Further Application of a Procedure for Molecular Weight and Molecular Weight Distribution Measurement of Polydisperse Polymers from Their Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectra

Daniele Vitalini* and Placido Mineo

Istituto per la Chimica e la Tecnologia dei Materiali Polimerici, CNR—Catania,
Viale A. Doria, 6-95125 Catania, Italy

Emilio Scamporrino

Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria,
6-95125 Catania, Italy

Received February 18, 1997; Revised Manuscript Received May 27, 1997[⊗]

ABSTRACT: A recently reported off-line procedure to estimate molecular weight (MW) averages and molecular weight distribution (MWD) index, also for polydisperse polymers, directly from their matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra was applied here to poly(bisphenol A−carbonate) (PC), a poly(ether−sulfone) resin (PES), and poly(dimethylphenylene oxide) (PDMPO), all having a wide polydispersity index. The MW and MWD obtained values were compared with those determined by GPC or supplied by makers. A structural characterization of these polymers was also performed by examining their MALDI-TOF mass spectra.

Introduction

The soft ionization occurring in the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) technique, strongly reducing the ion fragmentation, allows the desorption and detection of very large molecules, so that the information obtained by MALDI spectra is of particular importance in determining the composition of the examined samples.[1−14]

Because polymer molecules are different in molecular weight and/or kind of end groups, if ionization yield, desorption, and detection responses are independent of the mass of the molecules over a wide range of abundances, peak intensities of a MALDI-TOF mass spectrum (obtained in linear mode) should reflect the composition of the polymer. Therefore, accurate polymer molecular weight (MW) averages and molecular weight distributions (MWD) could be directly estimated from their MALDI-TOF mass spectra. However, it has been reported that MALDI molecular weights agree with the values obtained by other common techniques only in the case of polymers with a narrow polydispersity,[8,12−18] whereas, for polydisperse polymers, MALDI fails to yield reliable MW estimates.[14−23]

On the contrary, we have recently developed a new off-line procedure able to measure MW averages and MWD indexes of polymers having a large polydisperse index by direct examination of their MALDI-TOF mass spectra.[24] The method can be summarized in three points: (i) a smoothing operation[25] necessary to improve the recorded trace of the spectrum up to high *m/z* values; (ii) a subtraction of the offset contribution to the signal intensities, which renders the MALDI signals representative of the abundance of the species present in the sample; (iii) a recording of the MALDI spectra up to the higher *m/z* values possible for more accuracy in the MW evaluation. The combined effect of these operations determines a considerable advantage, allowing the measurement of reliable MW and MWD values for both narrow and wide disperse polymers directly from their MALDI spectra.

In the present paper, the structural characterization of a poly(bisphenol A-carbonate) (PC), a poly(ether−sulfone) resin (PES), and a poly(2,5-dimethyl-1,4-phenylene) oxide (PDMPO) by MALDI-TOF analysis and the measurement of their MW and MWD values using the above-mentioned method is reported.

Experimental Section

Materials. All solvent and basic materials were commercial products appropriately purified before use. Poly(bisphenol A−carbonate) (PC), a poly(ether−sulfone)resin (PES), and poly(2,5-dimethyl-1,4-phenylene oxide) (PDMPO) were commercial polydisperse polymers obtained from Aldrich Chemical Co.

GPC Analysis. A Polymer Laboratories PL-GPC 110 thermostated system, equipped with three PL-gel 5 μm columns (two Mixed-D and one Mixed-E) attached in series, was used. The analyses were performed using toluene (80.0 ± 0.1 °C) or tetrahydrofuran (THF) (35.0 ± 0.1 °C) as eluant at a flow rate of 1 mL/min. A differential refractometer (Polymer Laboratories) was used as the detector. The instrument was calibrated with a mixture of seven polystyrene standards (Lab Service Analytica, Polymer Laboratories; molecular weights between 2000 and 1 200 000) using a PL Caliber GPC software for the average molecular weight and polydispersity determination of the polymer samples.

MALDI Sample Preparation. The MALDI samples were prepared by mixing directly on the probe tip 0.2 μmol of 2-[(4-hydroxyphenyl)azo]benzoic acid (HABA), used as a matrix, and about 0.1 nmol of each polymer, both dissolved in THF. Before the MALDI analysis, the solvent was evaporated under a N_2 stream. To obtain the best MALDI mass spectrum, several experiments, changing in each case the polymer/matrix molar ratio, were performed.

MALDI-TOF Mass Spectrometric Analysis. The MALDI-TOF mass spectra were performed by a Bruker reflex mass spectrometer equipped with a nitrogen laser (emission at 337 nm, for 3 ns), a flash ADC (time base 8 or 16 ns), and a double-plate microchannel detector. The accelerating voltage was 30 kV. The laser irradiance was slightly above threshold (ca. 10^6 W/cm^2). The detection was in the linear mode by means of a

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* Author to whom correspondence is addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

S0024-9297(97)00220-9 CCC: $14.00

Table 1. Molecular Weight (MW) Averages and MW Distribution (MWD) Obtained by MALDI-TOF Mass Spectrometric and GPC Analysis for the Examined Polymers

sample	technique	M_w	M_n	MWD
PC	GPC	34 600	17 300	2.00
	MALDI-TOF	60 000	15 000	4.00
	GPC/MALDI[a]	75 500		
PES	GPC	53 900	28 000 (7800[b])	1.90
	MALDI-TOF	76 700	15 300	5.00
	MAKER[c]	67 000	20 400	3.3
PDMPO	GPC	37 100	10 200	3.6
	MALDI-TOF	31 900	6200	5.1

[a] MW values of a GPC eluted fraction, collected in correspondence with the GPC maximum, determinated by MALDI-TOF. [b] M_n value obtained including, in the GPC average computation, the low molecular weight oligomer region. [c] MW value supplied by the manufacturer (Aldrich).

HIMASS detector. It has a venetian-blind steel dynode that performs ion-to-electron conversion. Electrons pass through a 6000 V potential difference and hit first a single-plate microchannel detector and then a cesium iodine scintillator that surmounts the entrance window of a photomultiplier. The conversion dynode enables the detection of high mass ions. The scintillator avoids detector saturation by providing a very wide dynamic range. The HIMASS detector has a low temporal resolution.

The MALDI mass spectra were processed with the XMASS program from Bruker and with our software (compiled with Quick Basic Version 4.5) to obtain molecular weight averages and polydispersity indexes.

MALDI Mass Spectra Elaboration and Molecular Weight Calculations. The MALDI spectra were calibrated with two external standards:[11,26] tetrakis[(*p*-dodecanoxy)phenyl]porphyrin (MW = 1350; our preparation)[11] and 4-*tert*-butylcalix[4]arene−tetraethylester (MW = 992; Janssen). Then all the raw spectral data were elaborated according to an off-line procedure described elsewhere.[24]

To evaluate the M_w and M_n of a polymer by its MALDI-TOF mass spectrum, a nonlinear regression analysis was used here.[27] The trend of the experimental M_w and M_n values, calculated by eq 1a and 1b (where m_i = molecular weight and N_i = molar fraction, proportional to the ion peak intensity) fixing different upper mass limits in the elaborated

$$M_w = \frac{\sum_i m_i^2 N_i}{\sum_i m_i N_i} \tag{1a}$$

$$M_n = \frac{\sum_i m_i N_i}{\sum_i N_i} \tag{1b}$$

$$\text{MWD} = M_w/M_n \tag{1c}$$

MALDI-TOF mass spectrum and plotted as a function of these *m*/*z* limits, was described by the following equation:

$$y_{(\text{calc})n} = 1/[P_1 + (P_2/x_n) + (P_3/x_n^2) + (P_4/x_n^3)] \tag{2}$$

where $y_{(\text{calc})n}$ = MW at the designed x_n value, P_1−P_4 = parameters calculated with the fitting program, and x_n = array of the molecular weight.

To determine P_1−P_4 parameters for different examined polymers, a LIANA program[28] was used. Pertinent *P* values are reported in Table 1, in addition to the $R_{(\text{Hamilton})}$ values, representative of the very good fit, calculated according to eq 3

$$R_{(\text{Hamilton})} = [\textstyle\sum(\text{res}_n)^{1/2}/\sum(y_{(\text{exp})n})^{1/2}]^{1/2} \tag{3}$$

$$\text{res}_n = y_{(\text{exp})n} - y_{(\text{calc})n}$$

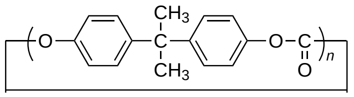
where res_n = residual, $y_{(\text{exp})n}$ = experimental data obtained from eq 1a or 1b, and $y_{(\text{calc})n}$ = calculated data from eq 2.

All M_w and M_n values reported in this work are calculated at *m*/*z* 500 000, fixed as the upper mass limit for our mass spectrometer.

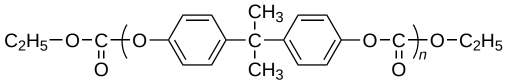
Results and Discussion

In the polymer field, the MALDI-TOF analysis, because of the absence of a substantial ion fragmentation, can allow the direct detection of molecules also at very high molecular weight, thus permitting the determination of polymer chain structure and the kinds of end groups.[1−14]

The MALDI-TOF mass spectrum, acquired in linear mode, of a polydisperse poly(bisphenol A-carbonate) (PC) is reported in Figure 1. The spectrum consists of two series of peaks (see inset in Figure 1) corresponding to molecular ions, detected as MNa^+, of cyclic oligomers (**I**), peaks at *m*/*z* n254 + 23, and open-chain ethyl carbonate terminated compounds (**II**), peaks at *m*/*z* n254 + 141 (peaks corresponding to MK^+ ions are also present with minor intensity).



I



II

The first peak in each series, observed in the spectrum of Figure 1 at *m*/*z* 3579 and 3697, respectively, corresponds to a cyclic or open-chain oligomer with *n* = 14.

Remarkably, the presence of these last compounds (**II**) in the polymer sample indicates that the polymerization reaction of PC was stopped by addition of ethanol.

From the GPC trace of this PC sample, omitted for brevity, the following values were obtained: M_w = 34 600; M_n = 17 300; MWD = 2.0 (by calibration with polystyrene standards). Differently, in the MALDI mass spectrum (Figure 1), only signals centered at about *m*/*z* 5000, which become negligible beyond 15 000 daltons, appear. Assuming, as an example, a limit of 15 000 in the MW averages calculation (according to common procedure) much lower values with respect to GPC values are obtained.

On the basis of this behavior, widely documented in the literature, several researchers have suggested that the direct MALDI-TOF analysis fails to yield reliable molecular weight estimates for polydisperse polymers,[14−21] whereas, for narrow disperse polymers, this technique gives MW values in good agreement with those obtained by other methods.[8,12−18]

We retain that the erroneous results obtained are due to an incorrect interpretation of MALDI mass spectra. Consequently, we have recently elaborated a procedure which allows reliable MW and MWD values also for polydisperse polymer samples directly from their MALDI-TOF mass spectra.

Since numbers of ions are counted by the time-of-flight detection, MALDI-TOF gives a molar response. Thus, in the MALDI spectra of samples having a broad

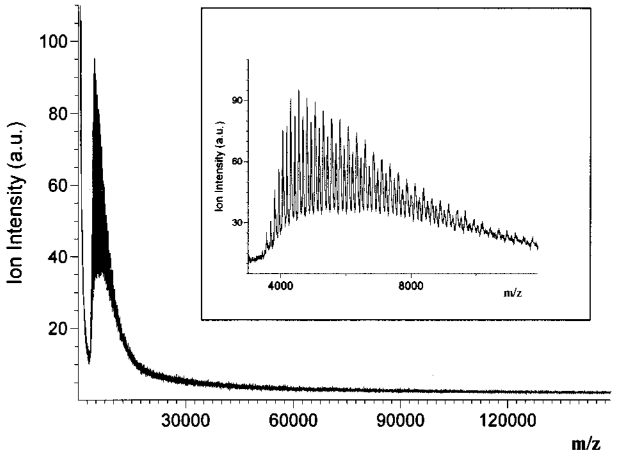


Figure 1. Positive "uncorrected" MALDI-TOF mass spectrum of poly(bisphenol A-carbonate) (PC). The low molecular weight region of the spectrum is reported in the inset.

MW distribution, a rapid decay of the signals is expected, so that the peaks corresponding to higher masses are often lost in the baseline noise. To improve the recorded trace up to high *m*/*z* values and to avoid the underestimation of higher mass species, the spectra were submitted to a simple smoothing. In addition, the arbitrary offset, introduced by the computer in the analogical/digital conversion of the signal recorded, provokes a strong distortion of the relative intensity of the peaks originally detected, especially of those at lower intensity. This alteration is, in fact, responsible for the observed failure in the MW computation. In our procedure,[24] a subtraction of this misleading offset contribution is made by fixing a new ordinate zero baseline in correspondence with the lower signal recorded in each spectrum. Combined effects of smoothing and offset subtraction allow one to obtain significative signals up to very high *m*/*z* values, thus allowing more accurate determination of MW.

The MALDI-TOF mass spectrum of the PC sample after the above-described procedure is reported in Figure 2a. In Figure 2b the variations of the calculated M_w and M_n values as a function of the upper mass limit selected in the spectrum of Figure 2a, are reported. As expected, the M_n trace reaches a plateau rapidly because this average is principally affected by low molecular weight compounds, whereas for M_w measurement high *m*/*z* values in the spectrum need to be acquired. It can be observed that the spectrum of Figure 2a is very similar to that of Figure 1, but as a consequence of the concerted smoothing, offset removal and examination of the signals up to higher *m*/*z* values, M_w and M_n, calculated in correspondence to the asymptotic values of the curves in Figure 2b, result in about $M_w = 60\,000$ and $M_n = 15\,000$ (MWD = 4.0).

The different MW values, with respect to those obtained by GPC (Table 1), can be explained by considering the different structures of polystyrene standards, used to calibrate the GPC, with respect to that of polycarbonate. However, to ascertain the exact MW values, a GPC fraction eluted in correspondence with the maximum exhibited by the GPC trace for PC was collected and its MALDI-TOF mass spectrum was then acquired. The MALDI mass spectrum of this GPC fraction (omitted for brevity) yielded $M_w = 75\,500$ (with $M_n = 67\,600$ and MWD = 1.1) which is comparable with the MALDI data above reported.[11,12,18,22]

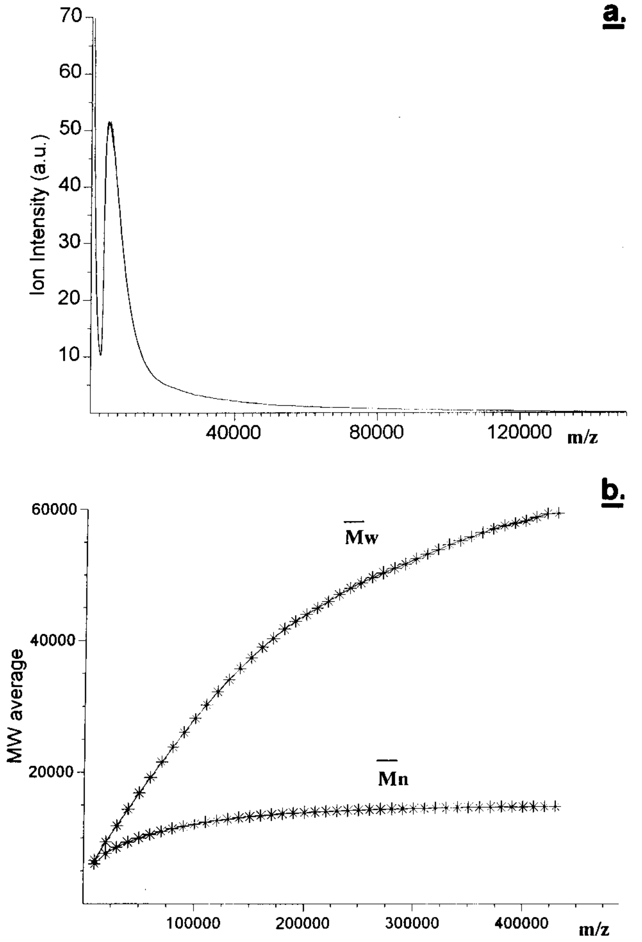
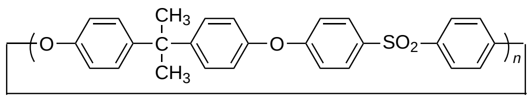


Figure 2. (a) Elaborated MALDI-TOF mass spectrum of PC. (b) Molecular weight averages (M_w and M_n) of PC calculated from its elaborated MALDI-TOF mass spectrum at different *m*/*z* upper limits and reported as a function of those *m*/*z* values.

A poly(ether−sulfone) resin (PES) was also investigated; its elaborated MALDI-TOF mass spectrum and, in the inset, the extended first region of the spectrum are reported in Figure 3a. The spectrum is essentially constituted by a series of peaks, corresponding to molecular ions of cyclic oligomers (**III**) detected as MNa^+ ions at *m*/*z* n442+23, whose intensities rapidly decrease and become very weak at about *m*/*z* 10 000. The first peak present in the spectrum is due to a cyclic tetramer ($n = 4$) detected at *m*/*z* 1791.



III

In Figure 3b the M_w and M_n curves, calculated by fixing the upper mass limit of the signals in the MALDI spectrum of Figure 3a at different *m*/*z* values, show a plateau, in correspondence to which, by the nonlinear regression analysis, $M_w = 76\,700$ and $M_n = 15\,300$ (MWD = 5.0) were calculated. For this sample the manufacturer specifies $M_w = 67\,000$ (by light scattering) and $M_n = 20\,400$ (by GPC), whereas from our GPC curve of Figure 4 $M_w = 53\,900$ and $M_n = 28\,000$ result. Comparing these data with those obtained by MALDI (see also Table 1), the agreement between the M_w calculated by MALDI and light scattering can be observed. The lower M_n value measured by MALDI may be due both to the relative calibration of GPC (with polystyrene standards) and, more probably, to having excluded from the MW computation the region of the

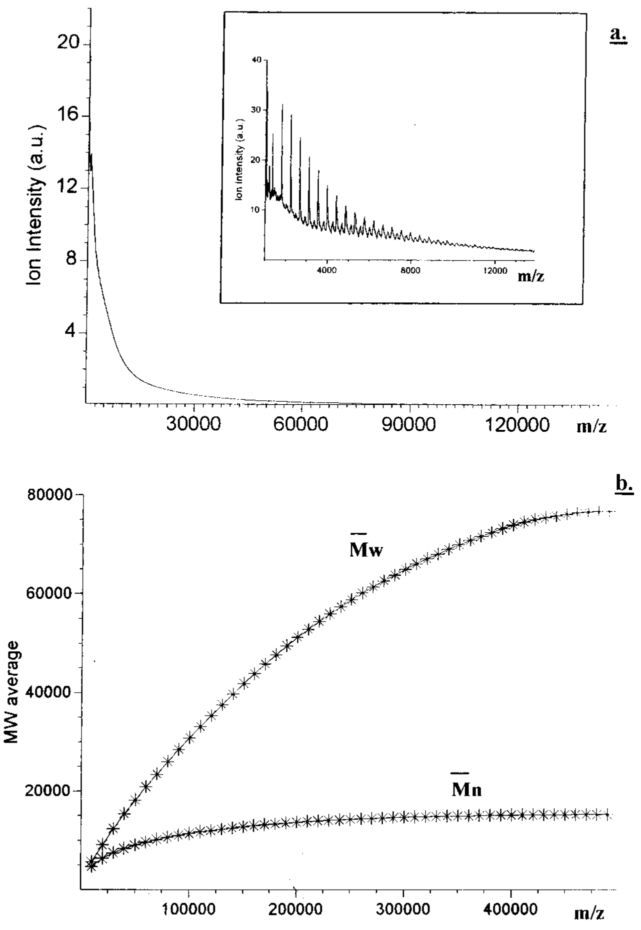


Figure 3. (a) Positive elaborated MALDI-TOF mass spectrum of a poly(ether−sulfone) resin (PES). The low molecular weight region of the spectrum is reported in the inset. (b) Molecular weight averages (M_w and M_n) of PES calculated from its elaborated MALDI-TOF mass spectrum at different *m*/*z* upper limits and reported as a function of those *m*/*z* values.

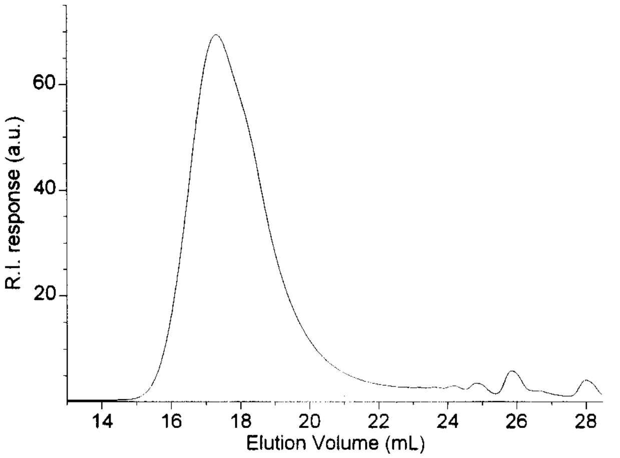


Figure 4. GPC of a poly(ether−sulfone) resin (using THF as eluant).

GPC curve (Figure 4) corresponding to low molecular weight oligomers. In fact, if M_n is calculated again including also these oligomers, an M_n value of only 7800 (M_w = 45 600, and MWD = 5.8) is obtained.

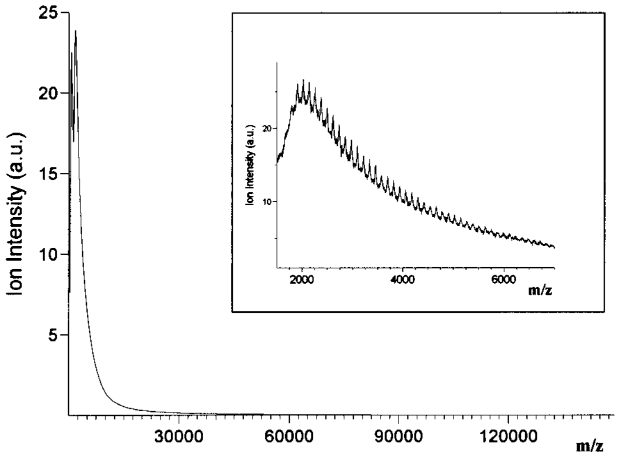
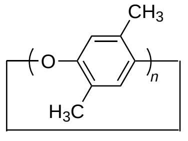


Figure 5. Positive "cleaned" MALDI-TOF mass spectrum of poly(2,5-dimethyl-1,4-phenylene oxide) (PDMPO). The low molecular weight region of the spectrum is reported in the inset.

In Figure 5, the elaborated MALDI-TOF mass spectrum of poly(2,5-dimethyl-1,4-phenylene oxide) (PDMPO) and, in the inset, the extended first part of the spectrum are reported. The spectrum is constituted by a series of broad peaks, probably due to the overlap of Na and K adducts, from *m*/*z* 1943 up to about *m*/*z* 7000 separated from each other by 120 (molecular weight of PDMPO repeating unit), which correspond to molecular ions of cyclic oligomers **IV**.



IV

From the MALDI-TOF MW plots (omitted for brevity) M_w = 31 900 and M_n = 6200 (with MWD = 5.1) were obtained which are comparable to the MW values measured by GPC trace (omitted for brevity): M_w = 37 100 and M_n = 10 200 (MWD = 3.6).

The above-reported data confirm the validity of our method to measure MW averages also for polydisperse polymers directly from their MALDI-TOF mass spectra. Although GPC is certainly the most common and immediate way to visualize the mass distribution of a polymer sample, the necessity that the sample is soluble in a suitable solvent considerably reduces the number of polymers that can be examined with this technique. Besides, for calibration problems, only relative MW values are usually obtained. On the contrary, although MALDI-TOF analysis requires, according to the sample, a careful choice of experimental conditions (such as type of matrix, matrix/product ratio, sample preparation, laser power and focusing, etc.),[5,7,20,28,29] many more solvents (as DMF, NMP, etc.) can be used, so that fewer limitations occur in this technique. Moreover, the MW measurements are absolute values and the polymer structure or polymer sample composition can often be inferred.

All these reasons make the MALDI technique of more general use. Furthermore, the restriction regarding the ability of MALDI-TOF to give exact MW values only for narrow disperse polymers has been overcome by our above-mentioned procedure which allows one to obtain reliable MW estimates also for polymers with very wide polydispersity.

Nevertheless, in MALDI analysis, a number of problems such as the matrix contribution to MW calculation and the exact MW evaluation of very high polymers (>500 000) must still be resolved. In fact, several matrices produce very intense signals at low mass (around *m*/*z* 500) and often maintain a significant intensity up to high m/z values. These signals, added to those of the sample, play a considerable effect in lowering the M_n and, to a lesser extent, M_w values of a polymer, thus indicating a major polydispersity index for the sample (as observed in the above-reported cases; Table 1). At the present time, work on the solution of this problem is in progress.

Acknowledgment. Partial financial support from the Italian Ministry of University and Scientific and Technological Research (40% and 60%), P. O. CNR-MURST (1994−95), and financial contribution from the Progetto Strategico "Tecnologie Chimiche Innovative" (CNR, Rome) are gratefully acknowledged.

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MA9702206