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# Characterization of Synthetic Polymers Using Matrix-Assisted Laser Desorption/Ionization−Time of Flight Mass Spectrometry

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ABSTRACT: Matrix-assisted laser desorption/ionization−time of flight mass spectrometry was used for a detailed characterization of three synthetic polymers. It has been demonstrated that the necessary components of the matrix required for effective desorption of intact oligomer ions depend on the properties of the synthetic polymer. Molecular weight averages were obtained for polystyrene and poly(ethylene glycol) samples by calculating the centroid of the distribution. Polyesters, synthesized from enzymatic polytransesterification of adipic acid esters with 1,4-butanediol, were characterized in detail to obtain significant structural information. Intact oligomer ions, cationized with $Na^+$ were detected in the mass range 200−9000. The polyester species detected were terminated at both ends either with OH groups or by a COOH group and an OH group. The presence of these species was confirmed by quantifying the isotopic abundances of these cations and verifying them with theoretical predictions. The presence of -COOH termination was not detected using $^1$H-NMR, even at low polymer molecular weights. The repeat unit of the polyester was confirmed from the spacing between consecutive peaks with the same end groups. The presence of acid-terminated species was also confirmed by direct titration of the polyester.

## Introduction

The use of mass spectrometry for the analysis of synthetic polymers can be divided into degradational characterization of polymers and direct analysis of molecular (or quasimolecular) ions of intact polymers. Chemometric pyrograms can be used to explain the mechanism of decomposition for polymers, but in order to obtain structural information or molecular weight averages and end groups, it is crucial to avoid fragmentation during desorption and ionization. Such an analysis is possible given the development of various “soft” desorption−ionization techniques.[1,2]

The use of mass spectrometry for qualitative and quantitative characterization of polymer properties has been the goal of much previous research. Determination of the absolute molecular weight averages and the molecular weight distributions of various oligomeric systems have been investigated. Notable among these studies are the analyses of polyglycols,[3−5] polystyrene,[6,7] poly(dimethylsiloxane),[7] polyamide,[7] and poly(ethylenimine).[7]

Laser desorption mass spectrometry (LDMS), because of the fast analysis time and ease of sample preparation compared to other soft ionization methods, has received considerable attention for the analysis of nonvolatile and thermally labile biological compounds.[1,8] Previous reports on calculating molecular weight averages and dispersities using LDMS−TOF (TOF, time of flight) techniques were encouraging when compared with other techniques for polyglycol,[5] polystyrene,[7] and poly(ethylenimine)[5] systems. For a variety of other polymer systems investigated by LDMS, identification of fragmentation patterns was the focus of the research.[9]

It is well known that electrohydrodynamic ionization mass spectrometry (EHMS) requires a supporting matrix. Formation of cluster ions of the matrix with the sample results in a complex spectra. EHMS utilizes a solvent with an added electrolyte (for example, an alkali halide), which is particularly helpful for generating cations and has been successfully applied to poly(ethylene glycol)[10,11] and poly(ethylenimine) samples.[12]

Earlier research in laser-induced desorption experiments indicated that efficient energy transfer to the sample requires resonant excitation of molecules,[13] the type of excitation being dependent on the wavelength of the laser. To avoid thermal decomposition during this process, energy must be transferred within a short time. It was realized that efficient energy transfer for resonant excitation results in energy transfer to photodissociation channels. Hence, the use of a solid or liquid matrix consisting of a small highly absorbing species[14,15] can spare the analyte molecules from excessive energy that could otherwise lead to their photodissociative fragmentation. Dilution of a sample can also prevent the association of analyte molecules which would form complexes of masses too large to be desorbed and analyzed. This method, known as matrix-assisted laser desorption/ionization (MALDI), has been successfully used for the characterization of a variety of biological molecules.[16] Applications of MALDI−TOF have also been discussed for characterization of synthetic polymers[17,18] and polypeptides.[19] In order to obtain information of polymer properties, desorption of intact oligomeric species is necessary.

We have investigated the use of MALDI−TOF spectrometry for characterization of polystyrene, poly(ethylene glycol), and oligomeric polyesters. We have also characterized polyesters in detail. The polyesters we have studied ($M_w$ < 10 000), synthesized biocatalytically[20] from adipic acid esters and 1,4-butanediol (poly(1,4-butylene adipate)), are used as starting materials for synthesis of elastomeric polyurethanes.

## Experimental Section

**Polymers.** Polystyrene samples were obtained from Polymer Laboratories. α-Vinyl ω-*N*-hydroxysuccinimidyl poly(ethylene glycol) was kindly donated by Shearwater Polymers Inc. A commercial polyol (poly(1,4-butylene adipate)) sample was provided by Bayer, Pittsburgh, PA.

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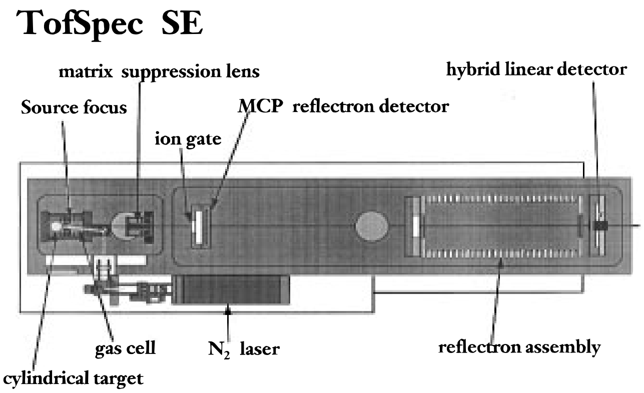
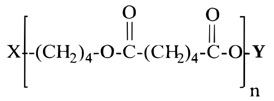


**Figure 1.** Schematic diagram of the MALDI−TOF spectrometry unit.

**Synthesis of Polyesters.** Polyesters were synthesized by enzyme-catalyzed polytransesterification using either bis(2,2,2-trichloroethyl) adipate[20] or divinyl adipate as starting diesters and 1,4-butanediol as the diol. The general structure of the resulting polyester is shown below:



$$X\left[(CH_2)_4\text{-O-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-O}\right]_n Y$$

where X and Y are the end groups of the polyester. The following six combinations are possible: ester−ester, ester−hydroxyl, hydroxyl−hydroxyl, ester−carboxyl, carboxyl−hydroxyl, and carboxyl−carboxyl end groups.

All reactions were performed in tetrahydrofuran (THF) at 30−35 °C. Reaction products were recovered and analyzed using MALDI−TOF. Some of the polymers were also washed with methanol to remove low molecular weight fraction prior to MALDI−TOF analysis. All the oligoesters with molecular weights less than around 800−1000 are soluble[21] in methanol and were not detected in the polymer after methanol wash by MALDI−TOF.

**Polymer Characterization.** Gel permeation chromatography (GPC) measurements were performed in THF at 35 °C at a flow rate of 1.0 mL/min. The instrument (Waters 150CV) was equipped with ultrastyragel columns with pore sizes of $10^4$, $10^3$, 500, and 100 Å in series. Polystyrene standards in the molecular weight range of 162−11 600 were used for calibration. Nuclear magnetic resonance (NMR) spectra were taken using a Bruker MSL-300 instrument.

The acid numbers of polyesters were also determined by direct titration.[22] Accurately weighed quantities of polyester were dissolved in a 1:1:1 mixture of 2-propanol, toluene, and methanol. The above solution was then titrated against standardized methanolic potassium hydroxide using phenophthalein as an indicator. Color change from clear to pink is observed, when all the acid groups present have been neutralized.

**Mass Spectrometry Instrumentation.** A Fisons VG Tofspec E spectrometer was used for the MALDI analysis of all the synthetic polymers. Light from a pulsed nitrogen laser ($\lambda = 337$ nm, 4 ns pulse width) is focused onto the target. The instrument is equipped with a single stage reflectron to give increased mass resolution. A computer-controlled "ion" gate allowed selection of a precursor ion, and a full postsource decay spectrum was obtainable. The instrument has a 1.0 m linear time of flight mass spectrometer with a 30 kV source voltage. With the reflectron engaged, the effective path length is 2.3 m. The detector is a high mass hybrid microchannel plate/electron multiplier (Figure 1).

Hercules and Mattern (1985) have reported that for the analysis of polyglycols, the molecular weight distribution obtained could be skewed to lower masses if the postacceleration voltage is too low. This effect has been related to the failure of electron multipliers to respond linearly for lower ion velocities at higher masses. By increasing the source extraction lens voltage from the normal 6 to ∼10 kV, this problem was alleviated. We have collected spectra in both linear and reflectron mode. In linear mode, the source extraction lens voltage was 10 kV. In reflectron mode, the source voltage, source extraction lens voltage, and reflectron voltage were 25, 8.333, and 29 kV, respectively. Preferential desorption of oligomers can also skew obtained molecular weight distributions toward lower masses. We therefore carefully compared molecular weight distributions from MALDI−TOF spectra to those collected by GPC. No evidence of changes in distribution was observed.

Laser power densities from 1 to 90 MW/cm$^2$, about 10 times lower than those usually used for laser pyrolysis studies using LAMMA instruments,[23] were employed for our work. The laser power density required for efficient desorption depends on polymer and matrix compositions. For all samples, dithranol (1,8,9-anthracenetriol) was used as the matrix.

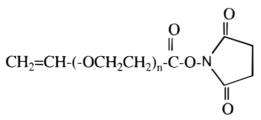
**Sample Preparation.** Samples were prepared by mixing dithranol (10 mg/mL in THF), silver trifluoroacetate (1 mg/mL in THF), and polymer (10 mg/mL in THF) in the ratio of 8:1:1, respectively. Enough of this mixture was applied to the sample position to cover the 2.5 mm diameter sample position (typically 0.3 $\mu$L). The spot was allowed to air-dry without assistance. For some of the samples, sodium iodide (1 $\mu$L of 1 $\mu$g/$\mu$L solution) was added at the premixing stage. Differences in the cationic species observed in the spectra are explained below.

## Results and Discussion

**Selection of Polymers.** It is known that low concentrations of alkali halides can improve the ionization of polar-desorbing species.[9] In field desorption mass spectrometry, nonpolar organics yield odd-electron molecular ions (cations or anions). Polar organics (for example, aliphatic amines, alcohols, and acids), on the other hand, normally form ions by cation attachment. Polymers that were selected for our study varied in their polarity. Polystyrene is nonpolar, poly(1,4-butylene adipate) is relatively polar, and poly(ethylene glycol) is amphiphilic.

**Effect of Matrix Composition.** The expected molecular weights of intact polystyrene chains (with *n*-butyl end group) are given by $58 + 104n$, where $n$ is the number of repeat units. MALDI−TOF spectra indicated the presence of $(M + Ag)^+$ cationic species with molecular masses following the general formula $104n + 166$ (Figure 2). It is important to note that no protonated molecular ions were detected, thus improving our ability to determine molecular weight averages and polydispersity index of the material. Residual peaks such as fragmented series or alternatively cationized species were not observed. The presence of another series of peaks would result in a lower yield of identically cationized species, thus reducing the sensitivity. Additionally, unless the intensities of each series of peaks are equivalent to the relative concentrations of the species, it would be difficult to estimate molecular weight averages based on one particular type of ionic species. In the presence of sodium iodide and silver, an additional series with general formula $104n + 16$ was observed (Figure 3) as a result of fragmentation.

Vinyl *N*-hydroxysuccinimidyl poly(ethylene glycol) has the following structural formula:



with the molecular weight series being $44n + 169$. For the amphiphilic polymer in the absence of

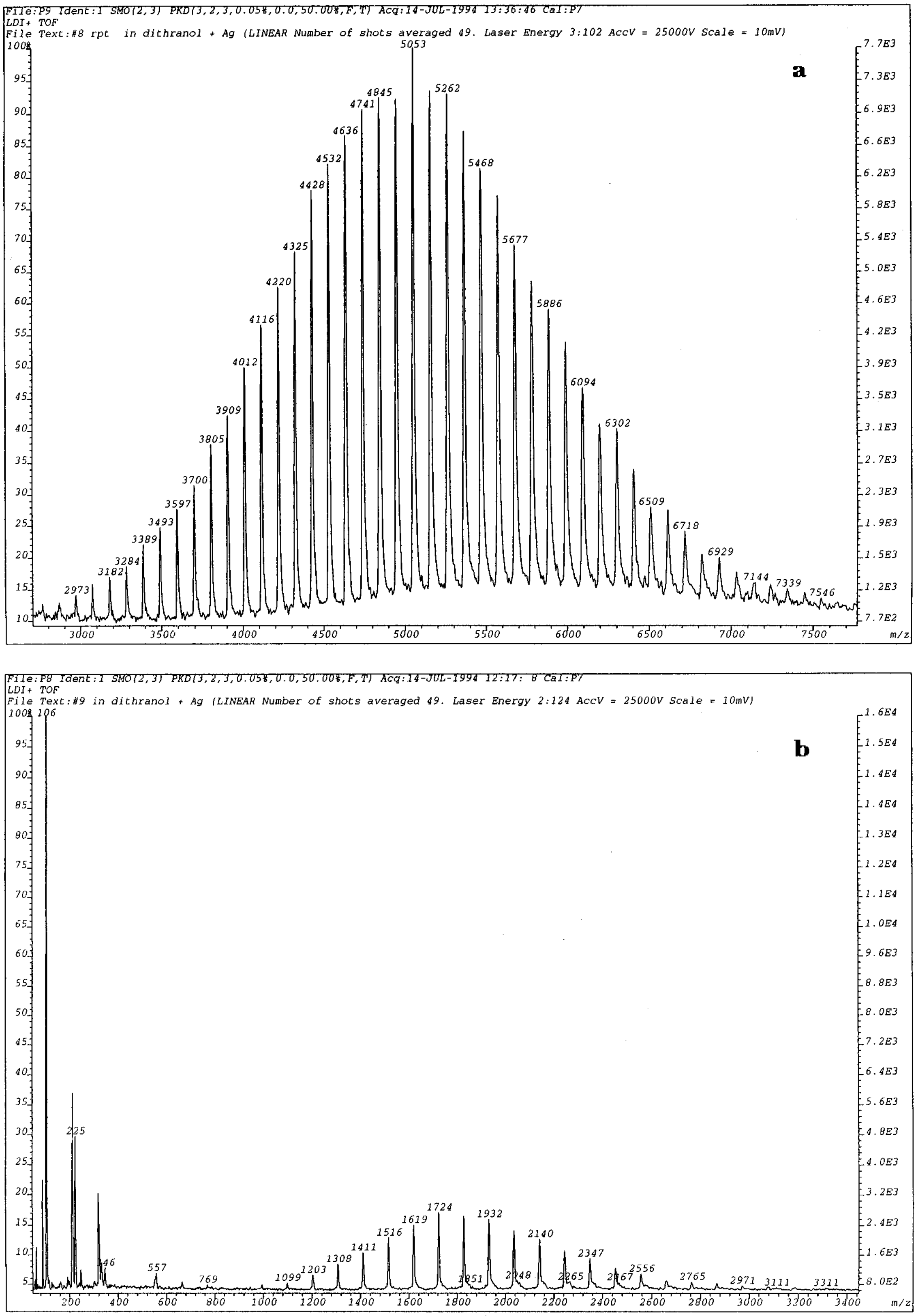


**Figure 2.** (a) Positive ion MALDI–TOF spectrum of polystyrene ($M_p$ = 5050, matrix = dithranol + silver, laser power density = 62.4 MW/cm$^2$). (b) Positive ion MALDI–TOF spectrum of polystyrene ($M_p$ = 1720, matrix = dithranol + silver, laser power density = 36.9 MW/cm$^2$).

sodium iodide in the matrix, but with silver, we observed reduced fragmentation and better desorption characteristics at lower laser intensities. Also, molecular weights of cations M + 170, corresponding to a single series of $(M + H)^+$, were detected. It is interesting to note that no $(M + Ag)^+$ peaks were detected (Figure 4). A series of contaminating PEG's (44*n* + 144) were also observed.

Telechelic polyesters are routinely characterized for molecular weight averages and nature of their end groups. Since polyesters are polar in nature, when silver is used as a matrix component, the desorption of an intact molecule requires higher laser intensities, potentially resulting in fragmentation. The interpretation of such a fragmented spectra is difficult, and only limited information can be generated (Figure 5a). Ad-

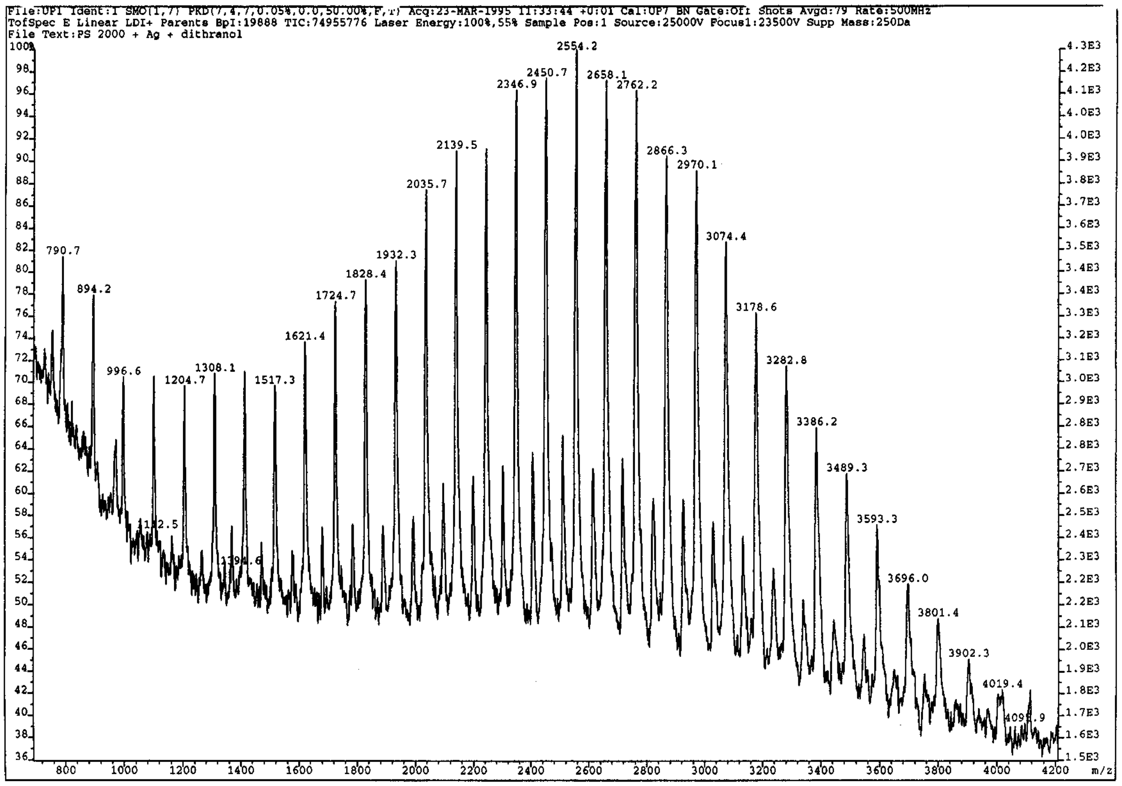


**Figure 3.** Positive ion MALDI−TOF spectrum of polystyrene ($M_p = 2000$, matrix = dithranol + silver + sodium iodide, laser power density = 36.3 MW/cm$^2$).

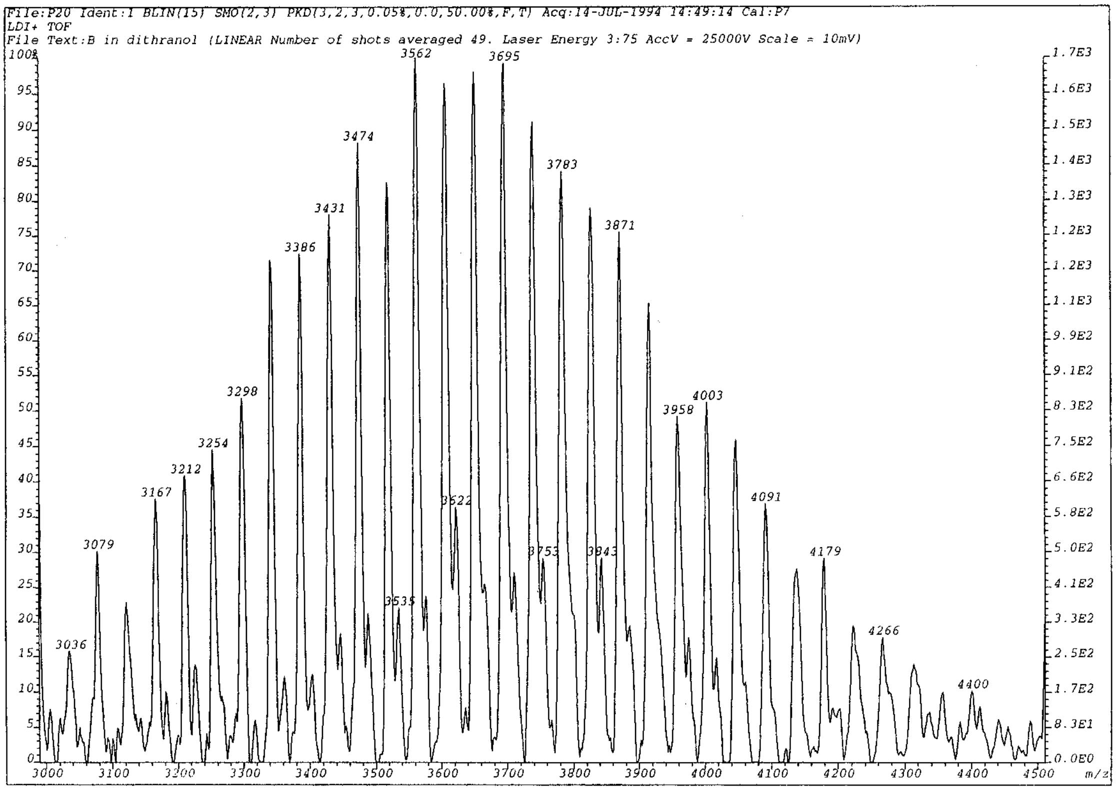


**Figure 4.** Positive ion MALDI−TOF spectrum of poly(ethylene glycol) (matrix = dithranol + silver, laser power density = 33.8 MW/cm$^2$).

dition of sodium halide to silver, however, improves the desorption of the intact polyester from the matrix (Figure 5b). Reducing polymer loading from 10 to 1 mg/mL also results in improved desorption/ionization efficiency (Figure 5c). Similar results were obtained forboth the enzymatically synthesized and the commercial polyols (Figures 6 and 7).

We hypothesize that as a result of partial preionization of the polymer, the desorption properties of poly(1,4-butylene adipate) are improved by the addition of sodium halide to the matrix. Interestingly when a nonpolar polymer such as polystyrene is used, the addition of sodium halide to the matrix does not give encouraging results (Figure 3). Fragmentation of poly-

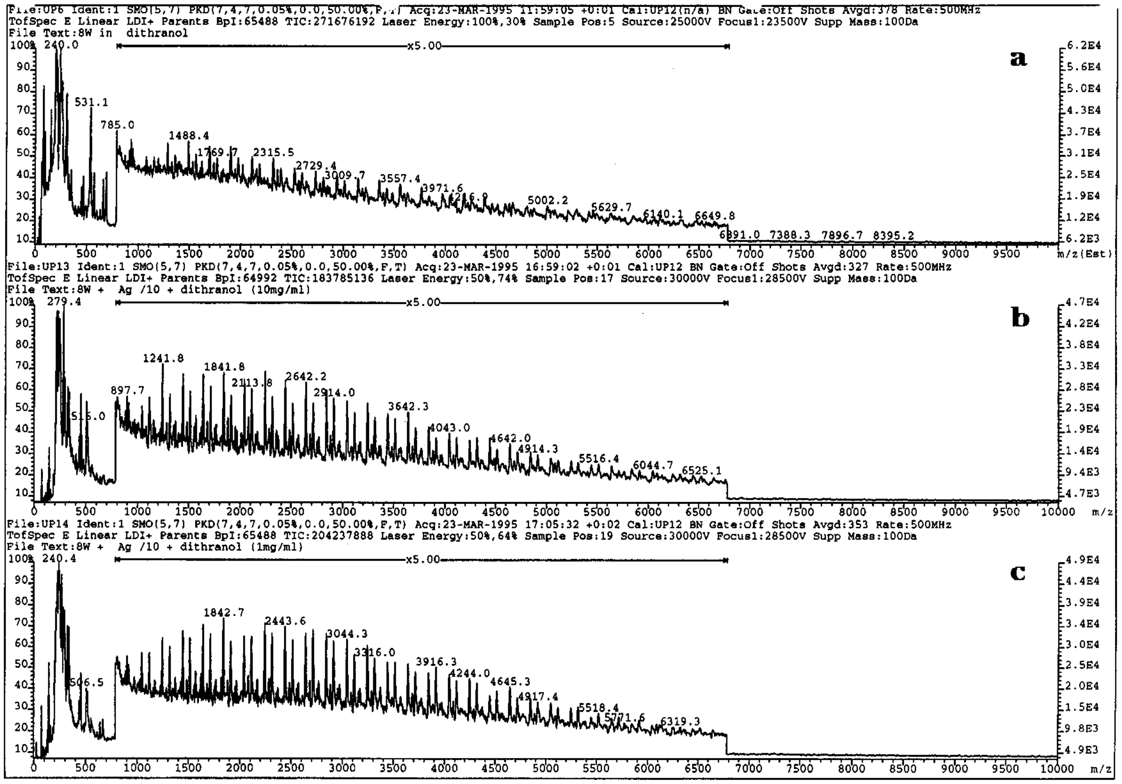


**Figure 5.** (a) Positive ion MALDI−TOF spectrum of poly(1,4-butylene adipate) (enzyme-catalyzed synthesis, matrix = dithranol + silver, laser power density = 10.8 MW/cm$^2$). (b) Positive ion MALDI−TOF spectrum of poly(1,4-butylene adipate) (enzyme-catalyzed synthesis, matrix = dithranol + silver + sodium iodide, laser power density = 32.8 MW/cm$^2$, polymer = 10 mg/mL). (c) Positive ion MALDI−TOF spectrum of poly(1,4-butylene adipate) (enzyme-catalyzed synthesis, matrix = dithranol + sodium iodide + silver, laser power density = 24.6 MW/cm$^2$, polymer = 1 mg/mL).

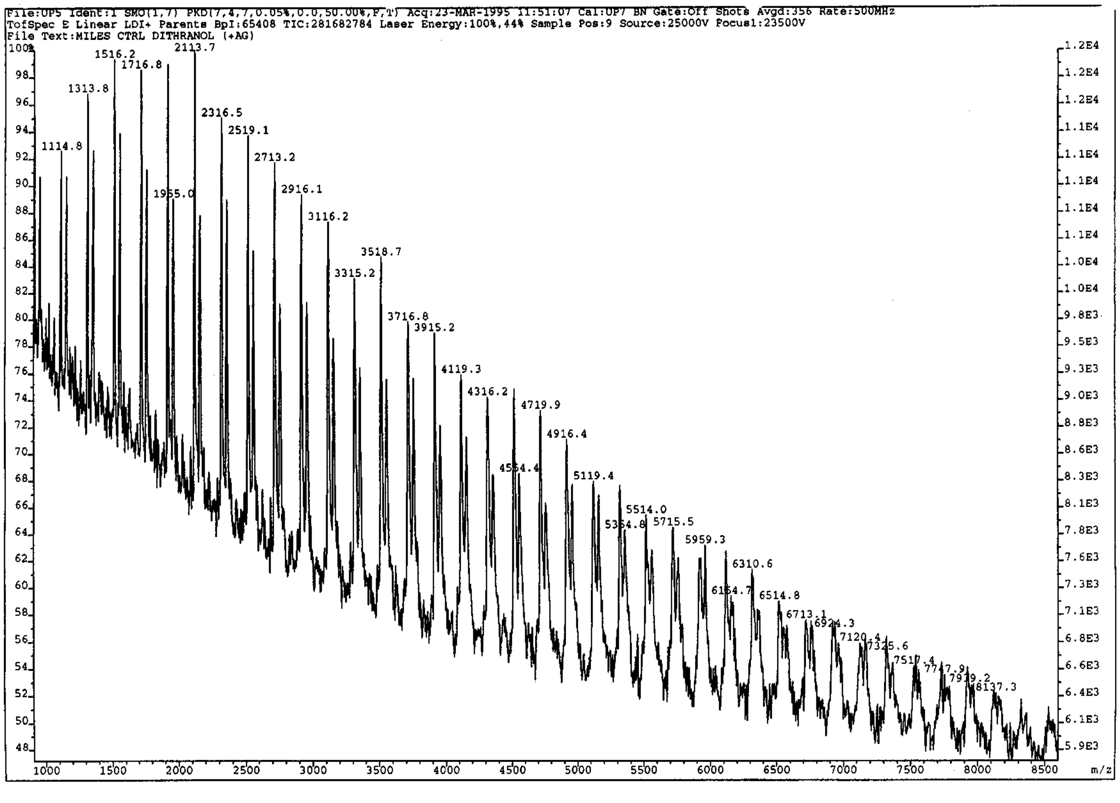


**Figure 6.** Positive ion MALDI−TOF spectrum of a polyol (dithranol + silver, laser power density = 23.2 MW/cm$^2$, $M_n$ = 2010 by GPC analysis).

(ethylene glycol) does not occur when only silver is added to the matrix. A summary of the effect of matrix components and the type of polymer analyzed is shown in Table 1.

**Interpretation of Spectra: Polystyrene and Polyglycols.** MALDI−TOF spectra of polystyrene samples with peak molecular weights of 1720 and 5050 (determined by GPC) were carefully analyzed. Intact

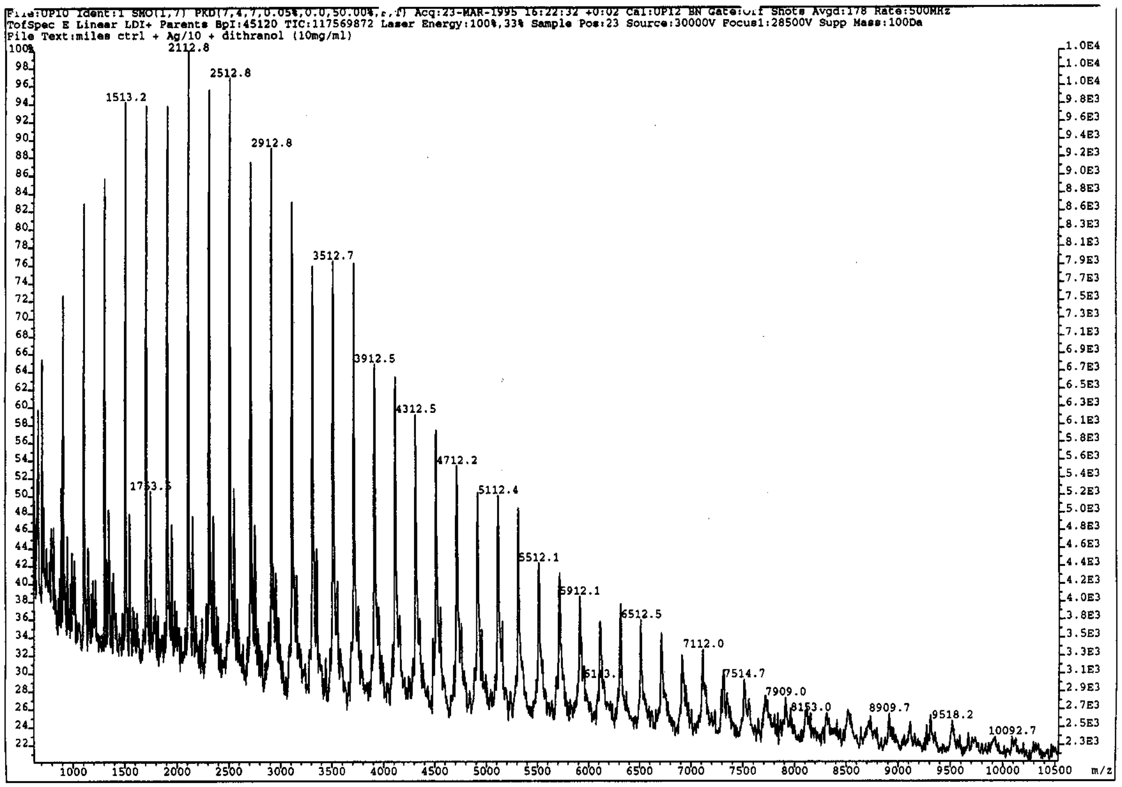


**Figure 7.** Positive ion MALDI−TOF spectrum of a polyol (dithranol + silver + sodium iodide, laser power density = 13.1 MW/cm$^2$, $M_n$ = 2010 by GPC analysis).

oligomeric cations were observed, and the molecular weight averages and polydispersity indices were calculated using the following formulae:

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$D = \frac{M_w}{M_n}$$

where $N_i$ (taken as a percent from each scan) is the number of molecules having molecular weight $M_i$. $M_n$ and $M_w$ are number- and weight-average molecular weights, and $D$ is the polydispersity index. This approach is valid for the low molecular weights analyzed but would have to be adapted for high molecular weight species.

The molecular weights and dispersities of the polystyrene samples calculated using MALDI−TOF and GPC data are compared in Table 2. The agreement between the molecular weight averages determined using GPC and MALDI is striking. The values of polydispersity index for both the samples are also similar.

For poly(ethylene glycol), the cationic series, $(M + H)^+$ was used for the calculation of molecular weight averages. The molecular weight average, which was calculated from MALDI−TOF data ($M_n$ = 3648), agreed well (within 10%) with that reported by manufacturer ($M_n$ = 3400, as measured by GPC).

**Table 1. Summary of Matrix Composition and Type of Cations Detected for Different Types of Polymers**

| polymer | type | matrix with | observations |
|---|---|---|---|
| polystyrene | nonpolar | Ag | $(M + Ag)^+$ cations only |
| | | Ag + NaI | $(M + Ag)^+$ cations, unidentified fragments |
| poly(ethylene glycol) | amphiphilic | Ag | intact $(M + H)^+$ ions only |
| poly(1,4−butylene adipate) | polar | Ag | extensive fragmentation |
| | | NaI | $(M + Na)^+$ ions, fragments |
| | | Ag + NaI | $(M + Na)^+$ ions only |

**Table 2. Molecular Weights of Polystyrene as Calculated Using MALDI**[a]

| polystyrene sample | values | |
|---|---|---|
| | actual (by GPC) | determined by MALDI |
| 1 | $M_p$ = 1720, $D$ = 1.04 | $M_n$ = 1724, $D$ = 1.08 |
| 2 | $M_p$ = 5050, $D$ = 1.05 | $M_n$ = 5010, $D$ = 1.04 |

[a] $M_p$ represents peak molecular weight within polystyrene standard (as calculated by GPC).

**Polyester Polyols.** Polyester polyols[24] and polyol fragments from polyurethanes[25,26] have been characterized previously by Hercules and co-workers using TOF−SIMS. In all cases, cation adducts of either intact oligomers, repeat units, or various fragments of polyesters or polyols (in the case of polyurethanes) were observed and extensively characterized. This was also true for TOF−SIMS of substituted polystyrenes[27] and polyamides,[28] and silver clusters were also formed for these studies.

Using MALDI, and an appropriate matrix, the fragmentation was either minimized or eliminated. Indeed when sodium halide and silver were added to matrix, cations, $(M + Na)^+$, were exclusively detected (Figure 7). For example, in Figure 7 all the observed peaks

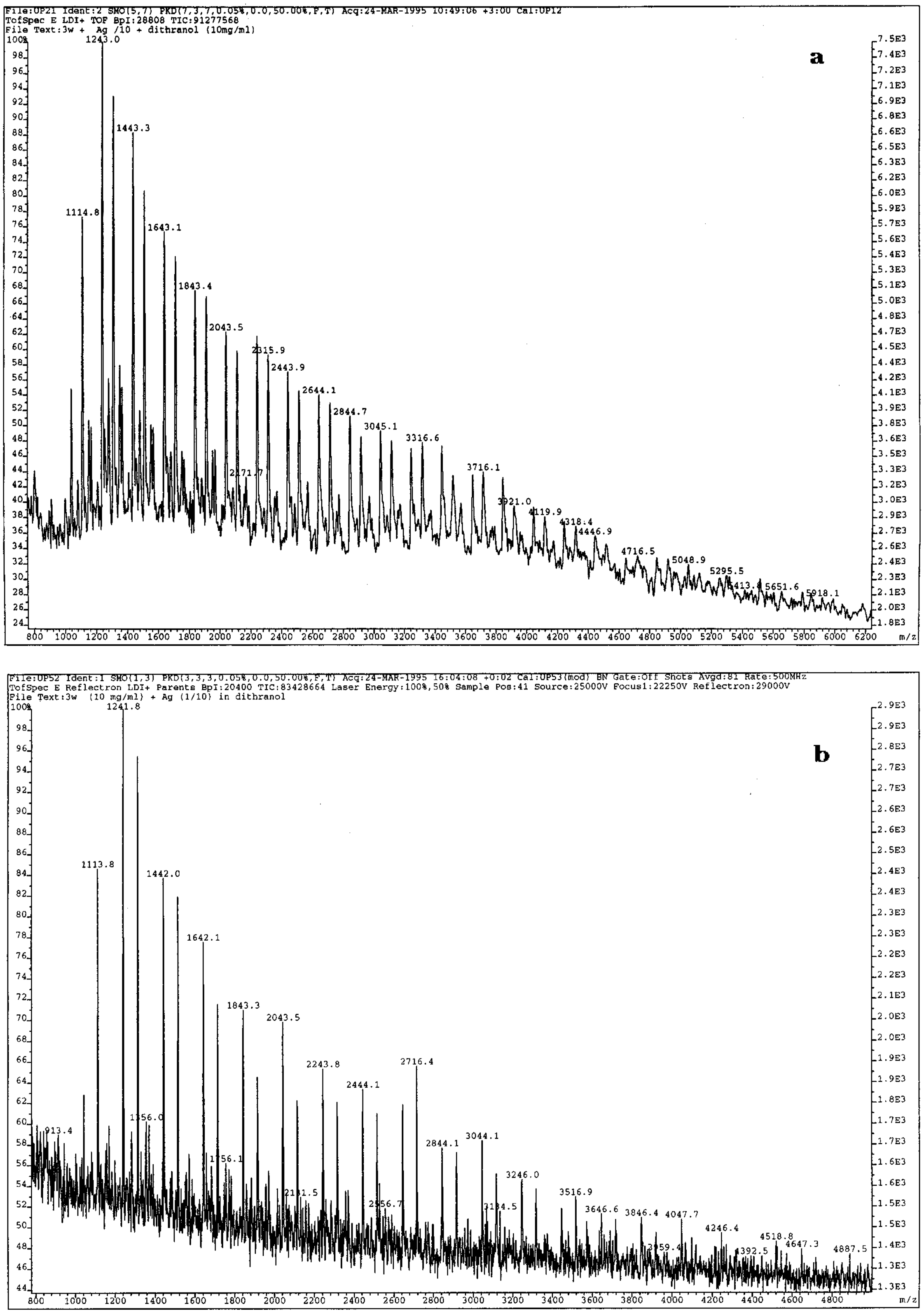


**Figure 8.** (a) Positive ion MALDI−TOF spectrum of polyester synthesized by enzymatic polycondensation (TOF in linear mode, $M_n$ = 2300 by GPC analysis). (b) Positive ion MALDI−TOF spectrum of polyester synthesized by enzymatic polycondensation (TOF in reflectron mode, $M_n$ = 2300 by GPC analysis).

result from intact sodium-containing oligomers (200*n* + 90). The identity of these species was substantiated by a series of compelling isotopic abundance studies as described below.

We note the presence of a low-intensity fragmentation series in Figure 7 at *m/z* values between 1154 + 200*n* and 1954. This fragmentation series can not result from intact oligomers attached to $Ag^+$ cations as is the case in TOF−SIMS,[24] since the difference between $Na^+$ and $Ag^+$ ions is 84. The identity of these species is currently under investigation.

Polyesters that were synthesized enzymatically were also analyzed. As for commercial polyols, there is a series of intact oligomers cationized with $Na^+$ ($C_{10n+4}H_{16n+10}O_{4n+2}$). However, the spectra of enzymatically synthesized polyesters also contains a series corresponding to intact oligomers in which one end could be a carboxylic acid group and the other end group could

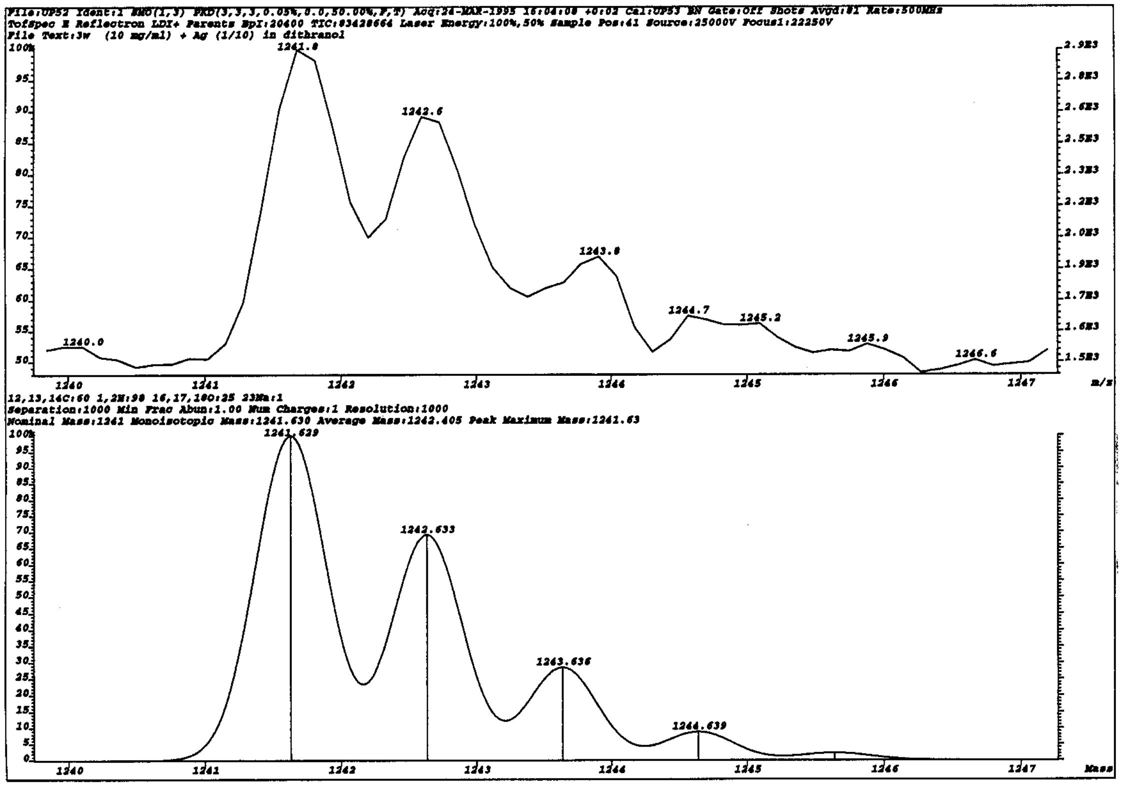


**Figure 9.** Isotopic abundance spectrum of carboxyl–hydroxyl-terminated polymer cation ($C_{60}H_{98}O_{22}Na^+ = 1241.8$) (top) and its comparison with a theoretically derived spectrum (bottom).

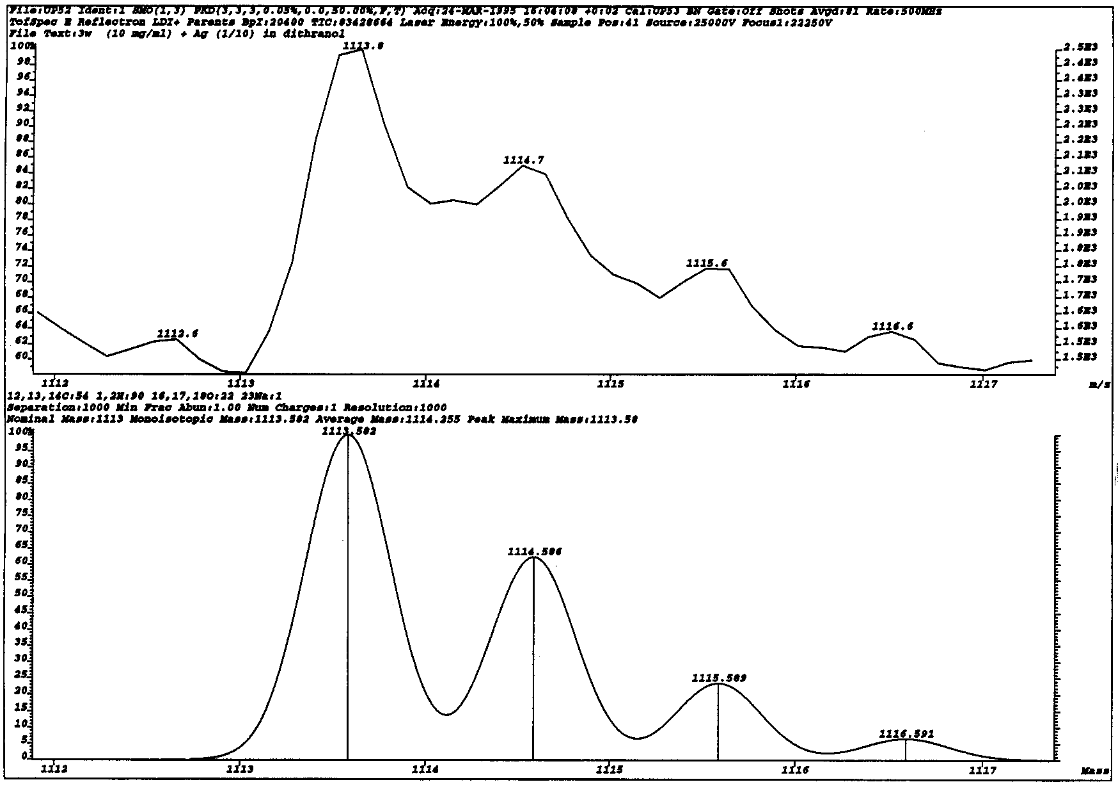


**Figure 10.** Isotopic abundance of hydroxyl–hydroxyl-terminated polymer cation ($C_{54}H_{90}O_{25}Na^+ = 1113.8$) (top) and its comparison with a theoretically derived spectrum (bottom).

be a hydroxyl group ($C_{10n}H_{16n+2}O_{4n+1}$). Once again, cations with $Na^+$ were detected.

End-group analysis is particularly relevant for polyester polyols as their final use, condensation with isocyanates to polyurethane elastomers, is dependent on hydroxy termination. End-group analysis for low molecular weight polymers is often performed by $^1$H-NMR, but acid termination of polyesters is difficult to detect at low levels. Hence polyesters with carboxylic acid end groups are characterized for acid content via titration, which requires large amounts (hundreds of grams of sample) if the acid content of the polyester is very low (<5%). Determination of trace amounts of acid-terminated polyester species in the sample is virtually impossible using this method, but such information would be of significant value. Hence a highly sensitive technique for the end-group analysis of polyesters is desirable.

For polyesters that were synthesized by the enzymatic route, spectra were collected in both linear (Figure 8a) as well as reflectron mode. In linear mode, the ions formed in the ionization region are accelerated in the drift tube before they strike the detector plate. The main purpose of the reflectron is to gain higher mass resolution in order to resolve isotopes. In addition mass accuracy and reproducibility in reflectron mode increases by a factor of 10 over data calibrated in linear mode (from 0.2% to 0.02%). For a reflectron mass spectrometer, the ions are reflected once by a reverse electric field, and relatively fast ions penetrate deeper into the reflecting field and take a longer time to return than slow ions. This compensates for their faster velocity in the drift tube. Hence, fast or slow ions can be focused at the detector. In order to confirm the presence of both carboxyl−hydroxyl- and hydroxyl−hydroxyl-terminated species in the sample (as implied by the linear mode spectra), a single molecular weight species of each ion type was selected using an ion gate prior to being deflected to the mass analyzer.

Isotopic abundance spectra of these species can be theoretically predicted[29] based on the natural abundance ratios of the isotopes. Isotopic abundance spectra of a carboxyl−hydroxyl-terminated intact oligomer chain cationized with $Na^+$ ($C_{60}H_{98}O_{25}Na$, molecular mass = 1241.8) are compared to the theoretical spectra for that formula in Figure 9. Similarly, isotopic abundance data and the prediction for the hydroxyl−hydroxyl-terminated oligomer chain, cationized with $Na^+$ ($C_{54}H_{90}O_{22}Na$, molecular mass = 1113.8), are compared in Figure 10.

Excellent agreement in the positions of isotopic peaks is observed. Quantitatively, the difference in positions of isotopic forms with that predicted theoretically was <0.02% of the molecular mass value for both the carboxyl−hydroxyl- and the hydroxyl−hydroxyl-terminated chains. Presence of acid termination in the polymer was further confirmed by performing titration analysis. The calculated acid number for sample described in Figure 8 using titration was 20.2 mg of KOH/g of sample. Using MALDI−TOF, the equivalent calculated value was 18.2 mg of KOH/g of sample. This implies that the relative intensities of both series of peaks are equivalently concentration dependent. Further, for this matrix and polymer, there is no end-group dependent preferential desorption.

## Conclusion

We have demonstrated the use of MALDI−TOF spectrometry for the analysis of synthetic polymers and have performed end-group analysis of a synthetic polymer using this technique. Intact oligomeric ions were obtained within molecular weight range of 200−9000. By changing matrix components, it is possible to perform the desorption of intact polymers of varying polarity. The type of cations that are detected are not only dependent on the properties of the polymer but also on the matrix composition. MALDI−TOF provides a versatile method for the desorption and analysis of intact polymer ions. Detection of unfragmented oligomer ions is particularly helpful for the determination of molecular weight distributions of the polymer.

For oligomeric poly(1,4-butylene adipate), MALDI−TOF experiments showed the presence of $Na^+$-cationized species. Polyesters that were synthesized enzymatically are different from commercial polyols because of the presence of carboxyl-terminated species. Isotopic abundance spectra of carboxyl−hydroxyl- and hydroxyl−hydroxyl-terminated species were compared with theoretical predictions to confirm the presence of each species.

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## References and Notes

(1) Schulten, H.-R.; Lattimer, R. P. *Mass Spectrom. Rev.* **1984**, *3*, 231−315.
(2) Brown, R. S.; Wilkins, C. L. In *Lasers in Polymer Science and Technology: Applications*; Fouassier, J.-P., Rabek, J. F., Eds.; CRC Press: Boca Raton, FL, 1990; Vol. 4, Chapter 1.
(3) Mattern, D. E.; Hercules, D. M. *Anal. Chem.* **1985**, *57*, 2041−2046.
(4) Lattimer, R. P.; Hansen, G. E. *Macromolecules* **1981**, *14*, 776−780.
(5) Cotter, R. J.; Honovich, J. P.; Olthoff, J. K.; Lattimer, R. P. *Macromolecules* **1986**, *19*, 2996−3001.
(6) Matsuo, T.; Matsuda, H.; Katakuse, I. *Anal. Chem.* **1979**, *51*, 1329.
(7) Holm, R.; Karas, M.; Vogt, H. *Anal. Chem.* **1987**, *59*, 371−373.
(8) Hercules, D. M.; Day, R. J.; Balasanmugam, K.; Dang, T. A.; Li, C. P. *Anal. Chem.* **1982**, *54* (2), 280A.
(9) Gardella, J. A.; Graham, S. W.; Hercules, D. M. In *Structural characterization of polymeric materials by Laser Desorption Mass Spectrometry*; Craver, C. D., Ed.; Advances in Chemistry Series 303; American Chemical Society: Washington, DC, 1983; p 635.
(10) Lai, S.-T. F.; Chan, W. S.; Cook, K. D. *Macromolecules* **1980**, *13*, 953.
(11) Chan, K. W. S.; Cook, K. D. *Macromolecules* **1983**, *16*, 1736.
(12) Lattimer, R. P.; Harris, R. E.; Schulten, H. R. *Rubber Chem. Technol.* **1985**, *58*, 577.
(13) Hillenkamp, F.; Karas, M.; Beavis, R. C.; Chait, B. T. *Anal. Chem.* **1991**, *63* (24), 1193A.
(14) Tanaka, K.; Bachmann, D.; Bahr, U.; Hillenkamp, F. *Int. J. Mass Spectrom. Ion Proc.* **1988**, *2*, 151−153.
(15) Karas, M.; Hillenkamp, F. *Anal. Chem.* **1988**, *60*, 2299−3001.
(16) Karas, M.; Bachmann, D.; Bahr, U.; Hillenkamp, F. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *78*, 53−68.
(17) Bahr, U.; Deppe, A.; Karas, M.; Hillenkamp, F. *Anal. Chem.* **1992**, *64*, 2866−2869.
(18) Blais, J. C.; Tessier, M.; Bolbach, G.; Remaud, B.; Rozes, L.; Guittard, J.; Brunot, A.; Marechal, E.; Tabet, J. C. *Int. J. Mass Spectro. Ion Proc.* **1995**, *144*, 131−138.
(19) Chait, B. T.; Wang, R.; Beavis, R. C.; Kent, S. B. H. *Science* **1993**, *262*.
(20) Chaudhary, A. K.; Beckman, E. J.; Russell, A. J. *J. Am. Chem. Soc.* **1995**, *117* (13), 3728−3733.
(21) Uyama, H.; Kobayashi, S. *Chem. Lett.* **1994**, 1687−1690.
(22) Taylor, R., Bayer Corp. Personal communication.
(23) Denoyer, E.; Van Grieken, R.; Adams, F.; Natusch, D. F. *Anal. Chem.* **1982**, *54* (1), 26A.
(24) Kim, Y. L.; Hercules, D. M. *Macromolecules* **1994**, submitted for publication.
(25) Bletsos, I. V.; Hercules, D. M.; VanLeyen, D.; Benninghoven, A.; Karakatsanis, C. G.; Rieck, J. N. *Anal. Chem.* **1989**, *61*, 2142−2149.
(26) Bletsos, I. V.; Hercules, D. M.; VanLeyen, D.; Benninghoven, A.; Karakatsanis, C. G.; Rieck, J. N. *Macromolecules* **1990**, *23*, 4157−4163.
(27) Chiarelli, M. P.; Proctor, A.; Bletsos, I. V.; Hercules, D. M. *Macromolecules* **1992**, *25*, 6970−6976.
(28) Bletsos, I. V.; Hercules, D. M.; Greifendorf, D.; Benninghoven, A. *Anal. Chem.* **1985**, *57*, 2384−2388.
(29) Matsuo, T.; Matsuda, H. *Anal. Chem.* **1979**, *51*, 1329−1331.

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