

International Interlaboratory Comparison of Mixtures of Polystyrenes with Different End Groups Obtained by Matrix Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF-MS): Preliminary Results

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Introduction

National Institute of Standards and Technology (NIST) has sponsored a MALDI-TOF-MS interlaboratory comparison (IC) of mixtures of synthetic polymers of the same repeat unit and with closely matching molecular masses but with different end groups. This IC was designed to determine how well a group of laboratories from all over the world agree on the percent composition of each polymer in the mixture. In an earlier IC, NIST studied the molecular mass distribution (MMD) and the moments obtained by MALDI on a polystyrene (PS) and compared the results with classical methods.¹ In the current IC, PS's of a molecular mass around 9000 u with two different end groups were used. The PS's were both initiated with butyl initiator. One was terminated with H (PSH) and the other was terminated with a CH₂CH₂OH (PSOH). Five mixtures of these were made up with mass ratios between approximately 95:5 to 10:90 PSOH:PSH. Samples of these five mixtures were sent to institutions requesting a sample set. A total of 14 institutions participated in the IC.

Materials And Sample Preparation

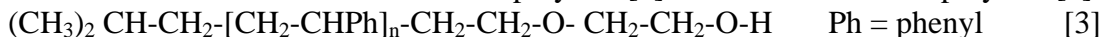
The PSH and PSOH used in this IC were obtained from commercial sources. The products as received from the suppliers are called PSOH-material and PSH-material in the rest of the text. From the preparation chemistry indicated by the suppliers, we expected the PSH-material to be polymer [1].



For the PSOH-material, we expected the polymer to be mainly PS polymer [2].



Due to the difficulty in producing fully functionalized polymer it is expected that some of the PSOH-material could contain some amount of polymer [1] and some amount of polymer [3].



An initial MALDI study by us indicated that about 5 % by mass fraction of polymer [1] was present in the PSOH-material and less than 1 % by mass fraction of polymer [3] was present. An earlier MALDI study by Weaver et al² indicated that [3] was very easily detected by MALDI suggesting that we have little or none of polymer [3] in material-PSOH.

It should be noted that the PSOH-material as supplied was found to have a within bottle variation for its MMD indicating that the sample within the bottle was inhomogeneous. Thus to avoid such variations, toluene solutions were made up of all polymer materials and these were mixed in weighed proportions to make up the final solutions. About 0.5 mL of the toluene solutions were put into 4 mL vials; the solvent was then evaporated off. These vials were sent to each IC participant with instructions to add at least 0.5 mL of solvent to dissolve all the material for the MALDI sample preparation.

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NMR and FTIR done at NIST confirmed the gravimetric mass ratio. NMR was used to estimate the fraction of PSOH polymer and PSH polymer in the PSOH-material. NMR gave between (4 to 9) % PSH polymer in the PSOH-material. This is close to the value obtained from the initial MALDI analysis done at NIST

Method

Each participating laboratory was asked to perform MALDI mass spectrometry on each of the five mixtures using two distinct protocols: one using all-trans retinoic acid with defined concentrations of matrix:analyte:salt and a second protocol defined by the user as their preferred method for analyzing polystyrene. Each laboratory was asked to do two repeats of each protocol for each mixture to check for interlaboratory variability. Each laboratory was asked to send the estimated ratio of the mass of PSH to the mass of PSOH in each mixture and data sets listing mass versus the integrated peak area of the mass spectra.

Preliminary Data

Figure 1 below shows a plot of the "Theoretical Mixture PSOH" polymer fraction assuming 7 % PSH polymer in the PSOH material from the NMR. This result is compared to MALDI data from some of the participating laboratories. The agreement is generally good but the data show a wide range of variability among the laboratories. Deviation of the data from the expected percentages was found widest at the extremes of concentration of 95:5 and 10:90 PSOH: PSH, but even at the 50:50 ratio the deviation was as high as 10 %.

The agreement and standard deviation of data are shown in Table 1. The fraction of PSOH polymer in each mixture is given in the 2nd column. This column assumes the PSOH-material is 7 % PSH polymer and 93 % PSOH polymer . Seven percent is the mid point of the range assigned by the NMR. It is seen from both Fig. 1 and Table 1 that the agreement between the MALDI and the gravimetric results for the fraction of PSOH polymer in each mixture is good when judged by the standard deviation of the MALDI results. Finally, a preliminary study on the effect of various parameters in an ANOVA study of the data indicates that the lab-to-lab variation is important. As in our earlier interlaboratory comparison, we also found there was a mass axis calibration problem with many participating laboratories. Some labs had calibrations off by 30 u for polymers with a number average molecular mass of about 9000 u.

1. C. M. Guttman et al., Analytical Chemistry, vol. 73, p1252-1262 (2001)
2. A. Weaver et al., Proceeding of 50th ASMS Conference on Mass Spectrometry and Allied Topics, June 2002, Orlando, FL.

Table 1
Fraction of PSOH-polymer

| | | Ave | Stdev |
|-------|-------|-------|-------|
| Mix A | 0.93 | 0.933 | 0.051 |
| Mix B | 0.716 | 0.746 | 0.086 |
| Mix C | 0.481 | 0.47 | 0.041 |
| Mix D | 0.284 | 0.259 | 0.051 |
| Mix E | 0.086 | 0.117 | 0.2 |

Figure 1

