air absorbs weakly.

The net photochemical process in an organic polymer when radiation in the 180–200 nm region is used is dependent upon the intensity of the radiation. The similarities and differences between low-intensity, continuous light from a mercury resonance lamp and high intensity, pulsed light from an excimer laser are best discussed in terms of a schematic diagram (Figure 1). The absorption of the photons by the polymer (Figure 1a) is observed to be governed by Beer's Law in both cases as

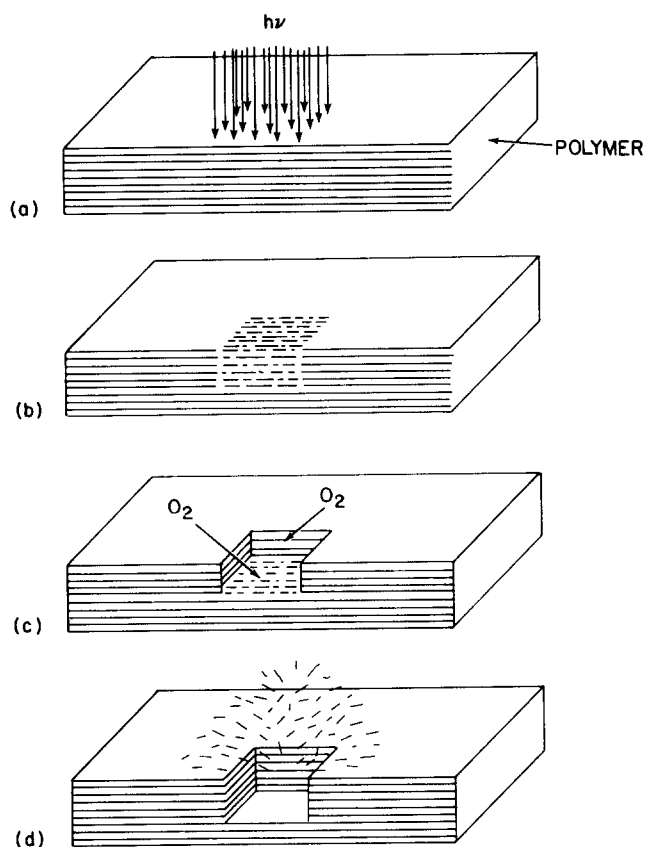


Figure 1 Schematic representation of action of far-ultraviolet radiation on a polymer surface

long as the laser fluence (energy/unit area in the lifetime of the pulse) does not exceed 0.5 J cm^{-2} for pulses of $12\text{--}14 \times 10^{-9} \text{ s}$ half-width. The radiation must therefore penetrate to the same depth in both cases. Figure 1b shows that there will be numerous bond-breaks in the irradiated volume in both cases. Typically, radiative lifetimes of organic molecules in the wavelength region of interest can be calculated to be $\approx 0.1 \text{ ns}$ but since fluorescence is rarely observed, the lifetimes for decomposition must be of the

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order of picoseconds. The course of photochemistry at this point is determined by the rate at which the photons are delivered to the irradiated volume.

If the photons are delivered in a slow but continuous stream from a mercury lamp, and air is excluded, the breaking of the bonds in the polymer chain is rapidly followed by recombination processes so that the net reactions are the loss of the small gaseous molecules (CO , CO_2 , H_2) and degradation of the polymer by the disruption of its linear structure. In the presence of air (Figure 1c), the oxygen traps the radical ends to give initial oxidation products which can undergo further photolysis to give smaller fragments. Prolonged irradiation results in the controlled etching of the polymer². These reactions are closely related to the photodegradation of the same polymers in the mid-u.v. which have been intensively studied³⁻⁵ and also to the modification of polymer surfaces by ion bombardment in plasmas⁶⁻⁸. The use of far-ultraviolet radiation offers a greater degree of control in terms of speed, minimization of damage to the bulk and simplicity than these alternative methods, as will be discussed.

When the photons are delivered in an intense pulse of short duration, (Figure 1d) the concentration of fragments in the irradiated volume presumably reaches a high value which, when it exceeds a threshold level, results in the spontaneous ejection of the fragments into the gas phase⁹⁻¹⁴. This process is termed 'ablative photodecomposition' because the ablated material carries away a high percentage ($\approx 90\%$ at 0.5 J cm^{-2}) of the energy of the photon that is not consumed in the bond breaking. The result is a clean etching of the surface in a geometry defined by the light beam.

IRRADIATION AT 185 nm WITH CONTINUOUS MERCURY LAMPS

Experimental

Light source. The samples were irradiated with a BHK mercury vapour grid lamp, providing a 185 nm line, the intensity of which was 2.5 mW cm^{-2} at a distance of 2 cm. The 254 nm radiation was not filtered out.

Samples. The polymer samples were commercially available films of poly(methyl methacrylate) (PMMA)*, poly(ethyleneterephthalate) (PET)[†] and polyimide. The last two (Mylar[®] and Kapton[®]) were purchased from DuPont. The size of the samples was $6 \times 12\text{ mm}$ which was chosen to fit the XPS sample holder.

E.s.c.a. equipment. The XPS spectra were recorded on a standard Hewlett-Packard 5950 B spectrometer which was equipped with all the computing facilities as described in ref. 15.

Procedure. The photoetching rate was obtained by measurement of the depth of a hole which resulted from exposure to radiation for a given time through a contact mask. The depth measurements were performed on a Tencor Depth Gauge.

Results

The simplest experiment consisted of irradiation of polymer samples in the presence of air with the mercury

* The commercial sample of PMMA had a molecular weight of 200 000
 † The sample of PET had a molecular weight of 20 000 and was free of plasticizer

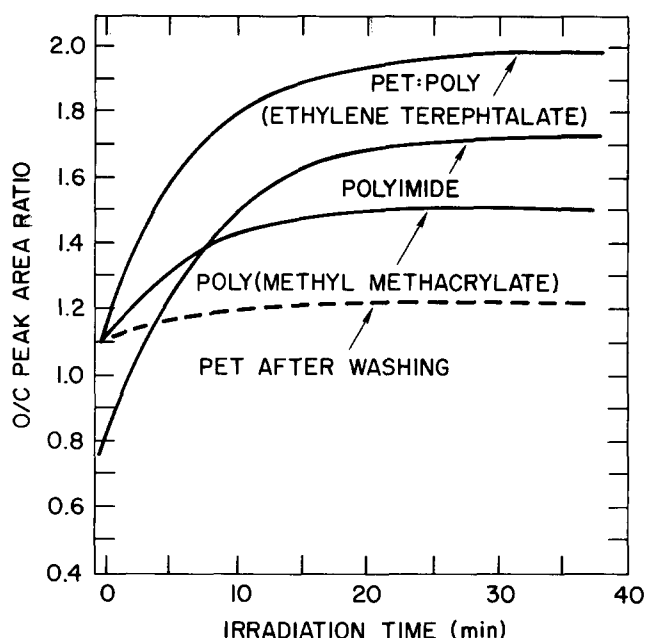


Figure 2 Ratio of O/C peaks in e.s.c.a. as a function of irradiation time (185 nm continuous radiation)

resonance lamp (185 nm). The increase in oxygen content as monitored by the O/C e.s.c.a. peak area ratio is displayed as a function of the irradiation time in Figure 2. For all three polymers, the O/C values reached a maximum value within ≈ 10 min of irradiation. PET and PMMA which have the same original oxygen content according to the formulae of their repeat units (C_{10}O_4 for PET and C_5O_2 for PMMA) show different oxygen contents at the photostationary state. This difference can be explained by their different susceptibility to photooxidative etching, a fragmentation process which, in air, competes with oxidation. Under the experimental conditions, the etch rate of PMMA was 85 \AA min^{-1} whereas for PET it was only 14 \AA min^{-1} . Polyimide showed photooxidation to a degree comparable to that of PET.

These results show the efficiency of the 185 nm CW radiation in photooxidizing the polymer surfaces. This can be compared to other surface treatments such as electrical discharges in air or oxygen⁶⁻⁸. Plasma modification of the surface also leads to oxidation as seen by e.s.c.a. but neither the active species nor the precise mechanism of this reaction is known. Recent work¹⁶ shows that an oxygen ion beam with 1 KeV energy causes a significant decrease in the oxygen content of PET rather than oxidation. Irradiation of polymers using wavelengths $\geq 254\text{ nm}$ have been performed by other groups³⁻⁵, but the required exposure time is necessarily longer since the depth of penetration of the photon at these wavelengths is greater than in the far-u.v. and the photon is less reactive photochemically.

The oxidized surface obtained by far-u.v. irradiation displayed some characteristic chemical properties. The oxygen-rich layer was able to oxidize a potassium iodide solution to yield iodine. This oxidizing power may be attributed to the presence of hydroperoxy and/or peracid groups in the irradiated layer¹⁶. It was further found that these oxidizing groups were contained in small fragments on the surface of the polymer since they could be washed away simply by soaking the irradiated sample in a liquid

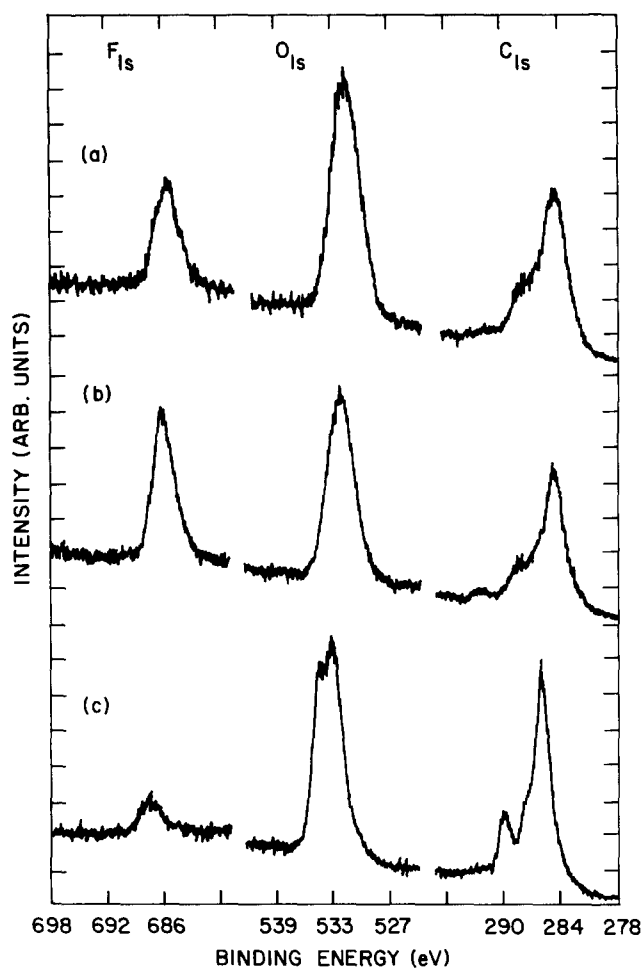


Figure 3 E.s.c.a. spectra of polymer surfaces after far-u.v. exposure followed by treatment with trifluoroacetic anhydride. (a) 185 nm Continuous radiation in air; (b) 185 nm continuous radiation in vacuum; (c) 193 nm pulsed laser radiation

(H_2O , CH_3OH). This phenomena was further confirmed by e.s.c.a. which showed (Figure 2 for PET) a considerably lower oxygen content after washing. The reaction of the irradiated surface with trifluoroacetic anhydride¹⁷ gave confirmatory evidence that new functionalities had been created, since unirradiated samples did not show any affinity for this reagent. For example a PET sample, after 10 min of exposure in air, was dipped in a 10% KI solution and then transferred to a trifluoroacetic anhydride solution in toluene buffered with pyridine. After extensive washing with anhydrous toluene, the e.s.c.a. analysis of the sample (Figure 3) revealed the presence of an important fluorine peak whereas PET as received did not show any fluorine peak after the same treatment. It has been shown¹⁷ that the introduction of fluorine by reaction with this reagent is indicative of the presence of both carboxylic and hydroxyl groups. The hydrolysis of the mixed anhydride formed with the acid groups is achieved by soaking the samples in methanol. After this treatment e.s.c.a. still showed a residual fluorine peak corresponding to the non-hydrolysable trifluoroacetate formed with the hydroxyl groups. This technique allowed the relative amounts of hydroxyl and carboxylic groups to be determined. Figure 3 shows three PET samples, the first of which was irradiated in the presence of air and was found to contain hydroxyl and carboxylic groups in equivalent amounts. The second sample, similarly irradiated under vacuum, displayed only carboxylic groups and very few hydroxyls. Similarly after laser ablation (described below)

the PET surface (Figure 3c) showed a small extent of carboxylic functionalities but no hydroxyls.

IRRADIATION OF POLYMER SURFACES WITH PULSED 193 nm LIGHT AT LASER INTENSITY

Experimental

The source of laser radiation at 193 nm was a Lambda-Physik (Goettingen) Excimer Laser filled with a mixture of argon, fluorine and helium. It could be repetitively pulsed from 1 to 80 Hz to yield pulses of 14 ns half-width. The output at low repetition rates was ≈ 200 mJ/pulse over an area of ≈ 1.5 cm². Although this laser could provide other wavelengths in the ultraviolet with appropriate gas fillings, in this article, only results obtained with 193 nm radiation will be reported.

The materials and analytical methods were exactly the same as those described in the previous section. All exposures were performed in air except when it was specially necessary to use a low vacuum ($p \approx 15$ μm).

Results

The kinetics of the ablative photodecomposition of four common photopolymers have been detailed elsewhere¹¹ and analysed in terms of a standard photodegradation scheme¹². It is sufficient to point out here that the depth of the polymeric material that is removed (etched) by each successive pulse is exactly the same over hundreds of pulses and the magnitude of the etch depth/pulse can vary from a few hundred to a few thousand Angstroms when fluences are in the range 50–500 mJ cm⁻². A plot of log fluence vs. etch depth is a straight line for four polymers and the slopes fall within a narrow range irrespective of the chemical composition. The intercepts which represent the fluence threshold at which ablative photodecomposition commences can vary from ≈ 10 mJ cm⁻² for PMMA to ≈ 60 mJ cm⁻² for a condensation polymer such as a polycarbonate. Satisfactory correlations between the chemical composition of a polymer and either its threshold for photoablation or the slope of its log fluence vs. etch depth have not been found. The dynamics of ablation has been modelled¹³ and the parameters for the ablated material have been measured¹⁴. It has been found that the ablated material is ejected from the surface at supersonic velocities in a narrow cone with a solid angle of $\pm 30^\circ$ to the normal.

The chemistry of the surface following ablative photodecomposition will be the main concern of this article. In Figure 4, the e.s.c.a. of a sample of PET before and after exposure to laser radiation is shown. In contrast to continuous radiation at 185 nm, pulsed laser radiation produces a surface that is relatively depleted in oxygen. Since both the absorption (Figure 1a) and bond-breaking (Figure 1b) under both sets of conditions are not likely to differ significantly, the oxygen-depleted surface that is produced by ablative photodecomposition is attributable to the high-velocity stream of ablated material that is ejected normal to the surface (Figure 1d). It will effectively prevent oxygen from the atmosphere from diffusing to the surface and reacting with the radical ends. This is consistent with the observed uniformity in the etch depth/pulse in air and in a vacuum¹¹ for PET and with the inability to quench totally the formation of benzene which is the major product¹⁰ even when laser exposure is carried out in pure oxygen at 200 Torr pressure.

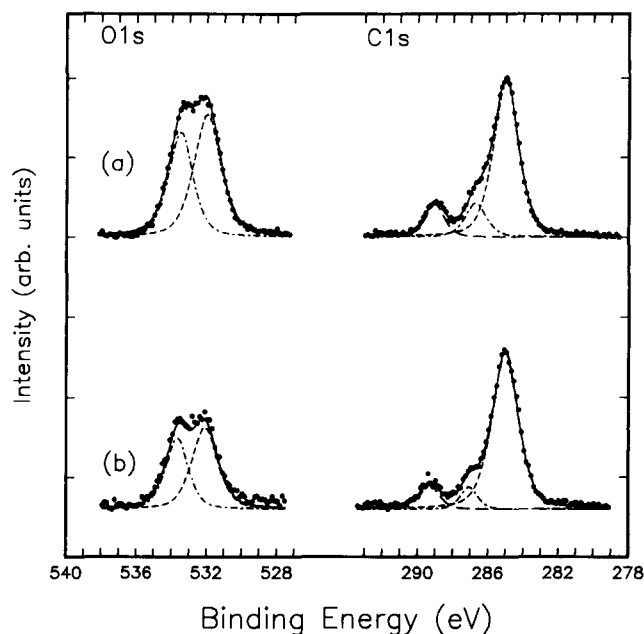


Figure 4 E.s.c.a. spectrum of poly(ethylene terephthalate) (PET). (a) Untreated; (b) after laser irradiation at 193 nm in air

The depletion of oxygen atoms at the surface of the polymer film indicates that while ablative removal etches the film to a finite depth as shown schematically in *Figure 1d*, photolysis extends below this surface since the photons penetrate to a greater depth. A similar decrease in O/C ratio was observed in polyimide films but not in PMMA which decomposed principally into monomer units¹⁶. It may be pointed out that ablative photodecomposition is not exactly a method for the modification of a polymer surface at an atomic level since it totally eliminates the atoms at the surface and creates a fresh surface.

Scanning electron microphotographs of PET films modified by oxidative photoetching at 185 nm and by ablative photodecomposition show a surface roughness (*Figure 5*) which is probably related to a small difference in the sensitivity to etching of the crystalline and amorphous regions. The dimensions of the hills and valleys seen in the photograph would fit this interpretation. However, surface contour measurements show that oxidative photoetching leaves asperities only 200–400 Å high whereas laser ablation leaves hills which can be as high as 800–1000 Å.

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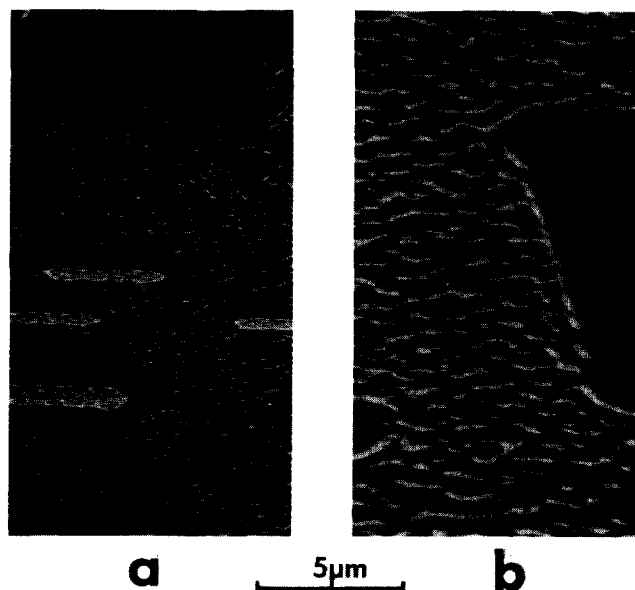


Figure 5 Scanning electron microphotographs of poly(ethylene terephthalate) (PET). (a) Exposure to 185 nm continuous radiation in air; (b) laser radiation at 193 nm in air. The smooth surfaces represent unirradiated regions

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