Effect of molecular weight on the physicochemical modifications induced in the UV laser ablation of doped polymers

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Abstract. This work investigates the effect of polymer molecular weight $M_W$ on the UV ablation of iodo-naphthalene- and iodo-phenanthrene-doped poly(methyl methacrylate) PMMA, and polystyrene PS films following irradiation at 248 nm. For irradiation at weakly absorbed wavelengths, the ablation threshold increases with increasing $M_W$. However, at strongly absorbed wavelengths, the difference in the ablation thresholds is much smaller, or minimal. In parallel, bubble formation due to accumulation of gas produced by polymer and dopant decomposition differs depending on $M_W$. For highly absorbing PS, the differences of behaviour show a less dramatic dependence on $M_W$. These results are explained within the framework of the bulk photothermal model, according to which ejection requires that a critical number of bonds is broken. In all, they are of direct importance for the optimisation of laser processing schemes and applications and provide the first indication of explosive boiling in UV ablation of polymers.

1. Introduction

The molecular weight ($M_W$) of a polymer is an important parameter as it determines many of its physical characteristics such as transition temperatures and mechanical properties. In several applications, especially on real systems such as those encountered in medical and art laser applications, the $M_W$ of the treated polymeric-like substrates may vary a lot from case to case. However, only a few studies are available on the influence of $M_W$ on the laser ablation of polymers [1, 2 and references therein]. Lemoine et al. studied the effect of $M_W$ on the 248 nm photoablation of PS [3], and Lippert et al. reported an influence of the degree of polymerization [4] in their study on the ablation of PMMA at 308 nm. Masuhara et al. [5] have examined the temporal dynamics of the morphological changes of PS of different $M_W$ via time-resolved interferometry and have shown that the time-scale of expansion and contraction of films upon laser irradiation differs for different $M_W$ systems correlating this behaviour with their different glass-rubber transition temperature ($T_g$).

In this work we present a study on the effect of $M_W$ (in the range of 2-1000 kDa) on UV laser ablation (248 nm) of PMMA and PS, doped with the iodo-derivatives of the aromatics naphthalene (NapI) and phenanthrene (PhenI). To this purpose we have examined the physicochemical modifications induced by laser irradiation of the films of the doped polymers. Results obtained show a strong dependence of the ablation threshold, etching efficiencies and of bubble formation on $M_W$. However, the extent of this dependence is clearly mediated by the polymer optical absorption coefficient at the ablation wavelength. The implications of these
results for the mechanisms of polymer UV laser ablation are discussed. Furthermore, this sensitive dependence of processes on M_W occurring in a low absorbing polymer is of direct importance for the optimisation of laser processing schemes and applications (e.g. tissue processing, laser deposition, laser restoration, etc).

2. Experimental
Highly purified PMMA average M_W 2.5 kDa, 120 kDa and 996 kDa and PS 15.1 and 51.5 kDa, 280 kDa and 532 kDa (from Aldrich and Polymer Standard Services) are doped with NapI and PhenI (Aldrich). For preparation of the films, solutions of the purified polymer and of the dopant dissolved into dichloromethane are cast on quartz substrates. The dopant concentration varies from 0.5% to 1.2% by weight and the typical film thickness is in the range of 10-80 µm, as measured by a DEKTAK 3030 profilometer. Film absorption spectra were measured using a Perkin Elmer, Lambda 16-UV/VIS spectrometer.

The targets were irradiated by a KrF excimer laser (248 nm, 20 ns FWHM) focused at normal incidence to reach fluences up to 3 J/cm^2. Morphological changes on the surface of the irradiated films were established via optical microscopic examination by an optical Leica microscope and by standard profilometric measurements. To further investigate the time scale of the observed effects, we measured simultaneously the attenuation of two CW probe HeNe lasers, the first incident at 45º on the irradiated region and the second one propagating parallel and at 200 µm to the film surface. The intensities of both beams were monitored in real time by two identical fast photodiodes (response time 5 ns).

3. Results
UV irradiation results in swelling and/or etching of the films depending on the fluence. Thresholds, as determined by the profilometer, are displayed in Table 1 which also lists the measured absorption coefficients of the prepared films. The measured swelling and etching thresholds are lower for the films of low M_W polymer. Below threshold, swelling is observed for both NapI- and PhenI-PMMMA doped systems although swelling is much more pronounced for the higher M_W system (e.g., for the 1.2% NapI/PMMA the maximum swelling is 8 µm vs. ≈4 µm for the low M_W polymer). No swelling and lower ablation thresholds are obtained for the PS-based systems in correspondence with the higher absorption coefficient of this polymer (more than 30 times), as compared with PMMA.

Table 1. Swelling and ablation thresholds (in mJ/cm^2), typical bubble diameter (in µm) and linear absorption coefficients \( \alpha \) (in cm\(^{-1} \)) at 248 nm (or 308 nm when stated) of doped polymer films.

| M_W (kDa) | Swelling | Ablation | Typical bubble diameter at 300 mJ/cm^2 | \( \alpha \) |
|-----------|----------|----------|--------------------------------------|---------|
| 1.2% NapI/PMMA | 2.5 | 250 | 1100 | 25 | 360 ± 60 |
| 120 | 600 | 1500 | 5 |
| 996 | 600 | 1500 | 4 |
| 0.5% PhenI/PMMA | 2.5 | 200 | 500 | 16 | 570 ± 140 |
| 120 | 200 | 800-900 | 3 |
| 996 | 300 | 1000 | 2.5 |
| 1.2% PhenI/PMMA | 2.5 | 180 | 540 | 14 | 940 ± 100 |
| 120 | 180 | 800 | 5 |
| 996 | 180 | 850 | 4 |
| 0.5% PhenI/PS | 15.1 | - | 50 | <0.5 | 3380 ± 250 |
| 280 | - | 50 | <0.5 | 340 ± 30 at 308 nm |
| 532 | - | <0.5 | 30 at 308 nm |
Irradiation at 248 nm of the PMMA-based films gives rise to a foam-like layer as evidenced by optical micrographs taken on irradiated spots (fig. 1). This type of morphological modification of irradiated polymeric substrates has been reported by other authors [2,9]. The typical dimensions of the formed gas filled micro bubbles (Table 1) scale down with increasing optical absorption coefficient. In fact at 248 nm, where PS has a high optical absorption coefficient, no particular morphological changes can be detected in the optical microscopic examination, with the irradiated region appearing smooth. In contrast, similarly to what is observed in PMMA at 248, the irradiated substrates of doped PS at 308 nm (weakly absorbed wavelength) display morphological modifications of micrometric size. The diameter of the observed bubbles expectably grows with increasing laser fluence. The important result however is that for a given fluence, the bubbles are on average larger in the films of low M_W [2]. In fact, for low M_W polymer, the typical bubble diameter is comparable to the optical penetration depth, their size strongly decreasing at higher M_W values. As the optical absorption coefficient of films does not change with M_W (as determined experimentally), the differences in bubble size and number should be related to the M_W dependence on physical polymer properties. The formation of larger and more numerous bubbles in the lower M_W polymer can be ascribed to the larger free volume, lower viscosity and lower tensile strength, as well as more efficient gaseous product formation.

Yet, as mentioned earlier, the overall/maximum swelling is much more pronounced for the higher M_W system and therefore, considering the higher matrix stiffness of the high M_W polymer, this result demonstrates that a much higher production and decomposition degree is attained for effecting material ejection in this system.

The simultaneous measurements of the transmission of a CW laser through the irradiated film and through the ablation plume can provide further information of the time scale of the effects reported above. Figure 2 shows an example for films of 1.2% NapI/ PMMA 2.5 and 996 kDa. The duration of the observed transients scales up for lower polymer M_W. However significant attenuation by the plume is only observed above the ablation threshold of the films, when transmission by the substrate has already been severely attenuated. These results imply a slower plume evolution in the case of lower M_W polymer and also that the time scale of the transients in transmission by the substrate reflects the temporal evolution of the induced morphological modifications, i.e. the time scale involved in the growth of bubbles.
Figure 2. Time resolved attenuation of the transmission of a CW laser by the ablated substrate (thick line) and by the ablation plume (thin line) in 1.2 % NapI/PMMA films irradiated at 248 nm.

We consider now a likely explanation for the observed dependence on $M_W$. There is no doubt that for PMMA at 248 and 308 nm a photothermal mechanism is dominant for material ejection. These results are consistent with a bulk photothermal model [7], as more laser energy is needed to produce polymer fragments of the critical size from an initially longer polymer chain. Therefore, we can assume that material ejection involves thermal decomposition of the polymeric chains to oligomers or monomers that subsequently desorb. In fact, according to the bulk photothermal model, which appears to be the most appropriate for describing the ablation of polymers, the temperature rise can be estimated as

$$\frac{dT}{dt} = \frac{Q}{\rho c_p} + \frac{k}{\rho c_p} \frac{d^2 T}{dz^2}$$

where $k$ is the heat conductivity, $\rho$ the density, $c_p$ the specific heat, $V$ the velocity of surface recession and $Q$ the heat term given by

$$Q = \frac{\Delta H_b N_0 (1 - M_B) k_0 \exp(-E_b/k_BT)}{\rho c_p}$$

with $\Delta H_b$ the enthalpy per bond, $N_0$ the initial number density of bonds, $M_B$ the fraction of broken bonds, $k_0$ a constant, $E_b$ the activation energy and $k_B$ the Boltzmann constant. The rate of material removal is $V = V_0 \exp(-E_{bm}/k_BT)$ with the position $z$ of the interface determined by a critical number of broken bonds ($E_{bm}$ stands for energy of bonds per monomer, $M_s$ the fraction of broken bonds at the surface and $T_s$ the surface temperature). Clearly, the model implies a critical number of monomers, being intuitively evident that this number is reached very efficiently for low $M_W$, resulting in a much higher velocity of surface recession for the latter. It is also implied that energy removal is much less efficient for the high $M_W$, which then suggests that indeed higher temperatures must be attained. As confirmed in figure 2, a more adiabatic slower ejection of material occurs in the low $M_W$ system, ensuring efficient removal of excess energy. On the contrary, for the high $M_W$ system, ejection takes place suddenly in a shorter time interval as a consequence of photomechanical effects induced by the accumulation of degradation products in a more stiff matrix. In conclusion, we have analyzed the influence of $M_W$ on the 248 nm laser ablation of PMMA and PS films, doped with photoactive iodo-substituted derivatives, by examining the irradiated substrates with optical microscopy and real-time monitoring of the transmission of a CW laser. Results reveal that at weakly absorbed wavelengths morphological changes are observed, their extent being dependent on $M_W$. The bulk photothermal model, according to which ejection requires a critical number of broken bonds, is adequate to explain the observed behaviour. In all, these results are of direct importance for the optimisation of laser processing schemes and applications and provide the first indication of explosive boiling in UV ablation of polymers. Work is in progress for examining in more detail the dynamics of processes involved both in the substrate and in the ejection process.
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