End-Groups-Dependent MALDI Spectra of Polymer Mixtures

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ABSTRACT: During a work designed to use MALDI−TOF MS to determine the composition of an equimolar blend of nylon 6 (Ny6) and polybutyleneterephthalate (PBT), the MALDI−TOF mass spectrum showed a surprising strong imbalance between the two components. The predominance of Ny6 oligomers over the PBT oligomers terminated with hydroxyl end chains is signaled by the appearance of specific peaks in the MALDI−TOF mass spectra. Since the average molar mass and the polydispersion of the two polymers are comparable, the MALDI−TOF MS ionization efficiency is quite different for the two components of the blend. This finding prompted us to a more detailed study, and to synthesize a number of Ny6 and PBT samples terminated with different end groups, to analyze their equimolar blends by MALDI−TOF MS. The results reported in the present study may help clarifying some fundamental aspects about the mechanisms of ions formation, when MALDI−TOF mass spectrometry is applied to macromolecules. End groups ionization efficiency appears to be the most important parameter in determining the relative intensity of peaks in the MALDI−TOF mass spectra of the polymer blends investigated. End-groups-dependent ionization of MALDI−TOF mass species is the key to rationalize the relative peak intensity in MALDI−TOF mass spectra of polymer mixtures. Understanding of ionization efficiency mechanisms is essential to the quantitative applications of MALDI−TOF MS.

Introduction

Matrix-assisted laser desorption ionization−time-of-flight mass spectrometry (MALDI−TOF MS) has recently gained wide popularity in polymer research because of its high sensitivity and capability of detecting ions at high masses and is currently used as a powerful analytical tool in many applications such as molar mass measurements, structure identification, and characterization of polymer end groups.[1]

Although MALDI−TOF MS is meeting with increasing success in applications concerning the qualitative (structural) analysis of macromolecules, some problems have been encountered in extracting quantitative data from the MALDI−TOF mass spectra of synthetic polymers because of mass discrimination effects.[1]

The best known example of mass discrimination in MALDI−TOF mass spectra is the estimate of molar mass in polymers.[1−8] Values calculated from MALDI−TOF mass spectra agree with those obtained by conventional techniques only in the case of polymer samples with narrow distribution, whereas with polydisperse polymers MALDI−TOF MS fails to yield reliable values. As matter of fact, the intensities of the mass spectral peaks as a function of their mass values are far from the intensities expected from the actual molar mass distribution present in polydisperse polymer samples.[1−8]

In the quantitative analysis of polymers, the number of charged adducts revealed by the mass detector must reflect the number of polymeric chains actually existing in the sample. This requires that ion fragmentation, ion trasmittance, and ionization yield of the various oligomer species present in polymers must be independent of chain size.[1]

If mass discrimination would depend on a nonideal detector response, an obvious approach to solve the problem would be to design an ideal detector, capable of showing a constant response independent of mass value, but attempts in this direction have met with limited success.[9]

An explanation for the varying detector response observed in MALDI−TOF MS might reside in the fact that smaller oligomers contain a larger number of end groups, which would be ultimately responsible for the enhanced response observed. This rationalization would require a solid proof that the ionization efficiency of the oligomers depends on the chemical nature of their end groups. However, the data available do not allow one to decide, and the parameters determining ion formation and ionization efficiency in the MALDI−TOF MS desorption processes of synthetic polymers are still subject to speculation.[1−9]

Understanding the sources of ionization efficiency is essential to the quantitative applications of MALDI−TOF MS, and the results reported in the present study may clarify some fundamental aspects about the mechanisms of ions formation, when MALDI−TOF mass spectrometry is applied to macromolecules.

It occurred to us that if the ionization efficiency of the oligomers depends on the chemical nature of their end groups, polymers having specific end groups attached to the chain may show a higher ionization efficiency with respect to others, and therefore may yield more intense MALDI−TOF mass peaks.

When we used MALDI−TOF MS to detect the composition of equimolar blends of nylon 6 (Ny6) and

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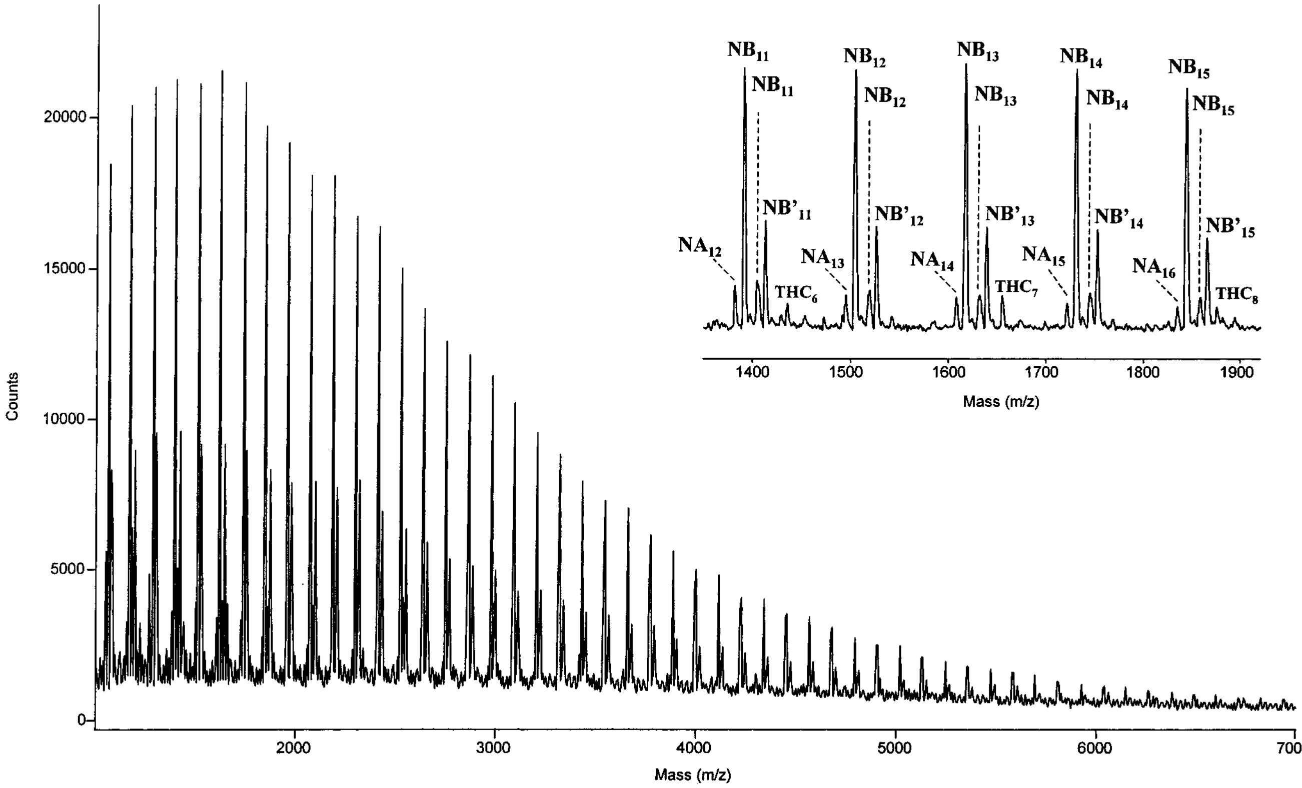
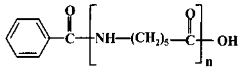
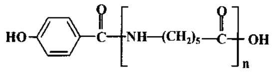
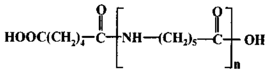
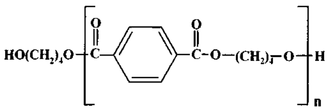
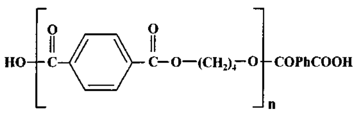


Figure 1. MALDI–TOF mass spectrum of an equimolar mixture of Ph–Ny6–COOH and HO–PBT–OH, registered in positive mode. In the inset is shown the mass range 1350–1920 Da. Peak assignments are reported in Table 2.

Table 1. Symbols and Molar Mass Values of the Ny6 and PBT Samples Used in This Work

Polymer	Symbol	Structure	η_{inh}[a]	[COOH] mol/Kg	[OH][d] mol/Kg	M_v[e]
1	Ph-Ny6-COOH		0.11	0.486[b]	----	2500
2	HOOC-Ar-Ny6-COOH		0.094	0.980[b]	----	2000
3	HOOC-R-Ny6-COOH		0.12	0.910[b]	----	2800
4	HO-PBT-OH		0.125	0.120[c]	0.96[d]	2300
5	HOOC-PBT-COOH		0.11	0.980[c]	----	2000

[a] The inherent viscosities (η_{inh}) were measured at 30.0 ± 0.1 °C (see Experimental Part). [b] Concentration of COOH end groups in the Ny6 samples were determined by conductometric methods (see Experimental Part). [c] Concentration of COOH end groups in the PBT samples were determined by potentiometric titration methods (see Experimental Part). [d] Concentration of OH end groups were determined by ^{1}H NMR analysis. [e] Viscosity-average molar masses were estimated using the Mark-Houwink equation (see Experimental Part).

polybutyleneterephthalate (PBT), the MALDI–TOF mass spectrum (Figure 1) showed a surprising strong imbalance between the two components. Since the average molar mass and the polydispersion of the two polymers are comparable, the MALDI–TOF MS ionization efficiency ought to be quite different for the two components of the blend. This finding prompted us to a more detailed study and to synthesize (Table 1) Ny6 and PBT samples terminated with different end groups, to examine their equimolar blends by MALDI–TOF MS.

The results obtained imply that ionization efficiency appears to be the most important parameter in determining the relative intensity of peaks in the MALDI–TOF mass spectra of the polymer blends investigated.

Experimental Section

Materials. Aldrich Chemical Co. (Italy) supplied the high molar mass analytical-grade PBT and Ny6 commercial samples, reagents and solvents used. The reagents were purified before use.

The MALDI matrix 2-(4-hydroxyphenylazo)benzoic acid (HABA) was analytical-grade material (Sigma Aldrich Chemical Co.), used as supplied.

Polymer Syntheses. Carboxyl-Terminated Ny6 Samples. (a) Ny6 with one carboxylic acid end group per chain, namely Ph−Ny6−COOH (polymer **1**, Table 1), was obtained by acidolysis of high molar mass (M_v = 45 000) Ny6 sample with benzoic acid, using a molar ratio 1/0.2 in phenyl sulfone (DPSO) as solvent, in an inert atmosphere at 240 °C. Typically, 10.00 g (90 mmol) of Ny6 and 10.00 g of DPSO were placed in a three-necked flask, with mechanical stirrer and under nitrogen flow. When the temperature was raised to 240 °C, 2.20 g (29 mmol) of benzoic acid were added to the liquid reaction mixture, and this mixture was reacted for 20 min. DPSO was extracted by refluxing with acetone overnight. The solid residue was filtered and dried at 60 °C in a vacuum oven.

(b) Ny6 sample terminated with one aliphatic and one aromatic acid end groups (HOOC−Ar−Ny6−COOH, polymer **2** in Table 1) was synthesized by acidolysis of a high molar mass (M_v = 45 000) Ny6 sample with terephthalic acid, in a molar ratio of 15/1 with respect to Ny6 repeat units, at 245 °C for 30 min, under N_2 flow, with a procedure similar to that described above.

(c) Ny6 sample terminated with both aliphatic acid groups (HOOC−R−Ny6−COOH, polymer **3** in Table 1) was prepared by reaction of high molar mass (M_v = 45 000) Ny6 sample with adipic acid, in a 10/1 molar ratio (with respect to Ny6 repeat unit), at 240 °C for 20 min under N_2 flow in DPSO as solvent. The synthetic procedure used is similar to that described above.

Dihydroxy-Terminated PBT. A PBT sample with hydroxyl terminal groups at both chain ends, namely HO−PBT−OH (polymer **4**, Table 1), was obtained by melt-polymerization, starting from terephthaloyl dichloride and an appropriate excess of 1,4-butanediol. Then 7.00 g (34.46 mmol) of terephthaloyl dichloride and 5.28 g (58.59 mmol) of 1,4-butanediol were placed in a three-necked flask and reacted at 160 °C for 2 h, under vigorous stirring. The reaction mixture was then heated at 200 °C and maintained for 1 h. After that time the temperature was raised at 250 °C for 1 h. The solid residue was dissolved in 50 mL of *sym*-tetrachloroethane (TCE), and the solution was then precipitated in 500 mL of acetone, filtered, washed several times with acetone, and dried at 60 °C in a vacuum oven, overnight.

Dicarboxylic-Terminated PBT. Synthesis of the PBT sample with both terephthalic acid as end groups, namely HOOC−PBT−COOH (polymer **5**, Table 1), was prepared by a two-steps polymerization in solution. In the first step, 10.00 g (49.21 mmol) of terephthaloyl dichloride in 100 mL of TCE solvent, were placed in a three-necked flask. Then, 4.22 g (46.86 mmoli) of 1,4-butanediol in 42 mL of TCE, and a stoichiometric amount of *N*,*N*-dimethylaniline (respect to terephthaloyl dichloride) in TCE, were simultaneously added dropwise to the acid solution, under stirring at 70 °C. The reaction mixture was maintained at these conditions for 24 h. After that time, an excess of terephthaloyl dichloride (1/10 molar ratio with respect to the initial amount) was added to the mixture, to cap eventually free hydroxyl end groups. In the second step, the solvent was removed by vacuum distillation, and the solid residue was dissolved in 100 mL of dimethylformamide (DMF), using a solution of *N*,*N*-dimethylaniline as protons acceptor. A portion of water (1 mL) was added under stirring, at 100 °C for 24 h. and under nitrogen flow, to hydrolyze the acyl chloride. After that, the solution was precipitated in 1 L of water, and it was filtered, washed several times with water, and dried at 60 °C in a vacuum oven.

MALDI−TOF Mass Spectrometry. Positive ion and negative ion MALDI−TOF mass spectra of the mixtures analyzed were recorded either in linear mode or in reflection mode, using a Voyager-DE STR instrument (Perseptive Biosystem) mass spectrometer, equipped with a nitrogen laser emitting at 337 nm, with a 3 ns pulse width. The spectra of Ny6/PBT blends were recorded using the same instrumental parameters selected for the MALDI−TOF MS analysis of PBT samples.

In the case of Ny6/Ny6 blends, the instrumental parameters was optimized in each analysis in order to obtain the higher mass resolution (expressed as the molar mass of a given ion divided by the full width at half-maximum). Changing some instrumental parameters, such as accelerating voltage, grid voltage, delay time, and laser intensity, does not vary the relative intensity of the peaks present in each mass spectrum of the Ny6/Ny6 and Ny6/PBT blends detected.

2-(4-Hydroxylphenylazo)benzoic acid (HABA), 0.1 M in hexafluoro-2-propanol (HFP), was used as the matrix. A concentration of about 2 mg/mL of all Ny6/PBT and Ny6/Ny6 mixtures was used in the HFP. Appropriate volumes of polymer solution and matrix solution were mixed in order to obtain a 1:1, 1:2 and 1:3 V/V ratio. 1 μL of each sample/matrix mixture was spotted on the MALDI−TOF MS sample holder and slowly dried to allow matrix crystallization.

Viscometry. The reduced viscosity (η_{spec}/C), and the inherent viscosity (η_{inh}), were measured using an Ubbelohde viscometer, at a concentration of 0.5 g/dL of a Ny6 or PBT sample in trifluoroethanol (TFE) and phenol/tetrachloroethane 60/40 w/w, respectively, at 30.0 ± 0.1 °C.

The pertinent values are reported in Table 1 together with the viscosity-average molar mass M_v of each samples calculated by the Mark-Howink equation ($\eta = KM^a$), where, for Ny6, $K = 30.3 \times 10^{-3}$ mL/g and $a = 0.75$ and, for PBT, $K = 2.15 \times 10^{-4}$ dL/g and $a = 0.82$.[10]

End Groups Determination. The concentration of end groups of the studied telechelic polymers, reported in Table 1, was carefully characterized using appropriate methods reported in the literature.[11−13]

The content of carboxyl groups in the Ny6 samples was determined by conductometric titration in trifluoroethanol (TFE) with a acqueous solution of sodium hydroxide (NaOH), 0.05 N.[11]

The amount of acid end groups in the PBT samples was determined by potentiometric titration.[12] Typically, 2 g of a PBT sample was dissolved in 100 mL of *o*-cresol at 90°, in a nitrogen atmosphere. After cooling at room temperature, 5 mL of water was added, and the titration was performed potentiometrically using a 0.05 N water solution of NaOH, under vigorous stirring.

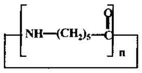
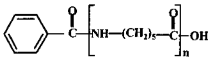
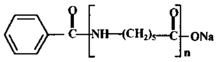
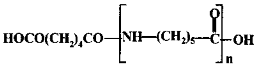
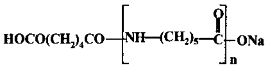
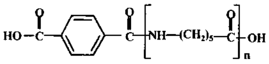
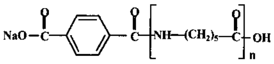
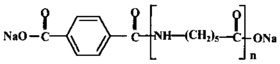
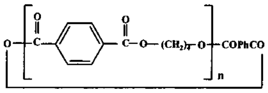
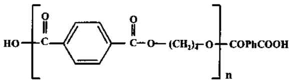
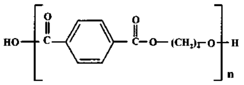
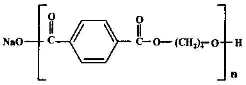
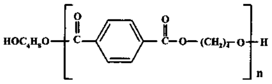
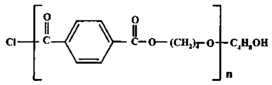
The concentrations of hydroxyl (OH) end groups in the PBT samples were determined by ^{1}H NMR analysis in deuterated tetrachlotoethane, at room temperature,[13] using the area of the signals at 4.38 and 3.67 ppm corresponding to the methylene groups linked to ester groups and methylene groups in α-position to OH, respectively.

Results and Discussion

In Table 1 is given a list of the polymer samples used here, together with their code names and respective molar mass estimates. The syntheses (see Experimental Section) were aimed to obtain polymer samples with comparable molar mass, to avoid possible mass discrimination effects[1] in the MALDI−TOF MS analysis.

In Figure 1 is reported the positive ion MALDI−TOF mass spectrum of an equimolar blend of Ph−Ny6−COOH and HO−PBT−OH, which shows a surprisingly strong imbalance between the two components. This effect is better seen in the expanded spectrum inset of Figure 1, where the predominance of carboxyl-terminated Ny6 oligomers (peaks assigned to species NB and NB′, Table 2) over the hydroxyl-terminated PBT oligomers (peaks assigned to species THC, Table 2) is signaled by the appearance of specific peaks in the MALDI−TOF mass spectra.

Table 2. Structural Assignments of the Peaks Displayed in the MALDI−TOF Mass Spectra Reported in Figures 1−4

Symbol	Species	Structure (M)	Positive mode			Negative mode
			$M+H^+$ (n)	$M+Na^+$ (n)	$M+K^+$ (n)	M^- (n)
Ph-Ny6-COOH	NA		----	1380 (12) 1493 (13) 1606 (14) 1719 (15) 1834 (16)	----	----
	NB		----	1389 (11) 1502 (12) 1615 (13) 1728 (14) 1841 (15) 2294 (19) 2407 (20) 2521 (21) 2633 (22)	1405 (11) 1518 (12) 1631 (13) 1744 (14) 1857 (15) 2310 (19) 2423 (20) 2536 (21) 2649 (22)	2270 (19) 2383 (20) 2496 (21) 2609 (22)
	NB'		----	1411 (11) 1524 (12) 1637 (13) 1750 (14) 1863 (15) 2316 (19) 2429 (20) 2542 (21) 2655 (22)	----	2270 (19) 2383 (20) 2496 (21) 2609 (22)
HOOC-R-Ny6-COOH	NC		----	1866 (15) 1979 (16) 2092 (17) 2205 (18)	1882 (15) 1995 (16) 2108 (17) 2221 (18)	
	NC'		----	1888 (15) 2001 (16) 2114 (17) 2227 (18)	---- ---- ---- ----	---- ---- ---- ----
HOOC-Ar-Ny6-COOH	ND		----	1886 (15) 1999 (16) 2112 (17) 2225 (18)	1902 (15) 2015 (16) 2128 (17) 2241 (18)	----
	ND'		----	1908 (15) 2021 (16) 2134 (17) 2247 (18)	----	----
	ND''		----	1930 (15) 2043 (16) 2269 (18)	----	----
HOOC-PBT-COOH	TCA		----	1933 (8) 2153 (9) 2373 (10) 2593 (11)	----	----
	TCB		----	1951 (8) 2171 (9) 2391 (10) 2611 (11)	----	----
HO-PBT-OH	THB		----	2243 (10) 2463 (11) 2683 (12))	----	----
	THB'		----	2265 (10) 2485 (11)	----	----
	THC		----	1435 (6) 1655 (7) 1875 (8) 2315 (10) 2535 (11)	----	----
	THD		----	2333 (10) 2553 (11)	----	----

The MALDI−TOF MS response is quite different for the two components of the blend and, since the molar masses of the two samples are comparable (Table 1), this evidence appears to indicate that the ionization

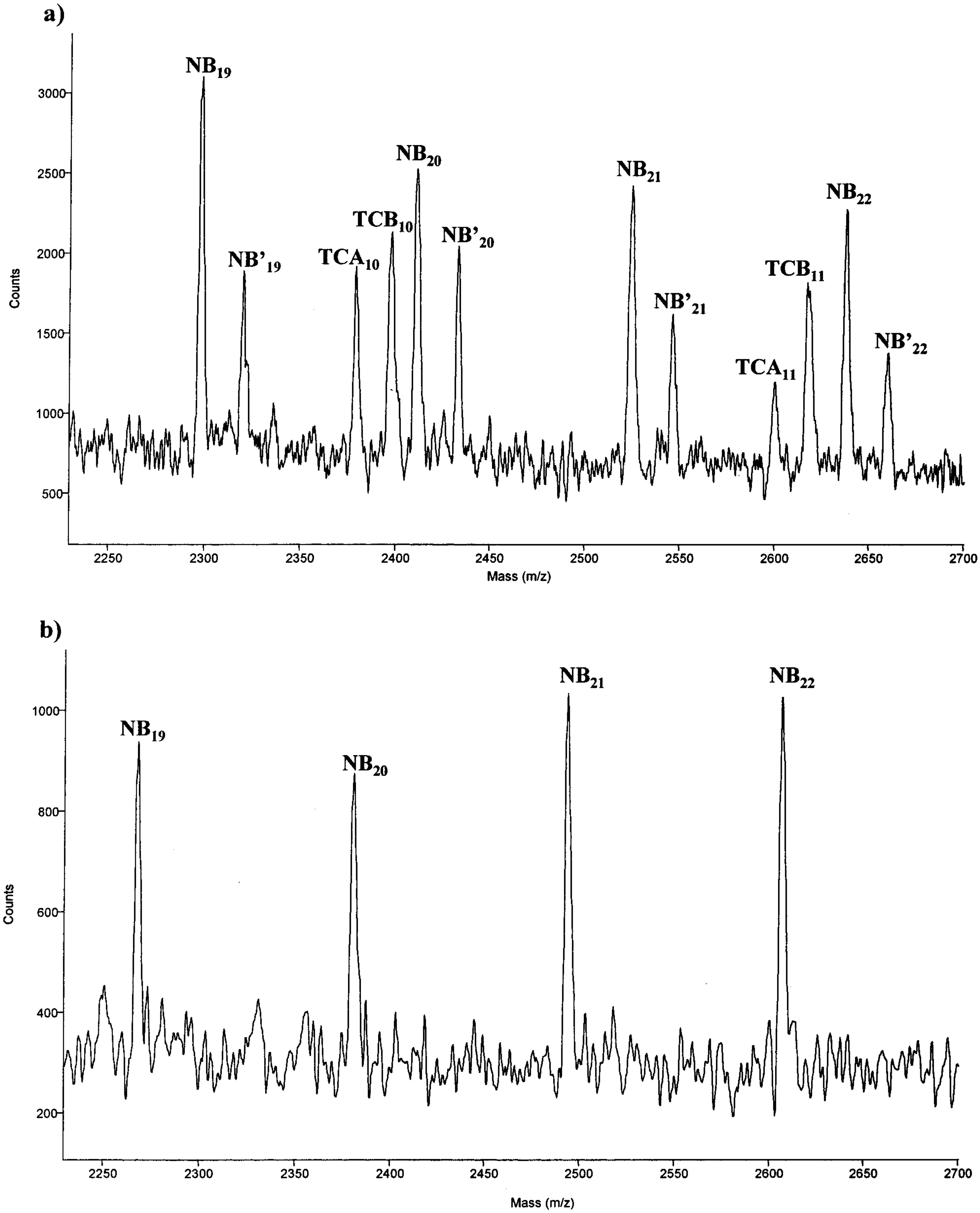


Figure 2. Enlarged regions of the MALDI−TOF mass spectra of an equimolar mixture of Ph−Ny6−COOH and HOOC−PBT−COOH, registered in (a) positive mode and (b) negative mode.

efficiency of the hydroxyl-terminated PBT polymer is much lower than of Ny6, so that the PBT signals result almost entirely suppressed.

In Figure 2a is reported an expanded portion of the positive ion MALDI−TOF mass spectrum of an equimolar blend of Ph−Ny6−COOH and HOOC−PBT−COOH. Compared with the spectrum in Figure 1, peaks TCA and TCB, assigned to species belonging to the PBT component (Table 2), appear much more intense, almost with the same intensity of peaks NB and NB′ due to Ny6.

The MALDI−TOF MS ionization efficiency of the carboxyl-terminated PBT oligomers is drastically changed with respect to the hydroxyl-terminated PBT oligomers, and this influences in a dramatic way the MALDI−TOF mass spectra of their equimolar mixtures with Ny6.

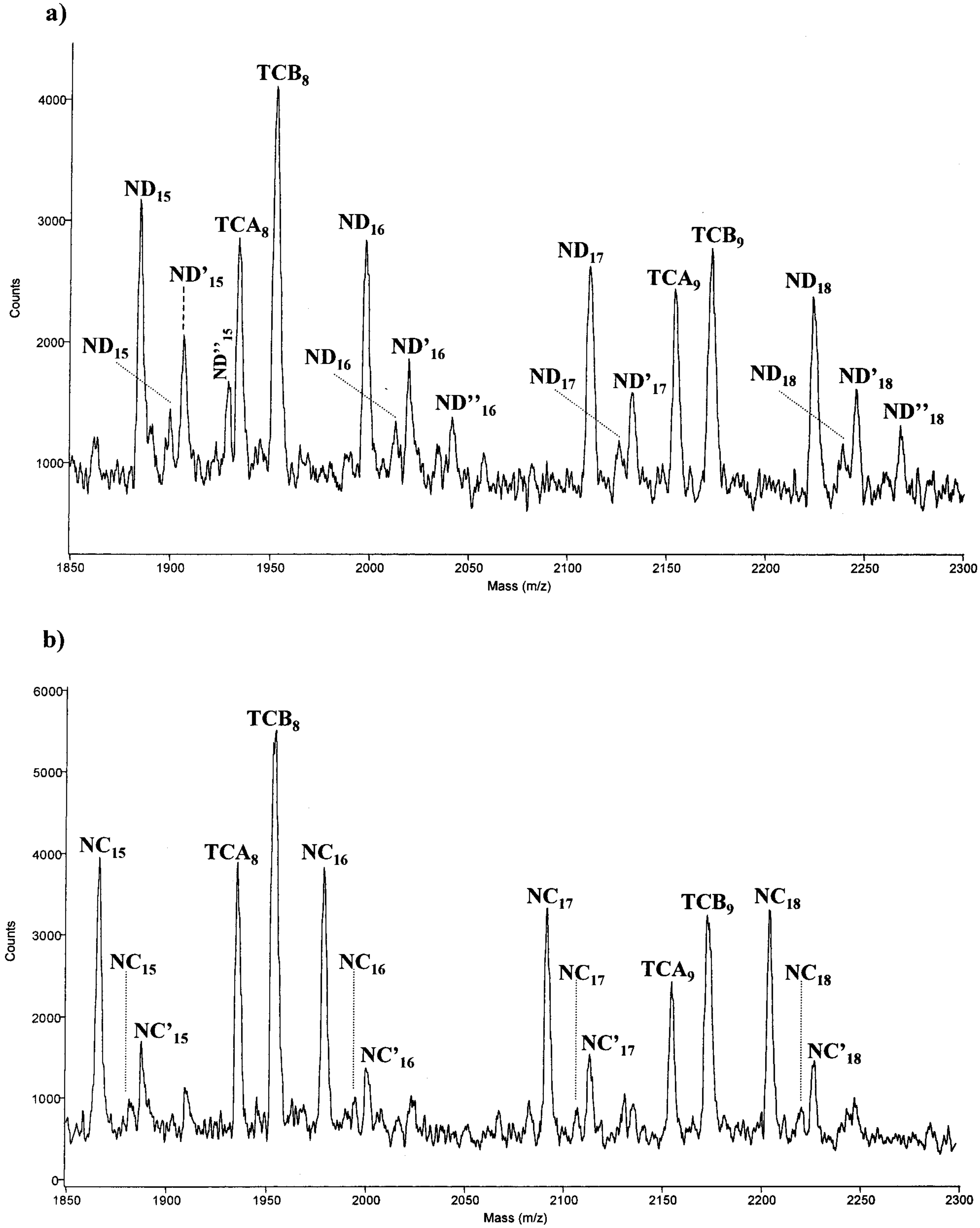


Figure 3. Enlarged regions of the MALDI–TOF mass spectra of equimolar mixtures of (a) HOOC–Ar–Ny6–COOH and HOOC–PBT–COOH and (b) HOOC–R–Ny6–COOH and HOOC–PBT–COOH, registered in positive mode.

Interestingly, in the negative ion MALDI–TOF mass spectrum of the Ph–Ny6–COOH/HOOC–PBT–COOH equimolar mixture (reported in Figure 2b) only peaks due to Ny6 (species B′, Table 1) are present, indicating that the relative ion efficiency of the two polymers in the blend varies considerably, subject to the positive- or negative-ion detection.

The variations observed in the spectra in Figures 1 and 2 are apparently due to the specific end groups terminating the PBT oligomers, and one is forced to conclude that PBT oligomers bearing carboxyl ends are able to induce a higher MALDI–TOF MS ionization efficiency with respect to PBT oligomers bearing hydroxyl ends in Ny6/PBT blends.

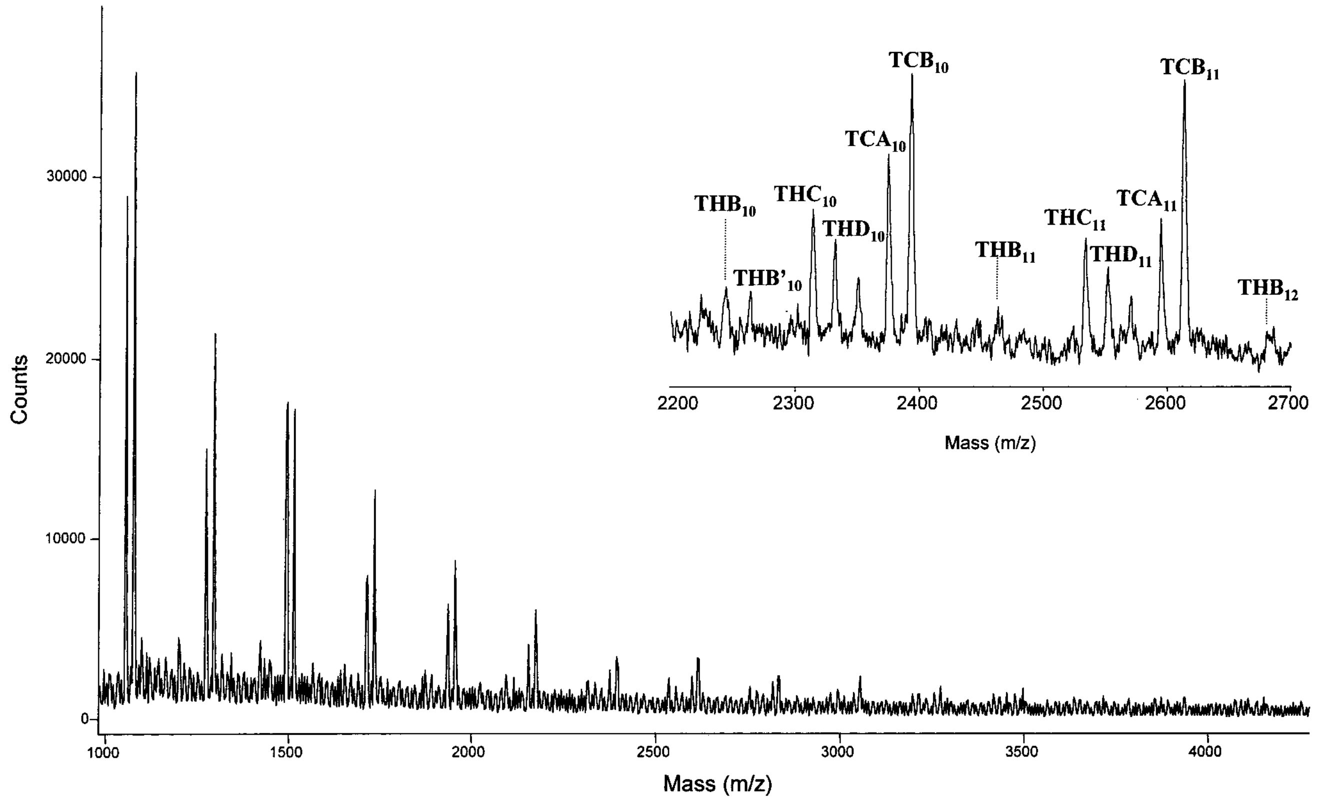


Figure 4. MALDI−TOF mass spectrum of an equimolar mixture of HO−PBT−OH and HOOC−PBT−COOH, registered in positive mode. In the enlarged region is shown the mass range 2200−2700 Da. Peak assignments are reported in Table 2.

Continuing in the investigation of the subtle effects of end groups on the MALDI−TOF mass spectra of Ny6/PBT blends, in Figure 3a we have reported an expanded portion of the positive ion MALDI−TOF mass spectrum of an equimolar blend of HOOC−Ar−Ny6−COOH and HOOC−PBT−COOH, while in Figure 3b is reported an expanded portion of the positive ion MALDI−TOF mass spectrum of an equimolar blend of HOOC−R−Ny6−COOH and HOOC−PBT−COOH.

In the first case, the Ny6 sample is terminated with one aliphatic group and one aromatic acid group (Table 1), whereas in the second case the Ny6 sample is terminated with two aliphatic carboxylic groups. This slight difference in end groups, with respect to the mixture shown in Figure 2, is sufficient to lower the response of Ny6 in the MALDI−TOF mass spectrum of the blends, and now the peaks belonging to the PBT component (TCA and TCB, Figure 3a,b), appear more intense with respect to peaks NC, ND, and ND′ due to Ny6.

At last, in Figure 4, is reported the positive ions MALDI−TOF mass spectrum of an equimolar blend of the two PBT samples investigated here: HO−PBT−OH and HOOC−PBT−COOH (Table 1). The higher intensity of peaks due to HOOC−PBT−COOH sample is apparent at the lower masses, whereas above 2000 Da, peaks due to the hydroxyl-terminated sample become stronger, as shown in the expanded portion of the spectrum in Figure 4. This result indicates the preponderant effect of the end groups on the oligomers ionization efficiency. As matter of fact, the intensities of peaks due to the two PBT samples tend to equalize as the number of end groups in both oligomers decreases at higher mass.

We have confirmed the results reported above by examining a higher number of polymer mixtures bearing different end groups (Ny6/Ny6, Ny6/PBT, etc.). The data are not discussed here for brevity, they have been reported elsewhere.[14]

Conclusion

The observations made on Ny6/PBT blends provide a way to investigate the phenomenon of mass discrimination in MALDI−TOF mass spectra. The results would appear to rule out the possibility that mass discrimination is produced by an imperfect detector. Instead, the data collected here indicate that the ionization efficiency of MALDI−TOF mass species is end groups dependent, and this lends a key to rationalize the relative peak intensity in these MALDI−TOF mass spectra. Our experiments appear to establish the relevance of end groups in the mechanism of ion desorption in MALDI−TOF MS.

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References and Notes

(1) For a review of current MALDI−TOF MS literature: Montaudo, G.; Montaudo, M. S.; Samperi, F. In *Mass Spectrometry of Polymers*; Montaudo, G., Lattimer, R. P., Eds.; CRC Press: Boca Raton, FL, 2001; Chapter 10.

(2) (a) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 453. (b) Montaudo, G.; Garozzo, D.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *Macromolecules* **1995**, *28*, 7983. (c) Garozzo, D.; Impallomeni, G.; Spina, E.; Sturiale, L.; Zanetti, F. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 937. (d) Montaudo, M. S.; Puglisi, C.; Samperi, F.; Montaudo, G. *Rapid Commun. Mass Spectrom.*,

1998, *12*, 519. (e) Montaudo, G. *Polym. Prepr.* **1996**, 290. (f) Montaudo, M. S.; Puglisi, C.; Samperi, F.; Montaudo, G. *Macromolecules* **1998**, *31*, 3839.

(3) Martin, K.; Spickermann, J.; Räder, H. J.; Müllen, K. *Rapid Commun. Mass. Spectrom.* **1996**, *10*, 1471.

(4) Schriemer, D. C.; Li, L. *Anal. Chem.* **1997**, *69*, 4169, 4176.

(5) Zhu, H.; Yalcin, T.; Li, L. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 275.

(6) Guo, B.; Chen, H.; Liu, R. X. *Rapid Commun. Mass. Spectrom.* **1997**, *11*, 781.

(7) Nielen, M. W.; Malucha, S. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 1194.

(8) Jackson, C.; Larsen, B.; McEwen, C. *Anal. Chem.* **1996**, *68*, 1303.

(9) (a) Larsen, B. S.; Byrd, H. C. M.; McEwen, C. N. *Polym. Prepr.* **1999.** (b) Byrd, H. C. M.; McEwen, C. N. *Anal.Chem.* **2000**, *72*, 4568. (c) McEwen, C. N.; Peacock, P. M.; Guan, Z. *Proc. 46th ASMS Conf. Mass Spectrom.* , **1998**, 409.

(10) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989.

(11) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *J. Polym. Sci., Polym. Chem.* **1996**, *34*, 47.

(12) Weidener, S.; Kuehn, G.; Werthmann, B.; Schoreder, H.; Just, U.; Borowski, R.; Decker, R.; Schwarz, B.; Schmuecking, I.; Seifert, I. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2183.

(13) Boutevin, B.; Khamlilichi, M.; Lusinchi, J. M.; Robin, J. J. *Macromol. Chem. Phys.* **1997**, *198*, 605.

(14) Alicata, R.; Montaudo, G.; Puglisi, C.; Samperi, F. *Rapid Commun. Mass Spectrom.* **2002**, *16*, 248.

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