

Experimental Investigations of Polymer Plasma Laser Ablation

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Experimental investigations of a diblock copolymer (polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP) film doped selectively with tetrakis(4-carboxyphenyl)porphine (TCPP) into the nanoscale spherical domains of P4VP) used as target in a Nd: YAG laser ($\lambda = 532$ nm) ablation process, were performed. The ionic current oscillations and the velocity of diblock copolymer plasma plume were experimentally obtained.

Keywords: polymer, laser ablation

Polymers are an interesting material for many different applications [1-2] due to their wide range of properties. The first laser ablation experiments using the polymers as targets were published in [3-4]. At that time, laser ablation of polymers was considered as an alternative to the conventional photoresist technology. This method never reached the breakthrough in industry due to the high ablation thresholds and the redeposition of the ablated material (debris). Since then other applications have been developed and are applied in the industry. For instance laser ablation of polyimide is being used by IBM to create via holes in multi-chip modules [5] and by several companies to structure nozzles for inkjet printer.

In 2004 papers on applications discussed the use of ablation in high-aspect-ratio LIGA process [5], in manufacturing of all-polymer photonic devices [6] and interconnections for optical printed circuit boards [7], in polymer jacket stripping of optical fibers [8], in fabrication of polymer micropumps [9] and in other types of micromachining [10-11].

Laser ablation is now suggested for use in micropropulsion [12-13]. Very intriguing is the application of laser ablation of soft polymers for the creation of micron-sized containers of alkali metal in light-induced atom desorption experiments [14].

In the present paper experimental investigations of polymer laser ablation were performed. Our analysis describes only the dynamics of a polymer plasma plume generated by laser ablation and not the chemical transformations that occur during the treatment.

Experimental part

Polymer Target Structure

Recently, laser ablation of polymer films has been extensively investigated both for application to their surface modification and thin-film deposition and for elucidation of the mechanism. Dopant-induced laser ablation of polymer films has also been investigated. This feature is that ablation is induced by excitation not of the target polymer film itself but of a small amount of the photosensitizer doped in the polymer film. By choosing a molecule with a large π -electronic conjugated system as a dopant, the ablation of polymer films is easily induced with longer wavelength lasers and lower fluences than those employed in laser ablation with excitation of the polymer film itself.

This mechanism is applied to molecules whose transient states have substantial absorption coefficients at the excitation wavelength. In the mechanism, the relaxation from the excited states of the transient states of a dopant to the transient states involves the internal conversion in the dopant and the subsequent intermolecular vibrational energy transfer from the dopant to the surrounding polymer matrix. Thus, the polymer matrix is heated up repeatedly during the multiphoton absorption. The irradiation of a laser with high fluences results in rapid thermal-decomposition of polymer matrix, i.e. ablation. Almost all investigations on the laser ablation of polymer systems have been restricted to homopolymer systems. A diblock copolymer consists of two different types of polymer chains connected by a chemical bond. The diblock copolymers have a wide variety of microphase separation structures such as spheres, cylinders, and lamellae on the nanoscale, and are expected to be new functional materials with nanostructures. Hence, it is interesting to investigate the laser-ablation modification of diblock copolymer films having nano-scale microdomain structures. In the present study, we used a thin diblock copolymer, polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP), film doped selectively with tetrakis(4-carboxyphenyl)porphine (TCPP) into the nanoscale spherical domains of P4VP as a target polymer film.

The diblock copolymer (PS-b-P4VP) used was purchased from Polymer Source Inc. (Quebec, Canada). The number-average molecular weights of the styrene and the 4-vinylpyridine blocks are 301000 and 19600, respectively; $M_w = M_n$ of 1.19. TCPP used as the dopant has a molar extinction coefficient of $3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at the maximum absorption peak of 420 nm. The chemical structures of the dopant and the diblock copolymer are shown in figure 1[15].

The doping conditions employed under the experiment from [15] result in the maximum concentration of dopant in films. Moreover, the second harmonic output (532 nm) of a Nd: YAG laser (Spectra-Physics, Quanta-Ray INDI-40 with full width at half maximum (FWHM) of ca. 10 ns) was used to induce ablation. Therefore, in our study we will use this type of laser.

Experimental technique

The experimental technique is based on a set-up (fig. 2 for a schematic view) developed mainly for analytical

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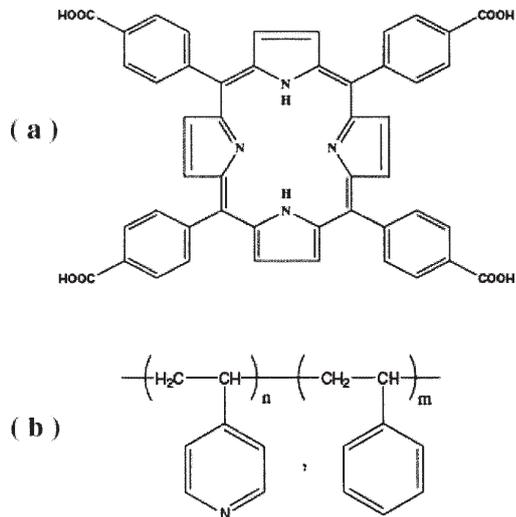


Fig. 1. Chemical structures of (a) diblock copolymer of PS-b-P4VP and (b) dopant of TCPP. TCPP has four carboxyl groups, which form hydrogen bonds ($-O-H\cdots N$) with nitrogen atoms of pyridyl groups (according to [15])

purposes and described in detail elsewhere [16- 17]. The experiments have been performed in a stainless steel vacuum chamber evacuated by means of a 450 l/s turbomolecular pump to a base pressure $< 10^{-6}$ Torr. A 10 ns Nd:YAG pulsed laser beam ($\lambda = 532$ nm) has been focused by a $f = 25$ cm lens on the polymer target (the polymer structure was presented in paragraph 2) placed in the vacuum chamber. The estimated spot diameter at the impact point has been $\sim 300 \mu\text{m}$. The laser beam energy (1-100 mJ/pulse) has been continuously monitored by an OPHIR joulemeter. The energy usually employed was ~ 40 mJ/ pulse; this leads to a typical laser intensity of ~ 5.7 GW/cm².

The formation and dynamics of the plasma plume (as a result of laser ablation) have been studied by means of an intensified CCD camera (PI MAX, 576X384, gating time 20ns) placed orthogonal to the plasma expansion direction. A Nikon lens has been used to image the plume onto the camera.

The total ionic current generated by the plasma expansion has been measured by a cylindrical Langmuir probe (stainless steel 0.8 mm diameter, 5 mm length), biased at -30 V (stabilized dc power source) and placed at a fixed position (see below for details). The transitory signals have been recorded by a 500 MHz digital oscilloscope (LeCroy 9350AM) and transferred to a PC for further analysis (LabView environment).

Results and discussions

In figure 3 the ICCD images of the expanding polymer plasma plume at different delays after the laser pulse are given. The images of this structure reveal the dynamics of the polymer plasma plume. According to [18], the well-localized plasma pattern has an electric double-layer structure. By analyzing the evolution presented in figure 3 we conclude that in the time interval 10-50 ns after the laser pulse, the visible emitting regions of the plasma are almost stationary and they form a structure corresponding to a maximum emissive zone and after this moment, the emitting structure flies away and eventually disappears, having an estimated life time of ~ 1500 ns. It was experimentally observed that this life time strongly depends on the laser beam energy. Such short phase explosion nucleation time lags (5 ns) have already been

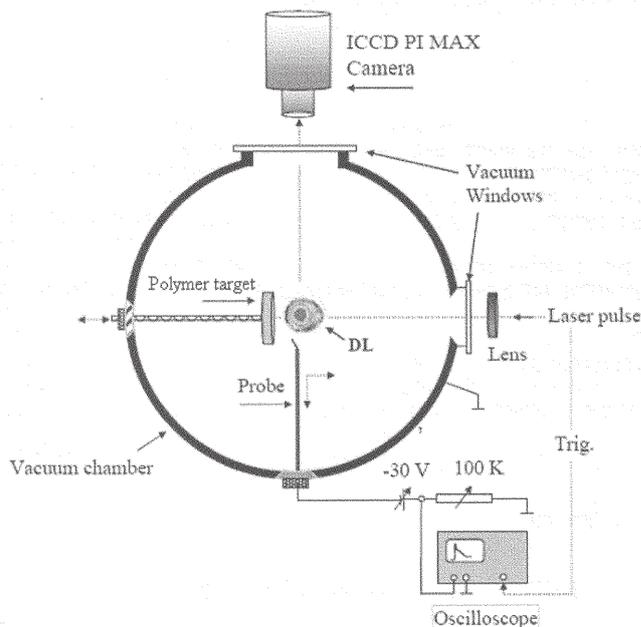


Fig. 2. Schematic view of the experimental set-up

demonstrated experimentally in nanosecond laser ablation with comparable fluences [19] and theoretically [20-28].

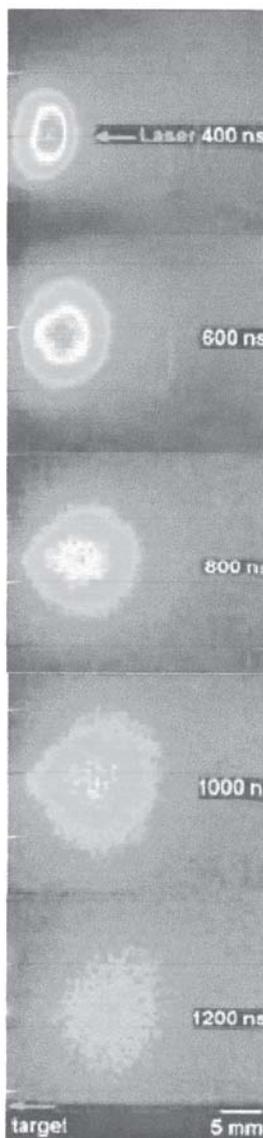


Fig. 3. The evolution of the visible emission from the polymer plasma plume recorded using an ICCD PI MAX camera (gating time 20 ns). Successive laser pulses of equal energy (40 mJ/pulse) were used to record the different shots

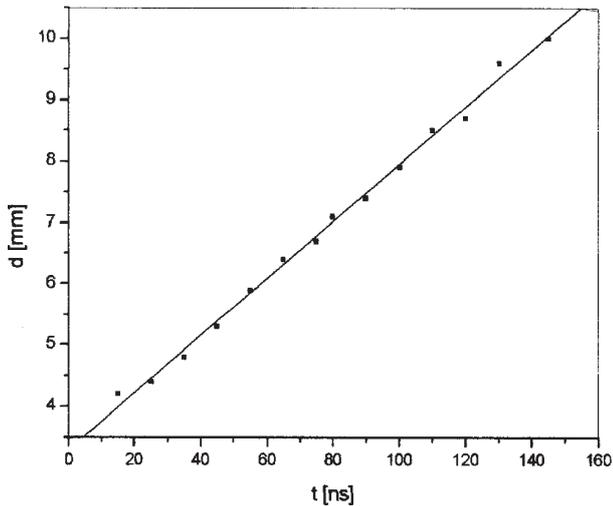


Fig. 4. The expansion velocity of the plasma structure. The position of the maximum emission region is plotted against the delay after the laser pulse

Using experimental data from optical diagnosis, the velocities of the plasma formation has been calculated by measuring the position of the maximum emissivity at different times. The results are given in figure 4. The experimental data were fitted by linear regression and the velocity of the structure has been estimated. We obtained $v_1 = 4.66 \cdot 10^4$ m/s for the plasma structure (fig. 4).

The transient ionic currents recorded by the Langmuir probe for 40 mJ/ laser pulse beam energy are plotted in figure 5. For this measurement, the probe was located on the expanding plasma symmetry axis (z), at $z = 19$ mm from the polymer target surface. Analyzing this profile, the resulted that the current recorded by the Langmuir probe has multi-peak structure. Thus, the first part of the transient signal takes about 2 μ s and has an oscillatory structure with the average period of 240 ns which does not depend on the laser energy (for details see [29]). The results obtained by the electrical probe are in good agreement with those recorded by optical methods.

An extension of the present results can be performed using the methodology [30, 31].

Conclusions

The laser ablation of the diblock copolymer (PS-b-P4VP) is experimentally investigated.

The velocity of the polymer plasma plume has been estimated. Also, the ion current oscillations were clearly highlighted. Obviously, the current recorded by the Langmuir probe has a multi-peak structure.

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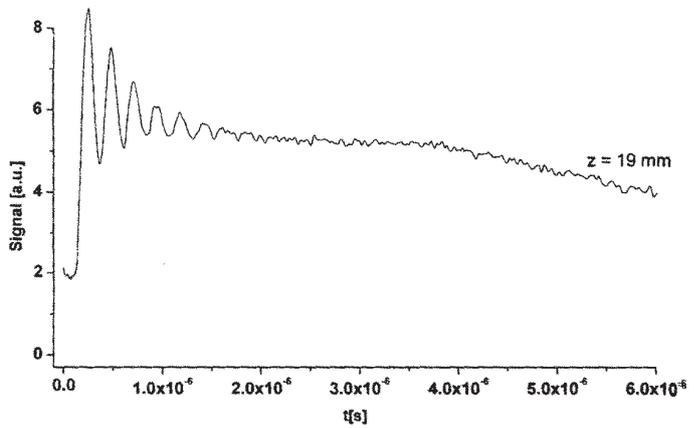


Fig. 5. Transient ionic current recorded by the Langmuir probe located at a fixed distance on the normal to the polymer target

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