Macromolecules **1994,** *27,* 7855-7871

Structural Characterization of Polyesters by Transesterification and Time-of-Flight Secondary Ion Mass Spectrometry

Yeonhee L. Kim and David M. Hercules*

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

Received February 15, 1994; Revised Manuscript Received August 2, 1994®

ABSTRACT: The structural characterization of a series of polyesters has been done by time-of-flight secondary ion mass spectrometry (TOF-SIMS) combined with transesterification. Polymer fragments and intact oligomers composed of large numbers of repeat units were observed. Transesterification of polyesters by trifluoroacetic acid (TFA) and chlorodifluoroacetic acid (CFA) was carried out to produce TOF-SIMS spectra. The shapes and intensities of clusters in transesterification spectra showed good agreement with theoretical isotope patterns. TOF-SIMS spectra were used to monitor the progress of the transesterification reaction. Transesterification products of branched poly(1,3-butylene adipate) were identified in the TOF-SIMS spectra, providing information about polymer branching.

Introduction

Polyesters are well-known polycondensation polymers and have been investigated by many research groups in the past few decades.[1-4] More recently, they have drawn increasing attention as a thermoplastic molding material to be used for new applications, e.g., blow molding for soft drink containers. As a result, new techniques of molecular and structural analysis have led to a high degree of understanding of the chemistry, physical behavior, and utility of polyesters.[5-9]

Pyrolysis mass spectrometry has been used to examine thermal degradation processes in polyesters. Typically, these studies have been done in the low mass range, generally below 250. The thermal decomposition mechanisms of several polyesters were studied by direct pyrolysis mass spectrometry, using low-energy electron ionization and chemical ionization.[10,11] These studies reported the predominant thermal fragmentation mechanisms of polyesters. Since its introduction in 1981, fast atom bombardment mass spectrometry (FAB-MS) has become widely used for the analysis of high molecular weight and thermally labile compounds. A limited investigated of polyesters and polyamides was done in the low mass range using FAB-MS.[12]

Mass spectrometry has become a valuable technique for characterization of synthetic polymers in the high mass range. This technique provides the molecular weight distribution, data on the sequence of repeat units, polymer additives, and impurities, and structural information. Many ionization methods have been applied in the structural characterization of high molecular weight polymers. They include field desorption,[13,14] fast atom bombardment,[15] electrohydrodynamic ionization,[16,17] plasma desorption,[18] electrospray ionization,[19] and matrix-assisted laser desorption/ionization (MALDI)[20,21] mass spectrometry. Of these methods, secondary ion mass spectrometry (SIMS) in combination with time-of-flight (TOF) mass analyzers has been used for structural characterization of various polymers.[22-24] The masses of the repeat unit and terminal groups and molecular weight distributions of polymers have been determined from their TOF-SIMS spectra. TOF-SIMS provides good sensitivity and structural specificity for high mass ions so that intact oligomers and large polymer fragments are observed.

The purpose of the present investigation was detailed analysis of the oligomers and fragment ions of polyesters and the transesterification products of polyesters with trifluoroacetic acid or chlorodifluoroacetic acid. Transesterification is potentially useful for characterization of high molecular weight and intractable polyesters. Transesterification of polyesters in trifluoroacetic acid (TFA) produced diesters of TFA and polyesters. Chlorodifluoroacetic acid was also used as a transesterification reagent to take advantage of the unique isotope clusters from multiple chlorine atoms. The progress of such reactions was monitored, and reaction products were identified using TOF-SIMS.

Experimental Section

A. Instrumentation. A time-of-flight secondary ion mass spectrometer (TOF-SIMS) was used to obtain mass spectra of the polyesters.[25,26] It has high transmission and detects ions in the mass range *m/z* 1-10 000 simultaneously. A continuous beam of primary argon ions is produced in a conventional electron impact source. The ions are accelerated to 10 keV and are focused by slit electrodes. The ion beam passes a 90° deflector which chops the beam into ion packets having widths of ca. 20 ns and deflects a short bunch of ions into a magnetic sector field. These pulses are time focused onto the target by a second pulsed capacitor, giving a final ion pulse with an optimal pulse length of 800 ps. This system produces packets of 100-2000 primary ions focused on the target with a spot diameter of about 5-50 μm. The argon ion beam has an energy of ca. 10-11.5 kV.

Secondary ions are extracted from the sample and accelerated by an ion lens operating at 3 kV into a time-of-flight (TOF) mass analyzer. The TOF uses a reflectron to reduce line widths and has a total flight path of 2 m. A single-stage ion mirror provides first-order energy focusing. The initial energy spread of the secondary ions is narrowed to the order of 1% or less, thus improving the mass resolution. The secondary ion beam is focused by an Einzel lens onto the detector. To enhance detection efficiency, especially for high masses, a postacceleration voltage of up to 10 kV is applied to the entrance of the detector unit.

The detector is combined with a channel plate which converts an ion into many electrons, a scintillator which functions by converting the electrons into photons, and a photomultiplier. The advantage of this detection system is high gain and sensitivity, especially in the high mass range. The detector is used in the single-ion counting mode which can efficiently enhance the signal-to-background ratio.

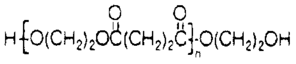
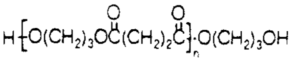
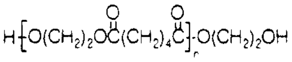
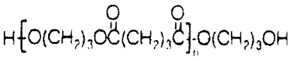
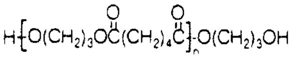
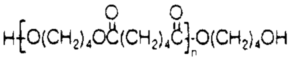
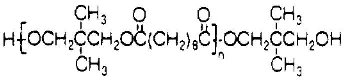
The recording system consists of a multistop time-to-digital converter (TDC), a fast buffer memory, and an accumulating memory board. The TDC memory size is 256K, with each

---

® Abstract published in *Advance ACS Abstracts,* November 15, 1994.

0024-9297/94/2227-7855$04.50/0

Table 1. Structures, Repeat Units, and Molecular Weights of Polyesters Studied

sample name	structure	repeat unit (*m/z*)	GPC M_w	GPC M_n	GPC M_w/M_n	NMR M_n
poly(ethylene succinate)	 $\mathrm{H\!\left[O(CH_2)_2O\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{O}{\overset{\|}{C}}\right]_n\!\text{-}O(CH_2)_2OH}$	144	2427	1510	1.61	1535
poly(trimethylene succinate)	 $\mathrm{H\!\left[O(CH_2)_3O\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{O}{\overset{\|}{C}}\right]_n\!\text{-}O(CH_2)_3OH}$	158	5224	2201	2.37	1803
poly(ethylene adipate)	 $\mathrm{H\!\left[O(CH_2)_2O\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\right]_n\!\text{-}O(CH_2)_2OH}$	172	7935	1830	4.33	1483
poly(trimethylene glutarate)	 $\mathrm{H\!\left[O(CH_2)_3O\overset{O}{\overset{\|}{C}}(CH_2)_3\overset{O}{\overset{\|}{C}}\right]_n\!\text{-}O(CH_2)_3OH}$	172	3618	1954	1.85	1484
poly(trimethylene adipate)	 $\mathrm{H\!\left[O(CH_2)_3O\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\right]_n\!\text{-}O(CH_2)_3OH}$	186	3378	961	3.51	1049
poly(butylene adipate)	 $\mathrm{H\!\left[O(CH_2)_4O\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\right]_n\!\text{-}O(CH_2)_4OH}$	200	9813	2540	3.86	2170
poly(neopentyl glycol sebacate)	 $\mathrm{H\!\left[OCH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}\right]_n\!\text{-}OCH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2OH}$	270	7107	2258	3.51	2182

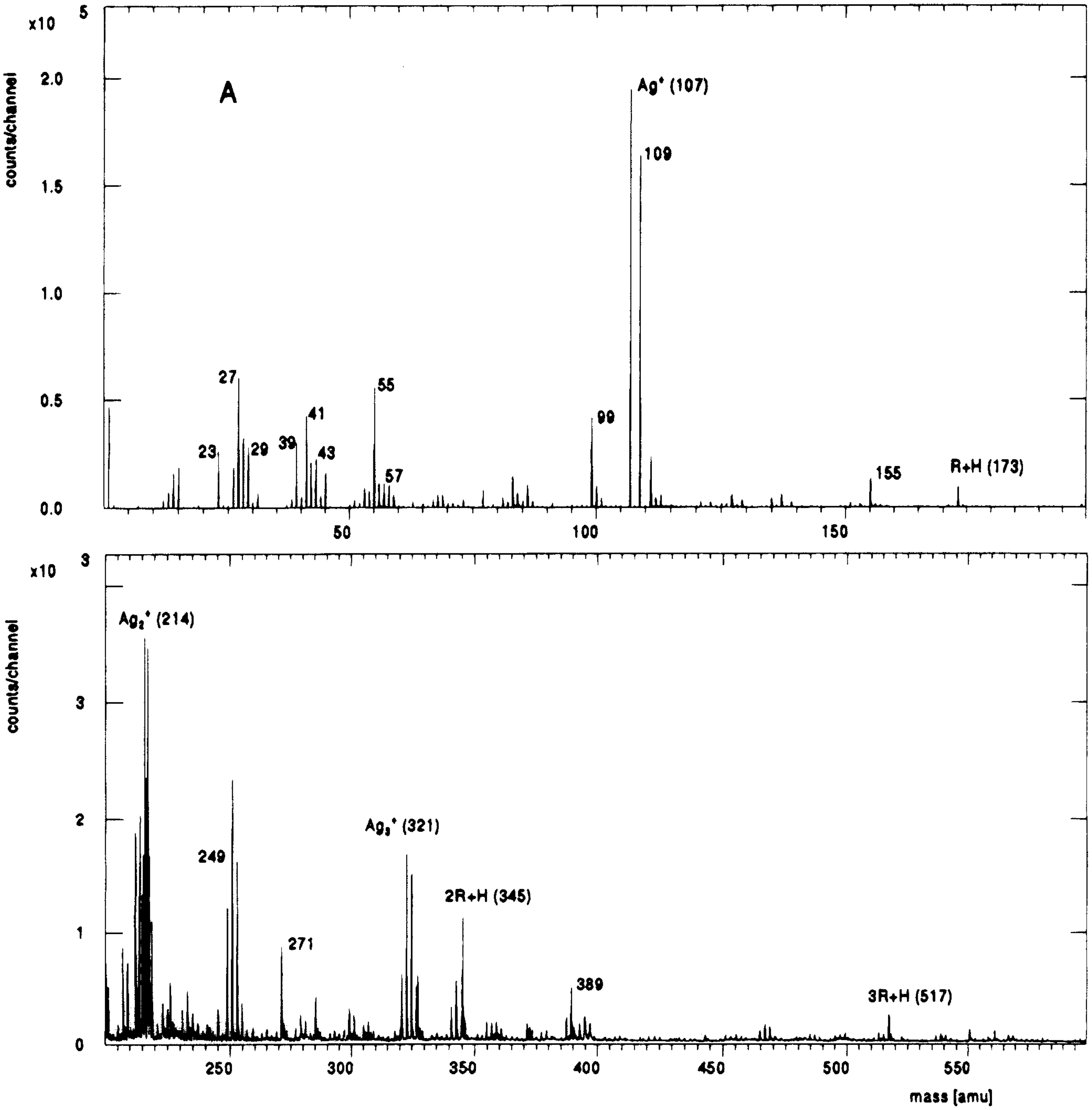


Figure 1. Positive-ion TOF-SIMS spectrum of poly(ethylene adipate) in the mass ranges (A) *m/z* 0–600, (B) *m/z* 600–2000, and (C) *m/z* 780–1080.

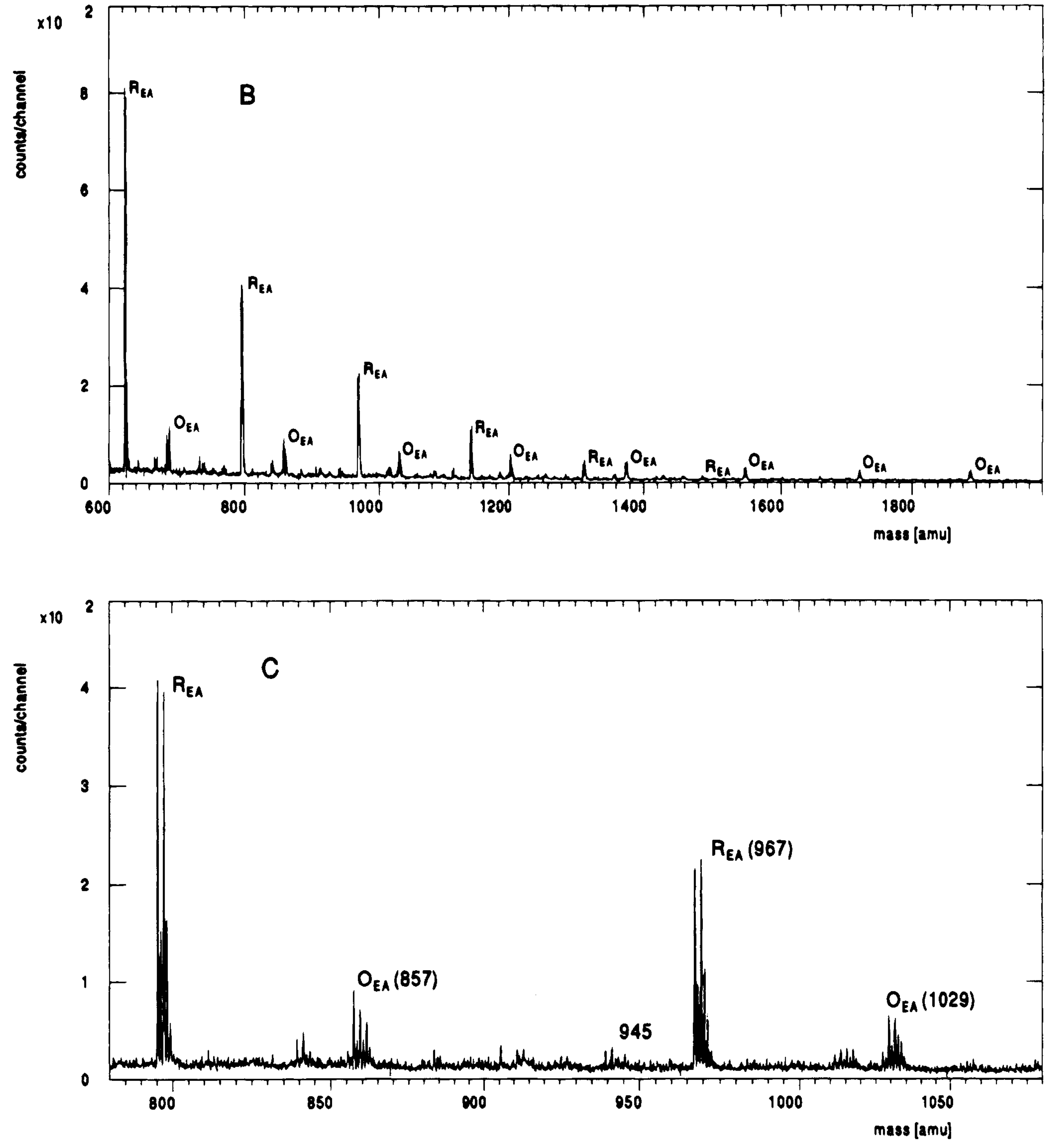


Figure 1. cont'd.

channel having a width of 1.25 ns. The TDC can measure flight times of up to 256 ions per cycle and record these events in its memory. The maximum total count rate is 2.5×10^6 counts/s.

The instrument is also equipped with a pulsed electron gun for charge compensation, which is pulsed after each primary ion pulse during the analysis of insulating samples. The electron flood gun provides low-energy electrons (10 eV) to the surface for a relatively long period of time.

B. Sample Preparation. The following polymer samples were obtained from Aldrich Chemical Co. (Milwaukee, WI): poly(ethylene succinate), poly(ethylene adipate), poly(neopentyl glycol sebacate). The source of poly(trimethylene adipate) and poly(butylene adipate) was Polysciences, Inc. (Warrington, PA). Poly(trimethylene succinate) and poly(trimethylene glutarate) were obtained from Scientific Polymer Products, Inc. (Ontario, NY). Branched poly(1,3-butylene adipate) was obtained from Miles Chemical Inc. (Pittsburgh, PA). The structures, repeat units, and molecular weights of the polyesters studied are shown in Table 1. TOF-SIMS spectra of polyesters were obtained from thin polymer films cast from solutions of polyesters in *N*,*N*-dimethylformamide (DMF) on a silver substrate. Transesterification of polyesters was carried out by dissolution in trifluoroacetic acid (TFA) or chlorodifluoroacetic acid (CFA) and allowing the reaction to occur for a specific time. The concentrations of polymers in DMF, TFA and CFA solutions were in the range of 1–2 mg/ml. After transesterification 1–5 μL of solution were deposited onto ca. 20 or 80 mm^2 of silver target that had been etched in 20% nitric acid and rinsed thoroughly with distilled water and methanol. Approximately 1–2 μg of each polyester was deposited on the silver substrate for analysis.

Gel permeation chromatography (GPC) measurements were carried out in THF at 35 °C at a flow rate of 0.35 mL/min, maintained by a Perkin-Elmer Series 100 pump. The GPC instrument was equipped with two Phenomenex narrow bore

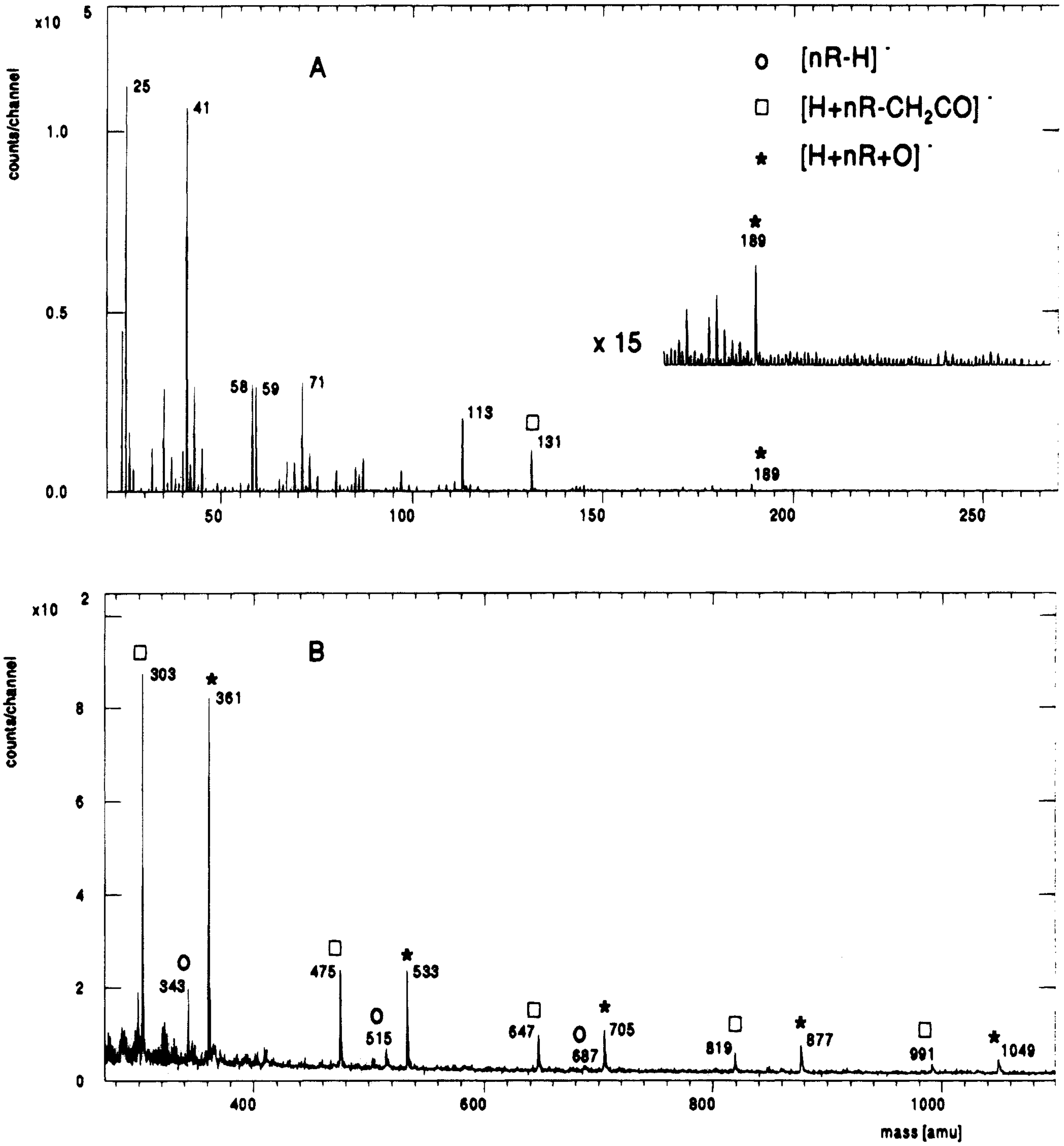


Figure 2. Negative-ion TOF-SIMS spectrum of poly(trimethylene glutarate) in the mass ranges (A) *m/z* 20–270 and (B) 270–1100.

GPC columns, a Waters 410 differential refractometer detector, and a Waters 745 data module. Calibration was performed using Polystyrene standards from Waters; the typical sample concentration was 5 mg/mL.

Nuclear magnetic resonance (NMR) spectra were taken on a Bruker Aspect-3000, AM-500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) to get the number-average molecular weights.

Results and Discussion

Polyester TOF-SIMS Spectra. TOF-SIMS spectra of the polyesters studied were obtained in the mass range *m/z* 1–3500. The peaks in the spectra can be resolved into three well-defined series: oligomer, repeat unit, and fragmentation series. Desorption of intact polyesters generates the oligomer series. The repeat unit series consists of an integral number of ester repeat units. Formation of large fragment ions from polyesters involves chain-breaking events to produce fragment molecules.

TOF-SIMS positive ion spectra of poly(ethylene succinate), poly(trimethylene succinate), poly(trimethylene glutarate), poly(ethylene adipate), poly(trimethylene adipate), poly(butylene adipate), and poly(neopentyl glycol sebacate) were studied. Interpretation of the spectra will focus on information for structural characterization. Most of the discussion will consider poly(ethylene adipate) as the example polymer; results for others are similar. Details can be obtained from the supplementary material. A segment from a typical spectrum of poly(ethylene adipate) in the mass range *m/z* 0–600 is shown in Figure 1A. The dominant peaks are $C_2H_3^+$ (*m/z* 27), $C_2H_5^+$ (*m/z* 29), $C_3H_5^+$ (*m/z* 41),

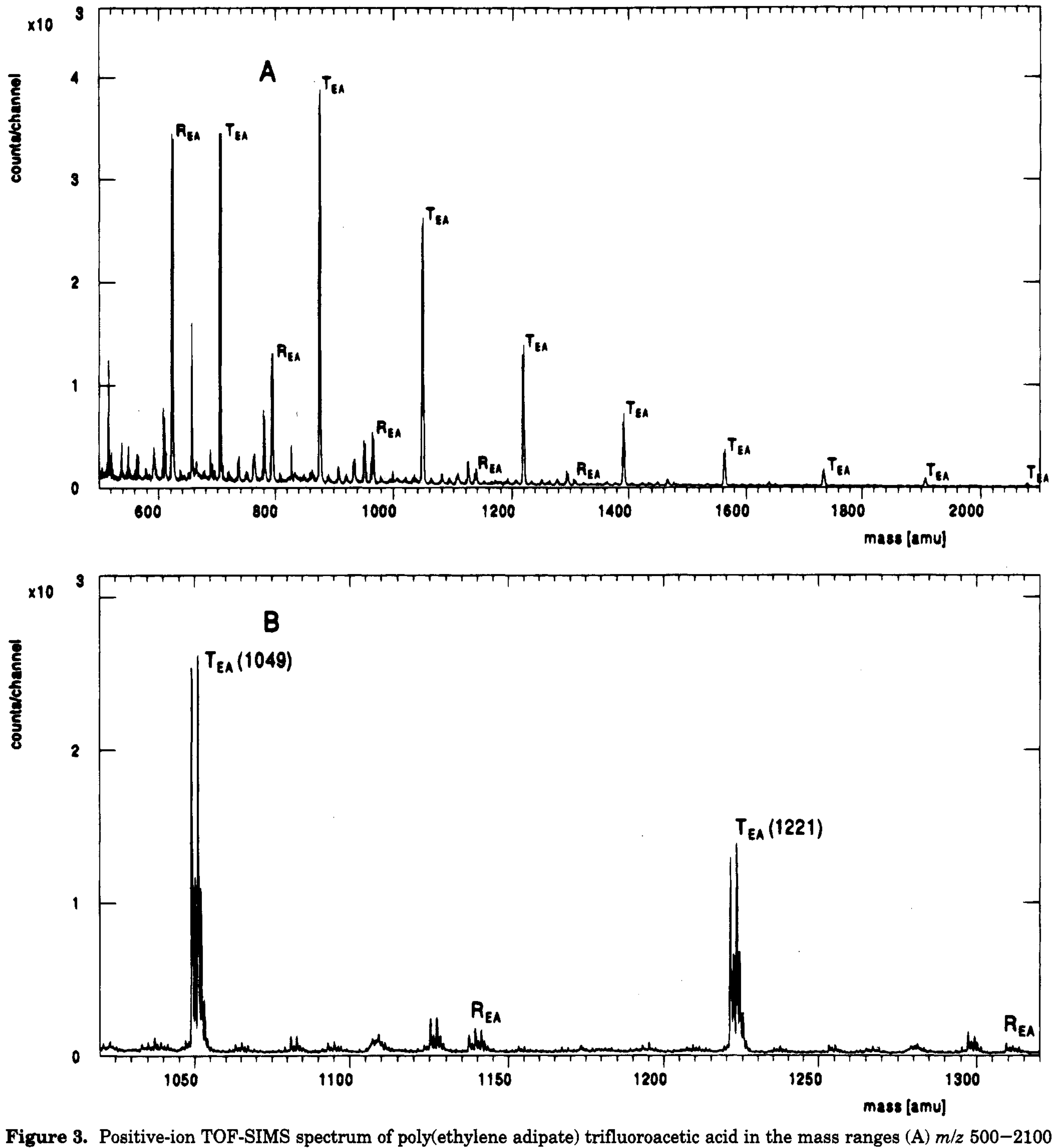


Figure 3. Positive-ion TOF-SIMS spectrum of poly(ethylene adipate) trifluoroacetic acid in the mass ranges (A) *m/z* 500–2100 and (B) *m/z* 1020–1320.

$C_3H_7^+$ (exact mass *m/z* 43.05), $C_2H_3O^+$ (exact mass *m/z* 43.02), $C_4H_7^+$ (exact mass *m/z* 55.05), $C_3H_3O^+$ (exact mass *m/z* 55.02), $C_4H_9^+$ (exact mass *m/z* 57.07), and $C_3H_5O^+$ (exact mass *m/z* 57.03). Na^+ (*m/z* 23) and K^+ (*m/z* 39) ions are also found in the spectra as well as Ag^+ (*m/z* 107 and 109) from the substrate. The other peaks in the lower mass range are due to carbon-, oxygen-, and hydrogen-containing ions which are found in the positive spectra of nearly all polymers. Silver clusters (Ag_2^+, Ag_3^+, etc.) and uncationized repeat unit ions are also found in this low region. For example, the spectrum of poly(ethylene adipate) shows Ag_2^+ (*m/z* 214), Ag_3^+ (*m/z* 321), and a peak of moderate intensity at *m/z* 173 which can be attributed to the monomer, R + H (R = repeat unit). There are also peaks corresponding to the dimer 2R + H, trimer 3R + H, tetramer 4R + H etc., at *m/z* 345, 517, and 689, respectively, with decreasing intensities. Fragment ions from the repeat units are found at *m/z* 99, 155, 271, and 389. These ions are characteristic for the structure of the repeat units of poly(ethylene adipate). The same types of ions are found in the low mass range of the other polyester spectra.

Figure 1B shows the TOF-SIMS spectrum of poly(ethylene adipate) in the mass range *m/z* 600–2000. Peaks of the oligomer and repeat unit series of poly(ethylene adipate) are labeled O_{EA} and R_{EA}, respectively; both oligomers and repeat units show peaks which are cationized with Ag^+ and Na^+. Desorption of intact polymer chains yields a series of peaks corresponding to $[H+nR+OCH_2CH_2OH + M]^+$, where R = repeat unit and M = Ag and Na. The oligomer series consists of an integral number of repeat units, two terminal groups, and the metal cation. The repeat unit series comes from

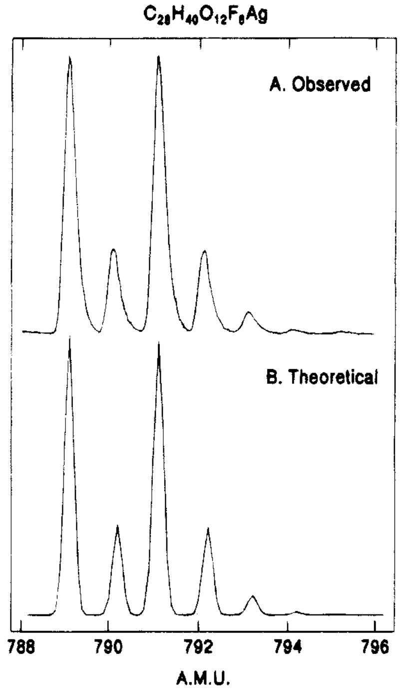
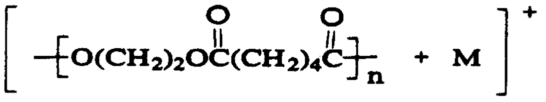


Figure 4. Comparison between the theoretical isotope pattern for $C_{28}H_{40}O_{12}F_6Ag$ and the positive-ion TOF-SIMS spectrum of poly(butylene adipate) for $n = 2$ and M = Ag at m/z 789.

an integral number of repeat units plus the metal cation, corresponding to $[nR + M]^+$ where R = repeat unit and M = Ag and Na. It results from fragments produced by cleavage of the COO bond along the polymer backbone. The structure of repeat unit series is shown below.



$$\left[-\!\left[O(CH_2)_2O\overset{\displaystyle O}{\overset{\|}{C}}(CH_2)_4\overset{\displaystyle O}{\overset{\|}{C}} \right]_n\!- \quad + \quad M \right]^+$$

A smaller segment of the spectrum is shown in Figure 1C. The spectrum is dominated by the repeat unit series, which extends to m/z 2000. Peaks in the oligomer series are of lower intensity than the repeat unit series, but the oligomer series extends to m/z 3000. The abundance of the oligomer series in the higher mass range indicates that desorption of intact oligomers of poly(ethylene adipate) occurs more readily than fragmentation to produce large fragments.

There are pairs of peaks in Figure 1C having a mass difference of $\Delta m/z$ 84 in a spacing of one repeat unit, which are oligomers or fragments cationized with both Ag^+ and Na^+. For example, in the oligomer series of poly(ethylene adipate) for $n = 5$, the mass difference between peaks for M = Na at m/z 945 and M = Ag at m/z 1029 is equal to $\Delta m/z$ 84, the mass difference between Na and Ag. The spacing between consecutive peaks involving the same cation in the oligomer or repeat unit series is the same mass as the repeat unit of polyesters. For example, in the oligomer series of poly(ethylene adipate) for M = Ag, the mass difference between peaks for $n = 4$ at m/z 857 and $n = 5$ at m/z 1029 is equal to $\Delta m/z$ 172, the mass of the repeat unit of poly(ethylene adipate). The mass difference between oligomer series peaks and repeat unit series peaks, which have the same number of repeat units and the same metal cation, is the combined masses of the terminal groups of the polyesters. For example, the mass difference between the O_{EA} peak at m/z 1029 and 1031 ($n = 5$, M = Ag) and the R_{EA} peak at m/z 967 and 969 ($n = 5$, M = Ag) is equal to $\Delta m/z$ 62, the combined masses of H and $O(CH_2)_2OH$. A listing of the peaks and their relative intensities of the oligomer and repeat unit series for the polyesters studied is available as supplementary material.

The negative-ion spectrum of poly(trimethylene glutarate) is the mass range m/z 20–1100 is shown in Figure 2. The peaks observed in the spectrum are due to $[nR - H]^-$, $[H + nR - CH_2CO]^-$, and $[H + nR + O]^-$, where R = repeat unit. $[H + nR - CH_2CO]^-$ is found at m/z 131, 303, 475, 647, 819, 991, 1163, etc. A series of peaks corresponding to $[H + nR + O]^-$ are m/z 189, 361, 533, 705, 877, 1049, etc. Peaks at m/z 343, 515, 687, etc., come from $[nR - H]^-$. Negative-ion spectra of polyesters give the information about the repeat unit and fragment series. However, oligomer series of polyesters are not seen in the negative-ion spectra.

Transesterification of Polyesters in Trifluoroacetic Acid. TOF-SIMS spectra of polymers are obtained from polymer solutions deposited on a silver substrate. If polymers are insoluble or of high molecular weight, it is difficult to characterize them using TOF-SIMS. For intractable high molecular weight polymers, selective cleavage reactions or chemical derivatization could be used if they occur at specific bonds, do not change the structure of the polymer, and produce chain segments that are large enough to contain information about more than one repeat unit. These reactions can be used to cleave specific bonds of intractable polymers or modify polymers by incorporating desirable chemical functions in the backbone. Studies on polyurethanes have demonstrated that transesterification can be used to selectively break bonds in copolymers.[27] The feasibility and progress of such reactions can be monitored by TOF-SIMS.

Transesterification of polyesters in trifluoroacetic acid (TFA) occurs at ester bonds and produces diesters of TFA and diols. The equation of the transesterification reaction for poly(ethylene adipate) with TFA is shown below. Products were identified from TOF-SIMS spectra of polyester thin films cast from TFA solutions.

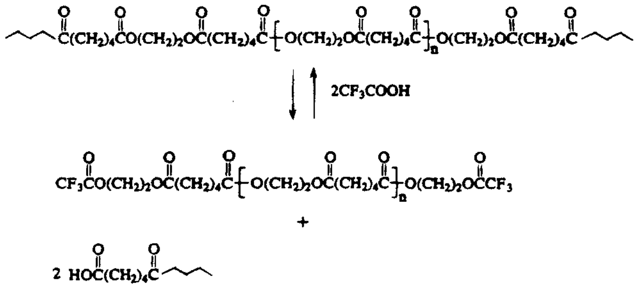
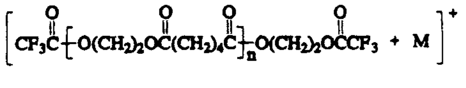


Figure 3A shows a spectrum of the transesterification products of poly(ethylene adipate) and TFA in the mass range m/z 500–2100 after 8 h of reaction. Figure 3B shows the structure of clusters in detail. Diester ions of poly(ethylene adipate) are labeled T_{EA}, while repeat unit peaks of poly(ethylene adipate) are labeled R_{EA}. Peaks of the oligomer for poly(ethylene adipate) are not observed in the spectrum after the reaction.

The T_{EA} ions arise from diesters of the diol and TFA. They consist of an integral number of polyester repeat units plus an additional ethanediol and two trifluoroacetates at the diol ends. The structure of T_{EA} which is cationized with Ag^+ or Na^+ is given below. The



$$\left[CF_3\overset{\displaystyle O}{\overset{\|}{C}}\!\left[O(CH_2)_2O\overset{\displaystyle O}{\overset{\|}{C}}(CH_2)_4\overset{\displaystyle O}{\overset{\|}{C}} \right]_n\!O(CH_2)_2O\overset{\displaystyle O}{\overset{\|}{C}}CF_3 \quad + \quad M \right]^+$$

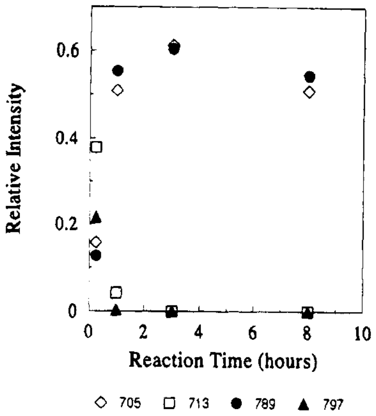


Figure 5. Relative intensities for [H + 2R + $O(CH_2)_4OH$ + Na]$^+$ (*m/z* 713) (☐), [H + 2R + $O(CH_2)_4OH$ + Ag]$^+$ (*m/z* 797) (△), [CF_3CO + 2R + $COCF_3$ + Na]$^+$ (*m/z* 705) (◇), and [CF_3CO + 2R + $COCF_3$ + Ag]$^+$ (*m/z* 789 (●) of poly(butylene adipate) for different reaction times with CF_3COOH.

spacing between consecutive T_{EA} peaks involving the same cation corresponds to the mass of the repeat unit of poly(ethylene adipate). For example, in the T_{EA} series of poly(ethylene adipate) for M = Ag, the mass difference between peaks for $n = 4$ at *m/z* 1049 and $n = 5$ at *m/z* 1221 is equal to Δ*m/z* 172, the mass of the repeat unit of poly(ethylene adipate).

The peaks in the transesterification spectra of other polyesters studied are listed in the supplementary material. Diester peaks of polyesters indicate that all polyesters studied reacted with TFA and produced fragments containing two tagged groups. Figure 4 shows the isotopic pattern for the di-TFA ester of poly(butylene adipate) for $n = 2$ and M = Ag at *m/z* = 789. The lower peaks represent the theoretical isotope pattern for $C_{28}H_{40}O_{12}F_6Ag$, and the upper peaks are for the ion observed in the TOF-SIMS spectrum. As can be seen, the peak pattern and intensities of the spectrum measured for poly(butylene adipate) after transesterification are quite consistent with the theoretical isotope cluster.

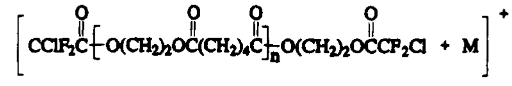
A negative-ion spectrum for the transesterification of poly(trimethylene glutarate) in TFA shows the dominant peaks which are F^- (*m/z* 19), C_2HO^- (*m/z* 41), CF_3^- (*m/z* 69), and CF_3COO^- (*m/z* 113). There are also [H + *n*R − CH_2CO]$^-$ (*m/z* 475, 647, 819, 991, etc.), [*n*R − H]$^-$ (*m/z* 515, 687, 859, 1031, etc.), [H + *n*R + O]$^-$ (*m/z* 533, 705, 877, etc.), [CF_3CO + *n*R + $O(CH_2)_3COCF_3$]$^-$ (*m/z* 612, 784, 956, 1128, etc.), and [CF_3CO + *n*R − CH_2CH_2CO]$^-$ (*m/z* 557, 729, 901, 1073, etc.).

Transesterification of polyesters was carried out in TFA for different reaction times. In order to get information about the progress of the transesterification reaction, TOF-SIMS spectra of poly(butylene adipate) were taken after 15 min, 1h, 3h, and 8h, respectively. Relative peak intensities for different times are shown in Figure 5. The oligomer series peaks, [H + 2R + $O(CH_2)_4OH$ + Na]$^+$ (*mz* 713) and [H + 2R + $O(CH_2)_4OH$ + Ag]$^+$ (*m/z* 797), still exist in the spectrum taken immediately after poly(butylene adipate) was dissolved in TFA. However, they have disappeared in the spectrum for 3 h of reaction; the relative intensities of diester ions, [CF_3CO + 2R + $COCF_3$ + Na]$^+$ (*m/z* 705) and [CF_3CO + 2R + $COCF_3$ + Ag]$^+$ (*m/z* 789), have increased after 1 h of reaction. The increasing abundance of two tagged ions indicates that the reaction has progressed with time.

Transesterification of Polyesters in Chlorodifluoroacetic Acid. Chlorodifluoroacetic acid was also investigated as a transesterification reagent for polyesters to take advantage of its unique isotope pattern. The $CClF_2CO$ (*m/z* 113) group in chlorodifluoroacetic acid provides a good mass marker, and cleaved fragments can readily be identified because of the chlorine isotope patterns.

When the peaks are weak, or the high mass fragments are not well-resolved, it is helpful to compare the spectrum of TFA transesterification and that of CFA transesterification for the same polyester. The mass difference between peaks including one CF_3CO group (*m/z* 97) and peaks including one $CClF_2CO$ group (*m/z* 113) is 16, and the mass difference of two labeled fragments is 32. Therefore, the peaks can be easily identified as the mass difference between them is 0 for not tagged, 16 for one-tagged, and 32 for two-tagged fragments.

Transesterification of polyesters in chlorodifluoroacetic acid selectively cleaves the ester bond and produces diesters of chlorodifluoroacetic acid and diols. Figure 6 shows spectra of poly(ethylene adipate), after transesterification with chlorodifluoroacetic acid, in the mass ranges *m/z* 600−2000 (A) and *m/z* 880−1180 (B). Chlorodifluoroacetates of poly(ethylene adipate) are labeled C_{EA}, and repeat unit peaks of poly(ethylene adipate) are labeled R_{EA}. Oligomer peaks for poly(ethylene adipate) are not seen in the spectrum after reaction, indicating that all oligomers have reacted. The C_{EA} ions arise from diesters of the diol and CFA, corresponding to an integral number of polyester repeat units plus an additional ethanediol and two chlorodifluoroacetates at the diol ends. The structure of cationized C_{EA} is given below. The mass difference between consecutive C_{EA} peaks with the same cation represents the mass of the repeat unit of poly(ethylene adipate). For example, in the C_{EA} series of poly(ethylene adipate) for M = Ag, the mass difference between peaks for $n = 3$ at *m/z* 909 and $n = 4$ at *m/z* 1081 is equal to Δ*m/z* 172, the mass of the repeat unit of poly(ethylene adipate).



$$\left[\mathrm{CClF_2\overset{O}{\overset{\|}{C}}\left[O(CH_2)_2O\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\right]_n O(CH_2)_2O\overset{O}{\overset{\|}{C}}CF_2Cl + M}\right]^+$$

The peaks in the $CClF_2COOH$ transesterification spectra of the polyesters studied are listed in the supplementary material. Diester peaks of polyesters indicate that all polyesters studied reacted with CFA and produced two-tagged fragments involving two chlorines. Figure 7 shows how the theoretical isotope pattern compares with that observed for a real spectrum. The isotopic pattern for the di-TFA ester of poly(butylene adipate) for $n = 2$ at *m/z* 821 in the TOF-SIMS spectrum is shown in the top of the figure, and the theoretical isotope pattern for $C_{28}H_{40}O_{12}F_4Cl_2Ag$ is at the bottom of the figure. Clearly there is good agreement.

The progress of transesterification of poly(ethylene adipate) in CFA was monitored at 15 min, 1 h, 3 h, and 11 h. Figure 8 gives relative intensities of important peaks for four different reaction times. The oligomer series peaks, [H + 4R + $O(CH_2)_2OH$ + Na]$^+$ (*m/z* 773) and [H + 4R + $O(CH_2)_2OH$ + Ag]$^+$ (*m/z* 857), are still found in the spectra taken immediately and after 3 h. The spectrum for the 11-h reaction does not have oligomer peaks. The relative intensities of chlorodifluoroacetate ions, [$CClF_2CO$ + 3R + $COCClF_2$ + Na]$^+$ (*m/z* 825) and [$CClF_2CO$ + 2R + $COCClF_2$ + Ag]$^+$ (*m/z* 737), increase after 1 h of reaction. This indicates that TOF-SIMS can potentially monitor the progress of such a reaction.

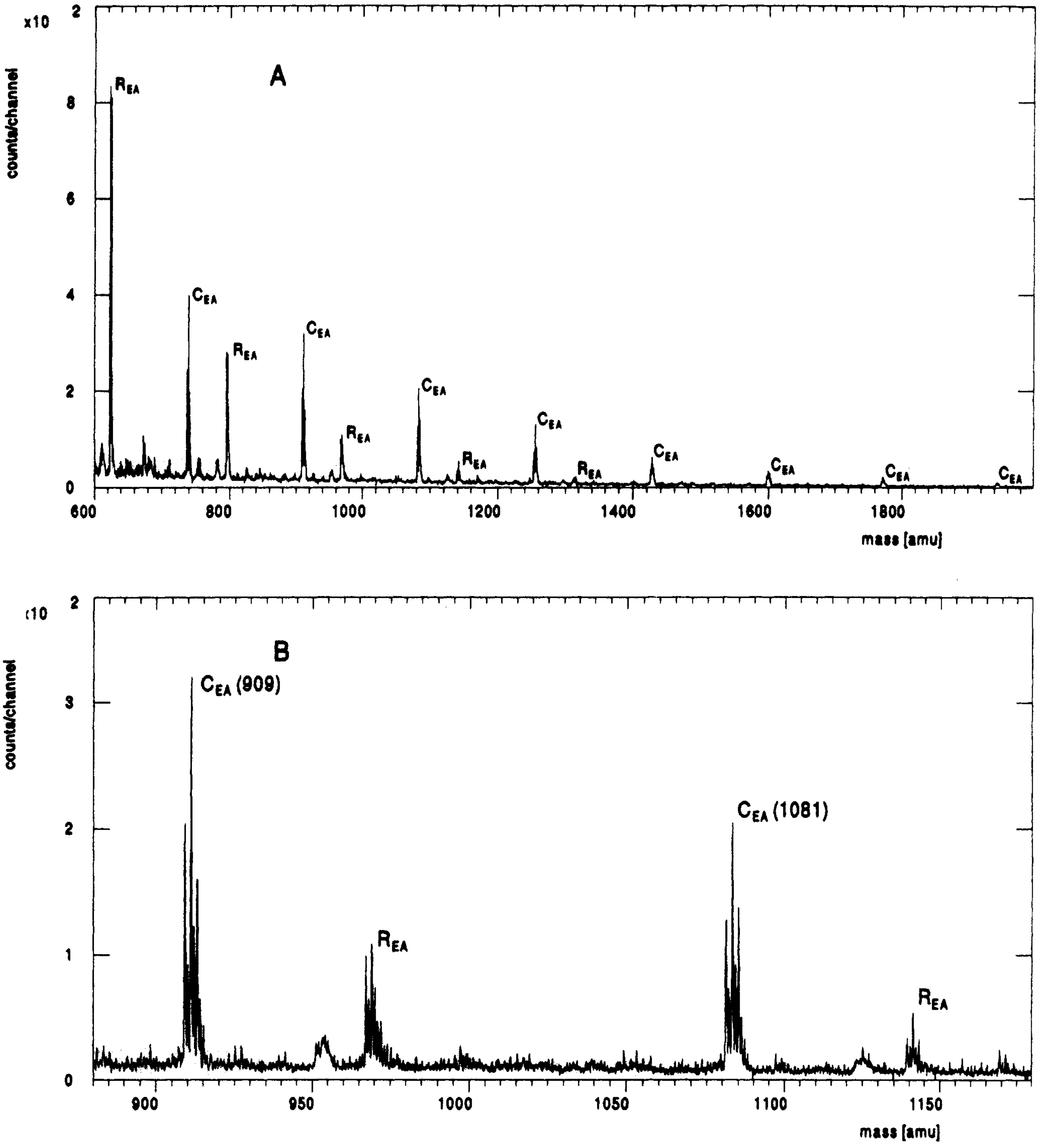


Figure 6. Positive-ion TOF-SIMS spectrum of poly(ethylene adipate) in chlorodifluoroacetic acid in the mass range (A) *m/z* 600−2000 and (B) *m/z* 880−1180.

Branched Polyester TOF-SIMS Spectra and Transesterification. Transesterification can be extended to study branched polyesters. For a branched polymer, branch points will give fragments containing three or more tagged groups per fragment; the linear part will show only two tags. The four- and five-tagged fragments can arise from branched or cross-linked polymers which have two and three branch points, respectively. Figure 9 shows a schematic diagram of how two-, three-, four-, and five-tagged fragments can be generated from branched polymers.

Branched poly(1,3-butylene adipate) was prepared from 1,3-butanediol, adipic acid, and trimethylol propane (TMP). The number-average molecular weight (M_n) for branched poly(1,3-butylene adipate) was 960, and the functionality was 2.8. The spectra of branched poly(1,3-butylene adipate) with and without transesterification by CF_3COOH or $CClF_2COOH$ were obtained for the mass range *m/z* 0−350. All three spectra show major peaks due to $C_2H_3^+$ (*m/z* 27), $C_2H_5^+$ (*m/z* 29), $C_3H_5^+$ (*m/z* 41), $C_3H_7^+$ (exact mass *m/z* 43.05), $C_2H_3O^+$ (exact mass *m/z* 43.02), $C_4H_7^+$ (exact mass *m/z* 55.05), and $C_3H_3O^+$ (exact mass *m/z* 55.02). Peaks from Na^+, K^+, Ag^+, Ag_2^+, and Ag_3^+ are also observed at *m/z* 23, 39, 107, 214, and 321, respectively. In the spectra of branched poly(1,3-butylene adipate) peaks at *m/z* 256 and 273 are from $[(CH_2)_4OCO(CH_2)_4COO(CH_2)_4]^+$ and $[HO(CH_2)_4OCO(CH_2)_4COO(CH_2)_4]^+$, respectively. The spectra of branched poly(1,3-butylene adipate) with CF_3COOH includes peaks from F^+ (*m/z* 19), CF_3^+ (*m/z* 69), $CF_3COO(CH_2)_4^+$ (*m/z* 169), and $CF_3COO(CH_2)_4OCO(CH_2)_4CO^+$ (*m/z* 297). Peaks from F^+ (*m/z* 19), Cl^+ (*m/z*

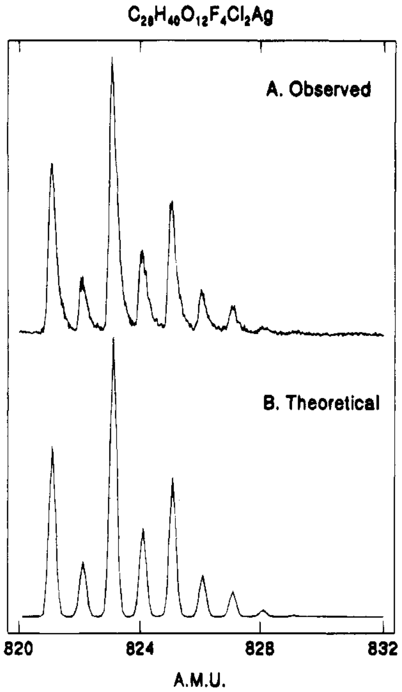


Figure 7. Comparison between the theoretical isotope pattern for $C_{28}H_{40}O_{12}F_4Cl_2Ag$ and the positive-ion TOF-SIMS spectrum of poly(butylene adipate) for $n = 2$ and M = Ag at *m/z* 821.

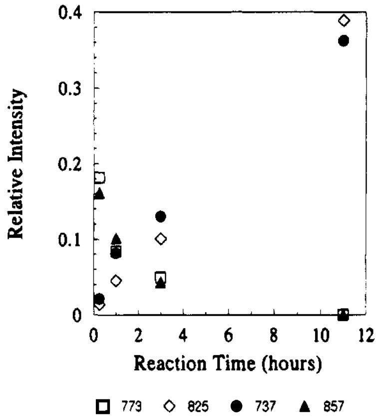
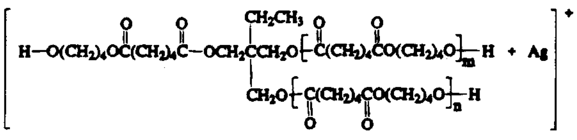


Figure 8. Relative intensities for $[H + 4R + O(CH_2)_2OH + Na]^+$ (*m/z* 773) (□), $[H + 4R + O(CH_2)_2OH + Ag]^+$ (*m/z* 857) (△), $[CClF_2CO + 3R + COCClF_2 + Na]^+$ (*m/z* 825) (◇), and $[CClF_2CO + 2R + COCClF_2 + Ag]^+$ (*m/z* 737) (●) of poly(ethylene adipate) for different reaction times with CF_3COOH.

35), $CClF_2^+$ (*m/z* 85), $CClF_2COO(CH_2)_4^+$ (*m/z* 185), and $CClF_2COO(CH_2)_4OCO(CH_2)_4CO^+$ (*m/z* 313) are observed in $CClF_2COOH$ transesterification spectra.

Parts A–C of Figure 10 show spectra in the mass range *m/z* 350–750 for branched poly(1,3-butylene adipate) and after transesterification with CF_3COOH and $CClF_2COOH$. In Figure 10A, peaks at *m/z* 507 and 707 come from $[2R + Ag]^+$ and $[3R + Ag]^+$, R = repeat unit. Oligomer and water-loss peaks are seen at *m/z* 597 ($[(H + 2R + OCH_2CH_2OH) + Ag]^+$) and 579 ($[(H + 2R + OCH_2CH_2OH) - H_2O + Ag]^+$), respectively. Peaks at *m/z* 441 and 641 correspond to the branched oligomer ionwhere $l + m + n = 1$ and 2, respectively; l, m, and n


$$\left[H{-}O(CH_2)_4OC(=O)(CH_2)_4C(=O){-}OCH_2C(CH_2CH_3)(CH_2O{+}C(=O)(CH_2)_4CO(=O)(CH_2)_4O{+}_nH)CH_2O{+}C(=O)(CH_2)_4CO(=O)(CH_2)_4O{+}_mH + Ag\right]^+$$

are the numbers of repeat units included in the branched oligomer. Loss of water from the ion at *m/z* 641 is observed at *m/z* 623. The dominant peaks in parts B and C of Figure 10 are not cationized with silver. The specific peaks and their structures in the spectra are shown in Table 2. Peaks at *m/z* 509, 709, 541, and 741 come from a fragment of the branched chain. In the low mass range peaks containing one and two chlorines can be readily distinguished as they show unique isotope patterns.

Parts A–C of Figure 11 illustrate the TOF-SIMS spectra of branched poly(1,3-butylene adipate) in the mass range *m/z* 750–1700 before and after transesteri-

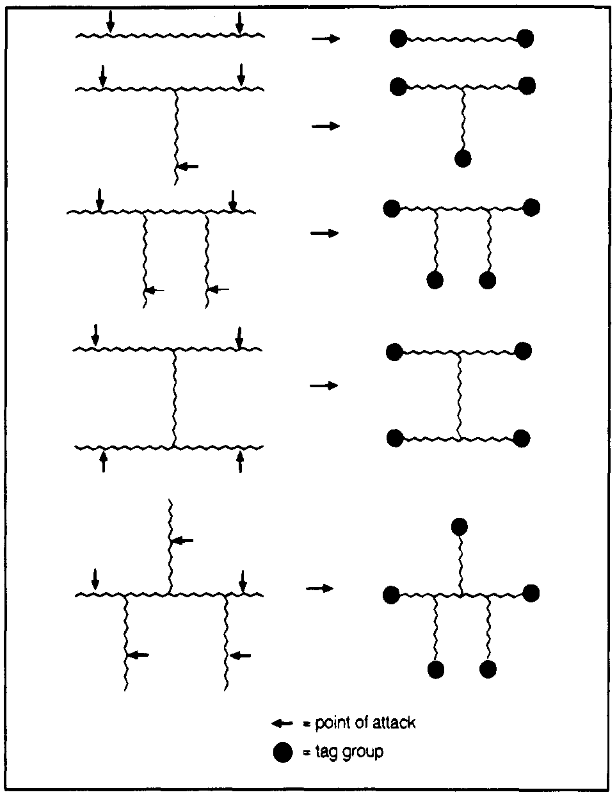
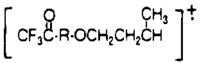
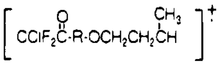
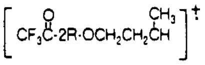
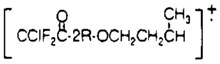
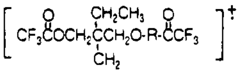
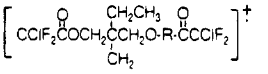
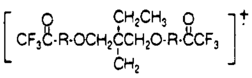
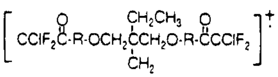
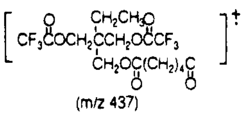
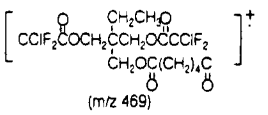


Figure 9. Schematic diagram of the two-, three-, four-, and five-tagged fragments from the branched polymers.

Table 2. Specific Fragment Ions of Branched Poly(1,3-Butylene Adipate) after Transesterification with CF_3COOH and $CClF_2COOH$ in the Mass Range *m/z* 350–750

CF_3COOH	$CClF_2COOH$
 $[CF_3C(=O)\text{-}R\text{-}OCH_2CH_2CH(CH_3)]^{+\cdot}$ (m/z 369)	 $[CClF_2C(=O)\text{-}R\text{-}OCH_2CH_2CH(CH_3)]^{+\cdot}$ (m/z 385)
 $[CF_3C(=O)\text{-}2R\text{-}OCH_2CH_2CH(CH_3)]^{+\cdot}$ (m/z 569)	 $[CClF_2C(=O)\text{-}2R\text{-}OCH_2CH_2CH(CH_3)]^{+\cdot}$ (m/z 585)
 $[CF_3C(=O)OCH_2C(CH_2CH_3)(CH_2)CH_2O\text{-}R\text{-}C(=O)CF_3]^{+\cdot}$ (m/z 509)	 $[CClF_2C(=O)OCH_2C(CH_2CH_3)(CH_2)CH_2O\text{-}R\text{-}C(=O)CClF_2]^{+\cdot}$ (m/z 541)
 $[CF_3C(=O)\text{-}R\text{-}OCH_2C(CH_2CH_3)(CH_2)CH_2O\text{-}R\text{-}C(=O)CF_3]^{+\cdot}$ (m/z 709)	 $[CClF_2C(=O)\text{-}R\text{-}OCH_2C(CH_2CH_3)(CH_2)CH_2O\text{-}R\text{-}C(=O)CClF_2]^{+\cdot}$ (m/z 741)
 $[CF_3C(=O)OCH_2C(CH_2CH_3)(CH_2OC(=O)(CH_2)_4C(=O))CH_2OC(=O)CF_3]^{+\cdot}$ (m/z 437)	 $[CClF_2C(=O)OCH_2C(CH_2CH_3)(CH_2OC(=O)(CH_2)_4C(=O))CH_2OC(=O)CClF_2]^{+\cdot}$ (m/z 469)

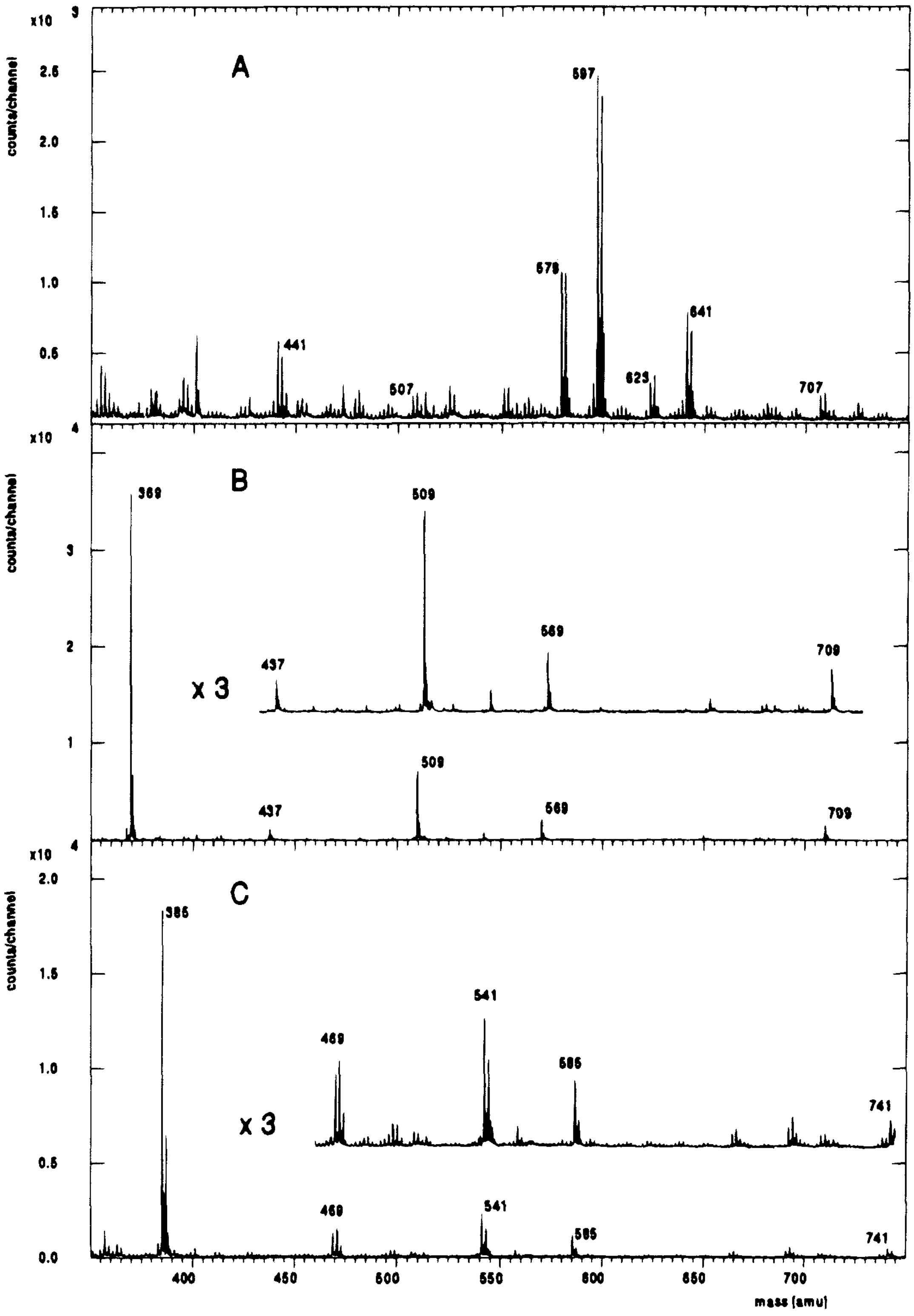


Figure 10. Positive-ion TOF-SIMS spectra of branched poly(1,3-butylene adipate) (A) without transesterification, (B) in trifluoroacetic acid, and (C) in chlorodifluoroacetic acid in the mass range *m/z* 350–750.

fication. Figure 11A shows oligomer and fragment peaks of the branched polymer which are cationized with silver ions. Codes R_{BA}, O_{li}, O_{1b}, and O_{2b} indicate repeat unit series, linear oligomer series, one-branched oligomer series, and two-branched oligomer series, respectively. In parts B and C of Figure 11 Ag cationized transesterification products containing two, three, and four tags are observed. T_{2t}, T_{3t}, and T_{4t} represent two-tagged, three-tagged, and four-tagged fragments with CF_3CO groups. C_{2t}, C_{3t}, and C_{4t} are two-tagged, three-tagged, and four-tagged fragments with $CClF_2CO$ groups. The characteristic peaks and the relative intensities of each spectrum are given in Tables 3–5. Tables 3–5 also show the structures of oligomers and fragments that generate the series of peaks in the TOF-SIMS spectra before and after transesterification. The mass difference between oligomers or fragments in the same series is the repeat unit of branched poly(1,3-butylene adipate).

Figure 12. shows the detail of the clusters for the H + 4R + $O(CH_2)_4OH$ (R = repeat unit) peak (A), CF_3CO + 4R + $COCF_3$ diacetate peak (B), and $CClF_2CO$ + 4R + $COCClF_2$ peak (C) in branched poly(1,3-butylene, adipate). The peak in Figure 12A is the linear oligomer (n = 4) for branched poly(1,3-butylene adipate). The peaks in parts B and C of Figure 12 are the linear

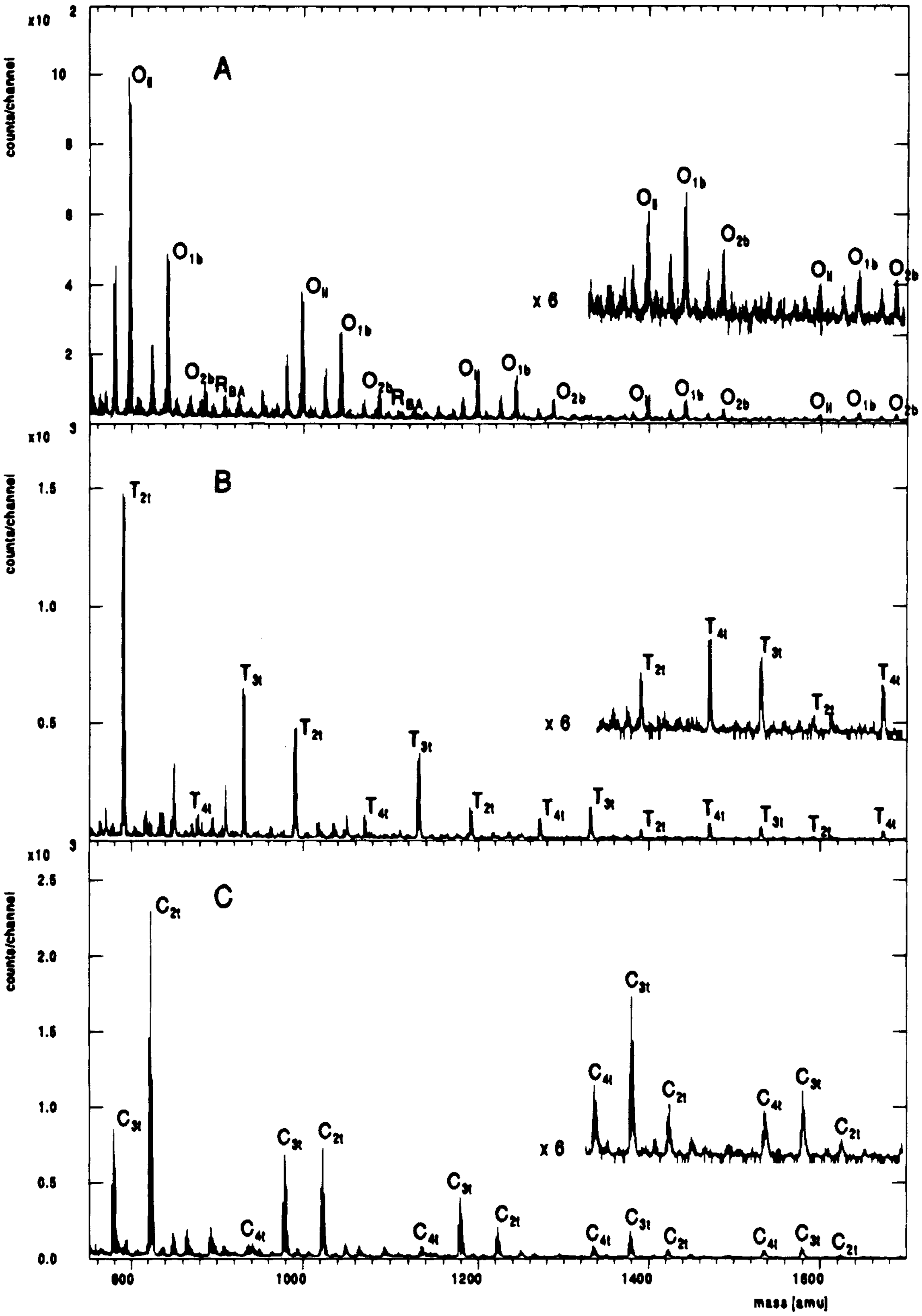


Figure 11. Positive-ion TOF-SIMS spectra of branched poly(1,3-butylene adipate) (A) without transesterification, (B) in trifluoroacetic acid, and (C) in chlorodifluoroacetic acid in the mass range *m/z* 750–1700.

diacetate ions ($n = 4$) formed from linear oligomers by transesterification. The theoretical isotopic distributions for the silver cationized ions of $C_{44}H_{74}O_{18}$, $C_{48}H_{72}O_{20}F_6$, and $C_{48}H_{72}O_{20}F_4Cl_2$ at *m/z* 997, 1189, and 1221 are also shown in the figure. Comparison with observed spectra shows that the comparable cluster patterns are almost identical.

Peaks can be identified by their *m/z* values and isotope patterns as shown in parts D–F of Figure 12. It shows detail of peaks for $l + m + n = 3$ and M = Ag for branched poly(1,3-butylene adipate) before and after transesterification with CF_3COOH and $CClF_2COOH$. Figure 12D shows the pattern for an oligomer having one branching point. Parts E and F of Figure 12 illustrate three-tagged fragments with CF_3CO and $CClF_2CO$ groups, respectively. The structure of each ion is shown above the spectrum. The theoretical isotope cluster of each peak is also given in the figure. As can be seen the isotope patterns of the peaks in TOF-SIMS spectra are almost identical to the theoretical isotope distributions.

A two-branched oligomer peak is shown in Figure 12G. This peak has two branching points and the terminal groups are hydroxyl groups. Figure 12H is the peak which comes from the four-tagged polyester reacted with CF_3COOH. Figure 12I shows a four-tagged

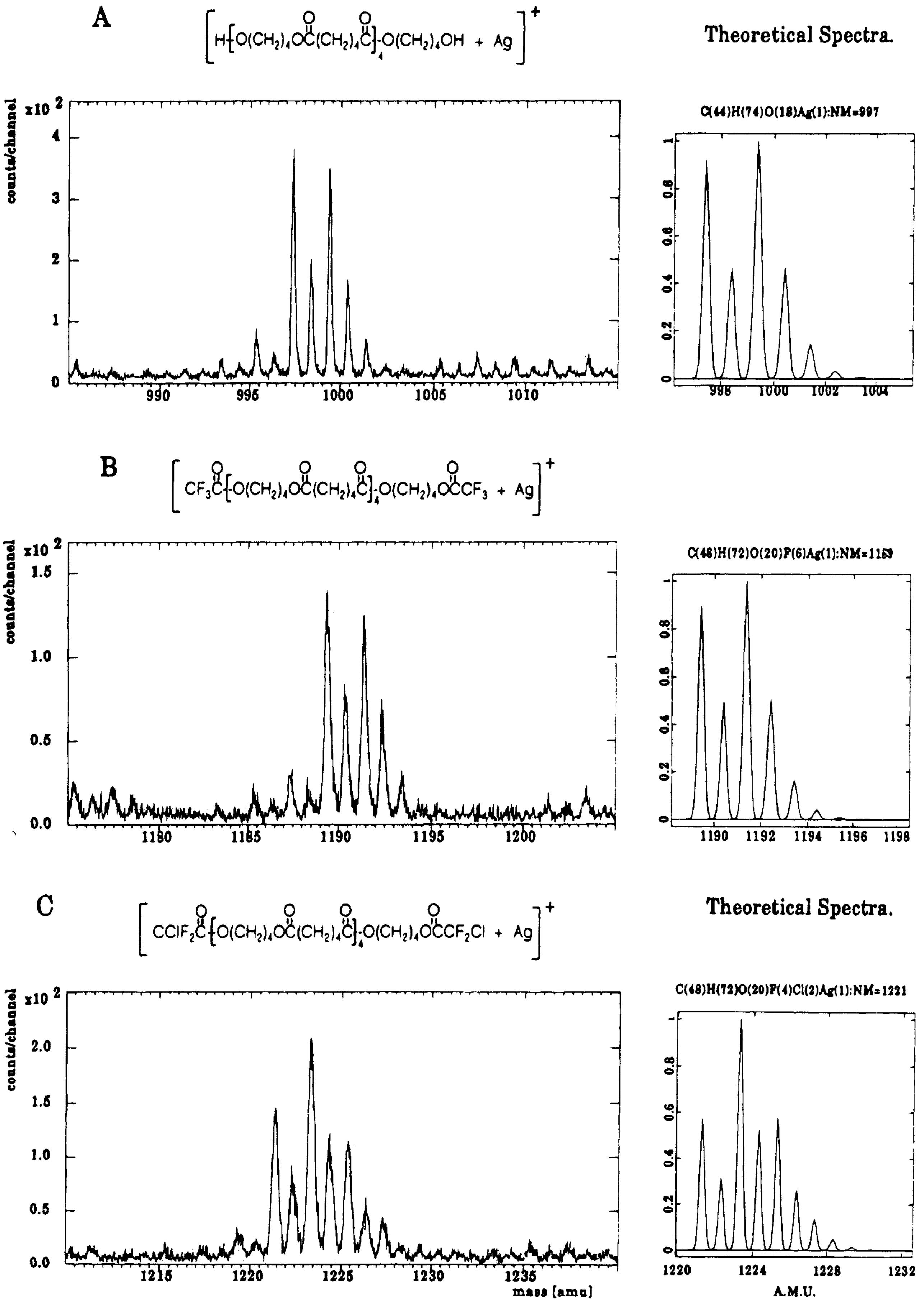


Figure 12. Detail of positive-ion TOF-SIMS spectra of branched poly(1,3-butylene adipate) for (A) linear oligomers without transesterification, (B) linear oligomers in trifluoroacetic acid, (C) linear oligomers in chlorodifluoroacetic acid, (D) one-branched oligomers without transesterification, (E) one-branched oligomers in trifluoroacetic acid, (F) one-branched oligomers in chlorodifluoroacetic acid, (G) two-branched oligomers without transesterification, (H) two-branched oligomers in trifluoroacetic acid, and (I) two-branched oligomers in chlorodifluoroacetic acid.

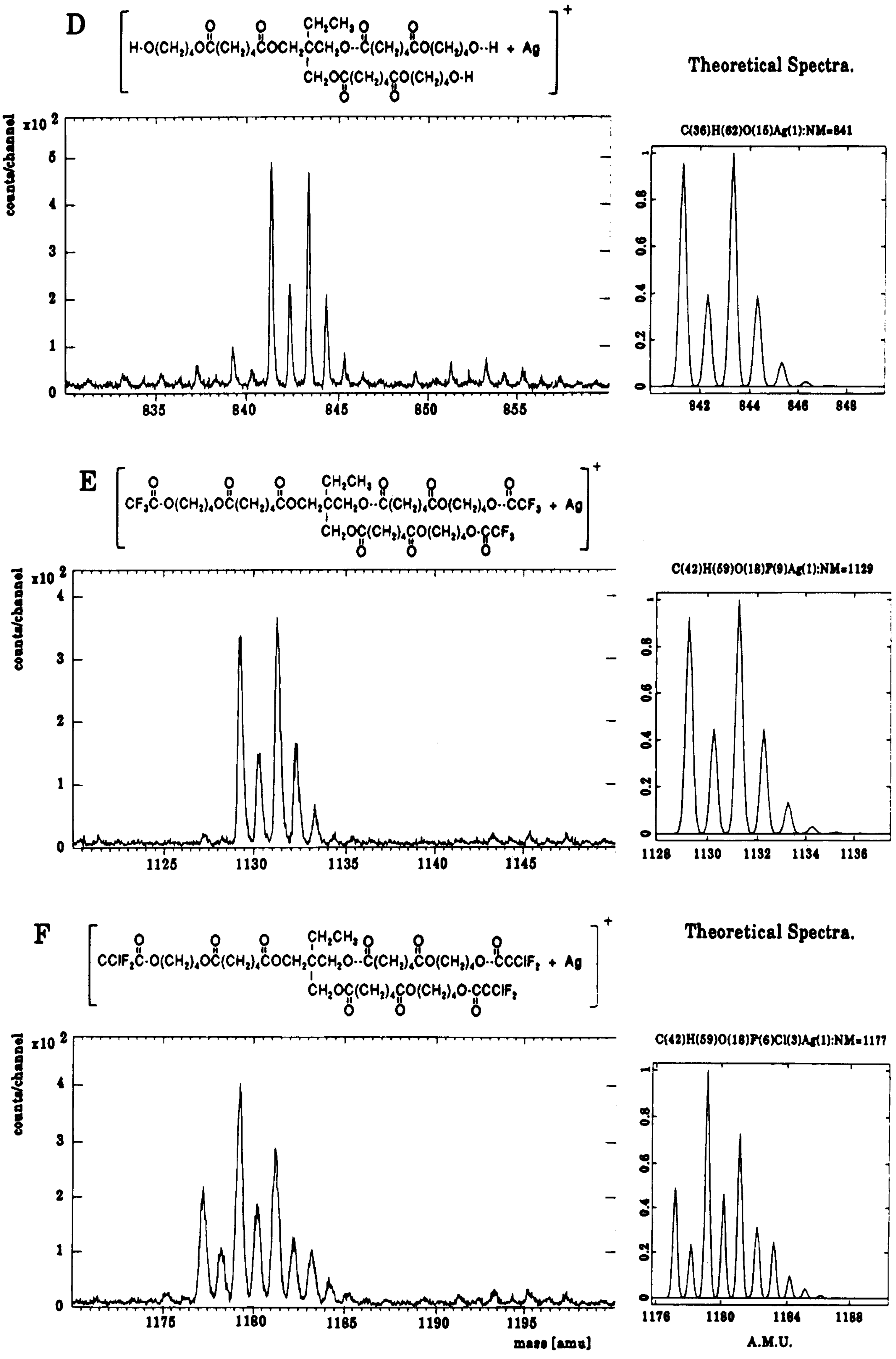


Figure 12. cont'd.

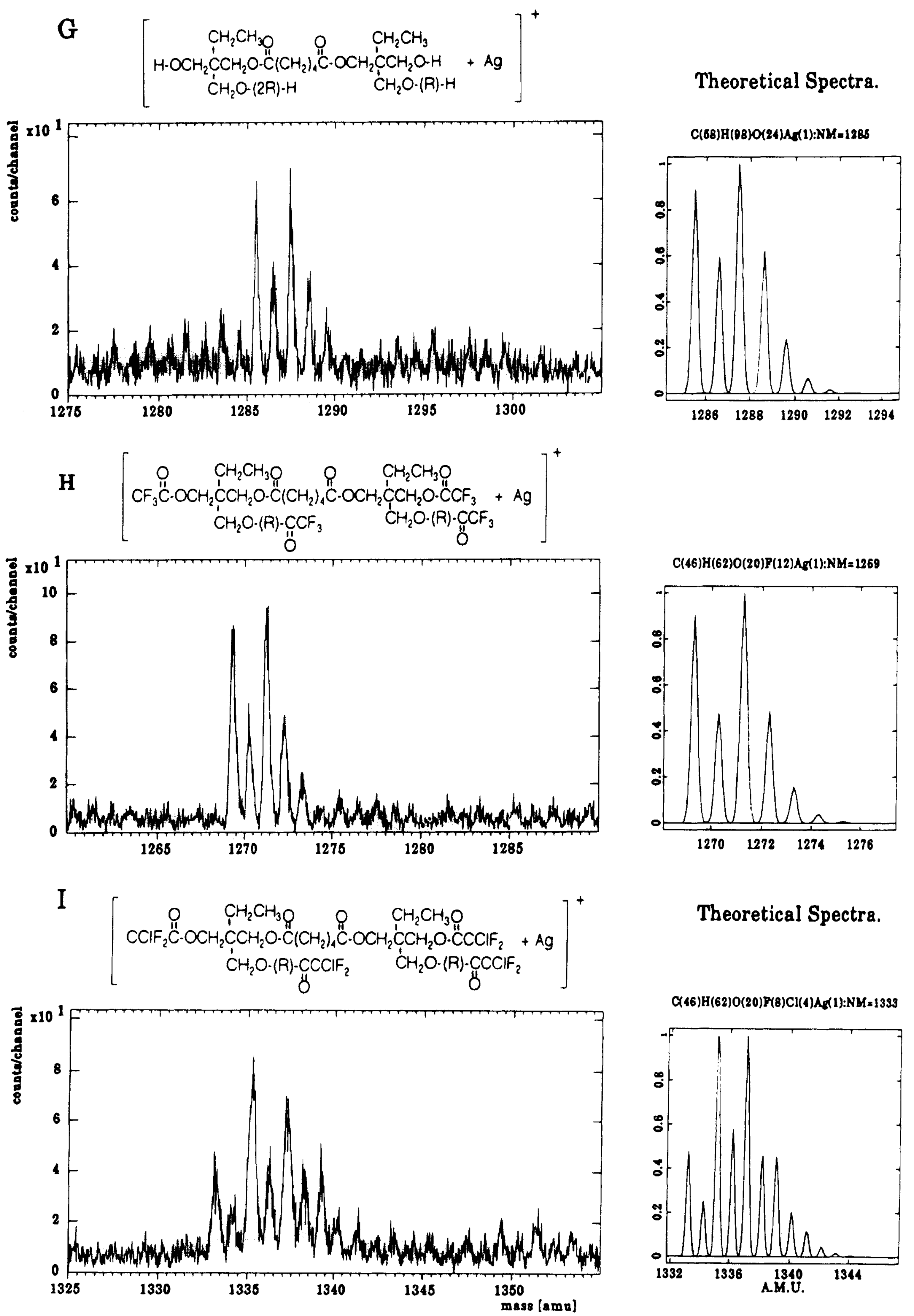
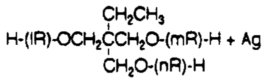


Figure 12. cont'd.

Table 3. Oligomers and Fragments of Branched Poly(1,3-butylene adipate) in the Mass Range *m/z* 750−1500

	code	n	m/z	intensity
nR + Ag	R_{BA}	4	907	937
		5	1107	491
$H\text{-}(nR)\text{-}O(CH_2)_4OH + Ag$	O_{1i}	3	797	9004
		4	997	3867
		5	1197	1698
		6	1397	754
		7	1597	229

	code	$l+m+n$	m/z	intensity
 $H\text{-}(lR)\text{-}OCH_2\underset{\underset{CH_2O\text{-}(nR)\text{-}H}{\vert}}{\overset{\overset{CH_2CH_3}{\vert}}{C}}CH_2O\text{-}(mR)\text{-}H + Ag$	O_{1b}	3	841	5043
		4	1041	3092
		5	1241	1440
		6	1441	569

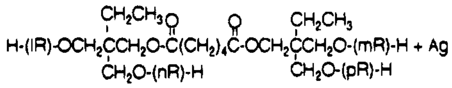
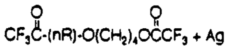
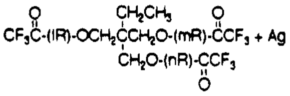
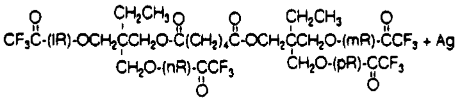
	code	$l+m+n+p$	m/z	intensity
 $H\text{-}(lR)\text{-}OCH_2\underset{\underset{CH_2O\text{-}(nR)\text{-}H}{\vert}}{\overset{\overset{CH_2CH_3}{\vert}}{C}}CH_2O\text{-}\overset{\overset{O}{\Vert}}{C}(CH_2)_4\overset{\overset{O}{\Vert}}{C}\text{-}OCH_2\underset{\underset{CH_2O\text{-}(pR)\text{-}H}{\vert}}{\overset{\overset{CH_2CH_3}{\vert}}{C}}CH_2O\text{-}(mR)\text{-}H + Ag$	O_{2b}	3	885	1326
		4	1085	1071
		5	1285	746
		6	1485	514

Table 4. Oligomers and Fragments of Branched Poly(1,3-butylene adipate) after Transesterification with CF_3COOH in the Mass Range *m/z* 750−1500

	code	n	m/z	intensity
 $CF_3\overset{\overset{O}{\Vert}}{C}\text{-}(nR)\text{-}O(CH_2)_4O\overset{\overset{O}{\Vert}}{C}CF_3 + Ag$	T_{2t}	2	789	16351
		3	989	6221
		4	1189	2144
		5	1389	707
		6	1589	120

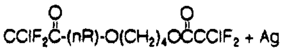
	code	$l+m+z$	m/z	intensity
 $CF_3\overset{\overset{O}{\Vert}}{C}\text{-}(lR)\text{-}OCH_2\underset{\underset{CH_2O\text{-}(nR)\text{-}\underset{\underset{O}{\Vert}}{C}CF_3}{\vert}}{\overset{\overset{CH_2CH_3}{\vert}}{C}}CH_2O\text{-}(mR)\text{-}\overset{\overset{O}{\Vert}}{C}CF_3 + Ag$	T_{3t}	2	929	7354
		3	1129	4621
		4	1329	2093
		5	1529	758

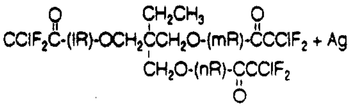
	code	$l+m+n+p$	m/z	intensity
 $CF_3\overset{\overset{O}{\Vert}}{C}\text{-}(lR)\text{-}OCH_2\underset{\underset{CH_2O\text{-}(nR)\text{-}\underset{\underset{O}{\Vert}}{C}CF_3}{\vert}}{\overset{\overset{CH_2CH_3}{\vert}}{C}}CH_2O\text{-}\overset{\overset{O}{\Vert}}{C}(CH_2)_4\overset{\overset{O}{\Vert}}{C}\text{-}OCH_2\underset{\underset{CH_2O\text{-}(pR)\text{-}\underset{\underset{O}{\Vert}}{C}CF_3}{\vert}}{\overset{\overset{CH_2CH_3}{\vert}}{C}}CH_2O\text{-}(mR)\text{-}\overset{\overset{O}{\Vert}}{C}CF_3 + Ag$	T_{4t}	0	869	784
		1	1069	1341
		2	1269	1285
		3	1469	902
		4	1669	462

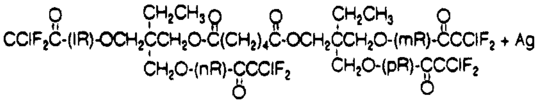
fragment after a two-branched polyester reacts with $CClF_2COOH$. The observed spectra compared with the ideal isotope distribution give similar isotope patterns and intensities. After transesterification with CF_3COOH or $CClF_2COOH$, the *m/z* values of peaks are different enough to characterize the transesterification products. Moreover, $CClF_2COOH$ transesterification has the additional benefit that the isotope patterns of linear, one-branched, and two-branched fragments are quite different after transesterification. Comparison of spectra A, B, D, E, G, and H in Figure 12 illustrates that the isotope patterns before and after CF_3COOH transesterification do not show any significant difference, although there is an absolute mass difference due to the presence of F atoms in place of hydrogen; also little difference between isotope patterns is observed for linear, one-branched, and two-branched oligomers. However, linear, one-branched, and two-branched fragments can be distinguished qualitatively by the isotope patterns after $CClF_2COOH$ transesterification as can be seen by comparison of parts C, F, and I of Figure 12. Therefore, transesterification of polyesters with $CClF_2COOH$ is very valuable for characterization of both linear and branched polyesters.

It would be desirable to have a less subjective method for comparison of patterns than visual inspection. To this end, we carried out cross correlation of the spectra for transesterification by chlorodifluoroacetic acid (parts C, F, and I of Figure 12), with their commensurate theoretical spectra. Given the similarity of the spectra, a high level of correlation was found for any measured spectrum with any theoretical pattern. However, the correlation coefficient for each measured spectrum with its theoretical pattern exceeded 0.99, while correlation

Table 5. Oligomers and Fragments of Branched Poly(1,3-butylene adipate) after Transesterification with $CClF_2COOH$ in the Mass Range *m/z* 750–1500

	code	*n*	*m/z*	intensity
 $\mathrm{CClF_2\overset{O}{\overset{\Vert}{C}}\text{-(nR)-}O(CH_2)_4O\overset{O}{\overset{\Vert}{C}}CClF_2 + Ag}$	C_{2t}	2	821	21268
		3	1021	8024
		4	1221	2617
		5	1421	987
		6	1621	235

	code	*l*+*m*+*n*	*m/z*	intensity
 $\mathrm{CClF_2\overset{O}{\overset{\Vert}{C}}\text{-(lR)-}OCH_2\overset{CH_2CH_3}{\underset{CH_2O\text{-(nR)-}\underset{O}{\underset{\Vert}{C}}CClF_2}{C}}CH_2O\text{-(mR)-}\overset{O}{\overset{\Vert}{C}}CClF_2 + Ag}$	C_{3t}	1	777	7517
		2	977	6222
		3	1177	3756
		4	1377	1766
		5	1577	395

	code	*l*+*m*+*n*+*p*	*m/z*	intensity
 $\mathrm{CClF_2\overset{O}{\overset{\Vert}{C}}\text{-(lR)-}OCH_2\overset{CH_2CH_3}{\underset{CH_2O\text{-(nR)-}\underset{O}{\underset{\Vert}{C}}CClF_2}{C}}CH_2O\text{-}\overset{O}{\overset{\Vert}{C}}(CH_2)_4\overset{O}{\overset{\Vert}{C}}\text{-}OCH_2\overset{CH_2CH_3}{\underset{CH_2O\text{-(pR)-}\underset{O}{\underset{\Vert}{C}}CClF_2}{C}}CH_2O\text{-(mR)-}\overset{O}{\overset{\Vert}{C}}CClF_2 + Ag}$	C_{4t}	0	933	774
		1	1133	1101
		2	1333	551
		3	1533	503
		4	1733	204

coefficients with other theoretical patterns were typically 0.92–0.94. Thus it appears (based on fragmentary evidence) that a correlation coefficient >0.99 can be applied to the identification of theoretical and measured patterns.

Conclusions

High-resolution time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a powerful technique for structural characterization of polyesters. TOF-SIMS spectra of a series of polyesters with different diols and diacids were obtained in the mass range *m/z* 0–3500. Intact oligomers and fragments consisting of a large number of repeat units were observed. The mass of the ester repeat unit can be determined from spacings between consecutive oligomer and/or fragment peaks.

Transesterification of polyesters by trifluoroacetic acid (TFA) and chlorodifluoroacetic acid (CFA) was studied. Diesters were produced by transesterification, giving a large number of peaks for polyester repeat units with an additional diol and two trifluoroacetates or chlorodifluoroacetates. The structural characteristics of the polymer backbone are retained after transesterification, providing definitive information about the repeat unit.

Transesterification products can be identified by peak patterns in TOF-SIMS spectra. The shapes and intensities of clusters in transesterification spectra show good agreement with theoretical isotope patterns. TOF-SIMS spectra were used to obtain information about the progress of the transesterification reaction. The increasing abundance of tagged ions indicates that the reaction has progressed with time.

Transesterification was also applied to branched poly(1,3-butylene adipate). Transesterification products such as two-, three-, and four-tagged fragments were identified in the TOF-SIMS spectra to give information about polymer branching. The $CClF_2CO$ group in chlorodifluoroacetic acid provides a good mass marker. Linear, one-branched, and two-branched polyesters tagged with $CClF_2CO$ groups can be readily identified from the unique chlorine isotope patterns. This study shows that TOF-SIMS combined with transesterification reactions is a potentially powerful technique for the characterization of highly branched or cross-linked copolymers.

Acknowledgment. We are grateful to Dr. Neil Nodelman of Miles Chemical Corp. for providing the branched poly(1,3-butylene adipate) and to Dr. Andy Proctor for help with cross correlation. This work was supported by the National Science Foundation under Grant No. CHE-9022135.

Supplementary Material Available: Tables of oligomer and repeat unit series for polyesters and of transesterification products of polyesters with trifluoroacetic acid and chlorodifluoroacetic acid (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Mark, H. F., Gaylord, N. G., Eds. *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons, Inc.: New York, 1969; Vol. 11.

(2) Manaresi, P.; Munari, A.; Pilati, F.; Alfonso, G. C.; Russo, S.; Sartirana, M. L. *Polymer* **1986**, *27*, 955–960.

(3) Manaresi, P.; Parrini, P.; Semeghini, G. L.; de Fornasari, E. *Polymer* **1976**, *17*, 595–600.

(4) Neff, B. L.; Overton, J. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *23*, 130–131.

(5) Montaudo, G.; Montaudo, M. S.; Scamporrino, E.; Vitalini, D. *Macromolecules* **1992**, *25*, 5099–5107.

(6) Plage, B.; Schulten, H.-R. *J. Anal. Appl. Pyrolysis* **1989**, *15*, 197.

(7) MacDonald, W. A.; McLenaghan, A. D. W.; McLean, G.; Richards, R. W.; King, S. M. *Macromolecules* **1991**, *24*, 6164–6167.

(8) Andruzzi, F.; Huilsted, S. *Polymer* **1991**, *32*, 2294–2299.

(9) Smith, C. G.; Nyquist, R. A.; Smith, P. B.; Pasztor, A. J., Jr.; Martin, S. J. *Anal. Chem.* **1991**, *63*, 11R–32R.

(10) Adams, R. E. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 119–129.

(11) Garozzo, D.; Giuffrida, M.; Montaudo, G. *Macromolecules* **1986**, *19*, 1643–1649.

(12) Ballistreri, A.; Garozzo, D.; Giuffrida, M.; Montaudo, G. *Anal. Chem.* **1987**, *59*, 2024–2027.

(13) Rollins, K.; Scrivens, J. H.; Taylor, M. J.; Major, H. *Rapid Commun. Mass Spectrom.* **1990**, *4*, 355–359.

(14) Jardine, D. R.; Nekula, S.; Than-Trong, N.; Haddad, P. R.; Derrick, P. J.; Grespos, E.; O'Donnell, J. H. *Macromolecules* **1986**, *19*, 1770–1772.

(15) Lattimer, R. P. *Int. J. Mass Spectrom. Ion Processes* **1983**, *55*, 221–232.

(16) Lai, S. T.; Chan, K. W. S.; Cook, K. P. *Macromolecules* **1980**, *13*, 953–956.

(17) Chan, K. W. S.; Cook, K. D. *Org. Mass Spectrom.* **1983**, *18*, 423–425.

(18) Feld, H.; Leute, A.; Zurmuhlen, R.; Benninghoven, A. *Anal. Chem.* **1991**, *63*, 903–910.

(19) Wong, S. F.; Meng, C. K.; Fenn, J. B. *J. Phys. Chem.* **1988**, *92*, 546–550.

(20) Hillenkamp, F.; Karas, M.; Beavis, R. C.; Chait, B. *Anal. Chem.* **1991**, *63*, 1193A–1203A.

(21) Bahr, U.; Deppe, A.; Karas, M.; Hillenkamp, F.; Giessmann, U. *Anal. Chem.* **1992**, *64*, 2866–2869.

(22) Bletsos, I. V.; Hercules, D. M.; Greifendorf, D.; Benninghoven, A. *Anal. Chem.* **1985**, *57*, 2384–2388.

(23) Bletsos, I. V.; Hercules, D. M.; vanLeyen, D.; Benninghoven, A.; Karakatsanis, C. G.; Rieck, J. N. *Macromolecules* **1990**, *23*, 4157–4163.

(24) Chiarelli, M. P.; Proctor, A.; Bletsos, I. V.; Hercules, D. M.; Feld, H.; Leute, A.; Benninghoven, A. *Macromolecules* **1992**, *25*, 6970–6976.

(25) Niehius, E.; Heller, T.; Feld, H.; Benninghoven, A. *J. Vac. Sci. Technol.* **1987**, *A5*, 1243–1246.

(26) Feld, H.; Zurmullen, R.; Leute, A.; Benninghoven, A. *J. Phys. Chem.* **1990**, *94*, 4594–4599.

(27) Bletsos, I. V.; Hercules, D. M.; vanleyen, D.; Benninghoven, A.; Karakatsanis, C. G.; Rieck, J. N. *Anal. Chem.* **1989**, *61*, 2142–2149.