Macromolecules **1995,** *28,* 7983–7989

Molecular and Structural Characterization of Polydisperse Polymers and Copolymers by Combining MALDI-TOF Mass Spectrometry with GPC Fractionation

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Received July 5, 1995; Revised Manuscript Received August 24, 1995[⊗]

ABSTRACT: Matrix assisted laser desorption ionization–time of flight mass spectrometry (MALDI-TOF MS) allows detection of large molecules such as those present in synthetic and natural macromolecules. Until recently, it was reported that MALDI-TOF measurements can provide correct molecular weight (MW) averages only for samples with a narrow MW distribution ($M_w/M_n \leq 1.20$). We have now developed a methodology for polydisperse samples. We recorded the GPC trace of two polydisperse polymeric samples, namely, poly(butylene adipate) (PBA) and poly(butylene adipate-*co*-butylene succinate) (PBAS), collecting about 40–50 fractions per run. Selected fractions were analyzed by MALDI-TOF, and the average MW of each fraction was determined, allowing calibration of the GPC curves against absolute MW. The two calibrated GPC traces were then used to compute average MW and molecular weight distributions (MWD) of the unfractionated samples. End group analysis from MALDI-TOF spectra revealed that the PBA sample is composed of seven different types of chains. For the copolymer sample, PBAS, analysis of the MALDI spectra established a random sequence distribution of comonomer units. The succinate/adipate molar ratio calculated from the MALDI spectra is in good agreement with the molar ratio found by NMR.

Introduction

Matrix assisted laser desorption ionization–time of flight mass spectrometry (MALDI-TOF MS) is a recently introduced[1,2] soft ionization technique that allows desorption and ionization of very large molecules, even if in complex mixtures. In polymer analysis,[3–15] the great promise of MALDI-TOF is to perform direct identification of mass-resolved polymer chains including intact oligomers, measurement of MW averages and MWD, and the simultaneous determination of structure and terminal groups in polymer samples.

All the conventional MW characterization techniques (viscosity, GPC, laser light scattering) are indirect measurements of molecular masses, and the perspective of direct measurements of MW and MWD has stirred much expectation among polymer scientists, but the characterization of synthetic polymers by MALDI MS is far from satisfactory. In fact, it has been found[15] 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,[15] whereas with polydisperse polymers MALDI MS fails to yield reliable MW values.

Recently,[16] polydisperse polymers such as dextrans were fractionated by GPC, yielding narrow distribution samples which, when analyzed by MALDI MS, were found to give good mass spectra with MW values in excellent agreement with those obtained by a conventional technique (high pressure size exclusion chromatography–low angle laser light scattering, HPSEC-LALLS). This finding opens the way to a new development of the technique, where the MALDI MS is used as the detector in the GPC fractionation of polydisperse polymer samples.

In this paper, we show how to obtain MW averages and MWD of polydisperse polymer samples by off-line coupling of the GPC apparatus with the MALDI mass spectrometer. The MALDI mass spectra of GPC fractions allow the computation of M_n and M_w of the fractions. This permits the calibration of the GPC curve against absolute molecular weights and the computation of MW averages from the GPC curve. The procedure yields correct MW and MWD estimates.

Furthermore, the MALDI spectra of the fractions containing the lowest molecular weight species show resolved oligomer signals, allowing the identification of the polymer structure and of the end groups present in the polymer chains. In the case of copolymers, MALDI spectra allow us also to determine both the composition of the copolymer and the sequence distribution.

Experimental Section

Materials. Dimethyl adipate, dimethyl succinate, adipoyl chloride, and 1,4-butanediol were supplied by Aldrich and purified by vacuum distillation, prior to use.

Polymer Synthesis. Poly(butylene adipate) (PBA) was synthesized by bulk polycondensation from an equimolecular mixture of adipoyl chloride and 1,4-butanediol. The monomers were mixed at room temperature under nitrogen flow, and the reaction mixture was allowed to reach 180 °C and maintained for 2 h. The HCl formed was removed with the nitrogen flow. The inherent viscosity measured in THF at 30 ± 0.1 °C was 0.16 dL/g.

Poly(butylene adipate-*co*-succinate) (PBAS) was synthesized by melt polycondensation using dimethyl adipate, dimethyl succinate, and 1,4-butanediol in a 1:1:2 ratio, respectively, in

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

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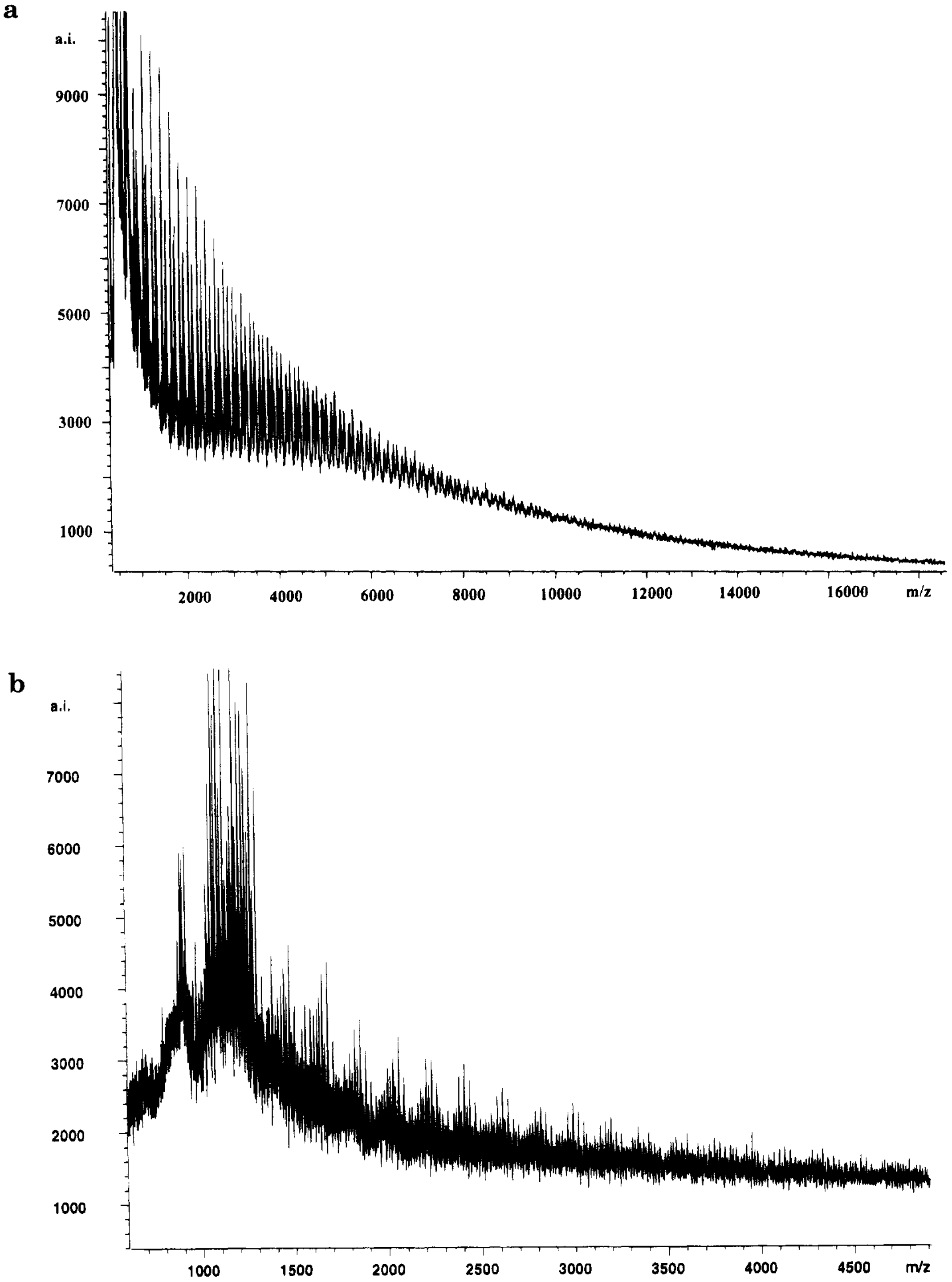

Figure 1. MALDI-TOF mass spectra of (a) poly(butylene adipate) and (b) poly(butylene adipate-*co*-butylene succinate).

the presence of a 1% mixture of $Sb_2O_3/Zn(CH_3COO)_2$ (4:1 w/w) as a transesterification catalyst. The reaction mixture was reacted at 180 °C under anhydrous condition for 2 h and then heated up to 230 °C for 5 h under vacuum (2 Torr) in order to remove the methanol and to shift the equilibrium toward higher molecular weight. The inherent viscosity of the crude copolymer in THF at 30 ± 0.1 °C was 0.19 dL/g. The composition calculated from ^{1}H and ^{13}C NMR spectra was 51% mol of butylene adipate.[17]

MALDI Sample Preparation. 2-[(4-Hydroxyphenyl)azo]-benzoic acid (HABA) or 2,4-dihydroxybenzoic acid (DHBA) was used as a matrix. The solvent was tetrahydrofuran (THF). Probe tips were loaded with 0.1 nmol of polymer sample and 0.3 μmol of matrix. No cationization agents were added.

MALDI-TOF Mass Spectra. A Bruker Reflex mass spectrometer 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 8 ns), and 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. Detection in the linear mode was achieved by means of a HIMASS detector. It has a venetian-blind steel dynode which 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 HIMASS detector has a low temporal resolution. The detection in the reflectron mode was achieved by the standard double-plate microchannel detector. Accelerating voltage was

Table 1. Determination of Molecular Weight Averages and of MW Distribution for PBA from the Analysis of MALDI-TOF Mass Spectra of the GPC Fractions of PBA

fraction	M_p[a]	M_n[b]	M_w[c]	M_w/M_n
2	39 000	36 600	37 200	1.02
4	29 840	29 900	29 960	1.01
7	22 080	22 550	23 020	1.02
10	16 800	17 163	17 529	1.02
16	9 570	10 252	11 135	1.09
21	6 190	6 454	6 721	1.04
26	4 500	4 113	4 342	1.06
30	3 200	3 060	4 036	1.07
36	2 700	2 460	2 680	1.09
40	1 180	1 820	2 000	1.10

[a] Most probable molecular weight. [b] $M_n = \Sigma n_iM_i/\Sigma n_i$. [c] $M_w = \Sigma n_iM_i^2/\Sigma n_iM_i$.

Table 2. Determination of Molecular Weight Averages and of MW Distribution for PBAS Copolymer from the Analysis of MALDI-TOF Mass Spectra of the GPC Fractions of PBAS

fraction	M_p[a]	M_n[b]	M_w[c]	M_w/M_n
1	64 000	66 000	69 000	1.04
3	46 500	47 500	48 500	1.02
6	29 300	29 900	30 600	1.02
10	18 070	18 490	18 920	1.02
14	10 800	11 690	12 600	1.08
19	6 420	6 360	6 500	1.02
25	3 510	3 530	3 650	1.03
31	2 350	2 350	2 410	1.03
34	1 450	1 400	1 500	1.07

[a] Most probable molecular weight. [b] $M_n = \Sigma n_iM_i/ \Sigma n_i$. [c] $M_w = \Sigma n_iM_i^2/\Sigma n_iM_i$.

30 kV. The laser irradiance was slightly above threshold (ca. 10^6 W/cm^2). Ions below m/z 350 were removed with pulsed deflection, and 100 transients were summed. The resolution at 5000 Da was 150 in the linear mode and 300–1500 in the reflectron mode.

Time-to-mass conversion of the time of flight mass spectra was achieved using the previously described[13] self-calibration method.

GPC Fractionation. The analyses were performed on a Waters 6000A apparatus, equipped with four μ-Styragel columns (in the order 1000, 500, 10000, and 100 Å pore size) attached in series, and a Waters R401 differential refractometer. Polymeric solution (60 μL of 15 mg/mL in THF) was injected. The flow rate was 1 mL/min THF. Fractions of 0.24 mL were collected, so that we obtained 42 fractions for PBA and 45 fractions for PBAS.

Molecular Weight Calculations. The MALDI mass spectra of ten selected fractions for PBA and nine selected fractions for PBAS were obtained and processed with the XMASS program from Bruker. The program uses mass spectral areas to compute the quantities known as most-probable molecular weight, number-average molecular weight, weight-average molecular weight, and polydispersity index (denoted as M_p, M_n, M_w, and M_w/M_n, respectively) of each selected fraction, as reported in Tables 1 and 2.

In order to calculate the molecular weight of PBA and PBAS, the $\log_{10}$ (M_n) obtained for each fraction was correlated with the corresponding eluted volume (V_e) in mL. The ten points for PBA are on a straight line. They were fitted with the line $\log_{10}$ $(M_n) = 8.008 - 0.1542V_e$. The nine points for the copolymer were fitted with the line $\log_{10}$ $(M_n) = 8.995 - 0.2026V_e$. The two GPC calibration lines were used to perform the following computation.[18] Based on the GPC traces of PBA and PBAS, an array of data points was constructed containing the weight fraction versus the eluted volume. A new array of data points was obtained by transforming the eluted volumes into masses. The latter array was used to compute M_n and M_w for the two samples. The result was M_n = 11 100, M_w = 16 000 for polyBA and M_n = 11 500, M_w = 20 600 for the copolymer.

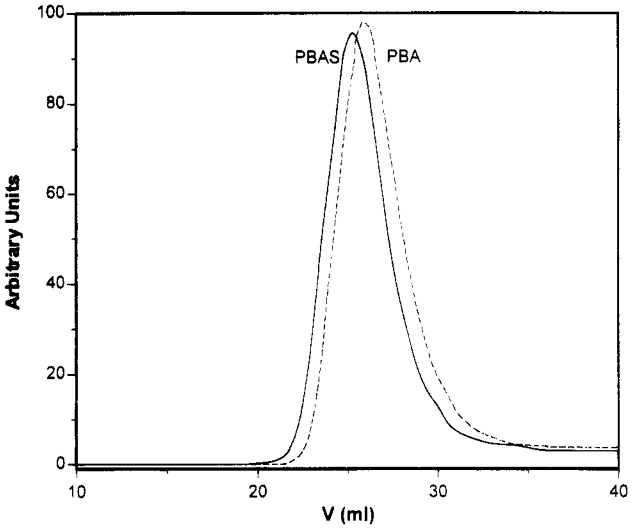

Figure 2. GPC recordings for poly(butylene adipate) (trace a) and poly(butylene adipate-*co*-butylene succinate) (trace b).

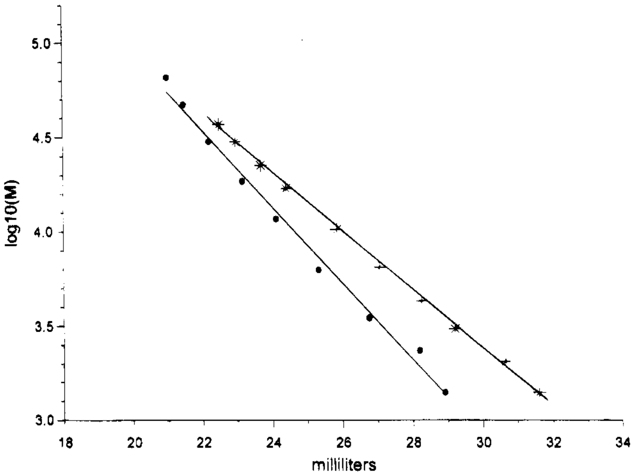

Figure 3. Calibration lines for GPC trace of poly(butylene adipate) (*) and for the copolymer (●) $\log_{10}$ (M) versus volume eluted (V_e) of each fraction.

Results and Discussion

Molecular Characterization of PBA and PBAS by MALDI-TOF MS. The ionization process in MALDI-TOF proceeds through the capture of a proton or a metal ion (usually lithium, sodium, or potassium), which forms a charged adduct with the molecular species.[3]

For the analysis of mass spectra of polymers, especially in quantitative applications, it has to be 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.

Synthetic polymers may show a wide range of molecular weight distributions, according to the synthetic method used in their preparation.

It has been recently found[15] that molecular weight estimates provided by MALDI-TOF measurements agree with the values obtained by conventional techniques, such as GPC, only in the case of polymer samples with very narrow MWD. When the polydispersity index reaches values around 1.20, the difference between the MW measured by GPC and MALDI spectra may amount to about 20%. At higher polydispersities, MALDI

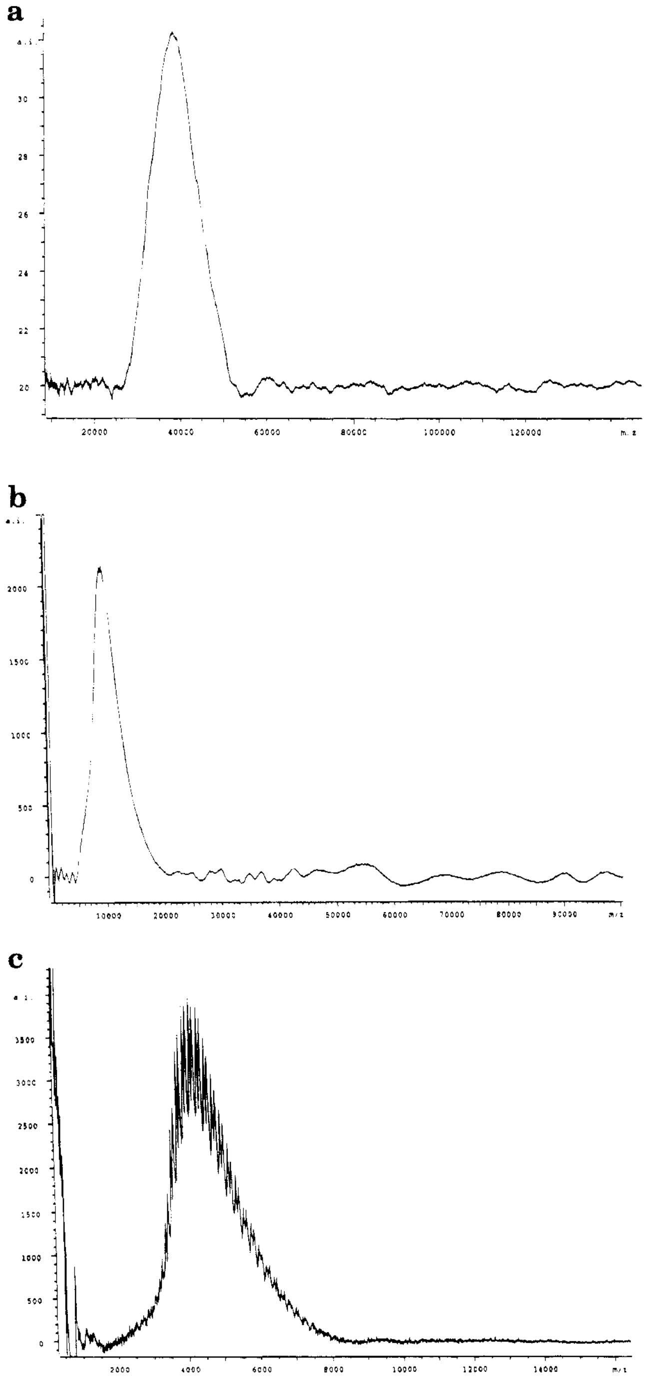

Figure 4. MALDI-TOF mass spectra of three selected fractions of PBA: (a) fraction 2, (b) fraction 16, (c) fraction 26.

spectra fail to yield reliable MW values, at least within the limitations imposed by the instrumentation used.[15] 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.

We have synthesized, by bulk polycondensation in the molten state, a polyester, poly(butylene adipate) (PBA), and a copolyester, poly(butylene adipate-*co*-butylene succinate) (PBAS), both with broad MWD.

Figure 1a reports the MALDI-TOF mass spectrum of the unfractionated PBA sample. A strong signal at low masses (1500 daltons) is present. As the mass grows, the signal intensity becomes lower and lower, until it reaches zero around 18 000 daltons and coincides with the base line. Similar behavior is observed for the MALDI-TOF mass spectrum of the unfractionated PBAS sample (Figure 1b), which shows a steep drop in signal intensity going from low masses to high masses and reaches the base line level around 5000 daltons. In the spectrum it is also possible to distinguish several clusters due to co-oligomers from pentamers to up twentymers.

Therefore, the MALDI spectra in Figure 1 indicate that the two polydisperse polyesters have very low molecular weights.

The GPC traces of the two samples, reported in Figure 2, show that PBA has a maximum at 25.7 mL of eluted

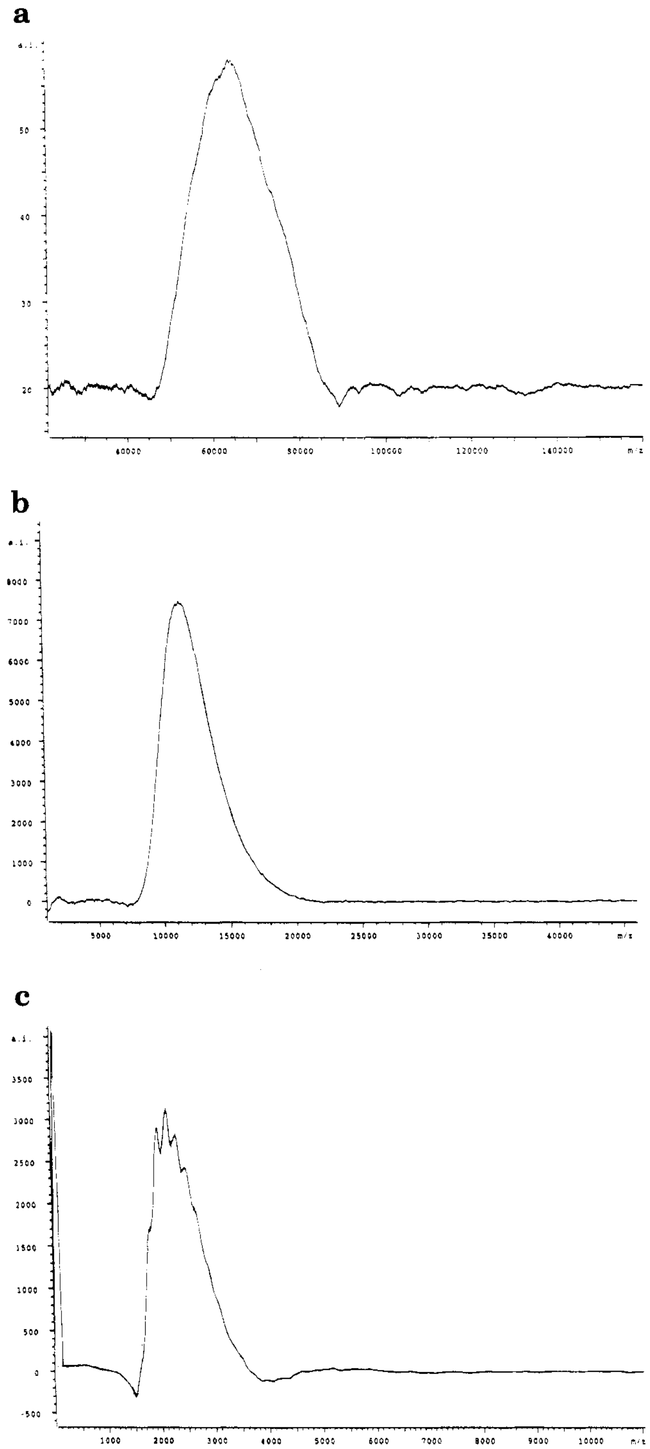

Figure 5. MALDI-TOF mass spectra of three selected fractions of PBAS: (a) fraction 1, (b) fraction 14, (c) fraction 31.

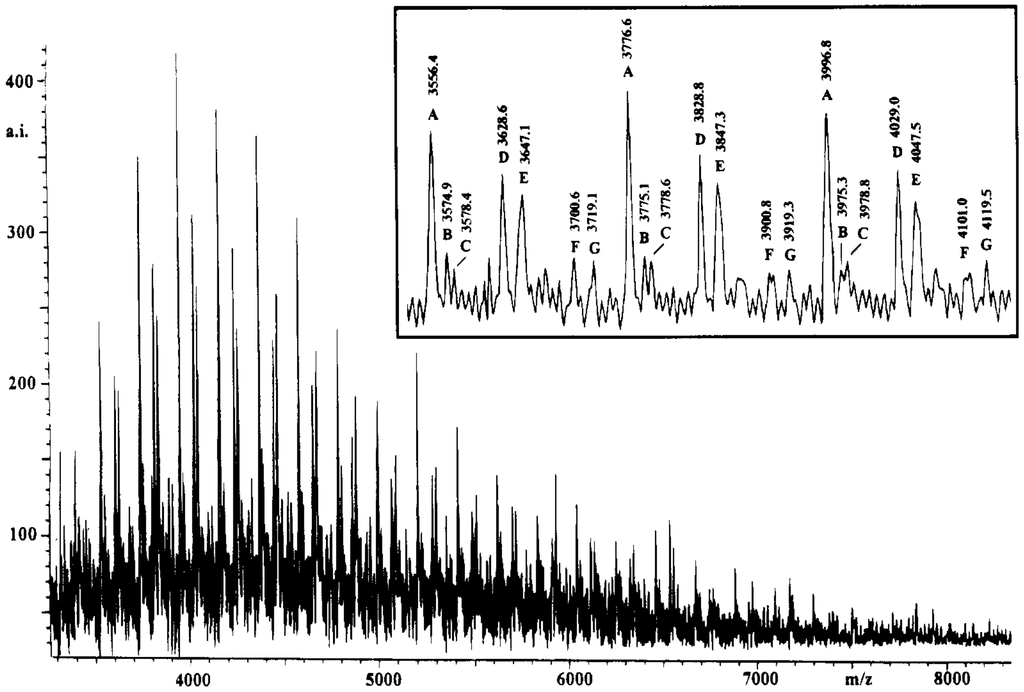

Figure 6. High resolution MALDI-TOF mass spectrum of a low MW fraction of polyester PBA (fraction 26, Table 1).

volume, whereas PBAS reaches a maximum for 25.3 mL. The weight average molecular weights of the two samples, roughly estimated through a GPC universal calibration curve,[19] are 14 200 for PBAS and 12 000 for PBA.

It can be also noted that the low molecular weight tail (between 30 and 40 mL of eluted volume, Figure 2) is quite low, thus hinting that low molecular weight oligomers (dimers, trimers, tetramers, and pentamers) are not very abundant in the two samples, which indicates a discrepancy with the results obtained by MALDI-TOF of the unfractionated samples (Figure 1). However, it will be shown below that this discrepancy is due to a MALDI artifact.

Since MALDI-TOF gives reliable and reproducible mass spectra for polymeric samples with narrow polydispersion,[15] we then decided to fractionate the GPC eluates of PBA and PBAS. We recorded the GPC traces of PBA and PBAS samples, collecting 42 fractions for PBA and 45 fractions for PBAS, each containing about 20 μg of polymeric material. Ten selected fractions of PBA and nine of PBAS were then analyzed by MALDI-TOF, and the average MW of each fraction was determined from the analysis of the corresponding MALDI mass spectrum (Tables 1 and 2, respectively), allowing the calibration of the GPC curves against absolute MW, as shown in Figure 3. The two calibrated GPC traces were then used to compute average MW and MWD of the unfractionated samples, as described in detail in the Experimental Section.

The results were as follows: M_n = 11 100, M_w = 16 000 in the case of PBA, and M_n = 11 500, M_w = 20 600 in the case of PBAS, in fair agreement with the GPC universal calibration estimates reported above.

The polymer fractions analyzed by MALDI-TOF yielded excellent spectra. Figure 4 reports the MALDI-TOF mass spectra of fractions 2, 16, and 26 of the PBA homopolyester. The overall pattern of the mass spectrum is similar for the three samples. It displays a single bell-shaped band. The center of the band falls at *m/z* 36 000 for fraction 2, at *m/z* 11 000 for fraction 16, and at *m/z* 4500 for fraction 26.

Figure 5 shows the MALDI-TOF mass spectra of fractions 1, 14, and 31 for the copolyester PBAS. The spectra have the same shape as above. The center of the band falls at *m/z* 64 000 for fraction 1, at *m/z* 10 800 for fraction 14, and at *m/z* 2300 for fraction 31.

Structural Characterization of PBA and PBAS by MALDI-TOF. The MALDI spectra of the GPC fractions containing the lowest weight molecular species present in the polymers show these oligomers as mass-resolved signals, allowing the assignment of each peak to a specific oligomer, and therefore allowing the identification of the structure of the polymer and of the end groups of the chains.

Figure 6 reports the MALDI-TOF mass spectrum of a low molecular weight PBA fraction (26, Table 1) recorded in the reflected mode. The width of the peaks is about 2 mass units. This implies that the resolution ($m/\Delta m$) is about 1500. Time-to-mass conversion of the time of flight mass spectra was achieved using the previously described[13] self-calibration method, with which the accurate mass peak calibration necessary for end groups analysis was obtained. Seven mass series are present in the mass spectrum in Figure 6, due to different end groups, and are assigned as reported in Table 3.

Figure 7 reports the mass spectrum of a low molecular weight PBAS copolyester fraction (31, Table 2) recorded in linear mode, using DHBA as a matrix. There are two mass series. The most intense one is due to oligomers terminated by methyl esters. They form ions of the following type: $H_3CO[CO(CH_2)_4COO(CH_2)_4O]_{0.55}[CO(CH_2)_2COO(CH_2)_4O]_{0.45}H...Na^+$. The other mass series is due to ions of the following type: $HO[CO(CH_2)_4COO(CH_2)_4O]_{0.55}[CO(CH_2)_2COO(CH_2)_4O]_{0.45}H...Na^+$.

In the case of copolymers, the chain statistic analysis of the mass spectra allows us to determine the composition and the sequence distribution of the comonomer units.[20] The relative intensity of the mass peaks depends on the copolymer composition and on the type of distribution along the chain. Therefore, assuming a theoretical distribution model and fitting the calculated

Table 3. Assignments for the Seven Mass Series Observed in the MALDI-TOF Mass Spectrum Reported in Figure 6 and Corresponding to PBA Oligomers

oligomer	structure	*n*	*m/z*[a]
A	$HO[CO(CH_2)_4COO(CH_2)_4O]_nCO(CH_2)_4COOH...Li^+$	17	3556.4
		18	3756.6
		19	3956.8
B	$Cl[CO(CH_2)_4COO(CH_2)_4O]_nCO(CH_2)_4COOH...Li^+$	17	3574.9
		18	3775.1
		19	3975.3
C	$NaO[CO(CH_2)_4COO(CH_2)_4O]_nCO(CH_2)_4COOH...Li^+$	17	3578.4
		18	3778.6
		19	3978.8
D	$HO[CO(CH_2)_4COO(CH_2)_4O]_nH...Li^+$	18	3628.6
		19	3828.8
		20	4029.0
E	$Cl[CO(CH_2)_4COO(CH_2)_4O]_nH...Li^+$	18	3647.1
		19	3847.3
		20	4047.5
F	$HO(CH_2)_4O[CO(CH_2)_4COO(CH_2)_4O]_nH...Li^+$	18	3700.6
		19	3900.8
		20	4101.0
G	$Cl[CO(CH_2)_4COO(CH_2)_4O]_n(CH_2)_4OH...Li^+$	18	3719.1
		19	3919.3
		20	4119.5

[a] Observed *m/z* values after calibration procedure.[13]

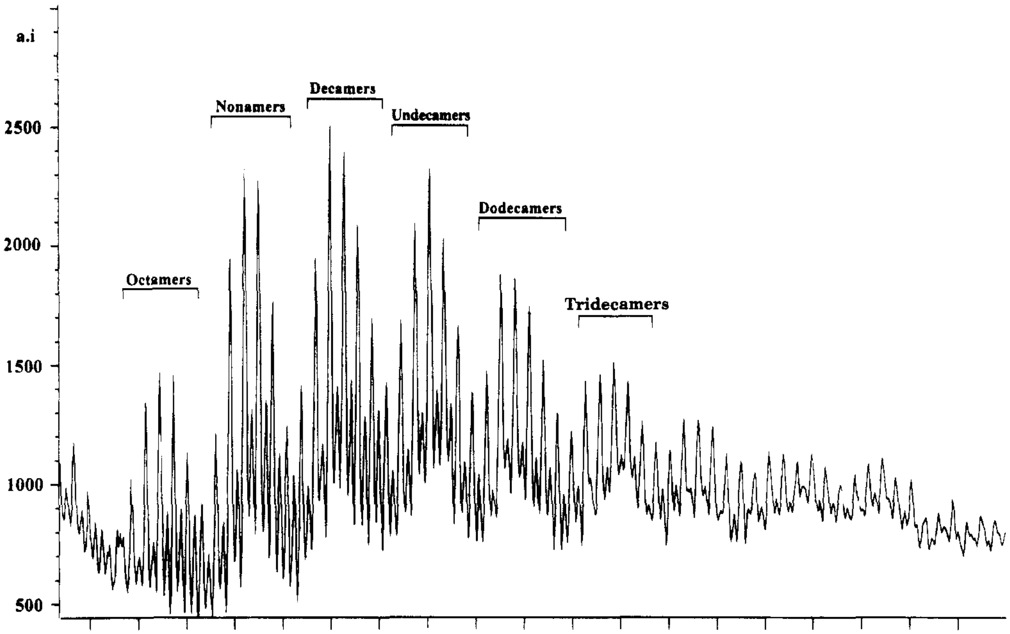

Figure 7. MALDI-TOF mass spectrum of a low MW fraction of copolyester PBAS (fraction 31, Table 2). Peak assignments are in Table 4.

oligomer abundances with the experimental peak intensities, the copolymer composition can be determined. A computer program (MACO4) is available to perform these calculations.[20]

The mass spectral peak intensities relative to the cooligomers of PBAS (Figure 7) were given as input to the program MACO4[20] to compute copolymer composition, assuming a Bernoullian distribution of the comonomer units along the chain. Spectral assignments and the results of the calculations are collected in Table 4. From these data the PBAS copolymer resulted in a random copolymer with a composition of 55/45 in favor of the adipate units, against a ratio of 51/49 found by NMR (see the Experimental Section).

Conclusions

Summarizing our findings, remarkable progress appears to have been made toward achieving a longtime goal in the characterization of polymeric materials, i.e., the direct measurement of MW and MWD of high polymers. The GPC eluate of a polydisperse polymer sample was fractionated; the fractions were analyzed by MALDI-TOF and yielded excellent spectra with narrow distributions. The computation of M_n and M_w from the MALDI spectra allowed us to calibrate the GPC traces against absolute molecular weights and to compute the MW averages from the GPC traces. The procedure yields absolute MW distributions.

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 of the terminal groups of the polymer chains. In the case of the copolyester (PBAS), measurement of the relative intensity of the co-oligomer peaks in the MALDI-TOF spectra allowed us to estimate both the composition

Table 4. Experimental and Calculated Relative Amounts of PBAS Oligomers

oligomer[a]	*m/z*[b]	exptl[c]	calcd[d]
	Octamers		
A2S6	1488.6	27	14
A3S5	1516.6	50	40
A4S4	1544.6	59	66
A5S3	1572.6	59	69
A6S2	1600.6	40	46
	Nonamers		
A3S6	1688.8	45	51
A4S5	1716.8	92	99
A5S4	1744.8	114	124
A6S3	1772.8	109	103
A7S2	1800.8	75	57
	Decamers		
A4S6	1889.0	81	83
A5S5	1917.0	115	121
A6S4	1945.0	105	120
A7S3	1973.0	86	84
A8S2	2001.0	60	40
	Undecamers		
A4S7	2061.2	58	52
A5S6	2089.2	83	86
A6S5	2117.2	97	100
A7S4	2145.2	78	83
A8S3	2173.2	55	49
	Dodecamers		
A4S8	2217.4	41	30
A5S7	2245.4	67	55
A6S6	2273.4	67	74
A7S5	3201.4	58	71
A8S4	2329.4	45	51
A9S3	2357.4	30	26
	Tridecamers		
A5S8	2433.6	39	29
A6S7	2461.6	40	44
A7S6	2489.6	43	48
A8S5	2517.6	38	40
A9S4	2545.6	27	25
AF = 15%[e]			

[a] A = butylene adipate, S = butylene succinate. [b] Observed *m/z* values after calibration procedure.[13] [c] Intensities of the MNa^+ ions in the MALDI-TOF spectrum of PBAS. [d] Intensities calculated using MACO4 program.[20] [e] AF = agreement factor[20] between experimental and calculated MALDI-TOF spectrum of PBAS.

of the copolymer and the sequence distribution.

Therefore, a complete structural and molecular characterization of polymers and copolymers is possible by combined MALDI-TOF/GPC experiments, a unique set of information hitherto not available by other techniques.

Acknowledgment. Partial financial support from the Italian Ministry for University and for Scientific and Technological Research (MURST), from Progetto Strategico Tecnologie Chimiche Innovative (CNR, Rome), and from the National Council of Research (CNR, Rome) is gratefully acknowledged.

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(19) The universal calibration curve was obtained using ten PS, ten PMMA, and five PEG samples. These samples were GPC standards obtained by anionic polymerization, and their MW were all accurately measured by independent techniques.[15]

(20) Montaudo, G.; Montaudo, M. S. *Macromolecules* **1992**, *25*, 4264.

MA950950I