

A Study of the Effects of MALDI Matrix and Laser Energy on the Molecular Mass Distribution of Synthetic Polymers

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Introduction

The characterization of synthetic polymers by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) has yielded inconsistent results, indicating that the MALDI-MS-determined molecular mass distribution (MMD) is sensitive to instrumental and sample preparation parameters used to obtain the polymer mass spectrum.¹⁻⁶ The disparity of these results produces questions as to the accuracy and repeatability of the MALDI-TOF-MS method creating a need to carefully define these parameters. We considered the effects of laser energy and matrix on the MMD of several polymers of varying thermal stability.

Method

Four synthetic polymers were analyzed: a 7 ku polystyrene (PS) sample, a 5 ku poly(ethylene glycol) (PEG) sample, an 8 ku poly(methyl methacrylate) (PMMA) sample, and an 8 ku poly(tetrahydrofuran) (PTHF) sample. The moments of each MMD obtained by MALDI-TOF-MS were obtained at different laser energies and in each of three different matrices; all-*trans*-retinoic acid (RA), dithranol and 2,5-dihydroxybenzoic acid (DHB). The estimated standard uncertainty of M_n obtained by MALDI-TOF-MS is 50 u.

Results and Discussion

The mass distributions for PEG, PMMA, and PTHF all show noticeable changes in different matrices, through a distinct secondary series, an increased tailing, or a varying distribution shape, as shown in Figure 1 for PTHF. The M_n values in Table 1 show little difference between those run in RA and dithranol, but the M_n values are always lower for the distributions obtained in DHB. PEG, PMMA and PTHF run in DHB at different laser energies show an increased low-mass tail at higher laser energies, and the PEG MMD shows a secondary series at higher laser energies.

Polymer	Matrix	Laser Energy	M_n
		$\mu\text{J/pulse}$	g/mol
PTHF	RA	0.87-2.12	7898
	DHB	2.32-5.52	6737
PMMA	RA	0.88-1.34	7316
	DHB	2.84-6.22	7011
PEG	RA	0.96-1.82	4359
	Dith	1.53-5.03	4339
	DHB	1.98-7.49	4219
PS	RA	1.03-2.30	6565
	Dith	1.34-3.31	6565
	DHB	3.46-5.52	6265

Table 1. The M_n and laser energy data for PS, PEG, PMMA, and PTHF in RA, dithranol and DHB.

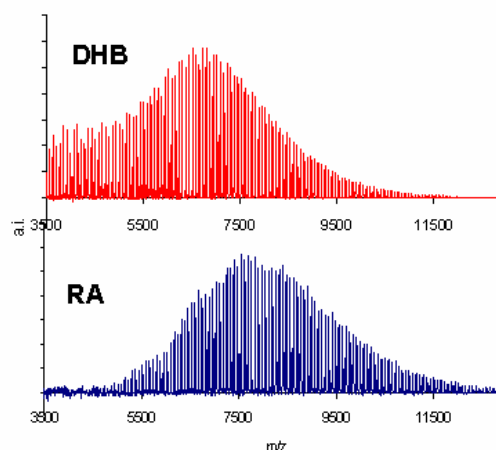


Figure 1. PTHF mass spectrum in DHB and RA

The secondary series in the PEG mass spectra arises from fragmentation. Fragmentation occurs at the oxygen-carbon bond of the PEG repeat unit.⁷ Each PEG oligomer which fragments produces two discernible fragment molecules. The fragmentation peak series is shifted sixteen mass units from the main series of the MMD. If the assumption is made that the PEG molecule is equally likely to fragment anywhere along the polymer chain, then the distribution of the fragmentation peaks with no end group

change should be the same as the distribution of the fragment ions with an end group change, allowing the fragmentation to be subtracted from the PEG MMD.

The molecular mass moments of the original data and those calculated after the fragmentation peaks were subtracted, which are shown in Table 2, are averaged over all laser energies for each matrix. Regardless of matrix, all the moments increase after the fragmentation is subtracted. Changes to the effect of laser energy on the molecular mass distribution due to the subtraction of the fragment peaks are considered in Figure 2. Each matrix seems to have a different effect on the molecular mass distribution of PEG.

Matrix	M _n	Corrected M _n
RA	4348	4385
Dithranol	4080	4206
DHB	4208	4416

Table 2. The original PEG M_n and the corrected PEG M_n in RA, dithranol and DHB.

When PEG is analyzed in RA, no effect of laser energy on the molecular mass distribution is seen. The fragmentation and change in the M_n for the PEG in RA is the same for all laser energies. When PEG is analyzed in DHB, the M_n decreases as laser energy increases. However, when the fragmentation peaks are subtracted from the mass distribution, the M_n remains constant, independent of laser energy. In dithranol, the original PEG data revealed an increase in M_n as laser energy increases. This trend in the data remains after the fragmentation peaks are subtracted from the PEG molecular mass distribution, indicating that although there is an effect of laser energy on the PEG mass distribution, it is not only due to fragmentation.

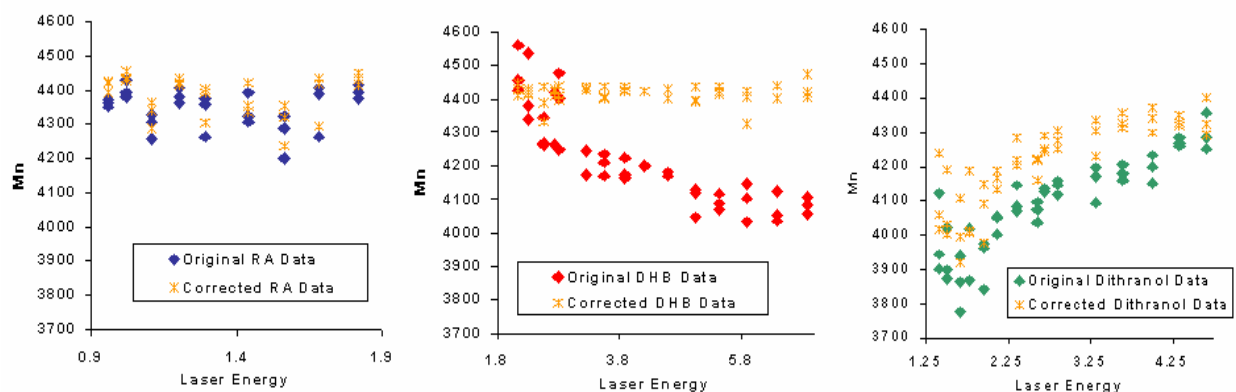


Figure 2. The M_n of the original PEG spectrum and the corrected PEG spectrum in RA, DHB and Dithranol as laser energy increases.

Conclusions

The analysis of the four polymers reveals an influence of both matrix and laser energy on the polymer mass distribution. The effect of the laser energy is matrix dependent. Little or no fragmentation is seen when the polymers are analyzed with RA or dithranol as the matrix, but a more intense fragmentation pattern is seen in the mass spectra when DHB was the matrix. The results of the analysis reveal that the matrix plays a greater role in the desorption/ionization process than just enabling desorption of intact polymer into the gas phase.

References

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