Characterization of Polyesters by Matrix-Assisted Laser Desorption Ionization Mass Spectrometry

John B. Williams, Arkady I. Gusev,† and David M. Hercules*,†

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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ABSTRACT: A series of aliphatic polyesters, characterized by assymetric oligomer distributions, heteroterminated linear chains, and cyclic oligomers, were studied using MALDI. The results from structural characterization of these materials was compared with those acquired using fast atom bombardment mass spectrometry (FAB-MS), electrospray ionization mass spectrometry (ESI-MS), nuclear magnetic resonance (NMR) spectroscopy, and end group titration. Information on the composition of these polymers obtained from MALDI, ESI-MS, and end group titration showed reasonable agreement. However, the MALDI ionization efficiency appeared to be higher for carboxyl-terminated oligomers. MALDI molecular weight determination were contrasted with those from GPC and NMR. Reasons for disparities in the results between the three methods are discussed. The feasibility of using acidolysis for structural characterization of high molecular weight or insoluble materials was explored. Reaction of the polyesters with trifluoroacetic acid (TFA) produced mono- and bis(trifluoroacetate) esters of the starting material. The products were characterized and the progress of the reaction was monitored using MALDI.

Introduction

Polyesters are a broad and important class of condensation polymers utilized in a variety of films and textiles. More recently, these polymers have been used as thermoplastic molding materials for the manufacture of blow-molded containers. Aliphatic polyesters are useful as plasticizers for poly(vinyl chloride) polymers and copolymers. Knowledge of the chemical structure, molecular weight distribution (MWD), and the presence or absence of additives or impurities is crucial to control of the synthesis and performance of these products. Mass spectrometry provides a tool for simultaneous measurement of the absolute mass to charge ratio and relative ion abundance; this supplies pertinent structural and molecular weight information for synthetic polymer samples. Pyrolysis mass spectrometry, using low energy electron and chemical ionization, has been used to examine thermal degradation processes of polyesters in the low mass range (<250 Da).[1−2] Fast atom bombardment mass spectrometry (FAB-MS) has been applied to the analysis of poly(ethylene adipate) and poly(ϵ-caprolactone).[3] An investigation of the microstructure of copolymers formed during the melt mixing of poly(ethylene terephthalate) and poly(ethylene adipate) was conducted using FAB-MS.[4] Time of flight secondary ion mass spectrometry (TOF-SIMS) has been applied to the characterization of poly(butylene adipate).[5] While FAB-MS and TOF-SIMS overcome the problems of low volatility and thermal lability, desorption/ionization efficiency and fragmentation[6] at higher masses limits the utility of these methods for determination of molecular weight values. Chemical derivatization can aid in the analysis of materials having high molecular weight or low solubility in common solvents. The structural characterization of a series of polyesters using acidolysis and TOF-SIMS has been reported.[6]

The innovation[7,8] and development[9,10] of matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) has considerably increased the accessible mass range for macromolecular analysis. Application of MALDI to lower molecular weight polymers (*ca.* 10^4) produces spectra consisting of discreet oligomer ion peaks. The distribution of intact oligomer ions, with little or no fragmentation, provides an accurate and reproducible tool for the measurement of MWD as well as information on molecular structure and purity of the polymer. MALDI spectra of higher molecular weight materials yield an envelope of unresolved molecular ions which can be used to estimate pertinent molecular weight values. Structural information may be obtained by controlled cleavage of the polymer backbone to produce lower mass oligomer observable in MALDI spectra.

This paper reports the application of MALDI-TOF-MS to the characterization of a series of aliphatic polyesters and derivatives of these materials. Mass measurements of the oligomer and fragments in MALDI spectra allow determination of the polyester repeat unit and terminal group masses. Structural information from MALDI spectra will be compared with that provided by nuclear magnetic resonance (NMR) spectroscopy, FAB-MS, TOF-SIMS, and electrospray ionization mass spectrometry (ESI-MS). Molecular weight information obtained from MALDI spectra will be contrasted to that provided by gel permeation chromatography (GPC) and NMR. Acidolysis of these materials with trifluoroacetic acid (TFA) provides additional structural information through mass measurement of product oligomer and offers a method to improve the solubility of analytes. This is the first report detailing the coupling of this type of derivatization with MALDI.

Experimental Section

I. Instruments. MALDI spectra were acquired using a modified LAMMA 1000 (Leybold-Heraeus GmbH) (TOF-MS) equipped with a N_2 laser (VSL 337 ND, Laser Science Inc., Boston, MA). The instrument has been described elsewhere.[11] Laser irradiance was controlled by diaphragm defocusing of the laser beam in the sample plane. The laser spot size was (30×50 to 100×150 μm). The positive ions were accelerated to 4 keV and space focused using an Einzel lens; ions were postaccelerated to 15 keV before detection by a discrete dynode type secondary electron multiplier (SEM). The signal from the SEM was amplified and stored in a 200-MHz 8×32K channels transient recorder (LeCroy, Inc., Spring Valley, NY) subsequent to transfer to a IBM compatible PC terminal. Typically, 50−500 shots were averaged to produce experimental spectra.

† Present address: Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

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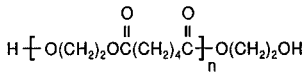
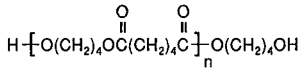
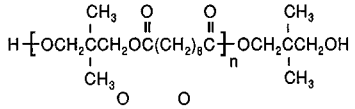
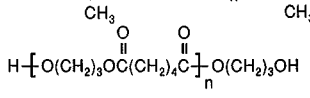
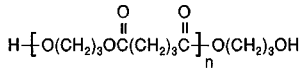
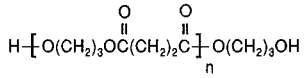
Table 1. Structures and Repeat Unit Masses of Dihydroxyl-Terminated Polyesters

poly(ethylene adipate) (PEA) repeat unit = 172 Da	
poly(butylene adipate) (PBA) repeat unit = 200 Da	
poly(neopentyl glycol sebacate) repeat unit = 270 Da (PNS)	
poly(trimethylene adipate) (PTA) repeat unit = 186 Da	
poly(trimethylene glutarate) (PTG) repeat unit = 172 Da	
poly(trimethylene succinate) (PTS) repeat unit = 158 Da	

ESI analysis was performed using a VG Autospec mass spectrometer (Fison Instrument, Manchester, U.K.) equipped with an Autospec ESI source. The analyzer had a three-sector, double-focusing geometry of the type ESA/magnet/ESA. The detector was a VG photomultiplier dual detector. The sample flow rate for ESI was 13.5 μL/min delivered from a Sage Industries 355 syringe pump. The bath and nebulizer gas was dry N_2. ESI samples were prepared by dissolution of 0.2 mg of the polyester in 1 mL of 1:1 v/v acetonitrile/water.

FAB spectra were acquired the VG Analytical 70-G dual sector mass spectrometer using a xenon ion gun. FAB samples were prepared by dissolution of the polyester (*ca.* 10 μg/mL) in methanol. The FAB matrix was *m*-nitrobenzyl alcohol.

GPC measurements were performed in THF at 35 °C at a flow rate of 0.35 mL/min maintained by a Waters 590 HPLC pump. Samples were prepared by dissolving 20 mg of the polyester in 2 mL of THF. The GPC instrument was equipped with 2 Phenomenex Phenogel columns (length = 300 mm and bore = 4.6 mm). The packing material of the first column consisted of 5−20 μm spheres having mixed pore sizes (10^2−10^6 Å). Similar packing in the second column had a pore size of 500 Å. A Waters 410 differential refractometer detector and a Waters 745 data module provided detection and data acquisition. Calibration was performed using poly(ethylene glycol) standards (Polyscience) of molecular weights 200, 1500, 5000, 9000, and 20000, at a typical sample concentration of 10 mg/mL.

Nuclear magnetic resonance (NMR) spectra were acquired using a Bruker Aspect-3000, AM-500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) under a long delay time (40 s) without nuclear Overhauser enhancement (NOE). Samples for ^{13}C NMR and ^{1}H NMR were prepared by dissolving 100−200 mg and 1−2 mg, respectively, of the polyester in 1 mL of $CDCl_3$. The number average molecular weight (M_n) was estimated by dividing the signal intensity of the carbon atoms in the repeat unit by a factor corresponding to the number of equivalent carbon atoms. The result was ratioed to the intensity of the signal from terminal carbon atoms, then multiplied by the repeat unit mass. The terminal group masses were then added.

II. Sample Preparation. A series of six aliphatic polyesters with molecular weights below 10^4 were investigated. Poly(butylene adipate) (PBA) was obtained from the Bayer Corporation, poly(ethylene adipate) (PEA) and poly(neopentyl glycol sebacate) (PNS) were purchased from the Aldrich Chemical Co., poly(trimethylene adipate) (PTA) was purchased from Polyscience, Inc., and poly(trimethylene glutarate) (PTG) and poly(trimethylene succinate) (PTS) were purchased from Scientific Polymer Products, Inc. The structures of dihydroxyl terminated oligomers and repeat unit masses of these materials are shown in Table 1.

MALDI matrices used for analysis of the polyesters were prepared using trans-3-indoleacrylic acid (IAA) from the Aldrich Chemical Co. A 0.2 M solution of IAA in acetone was vortex mixed with an equal volume of the analyte (1 mg/mL) in acetone. Then 2−3 μL of the mixture was slowly pipetted onto a stainless steel substrate allowing rapid formation of matrix crystals.[12]

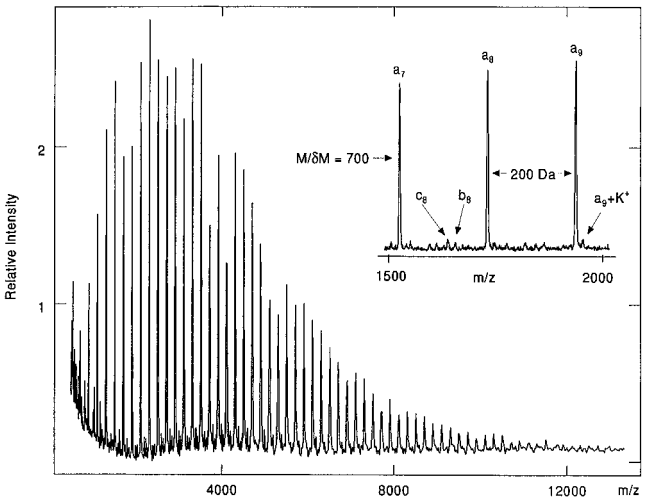


Figure 1. MALDI mass spectrum of PBA with an IAA matrix. The inset shows an expanded view of the 1500−2000 Da reagion of the spectrum.

Liquid matrices were employed for MALDI analysis of liquid phase derivatives using the absorber 2-cyano-5-phenyl-2,4-pentadienoic acid (CPPA) (Aldrich Chemical Co.). A 10 μL aliquot of of 0.2 M CPPA in methanol was added to 5 μL of the product.[13] The samples were vortex mixed and then vacuum centrifuged to remove the volatile solvent, yielding a final absorber concentration of 0.4 M in the liquid analyte. A 2−3 μL droplet of the mixture was placed on a stainless steel substrate and mounted in the instrument source.

Acidolysis of the above polyesters was carried out by dissolution of solid materials in concentrated trifluoroacetic acid (TFA), yielding an initial concentration of 1 mg/mL. Dilute reaction mixtures were prepared by adding 1 mL of TFA to 3 mL of a 1 mg/mL polyester solution in acetone. The reaction was terminated by vacuum centrifugation of a 0.5−1.0 μL aliquot of the mixture.

Results and Discussion

I. Structural Characterization. 1. Matrix Assisted Laser Desorption Ionization (MALDI) Mass Spectrometry. Positive ion MALDI-TOF spectra were obtained for all polyesters listed in Table 1. The spectrum of PBA (Figure 1) typifies the highly asymmetric and dispersed oligomer distributions observed from the polyesters studied; as expected for polycondensates. The mass range below 1000 Da (not shown) was dominated by peaks resulting from matrix, matrix fragments, clusters, and metal ions. The highest intensity peaks result from Na^+-cationized dihydroxyl terminated oligomers (a_n) and extend over the mass range 1000−13000 Da. Potassium-cationized oligomer peaks show a much weaker intensity. With a resolution of 700, calculated using the full width at half-maximum (fwhm) definition, the ^{13}C isotopic distribution is not discernible. The mass difference between adjacent homocationized oligomers was found to be 200 Da, consistent with that expected for the PBA repeat unit. After subtraction of the cation and total repeat unit mass, the combined terminal group mass was calculated to be 90 Da, which is in agreement with the structure shown in Table 1.

A series of low intensity peaks, designated as b_n in Figure 1, appear 72 Da below the mass of the dihydroxyl

Table 2. Averaged Intensities (Percentage of All Ion Types) of Carboxyl-Terminated Oligomers in MALDI and ESI Polyester Spectra[a]

	MALDI		ESI	
polyester	% b	% d	% b	% d
PBA	3.8 ± 0.2	0.0 ± 0.0	4.0 ± 0.4	0.0 ± 0.0
PEA	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
PNS	44.9 ± 3.6	40.6 ± 3.7	48.6 ± 6.5	37.1 ± 6.7
PTA	41.7 ± 8.9	8.3 ± 2.2	35.5 ± 1.8	5.3 ± 1.8
PTG	33.7 ± 3.6	6.0 ± 1.3	27.6 ± 9.2	6.6 ± 3.6
PTS	47.7 ± 6.8	29.5 ± 2.3	45.8 ± 12.5	22.8 ± 11.6

[a] Key: b, carboxyl and hydroxyl end groups; d, dicarboxyl end groups.

oligomer and are identified as the sodium cation of the monocarboxyl terminated oligomer. Peaks from monocarboxyl oligomers have also been seen in the MALDI analysis of this PBA sample using a Bruker REFLEX TOF-MS.[14] Additional weak peaks, designated as c_n in Figure 1, correspond to the masses of an integral number of repeat units plus sodium and are assumed to result from cyclic oligomers. Positive ion FAB mass spectra of the experimental polymers were characterized by intense proton cationized cyclic oligomers with the appearance of low intensity peaks from dihydroxyl oligomers minus water. Montaudo and co-workers have previously reported the presence of cyclic oligomers in the FAB spectra of polyesters.[3] These oligomers were believed to be the product of synthesis rather than fragmentation and were shown to have a high ionization efficiency relative to their linear counterparts.

The MALDI spectrum of PTS is presented in Figure 2. The mass separation of the sodium-cationized dihydroxyl oligomer (a_n) allowed determination of a repeat unit mass of 158 Da, as expected for PTS. Peaks corresponding to sodium-cationized cyclics (c_n) are also observed at moderate intensity. In addition, two series of peaks (b_n and d_n), separated by the mass of the repeat unit, appear 58 and 116 Da below each dihydroxyl oligomer. The positions of these peaks were consistent with the predicted mass of the sodium-cationized mono- and dicarboxyl-terminated oligomer having an identical number of repeat units. Acid-terminated oligomers were detected by MALDI in all polyesters studied, with the exception of PEA. The relative intensities of the heterogeneous oligomer peaks were consistent over the distribution of each polyester and are summarized in Table 2. These determinations were made by calculating the ratio of the intensity (peak height) of the mono- or dicarboxyl ion to the total intensity of all ions having the same degree of polymerization. These ratios were then averaged over the breadth of the distribution. A wide disparity in the end group composition of these materials is noted.

2. Nuclear Magnetic Resonance (NMR) Spectroscopy. The appearance of heterogenous oligomer peaks in MALDI spectra could arise from four sources: the products of polymer synthesis, impurities in starting materials, hydrolysis of the polyester during storage or sample preparation, or fragmentation of the polymer during mass spectrometric analysis. The end-group compositions of the polyesters were evaluated using ^{13}C and ^{1}H NMR. The position, intensities, and assignment of peaks in the NMR spectrum of PTS were 27.6 ppm (11.9), 28.7 ppm (27.0), and 61.1 ppm (25.1) (repeat unit methylene carbons), 31.3 ppm (1.0), 58.7 ppm (1.1), and 61.6 ppm (1.4) (terminal group methylene carbons), and 172.0 ppm (28.3) (ester carbonyls). Similar spectra were obtained from PBA, PEA, PTA, and PTG. PNS produced an additional peak at 178.2 ppm (4.5 ppm above the ester peak), having an intensity of *ca.* 8% of that of the hydroxyl terminus. This weak peak is believed to result from a carboxyl carbon. The ^{1}H NMR analysis of the same materials produced peaks corresponding to the aliphatic hydrogens (*ca.* 1.8, 2.4, and 4.1 ppm) and the hydroxyl hydrogens (*ca.* 3.5 ppm). No peaks from acid protons (expected in the 10−11 ppm region of the spectra) were found. The NMR response for acid and hydroxyl groups was evaluated using the model compound 10-hydroxydecanoic acid. A *ca.* 1:1 ratio was observed between the intensities of the hydroxyl and carboxylic hydrogens. Hence, NMR data indicate that the experimental polyesters consist predominately of dihydroxyl-terminated oligomers.

Polyesters are synthesized by condensation of the appropriate diacid with a selected diol. To produce polyesters of higher molecular weight, excess diol is added.[15] The products of this type of synthesis would be expected to produced MALDI spectra similar to those seen for PBA and PEA, i.e., spectra indicating a negligible presence of carboxylic end groups.

It is possible that the polyester samples may have been hydrolyzed during sample storage or preparation. The MALDI matrix (IAA) has carboxylic acid functionality and could be capable of catalyzing hydrolysis. However, acetone was used as the matrix and sample solvent, and the presence of adventitious water is unlikely to result in the extent of hydrolysis indicated by MALDI spectra. In addition, the large disparity between end group composition of experimental materials, subjected to identical sample preparation, suggests that hydrolysis during sample preparation is unlikely.

3. Fragmentation. It is also conceivable that the heterogeneity of the polyester terminal groups, as seen in MALDI spectra, could be a product of fragmentation. Polyesters fragment during thermal degradation *via* two major pathways:[16] intramolecular ester exchange and β-hydrogen transfer. Intramolecular exchange results in formation of a linear fragment identical to the oligomer of $n - 2$ repeat units and a cyclic dimer of the repeat unit. Hydrogen migration has been shown by electron ionization mass spectrometry to occur *via* β-H transfer (McLafferty rearrangement).[17]

TOF-SIMS spectra of the experimental polyesters[5,6] are characterized by three distinct series of peaks: oligomer, repeat unit, and a weaker intensity fragment series. The β-H transfer mechanism is responsible for the low-intensity fragment peaks seen in TOF-SIMS polyester spectra.[5] The repeat unit series seen in TOF-SIMS spectra has been shown to originate from cyclization via intramolecular ester exchange during ion formation.[5] This series also appears at low intensity in MALDI spectra.

Loss of fragments has occurred in the MALDI analysis of poly(butyl methacrylate) (PBMA) prepared with saturated butyl methacrylate terminal groups.[18] Since fragments are not seen at low masses, these losses appear to result from the single elimination of neutral butanol. In addition, neutral water loss has been observed in the MALDI spectra of poly(acrylic acid).[19] The features of MALDI polyester spectra, exemplified by Figure 2, are consistent with cleavage of one or both terminal group(s) accompanied by hydrogen transfer and the loss of a small neutral moiety.

4. Electrospray Ionization Mass Spectrometry (ESI-MS). The source of carboxyl termination was investigated using the soft ionization technique ESI-

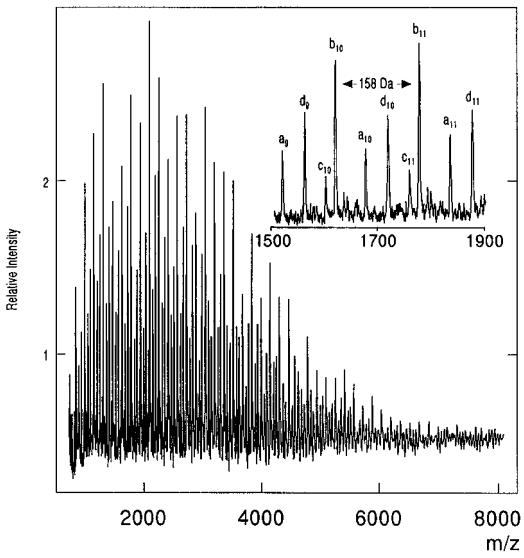


Figure 2. MALDI mass spectrum of PTS with an IAA matrix. The inset expands the range 1500−1900 Da.

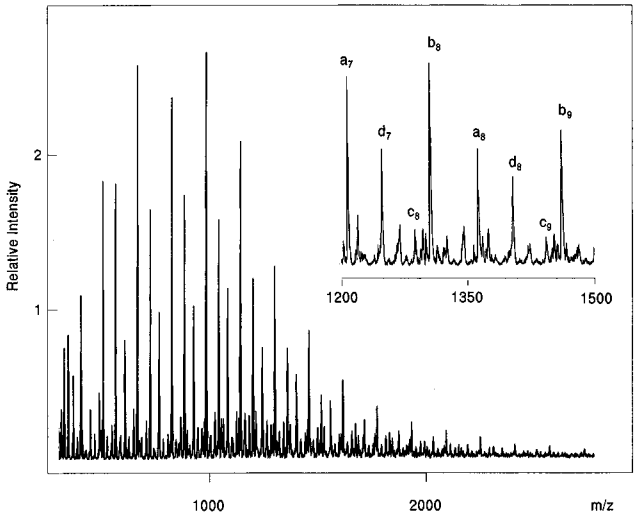


Figure 3. ESI mass spectrum of PTS in 1:1 v/v H_2O/acetonitrile. The inset expands the range 1200−1500 Da.

MS. The ESI mass spectrum of PTS is shown in Figure 3. The peaks represent the singly charged (Na^+) linear oligomer ions with dihydroxyl (a_n) and mono- (b_n) and dicarboxyl (d_n) endgroups, as well as cyclic oligomers (c_n). Higher intensity peaks resulting from cyclic oligomers are seen in the 200−1000 Da region of the spectrum. Other lower intensity peaks were identified as doubly charged ($2Na^+$) ions and were observed up to $m/z \approx 3000$ Da. In general, the characteristics of ESI spectra of the polyesters listed in Table 1 mimic those appearing in the 1000−3000 Da range of the MALDI spectra. The relative intensities of the heterotelechelic linear species calculated from ESI spectra are included in Table 2. It is seen that the MALDI and ESI determinations of relative abundance agree within limits of experimental error. However, the relative ionization efficiency of the carboxyl-terminated species appears to be somewhat higher in MALDI.

The extent of fragmentation in ESI analysis has been shown to vary with the skimmer voltage.[20] To evaluate the possibility of polyester fragmentation produced during ESI analysis, spectra of PTS were acquired over the range of skimmer voltages accessible through instrument control. Although the total ion current was diminished at lower voltages, there was negligible change in the relative intensities of the polyester peaks. This result indicates that the acid-terminated species are not the product of fragmentation but are instead present in the polyester sample.

Table 3. Percent of Polyester Carboxyl Termini

polyester	MALDI	ESI	titration
PBA	1.9 ± 0.1	2.0 ± 0.2	2.0 ± 0.2
PEA	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.2
PNS	63.2 ± 3.8	61.4 ± 6.8	55.6 ± 1.5
PTA	29.2 ± 4.4	23.1 ± 1.1	26.0 ± 1.0
PTG	22.9 ± 2.2	20.4 ± 5.9	19.9 ± 1.5
PTS	53.4 ± 5.0	45.7 ± 11.4	45.9 ± 2.0

5. End Group Titration. The degree of carboxyl termination was further evaluated by titration, in 1:1 v/v methanol/water using phenolphthalein as an indicator. Strict quantification of the carboxyl termini was not intended since an accurate value of the polymer molecular weights cannot be assessed. However, the titrations did allow estimation of the extent of carboxyl groups presence and are included, for comparison, with determinations the by MALDI and ESI in Table 3. Good agreement is seen between the ESI and titration results. However, the MALDI values are generally higher than those produced by titration of the polyesters, further supporting the possibility of a higher MALDI ionization efficiency for acid-terminated oligomers under the previously described experimental conditions.

The results from MALDI, ESI, and titration indicate that the acid-terminated oligomers seen in MALDI spectra of aliphatic polyesters were a product of polymer synthesis or the hydrolysis of these materials during storage. The conflicting results from NMR may have been the consequence of an inability to resolve the acid and ester carbonyl peaks, the low concentration of acid end-groups, or a decreased instrument response for the acid carbonyl and hydrogen.

II. Molecular Weight Determination. The masses of the oligomer peaks from mass calibrated spectra, combined with their relative intensities (height or area), allow accurate calculation of the **number average molecular weight** (M_n), the **weight average molecular weight** (M_w), and the **polydispersity** (M_w/M_n), which serves as an indication of the width of the mass range of the oligomer distribution. M_n and M_w are defined as

$$M_n = \sum N_i M_i / \sum N_i$$

$$M_w = \sum N_i M_i^2 / \sum N_i M_i$$

where N_i is the molar fraction of the molecular ion with a degree of polymerization i and M_i is the mass or, without resolution of the isotopic distribution, the average mass of the ith oligomer.

Molecular weight determinations from MALDI, GPC, and NMR analysis of the experimental polyesters are presented in Table 4. To examine the effect of peak broadening at higher masses in broad polymer distributions, molecular weight values from MALDI spectra of the polyesters were calculated using both the height and area of oligomer peaks. These values show good agreement (ΔM_n and $\Delta M_w < 6\%$), indicating that molecular weight determination for the polyesters was not affected by instrumental mass resolution.

Comparison of the MALDI and NMR M_n values reveals large differences ($\Delta\%_{NMR}$) in results obtained for PNS and PTS. MALDI, ESI, and titration indicate a

Table 4. Comparison of Polyester Molecular Weight Determinations

polyester	average	MALDI (height)	MALDI (area)	GPC	GPC Δ%	NMR	NMR Δ%
PBA	M_n	3445	3530	6945	49.1	4380	19.4
	M_w	4480	4510	10490	57.0	NA	NA
	M_w/M_n	1.30	1.28	1.51	15.2	NA	NA
PEA	M_n	3000	3180	4850	29.1	3040	−4.6
	M_w	4335	4325	7115	39.2	NA	NA
	M_w/M_n	1.44	1.36	1.47	7.5	NA	NA
PNS	M_n	2470	2515	3925	35.9	6980	64.0
	M_w	3360	3190	6030	47.1	NA	NA
	M_w/M_n	1.36	1.26	1.54	18.2	NA	NA
PTA	M_n	2090	2105	2430	13.4	2110	0.2
	M_w	2710	2550	3210	20.1	NA	NA
	M_w/M_n	1.29	1.21	1.32	8.3	NA	NA
PTG	M_n	2255	2305	1915	−20.4	2315	0.4
	M_w	2770	2855	2795	−2.1	NA	NA
	M_w/M_n	1.23	1.24	1.46	15.1	NA	NA
PTS	M_n	2710	2640	3450	23.5	4600	42.6
	M_w	3410	3240	4885	33.7	NA	NA
	M_w/M_n	1.26	1.23	1.42	13.4	NA	NA

large percentage of these two polymers are mono- or dicarboxyl terminated. NMR molecular weight calculations are based on the ratio of backbone to end group carbon. Thus, if the endgroups are undetected, the molecular weight estimated for the polymer will be too large. This idea is supported by the dissimilarity of MALDI and NMR M_n values from predominately carboxyl-terminated PNS and PTS.

Molecular weight estimations from GPC produced results that are significantly different than those calculated from MALDI spectra. The possible reasons for these differences $(\Delta\%)_{GPC}$ are discussed below.

The validity of MALDI molecular weight determinations is based on the assumption that ionization efficiency and detector response are independent of oligomer mass in a limited mass range. A recent study[21] of the relative intensities of MALDI peaks produced from a 1:1 mixture of the 2500 and 5000 Da oligomers of poly(methyl methacrylate) supports this assumption. However, the polyesters produced oligomers distributed over a wider mass range (up to *ca.* 13000 Da); thus, the possibility of diminution of detector efficiency at higher masses during the MALDI analysis of these materials cannot be ignored.

The large $\Delta\%_{GPC}$ of M_w values may also have resulted from inaccuracies in GPC determinations. GPC uses size exclusion for separation and requires calibration with molecules of the same type as the sample to convert the size-sorted chromatograms into molecular weight distribution curves. If suitable calibration standards are not available, universal calibration provides a method for correction of the differences in hydrodynamic volume of the dissimilar materials. Application of GPC to determination of polyester molecular weight suffers from both a need for effective calibration standards (narrow MWD polyglycols were utilized) and the nonavailability of appropriate Mark−Houwink constants (**K** and **a**) necessary to implement universal calibration. Under these experimental conditions, the reliability of GPC measurements is in question.[22]

III. Acidolysis. Reactions allowing selective cleavage or chemical derivatization can be used to provide structural information about insoluble or high molecular weight materials. These reactions must occur at specific bonds, produce large chain segments that provide information about multiple repeat units, and not change the backbone structure of the polymer. TOF-SIMS studies of polyesters[6] and polyurethanes[5,23] have demonstrated the use of selective bond scission with TFA.

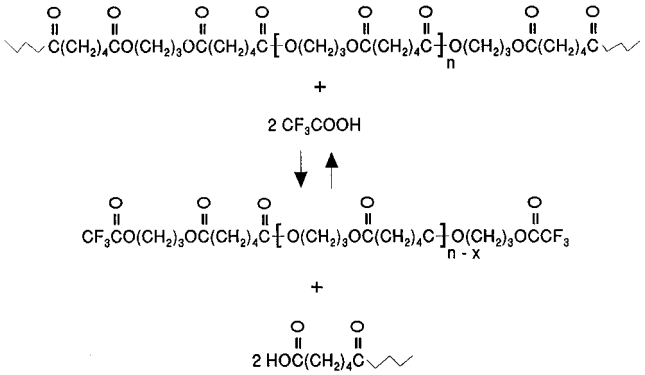


Figure 4. Acidolysis of PTA with TFA.

Table 5. Peaks from the Reactants and Products in the Mass Range 1500−1900 Da after Acidolysis of PTA for 15 min with Concentrated TFA

Species	n	m/z	Intensity
b,c*	8	1530	4135
	9	1716	2855
a	8	1588	3275
	9	1774	2040
f	7	1594	360
	8	1780	220
g	8	1626	1150
	9	1812	840
d	8	1658	1005
	9	1844	865
e	8	1684	1750
	9	1870	995

*Potassium cationized peak.

The sequence of PTA acidolysis with TFA is presented in Figure 4. The reaction, as shown, produces esters of TFA consisting of an integral number of repeat units and an acid-terminated oligomer. The liquid phase products were characterized by MALDI using solid and liquid matrices. Structural information related to both repeat unit and terminal groups may be gained from the mass disparity between reactant and product peaks.

The MALDI spectrum of PTA after 15 min of reaction with concentrated TFA is shown in Figure 5. The mass, intensity, and probable structure of species producing ions in the 1500−1900 Da region of the PTA spectrum are listed in Table 5. In addition to the oligomers of the starting material (a−d), peaks from mono- and bis-(trifluoroacetate)-substituted chains (e−g) are observed. There is also a significant increase in the relative intensity of the monocarboxyl (b) and dicarboxyl (d) oligomers. Thus, spectral detail is consistent with the expected products of the acidolysis reaction.

The MALDI mass spectrum of PBA after acidolysis for 3 h in 1:3 v/v trifluoroacetic acid/acetone mixture is shown in Figure 6. In contrast to the MALDI spectrum of unreacted PBA (Figure 1), ions were not detected above *ca.* 8000 Da after acidolysis. The effect of reaction time on the molecular weight of PBA was evaluated, with the results summarized in Table 6. MALDI spectra of polyester derivatives exhibited a decrease in signal from higher molecular weight oligomers with longer reaction times, resulting in a decrease in estimated molecular weight. This was accompanied by

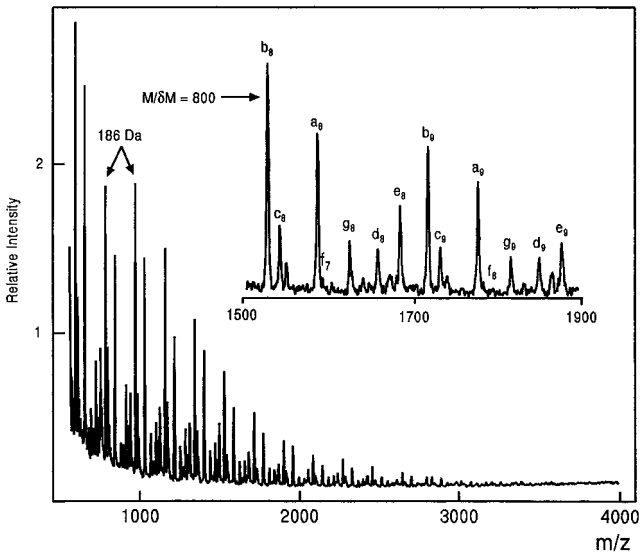


Figure 5. MALDI mass spectrum of PTA after 15 min of acidolysis with concentrated TFA. The liquid matrix was composed of the product mixed with a 2-fold volume of absorber solution (0.2 M CPPA). The inset expands the range 1500−1900 Da. The major peaks are identified in Table 5.

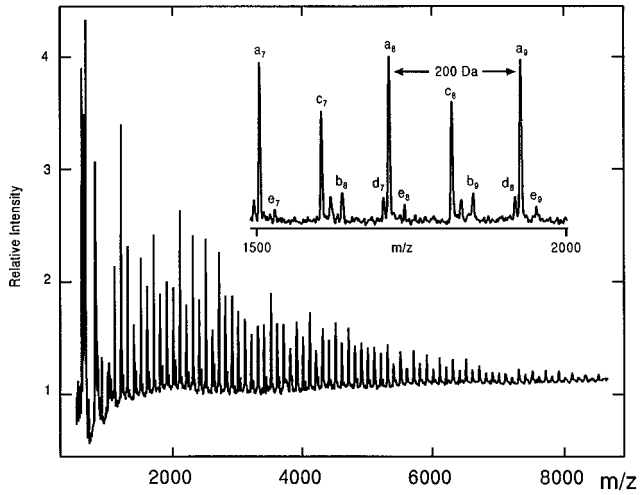


Figure 6. MALDI mass spectrum of PBA with an IAA matrix after 3 h of acidolysis with 1:3 v/v TFA/acetone. Major peaks from the reactant and products in the range 1500−2000 Da appear in the inset. The major peaks are identified as follows: a, the dihydroxyl-terminated oligomer; b, the monocarboxyl-terminated oligomer; c, the TFA/hydroxyl-terminated oligomer; d, the di-TFA-terminated oligomer; e, the TFA/carboxyl terminated oligomer.

Table 6. Effect of the Time of Reaction on the Molecular Weight of PBA

Δt (h)	M_n	M_w	M_w/M_n
0	3450	4490	1.30
0.25	2955	3840	1.30
1	2950	3645	1.20
2	2860	3680	1.29
3	2670	3245	1.22
5	2330	2885	1.24

growth of lower molecular weight products. The time dependent loss of signal at higher mass indicates that the mono- and disubstituted products may undergo subsequent reactions that further decrease the chain length of the oligomer.

The feasibility and progression of reactions that modify polymers to improve solubility or chemical functionality may be monitored by MALDI. Product growth during the reaction of PBA with 1:3 v/v TFA/acetone over the period 0−5 h in the mass range 1400−2000 Da is shown in Figure 7. The progress of the reaction is viewed through the steady increase in the intensity ratio of the $n = 7-9$ oligomer of the monosubstituted acidolysis product (M_{TFA}) and the dihydroxyl-terminated starting material (M_{NR}). Since derivatives may undergo subsequent reactions to form new products, assessment of rate parameters was not possible. However, the potential applicability of MALDI to kinetic problems is evident.

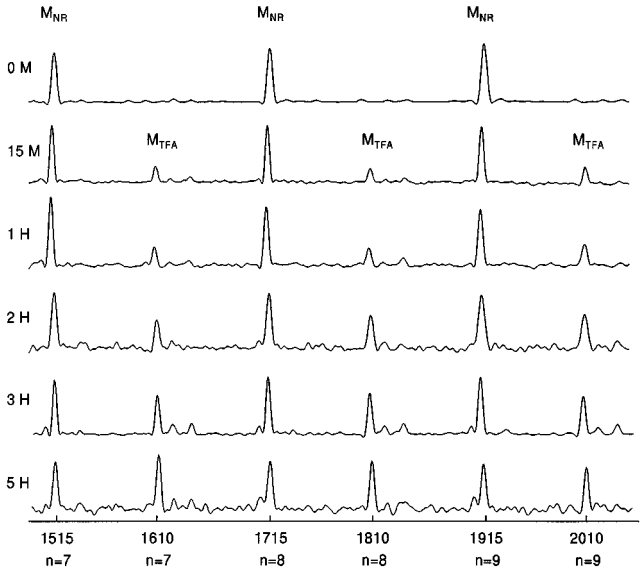


Figure 7. Progression of product formation during acidolysis of PBA in 1:3 v/v TFA/acetone using an IAA matrix.

Conclusions

A series of aliphatic polyesters were studied. The positions of the oligomer peaks allowed determination of the mass of the repeat unit and detection of cyclic oligomers consisting of an integral number of repeat units. MALDI analysis revealed a large disparity in the percentage of hydroxyl and carboxyl endgroups present within the polyester series. ESI-MS measurements and end group titration indicated that acid-terminated oligomers seen in MALDI spectra were a product of polymer synthesis or hydrolysis during storage and not the result of sample preparation or fragmentation.

Polyester M_n and M_w values determined using MALDI peak height and area showed good agreement (within 6%); thus, peak broadening at higher masses did not alter molecular weight determinations. Large differences between values of M_n determined by MALDI and NMR appear to result from the failure of NMR to detect carboxyl end groups. GPC molecular weight estimations were generally larger than those determined with MALDI.

Acidolysis with TFA was employed for further characterization of polyesters using MALDI. Progress of the acidolysis reaction was monitored using MALDI. The disappearance of higher mass oligomers with increasing reaction time indicated that products undergo additional reactions with TFA.

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References and Notes

(1) Adams, R. E. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 119.
(2) Garozzo, D,; Giuffrida, M.; Montaudo, G. *Macromolecules* **1986**, *19*, 1643.
(3) Ballistreri, A.; Garozza, D.; Giuffrida, M.; Montaudo, G. *Anal. Chem.* **1987**, *59*, 2024.
(4) Montaudo, G.; Montaudo, M.; Scamporrino, E.; Vitalini, D. *Macromolecule*s **1992**, *25*, 5099.
(5) Hittle, L. R. Ph.D. Thesis, University of Pittsburgh, 1994.
(6) Kim, Y. L.; Hercules, D. M. *Macromolecules* **1994**, *27*, 7855.
(7) Karas, M.; Bachman, D.; Bahr, U.; Hillenkamp, *F. Int. J. Mass Spectrom. Ion Processes* **1987**, *78*, 53.
(8) Tanaka, K.; Waki, H.; Ido, Y.; Akita, S.; Yoshida, Y.; Yoshida, T. *Rapid Commun. Mass Spectrom.* **1988**, *2*, 151.
(9) Hillenkamp, F.; Karas, M.; Beavis, R. C.; Chait, B. *Anal. Chem.* **1991**, *30*, 1193A.
(10) Karas, M.: Bahr, U.; Giessmann, U. *Mass Spectrom. Rev.* **1991**, *10*, 335.
(11) Gusev, A. I.; Wilkinson, W. R.; Proctor, A.; Hercules, D. M. *Anal. Chem.* **1995**, *67*, 1034.
(12) Danis, P. O.; Karr, D. E. *Org. Mass Spectrom.* **1992**, *28*, 923.
(13) Williams, J. B.; Gusev, A. I.; Hercules, D. M. *Macromolecules*,**1996**, *29*, 8144.
(14) Danis, P. O. Unpublished data.
(15) Rauve, A. *Principles of Polymer Chemistry*; Plenum Press: New York, 1995; p 209.
(16) Garrozo, D.; Guiffrida, M.; Montaudo, M. *Macromolecules* **1986**, *19*, 1643.
(17) McLafferty, F. W. *Interpetation of Mass Spectra*; University Science Books: Mill Valley, CA, 1980; p 201.
(18) Danis, P. O.; Karr, D. E.; Simonsick, W. J., Jr.; Wu, D. T. *Macromolecules* **1995**, *28*, 1229.
(19) Danis, P. O.; Karr, D. E.; Mayer, F.; Holle, A.; Watson, C. H. *Org. Mass Spectrom.* **1992**, *27*, 843.
(20) Katta, V.: Chowhury, S.; Chait, B. T. *Anal. Chem.* **1992**, *63*, 174.
(21) Larsen, B. S.; McEwen, C. N,; Simonsick, W.; Peacock, P. M. *Proceedings of the 42nd ASMS Conference on Mass Spectrometry and Allied Topics*; Chicago, IL, 1994; p 518.
(22) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 453.
(23) Blestos, I. V.; Hercules, D. M.; van Leyen, D.; Benninghoven, A.; Karakatsanis, C. G.; Rieck, J. N. *Anal. Chem.* **1989**, *61*, 2142.

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