

The effect of the matrix on film properties in matrix-assisted pulsed laser evaporation

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Thin films of polyethylene glycol of average molecular weight 1400 amu have been deposited by matrix-assisted pulsed laser evaporation (MAPLE). The deposition was carried out in vacuum ($\sim 10^{-6}$ Torr) with an ArF ($\lambda = 193$ nm) laser at a fluence of 220–230 mJ/cm². Films were deposited on NaCl plates and glass microscope slides. Both deionized water (H₂O) and chloroform (CHCl₃) were used as matrices. The physiochemical properties of the films are compared via Fourier transform infrared spectroscopy, and electrospray ionization mass spectrometry. The results show that the matrix used during MAPLE can greatly affect the chemical structure and molecular weight distribution of the deposited film. The infrared absorption spectrum shows evidence for C–Cl bond formation when CHCl₃ is used as a matrix, while there is little evidence in the IR data for photochemical modification when H₂O is used as a matrix. Time-of-flight analysis was performed using a quadrupole mass spectrometer to monitor evaporation of a frozen CHCl₃ target during laser exposure. Using this approach, we determined that the TOF spectra for $m/z = 35$ (Cl) and $m/z = 85$ (CHCl₂) differed significantly in both width and peak arrival time, indicating that neutral chlorine atoms were produced at the target surface. We attribute the reduction in molecular weight and structural modification of the film deposited using CHCl₃ to the presence of these highly reactive species. © 2002 American Institute of Physics. [DOI: 10.1063/1.1427138]

INTRODUCTION

Recently, matrix-assisted pulsed laser evaporation has been shown^{1–3} to be a viable alternative to conventional pulsed laser deposition (PLD) for polymers and other organics. There are a variety of important applications for thin polymeric and organic films including biomedical, electronic, chemical sensing, and optical applications. For example, polymer films have application as chemiresistors⁴ and chemoselective⁵ coatings on surface acoustic wave devices, and as drug delivery coatings.⁶ Specifically, for polyethylene glycol (PEG), there are many biomedical applications⁷ such as tissue engineering,⁸ spatial patterning of cells,^{9,10} and drug delivery coatings^{11,12} and anti-fouling coatings.¹³

In MAPLE, the material to be deposited is dissolved in a solvent (matrix), usually 0.1–2 wt % concentrated and then cooled below the solvent freezing temperature. The solid composite target is evaporated by a UV laser and the vaporized material is collected on a nearby substrate as a thin film. In a successful deposition, the vaporized solvent does not form a film and is pumped away. MAPLE is a process that is reminiscent of the analytical chemistry technique known as matrix-assisted laser desorption and ionization mass spectrometry (MALDI),¹⁴ except that in MAPLE the desorbed material is collected on a substrate and in MALDI the desorbed (and ionized) material is directed into a mass spectrometer. These processes are to be contrasted with conventional PLD, in which the UV laser beam directly interacts with the material to be deposited.

PLD has been an extremely successful technique for depositing thin films of a large variety of inorganic materials.¹⁵ More recently, the deposition of polymers via PLD has been

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explored.¹⁶ There is a large body of literature on PLD of polymers, particularly addition polymers which can be depolymerized by the intense laser beam and re-polymerize in the presence of radicals acting as catalysts.¹⁷ For a model polymer system such as PEG, we have recently shown MAPLE is far superior to PLD in terms of the physicochemical properties of the films.²

The role of the matrix in MAPLE has not been extensively investigated. The criteria for a suitable host is one that dissolves the guest material; one that, in the absence of a guest material does not undergo photochemical production of a film, and finally, one that does not photochemically interact with a guest. In view of the potentially strong photochemical interactions between both the host and guest materials,¹⁸ it is important to examine the influence of the host on the structure of the deposited film. In this paper, we show results for MAPLE films of PEG deposited using both H₂O and CHCl₃ as matrices. Water is an ideal matrix for MAPLE deposition of biological materials.³ CHCl₃ is a good solvent for a wide range of polymers. Both guests have the potential for photochemical reactivity with 193 nm excitation. The data show that the physicochemical properties of deposited material are strongly influenced by the solvent.

EXPERIMENT

An ArF excimer laser (Lambda Physik 305; $\lambda = 193$ nm; FWHM = 30 ns) was used for MAPLE. The experimental setup has been described in detail previously.¹ The laser was operated at a repetition rate of 10 Hz and the fluence was 220–230 mJ/cm². The target substrate distance was 3 cm. The spot size was varied between 0.03 and 0.06 cm² and the beam was rastered over the entire surface of the 1 in. diameter rotating target (35 rpm). Our starting material is PEG 1450 Carbowax (Alltech Associates, Deerfield, IL). CHCl₃ was used (Aldrich 32,024-2) as a matrix as well as deionized water ($R > 18$ M Ω). To form the composite targets for laser ablation approximately 2 wt. % solutions of PEG and solvent were poured into an aluminum target die. The die was inverted and placed on a metal plate and flash frozen in liquid nitrogen, producing targets with a smooth surface. During MAPLE, when CHCl₃ was used as a matrix, the target temperature was fixed at approximately -160 °C, and for H₂O it was -50 °C. The deposition rate has been found to vary with the temperature of the target when using water as a matrix. Holding the target at -50 °C as opposed to -160 °C (the coldest our system can achieve) increased the deposition rate by a factor of 3–5.

The evaporated material was collected on NaCl plates and glass microscope slides held at room temperature for post-deposition analyses. The background pressure in the chamber during deposition was between 10^{-5} and 10^{-6} Torr. A typical deposition rate for these conditions was 1.3–2.5 (ng/cm²·pulse), or 1–2 mg in an area approximately 1 in.² after 40 000 laser pulses. For comparison, performing UV PLD under nearly identical conditions yields a deposition rate of 10 (ng/cm²·pulse),² or about 4–8 times greater than during MAPLE.

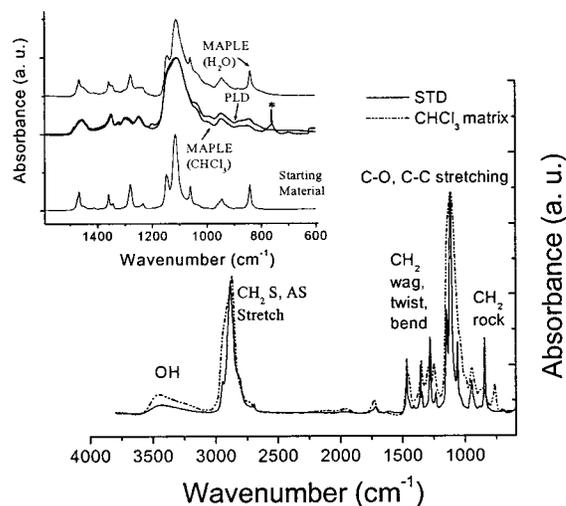


FIG. 1. Mid-infrared absorbance spectra of PEG starting material and MAPLE (CHCl₃) film. The position of major bands is marked in the spectrum. Inset: Expanded view of spectral region between 600 and 1600 cm⁻¹. For comparison, the spectrum of a film deposited using conventional PLD is added.

Polyethylene glycol samples were analyzed using FTIR, ESI,¹⁹ and MALDI.²⁰ Infrared spectra were recorded for the films using a Nicolet Magna-IR 750 Fourier transform infrared spectrometer. PEG samples were extracted from the surface with 1 ml of methanol, and then evaporated to dryness in a vial. The samples were re-dissolved in 25 μ L of methanol. For ESI, 20 μ L aliquots of the solution were mixed with an equal volume of KCl in water, to produce a final KCl concentration of 1 mM. Samples were electrosprayed and analyzed on a Thermoquest LCQ ion trap mass spectrometer.

In addition to the analyses performed upon the deposited films, quadrupole mass spectrometry (QMS) measurements were made during pulsed laser ablation of CHCl₃. The QMS apparatus has previously been described in detail.⁴

RESULTS AND DISCUSSION

The mid-infrared absorbance spectra of the starting PEG material and a MAPLE (CHCl₃) film are shown in Fig. 1. Clearly, the spectra are different in the 600–1600 cm⁻¹ region for the MAPLE (CHCl₃). An expanded view of this region is displayed in the inset. In particular, it can be noted that the MAPLE (CHCl₃) film has a similar mid-infrared absorbance spectrum as a film deposited by conventional pulsed laser deposition with nearly identical deposition parameters.² In fact, the MAPLE (CHCl₃) film's spectrum and the PLD film's spectrum have almost all absorbance bands appearing in the same ratio with the exception of one weak band appearing at 760 cm⁻¹ in the MAPLE (CHCl₃) film's spectrum. One possible assignment for this band is a C–Cl stretch.²¹

The mass spectra of the starting material and two MAPLE films (H₂O, CHCl₃) are compared in Fig. 2. The MAPLE (H₂O) and starting material appear to be very similar while the MAPLE (CHCl₃) shows evidence for chemical modification. The results are summarized in Table I. It is important to note that the manner in which the molecular weight averages are calculated affects the results. If the singly and doubly

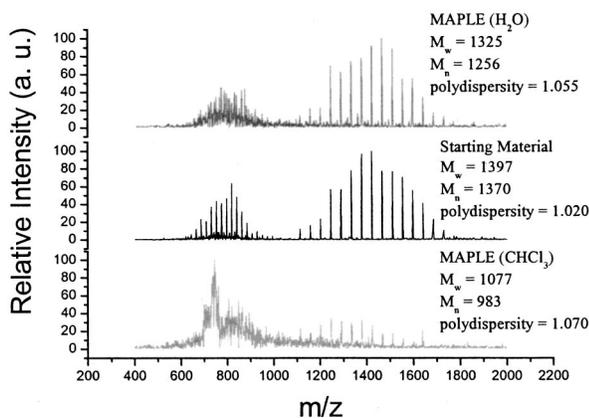


FIG. 2. ESI mass spectra of PEG 1400, and MAPLE (H_2O) and (CHCl_3) films.

charged ions are summed in order to calculate the masses, the contribution of doubly charged ions is overweighted and the results are skewed toward higher mass numbers. Practically speaking, this has the effect of masking some of the degradation that has occurred, particularly in the mass spectrum of the MAPLE (CHCl_3) film. If the mass averages are computed using only the singly charged ions, we see that the MAPLE (H_2O) film shows some slight degradation, while the MAPLE (CHCl_3) film shows more severe decomposition. When only using the singly charged envelope in order to compute the molar masses, M_n is reduced by 349 g/mol for the MAPLE (CHCl_3) film, while it changes by 144 g/mol for the MAPLE (H_2O) film and 64 g/mol for the starting material.

In the gas phase, during irradiation with 193 nm light, both CHCl_3 (Refs. 22, 23) and H_2O (Ref. 24) are known to photodissociate. In addition to gas phase studies on photofragmentation, there are a number of studies involving photoejection and fragmentation from solid cryogenic films that are relevant to the present work.^{25–28} In these studies on frozen molecular solids, the main mechanism of material ejection appears to be explosive photodesorption. In the gas phase, for CHCl_3 , the primary channel of photodissociation involves the creation of a dichloromethyl radical and a chlorine atom as follows:



Further, molecular elimination of HCl can occur:

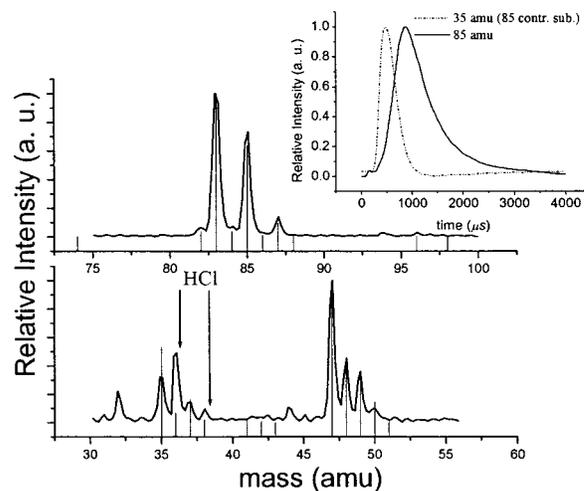


FIG. 3. Broadscan quadrupole mass spectrum during pulsed laser ablation of CHCl_3 , $\lambda = 193 \text{ nm}$, fluence = 200 mJ/cm^2 . See Ref. 29, electron impact mass spectrum for CHCl_3 plotted as vertical lines. Inset shows $m/z = 85$ peak and corrected $m/z = 35$ peak.



It is possible that the dissociation of CHCl_3 can occur in the plume or on the surface of the irradiated target. These two processes form the dominant scheme for photodecomposition of CHCl_3 into CHCl_2 , Cl , CCl , and HCl all of which are highly reactive species. It is also possible for HCl to be produced by reaction of the photofragment Cl with unfragmented CHCl_3 by hydrogen atom abstraction. In addition to the Cl atoms in the ground electronic state, Cl atoms are produced that are in excited electronic states. The branching ratios for photo-dissociated atoms in the gas phase have been documented.²³

In Fig. 3, we show the result of mass spectrum obtained during laser ablation of solid CHCl_3 at a fluence of 200 mJ/cm^2 . The mass spectrum appears to be very similar to that for the electron impact mass spectrum of CHCl_3 .²⁹ However, there are additional peaks at $m/z = 36$ and 38 which correspond to HCl . This is to be expected via Eq. (2). The TOF profiles for $m/z = 35$ amu and 85 are shown in the inset. The ion current at $m/z = 35$ has had the contribution from $m/z = 85$ [produced by the electron impact ionization of CHCl_3 (and CHCl_2)] subtracted from the total ion current. There-

TABLE I. Summary of ESI mass spectral characterization data for starting material and MAPLE films. S —calculated using singly charged ions only; $S+D$ —calculated using sum of singly + doubly charged ions.

Sample	S			$S+D$		
	M_n (g/mol)	M_w (g/mol)	M_w/M_n	M_n (g/mol)	M_w (g/mol)	M_w/M_n
Starting material	1370	1397	1.020	1434	1460	1.018
MAPLE (H_2O)	1256	1325	1.055	1400	1470	1.050
MAPLE (CHCl_3)	983	1077	1.096	1332	1467	1.101

fore, the $m/z = 35$ profile shown in the inset corresponds only to Cl produced at the surface of the target. The mean transit time of these neutral Cl atoms is approximately 480 μs , corresponding to a velocity of 2100 m/s. The collision-free recoil velocity obtained from Ref. 22 is 2300 m/s, thus showing that the Cl atoms have undergone relatively few collisions after leaving the surface of the target.

In contrast to CHCl_3 , H_2O appears not to photodissociate in our experiments. Even at fluences of up to 0.5 J/cm^2 , we do not observe any difference in the arrival time between the 17 and 18 amu peaks during laser ablation of ice. Not only are the peak arrival times the same, but the width of the time-of-flight distributions are identical. In photo-dissociation experiments it has been reported that the OH fragment carries away excess energy almost exclusively as translational kinetic energy.²⁴ This observation, coupled with ours, leads us to believe that H_2O is not photodissociating. In addition, when using H_2O as a matrix, we do not observe the type of modification in the FTIR spectrum and ESI mass spectrum that is observed when using CHCl_3 . For water-soluble polymers, H_2O is a superior MAPLE solvent to CHCl_3 .

CONCLUSION

We have used the polymer thin film growth technique known as MAPLE in order to deposit films of PEG while using two different matrices. The results of post-deposition analysis on the films show that the physicochemical properties can be greatly affected by the choice of matrix. Gas phase measurements during laser ablation of CHCl_3 confirm the presence of highly reactive species such as atomic Cl. We attribute the differences in film properties to the presence of these radicals and demonstrate that by properly choosing the matrix, one can greatly limit the damage done to the guest molecules during MAPLE.

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