

Comparison of Classical and MALDI-TOF-MS Analysis of a Polystyrene Interlaboratory Sample

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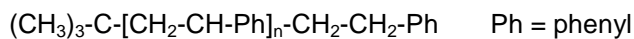
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Introduction

Over the past several years, the use of MALDI-TOF-MS for analysis of synthetic polymers has increased significantly. As the number of polymer analyses by MALDI has increased, scrutiny of the MALDI results in comparison to classically derived values for M_w , M_n and MWD, defined as the mass average molecular mass, the number average molecular mass and the molar mass distribution, respectively, has resulted. The results of MALDI and classical analysis do not always agree. In anticipation of the need for reference standards for calibration and intercomparison of current and future MALDI analytical methods, NIST has initiated an intercomparison of M_n and M_w determinations by MALDI.

Preparation and Bottling

The polystyrene (PS) polymer used in this interlaboratory comparison was prepared commercially for the NIST Polymers Division. A sufficiently large quantity was obtained to permit use of this polymer as a possible MS narrow distribution polymer standard. The polymer was specially prepared by anionic polymerization with well defined styrene and tertiary butyl end groups. From the preparation chemistry, we expected the polymer to be:



FTIR on the polymer independently confirmed that the end groups were as expected.

Homogeneity testing was done by size exclusion chromatography (SEC) with samples selected by stratified random sampling [1]. A Waters 150-C ALC/GPC Liquid Chromatograph (Waters Corp., Milford, MA) with a differential refractive index (DRI) detector was used in this study. Tetrahydrofuran (Mallinkrodt Specialty Chemicals, Paris, KY) with added antioxidant, 2,6-di-tert-butyl-4-methyl phenol (commonly known as butylated hydroxytoluene or BHT), was used as the solvent. Toluene at 0.3 g/L was added to the solvent used in preparing solutions as a SEC pump marker.

Two solutions in tetrahydrofuran were made from each polymer sample vial. The polystyrene samples were dissolved in the solvent at a concentration of approximately 1.0 g/L. The order of preparing the solutions and running the chromatograms was randomized. SEC was performed on these solutions using two injections from each solution.

After baseline subtraction, the SEC chromatograms were normalized to unit peak height and compared initially by overlaying to decide if there were visible differences outside the noise. The chromatograms from different solutions all superimpose on each other. This preliminary comparison showed that polymer samples taken from all the vials produced identical chromatograms. A statistical analysis on the chromatography confirmed these visual observations [1].

Light Scattering Methods

Light scattering measurements on toluene solutions of the PS were made on a Brookhaven Instrument Model BI-200 (Brookhaven Instrument Corp., Ronkonkoma, NY) light scattering apparatus with a 10 mw He-Ne laser light source. The temperature was controlled at 25.0 C in all light scattering experiments. In all experiments, the intensity measuring system was calibrated with the intensity of light scattered from the beam at a 90° angle by a benzene standard cell. The scattering intensity from each polymer solution sample was measured at ten angles in the range from 30.0° to 142.5°.

Light scattering data from polymer solutions of concentration c and scattering angle x was fit following normal Zimm Analysis [1]. The constant multiplying M_w depends quadratically on (dn/dc) , the change in refractive index of solution as a function of concentration. Normally for homopolymers (dn/dc) is independent of molecular mass. At lower molecular mass however, because the refractive increments from the end groups are different than that of the repeat units, we expect the (dn/dc) to have the form

$$dn/dc = A + B/M_n$$

For the PS polymer used in the intercomparison, we measured (dn/dc) and found it to be (0.1030 ± 0.0010) mL/g. Such dn/dc corrections are also important in SEC at low molecular masses of the polymer. With this (dn/dc) we estimate $M_w = (7300 \pm 600)$ u. The methods of data and uncertainty analysis used here are described in reference [1].

NMR Methods

Proton NMR spectra at 400 MHz were run at ambient temperature on a WM-400 spectrometer manufactured by Bruker Instruments, Inc. Resolution was found to be adequate for evaluating the integrals of interest, for both the 5% and the 13% solutions, under the following conditions. Spectra were taken with single pulse excitation. Pulse nutation ('tip') angle was 30 degrees and the delay between acquisitions was 20 s. This combination of conditions was confirmed to give quantitative results for all protons. Signal accumulations after 64 scans had adequate signal-to-noise in the Fourier Transform spectra for evaluating the integrals of interest. The Fourier transforms were made large enough, by zero-filling, so that the relative integrals, for even the narrowest lines, were reliable. Integrals on the NMR spectra of the intercomparison PS were measured. Based on the assumed structure for the PS polymer shown above, the integrals (of both aromatic and aliphatic PS protons plus the end-group methyl protons) measured from the NMR, yield an M_n of 7100 u based on measurements from the 5% solution and M_n of 7000 u, based on the measurements of 13% solution. The 13% solution had worse resolution, as expected from a more concentrated solution, but smaller corrections had to be made to the measured integrals than for the 5% solution. Thus the confidence level from each solution was similar. We estimate from NMR the $M_n = (7050 \pm 400)$ u.

MALDI

The spectra main peaks generally agree with the structure drawn above. There are some intermediate peaks perhaps indicating additional end groups. In another presentation at this meeting (MOA 11.35), those intermediate peaks are shown to result from polymer-matrix fragmentation. The overall M_w and M_n for the average of the interlaboratory data, with retinoic acid, is given as $M_n = 6600$ u with a standard deviation of 100 u and $M_w = 6700$ u, with a standard deviation of 90 u. No overall uncertainty can presently be estimated for these data. These results are discussed in detail in poster # ThPJ 275.

Conclusions

Within reported uncertainties, for this polymer, both the M_n and M_w derived from classical and MALDI techniques overlap.

References

1. Guttman, C. M.; Blair, W. R.; Maurey, J. R. Recertification of SRM 706a, a Polystyrene. Nat. Inst. Stds. and Tech. (U.S.) NISTIR 6091; 1998 March. 20 p.
2. Certain commercial items are identified in this paper in order to adequately specify the experimental procedure. This does not imply endorsement by N.I.S.T.