Macromolecules **1995,** *28,* 5601–5608

Characterization of Polyester Polyurethanes by Time-of-Flight Secondary-Ion Mass Spectrometry

Lucinda R. H. Cohen[†] **and David M. Hercules***[,‡]

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

Costas G. Karakatsanis and James N. Rieck

Bayer Corporation, Pittsburgh, Pennsylvania 15205

Received December 23, 1994; Revised Manuscript Received May 3, 1995[®]

ABSTRACT: A series of polyesters and polyester polyurethanes were analyzed using time-of-flight secondary-ion mass spectrometry (TOF-SIMS). Analysis of poly(butylene adipate) samples produced spectra containing oligomer ions and fragments corresponding to cyclization via intramolecular ester exchange. These cyclic fragments were also observed in the spectra of polyurethane [4,4,1] samples, along with cyclic ester–urethane fragments. The mass of the diisocyanate group within the polyurethane could be determined from the mass difference between the two major fragment-ion series in the spectrum. In general, only limited fragmentation within ester or urethane repeat units was observed. The sample molecular weight for both the polyesters and polyurethanes correlated with the relative intensity of the cyclic repeat unit series ions to the linear oligomer ions. Additionally, transesterification of polyesters and polyurethanes using trifluoroacetic acid was found to selectively cleave bonds between polyester repeat units in both types of polymers.

1. Introduction

Polyurethanes are an industrially important class of copolymers with a wide range of both applications and formulations. Typically, analytical characterization of polyurethanes involves multiple techniques, such as NMR, IR, and pyrolysis mass spectrometry, which provide complementary information about the sample. Polyurethane analyses using these techniques have been studied extensively and are reviewed elsewhere.[1–3] In general, the most important information to be gained from any type of analysis involves determination of the structure and molecular weight distribution of the polyurethane sample. Time-of-flight secondary-ion mass spectrometry (TOF-SIMS) has been used in polymer analysis to provide information about the mass of the repeat unit, terminal groups, chain extenders, and branching. A variety of polymers ranging from nylons[4] to polybutadienes[5] have been examined by TOF-SIMS. In particular, TOF-SIMS studies of model diol and polyester polyurethanes have been conducted to determine the structure of terminal groups, diol extenders, ester blocks, and diisocyanates.[1,2]

In addition to information about polymer structure, molecular weight distributions can be determined by mass spectrometry. Not only TOF-SIMS[6] but also field desorption,[7] electrospray,[8] and, recently, matrix-assisted laser desorption/ionization[9,10] mass spectrometries have been utilized to determine the molecular weights of various polymers. Poly(dimethylsiloxane) oligomers of up to 8000 Da[11] have been analyzed by TOF-SIMS, but, unfortunately, oligomers of many polymers are not observed above *ca.* 6000 Da. Instead, characteristic patterns are observed from ~500 to 3000 Da, resulting from silver-cationized fragments of the polymer chain. For certain types of polymers such as poly(propylene glycols)[12] and poly(dimethylsiloxanes)[13] these fragment patterns have been shown to change as a function of molecular weight. Previous work by Fowler *et al.* has also demonstrated that the M_n of Krytox samples can be obtained by using normalized intensities of specific high mass fragment ions in the TOF-SIMS spectrum.[14]

The purpose of the present study is to characterize a series of polyester polyurethanes with a range of molecular weights. Although the molecular weights of these samples are greater than the mass range accessible by TOF-SIMS, the fragment patterns of these polyurethanes will be compared as a function of molecular weight and the fragmentation mechanisms examined in detail. The polyester prepolymers will also be examined and compared with the polyurethanes. Transesterification reactions will be utilized to gain additional information about the structure and fragmentation mechanisms of polyesters and polyurethanes.

2. Experimental Section

2.1. Synthesis of Polyester Polyurethane [4,4,1]. Polyurethane (4,4,1) (PU[4,4,1]) samples were prepared using the polycondensation reaction of the diisocyanate, 4,4′-diphenylmethane diisocyanate (MDI), with poly(butylene adipate)s (PBA) of three different molecular weights. The nomenclature PU[4,4,1] is based on the length of the acid and alcohol moieties within the polyester repeat unit and the type of diisocyanate, as per the nomenclature described in ref 2. Varying amounts of polyester and tetrahydrofuran (THF) were added to a 500-mL three-neck flask, fitted with a thermometer, drying tube, and stirrer. After heating to 60 °C with stirring, an appropriate amount of 4,4′-diphenylmethane diisocyanate and 3–5 drops of stannous octoate catalyst were added. The reaction mixture was stirred overnight at 60 °C. Isocyanate detection paper was used to determine that all the isocyanate was reacted. The solutions were then removed from the flask (as 30% solids by mass in THF) and prepared for TOF-SIMS analysis. A total of nine PU[4,4,1] samples with different molecular weights were synthesized.

2.2. TOF-SIMS Instrumentation. The instrument used in these studies was a time-of-flight secondary-ion mass spectrometer, TOF-SIMS III, designed and manufactured by Ion-Tof GmbH, Münster, Germany. In essence, the instrument consists of two main components: (1) a pulsed Ar^+ primary ion source and (2) a TOF reflectron analyzer/detector system. The TOF-SIMS has been described in more complete

---

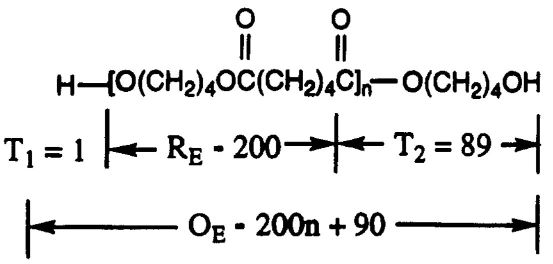
[†] Present address: Institute for Medical Physics and Biophysics, Robert Koch Strasse 31, University of Münster, D48149 Münster, Germany.

[‡] Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

[®] Abstract published in *Advance ACS Abstracts,* June 15, 1995.

0024-9297/95/2228-5601$09.00/0

Chart 1



$$H\text{-}[O(CH_2)_4OC(=O)(CH_2)_4C(=O)]_n\text{-}O(CH_2)_4OH$$

detail elsewhere.[15,16] The primary ion gun consists of a standard electron impact argon ion source combined with a pulsed 90° deflector for beam chopping and primary ion mass separation, followed by an axial buncher for pulse compression. The resultant mass-separated primary ion bunches have a typical pulse length of about 1 ns and a variable-spot diameter between 5 and 50 μm.

Secondary ions generated by a primary ion pulse on the target surface are extracted and accelerated to an energy of 3 keV. An Einzel lens and reflectron optics are integrated for focusing the secondary ion beam and for energy compensation, respectively. To achieve high detection efficiency, the ions are postaccelerated to 10 keV, where they are then detected by a channel plate–scintillator–photomultiplier combination. The data collection system consists of a time-to-digital converter, a fast buffer memory, and an accumulating memory board. The spectra are accumulated in the single ion counting mode with a maximum of 256 stops/pulse, a time resolution of 1.25 ns/channel, and a total time range of 320 μs. The cycle time was set at 200 μs, allowing investigation of ions from 1 to 4000 Da. During the analysis the target was bombarded by a 10-keV Ar^+ beam with an average pulsed primary ion current of 0.1–0.5 pA for a total collection time of 200 s. The total primary ion current density was less than 10^{13} ions/cm^2 (static SIMS). The typical mass resolution ($m/\Delta m$) was 8000 at m/z = 1000.

The samples were prepared for analysis by dissolving the polymer in tetrahydrofuran. Typical solution concentrations were 10^{-3} M with respect to the mass of the repeat unit. A total of 1 μL of the sample was deposited onto a silver target with an area of ~12 mm^2. The silver had been etched in nitric acid (20 vol %) and rinsed with deionized water and methanol. Transesterification reactions were carried out on the polyesters and polyurethanes using trifluoroacetic acid (TFA). An amount of 1 mL of TFA was reacted overnight with approximately 2 mg of the polymer. A total of 1 μL of this solution was deposited on an etched silver substrate and analyzed.

2.3. Gel Permeation Chromatography. The PBA and PU[4,4,1] samples were also characterized by gel permeation chromatography (GPC) using a Waters high-temperature gel permeation chromatograph. PU and PBA samples were dissolved in THF, and a 1% (wt %) sample solution was injected onto 10^4, 10^3, 500, 100, and 50 Å Ultrastyragel columns (in series). Polystyrene calibration standards were used for the polyurethanes and poly(ethylene glycol) standards for the polyesters.

2.4. Data Analysis. All of the data analysis procedures were performed using in-house-generated software (GOOGLY by Andrew Proctor) written for an IBM PC-compatible system operating under MS/DOS.

3. Results and Discussion

3.1. Poly(butylene adipate) Samples. Three poly(butylene adipate) (PBA) samples (shown in Chart 1) with molecular weights ranging from 1000 to 10 000 Da were analyzed by TOF-SIMS. For clarity, the term "oligomer" will refer to a polymer chain with an integral number of repeat units (R_E) and two terminal groups (T_1–R_B–T_2). A fragment ion, corresponding to an integral number of repeat units without any terminal groups (nR_E), will be called the repeat unit, or R_E, series. A representative spectrum for PBA is shown in Figure 1, illustrating a typical fragment pattern. By far the most intense ions observed in the PBA spectra are the repeat unit, R_E, and oligomer, O_E, series. These series of ions are each spaced 200 Da apart, which corresponds to the mass of the repeat unit. Some Na-cationized oligomer peaks were also observed, due to Na contamination in the sample. The R_E and O_E series have been observed as the only ions of significant intensity in the TOF-SIMS analysis of various other aliphatic polyesters.[17]

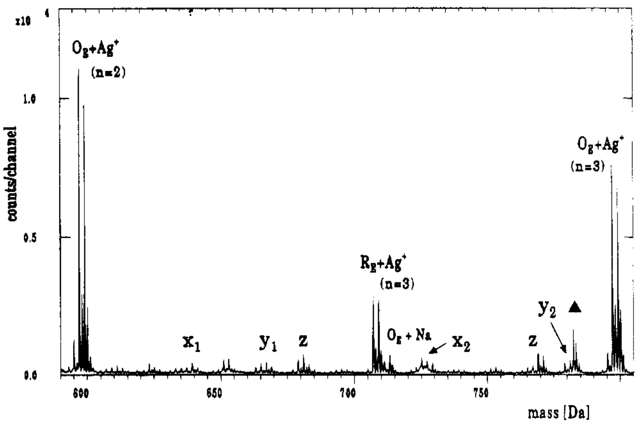


Figure 1. Portion of the TOF-SIMS spectrum of poly(butylene adipate), M_n = 2270, showing the fragment pattern. The contaminant peak at 783 Da is indicated by a filled triangle. Other symbols are as described in Scheme 2.

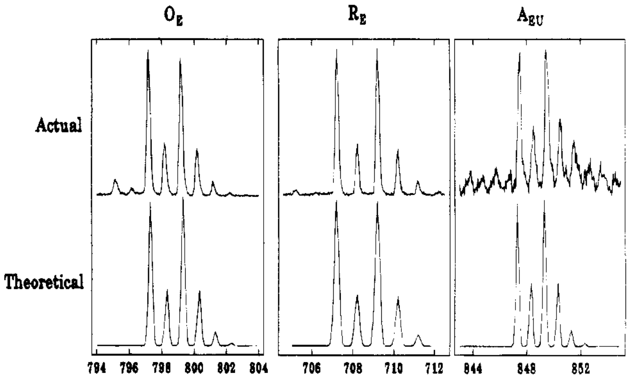
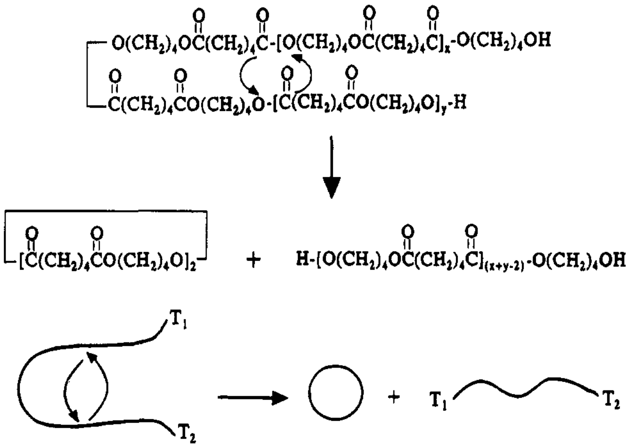


Figure 2. Cluster structures of poly(butylene adipate) and polyurethane [4,4,1] comparing theoretical and actual isotopic patterns.

The most striking feature of the polyester fragment pattern is the presence of essentially one, singly unsaturated, species for the $(R_E + M)^+$ and $(O_E + M)^+$ ions where M is the appropriate metal cation. The fragment clusters contained within the TOF-SIMS spectra of other C-, H-, and O-containing polymers such as polyglycols[12] or poly(alkyl methacrylates)[18] typically contain multiple species corresponding to varied degrees of unsaturation (0, 1, or 2 double bonds). A comparison of the theoretical and experimental isotopic patterns for $(R_E + Ag)^+$ and $(O_E + Ag)^+$ ions is shown in Figure 2; good agreement is seen between the theoretical and observed spectra. Linear least-squares regression analysis (LLSRA) showed a correlation coefficient of 0.985 between the theoretical and experimental patterns for the $(R_E + Ag)^+$ ion. A species with two unsaturations was detected as a low-intensity peak 2 Da below the $(O_E + Ag)^+$ and contributed *ca.* 5–10% to the overall peak envelope. The overall appearance and relative intensities of the peaks within the R_E and O_E patterns are the same regardless of the number of repeat units or the molecular weight of the sample.

Scheme 1. Fragmentation of Polyesters via Intramolecular Ester Exchange



One explanation for the absence of saturated or doubly unsaturated R_E fragments is that the R_E ions are cyclic species. Cyclization of polyester monomers, dimers, etc., occurs readily during pyrolysis mass spectrometry.[3,19,20] A fast atom bombardment (FAB) mass spectrometric study by Montaudo and co-workers[21] has shown that cyclic fragments have a much better ionization efficiency than linear oligomers, so much so that FAB-MS spectra can only be obtained for polyester samples which contain cyclic oligomers. Hagenhoff *et al.* have also observed better ionization efficiencies in TOF-SIMS for cyclic poly(dimethylsiloxanes) versus linear oligomers.[11] The amount of cyclic oligomers in the original polyester sample is determined by the reaction conditions,[22] and the polyesters examined in this study contained only trace amounts of cyclics, as was verified by GPC. Therefore, cyclic species observed in the TOF-SIMS spectra must be produced *during* ion formation.

TOF-SIMS polymer fragmentation mechanisms have previously been explained by homolytic radical cleavage mechanisms occurring in a more or less random fashion during ion formation. The fundamental assumption is that any skeletal bond may be broken, but the weakest bond will break more easily (*i.e.*, C−C bond cleavage is preferred over C=C bond cleavage). Analysis of polyglycol chain fracture mechanisms has suggested that C−O cleavage may be favored over C−C cleavage.[12] Preferential C−O cleavage may be favored over C−C cleavage.[12] Preferential C−O cleavage during polyester fragmentation should produce a greater number of fragments, with varying degrees of unsaturation, than is observed for the polyesters. If only the cleavage of C−O backbone bonds is considered, then the statistical model for the radical mechanism predicts that four major fragments should be produced: R_E, $R_E + \Delta$, $R_E + 5\Delta$, and $R_E + 6\Delta$ (where Δ corresponds to an oxygen or CH_n group). Random statistical cleavage of both the C−C and C−O bonds should produce a total of 12 different fragments. Since neither of these types of fragmentation patterns is observed for the PBAs, other types of fragmentation mechanisms must be considered.

Polyesters fragment during thermal degradation via two major pathways: intramolecular ester exchange and β-CH transfer.[3] Scheme 1 shows the cyclization of poly(butylene adipate) via intramolecular exchange. In this process, a linear oligomer undergoes ester exchange to produce a small cyclic fragment and another linear chain which is two units shorter. It should also be noted that there is no net energy change: two identical bonds are both broken and reformed. An alternative pathway to forming O_E and R_E segments would be cleavage of the C−O ester bond with hydrogen transfer. It seems unlikely that this is a major mechanism based on spectra for polymers reacted with trifluoroacetic acid.[17] Cleavage of the C−O ester bond should produce fragments containing one trifluoroacetate group, which is not observed.

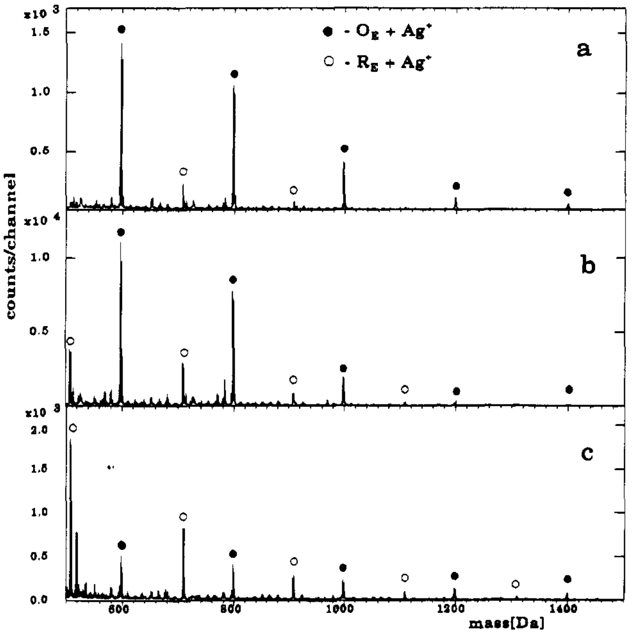


Figure 3. TOF-SIMS spectra of poly(butylene adipate)s. M_n: (a) 1290, (b) 2270, (c) 4040.

Other possible polyester fragmentation mechanisms involving hydrogen transfer are shown in Scheme 2. Electron ionization (EI) mass spectrometric studies of esters have shown that hydrogen transfer occurs via a McLafferty rearrangement.[23] Path A shows hydrogen transfer to produce two species: $O_E - 18$ and $R_E + 18$. Hydrogen transfer on the opposite side of the carbonyl group may also occur and is shown in path B, producing the species $O_E + 68$ and $R_E - 68$. Interpretation of these fragmentation mechanisms is complicated by the fact that these pathways may occur for any ester bond in the polymer. Each polyester repeat unit contains two ester bonds, so paths A and B will actually produce four fragments each, assuming equal ion formation probabilities. However, since the mass of the butylene diol terminal group ($HO(CH_2)_4O^-$) is the same as part of the polyester repeat unit, many of the fragments produced in paths A and B are actually isobaric. These fragments are summarized at the bottom of the scheme. For example, the x_1 fragment may result from C−C cleavage β to the carbonyl to yield the isobars $R_E - 68$ and $O_E + 42$. For both H-transfer pathways occurring at both ester bonds in a repeat unit, a total of four possible fragments will be produced. Examination of Figure 1 shows that, despite the multiple pathways which might produce these fragments, their intensities are quite low with respect to the R_E + Ag and O_E + Ag series. α-Cleavage adjacent to the carbonyl group also does not produce fragment ions of significant intensity (labeled "z" in the figure). Therefore, cyclization via intramolecular ester exchange shown in Scheme 1 is the major mode of fragmentation, and the H-transfer McLafferty rearrangements are only minor modes of fragment ion formation.

Figure 3 shows portions of the TOF-SIMS spectra for three different molecular weight PBAs. The Ag-cation-

Scheme 2. Fragmentation of Polyesters via McLafferty Rearrangements

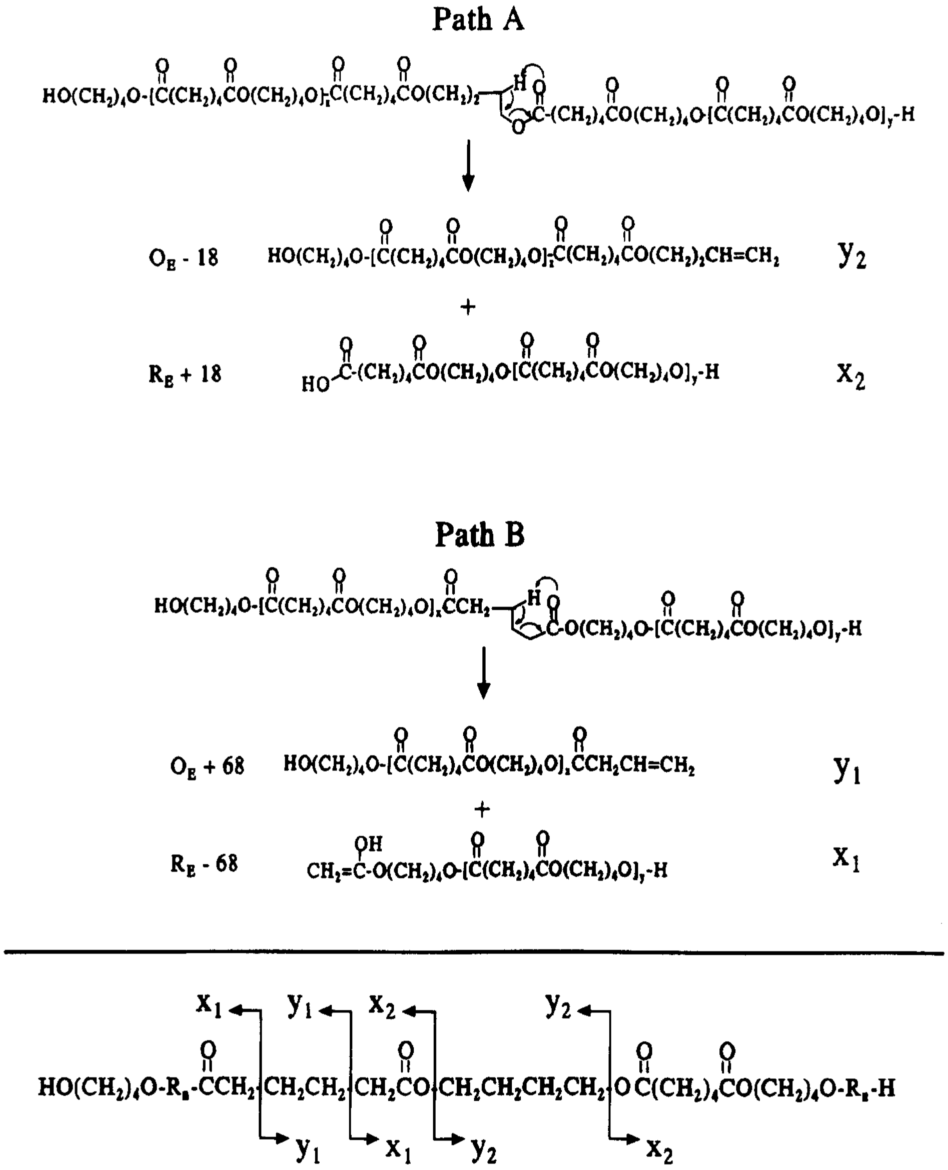


Table 1. Molecular Weight Determinations of Poly(butylene adipate) by GPC and TOF-SIMS

GPC			TOF-SIMS		
M_n	M_w	M_w/M_n	M_n	M_w	$O_E/(R_E + O_E)$
1290	2820	2.20	780	833	89 ± 2.7
2270	6200	2.74	734	771	72 ± 2.7
4040	12610	3.12	928	1053	28 ± 5.8

ized R_E series is indicated in the figure with open circles, and the Ag-cationized O_E series, by filled circles. The oligomer distributions for these spectra are nearly identical and are skewed toward lower masses, which is characteristic of condensation polymerization. Although the calculated M_n and M_w values from TOF-SIMS were quite similar, GPC analysis showed three different molecular weights for the PBA samples, which are listed in Table 1. Generally, TOF-SIMS analysis shows skewed molecular weight values for samples with broad molecular weight distributions ($M_w/M_n > 1.2$). Two different factors contribute to this effect: (1) lower detection efficiency and (2) lower transformation probabilities of intact high mass oligomers. An additional source of error is the fragmentation of higher molecular weight chains to produce ions which still contain the terminal groups but have fewer repeat units, which will skew the molecular weight distribution toward lower values.

The molecular weight of the sample can be estimated by comparing the relative intensities of the oligomer ions (O_E) to the fragment ions (R_E). The PBA with M_n = 1285 in Figure 3a shows intense O_E peaks, with less intense peaks for the R_E series. As the molecular weights of the PBA increases in parts b and c of Figure 3, the intensity of the O_E series decreases relative to that of the R_E series. The effect may be explained by considering the relative number of terminal groups compared to the number of repeat units, which decreases with increasing chain length. The relative intensity of the O_E series can thus provide an estimate of the polymer molecular weight. The relative intensity of the O_E ions was calculated by dividing the O_E peak area by the sum of the O_E and R_E peak areas. The $O_E/(O_E + R_E)$ values for the three PBA samples are listed in Table 1. As the PBA M_n values increased from 1285 to 4090, the relative intensity of the oligomer ions decreased from 89% to 28%. Direct measurement of accurate molecular weights by TOF-SIMS may not be possible for these samples, but the molecular weight can be semiquantitatively determined from the relative intensity of the O_E series.

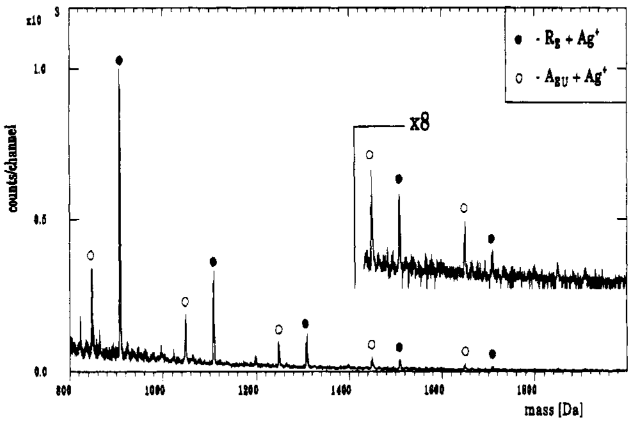


Figure 4. TOF-SIMS spectrum of polyurethane [4,4,1]. M_n = 40 000. Key: (○) $(A_{EU} + Ag)^+$; (●) $(R_E + Ag)^+$.

The change in the relative intensities of the O_E and R_E series with increasing molecular weight is consistent with the proposed cyclization mechanism of Scheme 1. Cyclization to produce cyclic dimers or trimers may involve multiple ester exchanges. As the chain length of the PBA oligomers increases, cyclization may proceed in a stepwise fashion, with the ratio of cyclics increasing in proportion to the number of shorter linear oligomers. For example, a PBA chain with $M_n = 1200$ will contain 6 repeat units. Two cyclic dimers and one oligomer with $n = 2$ could be produced (n = the number of repeat units). For a PBA sample with $M_n = 4000$ ($n = 20$), nine cyclic dimers and one shorter linear oligomer could be produced. Of course, this is a gross oversimplification since the oligomers may be desorbed intact, cyclic trimers or tetramers might be produced, and other minor fragmentation mechanisms might occur. Nevertheless, the general phenomenon of changes in the intensities of the R_E and O_E series with molecular weight can be explained by the cyclization mechanism.

3.2. Polyurethane [4,4,1] Samples. The polyurethane (PU) copolymers studied were produced by reaction of the PBA samples with 4,4′-diphenylmethane diisocyanate (MDI), resulting in the polyurethane shown in Chart 2. A typical TOF-SIMS spectrum of PU[4,4,1] is shown in Figure 4. Two intense fragment ion series were observed in the spectrum, corresponding to silver-cationized polyester fragments $(R_E + Ag)^+$ and polyurethane fragments $(A_{EU} + Ag)^+$. The mass of the diisocyanate group (340 Da) can be determined directly from the mass difference between the polyester and the polyurethane fragments. Depending on the molecular weight of the sample, the O_E peak series was also observed. These O_E species must be the shorter linear oligomers produced by cyclization/intramolecular ester exchange of the original (longer) oligomer chains, since GPC analysis indicated no unreacted PBA in the PU samples.

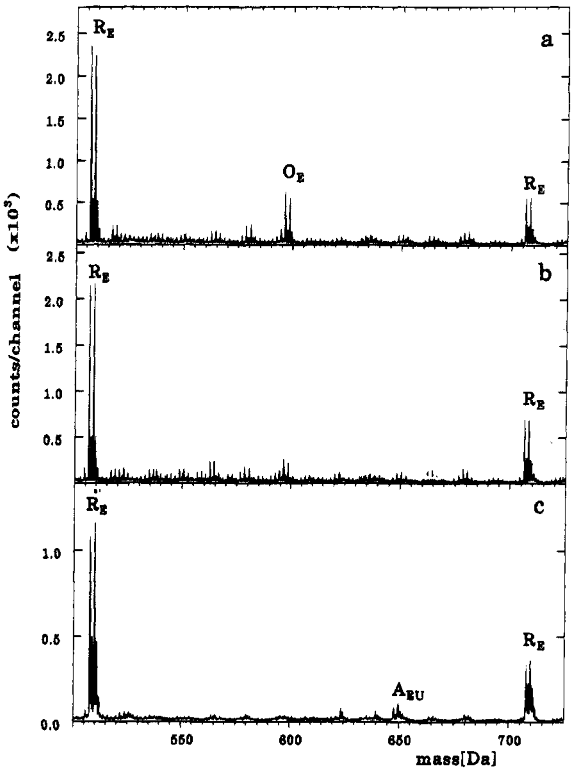
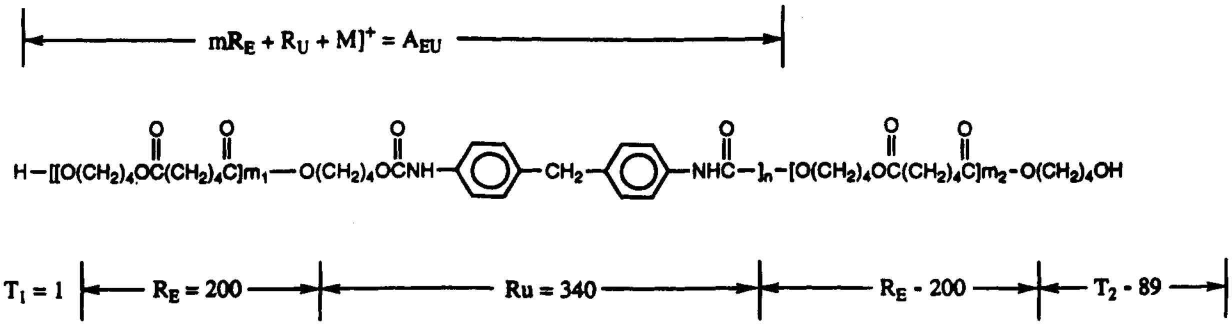


Figure 5. Fragment patterns for polyurethane [4,4,1] with M_n (a) 14 000, (b) 39 000, (c) 48 000.

In general, due to the high molecular weights of the PU samples, main-chain fragments rather than polyurethane oligomers were observed. The fragment patterns of PU[4,4,1] samples having three different molecular weights are shown in Figure 5. Examination of the cluster structure for the R_E, O_E, and A_{EU} series showed a singly unsaturated species, indicating that the cyclization/intramolecular ester exchange reaction of Scheme 1 is the major mode of fragmentation for polyester polyurethanes. The cluster structure of the A_{EU} ion and the corresponding theoretical pattern are shown in Figure 2. The R_E and O_E clusters in the PU samples were identical to those in the PBA samples. Similar to what was observed from the PBA samples, as the molecular weight of the PUs increased, the relative intensity of the oligomer (O_E) series decreased and the relative intensity of the fragment (R_E) series increased, indicating that fragmentation rather than desorption of intact oligomers predominates for higher molecular weight samples. The relative intensity of the A_{EU} series also increased as the PU molecular weight increased, although not in as dramatic a fashion as the R_E series, due to much lower absolute intensities for the A_{EU} ions.

Chart 2



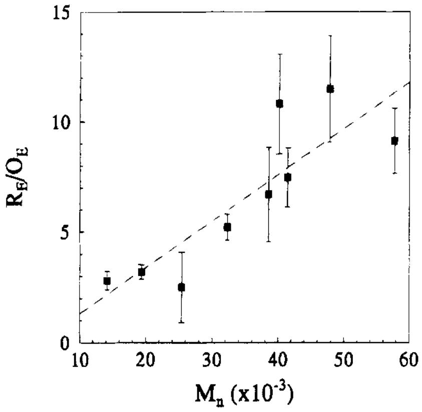


Figure 6. Relative intensity of R_E series versus O_E series as a function of molecular weight.

Table 2. Molecular Weight Determinations of Polyurethane [4,4,1] by GPC

sample ID no.	M_n	M_w	M_w/M_n
728–1	14 160	22 870	1.61
728–2	38 530	62 020	1.61
728–3	47 810	80 600	1.69
730–1	25 420	40 620	1.60
730–2	40 120	67 410	1.68
730–3	57 690	10 0270	1.74
732–1	19 340	30 730	1.59
732–2	32 280	51 450	1.59
732–3	41 430	70 670	1.71

The relative intensities of the O_E series versus those of the R_E series were calculated for the nine PU samples and are shown as a function of molecular weight (M_n) in Figure 6. M_n values were obtained by GPC; results are shown in Table 2. The results in Figure 6 are the averages of three replicate analyses. Linear least-squares regression showed a slope of 0.209 and a correlation coefficient of 0.851, which is significant at the 95% confidence level. For higher molecular weights, the scatter in the data is largely caused by the decrease in the absolute O_E peak intensities, which become more difficult to discern above the noise level. The error in the measurement therefore increases with molecular weight. Despite these difficulties, this method can provide a reasonable estimate of molecular weight. A similar relationship has been observed between cyclic and linear fragment ions for the poly(dimethylsiloxanes).[13]

Not surprisingly, the fragmentation behavior of the polyester polyurethanes appears to be quite similar to that of the polyesters. Once again, cyclization via intramolecular ester exchange is the major pathway for fragment ion formation, with the mechanisms in Scheme 2 producing ions of relatively low intensity in the PU fragment patterns. Thermal degradation of polyurethanes also occurs primarily via cyclization and intramolecular ester exchange.[3,20] The R_E and O_E cluster structures for the PUs reveal singly unsaturated species, as does the A_{EU} cluster. The A_{EU} series, although not shown in Figure 4, actually begins at 647 Da for a cyclic species consisting of one polyester (R_E) and one urethane (R_U) repeat unit. This is somewhat unexpected since the presence of two phenyl rings along the urethane backbone might be expected to prevent cyclization due to rigidity.

Analysis of other polyester polyurethanes by Bletsos *et al.*[2] has shown that the major ion series observed by TOF-SIMS correspond to polyester and polyurethane oligomers and R_E and A_{EU} fragments. Fragmentation within the polyester repeat unit occurred to a limited extent for poly(ethylene azelate)-, poly(butylene azelate)-, and poly(hexylene azelate)-based polyurethanes, producing fragments corresponding to $R_E + R_U + CO$, $R_E + R_U + O$, and $R_E + R_U + CO + O$. However, these fragments were not observed for polyurethanes based on poly(ethylene adipate), poly(butylene adipate), or poly(hexylene adipate), including PU[4,4,1]. Thus, the results from this study agree with those from Bletsos *et al.*[2] Fragmentation within the polyester repeat unit may be related to the length of the acid moiety, i.e., $HOOC(CH_2)_7COOH$ for azelaic acid versus $HOOC(CH_2)_4COOH$ for adipic acid.[2] Since the isotopic patterns of the fragment clusters in the original spectra by Bletsos *et al.* could not be resolved, the generality of the cyclization–ester exchange mechanism cannot be assessed from their data. Additional experiments under high-resolution conditions may help clarify this issue.

3.3. Transesterification Reactions. Transesterification is a particularly useful "derivatization" since it allows analysis of high molecular weight and branched polymers. In addition, transesterification offers the ability to cleave only the ester bond within the polyester chain. Using transesterification with chlorodifluoroacetic acid, Kim and Hercules have determined the number of branches in an unknown poly(1,3-butylene adipate) sample.[17] In the present study, transesterification of polyurethanes was conducted to compare the fragmentation behavior of transesterified polyurethane with unreacted samples. A diagram of the transesterification reaction is shown in Scheme 3. Transesterification of PBA produced spectra similar to those reported by Kim and Hercules[17] and Bletsos *et al.* for other polyesters.[2] The prominent peak series observed corresponded to termination on both ends of the PBA chain to produce $(R_{ET} + Ag)^+$ and $(R_{ET} + Na)^+$ ions, and less intense R_E peaks were also observed. O_E ions corresponding to unreacted polyester oligomers were not observed, since all of the samples were reacted overnight to ensure complete transesterification.

TOF-SIMS analysis of the transesterification products of PU[4,4,1] is shown in Figure 7. The most intense peak series correspond to the cyclic species R_E and transesterified R_{ET} (+ Na^+ and Ag^+) species. Examination of the R_E and R_{ET} cluster structures reveals a single species for both types of ions (results not shown). Less intense A_{EU} ions were also present, depending on sample molecular weight. In general, intense ions for transesterified PU fragments containing the diisocyanate group were not observed (A_{EUT} in Scheme 3). Due to the high molecular weights of the PBA chains within the polyurethanes, the ratio of the number of polyester repeat units to diisocyanate groups was very large ($\geq 70:1$). Transesterification must occur preferentially at the ester chain ends of the copolymer, producing predominantly R_{ET} species, and production of tagged species containing both ester and urethane units is not statistically preferred.

As with the unreacted PUs, the relative intensities of the major ion series in the spectra of transesterified PUs were highly dependent on the molecular weight of the sample. Figure 8 shows the spectra of three different molecular weight PUs following transesterification. The transesterified polyester fragments (R_{ET}) are the most intense series in Figure 8a. When the molecular weight is increased for the samples in parts b and c of Figure 8, the relative intensity of the R_E series increases and the relative intensity of the R_{ET} series

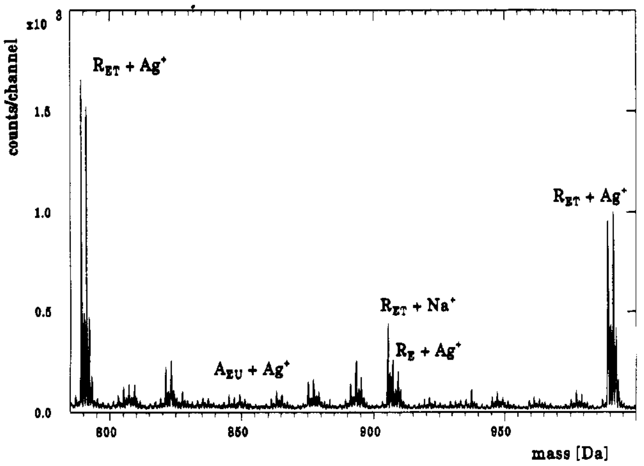


Figure 7. TOF-SIMS spectrum of polyurethane [4,4,1] after transesterification, showing details of a fragment pattern. Sample M_n = 14 160.

decreases. Unfortunately, the relative intensities of the R_E versus the R_{ET} ions do not display a linear relationship for the range of sample molecular weeights as was observed for the R_E versus the O_E ions in the unreacted polymers. This is caused by the additional complication of transesterification, which chemical cleaves or "digests" a high molecular oligomer into smaller TFA-tagged chains, which can then undergo further fragmentation during TOF-SIMS analysis. The number and size distribution of smaller tagged fragments from transesterification may not necessarily display a linear relationship with PU molecular weight.

Transesterification is not a suitable method for estimating the molecular weights of polyesters and polyurethanes, but it is a useful tool for comparison of the fragmentation mechanisms. The detection of singly saturated species in PBA, PUs, and transesterified PUs suggests that intramolecular ester exchange to produce cyclic fragments and short linear oligomers is the dominant mode of fragmentation for the PBAs and PUs, regardless of the identity of the terminal group ($CF_3C{=}O-$ versus $HO(CH_2)_4O-$). An additional justification for the cyclization mechanism is that cationization should occur more readily for cyclic polyesters, compared with linear chains. The functional groups in the polyester fragments should coordinate easily to the metal cation, similarly to what occurs for crown ethers.

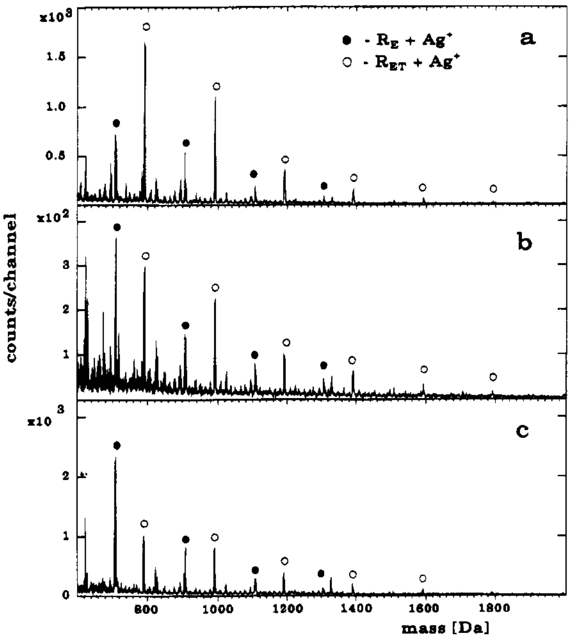


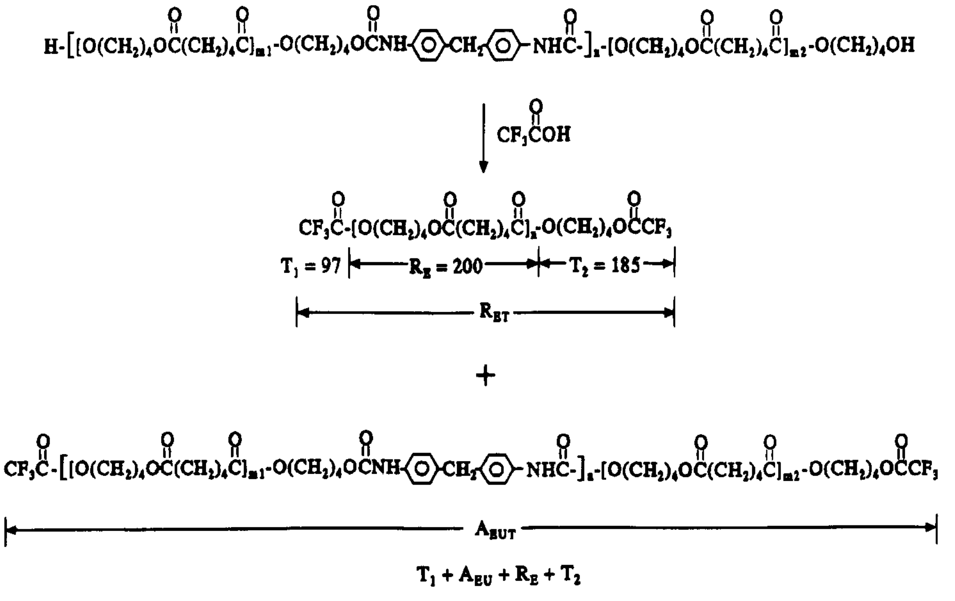
Figure 8. TOF-SIMS spectra of Transesterified Polyurethane [4,4,1] with M_n (a) 14 000, (b) 39 000, (c) 48 000. Key: (●) (R_E + $Ag)^+$, (○) (R_{ET} + $Ag)^+$.

4. Conclusions

TOF-SIMS analysis of poly(butylene adipate) samples produced spectra containing oligomer ions and fragments corresponding to cyclization via intramolecular ester exchange. These cyclic fragments were also observed in the spectra of polyurethane [4,4,1] samples, along with cyclic ester–urethane fragments. The mass of the diisocyanate group within the polyurethane could be determined from the mass difference between the two major fragment-ion series in the spectrum. In general, only limited fragmentation within ester or urethane repeat units was observed.

Although direct molecular weight determinations were not possible, the sample molecular weight for both the polyester and polyurethane samples could be esti-

Scheme 3. Transesterification of Polyurethane [4,4,1]



mated from the relative intensity of the cyclic repeat unit series ions to the linear oligomer ions. Additionally, transesterification of polyesters and polyurethanes using trifluoroacetic acid was found to selectively cleave bonds between polyester repeat units in both types of polymers. The spectra of transesterified polyurethanes followed the same trend as the unreacted polyurethanes, with the relative intensity of the R_E fragments to the $CF_3C{=}O-$ terminated fragments changing when the sample molecular weight was varied.

The fragmentation mechanisms of polyesters and polyurethanes, which are synthesized by stepwise condensation reactions, appear to be quite different from the fragmentation mechanisms of polymers produced by ionic or radical polymerization. Rather than random homolytic chain cleavages, fragmentation occurs via stepwise cyclizations, or, in essence, "depolymerization". Further investigations will be conducted to determine if the cyclization mechanism is generally applicable to other classes of condensation polymers.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-9022135. L.R.H.C. thanks Dow Chemical Co. for a graduate fellowship.

References and Notes

(1) Bletsos, I. V.; Hercules, D. M.; van Leyen, D.; Benninghoven, A.; Karakatsanis, C. G.; Rieck, J. N. *Anal. Chem.* **1989**, *1*, 2142–2149.
(2) Bletsos, I. V.; Hercules, D. M.; van Leyen, D.; Benninghoven, A.; Karakatsanis, C. G.; Rieck, J. N. *Macromolecules* **1990**, *23*, 4147–4163.
(3) Montaudo, G.; Puglisi, C. In *Developments in Polymer Degradation VII*; Grassie, N., Ed.; Elsevier Applied Science: London, Chapter 2, pp 35–79.
(4) Bletsos, I. V.; Hercules, D. M.; Greifendorf, D.; Benninghoven, A. *Anal. Chem.* **1985**, *57*, 2384–2388.
(5) Hittle, L. R.; Hercules, D. M. *Surf. Interface Anal.* **1994**, *21*, 217–225.
(6) Bletsos, I. V.; Hercules, D. M.; van Leyen, D.; Hagenhoff, B.; Niehuis, E.; Benninghoven, A. *Anal. Chem.* **1991**, *63*, 1953–1960.
(7) Lattimer, R. P.; Hansen, G. E. *Macromolecules* **1981**, *14*, 776–780.
(8) Nohmi, T.; Fenn, J. B. *J. Phys. Chem.* **1992**, *114*, 3241–3246.
(9) Bahr, U.; Deppe, A.; Karas, M.; Hillenkamp, F. *Anal. Chem.* **1991**, *63*, 1463–1466.
(10) Danis, P. O.; Karr, D. E. *Org. Mass Spectrom.* **1993**, *28*, 923–925.
(11) Hagenhoff, B.; Benninghoven, A.; Barthel, H.; Zoller, W. *Anal. Chem.* **1991**, *63*, 2466–2469.
(12) Hittle, L. R.; Altland, D. E.; Proctor, A.; Hercules, D. M. *Anal. Chem.* **1994**, *66* (14), 2302–2312.
(13) Dong, X.; Hercyles, D. M. Proceedings of the 42nd ASMS Conference on Mass Spectrometry and Allied Topics, Chicago, IL, 1994, p 530.
(14) Fowler, D. E.; Johnson, R. D.; van Leyen, D.; Benninghoven, A. *Anal. Chem.* **1990**, *62*, 2088–2092.
(15) Niehuis, E.; Heller, T.; Feld, H.; Benninghoven, A. *J. Vac. Sci. Technol. A* **1987**, *5* (4), 1243–1246.
(16) Niehuis, E.; van Veltzen, P. N. T.; Lub, J.; Heller, T.; Benninghoven, A. *Surf. Interface Anal.* **1989**, *14*, 135–142.
(17) Kim, Y.; Hercules, D. M. *Macromolecules* **1994**, *27*, 7855–7871.
(18) Zimmerman, P. A.; Hercules, D. M. *Anal. Chem.* **1993**, *65* (8), 983–991.
(19) Garozzo, D.; Guiffrida, M.; Montaudo, G. *Macromolecules* **1986**, *19*, 1643–1649.
(20) Foti, S.; Guiffrida, M.; Maravigna, P.; Montaudo, G. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1583–1598.
(21) Ballisteri, A.; Garozzo, D.; Guiffrida, M.; Montaudo, G. *Anal. Chem.* **1987**, *59*, 2024–2027.
(22) Semlyn, J. A. *Adv. Polym. Sci.* **1976**, *21*, 41–75.
(23) McLafferty, F. W. *Interpretation of Mass Spectra*; University Science Books: Mill Valley, CA, 1980; pp 201–205.

MA946308Q