Molecular weight effects on the 248-nm photoablation of polystyrene spun films

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Photoablation of spun polystyrene films was studied at 248 nm. The etching occurs on a submicrosecond time-scale, is strongly intensity dependent and is preceded by an incubation period. The chemical and photochemical properties of the polymer are not affected by its molecular weight. However the molecular weight changes the incubation behaviour of the samples. This last result is analysed as a physical effect in terms of the volume changes brought about by the ablation process.

(Keywords: photoablation; incubation; free volume)

INTRODUCTION

Since the first reports appeared in 1982, u.v.-laser photoablation of polymers has stimulated much interest and many studies, mainly due to its numerous microlithographic[1,2] and medical applications[3,4]. Several models have been proposed but the mechanisms of polymer ablation are still essentially unknown. The ablation phenomenon can be 'schematically' described as follows: the u.v.-laser pulse is absorbed by the material and this results in an explosive photodecomposition of the irradiated surface; often, a certain number of laser pulses (i.e. incubation shots)[5] must be incident on the polymer sample before this explosive photodecomposition can take place; after this the laser pulses then steadily etch the polymer surface.

The difficulties encountered in the understanding of polymer ablation are twofold. First, one must recognize the various molecular events of light absorption, and consequently bond breaking. These aspects are best accounted for by the Lambert–Beer law, multiphoton absorption, and more generally, the photochemistry of the molecule that is being considered. In this case, the chemical composition of the material is of great importance. Secondly, one must understand how the excitation of the species and the formation of the photoproducts lead to the 'explosion' of the polymer surface. This solid-state aspect is certainly the more problematical of the two and could also be related to the physical properties of the organic solid. It is this special aspect of polymer ablation which is addressed in this experimental study.

To this effect, we start by giving a brief description of the events of light absorption and bond breaking in the solid state. This quite general section is intended to outline the specific aspects of polymer ablation when compared to low-intensity irradiation and dilute phase photoreactions. Subsequently, results are presented for a number of selected dye and polymer thin films. These results show that the physical properties of the materials are also important. Finally, the possible physical parameters of the ablation process are pinpointed for the 248-nm ablation of polystyrene.

SPECIFIC ASPECTS OF POLYMER ABLATION

The photon flux interacts with a number of absorbing species (e.g. atoms, ions, molecules, etc.). On absorption of a photon, the species is excited to an upper energy level. The efficiency of this transition and the lifetime of the excited state are characteristics of the material and the photon energy. In this way, the transmission of the light beam and the excitation of the material is described by rate equations coupling the population of the different states and the photon flux. The occurrence of a photoreaction is accounted for by introducing product states. In general, many states participate in the transitions and the system does not have an analytical solution. However, the higher excited states are generally harder to populate (due to a lower cross-section and shorter lifetime). This means that, for low intensity, the absorption of light only results in the depopulation of the ground state and therefore can be described by a single rate equation. This rate process can either be considered in space or in time: the Lambert–Beer law expresses the spatial dependence of this process:

$$\mathrm{d}I = -\sigma N I \,\mathrm{d}x \qquad (1)$$

so

$$I_t = I_0 \exp(-\sigma N x) \qquad (2)$$

where N is the ground state population, σ is the cross section for absorption and I is the laser intensity. In this case, the transmission does not depend on the intensity, but it decreases exponentially with the sample thickness. An absorption coefficient (α) can be unambiguously

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defined in this case. In fact this simple law has been extensively used to explain the ablation process. This is because, for most of the polymers studied initially, such as polyimide, poly(ethylene terephthalate), poly(tetrafluoroethylene), and poly(methyl methacrylate), a high absorption coefficient meant a low ablation fluence theshold and a small etch depth. However, this is not true for every polymer.

In the general case, which must be considered when one uses intense laser pulses, other energy levels are also populated. The transmission and the different population densities thus depend on the intensity. The Lambert–Beer law is therefore invalid. Unfortunately, the time and spatial dependences of the different population densities and the photon flux are unknown since only very few parameters (cross section and lifetime) can be measured experimentally (by using absorption and fluorescence spectroscopy).

Because ablation also occurs in the solid state, the photoreactions are diffusion controlled (cage reactions) and therefore multimolecular processes must also be considered (e.g. annihilation and collisional recombination). This can be accounted for in the rate equations[6] but at the same time it can seriously complicate them, and the concept of a rate process loses a lot of its merit and utility when these multimolecular events are considered.

The complexity and the specificity of polymer ablation can be described as follows:

- due to the presence of multiphoton events and many different reaction pathways, it is very difficult to give a complete description of the absorption and bond-breaking events on the molecular level.
- because polymer ablation occurs in the solid state, molecular interaction between excited species and photoproducts do occur, and these are responsible for the explosive nature of the process.

INITIAL RESULTS

Mahan *et al.*[7] reported in 1988 that the ablation properties of polymers were independent of their absorption coefficients; this suggestion has also been made by others[8]. In *Figure 1* the ablation fluence thresholds (F_{th}) of a number of different materials are compared to their absorption coefficients (some of these values were measured by the present authors in earlier work). It can be seen that there is no apparent correlation between α and F_{th}.

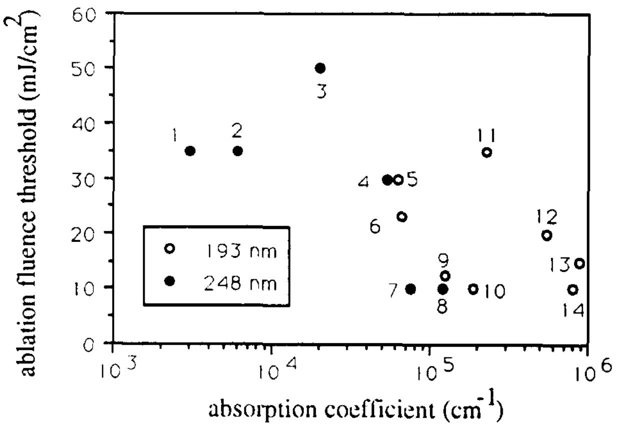

Figure 1 Ablation fluence threshold values of various polymers and their corresponding absorption coefficients: (1) polystyrene (this work); (2) bisphenol A polycarbonate (this work); (3) P3BCMU (ref. 9); (4) LB(dye+acetic acid) (ref. 10); (5) P3BCMU (this work); (6) LB(acetic acid) (ref. 10); (7) LB(dye) (ref. 10); (8) LB(polycondensate) (ref. 10); (9) LB(dye+acrylic acid (ref. 10); (10) LB(dye) (ref. 10); (11) polydiacetylene2d (ref. 9); (12) bisphenol A polycarbonate (ref. 9); (13) LB(polycondensate) (ref. 10); (14) polystyrene (this work)

In a previous paper describing the ablation of thin Langmuir–Blodgett (LB) films[10], Magan *et al.* observed that the etch rate changes with the film thickness and the proximity of the substrate. This suggests that molecular interactions play a role in the ablation process. In another paper[11], Lemoine and Blau also observed that polystyrene films doped with very small quantitites of Rhodamine 6G had different ablation properties to those of the pure polymer films, although the u.v. absorption characteristics of the doped and pure forms were similar. This result was interpreted as a physical effect, since the only change introduced by the dye is a change of free volume.

For these various reasons, the authors believe that a number of physical properties influence the ablation process. This was investigated by studying the effects of molecular weight on the ablation properties of polystyrene thin films. First, we will show that the molecular weight does not change the chemical and photochemical properties of the polymer, although it affects its physical properties. Secondly, the 248-nm ablation of polystyrene is studied. Some molecular weight effects are observed. These results are analysed in terms of the volume changes brought about by the ablation process.

CHARACTERIZATION OF THE POLYSTYRENE SAMPLES

Thin films were spun from styrene or cyclohexanone solution ($\sim 100\,\mathrm{g\,l^{-1}}$, $1500\,\mathrm{rev\,min^{-1}}$) onto glass or quartz substrates by using a commercial spin coater (Fell). The polystyrenes used in this study were selected from a range of monodisperse polymers (Aldrich Chemical Company), with molecular weights ranging from 2727–435 000 g mol^{-1} (measured by gel permeation chromatography, g.p.c.) (see later for details). The samples were characterized by glass transition temperature (T_g) and u.v. absorption coefficient (α) measurements.

Determination of the glass transition temperature

The T_gs of the samples were measured by differential scanning calorimetry (d.s.c.) (Perkin-Elmer DSC4, calibrated by using pure indium metal). A typical plot is shown in *Figure 2*. The heating rate was 10°C min^{-1} and the arrow indicates the direction of the endothermic reaction. The experiment was repeated for samples with different molecular weights, and the molecular-weight dependence of the T_g is shown in *Figure 3*.

Dilatometric and calorimetric measurements often show that the specific volume and T_g of polystyrene depend linearly on the inverse of the molecular weight:

$$v = v_0 + \frac{a}{M} \tag{3}$$

and

$$T_g = T_g^{\infty} - \frac{b}{M} \tag{4}$$

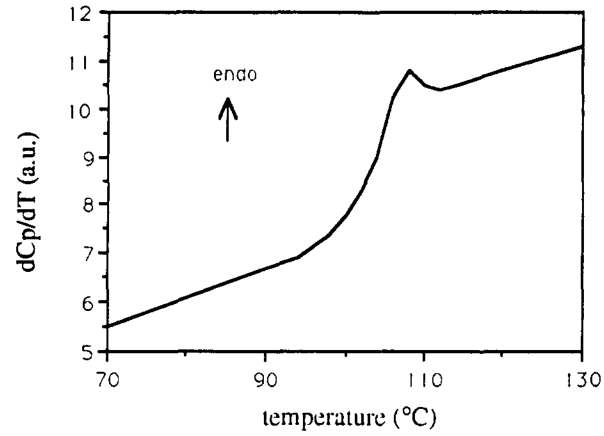

Figure 2 D.s.c. trace of a polystyrene powder with $M = 96000$ g mol^{-1}, using a heating rate of 10°C min^{-1}

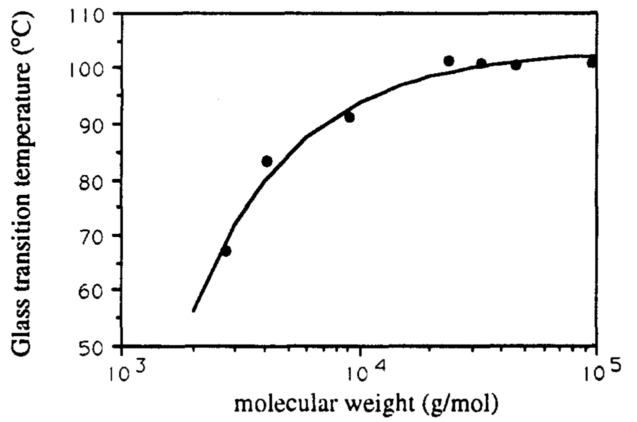

Figure 3 A typical curve of the molecular weight dependence of T_g for a polystyrene powder

where *a* and *b* are constants which are independent of the molecular weight. These equations can be justified using the concept of free volume[12]. In this analysis, it is assumed that the chain ends contribute to more free volume than the monomeric units present in the centre of the chain, and also that the molecular-weight dependence of the free volume is associated solely with the chain-end contributions. This last assumption has been challenged by François *et al.*[13], who showed that in a solution of a high-molecular-weight polymer ($M > 44000$ g mol^{-1}), the molecular weight also influences the partial specific volume associated with the non-end repeating units (i.e. packing of the segments). However, for solid samples the molecular-weight dependence of T_g is satisfactorily explained using equation (4) above[14,15]. If ρ is the density of the sample and M is its number-average molecular weight, then the number of chain ends per cm^3 is:

$$N_{ce} = \frac{2\rho N_a}{M} \tag{5}$$

where N_a is the Avogadro constant. If one chain contributes θ cm^3 to the free volume, then the free volume associated with the chain end (in cm^3) is:

$$V_{ce} = \frac{2\theta\rho N_a}{M} \tag{6}$$

The free volume associated with the chain ends corresponds to the increase of free volume when the molecular weight is varied from M to an infinite value. The expansion coefficient of the free volume is $\alpha_f = \alpha_r - \alpha_g$, where α_r and α_g are the expansion coefficients of the rubbery and glassy polymer, respectively. These two quantities are usually determined from thermal expansion measurements ($\alpha_f = 3.65 \times 10^{-4}$ °C^{-1})[16]. The equations relating these quantities are:

$$V_{ce} = \alpha_f[T_g(\infty) - T_g(M)] = (2\theta\rho N_a)/M \tag{7}$$

and therefore:

$$T_g(M) = T_g(\infty) - (2\theta\rho N_a)/(M\alpha_f) \tag{8}$$

Fitting the data points to equation (8) gives $\theta = 26$ Å^3, with this value agreeing with that measured by dilatometric methods (i.e. $\theta = 28$ Å^3)[17]. The values of the corresponding fractional free volume associated with the chain ends are $f_{ce} = 1$ and 0.03%, for $M = 3000$ and 100000 g mol^{-1}, respectively.

Since the T_g of a spun film can be different from that of a powder sample, an optical method was used to determine the T_g of thin films. As for all of the physical quantities which are related to density, both the refractive index increment (dn/dT) and the linear expansion coefficient (l^{-1})(dl/dT) of amorphous polymers changes at T_g; (dn/dT) is negative and $l^{-1}(dl/dT)$ is positive. Depending on how the light reflected from the back surface interferes with the light reflected from the front surface, the reflectivity of the film will change abruptly at T_g. In this work a polymer film spun on a glass substrate was fixed onto a small ceramic heater with silver paint; temperature was measured by a copper–Constantan thermocouple contacted to the front surface of the film, also with silver paint. The temperature control was only ±5°C. The temperature dependence of the He–Ne laser reflectivity (633 nm) of the polystyrene film is shown in *Figure 4*. In this case the reflectivity change at T_g was measurable and is shown in the figure. The line represents the calculated reflectivity with the following parameters[18]:

$$dn/dT_{T > T_g} = -3.5 \times 10^{-4}\ °C^{-1};$$
$$(1/l)dl/dT_{T > T_g} = 5.5 \times 10^{-4}\ °C^{-1}$$

and

$$dn/dT_{T < T_g} = -1.4 \times 10^{-4}\ °C^{-1};$$
$$(1/l)(dl/dT_{T < T_g} = 7 \times 10^{-5}\ °C^{-1}$$

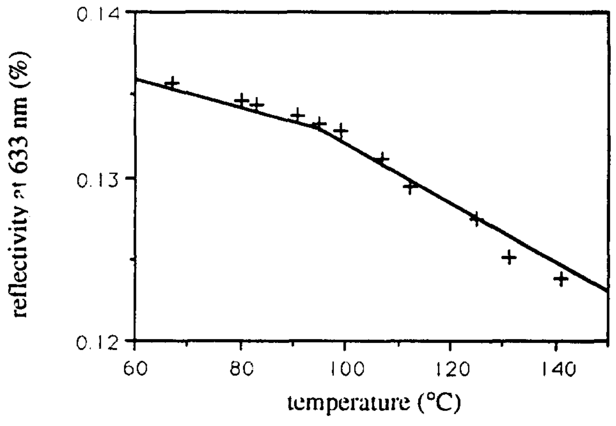

Figure 4 Temperature dependence of the 633-nm reflectivity of a polystyrene film ($M = 9100$ g mol^{-1}), using an incidence angle of 45° and a film thickness of 560 nm

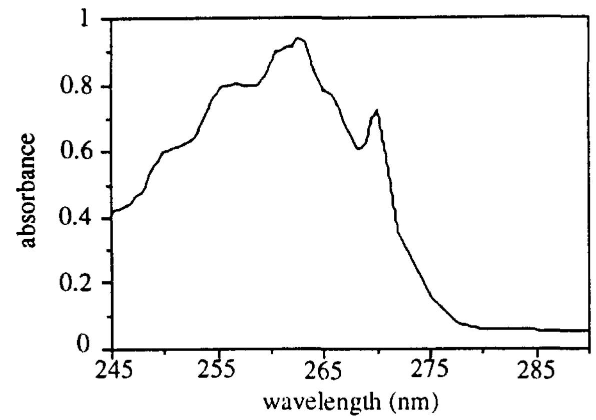

Figure 5 U.v. absorption spectrum of a polystyrene solution in 1,2-dichloroethylene (1 mm cell, 2.5 g l^{-1})

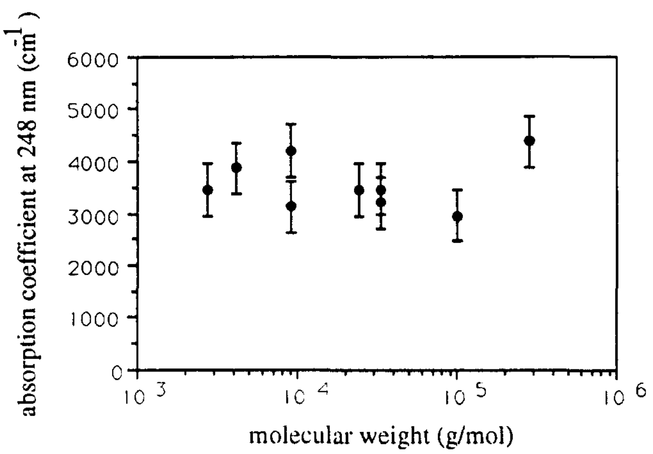

Figure 6 Molecular weight dependence of the 248-nm absorption coefficient of the polystyrene film

The film thickness at room temperature was 560 nm, measured from the visible interference spectrum. The value for T_g determined by this method agrees well with that determined from d.s.c. measurements (i.e. ~95°C).

U.v. absorption of polystyrene films

The u.v. absorption spectrum of a polystyrene solution, measured by a u.v.-visible spectrophotometer, is shown in *Figure 5*, and corresponds to the forbidden π–π^* transition of the phenyl ring (singlet to singlet transition)[19,20]. Absorptions from any charge-transfer oxygens (i.e. a tail at ~280–300 nm)[21] were not detected. More concentrated solutions (i.e. 100 g l^{-1}) and even thin solid films had similar spectral features, therefore showing no measurable tendency to aggregation. *Figure 6* shows that the u.v. absorption is essentially molecular-weight independent, and also indicates that there is no direct interaction between the phenyl rings or residual double bonds in the backbone, as has also been previously observed by others[20].

However, the absorption of a u.v. photon only constitutes the first step of the photoreaction. The photophysical (i.e. fluorescence, internal conversion, intersystem crossing, phosphorescence and energy transfer) and photochemical (reaction) processes are also determining steps in the bond-breaking mechanism. Therefore, one must examine how the molecular weight of the polymer can affect the photoreaction occurring in the solid sample. As outlined above the photoreactions occurring in organic solids are diffusion controlled. A chemical bond breaks irreversibly if the two radicals diffuse apart from each other by a distance ρ (the diameter of the recombination sphere) during their effective lifetimes. 'Small' chemical groups move by a simple 'Fick's law-type' diffusion, but polymeric radicals move by a process that was first described by De Gennes, and is called reptation[22]. This motion is much slower, so that a bond present in a pendant group is easier to break than the same bond which is present in a polymer backbone. Theoretical studies of intramolecular[23] and intermolecular[24] diffusion processes in condensed polymer melts showed that for a short reaction time ($t < \mu$s–ms), the molecular displacements are smaller than the distance between two entanglement points, i.e. the reaction is not affected by the reptational diffusion. Therefore, fast diffusion-controlled photoreactions in a 'high-value' polymer ($N > N_e$, where N_e is the number of monomers per entanglement point) should be nearly molecular-weight independent. However, these processes are still diffusion controlled and very much less efficient than in low-molecular-weight compounds. As has been observed by many authors, polymer ablation occurs over a submicrosecond time-scale. This will also be demonstrated below for the system studied here. Therefore, the yield for bond breaking should also be nearly molecular-weight independent.

Attempts were made to measure the u.v. absorption at higher intensities. These measurements were performed for a single laser shot to avoid etching of the polymer film, using a set-up similar to that used by Pettit and Sauerbrey[25]. Two 45°, u.v. dielectric mirrors (centred at 248 nm) were used as attenuators, and depending on the position of these mirrors (either placed before or after the sample) the intensity of the radiation on the sample could be varied from kW cm^{-2} to MW cm^{-2}. In this arrangement, the silicon photodiode (BPX65) always delivers a signal within its dynamic range and therefore optical saturation of this sensitive detector is avoided. Because of the micrometer thicknesses of the films, their high transmissions (60–90%) and good optical quality, the interference losses are comparable to the absorption losses. Since the calculation method that is used to extract the absorption coefficient of the film from this type of transmission measurement does not take into account any scattering losses, α was determined with relatively large errors, particularly for samples of small thickness. *Table 1* summarizes the values obtained for α at three different u.v. intensities, where it can be seen that the absorption coefficients of the polymer do not show any significant change.

Table 1 Values obtained for the absorption coefficient of polystyrene films measured at different u.v. intensities

Thickness (nm)	$\Delta\alpha/\alpha$ (%)	α_{248} (cm^{-1})		
		< 10 mW cm^{-2}	150 W cm^{-2}	6.5 MW cm^{-2}
2052	10	3400	3100	2800
1302	15	3300	3300	2800
948	20	3900	2800	3000
843	20	3500	2500	3100
751	25	3500	2500	3000
674	30	3900	2700	3000

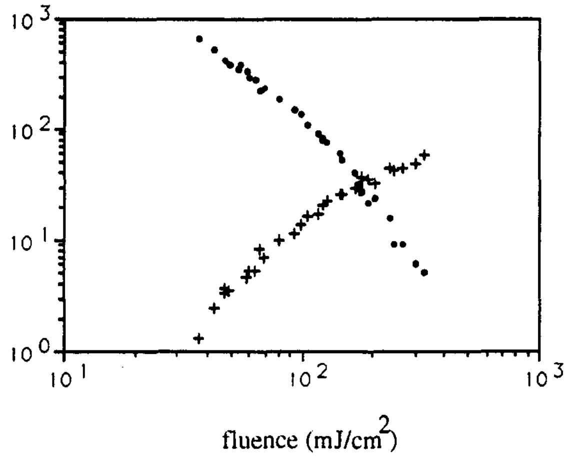

Figure 7 Etch and incubation curves of a polystyrene film at 248 nm: +, etch rate (nm per pulse); ●, number of incubation shots

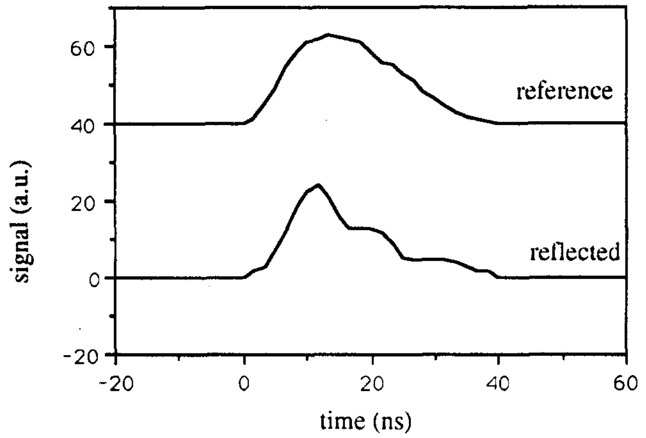

Figure 8 Transients of u.v. pulses incident on (top curve) and reflected from (bottom curve) a totally incubated polystyrene film, using a fluence of 300 mJ cm^{-2}

ABLATION RESULTS

As an example of the experimentally obtained data, the etch and incubation curves at 248 nm of a sample of high-molecular-weight polystyrene ($\bar{M}_n = 100000$ g mol^{-1}) are shown in *Figure 7*. The nonlinear trend of both sets of data points is obvious. The transformation of the surface during the incubation period is irreversible, and also independent of laser repetition rate (from 0.01 to 10 Hz). Even films left overnight showed no changes in their degree of 'incubation'.

Figure 8 shows typical u.v. transient changes in reflectivity during ablation. In this case, the fragments coming off the polymer surface attentuate (absorption plus scattering) the end of the laser pulse. This result shows that the 248-nm ablation of polystyrene is a fast process that starts before the end of the 20-ns laser pulse. Other workers have also studied the truncation on the reflection of u.v. pulses ablating polystyrene samples[26]. Although they do not take into account the effects of incubation (multipulse ablation), they also find that truncation occurs at fluences above the ablation fluence threshold.

The correlation that is always observed between incubation and etching can be better visualized from the data presented in *Figure 9*. This plot is an attempt to show a 'real quantum yield' for the ablation process. Since N_{sba} incubation pulses participated in the etching of the layer d (where d=etch rate), a quantum yield estimation must take into account the effect of these incubating pulses. Therefore, the quantity determined as a global quantum yield Φ_{gl} is the number of monomers generated per total number of photons incident on the polymer. This is expressed as:

$$\Phi_{gl} = \frac{10^5 dhc\rho N_a}{mN_{sba}F\lambda} \tag{9}$$

where d is the etch rate (nm per pulse), h is the Planck constant (SI units), c is the speed of light (m s^{-1}), ρ is the density of the polymer, N_a is the Avogadro constant (SI units), m is the molar mass of the monomer (g mol^{-1}), F is the laser fluence (mJ cm^{-2}), and λ is the laser wavelength (nm). In this parameter the combined effects of incubation and etching are brought together, and the definite power law ($\Phi_{gl} \sim I^3$) observed in *Figure 9* indicates that incubation and etching are both part of the same phenomenon, namely ablation. In other words, the incubation process is not a low-intensity side reaction which is concurrent with the etching process.

The molecular weight effects on the etch rate were weak and difficult to measure. On the other hand, the dependence of the molecular weight on the number of incubation shots has been determined and is shown in *Figure 10* for different laser fluences. It can be seen that as the molecular weight of the polystyrene film increases, the number of incubation shots decreases.

DISCUSSION

The results described in the previous sections can be summarized as follows. The u.v. transmission of polystyrene films irradiated by one laser pulse is independent of intensity. The quantities measured to describe the ablation efficiency (etch rate and incubation), however, have a superlinear dependence on the laser fluence. The etch rate is always much smaller than the absorption depth ($d < 0.1$ μm and $1/\alpha = 3$ μm). If the degradation was to be confined to a depth comparable to the etch rate, this bond-breaking process would be extremely nonlinear. An obvious question arises from this result, i.e. is the bond breaking also confined to the surface?

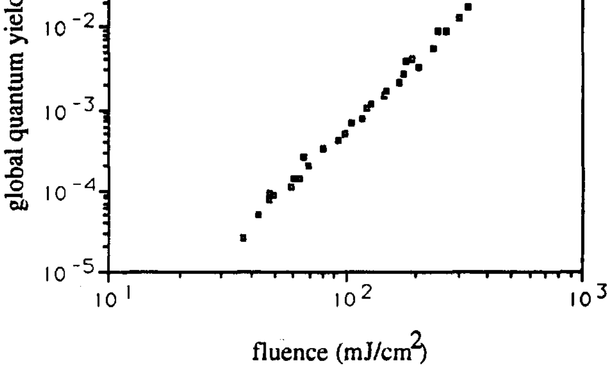

Figure 9 Global quantum yield curve for the ablation of a polystyrene film at 248 nm

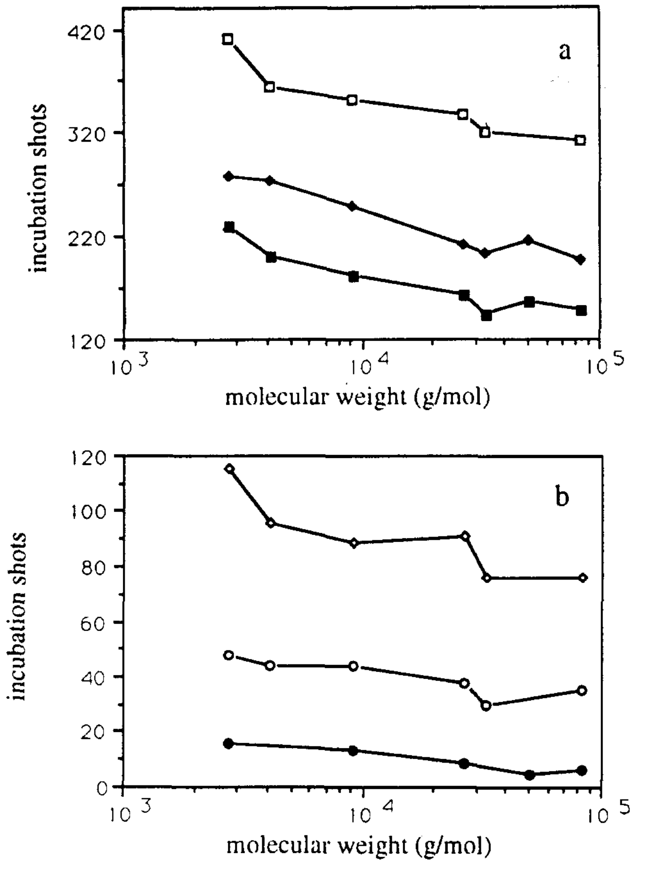

Figure 10 Molecular weight dependence of the number of incubation shots for the 248-nm ablation of polystyrene films shown for different laser fluences; the lines between the data points have been added as a guide to the eye. a, □, 48 mJ cm^{-2}; ◆, 71 mJ cm^{-2}; ■, 80 mJ cm^{-2}; b, ◇, 97 mJ cm^{-2}; ○, 132 mJ cm^{-2}; ●, 217 mJ cm^{-2}

If one were to describe the ablation process by using rate equations, this question could be answered in the following way. The absorption of a u.v. photon is apparently independent of intensity but the population of some product states depends nonlinearly on the intensities. In fact, this can occur when the absorption from the excited state matches the absorption from the ground state ($\sigma_{gs}=\sigma_{ex}$). It must also be noted that multipulse irradiation may cause some change in the u.v. transmission of the films if chromophoric changes were to take place over successive laser pulses.

Experimentally, the depth of the ablative degradation was probed by determining the molecular weight distribution of material recovered from untreated and laser-treated PS films, by using g.p.c. Films of polystyrene of different molecular weights were spun (70 g l^{-1}, 1600 rev min^{-1}) onto 2×2 cm^2 glass substrates; the resulting film thicknesses varied from 0.5 to 1 μm. The films were recovered in a small volume ($\sim$2 ml) of THF with the concentrations of the solutions thus obtained varying from 0.1 to 0.2 g l^{-1}. In the case studied here, two g.p.c. columns were used in series, giving a range of molecular weights which varied from 4000 to 450 000 g mol^{-1}.

A first observation to be made concerning the laser treatment is that even for these very low concentrations not all of the treated PS film was recoverable as a polymer solution. When subjected to ultrasonics, these 'unrecoverable' parts of the films lifted off the substrate and appeared as a suspension in the solution. These yellow suspensions could be retained by 0.45 μm filter paper.

The laser treatment was performed at a fluence of 100 mJ cm^{-2} using a hundred laser shots so that all of the polymer surface was fully incubated. The molecular weight distributions thus obtained are shown in *Figure 11*, where it can be clearly seen that no significant chain scission is observed. However, additional high-molecular-weight compounds always appear and seem to peak at around 100 000 g mol^{-1}. Incidentally, it should be noted that the sample with an initial molecular weight of 84 000 g mol^{-1} only broadens its distribution after u.v. irradiation.

These results, plus the observation of the yellow unrecoverable parts of the irradiated film, show that an appreciable crosslinking of the bulk of the polymer film occurs on u.v. irradiation. In fact, this crosslinking is certainly more important than is indicated by the g.p.c. traces since the solvent used in this case is unable to recover the very high-molecular-weight species. The low-intensity photochemistry of polystyrene has been studied by various authors[21,27–31]. The u.v. photons are absorbed in the phenyl ring and correspond to the transition from the ground state to the first excited singlet state (π–π* transition). It is generally found, owing to the great stability of the ring and the efficiency of the energy transfer process to adjacent bonds, that this polymer is photochemically very stable. Most of the excited species deactivate by internal conversion or excimer fluorescence. Nevertheless, some photoreactions occur (such as chain scission, crosslinking, substituent elimination, etc.), but they have a very low yield (10^{-4} mol per Einstein) and rarely lead to a direct breaking of the phenyl ring[21,27]. In the presence of oxygen, photo-oxidation may also occur, which often results in the formation of polyene structures in the polystyrene backbone[21,31], causing yellowing of the sample. This could explain the yellow colour of these crosslinked species. Nevertheless, this bulk crosslinking of the film could not be the phenomenon that is responsible for the ablation of the surface layer since, in all of the cases studied, mass spectrometry of the ablation products shows that the ablation is a decomposition reaction leading to products of a lower molecular weight than the pristine polymer.

At the very high photon flux employed in the ablation experiment (6×10^{24} phot cm^{-2} s^{-1} for ablation and 10^{15} phot cm^{-2} s^{-1} for low pressure Hg-lamp irradiation) the photochemistry of polystyrene could derive from highly excited states (multiphoton bond breaking). This could lead to ring opening and also to chain scission, and these reactions would in turn effectively lead to decomposition of the polymer surface. However, these reactions are not observed to occur in the bulk. Therefore, the ablative degradations must be confined to layers smaller than the film thickness. At this present time the reason for this confinement is not clear. The degradation could be highly intensity dependent, but could also be due to some mechanical effect which confines the bond-breaking process to the actual surface of the sample.

Examining now the molecular weight dependence of the incubation shots, one can see that the low-molecular-weight samples are harder to incubate than the high-molecular-weight species. It was also shown that the spectroscopic and photochemical properties of the polystyrenes are independent of the molecular weight.

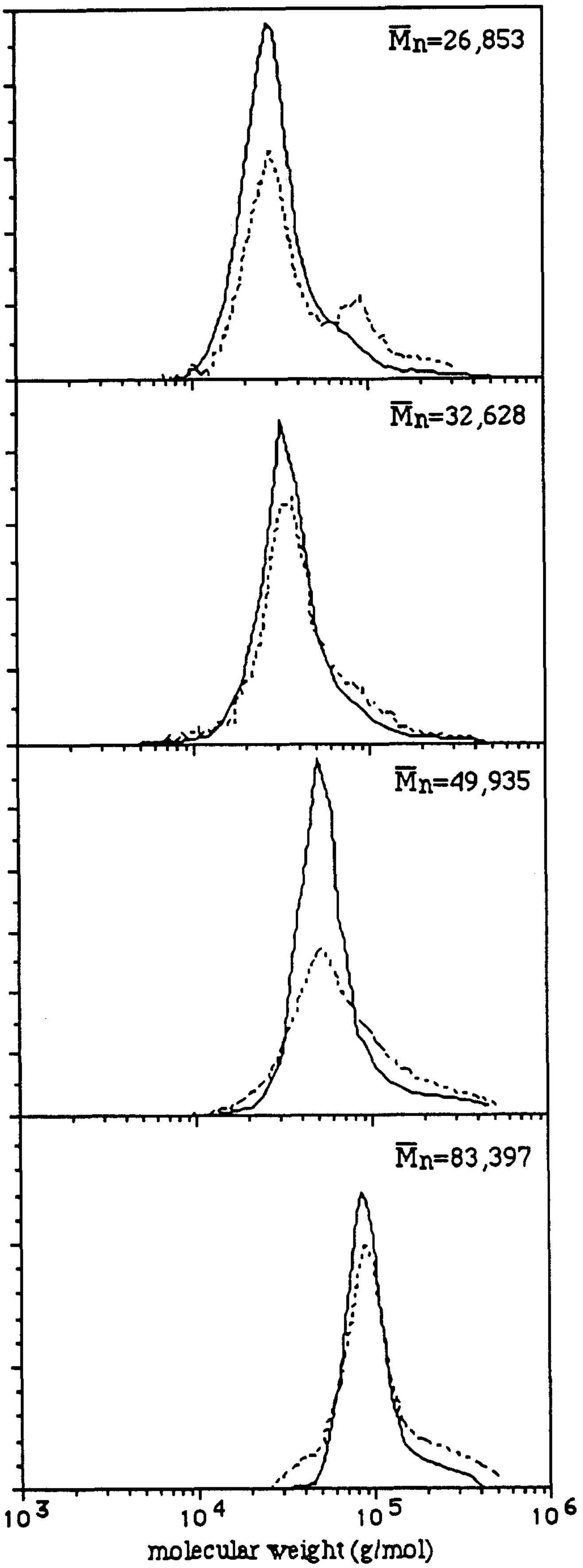

Figure 11 Molecular weight distributions of four polystyrenes recovered from spun film samples, as determined by g.p.c. The number-average molecular weights (M_ns) of the untreated sample are shown by a solid line, while values for the treated samples are shown as a dotted line; the latter were irradiated with one hundred Kr-F excimer laser pulses at 100 mJ cm^{-2}

Table 2 Diffusion of simple gases into glassy polystyrene at room temperature[33]

Gas	Diffusivity ($\times 10^8$) (cm^2 s^{-1})	Diffusion length for 1 s (μm)
Oxygen	11	4.7
Carbon dioxide	5.8	3.4
Water vapour	3.5	2.6
Methanol	0.67	1.2
Ethanol	0.028	0.24

Therefore, it is necessary to try to understand how the physical properties of the polymer affect the ablation of the irradiated film.

It has often been suggested that the explosive photodecomposition originates from the accumulation of small gaseous products. Certainly, for a polymer such as polyimide which shows single-pulse ablation and entirely decomposes into small gaseous products[32], this interpretation is justified. However, the case which is being considered here is different.

First, it is not at all obvious that the fragments are predominantly gaseous products. In fact, observation of the crosslinks shows that this is not the case. Secondly, at room temperature gases diffuse quite well into glassy polymers and a buildup of pressure in the polymer matrix will rapidly dissipate. *Table 2* shows the diffusion length of a few simple gases in glassy polystyrene. It can be seen that any gaseous pressure accumulating in a micron-thick film would disappear after only a few seconds. However, the number of incubation shots was found to be independent of the laser repetition rate (0.05–10 Hz). Even films that had been left overnight showed no changes in their degree of 'incubation'. Thus the incubation is an irreversible phenomenon and could not be caused by the accumulation of gaseous pressure within the layer. The importance of gas-product diffusion is rarely noted in ablation studies. However, Weir and Milkie[29], in their studies of the photo-oxidation of substituted PS, showed that the rate of gas product formation is significantly controlled by the rate at which these gas products diffuse out of the polymeric solid. This dependence was established by mass spectrometry long before polymer ablation was demonstrated.

On the other hand, the explosive nature of the process could be explained in another way. Photoreactions always correspond to a change in reaction coordinate. In some cases this change is negative and the products occupy less volume than the fragments (e.g. the ring closure of spiropyran[34]). However, for most bond-breaking reactions, this change is positive and the direct effect of the reaction is an increase of volume. Often the fragments are radicals and they can also abstract hydrogen from a neighbouring atom or another photoproduct, which can cause a further increase in the product volume.

For an amorphous polymer irradiated by non-polarized u.v. light, there is no preferential alignment or orientation of the fragments and the global physical effect of these molecular 'product swells' is the buildup of an effective isotropic strain in the polymer surface. Stresses will then develop and eventually cause the explosion of the surface. In this description, the ablation process is clearly viewed as a volume explosion; this is a mechanism whereby the application of a strain (volume increase) causes the buildup of a stress (pressure). Since these product swells occur on the nanosecond time-scale and are irreversible, this corresponds to the rheological behaviour known as stress relaxation, i.e. the temporal response of a stress when a constant strain is applied. On the other hand, the alternative interpretation concerning the buildup of a gaseous pressure in the polymer is analogous to the rheological behaviour known as creep relaxation i.e. the temporal response of a strain when a constant stress is applied. Already, a simple quantitative figure can be cited in favour of this description. In glassy polymers, the free volume accounts for approximately 10% of the total volume[35]. If the chain-scission reaction is extensive (100% monomer conversion), just a 10% increase in product volume is almost nearly enough to completely fill up the free volume present in the polymer sample.

This analysis qualitatively explains the molecular weight dependence of N_{sba}. If the initial molecular weight of a polymer sample is high then the available free volume is relatively small. Consequently, less laser shots are needed to incubate a surface of high molecular weight than one of low molecular weight. As shown above, the chain-end-associated free volume only accounts for, at the most, 3% of the total polymer volume (for a total free volume of 10%). Therefore, these molecular weight effects should be small, and, this is indeed what is observed.

A quantitative description of the different volume changes is more complicated and still remains to be properly developed. This is because as the chain-scission reaction proceeds, the molecular weight of the polymer decreases and therefore the chain-end-associated free volume increases, which effectively plasticizes the polymer glass. These volume recoveries occur by segmental motion[36]; as such, they are independent of sample size[37] and have a time-relaxation spectrum that depends strongly on the molecular weight of the sample ($\tau \propto M^3$). Experimentally, each polymer is characterized by a molecular weight, M_e, below which this relaxation time changes dramatically (the entanglement effects are small). For polystyrene, $M_e = 28\,000\ \mathrm{g\ mol^{-1}}$ (ref. 38). This effect renders an analytical formulation for the chain-end-associated free volume rather complicated. At the laser repetition rate that is usually used in the ablation experiments, the time that elapses between two successive laser pulses varies from 0.1 to 1 s, but these free volume redistributions can occur over a very large time-scale (10 ns to 10^3 s)[39]. Thus the plasticizing effect should have less of an effect on the first laser pulse (when the molecular weight of the polymer is high) than subsequent ones. For the same reason, a low-molecular-weight polymer will plasticize more than a high-molecular-weight material.

Qualitatively, it can be seen how the successive laser pulses decrease the free volume (the product swell) and how this effect competes with the plasticization of the polymer sample. It is not yet clear how large the decrease of free volume (strain) must be to promote the expulsion of the fragments. For most polystyrenes, the stress at break corresponds to a pressure of several hundred atmospheres and a strain of only a few percent (strain < 10%)[40]. Photoacoustic measurements show that the pressure generated in the polymer surface during ablation could reach several hundred atmospheres[41], and thus expulsion of the fragments could very well occur before the free volume (10%) is totally suppressed. When the free volume reaches a critical value, the stresses developed in the polymer surface cause the expulsion of fragments. Since this expulsion occurs on a nanosecond time-scale, the stress generated by this last pulse must also develop within a nanosecond time-scale. In fact, the temporal response of a stress to a strain is defined by the sonic velocity in the polymer ($v = 2100\ \mathrm{m\ s^{-1}}$ in the case of PS), and therefore the stress could travel over 42 μm during the 20 ns laser pulse, a distance which is far greater than the degradation depth (a few hundred nanometres, at the maximum).

CONCLUSIONS

In these investigations the 248 nm ablation properties of spun polystyrene films have been studied. The molecular weight effects that are observed are interpreted in terms of a volume relaxation. The polymer bonds break, the fragments occupy more volume than the reactant and this strain promotes the expulsion of the fragments. This mechanical explanation of the ablation process contrasts with current views, which emphasize the production of a gaseous pressure to explain the incubation process. Nevertheless, it conveniently accounts for the multipulse incubation observed in the samples and it is also consistent with the volumetric and mechanical properties of the polymers. Unfortunately, it was not possible to compare the data with a quantitative model based on these ideas. The dynamics of these volume recoveries are very complex in polymeric solids, and even for a simple system like polystyrene, very little is known about the different photoproducts formed during the ablation process.

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