The Influence of Laser Energy of MALDI on the Molecular Mass Distribution of Synthetic Polymers

Stephanie J. Wetzel[1], Charles M. Guttman[2] and James E. Girard[1]

[1]American University, Department of Chemistry, Washington, D.C.
[2]National Institute of Standards and Technology, Polymers Division, Gaithersburg, MD 20899

Introduction

The desorption/ionization process of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) is not completely understood. Characterization of synthetic polymers by MALDI-TOF-MS is very sensitive to the instrument and sample preparation parameters that are needed to obtain a mass spectrum. The molecular mass distribution (MMD) that is obtained in polymer characterization may be biased by preferential desorption/ionization of low mass polymer molecules, preferential ion attachment to larger polymers, or degradation and fragmentation due to the desorption process. In this study we focus on the effect of the laser energy on the molecular mass distribution of three narrow synthetic polymers of varying thermal stabilities.

Method

Three synthetic polymers were analyzed by MALDI-TOF-MS: SRM2888, a 7 ku polystyrene (PS) sample, a 5 ku polyethylene glycol (PEG) sample, and SRM1487, a 6 ku polymethylmethacrylate (PMMA) sample. Of these three polymers, polystyrene has the highest relative thermal stability, and PMMA has the lowest relative thermal stability [1]. Each polymer sample was run in two different matrixes. PS was run in dithranol and *all trans*-retinoic acid (RA) and silver trifluoroacetate (AgTFA) was added for cationization. The PEG sample was run in 2,5-dihydroxybenzoic acid (DHB) and dithranol, and a sodium trifluoroacetate (NaTFA) salt was added. The PMMA sample was run in DHB and *trans*-3-indole acrylic acid (IAA) with NaTFA added. The polymer samples using dithranol as the matrix were electro-sprayed onto the MALDI probe. All other polymer samples were hand-spotted onto the MALDI probe.

The polymer mass spectra were obtained using a Bruker Reflex II MALDI-TOF-MS [2]. The laser power was varied between 1 μJ and 8 μJ. The laser power range for each sample was defined by the ability to obtain mass signal. Three MALDI mass spectra were obtained for each laser power.

The polymer mass distributions obtained by MALDI-TOF-MS were divided into six equal bins for each polymer sample. The area of the MMD in each bin is then determined and normalized before comparison. Analysis of variance (ANOVA) was used to determine which bins were influenced by the changes in laser power. The significance level of the ANOVA (α) was chosen to be 0.05. ANOVA compares the bin fraction or moment variance within a laser power with the bin fraction or moment variance among laser powers to determine if there is a significant influence of laser power on the moment or bin fraction of the polymer distribution. A bin or moment is said to have a significant variation when the variance among laser powers is greater than the variance of the bin fraction or moment at a given laser power. Trends in the data explain possible effects of laser power.

Results

In the analysis of polystyrene, the M_n was analyzed as well as the six bins. The moments of polystyrene as laser power increases are seen in figure 1. The polystyrene moments in dithranol and RA

were both found to vary significantly by ANOVA. The M_n increases to a maximum and then decreases as the laser power is increased. The analysis of the bins of PS in dithranol reveals that the
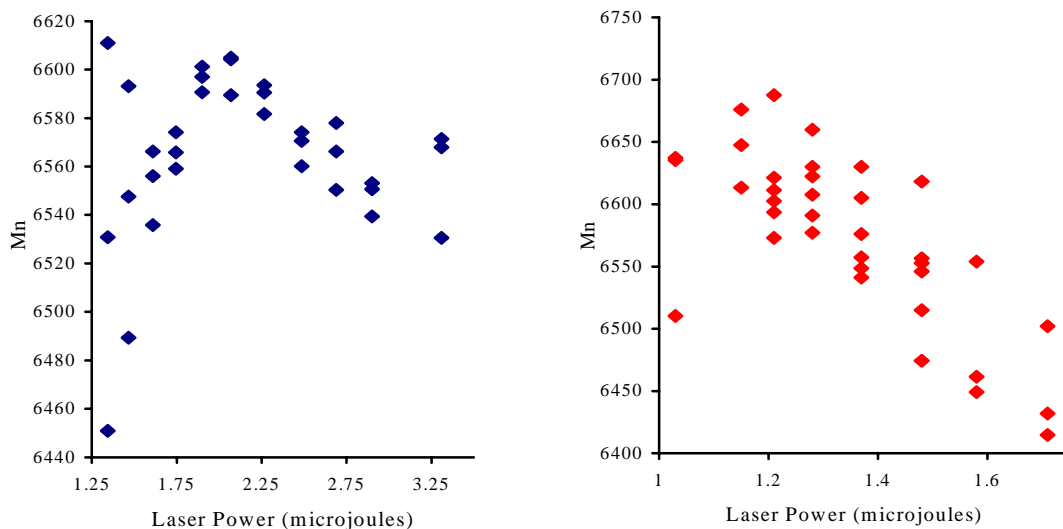

Figure 1. (a) A graph of the M_n of polystyrene in a dithranol matrix vs. laser power. (b) A graph of the M_n of polystyrene in RA vs. laser power.

fractions of the MMD in bins 5 and 6 increase until a laser power of about 2.5 µJ is reached and then level off. This increase in the fraction of the MMD contained in the high mass bins also occurs in the bins of PS in RA.

The analysis of PEG in DHB showed that all six bins were significantly influenced by laser power. The MMD fractions in bin 1 increased, the fractions in bins 2 and 3 increase to a maximum and then decrease, the fraction in bin 4 decreases and the fractions in bins 5 and 6 decrease and level off as laser power is increased. This indicates that the PEG sample is fragmenting as the laser power increases. The analysis of the bins of PEG in dithranol revealed that only bins 1,2,3 and 5 are significant. The MMD fraction in bins 1 and 5 increase and the fractions in bins 2 and 3 decrease as laser power increases.

The analysis of the PMMA in DHB data revealed that bins 2, 5 and 6 are influenced significantly by changes in laser power. The bin 2 fractions decrease with increased laser power and the MMD fractions in bins 5 and 6 increase with increased laser power. This increase in the high mass bin fractions indicates that as the laser power is increased more high mass polymer is desorbed into the gas phase. The analysis of PMMA in IAA yielded no bins that were significantly influenced by laser power. Since PMMA has the lowest thermal stability of the three polymers, it is unexpected that there is no degradation of PMMA apparent in the bin analysis. If any fragmentation peaks exist though, they are in the matrix region of the mass spectrum and are not included in the bin data.

Conclusions

The analysis of PS reveals that as laser power is increased, the moments and the high mass bins increase to a maximum. This may be due to more high mass polymer desorption at higher laser powers. As laser energy is increased, fragmentation begins to occur, causing a decrease in the polymer moment and the high mass bins. The analysis of the bins of PEG reveals that the polymer sample is fragmenting, and more fragmentation is seen as laser power is increased. The PMMA analysis shows that as laser power is increased, the high mass bins are increasing. This is due to increased desorption of the high mass polymer molecules as laser power is increased.

1. Madorsky, Samuel, L., *Thermal Degradation of Organic Polymers*. Interscience Publishers: New York, 1964.
2. Certain commercial items are identified in this paper in order to adequately specify the experimental procedure. This does not imply endorsement by NIST.