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Molecular Weight Determination and Structural Analysis in Polydisperse Polymers by Hyphenated Gel Permeation Chromatography/Matrix-Assisted Laser Desorption Ionization—Time of Flight Mass Spectrometry

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Molecular Weight Determination and Structural Analysis in Polydisperse Polymers by Hyphenated Gel Permeation Chromatography/Matrix-Assisted Laser Desorption Ionization—Time of Flight Mass Spectrometry

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A method for the determination of molecular weight distribution data for polydisperse polymer samples by MALDI-TOF is reported that involves the fractionation of polydisperse samples through analytical GPC columns and collection of fractions. Selected fractions are then analysed by MALDI-TOF and the mass spectra of these nearly uniform samples allow the determination of M_n and M_w averages. The GPC tracing, calibrated against molecular weight values obtained by MALDI, was used to compute molecular weight distribution data of the unfractionated sample. To test the reliability of the molecular weight estimates by the GPC/MALDI-TOF method, a sample of poly(methyl methacrylate) and two samples of poly(dimethyl siloxane), both with wide polydispersity, were analyzed. The results show that the molecular weights of PMMA fractions obtained by MALDI coincide with the GPC calibration plots obtained with anionic PMMA standards. In the case of the two poly(dimethyl siloxanes), two slightly different GPC calibration plots were obtained owing to the different structures of the polymer chains of the two samples. In fact, the MALDI spectra of low MW fractions of these polymers, showed that one sample consists essentially of linear oligomers, whereas the other sample contained cyclic oligomers.

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Keywords: Molecular weight distribution, MALDI-TOF, GPC fractionation, cyclic and linear poly(dimethyl siloxanes), poly(methyl methacrylate)

INTRODUCTION

Matrix assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF MS) [1,2], allows desorption and ionization of very large molecules, even in complex mixtures. The ionization process in MALDI-TOF proceeds through the capture of a proton or a metal ion (usually lithium, sodium, potassium), which forms a charged adduct with the molecular species. For the analysis of mass spectra of polymers [3–13], especially in quantitative applications, it is assumed that the number of charged adducts reflects the number of polymeric chains. In particular, the ionization yield of the various oligomer species present in polymers must not undergo any discrimination with respect to their mass values, and the MALDI-TOF detector should show a constant response to ions over a wide range of mass numbers. However, it has been found [10] that molecular weight estimates provided by MALDI MS agree with the values obtained by conventional techniques only in the case of samples with narrow MWD, whereas with polydisperse polymers MALDI MS fails to yield reliable MW values [10]. This implies that the relative intensity of the MALDI signals as a function of their m/z values is far from that expected from the actual MWD of the polymer sample, and indicates that lighter molecules are preferentially desorbed and ionized in the MALDI process, suppressing the desorption and ionization of larger molecules. Synthetic polymers may show a wide range of molecular weight distributions, according to the method of synthesis used in their preparation, and therefore the application of the MALDI MS technique for the MW measurements appears limited to narrow distributions [10,11].

A methodology for the MW determination in polydisperse polymer samples by MALDI consists of analytical GPC fractionation of polydisperse samples to collect numerous fractions per run [12,13]. Typically, by injecting 0.5mg of polymer into the GPC system and collecting about 100 fractions, the amount of sample present in each fraction (about 5 μ g, on average) exceeds many times the quantity needed for a MALDI spectrum. Selected fractions are then analysed by MALDI-TOF and the mass spectra of these nearly uniform samples allow the computation of reliable values of

M_n and M_w corresponding to the fractions. The calibrated GPC trace can then be used to compute average MWs and molecular weight distributions (MWD) of the unfractionated sample. We have proposed this approach earlier [12,13], and the first results obtained were encouraging.

We have now furthered our studies on this hyphenated GPC/MALDI method, testing the reliability of the MW estimates thus obtained, and exploring some peculiar aspects of the MALDI response to the phenomenon of molecular association in polymers.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA) GPC standard samples were supplied by Polymer Laboratories (Shropshir UK). Polydisperse PMMA sample (PMMA-W1) were supplied by the Aldrich Chemical Co. (Milwaukee, WI) Poly(dimethyl siloxane)(PDMS1) was a high-molecular-weight sample supplied by the Aldrich Chemical Co. PDMS2 sample was obtained from a PDMS1 sample equilibrated with 0.2% (w/w) of NaOH at 250°C for 2h. The reaction mixture was treated with 10 mL of the HCl 1M in methanol, and then was washed several times with fresh methanol and dried at 40°C overnight.

MALDI Sample Preparation

PMMA samples were dissolved in acetone and all *trans* 3-indoleacrylic acid was used as a matrix. 2-(4-hydroxyphenylazo)benzoic acid (HABA) and 2,5-dihydroxybenzoic acid (DHB) were used as a matrix for poly(dimethyl siloxane) samples. Probe tips were loaded with 0.3 μmol matrix and 0.1 nmole of polymer sample; whereas, for polymer fractions with molecular weight above 100 kDa, 0.01 nmole of sample were used.

MALDI-TOF Mass Spectra

A Bruker Reflex mass spectrometer (Bremen, Germany) was used to obtain the matrix-assisted laser desorption ionization-time of flight mass spectra. The spectrometer is equipped with a nitrogen laser (337 nm, 5 ns), a flash

ADC (time base 4 ns), and with two detectors. The first detector works when the reflectron device is off and allows the detection of ions in the linear mode; whereas, the second detector is placed at the end of the second flight tube, and allows the detection of ions in the reflectron mode. The detection in the linear mode was achieved by means of a Himas detector, which 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 iodide scintillator which 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 Himas detector has low temporal resolution. The detection in the reflectron mode was achieved by the standard double-plate microchannel detector. Accelerating voltage was 30 kV. The laser irradiance was slightly above threshold (ca. 10^6 W/cm²). Ions below m/z 350 were removed with pulsed deflection and 100 transients were summed. The resolution at 5000 Da was 200 in the linear mode and 400 in the reflectron mode. Time-to-mass conversion of the time-of-flight mass spectra was achieved using a previously described self-calibration method [8].

GPC Fractionation

The analyses were performed on a Polymer Laboratory GPC apparatus, equipped with four μ -Styragel columns (7.8×300 mm) (in the order 1000, 500, 10000 and 100 Å pore size) (Waters Corp., Milford, MA) attached in series, using a Polymer Laboratories differential refractometer. Injection volume was 60 μ L of polymeric solutions (15 mg/mL in THF). The flow rate was 1 mL/min. Fifty fractions of 0.24 mL were collected for PMMA and the equilibrated sample of PDMS; whereas, 81 fractions were collected for the high-molecular-weight PDMS sample (1–61, 0.10 mL; 62–81, 0.30 mL). Stabilized THF was used.

Molecular Weight Calculations

The MALDI mass spectra of the GPC fractions were processed with the XMASS program from Bruker. The program uses mass spectral intensities to compute the most-probable molecular weight M_p , number-average molecular weight M_n , weight-average molecular weight M_w , and polydispersity index (M_w/M_n) of each fraction, as reported in Tables I and II.

TABLE I Molecular weight distribution data for (polymethyl methacrylates)

| Polymer Sample | M_p | | M_n | | M_w | | M_w/M_n | | V_R^d |
|----------------------|--------|--------------------|--------|--------------------|--------|--------------------|-----------|-------|---------|
| | SEC | MALDI ^a | SEC | MALDI ^b | SEC | MALDI ^c | SEC | MALDI | |
| PMMA2400 | 2400 | 2100 | 2200 | 2000 | 2360 | 2200 | 1.08 | 1.10 | 30.3 |
| PMMA3100 | 3100 | 2700 | 2770 | 2700 | 3000 | 3000 | 1.09 | 1.11 | 29.4 |
| PMMA4700 | 4700 | 4200 | 4300 | 4100 | 4600 | 4450 | 1.10 | 1.08 | 28.6 |
| PMMA6540 | 6540 | 5200 | 5800 | 5200 | 6300 | 5800 | 1.09 | 1.11 | 27.9 |
| PMMA9400 | 9400 | 8400 | 8100 | 8100 | 8900 | 8700 | 1.10 | 1.08 | 27 |
| PMMA12700 | 12700 | 10400 | 11000 | 9300 | 11800 | 10300 | 1.08 | 1.10 | 26.3 |
| PMMA17000 | 17000 | 15000 | 16100 | 14900 | 17100 | 15400 | 1.06 | 1.03 | 25.8 |
| PMMA29400 | 29400 | 27000 | 28000 | 26000 | 29600 | 26300 | 1.06 | 1.01 | 24.6 |
| PMMA48600 | 48600 | 47000 | 47000 | 46400 | 49100 | 47000 | 1.05 | 1.01 | 23.6 |
| PMMA95000 | 95000 | 91000 | 92000 | 84000 | 95100 | 85600 | 1.04 | 1.02 | 22.5 |
| PMMA218600 | 218600 | 209000 | 209700 | 208000 | 218600 | 209000 | 1.05 | 1.007 | 21.4 |
| PMMA_W1 ^c | 33000 | 2200 | 11450 | | 32700 | | 2.85 | 1.15 | 25.2 |

TABLE I (continued)
SEC Fractions of PMMA-WI

| | | | | | |
|---------|-------|-------|-------|-------|-------|
| PMMAF5 | 99000 | 99300 | 99500 | 1.002 | 22.6 |
| PMMAF7 | 87000 | 83000 | 84000 | 1.012 | 23.04 |
| PMMAF9 | 64000 | 63600 | 64300 | 1.011 | 23.48 |
| PMMAF11 | 56000 | 55100 | 55900 | 1.014 | 23.92 |
| PMMAF13 | 42000 | 41800 | 42600 | 1.02 | 24.36 |
| PMMAF15 | 35000 | 34600 | 35200 | 1.017 | 24.80 |
| PMMAF17 | 28500 | 28300 | 29000 | 1.025 | 25.24 |
| PMMAF19 | 24500 | 23000 | 23300 | 1.013 | 25.68 |
| PMMAF21 | 19300 | 19700 | 20200 | 1.025 | 26.12 |
| PMMAF23 | 14800 | 14800 | 15000 | 1.013 | 26.56 |
| PMMAF25 | 12400 | 13100 | 13400 | 1.023 | 27 |
| PMMAF32 | 5000 | 4900 | 5100 | 1.04 | 28.54 |
| PMMAF34 | 4400 | 4400 | 4500 | 1.023 | 28.98 |

a: most probable molecular weight:

b: $M_p = n \sum n_i M_i / \sum n_i$

c: $M_w = \sum n_i M_i^2 / \sum n_i M_i$

d: V_R = retention volume of each fraction

e: obtained by free-radical polymerization

TABLE II Molecular weight distribution data of GPC fractions of commercial and equilibrated PDMS, obtained by the MALDI-TOF mass spectra.

| Fractions | M_p^a | M_n^b | M_w^c | M_w/M_n | V_R^d |
|--------------|---------|---------|---------|-----------|---------|
| PDMS1 | | | | | |
| 15 | 300000 | 296000 | 300000 | 1.01 | 20.71 |
| 18 | 275000 | 267000 | 274000 | 1.03 | 21.01 |
| 21 | 230000 | 222000 | 227000 | 1.02 | 21.32 |
| 25 | 190000 | 198500 | 206000 | 1.04 | 21.72 |
| 29 | 155000 | 150000 | 157000 | 1.05 | 22.12 |
| 33 | 140000 | 142000 | 151000 | 1.06 | 22.53 |
| 35 | 128000 | 127500 | 134000 | 1.05 | 22.73 |
| 38 | 100000 | 100500 | 106500 | 1.06 | 23.03 |
| 44 | 78000 | 77000 | 81500 | 1.06 | 23.64 |
| 50 | 49000 | 51000 | 54000 | 1.06 | 24.24 |
| 54 | 42000 | 43000 | 45000 | 1.05 | 24.64 |
| 66 | 16000 | 16500 | 18000 | 1.09 | 26.88 |
| 70 | 6300 | 9000 | 9800 | 1.09 | 28.10 |
| 75 | 3300 | 5200 | 5800 | 1.11 | 29.63 |
| PDMS2 | | | | | |
| 3 | 211000 | 209000 | 213000 | 1.019 | 22.22 |
| 5 | 170000 | 172000 | 176000 | 1.023 | 22.70 |
| 7 | 122000 | 124000 | 127000 | 1.024 | 23.18 |
| 9 | 87000 | 88200 | 89600 | 1.016 | 23.66 |
| 10 | 90000 | 87400 | 92200 | 1.055 | 23.90 |
| 12 | 56000 | 56800 | 57600 | 1.014 | 24.38 |
| 14 | 47000 | 48200 | 48800 | 1.012 | 24.86 |
| 16 | 35000 | 37200 | 37500 | 1.008 | 25.34 |
| 18 | 30000 | 31000 | 31500 | 1.016 | 25.82 |
| 20 | 26500 | 26100 | 26600 | 1.019 | 26.30 |
| 22 | 22000 | 22000 | 22500 | 1.023 | 26.78 |
| 24 | 17600 | 18200 | 18800 | 1.033 | 27.26 |
| 26 | 15000 | 14300 | 14800 | 1.035 | 27.74 |
| 28 | 11500 | 11800 | 12100 | 1.025 | 28.22 |
| 30 | 9000 | 10200 | 10900 | 1.068 | 28.70 |
| 32 | 8300 | 8450 | 8500 | 1.006 | 29.18 |
| 34 | 7100 | 7100 | 7230 | 1.018 | 29.66 |
| 36 | 5700 | 5760 | 5830 | 1.012 | 30.14 |
| 38 | 5000 | 4800 | 4880 | 1.017 | 30.62 |
| 40 | 4400 | 4000 | 4100 | 1.025 | 31.10 |
| 42 | 3100 | 3100 | 3150 | 1.016 | 31.58 |

a: most probable molecular weight;

b: $M_n = \sum n_i M_i / \sum n_i$ c: $M_w = \sum n_i M_i^2 / \sum n_i M_i$ d: V_R = retention volume of each fraction

The molecular weight data of the unfractionated polymer samples were calculated from the GPC curves by the Polymer Lab Caliber software. GPC calibration plots for PMMA-W1, PDMS1, and PDMS2 samples were obtained by the correlation of the log of M_w , obtained by MALDI, of each fraction with the corresponding eluted volume (V_e) in mL.

PDMS1 GPC fractions measured after six weeks (see text) showed the following values: $V_R = 21.22$, $M_w = 424,000$; $V_R = 21.51$, $M_w = 388,000$; $V_R = 21.80$, $M_w = 346,000$; $V_R = 22.08$, $M_w = 291,000$; $V_R = 22.37$, $M_w = 260,000$; $V_R = 22.66$, $M_w = 251,000$; $V_R = 22.23$, $M_w = 202,000$; $V_R = 24.38$, $M_w = 131,000$; $V_R = 24.67$, $M_w = 96,000$; $V_R = 26.96$, $M_w = 42,000$; $V_R = 29.26$, $M_w = 15,400$; $V_R = 29.83$, $M_w = 12,100$; $V_R = 30.41$, $M_w = 10,400$; $V_R = 31.55$, $M_w = 7200$; $V_R = 32.13$, $M_w = 5850$.

Viscometry

Inherent viscosities ($\eta_{inh} = c^{-1}l_n\eta_r$; $c = 0.5\text{g/dL}$) were measured in a Desreux-Bishoff suspended-level viscometer at $30 \pm 0.1^\circ\text{C}$. The solvent was toluene for poly(dimethyl siloxane) samples and tetrahydrofuran for the PMMA sample. Viscosity values for poly(dimethyl siloxane) were: PDMS1: $\eta_{inh} = 0.22$; PDMS2: $\eta_{inh} = 0.12$. The universal calibration curve for our GPC apparatus gave following equation: $\log(\eta M) = 0.016(V_e)^2 - 1.76 V_e + 22.7$

RESULTS AND DISCUSSION

Poly(Methyl Methacrylates)

A PMMA sample (denoted as PMMA-W1 in Table I) synthesized by free radical polymerization, with a polydispersity index of 2.5, was analysed by GPC/MALDI-TOF. The MALDI-TOF mass spectrum of this sample displays a most probable molecular weight of 2.2 kDa. This value falls well below the correct value (33 kDa), leaving open the problem of how to estimate the M_w of a polydisperse polymer sample by MALDI-TOF.

The PMMA-W1 sample was then injected into the GPC apparatus, and about 50 fractions were collected from the eluate. These fractions were analysed by MALDI-TOF and yielded excellent spectra with narrow distributions, up to high molecular masses, from which the corresponding MW

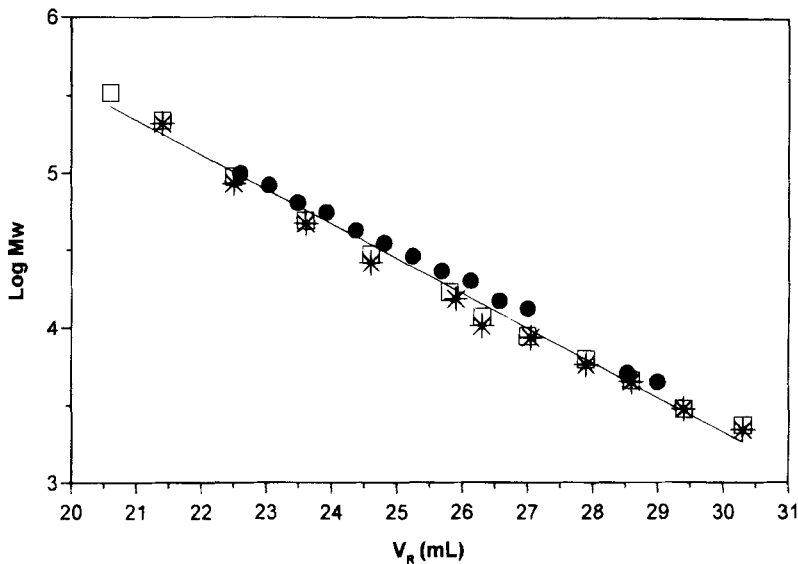


FIGURE 1 GPC calibration plots of the PMMA samples: □ M_w of the PMMA GPC standards as indicated by the supplier, * M_w of the PMMA GPC standards obtained by MALDI-TOF spectra, ● M_w of the PMMA-W1 fractions obtained by MALDI-TOF spectra.

could be calculated. These M_w values are collected in Table I. The log M_w of the PMMA-W1 fractions show a linear correlation with the elution volume of each fraction which allowed the calibration of the GPC tracing against absolute molecular weights (Figure 1). The computed MW averages of PMMA-W1 sample are $M_n = 12,000$; $M_w = 33,000$, and compare well with the values given by the manufacturer: $M_n = 13,000$ and $M_w = 33,000$.

In order to test the accuracy of M_w estimates obtained by GPC/MALDI-TOF, several anionic PMMA samples with well characterized molecular weights (GPC standards) were injected in the GPC apparatus, and the retention volumes V_R at the GPC maxima were plotted against M_w as shown in Figure 1. This independent set of data is nearly coincident with the GPC calibration curve obtained from the GPC fractionation of sample PMMA-W1, supporting the accuracy of the hyphenated method proposed. Data in Table I show also a reasonable agreement between the M_w values estimated from MALDI mass spectra and those determined by conventional techniques for the anionic PMMA standards.

Poly(Dimethyl Siloxane)

The GPC calibration curves of linear and cyclic polydimethylsiloxanes against absolute MW have been reported [14] and it has been shown that, cyclic oligomers are eluted at slightly higher retention volumes with respect to linear oligomers of the same MW; the ratio $(M_{cyclic}/M_{linear})_{Ve}$ was 1.24. This effect is caused by the smaller hydrodynamic volume of cyclics. The detection of this subtle difference appeared to offer an interesting test for the accuracy of GPC/MALDI-TOF. Therefore, in a second set of experiments, we analyzed two poly(dimethyl siloxane) samples: PDMS1 and PDMS2 (Fig. 2). PDMS1 is a polydisperse linear polymer, showing a bimodal distribution (Fig. 2a); whereas, PDMS2 is a lower MW sample obtained by partial alkaline hydrolysis of PDMS1 (Figure 2b). Besides lowering the molecular weight, the base also induces a ring-chain equilibration process and end-to-end cyclization into the polymer [14], and thus producing a polydisperse cyclic polymer. [13]

GPC fractionation of the two samples afforded a number of fractions which were analysed by MALDI-TOF, allowing the determination of their MW (Table II). Figure 3 reports $\log M_w$ versus elution volumes for PDMS1 and PDMS2 fractions. Owing to the different structure of the two samples (linear and cyclic chains, respectively), two slightly different GPC calibration lines are observed (Fig. 3).

The calibrated GPC tracings against absolute molecular weight of PDMS1 and PDMS2 were then used to compute the average molecular weight and MWD of these unfractionated samples. For sample PDMS1 these values are $M_n = 33,000$, $M_w = 130,000$, $M_p = 169,000$, $D = M_w/M_n = 3.94$ (an apparent value for the bimodal polymer), (Fig.2a); whereas for sample PDMS2 these values are $M_n = 19,000$, $M_w = 52,000$, $M_p = 57,000$, $D = M_w/M_n = 2.7$, (Fig.2b). The $M_w = 130,000$ value, obtained for PDMS1 by the hyphenated GPC/MALDI-TOF method, compares fairly well with the rough estimates computed from the GPC universal calibration curve. In fact, the GPC tracing of PDMS1 (Fig. 2a), shows a maximum at 22.3 mL, which corresponds to a weight average molecular weight $M_w = 180,000$, estimated from the inherent viscosity $[\eta] = 0.22$, through GPC universal calibration curve (see experimental section). Analogously, the GPC tracing of PDMS2 (Fig. 2b), shows a maximum at 24.8 mL, which corresponds to $M_w = 30,000$, estimated from the inherent viscosity $[\eta] = 0.12$, through GPC universal calibration curve, against a value of $M_w = 52,000$ obtained

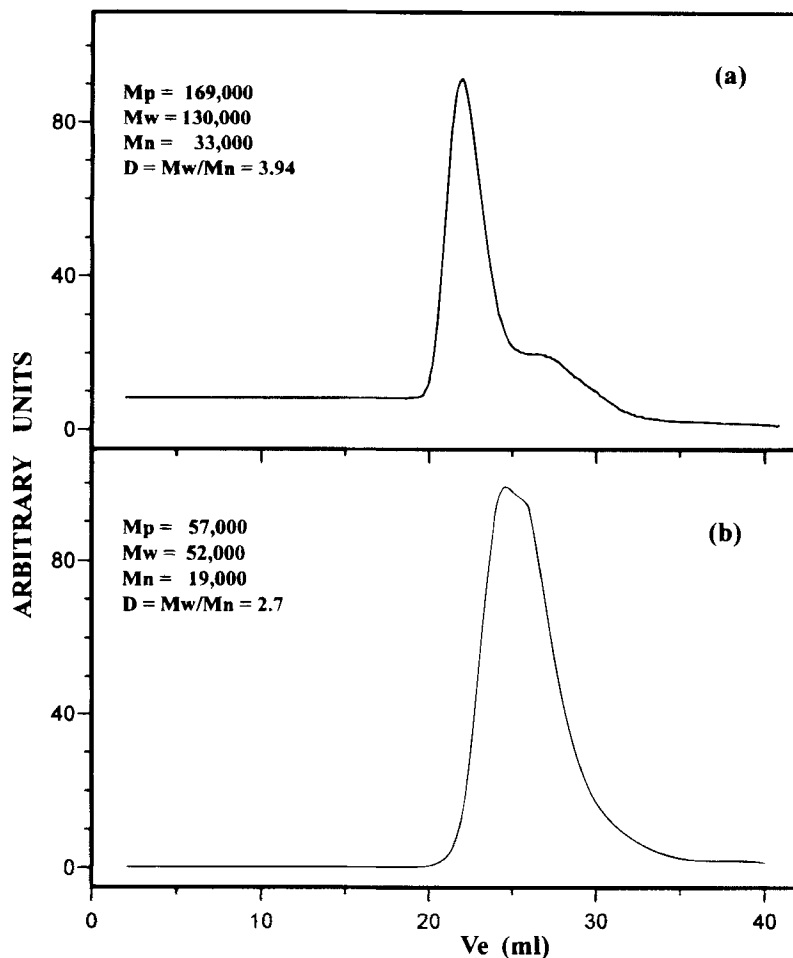


FIGURE 2 GPC in toluene of: (a) PDMS1 sample, (b) PDMS2 sample.

from the GPC/MALDI-TOF method. As expected, molecular weight data obtained from universal calibration are only indicative.

In a duplicate experiment, the PDMS1 sample was fractionated by GPC, and the elution tracing was identical to the previous one. However, the single GPC fractions were analysed by MALDI-TOF six weeks after the actual fractionation experiment. During this time, the solvent slowly evaporated and the fractions remained for relatively long time in the solid state.

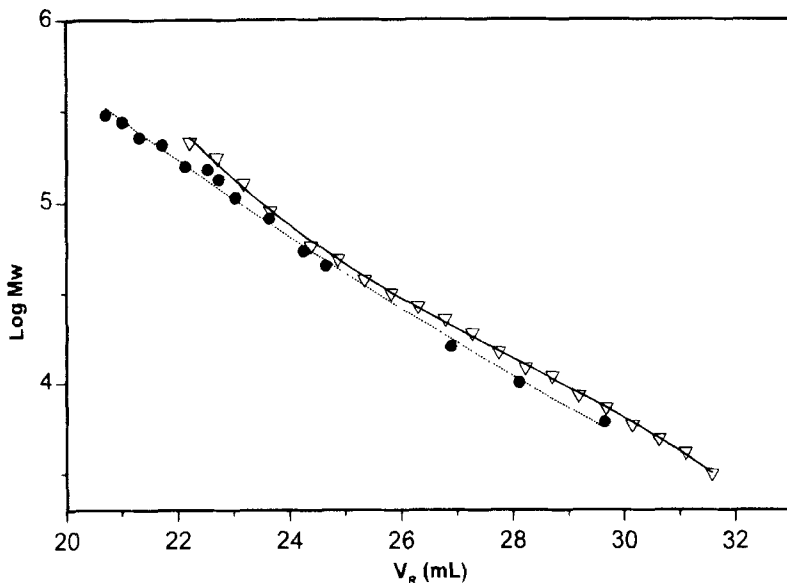


FIGURE 3 GPC calibration plots for poly(dimethyl siloxanes) MALDI-TOF molecular weights versus retention volume V_R of each GPC fractions. ● PDMS1 ∇ PDMS2.

These fractions gave excellent MALDI Spectra and four of them are shown in Figure 4 (a–d). Fraction 6 ($V_R = 21.22$) gave $M_w = 424,000$; fraction 8 ($V_R = 21.80$) gave $M_w = 346,000$; fraction 17 ($V_R = 24.38$) gave $M_w = 131,000$ Da; and fraction 26 ($V_R = 26.96$) gave $M_w = 42,000$. A comparison with the MW curve in Figure 3 (circles) shows that the MALDI spectra of these fractions display MW values roughly doubled with respect to fresh fractions which elute at same volume in GPC analysis.

This effect is not easily explained, except by assuming the occurrence of molecular association of PDMS chains in the condensed state. This association needs not to be complete in order to get doubled molecular weights by the MALDI technique. Dimeric, or even higher, polymer species have been often observed in the MALDI spectra of PMMA, polystyrenes, and poly(ethylene glycols) [8–10]. In these cases, the peak corresponding to dimeric (or higher) species, usually appear in the MALDI spectra as weak or medium intensity peaks. It is not surprising, therefore, that in the presence of even partial molecular association, the dimer peak becomes the most intense in the MALDI spectrum, justifying the observed doubling of MW.

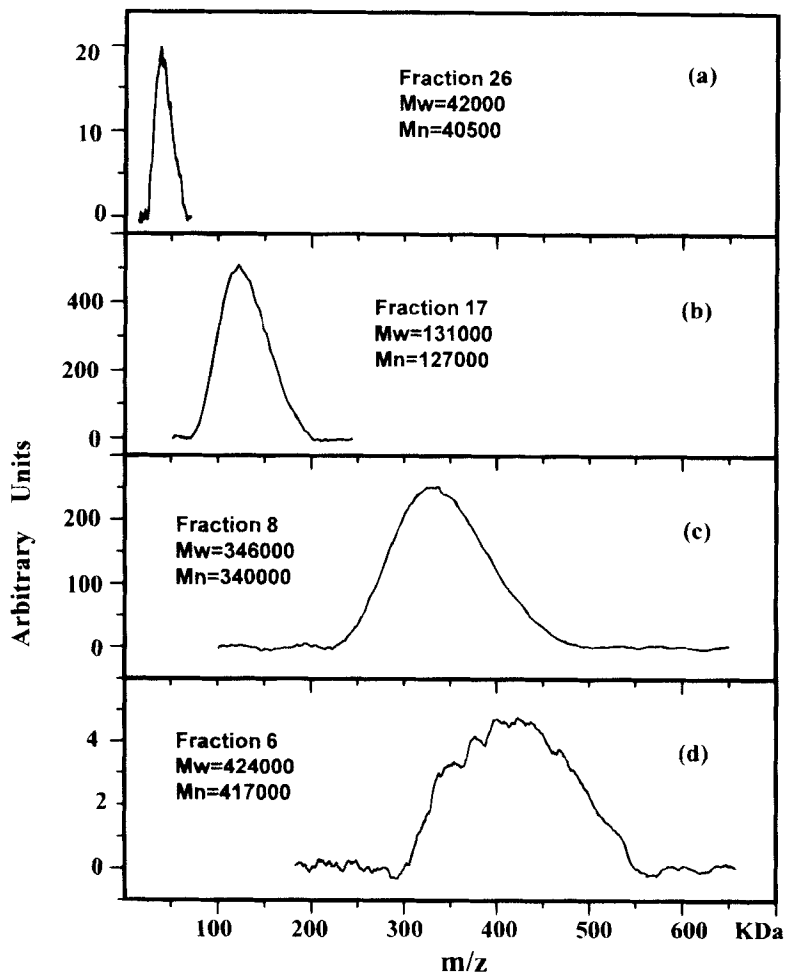


FIGURE 4 MALDI-TOF mass spectra, obtained in the linear mode, of four selected PDMS1a fractions: (a) fraction 26, (b) fraction 17, (c) fraction 8, (d) fraction 6.

Structural Characterization of PDMS by MALDI-TOF

The MALDI spectra of the GPC fractions containing the lowest molecular species present in the polymers show these oligomers as mass-resolved signals, allowing assignment of each peak to a specific oligomer and the identification of the structure of the polymer and the end groups of the

chains. The MALDI spectra of the GPC fractions containing very high-MW-polymer chains show unresolved mass signals, because at higher masses (>15 kDa) the molecular peaks in the MALDI-TOF spectra become progressively broader and the signals begin to overlap. Therefore, in these spectra it is not possible to distinguish the structure of the polymer (cyclic or linear).

Figure 5a gives the MALDI-TOF mass spectrum of a low-molecular-weight PDMS1 fraction in the reflected mode, showing peaks roughly in the region 5–10 kDa. After accurate mass calibration, peaks in Figure 5a were assigned to a single mass series: that is, linear PDMS oligomers terminated by trimethylsilyl groups. Figure 5b gives the spectrum of a lower MW fraction of PDMS1 (showing peaks in the mass range 1.7–6.0 kDa), which shows instead the presence of two mass series having a different molecular weight distribution. After accurate mass calibration, the most intense peak series in Figure 5b was assigned to linear PDMS oligomers terminated by trimethylsilyl groups, whereas the other mass series was assigned to cyclic dimethylsiloxane oligomers.

Conclusion

Progress appears to have been made in achieving a long-time goal in the characterization of polymeric materials, in which the MW and MWD of high polymers can be measured directly. The MALDI spectra of the GPC fractions containing the lowest molecular species present in the polymers show these oligomers as mass-resolved signals, therefore allowing the identification of the polymer structure and the terminal groups of the polymer chains. Therefore, the structural and molecular characterization of polymers are possible by combined GPC/MALDI-TOF experiments, giving a unique set of information not available by other techniques.

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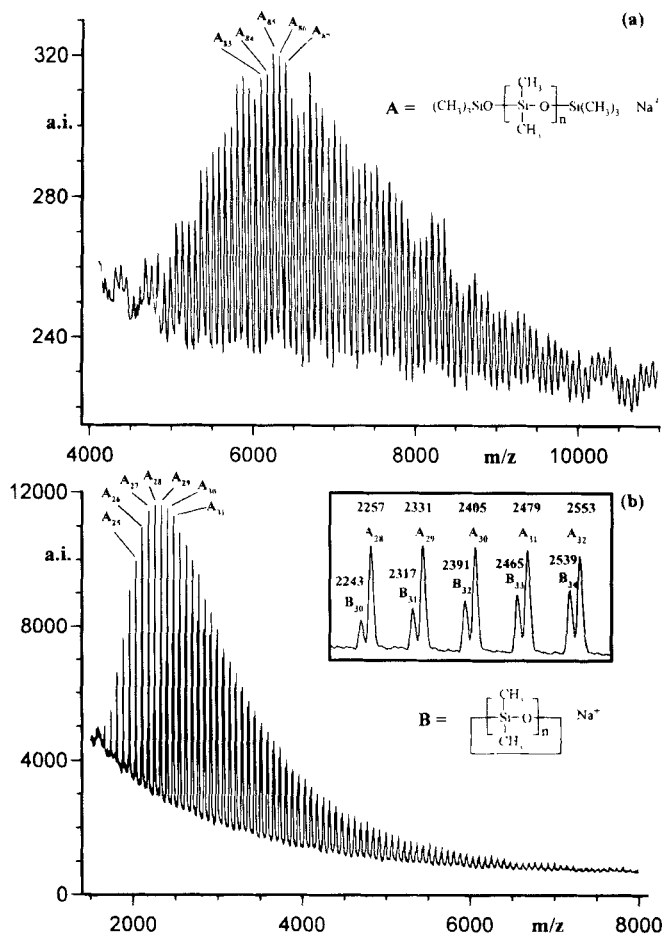


FIGURE 5 Reflectron MALDI-TOF mass spectra of PDMS1 fractions: (a) fraction 70 (b) fraction 78.

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