

An X-ray photoelectron spectroscopy study of poly(methyl methacrylate) surface modified by 193-nm laser radiation

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Summary

The chemistry of poly(methyl methacrylate) subjected to 193-nm radiation, emitted by an argon-fluorine excimer laser, was studied by X-ray photoelectron spectroscopy. From the O/C atomic ratios measured at two different sampling depths, it is concluded that the role of depolymerization in the laser ablation process may be less important than previously suggested.

Introduction

As the most convenient sources of intense, monochromatic and coherent ultraviolet (UV) radiation, the excimer lasers are increasingly used in the processing of microelectronic components by the controlled direct etching of polymers. The radiation with a wavelength of 193 nm, produced by the argon-fluorine excimer laser, has received a great deal of interest. The spontaneous removal and ejection of material (ablation) at the surface of polymers, caused by UV laser radiation is known as *ablative photodecomposition* [1,2]. Although ablation is customarily explained by the mechanisms proposed by Srinivasan *et al.* [1-8], the detailed chemistry of this process obviously requires more investigation. The experimental etch curve, i.e., the plot of ablation rate (in μm per pulse) versus fluence of radiation (in mJ/cm^2), has been frequently used as a tool to investigate the mechanism of ablation. It was noticed earlier [9,10] that the etch curve of poly(methyl methacrylate) (PMMA) was discontinuous, unlike the curves displayed by condensation polymers such as polyimides or poly(ethylene terephthalate) (PET). Subsequent experiments revealed two points of inflection in the PMMA etch curve [7,8]. It was assumed that only addition polymers with a great susceptibility to thermal depolymerization displayed points of inflection in the etch curves. We have confirmed the existence of two discontinuities in the etch curve of PMMA [11], and in that of poly(2-hydroxyethyl methacrylate) (PHEMA) [12], the latter not investigated previously in this respect.

X-Ray photoelectron spectroscopy (XPS) has been considered a useful alternative for the study of chemical modifications of polymer surface induced by excimer laser radiation, especially by that emitted by argon-fluorine laser (193 nm) [13-19]. While the ablated surface of condensation polymers (polyimides, PET, polycarbonates) was found poorer in oxygen (decreasing O/C atomic ratio), probably due to the loss of volatile species such as CO and CO₂ [13,14,16,18,19], the behaviour of addition polymers could not be generalized. For instance, fluorinated polymers underwent defluorination and oxidation during irradiation [17,18]; poly(α -methylstyrene) showed a loss of aromaticity and slight oxidation [15]. However, the O/C ratio in

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both exposed and unexposed PMMA was always found unchanged [13-15]. It was suggested that this is a consequence of depolymerization since (a) the ejected species include mainly monomers, and probably oligomers, with a stoichiometric composition indistinguishable from that of polymer [8], and (b) the large amount of monomer, generated rapidly and ejected at high speed, prevents the access of surrounding oxygen to the polymer surface, therefore secondary oxidative processes. However, the same argument is valid for polytetrafluoroethylene and poly(α -methylstyrene), both being able to depolymerize quantitatively. Unchanged C/F or $C_{\text{sat}}/C_{\text{arom}}$ ratios, respectively, would then be expected, but this has not been confirmed by experiments so far.

Previously we analyzed by XPS the surface of PHEMA exposed to 193-nm excimer laser radiation [20]. Two different take-off angles were used in XPS experiments enabling us to examine separately the changes in the top 2-nm thick layer as well as in the subsurface (*ca.* 12 nm in depth). Unlike the results previously reported for another acrylic polymer (PMMA), we found that the O/C ratio was dependent on both the fluence of radiation and the probing depth. At higher fluences there was no significant change in the O/C ratio in the bulk, and only a slight decrease in the top surface, which suggested a predominance of depolymerization during ablation. At lower fluences, the oxygen loss was substantial, especially in the bulk. The latter result conflicts with the general tendency noticed previously in PMMA [13-15]. This may be due to the scission of 2-hydroxyethoxycarbonyl pendant group and subsequent generation and ejection of oxygen-containing molecules. Presumably, this process would be diminished in PMMA where the pendant group is methoxycarbonyl. However, this assumption must be substantiated. We present here a study by XPS of the PMMA surface exposed to 193-nm laser radiation. Differing from previous reports for PMMA, two fluences of laser radiation and two sampling depths in XPS analysis have now been used.

Experimental

Materials

Square slabs (25 x 25 mm) were cut from a 1.7-mm thick PMMA sheet (Acrypoly®, Chi Mei Industrial Co. Ltd., Taiwan). This material was proved [11] to be pure and devoid of any additives. The slabs were extensively washed in cyclohexane and then diethyl ether, and finally dried in a vacuum oven at 50°C, under a static vacuum of 170 mm Hg, for 48 hours.

Laser exposure conditions

Pulsed 193-nm radiation was produced by a Questek Model 2820 (USA) argon-fluorine laser. The duration of a pulse was about 20 ns. The technique and setup for the exposure of polymer to laser radiation have been comprehensively described in our previous reports [11,12]. The entire area of one face of every PMMA slab was scanned with a laser beam of 5 mm in diameter, assuring that every point on the surface was exposed to *ca.* 50 pulses. The polymer was irradiated at two different fluences: 80 mJ/cm² (in the region of the first threshold identifiable on the etch curve [11]), and 280 mJ/cm² (above the second break in the etch curve [7,8,11]).

Both exposed and unexposed PMMA samples were stored in clean sealed glass jars prior to XPS analysis.

X-Ray photoelectron spectroscopic analysis

XP spectra were obtained with an Escalab MkII (Vacuum Generators Ltd., UK) spectrometer using MgK α radiation. The parameters and procedure were described in detail elsewhere [20].

Two different take-off angles (from the surface normal) were used in XPS experiments. At an angle of 0° from the normal, 90% of the observed photoelectron signal originated in the top *ca.* 12 nm of material; at 80° , the same amount of signal originated in the first few monolayers only, to a depth of *ca.* 2 nm. Henceforth, these regions will be referred to as the "subsurface" and "surface", respectively.

Results and discussion

The C 1s X-ray photoelectron spectra of unexposed original PMMA is shown in Fig. 1 at take-off angles of 0° and 80° . (The O 1s spectra are unremarkable, therefore not shown.) The C 1s peak is a composite of three C 1s signals corresponding, respectively, to aliphatic polymer backbone carbon, carbon linked to either oxygen in the ester group, and carbonyl carbon. It should be noted that the surface material (80° take-off angle) displays a larger carbonyl peak at *ca.* 288.5 eV, generally attributable to surface oxidation and expected in polymers kept in air for some time.

Fig. 2 shows a comparison between C 1s photoelectron spectrum of original PMMA and spectra of two samples ablated at 80 mJ/cm^2 and 280 mJ/cm^2 , respectively, all recorded at a take-off angle of 0° (subsurface). Spectra of the same samples, recorded at a take-off angle of 80° , are shown in Fig. 3. The experimental values for O/C ratios, corrected for sensitivity factors and for inelastic mean free path (IMFP) of photoelectrons, are given in Table 1.

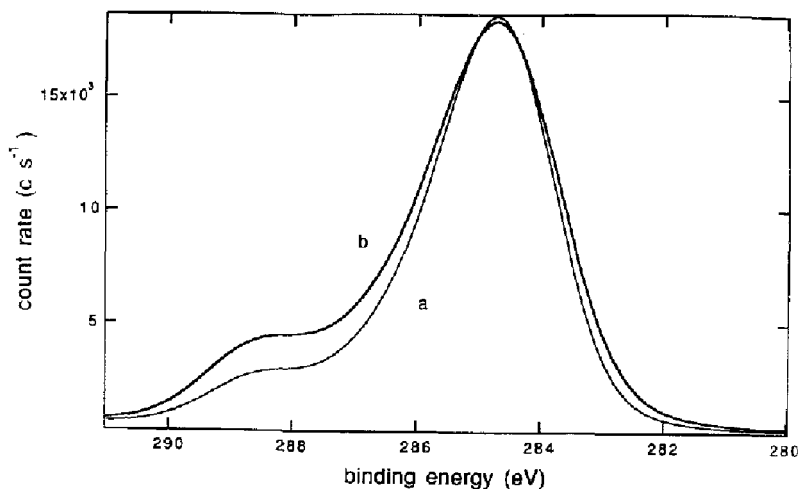


Fig. 1: X-Ray photoelectron C 1s spectra of non-irradiated PMMA, collected at take-off angles of 0° (a) and 80° (b), both normalized to the same intensity at *ca.* 284.6 eV.

A notable feature is the increase of O/C ratio with fluence in the subsurface, from 0.40 in the original polymer to 0.48 (at 80 mJ/cm^2) and 0.59 (at 280 mJ/cm^2) in the ablated polymer. This change, quite different from that found in PHEMA [20], cannot be ascribed to oxidation.

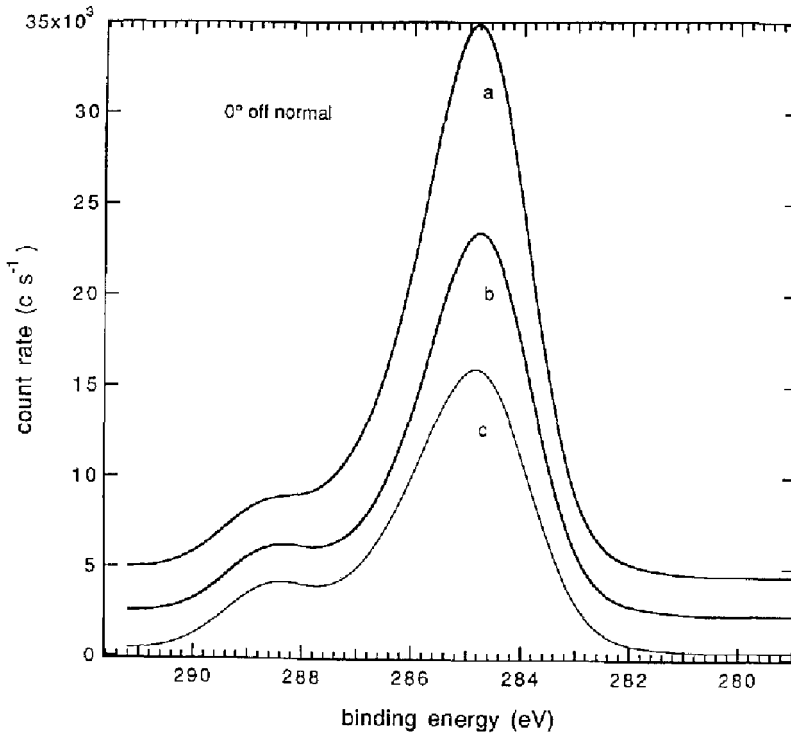


Fig. 2: X-Ray photoelectron C 1s spectra of PMMA before (a) and after (b,c) laser irradiation, at a take-off angle of 0°. Normalized at ca. 288.5 eV and displaced from each other by 2000 cps. Fluences, 80 mJ/cm² (b), and 280 mJ/cm² (c).

Previous studies [13,14,20] implied that ejecta from ablation prevented oxygen from diffusing to the surface of material. Braren *et al.* [21] showed that the process of ejecta release continues for at least 6 μ s (which is ca. 500 times the laser pulse duration), probably due to heat retention rather than ongoing bond scissions. It is unlikely that reactive species are formed with a life time sufficiently long to react with diffusing oxygen after the ejecta release has ceased. Another argument against oxidation in the subsurface is presented by the decrease of O/C ratio at the surface following ablation. In the original PMMA the surface clearly underwent some oxidation due to storage of samples in the atmosphere, as indicated by an O/C ratio of 0.48, compared to a theoretical value for PMMA of 0.40. After ablation, the O/C ratio decreased significantly (Table I). It is difficult to accept that, following the same treatment, the subsurface was enriched in oxygen while the region above was depleted. Therefore, the oxygen gain in the subsurface can only be attributed to a carbon loss. For instance, a scission of either of the two methyl groups in PMMA would lead to an increase in the O/C ratio up to 0.50. The larger carbonyl carbon peak in the C 1s spectrum of the ablated PMMA (Fig. 2) supports this hypothesis.

Table 1: XPS total O/C atomic ratios in laser-irradiated (193 nm) PMMA^a

Take-off angle (degrees)	Unexposed polymer (controls)	Polymer irradiated at 80 mJ/cm ²	Polymer irradiated at 280 mJ/cm ²
0 ^b	0.40	0.48	0.59
80 ^c	0.48	0.29	0.32

^aTheoretical O/C ratio is 0.40

^bSubsurface (*ca.* 12 nm)

^cSurface (*ca.* 2 nm)

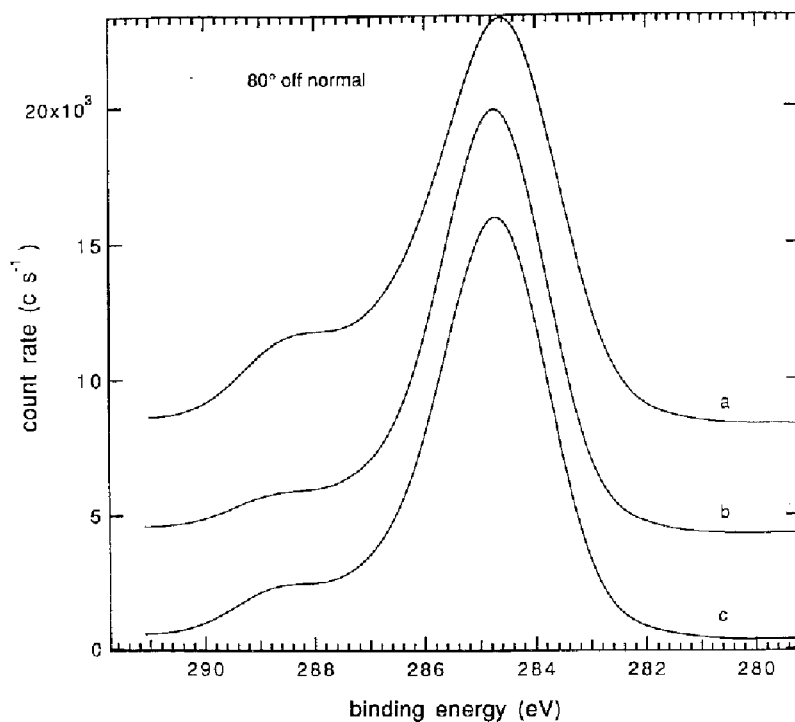


Fig. 3: X-Ray photoelectron C 1s spectra of PMMA before (a) and after (b,c) laser irradiation, at a take-off angle of 80°. Normalized at *ca.* 284.6 eV and displaced from each other by 4000 cps. Fluences, 80 mJ/cm² (b), and 280 mJ/cm² (c).

It has been also shown that the 193-nm photons, having energies larger than 6 eV, thus exceeding the bond dissociation energies of most covalent bonds in a polymer, are very effective in bond breaking with a high quantum yield. The photons at higher wavelengths have less energy and thermal processes are predominant in the ablation. When 193-nm radiation is involved, it is plausible that a direct photochemical bond scission precedes the ablation. (Of course, some thermal processes also become important especially at higher fluences.)

It is conceivable that C-C and C-O single bonds "resonately" absorb the 193-nm radiation and readily dissociate, since their bond energies are lower than the energy of the impinging photons. The scission of C-O bond is probably essential in this context to explain to some extent the different subsurface behaviour of PMMA as compared to PHEMA. When this bond is broken on either side of oxygen in PHEMA, oxygen-containing molecules are ejected, leading to an oxygen depletion in the remaining material. On the contrary, the leaving group (methyl) in PMMA does not contain oxygen, therefore the only possible depletion to occur is that of carbon. Nevertheless, a scission can also be imagined leading to the ejection of a methoxy group. Our findings support rather the generation of methyl groups, probably augmented by the cleavage of the second methyl group linked directly to the main polymer chain. The ejection of the whole ester group is unlikely, because this would actually result in a significant decrease of the O/C ratio, and also because of the obvious increase of the carbonyl peak (Fig. 2).

These arguments cannot explain, however, why at a fluence (280 mJ/cm²) higher than the presumed onset of massive depolymerization (ca. 230 mJ/cm² [7,8,11]), the depolymerization of PMMA does not become dominant over the scission processes; it happens in PHEMA at the same fluence [20], resulting in an O/C ratio identical to that in the unablated polymer. This question, yet to be answered, was obviously ignored by previous researchers who did not use different XPS sampling depths. It would seem that this point of inflection is not due to a switch to a depolymerization mechanism of ablation.

The second important feature of our present XPS analysis was revealed by *the decrease of O/C ratio at the surface*, i.e., within the first ca. 2 nm of polymer (Fig. 3, Table 1). The same phenomenon was noticed in PHEMA and explained by the preferential scission of 2-hydroxyethoxycarbonyl pendant group at the surface, presumably resulting in a great variety of oxygen-containing ejected species [20]. A similar explanation is probably valid for PMMA too. The methoxyl or methoxycarbonyl group may be removed and further decomposed, resulting in a depletion of oxygen. The decrease of the post-ablation carbonyl C 1s peaks in the XPS spectra (Fig. 3) supports such a scenario. It appears again, as in the subsurface region, that depolymerization is not the main contributor to the ablation mechanism at these radiation fluences. A possible explanation for the difference between the surface and subsurface results is the exposure of the polymer to nonphotochemical processes occurring during laser irradiation, such as thermal decomposition, reactions in shock wave, and ultrasound-induced reactions, as well as plasma formation and associated processes. Their extent during ablation is unknown, but they are probably highly dependent on the applied fluence and can influence the overall mechanism and the nature of ejected products. The possible migration of some reactive species from subsurface to surface, where they can react with other species, can also complicate the chemistry of ablation. All these factors suggest that either a prediction of O/C ratio or a conclusion on the mechanism of ablation based on measured chemical changes in the polymer surface would be unrealistic. After all, the depolymerization may take place with no restraint, but the constancy of the O/C ratio cannot be obtained experimentally because of many possible interfering processes.

Our results clearly contradict those previously reported for PMMA [13-15] which show unchanged post-ablation O/C atomic ratio. At closer examination of these reports, some discrepancies become obvious. For instance, in two papers [14,15] information was not given on

the take-off angles employed in the XPS analysis, so that the sampling depth remains unknown. (In fact, no details beyond the XPS instrument manufacturer's name were given in one report [14].) Some researchers found an O/C ratio of 0.32 in the original PMMA [15], significantly lower than the theoretical 0.40; it is hard to accept oxygen depletion in a polymer specimen stored in air, as proved both in our present study and in a previous report [13]. Whenever disclosed, the number of laser radiation pulses was lower than that used in our experiments. It can take a large number of irradiation pulses before any chemical changes beneath the ablated surface will reach a steady state condition, particularly for low fluences. We suggest that our results may be different from those previously reported [13-15] due in part to different experimental conditions used in our work, during both the laser exposure and XPS analysis. Inescapably, we also suggest that the post-ablation O/C ratio in PMMA, as measured by XPS analysis, is not actually identical to that found in the unablated polymer, thus casting some doubt upon the presumed dominant role of depolymerization during the ablation process.

Conclusions

Based on O/C atomic ratios measured by XPS analysis in PMMA ablated by excimer laser irradiation, it appears that depolymerization does not play a predominant role in the chemistry of ablation. At the surface, the polymer suffers a loss of oxygen due to the removal of pendent methoxycarbonyl groups. In the subsurface, the polymer gains oxygen-containing functions. Rather than a result of oxidation, this could be caused by carbon loss due to removal of methyl groups by C-C and C-O scissions.

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References

1. Srinivasan R, Mayne-Banton V (1982) *Appl Phys Lett* **41**: 576
2. Srinivasan R, Leigh W J (1982) *J Am Chem Soc* **104**: 6784
3. Srinivasan R (1984) Ultraviolet laser ablation of organic polymer films. In: Bauerle D (ed.) *Laser processing and diagnostics*. Springer, Berlin Heidelberg New York (Springer series in chemical physics, vol 39, pp 343-354)
4. Garrison B J, Srinivasan R (1984) *Appl Phys Lett* **44**: 849
5. Garrison B J, Srinivasan R (1985) *J Appl Phys* **57**: 2909
6. Srinivasan R (1986) *Science* **234**: 559
7. Srinivasan R, Braren B, Dreyfus R W, Hadel L, Seeger D E (1986) *J Opt Soc Am B* **3**: 785
8. Srinivasan R, Braren B, Seeger D E, Dreyfus R W (1986) *Macromolecules* **19**: 916
9. Srinivasan R (1983) *J Vac Sci Technol B* **1**: 923
10. Srinivasan R, Braren B (1984) *J Polym Sci Polym Chem Ed* **22**: 2601
11. van Saarloos P P, Constable I J (1990) *J Appl Phys* **68**: 377
12. Chirila T V, van Saarloos P P (1992) *J Appl Polym Sci* **44**: 1355

13. Lazare S, Hoh P D, Baker J M, Srinivasan R (1984) *J Am Chem Soc* **106**: 4288
14. Srinivasan R, Lazare S (1985) *Polymer* **26**: 1297
15. Burrell M C, Liu Y S, Cole H S (1986) *J Vac Sci Technol A* **4**: 2459
16. Lazare S, Srinivasan R (1986) *J Phys Chem* **90**: 2124
17. Novis Y, De Meulemeester R, Chtaib M, Pireaux J J, Caudano R (1989) *Br Polym J* **21**: 147
18. Chtaib M, Roberfroid E M, Novis Y, Pireaux J J, Caudano R, Lutgen P, Feyder G (1989) *J Vac Sci Technol A* **7**: 3233
19. Occhicchio E, Garbassi F, Malatesta V (1989) *J Mater Sci* **24**: 569
20. Vernon C F, Klauber C, van Saarloos P P, Chirila T V (1992) *Polym International* **27**: 243
21. Braren B, Casey K G, Kelly R (1991) *Nucl Instr Meth Phys Res B* **58**: 463

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