

Resonant IR-Pulsed Laser Deposition of Polymer Films Using a Free-Electron Laser

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Abstract

Thin films of polyethylene glycol (MW 1500) have been prepared by pulsed laser deposition (PLD) using both a tunable infrared ($\lambda = 2.9 \text{ } \mu\text{m}$, $3.4 \text{ } \mu\text{m}$) and an ultraviolet laser ($\lambda = 193 \text{ nm}$). A comparison of the physiochemical properties of the films by means of Fourier transform infrared spectroscopy, electrospray ionization mass spectrometry, and matrix-assisted laser desorption and ionization (MALDI) shows that when the IR laser is tuned to a resonant absorption in the polymer, the IR PLD thin films are identical to the starting material, whereas the UV PLD show significant structural modification. These results are important for several biomedical applications of organic and polymeric thin films.

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Introduction

Polyethylene glycol (PEG) is a technologically important polymer with many biomedical applications¹. Examples include tissue engineering², spatial patterning of cells^{3,4}, drug delivery coatings^{5,6}, and anti-fouling coatings⁷. In these applications a need exists for a technique capable of depositing thin, uniform, and adherent coatings of PEG. Whereas in some cases it is acceptable to deposit chemically modified PEG polymeric material^{7,8}, in drug delivery and *in vivo* applications it is important that there is no difference in the chemical and structural properties of PEG films compared with the bulk polymer.

In this paper, we report the first successful pulsed-laser deposition (PLD) of thin polyethylene glycol (PEG) films using a tunable IR source in the mid-infrared. A direct comparison is made between PEG films grown with an UV laser (193 nm) and a tunable infrared laser (2.9, 3.4 μm). The IR laser is tuned to be resonant with the O-H or C-H stretch mode in PEG. The films were characterized by means of Fourier Transform Infrared Spectroscopy (FTIR), electrospray ionization mass spectrometry (ESI), and matrix-assisted laser desorption and ionization time of flight mass spectrometry (MALDI). The comparisons shows that when the IR laser is tuned to a resonant feature in the organic material, the IR-PLD films retain the optical, structural and physical characteristics of the bulk PEG material, whereas the UV-PLD deposited PEG materials do not. In addition, the results also show clearly that the mechanism of IR-PLD is fundamentally different than UV-PLD. These results are very important in the context of such biomedical technologies as drug-delivery coatings and *in vivo* applications where it is crucial to effect transfer of polymeric coatings without significant chemical or physical modification to the polymer.

Background

Pulsed Laser Deposition (PLD) has been an extremely successful technique for depositing thin films of a large variety of inorganic materials⁹. PLD has also been applied to the growth of thin polymeric and organic films, albeit with varying degrees of success. For example, when PLD is used to fabricate chemical sensors from polymer-carbon nanocomposites, both the molecular weight distribution and the chemical structure of the polymeric material are substantially altered, but the required functional groups for the sensor remain intact¹⁰. In other cases, the damage caused during UV ablation is limited to a reduction in the molecular weight with the chemical structure remaining intact¹¹. It has been shown that certain polymers such as poly-methyl methacrylate (PMMA), poly-tetrafluoroethylene (PTFE), and poly-*a*-methyl styrene (PAMS), undergo rapid depolymerization during UV laser ablation, with the monomer of each strongly present in the ablation plume^{12,13,14}. For these polymers, the molecular weight distribution of the deposited thin film material can be increased by simply raising the substrate temperature¹⁵. Therefore, even in the most successful cases of UV PLD of polymers there is an intense interaction between the target material and laser resulting in chemical modification of the polymer during ablation. If repolymerization is incomplete at the substrate, this can lead to both a reduction of molecular weight and a change in chemical structure.

The mechanism for UV ablation of organic materials has been debated for some time. In the photochemical model of ablation^{16,17}, absorption of a UV photon leads to direct bond dissociation and fragmentation of the organic molecule. In the photothermal model^{18,19}, the energy absorbed by the UV photon is rapidly converted to heat and the polymer undergoes pyrolysis. Rapid pyrolysis results in depolymerization of target material in the plume;

repolymerization occurs on the substrate, possibly initiated by the presence of free radicals^{12,13,14,15,19}.

Ablation may also proceed through the absorption by extrinsic²⁰ or laser-generated impurities such as color centers²¹. Extrinsic impurities may absorb the light directly resulting in local heating by electron-phonon coupling, or the interaction length may be increased through scattering, resulting in absorption by the polymer. Thin films of polystyrene doped with anthracene²², and polyethylene oxide with a ZrO additive²³ have been successfully ablated in this way.

In general, the interaction between organic molecules and UV light is very complicated, occurring as it does with extreme rapidity²⁴ and through many different excitation-relaxation pathways²⁵. This certainly seems to present a number of challenges to polymer film growth using UV lasers.

MOTIVATION (for this experiment)

For organics, an alternative approach to PLD with UV lasers is matrix-assisted pulsed laser evaporation (MAPLE) in which roughly 0.1 to 1% of a material to be deposited is dissolved in an appropriate solvent and frozen to form an ablation target^{26,27,28}. The UV laser light interacts mostly with the solvent and the guest material is thus ablated much more gently than in conventional PLD. While this can result in smooth uniform films suitable for a variety of applications, it nevertheless requires that the polymer of interest be soluble in a non-interacting solvent. The one serious disadvantage to MAPLE is that the deposition rate is about an order of magnitude lower than in conventional PLD²⁶.

In the early days of PLD, IR lasers were extensively used for deposition^{29,30}, although UV lasers have now become the workhorse of PLD research in inorganic materials. The complexity of the UV-induced photo-ablation and photodecomposition channels leads one to wonder whether IR-PLD might be an appropriate alternative for deposition of organic materials. This is particularly true given the availability of broadly tunable, high-average-power sources such as the free-electron laser in the mid-infrared.

A form of PLD of organics and polymers that allows one to access only vibrationally excited states would be very valuable. The use of mid-IR laser pulses between 2-10 μm as a means of ablating material offers just such a possibility. This has been successfully applied to the matrix-assisted laser desorption and ionization (MALDI) mass spectroscopic technique³¹.

Experimental

The light source for the IR PLD films was the W. M. Keck Foundation Free-Electron Laser (FEL) at Vanderbilt University. The Vanderbilt FEL produces a 4 μs macropulse at a repetition rate of 30 Hz; the macropulse in turn comprises some 30,000 1-ps micropulses separated by 350 ps. The energy in each macropulse is of order 10 μJ , so that the peak unfocused power in each micropulse is very high. The average power of the FEL is of order 2-3 W. The FEL is also continuously tunable over the range 2 – 10 μm .

The characteristics of the laser are discussed in greater detail elsewhere^{31,32}. For the IR PLD films the fluence was between 2 – 3 J/cm^2 , the target substrate distance was 3 cm, and the spot size was 0.028 cm^2 . The background pressure in the chamber during deposition was

between 10^{-5} and 10^{-6} torr. A typical deposition rate for these conditions ($\lambda = 3.4 \text{ } \mu\text{m}$, fluence = $2.7 \frac{\text{J}}{\text{cm}^2}$, spot size = 0.028 cm^2) was $3.5 \frac{\text{mg}}{\text{cm}^2 \cdot \text{macropulse}}$.

For purposes of comparison, an ArF excimer laser (Lambda Physik 305; $\lambda = 193 \text{ nm}$; FWHM = 30 ns) was used for UV PLD. The experimental setup has been described in detail previously²⁶. The laser was operated at a repetition rate of 10 Hz with the fluence varied between 150 to 300 mJ/cm². The target substrate distance was 3 cm. The spot size was between 0.06 and .13 cm² and the beam was rastered over the entire surface of the 1" diameter rotating target (35 rpm). Our starting material is PEG 1450 Carbowax (Alltech Associates, Deerfield, Ill.). 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 (fluence = $200 \frac{\text{mJ}}{\text{cm}^2}$, spot size = .13 cm²) was $0.01 \frac{\text{mg}}{\text{cm}^2 \cdot \text{pulse}}$.

Polyethylene glycol samples were analyzed using FTIR, ESI³³ and MALDI³⁴. Infrared spectra were recorded for the films using either a Bruker IFS 66 or 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 μL of methanol. For ESI, 20 μL 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. For MALDI, 2 μL of the reconstituted sample was mixed with saturated matrix solution (2-(4-hydroxyphenylazo)benzoic

acid, HABA, or dithranol/silver trifluoroacetate) and evaporated on the probe tip. Samples were desorbed with a 337 nm laser and spectra were obtained on a time-of-flight mass spectrometer.

Discussion and Results

The mid-infrared absorbance spectra of a drop cast, UV PLD, and IR PLD film are shown in Figure 1. For the sake of comparison, the absorbance spectra have been normalized to the CH₂ symmetric stretching feature at 2880 cm⁻¹. The spectra of the films deposited using IR light are identical, so only one ($\lambda = 3.4 \text{ }\mu\text{m}$) is shown for the sake of clarity. At 3.4 μm , the IR laser is resonant with the C-H stretch in the hydrocarbon. The spectra of the starting material and the IR PLD films' spectra exhibit no discernible differences. The spectrum of the film deposited using UV light, however, has changed dramatically. The OH absorbance has increased by a factor of 2.5 relative to the starting material and IR PLD film, while the maximum is shifted to higher wavenumber ($\Delta\omega = 20 \text{ cm}^{-1}$). The C-O-C symmetric stretching band at 1110 cm⁻¹ is reduced in intensity and the absorbance maximum of the symmetric CH₂ stretch is shifted ($\Delta\omega = -15 \text{ cm}^{-1}$) to 2867 cm⁻¹. Figure 2 shows an expanded view of the fingerprint region in which the CH₂ wag, twist, and bend modes are modified significantly in the UV-PLD experiment. We have used Refs. 23 and 35 as aids in spectral assignment.

One possible explanation of the shifts observed in the UV PLD films' spectrum involves scission of a C-O bond in the middle of the polymer. One fragmented chain could abstract a proton from the other fragmented chain, resulting in a terminal double bond on one of the fragments and an additional OH group on the other. There is an additional small band at 1650 cm⁻¹ that is consistent with the appearance of a terminal alkene. Fully understanding the exact nature of the chemical modification of the UV PLD films, however, will require further study.

Both ESI and MALDI have been used to determine the molecular weight distributions in the IR and UV-PLD films. In Fig. 3, the ESI results are shown. The UV PLD film shows almost no recognizable pattern relative to the standard in the mass spectrum. In contrast, the IR PLD film has a very similar mass spectrum to the starting material. By calculation based on the position of the peaks, we see that the mass average for starting material (1538) and IR PLD (2.9 μm = 1518; 3.4 μm = 1528) are identical to well within one monomer unit (44 amu). Additionally, the number average for starting material (1500 amu) and IR PLD (2.9 μm = 1508 amu; 3.4 μm = 1507 amu) are similarly close. The polydispersity ($\frac{M_w}{M_n}$) for the IR PLD films (1.01 – 1.05) is nearly the same as the starting material (1.03).

We note that there are some differences between the ESI spectrum of the IR PLD and standard samples in the ratios of singly and doubly-charged envelope of ions. These differences can be attributed to variations in the ratio of added KCl to polymer in the ESI samples. As this ratio increases, more multiply-charged ions are observed. Since the amount of polymer extracted from the surfaces varies from sample to sample, it is difficult to standardize this ratio. However, M_n and M_w values are calculated based on the contributions from singly, doubly and triply-charged ions, and thus account for shifts in the charge state distribution. ESI spectra obtained with various ratios of KCl to PEG standards shown that M_n and M_w will vary somewhat with this ratio; consequently, while small variations in molecular weight from sample to sample are not significant, large changes would be apparent.

MALDI measurements have also been performed on all three films. These results agree with the ESI mass spectra. They also verify that the region between $m/z = 600$ and $m/z = 1200$

of the UV PLD sample is largely comprised of singly charged ions, thus suggesting that we may bracket the mass average of the UV PLD film between 900 and 1000 amu.

It was also necessary to obtain the MALDI spectrum of the UV PLD sample under completely different conditions (using dithranol/silver trifluoroacetate) in order to observe signals. The ions observed are different in chemical composition than those formed from the PEG standard. This is consistent with the observation that most of the ions observed in the ESI spectrum of the PLD sample cannot be related to the starting material in a simple way. Similar to the FTIR spectra, the mass spectra show that IR PLD films and the starting material are nearly identical whereas the UV PLD film is shifted lower in molecular weight and chemically altered.

The mass and FTIR spectra indicate that in IR-PLD the polymer chains are transferred intact with the same physicochemical properties as the starting material. This is in stark contrast to UV PLD in which the initial electronic excitation is either converted to heat which results in depolymerization and subsequent re-polymerization^{12,13,14,15,18,19,21} on the substrate, or results in bond rupture and the deposition of modified oligimeric fragments^{16,17}. The fact that individual FEL micropulses are separated by 350 ps indicates that the anharmonic vibrational modes excited by the laser are probably fully relaxed between micropulses³⁶; however, since thermal diffusion times are comparable to the duration of the macropulse, it is also likely that the temperature of the ablation target is gradually rising throughout the macropulse. This complicates the analysis of the ablation mechanism. Rapid relaxation of anharmonic vibrational modes could mean that the ablation is a single photon process; on the other hand, heating of the target material during the macropulse could produce efficient ablation by “preheating” or more effective heating by strong coupling between local and dispersed phonon modes. Experiments are underway using different FEL pulse structures in order to investigate these questions. If it is

in fact the case that the ablation is primarily initiated by a single-photon excitation, then polymer chains must surely be transferred intact because the photon energy involved (0.36 - 0.42 eV) is far below the energy required for electronic excitation and direct bond rupture.

Conclusion

Analysis of thin films of PEG deposited by laser ablation using an infrared tunable source shows that the IR source is tuned to a resonant absorption in the polymer, the polymer is transferred to the growth surface without chemical or structural modification. In contrast, the use of a UV laser for deposition results in severe photochemical modification of the polymer material appearing in the films. Such physical and chemical rearrangement of the polymer renders UV-PLD unsuitable for applications such as drug delivery coatings and *in vivo* applications in which the polymer coating is required to be unchanged from the bulk material. Moreover, the use of a resonantly tunable infrared source provides a potentially more general approach to polymer thin film deposition than either UV-PLD, where undesirable photochemical or photothermal effects can occur, or MAPLE, which requires a non-interactive, light-absorbing matrix for film deposition. In addition, tunable infrared laser sources such as free electron lasers with their high macropulse energies and high average powers may well provide new opportunities for studying the mechanisms of polymer ablation and mode specific chemistry in such processes as IR-PLD.

Figure Captions

Fig. 1 Infrared Spectrum of (a) starting material, (b) UV PLD ($\lambda = 193$ nm), and (c) IR PLD film ($\lambda = 3.4$ μm). In (a), important modes are labeled (S = symmetric, AS = anti-symmetric).

Fig. 2 Expanded view of fingerprint region of infrared spectra. Note the agreement between the IR PLD and drop cast films' spectra. The UV PLD film's spectra shows evidence for chemical modification.

Figure 3 Electrospray ionization mass spectrum of (a) starting material, (b) UV PLD ($\lambda = 193$ nm), and (c) IR PLD film ($\lambda = 2.9$ μm). The UV PLD film's spectra is not recognizable compared to the starting material. The calculated molecular weights of the IR PLD film and the starting material are in very close agreement.

REFERENCES

- ¹ J. M. Harris, J. M. Dust, R. A. McGill, P. A. Harris, M. J. Edgell, R. M. Sedaghat-Herati, L. J. Karr, and D. L. Donnelly, in *Water-Soluble Polymers*, edited by S. W. Shalaby, C. L. McCormick, and G. B. Butler (ACS Symposium Series **467**, ACS, Washington, D. C. 1991), pp. 418-29.
- ² L. J. Suggs, E. Y. Kao, L. L. Palombo, R. S. Krishnan, M. S. Widmer, and A. G. Mikos, in *Polymers for Tissue Engineering*, edited by M. S. Shoichet and J. A. Hubbell (VSP, Utrecht, Netherlands, 1998), pp. 99-112.
- ³ N. Patel, R. Padera, G. H. W. Sanders, S. M. Cannizzaro, M. C. Davies, R. Langer, C. J. Roberts, S. J. B. Tendler, P. M. Williams, and K. M. Shakesheff, *FASEB J.* **12**, 1447 (1998).
- ⁴ S. O. Vansteenkiste, S. I. Corneille, E. H. Schact, X. Chen, M. C. Davies, M. Moens, and L. V. Vaeck, *Langmuir* **16**, 3330 (2000).
- ⁵ Y. Kaneko, K. Sakai, and T. Okano, in *Biorelated Polymers and Gels*, edited by T. Okano, (Academic Press, New York, 1998), pp. 29-69; M. Yokoyama, in *Biorelated Polymers and Gels*, edited by T. Okano, (Academic Press, New York, 1998), pp. 193-229.
- ⁶ C. M. Henry, *Chem. Eng. News* **78**, 49 (2000).
- ⁷ M. N. Mar, B. D. Ratner, and S. S. Yee, *Sensors and Actuators B* **54**, 125 (1999).
- ⁸ P. Favia and R. d'Agostino, *Surface and Coatings Technology* **98**, 1102 (1998).

- ⁹ *Pulsed Laser Deposition of Thin Solid Films*, edited by D. B. Chrisey, and G. K. Hubler (John Wiley & Sons, Inc., New York, 1994).
- ¹⁰ D. M. Bubb, R. A. McGill, J. S. Horwitz, J. M. Fitz-Gerald, E. J. Houser, R. M. Stroud, P. W. Wu, B. R. Ringeisen, A. Piqué and D. B. Chrisey, in press, *Journal of Applied Physics*.
- ¹¹ S. G. Hansen and T. E. Robitaille, *J. Appl. Phys.* **64**, 2122 (1988).
- ¹² G. B. Blanchet and S. I. Shaw, *Appl. Phys. Lett.* **62**, 1026 (1993).
- ¹³ G. B. Blanchet, C. R. Fincher Jr., C. L. Jackson, S. I. Shah, and K. H. Gardner, *Science* **262**, 719 (1993).
- ¹⁴ G. B. Blanchet, *Macromolecules* **28**, 4603 (1995).
- ¹⁵ G. B. Blanchet, *J. Appl. Phys.* **80**, 4082 (1996).
- ¹⁶ R. Srinivasan and W. Mayne Banton, *Appl. Phys. Lett.* **41**, 576 (1982).
- ¹⁷ H. H. G. Jellinek and R. Srinivasan, *J. Phys. Chem.* **88**, 3048 (1984).
- ¹⁸ J. H. Brannon, J. R. Lankard, A. I. Baise, F. Burns, and J. Kaufman, *J. Appl. Phys.* **58**, 2036 (1985).
- ¹⁹ G. B. Blanchet and C. R. Fincher Jr., *Appl. Phys. Lett.* **65**, 1311 (1994).
- ²⁰ H. R. Philipp, H. S. Cole, Y. S. Liu, T. A. Sitnik, *Appl. Phys. Lett.* **48**, 192 (1986).
- ²¹ G. B. Blanchet, P. Cotts, C. R. Fincher, Jr., *J. Appl. Phys.* **88**, 2975 (2000).
- ²² Y. Tsuboi and A. Itaya, *Appl. Phys. Lett.* **74**, 3896 (1999).
- ²³ P. Manoravi, M. Joseph, and N. Sivakumar, *J. Phys. Chem. Solids* **59**, 1271 (1998).

- ²⁴ J. C. Owrutsky and A. P. Baronavski, *J. Chem. Phys.* **111**, 7329 (1999).
- ²⁵ H. Kaczmarek, *Eur. Poly. J.* **31**, 1175 (1995).
- ²⁶ A. Piqué, R. A. McGill, D. B. Chrisey, D. Leonhardt, T. E. Mslna, B. J. Spargo, J. Callahan, R. W. Vachet, R. Chung, and M. A. Bucaro, *Thin Solid Films* **355-356**, 536 (1999).
- ²⁷ D. M. Bubb, B. R. Ringeisen, J. H. Callahan, M. Galicia, A. Vertes, J. S. Horwitz, R. A. McGill, E. J. Houser, P.K. Wu, A. Piqué, and D. B. Chrisey, submitted to *Journal of Materials Research*.
- ²⁸ B.R. Ringeisen, J. Callahan, P. Wu, A. Piqué, B. Spargo, R.A. McGill, M.Bucaro, H. Kim, D.M. Bubb, and D.B. Chrisey, in press, *Langmuir*.
- ²⁹ R. Srinivasan, *J. Appl. Phys.* **73**, 2743 (1993).
- ³⁰ B. G. Sumpter, D. W. Noid, and B. Wunderlich, in *Laser Ablation: Mechanisms and Applications*, Eds. J. C. Miller and R.F. Haglund, (Springer-Verlag, New York, 1999), pps. 334 – 343.
- ³¹ R. Cramer, R. H. Haglund, Jr., and F. Hillenkamp, *Int. J. Mass Spectrom. Ion Proc.* **169/170**, 51 (1997).
- ³² G. Edwards, in *Laser Ablation: Mechanisms and Applications*, Eds. J. C. Miller and R.F. Haglund, (Springer-Verlag, New York, 1999), pps. 457- 468.
- ³³ T. Nohmi, J.B. Fenn *J. Am. Chem. Soc.* **114**, 3241 (1992)

- ³⁴ G. Montaudo, MS Montaudo, C. Puglisi, F. Samperi *Rapid Comm. Mass Spectrom.* **9**, 453 (1995).
- ³⁵ Brian Smith, *Infrared Spectral Interpretation*, (CRC Press, New York, 1999).
- ³⁶ Nicholas J. Turro, *Modern Molecular Photochemistry* (University Science, Sausalito, CA, 1991), pg. 174.

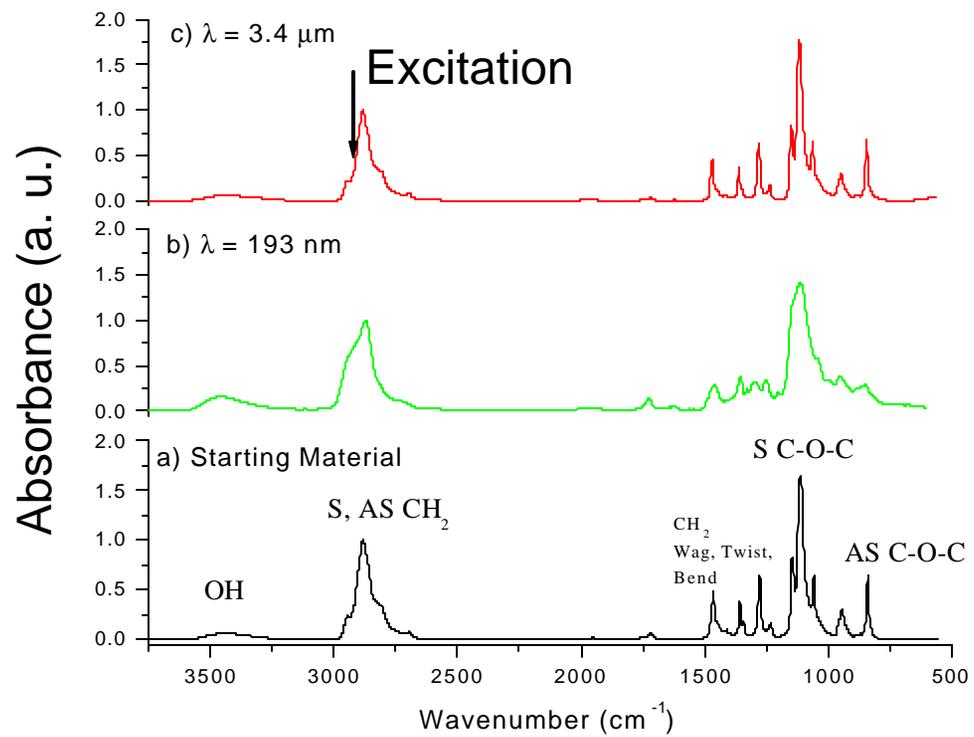


Fig. 1

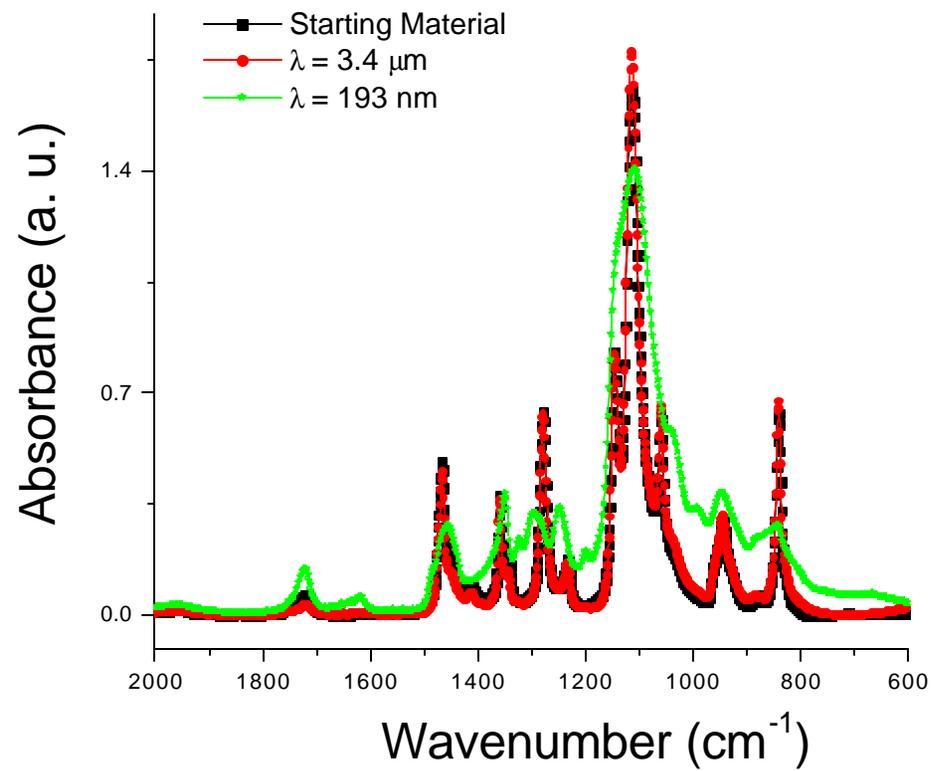


Fig. 2

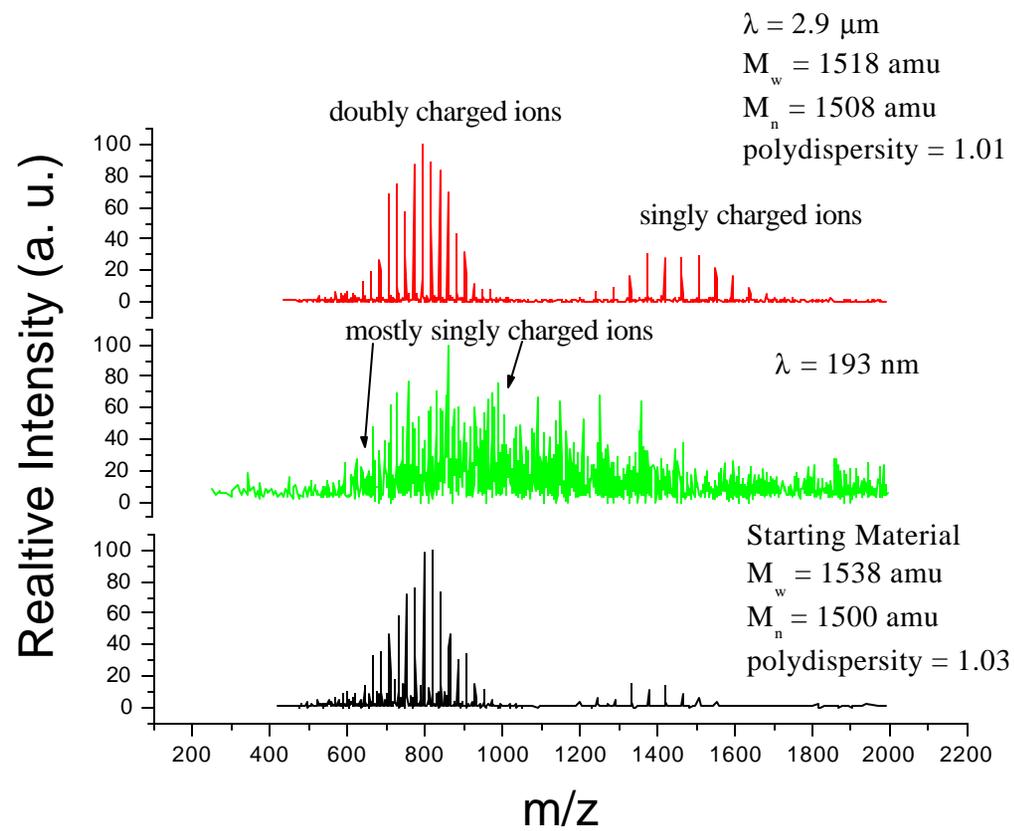


Fig. 3