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Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry: determining Mark–Houwink–Sakurada parameters and analyzing the breadth of polymer molecular weight distributions

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Abstract

Polystyrene, poly(methyl methacrylate), and poly(ethylene glycol) standards were characterized via matrix-assisted laser desorption/ionization (MALDI) mass spectrometry. This study develops two new contributions to the rapidly growing body of data appearing in recent literature. First, MALDI was found to be an optimum absolute molecular weight technique accompanying viscosity measurements for determining Mark–Houwink–Sakurada parameters. Second, since MALDI provides the mass spectra of polymer molecules without fragmentation, a new method of describing the breadth of the distribution of polymer standards is presented. The ratio of the distribution breadth at half-height to the molecular weight of the monomer unit, polymer spread, is shown to more clearly represent the molecular weight distribution than the customary ratio, M_w/M_n. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Matrix-assisted laser desorption/ionization; Mark–Houwink–Sakurada parameters; Molecular weight distribution

1. Introduction

In the late 1980s, the development of the soft ionization technique, matrix-assisted laser desorption, made it possible to ionize and desorb macromolecules without fragmentation [1]. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry was first used to characterize biopolymers [1–4]. MALDI studies were soon extended to the characterization of synthetic polymers and dendrimers, since it provides absolute molecular weight distributions, as well as important structural information [5–10]. Conventional techniques, such as light scattering and membrane osmometry are termed ‘absolute’ techniques and yield molecular weight averages, but provide no information on distributions. Gel permeation chromatography provides relative molecular weight distributions, however, data are complicated by polymer–solvent interactions and must be accompanied by calibration with narrow molecular weight standard polymers. More intensive studies supplement GPC data with light scattering and universal calibration curves [11,12]. MALDI allows the rapid determination of number (M_n) and weight average molecular weights (M_w), and absolute molecular weight distribution, or polydispersity (PD) via one simple but sophisticated experimental measurement. The classic definitions of polymer molecular weight are [13]:

$$M_n = \frac{\sum N_x M_x}{\sum N_x} \tag{1}$$

and

$$M_w = \frac{\sum N_x M_x^2}{\sum N_x M_x} \tag{2}$$

where M_x is the molecular weight of a molecule corresponding to a degree of polymerization x, N_x the total number of molecules of length x, M_n the number average molecular weight, and M_w is the weight average molecular weight. The PD is used to estimate the breadth of the distribution and is calculated as given by Eq. (3)

$$\mathrm{PD} = \frac{M_w}{M_n} \tag{3}$$

MALDI also provides the modal or maximum value of the molecular weight. A logical term to give the modal is the most probable molecular weight (M_p), which has been used in GPC and in other MALDI experiments in conjunction with the standard terms, M_n and M_w. M_p values tend to be about two monomer units less than values determined by

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GPC [6,14]; however, in a study conducted by Jackson and Larsen [15], the most probable peak values were shown to remain consistent for each of several polymer standards analyzed in different labs with varying procedures.

MALDI studies began and continue to focus on refining techniques and identifying new matrices to be used with synthetic polymers [16–20]. Several authors described studies characterizing oligomers and low molecular weight polymers via this technique [16,21–24], and as research continued, the molecular weight range examined soon extended to the hundreds of thousands and has been documented to a weight of 1.5 million for polystyrene (PS) [8,25–27]. While the use of MALDI to obtain polymer molecular weights increased throughout the 1990s, a conclusion resulted from all of these studies—MALDI is an optimum technique for polymers with narrow molecular weight distributions, while problems emerge with polydisperse polymers [7,8,21,22,24,25,28–31]. Different data processing schemes have been tried with limited success on broad molecular weight polymer spectra [32,33]. There are several problems encountered with MALDI measurements on polydisperse samples. These problems include: the signal being spread over many molecular weight species giving rise to a low signal to noise ratio, the different chain lengths require different intensities of laser power (when the laser power is increased to compensate for the low signal of the longer chain lengths, fragmentation of the shorter chain lengths increases, distorting the signal), and for most polymers the ionization process produces dimers and trimers along with multi-charged species, creating the possibility of overlap of these spectra [19,31].

Montaudo et al. developed a methodology for analyzing polydisperse samples by coupling gel permeation chromatography results with MALDI data [17]. Via this method, GPC fractions are analyzed by MALDI, determining the average molecular weight of each fraction. These molecular weights are then used to calibrate the GPC curves. These findings have led to the use of MALDI as a detector in size exclusion chromatography fractionations of polydisperse polymers [6,34–36].

Since MALDI is particularly suited for measuring narrow molecular weight polymers, it is a logical choice for characterizing polymer standards [29]. While GPC–MALDI studies have previously been conducted to determine molecular weights of polymers [6,34–36], this paper takes a novel approach, utilizing the MALDI technique along with viscosity measurements, to generate Mark–Houwink–Sakurada (MHS) parameters. The MHS relationship shown below is widely used in polymer science to obtain molecular weight information [37,38]. Viscosity average molecular weights (M_v) are calculated from this relationship. First, however, the constants, K and α, must be determined from a series of narrow molecular weight distribution polymers that have been characterized by another absolute weight technique, usually light scattering. The intrinsic viscosity ($[\eta]$) of each of these polymer standards is determined using the relationship [38]:

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 c} \tag{4}$$

where η_0 is the solvent viscosity, η the dilute solution viscosity, and c is the concentration. Intrinsic viscosities of the standard samples are then used to determine the parameters, K and α via equation

$$[\eta] = KM^{\alpha} \tag{5}$$

where K and α are constants determined from logarithmic plots of intrinsic viscosity versus the molar mass (M) as determined by light scattering. These constants are then used to calculate the molar masses of additional samples of unknown molecular weight. The only measurement required is the intrinsic viscosity. Molar masses calculated this way are viscosity average molar masses (M_v). While this study determines M_v, in place of M_n or M_w, its importance lies in the ability to determine the molecular weight of polymer standards without the use of sophisticated equipment once the K and α values have been determined.

The constants, K and α, are specific to polymer chemistry, configuration, molar mass distribution, solvent and temperature. Elias [39] summarizes theoretical predictions for α. This α depends on the shape and segmental distributions of the molecules. According to theory, $\alpha = 0$ for spherical molecules and 0.5 for unperturbed coils. Unperturbed coils are generated in theta solvents (solvents in which the intermolecular forces are similar in magnitude to the intramolecular forces, thus generating the unperturbed coil [40]), whereas, $\alpha = 0.764$ in good solvents. Infinitely thin, rigid rods have α values of 2.0. Worm-like polymer chains exhibit α values that range from 0.764 to 2.0. High values are encountered with rigid chains of low molar mass. High molar mass, flexible chains have lower α values [39].

Dilute solution viscosity is the most economical and technologically simplest technique for measuring molecular weights. It is valuable to identify an easy, optimum method for determining the absolute molecular weights of the standards used to determine the parameters, K and α. Light scattering is very time consuming, whereas MALDI molecular weights are determined rapidly. In addition, the use of the MALDI technique extends down to molecular weights in the range of 1000 Da. Whereas, light scattering data are limited to molecular weight of 10,000 Da and higher. In this paper, MHS parameters are calculated using MALDI to determine absolute molecular weights of a series of narrow molecular weight distribution PS. While the molecular weight ranges for which the MHS relationship holds true has been an area of debate, these data agree with parameters determined by other absolute methods and are determined using standards falling within previously published molecular weight ranges [38,39,41,42]. Some additional comments are made concerning the use of the ratio of the molecular weight of the monomer to the distribution breadth at half-height to represent the molecular

Table 1
Molecular weight data

	Sample	Manufacturer's data			MALDI data			M_p	PSp	$[\eta]$ (cm^3/g)
		M_n	M_w	PD	M_n	M_w	PD			
1	PS[a]	3600	–	–	4400	4700	1.05	4500	21	6.3
2	PS[a]	9100	–	–	7700	8400	1.10	8200	54	8.1
3	PS[a]	18,900	19,400	1.03	20,000	20,400	1.02	20,000	64	15.9
4	PS[a]	50,400	52,100	1.03	52,200	52,600	1.01	52,500	123	27.5
5	PS[a]	92,600	93,050	1.00	92,900	93,100	1.00	91,800	94	39.0
6	PS[b]	93,900	114,900	1.22	115,800	116,400	1.01	115,200	154	–
7	PS[a]	217,000	254,000	1.17	–	–	–	–	–	91.0
8	PS[a]	564,000	612,000	1.09	–	–	–	–	–	135.0
9	PMMA[c]	6400	6800	1.06	6000	6100	1.00	7300	22	–
10	PMMA[d]	11,500	12,000	1.04	11,900	12,200	1.02	11,900	42	–
11	PMMA[b]	48,800	52,700	1.08	51,300	51,700	1.01	51,000	116	–
12	PMMA[b]	74,200	78,700	1.06	74,000	74,800	1.01	78,500	121	–
13	PEG[b]	2000	2100	1.05	1900	2000	1.06	2100	15	–

[a] Perkin–Elmer.
[b] Scientific Polymer Products.
[c] Polymer Source.
[d] Polysciences.

weight distributions in these narrow molecular weight distribution polymers.

2. Experimental

2.1. Materials

The matrix chemicals, 3,5-dimethoxy-4-hydroxycinnamic acid (SA) and 1,8,9-anthracenetriol, were purchased from Aldrich (Milwaukee, WI). 3-β-Indoleacrylic acid, bovine insulin, bovine serum albumin, and cytochrome C were purchased from Sigma (St Louis, MO). Silver trifluoroacetate (98%) was purchased from ACROS (via Fisher Scientific in Pittsburgh, PA), and potassium chloride was purchased from T.J. Baker Chemical Corporation. Standard, narrow molecular weight distribution samples described in Tables 1 and 2 were obtained from Perkin–Elmer (polystyrene kit No. 0254-0074) (Norwalk, CT), from Scientific Polymer Products (poly(ethylene glycol), Cat#STD-2) (PEG) (Ontario, NY), and from Polysciences (poly(methyl methacrylate)) (PMMA) (Warrington, PA). Analytical grade tetrahydrofuran (THF) purchased from Fisher Scientific (Pittsburgh, PA), spectrophotometric grade acetonitrile was purchased from ACROS (via Fisher Scientific in Pittsburgh, PA), and reagent grade ethyl alcohol was purchased from Aldrich (Milwaukee, WI). All materials were used without further purification.

2.2. MALDI sample preparation

PMMA and PS analytes were dissolved in THF at the

Table 2
MHS parameters and viscosity molecular weights

Source	Molecular weight range ($\times 10^{-3}$)	α	K	PS standards		
				M_v ($M_w = 612{,}000$, $M_n = 556{,}000$, $[\eta] = 135$ cm^3/g)[a]	M_v ($M_w = 114{,}920$, $M_n = 93{,}924$, $[\eta] = 47$ cm^3/g)[b]	M_v ($M_w = 59{,}176$, $M_n = 53{,}588$, $[\eta] = 29$ cm^3/g)[b]
MALDI plot	4.7–93.1	0.63	0.031	597,200	111,900	52,000
Light scattering plot	20–610	0.65	0.026	519,900	102,600	48,800
Ref. [38]	10–1600	0.69	0.017	448,800	97,300	48,300
Ref. [38]	70–1500	0.71	0.013	434,900	98,400	49,800
Ref. [38]	40–520	0.75	0.0085	399,200	97,800	51,400
Ref. [38]	0.5–5	0.50	0.10	1,823,000	220,900	84,100
Ref. [38]	5–45	0.65	0.044	231,400	45,700	21,700
Ref. [38]	120–2800	0.75	0.0075	471,700	115,500	60,700
Ref. [38]	50–800	0.78	0.0075	285,400	73,800	39,730

[a] Perkin–Elmer standard with manufacturer's M_w and M_n.
[b] ^{2}Scientific Polymer Products standards with manufacturer's M_w and M_n.

following concentrations: samples <6 kDa, 0.8–1.2 mg/ml; samples 6–20 kDa, 1.5–2.0 mg/ml; samples 50–80 kDa, 2.8–3.8 mg/ml; and samples >90 kDa, 3.8–5.2 mg/ml. The PEG sample (1 mg) was dissolved in ethanol/water (1:4) (1 ml). The matrix solutions were prepared by dissolving 1,8,9-anthracenetriol (30 mg) in THF (1 ml), 3-β-indoleacrylic acid (20 mg) in THF (1 ml), or 3,5-dimethoxy-4-hydroxy-cinnamic acid water/acetonitrile (1:4) to form a saturated solution. Silver trifluoroacetate (5 mg) was dissolved in THF (1 ml), and a saturated solution of potassium chloride in ethanol was prepared. For PMMA and PS, matrix, silver trifluoroacetate or potassium chloride, and polymer solutions were mixed in the ratios 10:5:10 μl, respectively. For PEG, matrix, potassium chloride, and polymer solutions were mixed in the ratio of 10:1:5 μl. Samples (1–2 μl) were then spotted on the MALDI targets and allowed to air dry. 3-β-Indoleacrylic acid and 3,5-dimethoxy-4-hydroxy-cinnamic acid were the matrices used for PMMA and PEG, respectively. Potassium chloride was the salt used for both PMMA and PEG. For PS, 1,8,9-anthracenetriol and silver trifluoroacetate were the matrix and salt used.

2.3. Mass spectrometry

Polymer mass spectrum data was obtained on a Bruker REFLEX II MALDI-TOF instrument. The system is equipped with the Scout source, high mass detector®, delayed extraction, and XMASS data processing software [43]. The digitizer is 500 MHz in the linear mode used in these studies. The variable ND: Yag laser source was set to 355 nm. The spectrometer was calibrated using insulin for molecular masses <9 kDa, cytochrome C for molecular masses 9–20 kDa, and BSA for molecular masses >50 kDa.

2.4. Viscosity measurements

Dilute solution viscosity measurements were taken using a Ubbleholde viscosity tube as described in Billmeyer [43]. The data was collected at 25 °C in toluene.

2.5. Calculations

The MALDI data was processed using the XMASS [41] data processing software available from Bruker to calculate M_n, M_w, and PD. The $[\eta]$ was found by plotting concentration against inherent and reduced viscosities, and the MHS parameters were determined through plotting the logarithm of M_w versus the logarithm of $[\eta]$.

3. Results and discussion

3.1. Mark–Houwink–Sakurada parameter study

Table 1 summarizes MALDI data for PS, PMMA, and PEG standards. Included in the table are the number and weight average molecular weights provided by the supplier and the same determined by MALDI. The MALDI molecular weight values are very close to those determined by the supplier. These data illustrate an important advantage derived from using the MALDI technique. Both weight and number average molecular weights can be determined for the low molecular weight Samples 1 and 2. This is the only absolute molecular weight technique that provides M_w for such low molecular weight samples.

MALDI weight average molecular weights were used to calculate MHS parameters. Fig. 1(a) is a logarithm plot of intrinsic viscosity versus molecular weight. Included in the figure are the linear fit and the resulting equation with the correlation coefficient. In Fig. 1(b), a similar plot was generated using the light scattering molecular weights provided by the supplier of the standards. The correlation coefficient for the MALDI data is comparable to that obtained using light scattering data obtained from the manufacturer.

The constants, K and α, are particular to the polymer–solvent–temperature range chosen. These parameters were obtained from the slope and intercept of logarithm plots of intrinsic viscosity versus molecular weight. Table 2 lists intrinsic viscosities, K and α parameters and molecular weights determined using these parameters. In this table, MALDI K and α parameters are compared with those found in the literature for PS in toluene at 25 °C [38]. The molecular weight range of samples used to determine the parameters is also included. Note the broad range in K and α values, this is due to the dependence on configuration, molecular weight distribution, method by which molecular

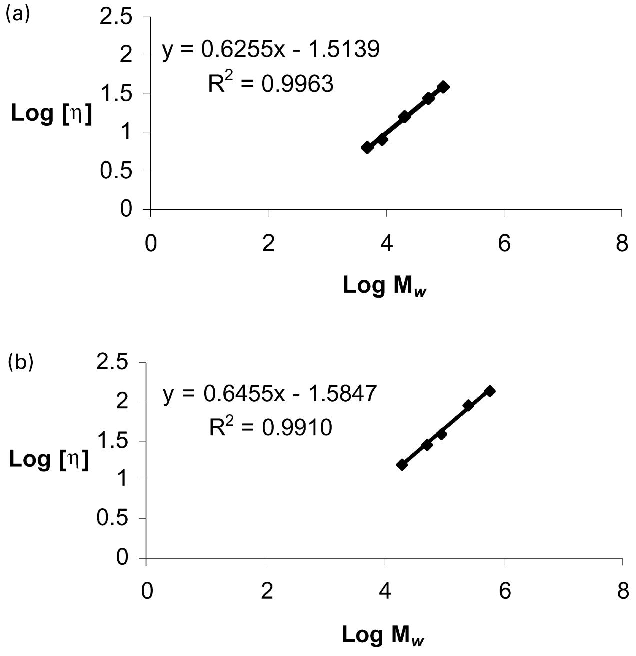

Fig. 1. Logarithm plot of intrinsic viscosity versus molecular weight used to calculate MHS parameters: (a) MALDI molecular weight data and (b) light scattering data determined by the manufacturer.

weight was determined, and branching in addition to the dominant solvent and temperature effects [39,41].

Literature values for α range from 0.50 to 0.78. The 0.50 value was obtained using low molecular weight standards. The α calculated using MALDI molecular weight data, 0.63, is within the range obtained for polymers of high molar mass in non-theta solvents. It is slightly lower than the value obtained from the manufacturer's light scattering data, 0.65. K values obtained from both MALDI (0.031) and light scattering (0.026) are also within the range of those reported in the literature for this system.

The equations generated in Fig. 1 and intrinsic viscosity data were used to calculate the molecular weights of three additional samples of PS (Table 2). The 612K M_w PS standard yielded a viscosity average molecular weight of 597K via MALDI–MHS data. Re-inserting into the light scattering MHS equation resulted in a molecular weight of 520K. The 115K M_w standard yielded viscosity molecular weights of 112K and 103K using the MALDI–MHS and light scattering MHS equations, respectively. Lastly, a 59K M_w standard gave 52K and 49K molecular weights for the same. In examining the wide range of viscosity, molecular weights calculated using literature MHS parameters (Table 2) it is necessary to realize that the polymers used to determine the parameters are not monodispersed, and more that one average molecular weight may have been used in the plots.

The following expression for the viscosity average molecular weight has been derived [44]:

$$M_v = \left[\frac{\sum N_x M_x^{(\alpha+1)}}{\sum N_x M_x} \right]^{1/\alpha} \tag{6}$$

In a theta solvent, $\alpha = 0.5$ and the following molecular weight ratios are expected [44]:

$$M_n/M_v/M_w = 1 : 1.67 : 2 \tag{7}$$

In good solvents, such as toluene used in this study, M_v approaches M_w. The MALDI data also generated viscosity molecular weights that were closest to the weight average molecular weights. The light scattering plot generated in this research from the manufacturer's data yielded a viscosity molecular weight second closest to the weight average molecular weight for the 612K M_w. The MALDI generated data was first in approach to M_w with a M_v of 597K. The MALDI data also generated viscosity molecular weights that were comparatively close to weight average molecular weights for the 115K M_w and the 59K M_w samples. All of this indicates that easily generated MALDI parameters are adequate for determining molecular weights from viscosity for the system chosen. This study should be extended to other polymers and molecular weight ranges. In Section 3.2, the description of molecular weight distribution is re-examined.

3.2. Polymer distribution

As mentioned earlier, polymer weights are described using number average molecular weight (M_n), weight average molecular weight (M_w), and the term PD (M_w/M_n); these terms were adopted from the methods available many years ago. The data in Table 1 illustrate the fact that weight average molecular weights calculated via light scattering measurements of the size of particles and number average molecular weight calculated by measuring the number of particles via osmotic pressure differ somewhat from M_n and M_w determined by the absolute method, MALDI. Furthermore, the PD values in Table 1 vary only slightly with sample or with the method used to determine PD. After considering the previous work of the MALDI pioneers, viewing the MALDI spectra presented in this paper, and comparing the spectra with the corresponding PD values, it is apparent that a new approach describing PD of narrow molecular weight polymer standards is needed. PD is intended to represent the width of the polymer spectrum; however, when PD values are calculated, the values for higher molecular weight polymers remain similar to lower molecular weight polymers even though the width of the spectrum increases. For example, two different molecular weight polymers may have the same or similar PDs, but may have very different MALDI spectra. This discrepancy occurs because as M_n and M_w increase, the difference between them can increase without being reflected in the PD. This paper proposes a method to define the width of the spectrum without bias being caused by the magnitude of the molecular weight of the polymer. While it may be understood that a higher molecular weight polymer has a larger spectrum width than a lower molecular weight polymer with the same PD, the use of this spectrum approach makes the difference easier to visualize. This value will be defined as the polymer spread (PSp). It is important to note there is a mathematical relationship between the standard deviation and PD [45] and the PSp is only applicable for symmetric distributions; however, it can be used, through the use of MALDI as an ideal method of determining the breadth of the polymer spectrum, to describe the spectrum width of polymer standards in a more meaningful way than using molecular weight ratios.

For each polymer studied, we have determined the breadth of the spectrum. From the standard practice used in analytical chemistry, the width at half-height on the MALDI curve defines the breadth. This is an approximation of the standard deviation. Twice the width takes into account 95% of the individual molecular weights. To make this number more meaningful and universal from polymer to polymer, it is divided by the molecular weight of the monomer. When describing a polymer with the term PSp, the number of different chain lengths within one standard deviation of the M_p can be determined, giving a much more descriptive value by which to classify polymers. Table 1 shows the PD and PSp as determined by MALDI for three different polymers, PS, PMMA, and PEG. The PDs are all very similar; however, when looking at the PSp, it is obvious the width of the spectrum increases as the

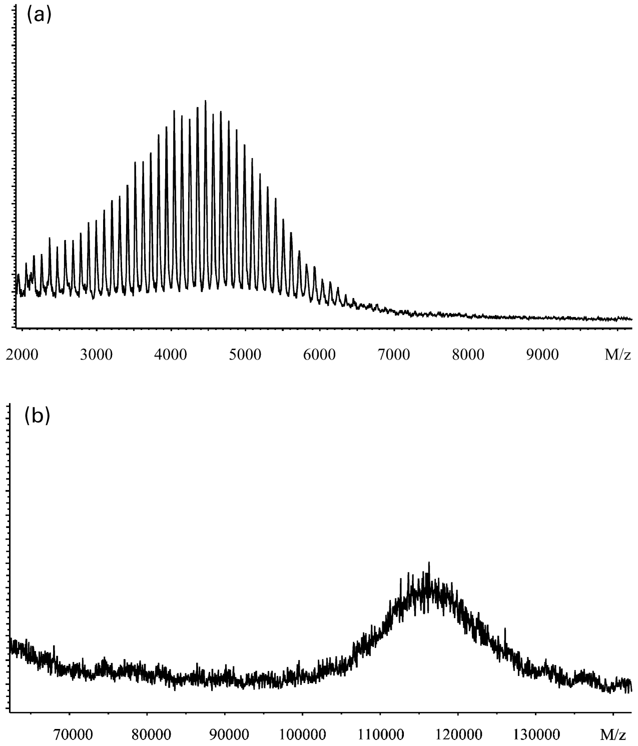

Fig. 2. MALDI molecular weight spectra for PS: (a) $M_w = 4700$, PD = 1.05, and PSp = 21 and (b) $M_w = 116{,}400$, PD = 1.01, and PSp = 154.

molecular weight increases. The MALDI spectra for Sample 1 is shown in Fig. 2(a) and the MALDI spectra for Sample 6 is shown in Fig. 2(b). For Sample 1, the PD is 1.05, a similar, but larger, value than the PD for Sample 6. If the MALDI spectra are compared, it is obvious that the distribution of the spectra for Sample 6 is actually much larger than that for Sample 1, the opposite of what is related by the PD. This increase is very clearly illustrated by the PSp seen in Table 1. If the PD and the spectra (Fig. 3(a) and (b)) for Samples 9 and 12 are compared, the same trend is evident. The two PD values are almost identical, 1.00 and 1.01, respectively, but the spectra are very different. The larger spectrum width of the higher molecular weight sample is once again demonstrated by the PSp value seen in Table 1. PSp, then, is a much more descriptive way to classify polymers.

4. Conclusions

In this initial study, MALDI spectra were found to be very useful in generating molecular weight spectra for use in determining MHS parameters. The useful molecular weight range extends below that possible using the light scattering technique. Most importantly, MALDI spectra can be generated with much less effort than those obtained via light scattering. In the future, this study will be expanded to include additional polymers.

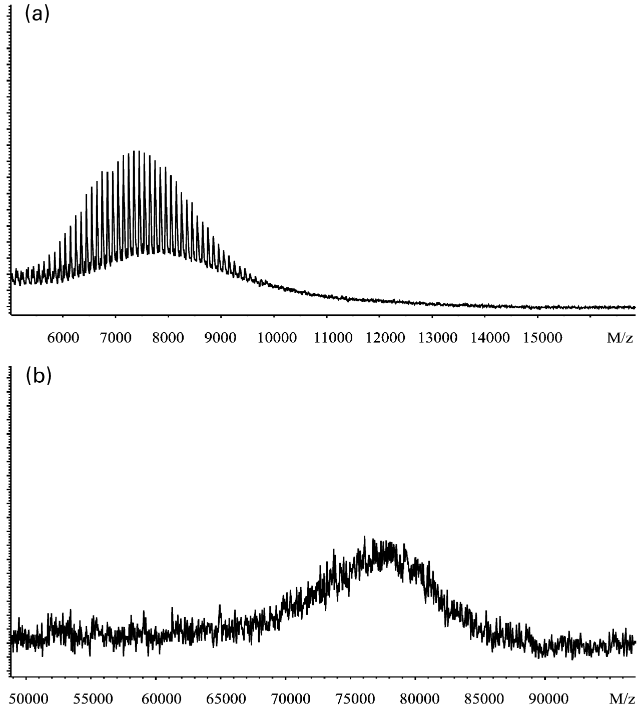

Fig. 3. MALDI molecular weight spectra for PMMA: (a) $M_w = 6100$, PD = 1.00, and PSp = 22 and (b) $M_w = 74{,}800$, PD = 1.01, and PSp = 121.

A new way of assessing polymer molecular weight distributions has been presented. The PSp method described in this paper uses narrow polymer standards as a basis for evaluating the broadness of molecular weight distributions in MALDI samples.

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