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## Pulsed Laser Deposition of Polymers Doped with Fluorescent Probes. Application to Environmental Sensors

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**Abstract.** Pulsed laser deposition (PLD) has been used to obtain thin films of poly(methyl methacrylate) and polystyrene doped with fluorescent probes, amino aromatic compounds S5 and S6, that could be used to sense the presence of contaminating environmental agents. These dopants both in solution and inserted in polymeric films are sensitive to changes in pH, viscosity and polarity, increasing their fluorescence emission and/or modifying the position of their emission band. Films deposits on quartz substrates, obtained by irradiating targets with a Ti:Sapphire laser (800 nm, 120 fs pulse) were analyzed by optical and Environmental Scanning Electron Microscopy, Fluorescence Microscopy, Laser-Induced Fluorescence, Micro Raman Spectroscopy and Flow Injection Analysis-Mass Spectrometry. The transfer of the polymer and the probe to the substrate is observed to be strongly dependent on the optical absorption coefficient of the polymeric component of the target at the irradiation wavelength.

### 1. Introduction

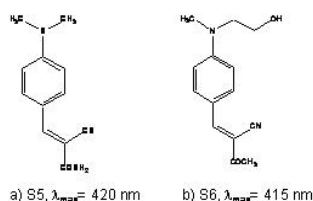
Pulsed laser deposition (PLD) of thin films of polymeric materials and biomaterials in the new domain of nanoprocesed and nanostructured deposits provides innovative solutions for the pharmaceutical industry, bioengineering and development of gas sensors [1-4]. Sensors based in thin polymeric films offer a series of advantages in comparison with other alternatives, as the diffusion time of the contaminant is shortened, increasing the capacity for real time monitoring. Moreover, the possibility of growing nanostructures by PLD increases the surface of interaction and consequently reduces the measurable concentration of contaminant lowering the detection threshold. This implements a clear advantage for pollutants when critical concentrations are below the detection capacities of the available techniques. The use of ultrashort femtosecond laser pulses in PLD experiments reduces the thermal effects and minimizes laser cluster production in the plasma, thus allowing optimal control of material removal and deposition [1,5].

Several studies have been devoted to the characterization of the ablation plume and deposited materials by PLD of poly(methyl methacrylate) (PMMA) and other polymers [4-8]. In this work, PLD has been used to grow films of polymers doped with fluorescent probes that could serve as sensors for the presence of environmental contaminating agents. As starting materials we have used polymeric matrices of PMMA and polystyrene (PS) doped with the amino aromatic compounds S5 and S6. These dopants have been shown to be sensitive, both in solution and inserted in polymeric films, to changes in pH, viscosity and

polarity, increasing their fluorescence emission and/or modifying the position of their emission band [9,10]. PLD was performed at room temperature with a Ti:Sapphire laser (800 nm, 120 fs). Analysis and characterisation of the obtained deposited films on quartz substrates by microscopic, micro Raman and mass spectrometric techniques have revealed the transfer of the polymer and the probe to the substrate and have shown that the properties of the film deposits including thickness and composition are strongly dependent on the absorption coefficient of the polymeric matrix at the laser wavelength.

## 2. Experimental

The targets for PLD were prepared by incorporating the fluorescent molecular probes in PMMA (average  $M_w$  120 kDa, Aldrich) and PS (average  $M_w$  280 kDa, Aldrich). As fluorescent probes, amino aromatic compounds S5 and S6 (figure 1) were used. Solutions of 1.0 g of polymer and 0.1 g of the probe in approximately 10 ml of chloroform were prepared and poured into a Teflon mould until the solvent was completely evaporated. The resulting disks of 3 cm diameter and a typical thickness of 1-2 mm were used as targets.



**Figure 1.** Formulae of fluorescent probes: a) (2Z)-3-[4-(dimethylamino)phenyl]-2-methylacrylonitrile (S5) and b) (2E)-2-acetyl-3-{4-[(2-hydroxyethyl) (methyl)amino]phenyl}acrylonitrile (S6). The wavelength of maximum absorption of a solution of the probe in chloroform is indicated.

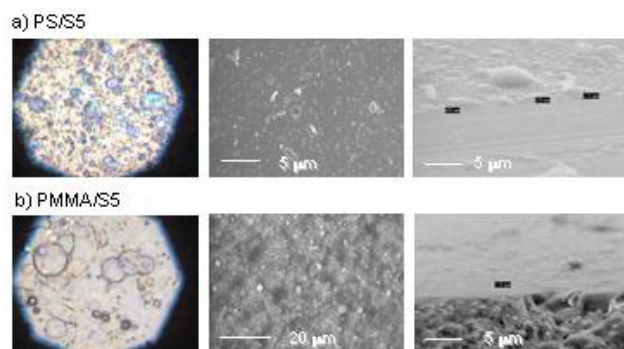
The targets, rotated during deposition for uniform cratering, were placed inside a vacuum chamber, evacuated down to a pressure of  $5 \cdot 10^{-5}$  mbar, at a distance of ca. 20 mm from a quartz flat of 25 mm diameter used as the substrate. The Ti:Sapphire laser, delivering 120 fs pulses of linearly polarized light,  $\lambda=800$  nm at 1 kHz, was focused by a  $f=30$  cm lens on the target at an incidence angle of  $45^\circ$ . To obtain the film deposits, the targets were typically irradiated in continuous-shot mode at fluences ranging from  $0.5\text{--}3 \text{ J/cm}^2$  for 2-4 minutes. For the samples of PS, low fluences were employed to avoid carbonisation of the targets, while for PMMA, higher irradiation fluences were necessary (and sometimes double irradiation of the same substrate) to get thicker films.

Several techniques were employed for the physicochemical characterization of the film deposits. The morphology was characterized by optical microscopy and Environmental Scanning Electron Microscopy (ESEM, Philips XL30). Fluorescence microscopy was used to check the presence of the fluorescent probes in the films. Fluorescent images were obtained using a microscope (Nikon Eclipse E400). The excitation source was an average pressure mercury lamp (Macam Flexicure-Silvana lamp, 400 W) coupled with a quartz optical fibre for light collection. Images were recorded with a CCD camera (Sony CCD-Iris). LIF spectra were obtained by illuminating the surface of the film deposits with a KrF laser at 248 nm and collecting the time integrated induced fluorescence with a 0.30 m spectrograph (TMc300 Benthams, grating of 300 grooves/mm) coupled to an intensified charge coupled device detector (2151 Andor Technologies). The film deposits were also characterized by micro Raman spectroscopy. The Raman spectra were recorded with a Renishaw Raman Microscope System RM1000 coupled to an optical Leica microscope. The Raman system was equipped with an electrically refrigerated CCD camera and a diode laser at 785 nm as the excitation source, operating at a power level of 30 mW. The spectra were acquired by collecting scattered light from a surface area of  $1 \mu\text{m}$  diameter in backscattering geometry. Finally, Flow Injection Analysis-Mass Spectrometry (FIA-MS) on a LC-MS (Thermo Electron) system was used for further chemical characterization of the film deposits.  $MS^2$  spectra were obtained by isolating and

fragmenting individual molecular ions in the ion trap. Isolation and further fragmentation of a second ion produced a  $MS^3$  spectrum. These  $MS^2$  and  $MS^3$  spectra were used to confirm the presence and the structure of the probes in the targets.

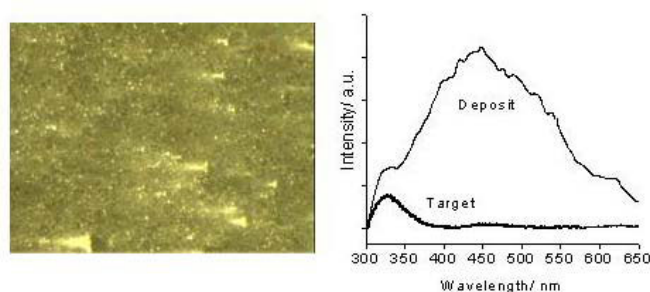
### 3. Results and discussion

The deposits obtained were films of variable roughness (between 600 and 2500 nm) with presence of submicron particles. Figure 2 shows optical and ESEM pictures of the S5 system. Inspection of the films by fluorescence microscopy indicates the existence of scattered fluorescence sites (figure 3). LIF spectra of the film deposits confirm the transfer of the polymer component to the substrate. This is observed for the PS/S5 sample (figure 3) where the characteristic PS emission band appears at 320 nm. Irradiation of PS targets results in carbonisation of the irradiated region. Discoloration of the irradiated regions is observed in PMMA-based targets, which in turn gives thinner films than PS targets under the same irradiation conditions. At 800 nm PS is a weaker absorber than PMMA [11], the difference in absorption coefficient could influence the nature and velocity of ejection of material giving rise to a less dense gaseous ablation plume from the PMMA-based target [12] and therefore less deposited material.

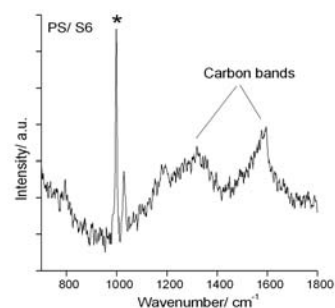


**Figure 2.** Optical (left) and ESEM pictures (center and right) of films obtained from targets of doped polymers, magnification 50x: a) PS/S5 (Ti:Sapphire, 3.5 J/cm<sup>2</sup>, 2 min, 1 kHz), thickness 680 to 1100 nm; b) PMMA/S5 (Ti:Sapphire, 3.5 J/cm<sup>2</sup>, 3 min, 1 kHz), thickness 1250 nm.

Micro Raman spectra of film deposits give further evidence of the transfer of the polymer to the substrate, although no Raman bands of the probe could be assigned. In figure 4 the band associated with the side chain benzene ring breathing mode of PS is observed at 997 cm<sup>-1</sup>. Additionally bands at 1340 and 1580 cm<sup>-1</sup> are assigned to polycrystalline graphitic carbon [14], indicating that dark film deposits may contain some carbonaceous material.



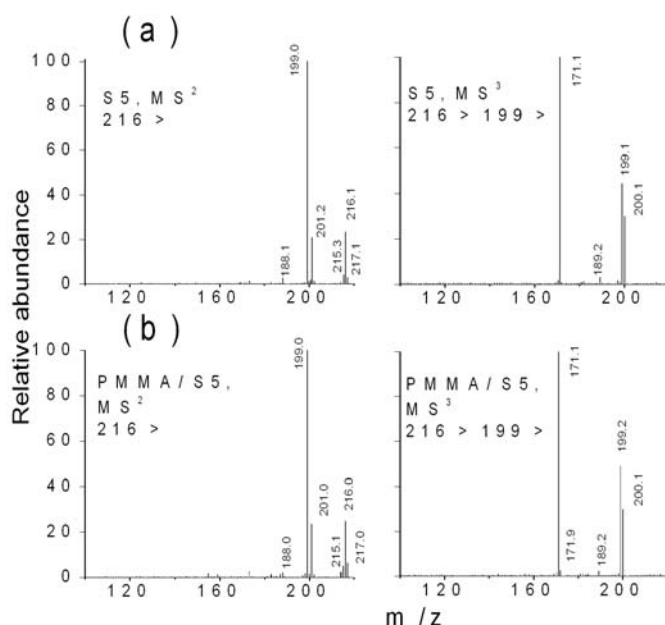
**Figure 3.** Fluorescence microscopy images of film deposits (magnification 60x) (left) and LIF spectra (right), excitation at 248 nm, of PS/S5 target and deposit (Ti:Sapphire, 3.5 J/cm<sup>2</sup>, 2 min, 1 kHz).



**Figure 4.** Micro-Raman spectra (resolution 4 cm<sup>-1</sup>, integration time 10 s, 3 accumulations) of film deposits (Ti:Sapphire, 0.3 J/cm<sup>2</sup>, 2 min, 1 kHz) of PS/S6. The asterisk indicates the ring breathing mode of PS.

To ascertain the transfer of the fluorescent probes to the substrates, the material deposited on the quartz substrate was extracted with methanol to carry out ESI+-MS analysis (electro spray ionization interphase with acid mobile phase). Mass spectra  $MS^2$  and  $MS^3$  were compared with the corresponding ones taken in a methanol solution of the pure dopant. As an example, Figure 5 displays a comparison of the spectra of the S5 probe dissolved in methanol (Figure 5a) with the spectra of the deposit obtained upon irradiation of the PMMA/S5 target with the Ti:Sapphire system (Figure 5b). For S5 (molecular mass 215 Da) the protonated parent ion of mass 216 Da is isolated in the ion trap to obtain a characteristic  $MS^2$  spectrum in which the main peak corresponds to the 199 Da ion. On a second step, this ion is further fragmented resulting in a characteristic  $MS^3$  fragmentation pattern. As seen, the sequential  $MS^2$  and  $MS^3$  pattern, which gives a unique signature of the compound, is clearly reproduced in the spectra of the material extracted from the deposit of the PMMA/S5 target, confirming that transfer of the intact probe to the substrate takes place in the PLD process. Similar results are obtained for the PS/S5 targets.

In conclusion, the morphological and chemical analysis performed by combining microscopic and spectrometric techniques confirms the efficient transfer by PLD of both the polymeric and fluorescent probe to constitute the film deposits. Differences of thickness of film deposits (thinner from PMMA- than for PS-based targets) are strongly correlated with optical absorption coefficient of the polymer at the laser irradiation wavelength; at 800 nm, the absorption coefficient of PS being significantly lower [11] than that in PMMA. Work is in progress to characterize the fluorescence response of the obtained films by exposure to a contaminating gaseous agent.



**Figure 5.**  $MS^2$  and  $MS^3$  spectra confirm the presence and the structure of the probes in the targets: a) S5 in methanol and b) PMMA/S5. The masses chosen for the analyses are indicated in the spectra.

### Acknowledgements

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