Quantitation of Polymer End Groups Using MALDI TOF MS

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Introduction
Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI TOF MS) offers a unique probe of the end group functionality of synthetic polymers with resolution of oligomeric species distinguished according to their individual lengths. Although there have been reports in which researchers demonstrated the ability to identify end groups within a mixture of polymers, little work has been done to examine the relative peak intensities in the spectra of these mixtures and whether the peak areas are representative of the weight proportion of each polymer in the sample. Our approach in this work is not simply to identify the end groups present in a mixture of polymers. Rather, we wish to determine of we can quantitatively measure a mixture of polymers with repeat units which are chemically the same but with end groups which are chemically different.
In this study we consider vary the mass of each polymer in a mixture of polymers from 75% of one to 75% of the other. We consider the effect of mass of each polymer and two important parameters in the development of MALDI, the matrix used with the polymer and the laser energy.

Method
MALDI TOF MS has been employed to analyze mixtures of polystyrenes of molecular mass ca. 4000 u. The component polymers of these mixtures are identical except for their end groups. The total mass of hydrogen-terminated polystyrene (PS) and monohydroxy-terminated polystyrene (PSOH) were prepared in various mixtures ranging from 75% of one to 75% of the other and analyzed by MALDI TOF MS. Each polymer mixture was measured using 2,3-dihydroxybenzoic acid (DHB), dithranol, all-trans retinoic acid, and trans, trans-1,4-diphenyl-1,3-butadiene matrices. Silver trifluoroacetate (AgTFA) salt was used as a cationization agent.
The MALDI TOF mass spectrometry data were obtained using a Brucker Reflex II (Billerica, MA) TOF mass spectrometer, operated in reflectron mode. The laser energy was varied between $0.7\mu J$ and $3.8\mu J$. The range of laser powers chosen for each matrix was based on the intensity of the polymer signal obtained.
The relative amount of each type of polystyrene contained in the samples were inferred by computing the peak areas from the mass spectral data. The ratios of the peak areas of each type of polystyrene in the mixture were then compared to the mass fractions of the polymers.

Results
Figure 1 shows a MALDI TOF mass spectrum of a mixture of hydrogen-terminated polystyrene (PS) and monohydroxy-terminated polystyrene (PSOH) in a 50%PS:50%PSOH (1:1) mass ratio. The overall shape of the distribution of the mixture appears the same as those of the individual polymers, since they both contain the same average molecular mass and polydispersities. Figure 2 shows an inset of the mass spectrum of the mixture. Although two polymer masses were measured during the preparation of the mixture, the inset shows that the distribution actually contains three major series of peaks. One series corresponds to hydrogen-terminated polystyrene, while the other two series correspond to the monohydroxy-terminated polystyrene. The dominant series from the monohydroxy-terminated polystyrene peaks represent the polymers in the mixture containing an ethanol termination (PSOH). The minor series from the monohydroxy-terminated polystyrene peaks represent the polymers containing an ethoxy-ethanol termination (PSOHOH).
The ratios computed from polystyrene mixtures in DHB matrix are shown in figure 3. It contains a comparison of the ratio values obtained by integrating the peaks corresponding to each type of polymer in the spectra measured in DHB matrix to the mass fractions of the polymers used to prepare the mixtures. A linear relationship of the type expected appears to exist between the calculated ratio and the mass ratio until a ratio of 65%PS:35%PSOH is reached. At this point, the deviation from linearity and the variance in the data increases significantly. This pattern of increasing variance with decreasing relative amount of PSOH was present in all of the matrices studied.

Figure 4 shows the peak area ratios as a function of laser energy for the mass spectra measured in DHB matrix. There did not seem to be any significant change in the ratios computed across this range of laser powers employed for samples studied in DHB matrix. The consistency in the peak ratios across changes in laser energy was present in all of the matrices studied.

Conclusion

The results of this experiment show that the peak areas in the MALDI spectrum do not directly represent the mass fractions of the component polymers in the mixtures analyzed. This has been demonstrated by the fact that a linear relationship with a slope proportional to the ratio of the number average molecular mass moments of the polymers was not observed between the calculated ratios of the areas and the mass fractions of the polymers.
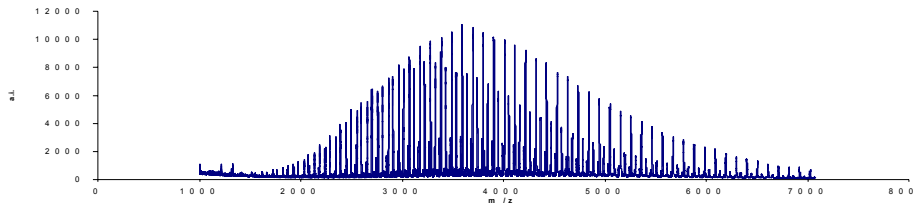

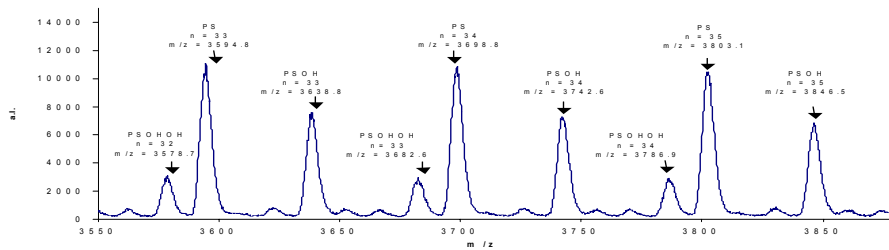Figure 1. MALDI TOF mass spectrum of a mixture of PS and PSOH in a 50%PS:50%PSOH mass fraction.

Figure 2. Inset of the region m/z 3550-3900 of the MALDI TOF mass spectrum of a mixture of 50%PS:50%PSOH.
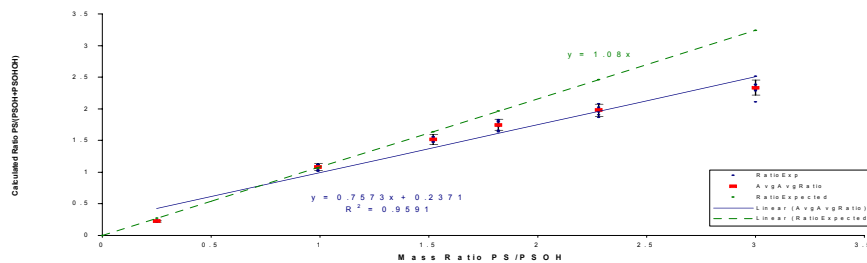

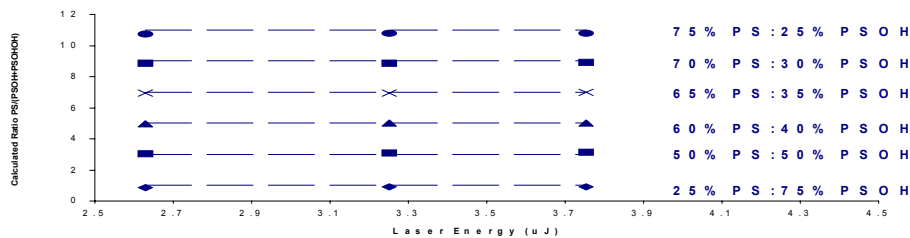Figure 3. Polystyrene ratios measured in DHB matrix.

Figure 4. Peak area ratios computed in DHB matrix as a function of laser energy.