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Structural Characterization of Model Polyester Polyurethanes Using Time-of-Flight Secondary Ion Mass Spectrometry

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ABSTRACT: Time-of-flight secondary ion mass spectra (TOF-SIMS) of a polyester and polyurethanes based on polyesters and diisocyanates were obtained from thin films cast from solution on silver substrates. Intact polyester or polyurethane oligomers and large fragments characteristic of the ester and ester–urethane blocks in polyurethanes, both cationized with Ag^+ and Na^+, were detected in the mass range m/z = 500–3300. The mass of the repeat unit of the polyester in a polyurethane can be determined from the spacing between oligomer or fragment peaks cationized with the same cation. The mass of the urethane can be determined by comparing fragments characteristic of ester and ester–urethane blocks consisting of the same number of repeat units and cationized with the same cation. The combined mass of the terminal groups can be determined from the mass difference between oligomer and fragment ions characteristic of the ester–urethane parts. The masses of unknown alcohol extenders in polyurethanes were determined from m/z values of fragment ions by subtracting the masses of ester and urethane repeat units and cation. The transesterification products of polyester polyurethanes and trifluoroacetic acid were identified from the spectra to be diesters of trifluoroacetic acid and the diol in the polyurethane; they consist of an integral number of ester repeat units with or without a urethane and an additional diol. Differences and similarities between various polyurethanes can be assessed by comparing their fragmentation patterns. Diols and diisocyanates can be identified by comparing fragments with or without a urethane and transesterification products.

Introduction

Polyurethanes (PUR's) are an important class of polymers. Because of the many formulations suitable for a wide variety of applications, PUR's are often difficult to characterize. Hydrolysis, infrared spectroscopy, and nuclear magnetic resonance spectroscopy have been used to determine functional groups in PUR's.[1-4] Pyrolysis mass spectrometry and pyrolysis chromatography mass spectrometry have been used to characterize many PUR's,[5,6] and PUR pyrolytic mechanisms have been proposed.[7] Various spectroscopic techniques used to characterize PUR's and other polymers have been reviewed in detail in previous papers.[8-10] These techniques can provide general information about functional groups in PUR's. More detailed characterization, however, can be difficult and time consuming, and in cases of complicated PUR formulations, standard PUR's must be prepared for comparison purposes. Therefore, the need for more definitive rapid and detailed structural characterization of PUR's still exists.

Successful structural characterization of PUR's includes identification of the repeat unit, its hydroxy and isocyanate components, and chain extenders, their sequence in

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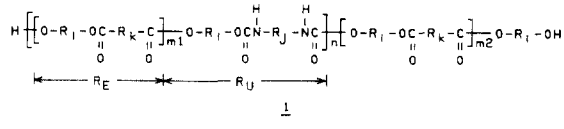
the PUR backbone, determination of the size of polyol or polyol–urethane blocks, and molecular weight distributions. Mass spectrometry has been used widely to study PUR's as well as other polymers. Research in this area has expanded lately, paralleling development of solid-state ionization sources. Some representative references are given.[11-13]

The utility of time-of-flight secondary ion mass spectra (TOF-SIMS) for structural characterization of various polymers has already been demonstrated.[8,9] Polymer fragments and intact oligomers composed of large numbers of repeat units have been observed up to m/z = 10 000. 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 combines good sensitivity and structural specificity for high masses, such that intact oligomers and large polymer fragments are detected, from which PUR's can be identified. Characterization of model polyurethanes (PUR-I's) has been reported in an earlier paper.[10] In the present report TOF-SIMS is used for the characterization of a polyester (PE) and polyurethanes (PUR-II's) prepared from polycondensation of PE's and diisocyanates. Large PUR-II and PE fragments and intact oligomers, both cationized with Ag^+ and Na^+, are detected in the mass range m/z = 500–3300. Fragments are characteristic of the ester for PE and the ester or ester–urethane blocks for PUR-II's. The mass of the repeat unit for PE and PUR-II's can be measured from the spacing between consecutive oligomer or fragment peaks in the spectrum or from m/z values of peaks, by accounting for the masses of known structures involved. The combined masses of the terminal groups can be determined from comparison between oligomers and fragments. The mass of the urethane part of a PUR-II can be obtained from comparison between fragments characteristic of ester and ester–urethane blocks, as can the sequence of PE blocks, diol extenders, and urethane repeat units. Unknown diol extenders were identified from fragmentation patterns in TOF-SIMS spectra of PUR-II's; products of transesterification also were identified. In summary, a single technique, namely TOF-SIMS, can provide rapid and detailed structural characterization of PURs based on polyesters and diisocyanates.

Experimental Section

I. Synthesis of PUR-II's. Twenty-six PUR-II's were prepared by using well-known polycondensation reactions for each of six PE's with each of four diisocyanates. The PE's were poly(ethylene adipate), poly(butylene adipate), poly(hexylene adipate), poly(ethylene azelate), poly(butylene azelate), and poly(hexylene azelate). The number-average molecular weight for each PE based on hydroxyl number was 500. The diisocyanates were 4,4′-diphenylmethane diisocyanate (MDI), 1,6-hexamethylene diisocyanate (HX), dicyclohexylmethane diisocyanate (RMDI) (94% 4,4′ and 6% 2,4′ isomers), and toluene diisocyanate (TDI) (80% 2,4 and 20% 2,6 isomers). Figure 1 shows the structures of PE's, $HOR_iOC(=O)R_kC(=O)R_iOH$, major isomers of diisocyanates used, $OCNR_jNCO$, and some typical PUR-II's. For identification purposes the PE's have been given indices i and k and the diisocyanates an index j. A PUR-II will be subsequently referred to as PUR(i,k,j). The general formula of PUR-II's is given by 1.



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Two sets of four PUR-II's having unknown diol extenders were examined, and the masses of the extender diols were obtained.

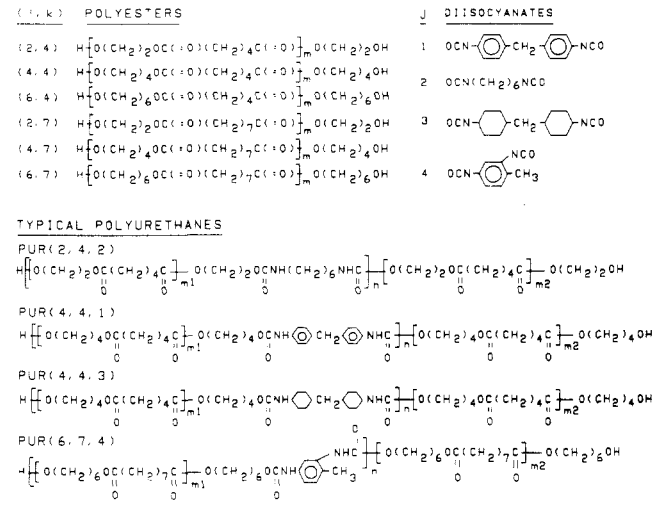


Figure 1. Structures of polyesters, major isomers of diisocyanates used, and some typical polyurethanes.

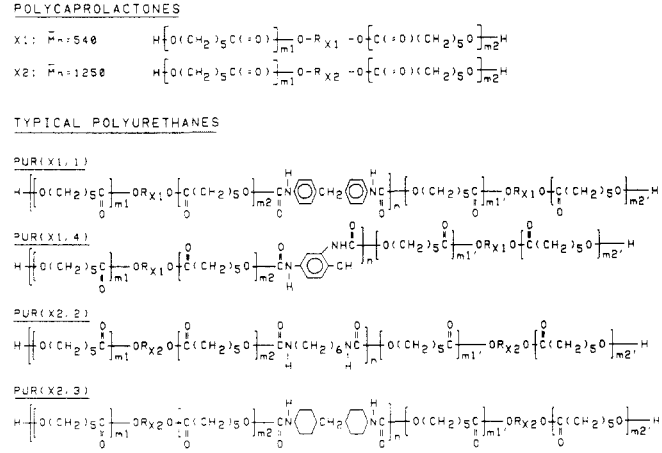
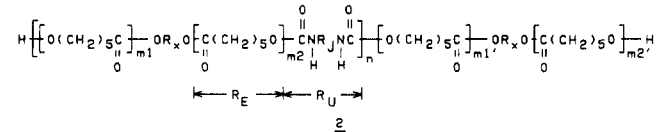


Figure 2. Structures of polycaprolactones having unknown diol extenders, and some typical polyurethanes.

These eight PUR-II's, identified in general as PUR(x_1,j) and PUR(x_2,j), were based on two polycaprolactones, PE(x_1) and PE(x_2), and MDI, HX, RMDI, and TDI. PE(x_1) and PE(x_2) have unknown diol extenders and number-average molecular weights 540 and 1250, respectively. The structures of PE(x_1) and PE(x_2) and some typical PUR(x_1,j) and PUR(x_2,j) are shown in Figure 2. The general formula of PUR(x_1,j) and PUR(x_2,j) is given by 2.



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Polyurethanes were prepared from diisocyanates and polyesters or polycaprolactones by heating the diol to 80 °C in a dried container, followed by addition of diisocyanate with stirring to give an average NCO/H ratio of 0.983 ± 0.004. The diisocyanates were all at room temperature at the time of addition to diol, except for MDI, which was melted at 41–42 °C and subsequently heated to 50 °C before addition. There was no catalyst used in the reactions. After it was stirred for 1 min, the reaction mixture was poured onto a Teflon-lined tray and cured for 30 min and 110 °C, followed by cooling to room temperature. Then polymer samples were collected for subsequent characterization using TOF-SIMS. Representative PE's and PUR's were also characterized by gel permeation chromatography.

II. Sample Preparation and Instrumentation. TOF-SIMS spectra of PUR-II's were obtained from thin polymer films cast from solutions of PUR-II's in N,N-dimethylformamide (DMF) on a silver substrate. TOF-SIMS spectra of poly-

(ethylene adipate) were obtained similarly. Transesterification of PUR-II's was carried out in trifluoroacetic acid (TFA) overnight. The concentrations of polymers in DMF and TFA solutions were in the range 1×10^{-2}–1×10^{-3} M based on molecular weights of poly(ethylene adipate) having one repeat unit and PUR(i,j,k) having $m_1 = m_2 = n = 1$ in 1. For unknown PUR's the concentrations were based on the molecular weights of PUR(x_1,j) and PUR(x_2,j) having $n = m_1 = m_2 = m_1' = m_2' = 1$ in 2, disregarding the unknown extenders R_x. A 1–5-μL quantity of each solution, corresponding to approximately 1–40 μg of polymer, was deposited on 100 mm² of a silver substrate, which had been previously cleaned by etching in nitric acid (20 vol %). After evaporation of the solvent, spectra of the polymers were obtained by using a TOF-SIMS instrument, which has been described in detail elsewhere.[14] The instrument has a resolution (M/ΔM) of 800. Peak location is better than ±1 amu at m/z = 1000 (by merging several spectra), but resolution of two peaks differing by 1 amu (one hydrogen) is limited to lower than m/z = 1000. All spectra were accumulated for 5 min.

The presence of low molecular weight oligomers in PUR's and PE's was determined by gel permeation chromatography (GPC). PUR and PE samples were dissolved in tetrahydrofuran (THF). A 100-μL aliquot of a 1% solution in THF was injected onto four Ultrastyragel columns (i.e., 10^4, 10^3, 500, and 500 Å) at a flow rate 1.0 mL of THF/min. A refractive index detector was used, and the calibration was based on polystyrene standards.

Results and Discussion

I. TOF-SIMS Spectra. TOF-SIMS spectra of the polymers studied were obtained in the medium mass range m/z = 500–3300. The peaks in the spectra can be resolved into three well-defined series: oligomer, repeat, and fragmentation series. Desorption of intact PE and PUR-II oligomers generates the oligomer series. The repeat unit series is due to fragments consisting of an integral number of ester (R_E) or a combination of ester (R_E) and urethane (R_U) repeat units; R refers to the repeat unit, E and U refer to ester and urethane, respectively (see 1 and 2), and EU refers to ester–urethane. PUR-II fragments consisting of an integral number of ester repeat units, with or without a urethane repeat unit, plus a smaller part of an additional ester repeat unit, give rise to the fragmentation series.

Consecutive peaks due to intact oligomers of PE's or PUR-II's in TOF-SIMS spectra are spaced apart by the mass of one ester repeat unit R_E. Cleavages occurring at the same bonds in consecutive repeat units along the polymer backbone produce fragments that differ by one repeat unit. The spacing between such fragments or oligomers defines the mass of one repeat unit. Within a spacing of one repeat unit there are pairs of peaks having a mass difference of $\Delta m/z$ = 84, because oligomers and fragments are cationized with both Ag^+ and Na^+. Peaks at m/z values equal to an integral multiple of the repeat unit, plus the mass of the metal cation, comprise the repeat unit series. Peaks appearing on the high mass side of the repeat unit series, at m/z values equal to an integral number of repeat units, plus some mass to account for the combined masses of the two terminal groups, plus the mass of the metal cation, comprise the oligomer series. Peaks of the fragmentation series appear on either side of the peaks of the repeat unit series. The mass differences between fragments of the repeat unit and fragmentation series correspond to groups typical of the ester and urethane functions (e.g., CO, CO + O, etc.). With use of these characteristic features of the TOF-SIMS spectra of PUR-II's, peaks can be easily grouped into their respective series.

TOF-SIMS spectra of a PE, PUR-II's, and unknown PUR-II's will be presented. Interpretation of the spectra will focus on information they provide for structural characterization of these polymers.

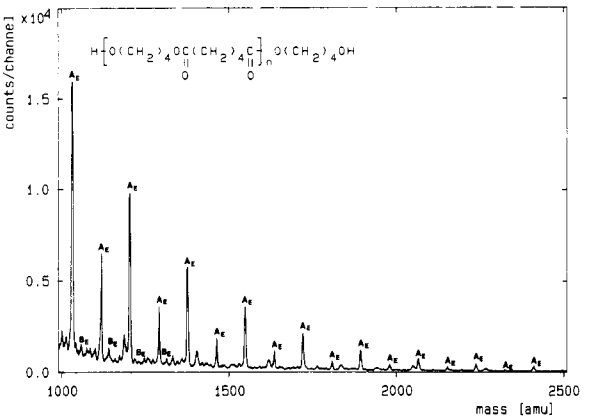
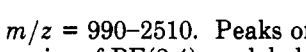


Figure 3. TOF-SIMS spectrum of poly(ethylene adipate) in the mass range m/z = 990–2510. The oligomer series is identified by A_E and the repeat unit series by B_E.

A. Poly(ethylene adipate). Figure 3 shows the TOF-SIMS spectrum of poly(ethylene adipate), PE(2,4) (3), in



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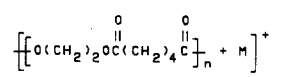
the mass range m/z = 990–2510. Peaks of the oligomer and repeat unit series of PE(2,4) are labeled A_E and B_E, respectively, in Figure 3. The spectrum is dominated by the oligomer series, which extends to m/z = 3300; a listing of the peaks and their relative intensities is available as supplementary material. Peaks in the repeat unit series are of lower intensity than the oligomer series. The repeat unit series extends to m/z = 1300. The prominence of the oligomer series indicates that desorption of intact oligomers of PE(2,4) occurs more readily than fragmentation. Oligomer distributions of PE prepolymers will be presented in a subsequent paper. Fragments of the repeat unit series are produced by cleavage at every other ester bond and consist of an integral number of PE(2,4) repeat units. The structure of repeat unit fragment B_E is given in 4 where M = Ag and Na. The fragmentation series is not observed for PE(2,4).



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The spacings between consecutive peaks involving the same cation in the oligomer or repeat unit series correspond to the mass of the repeat unit of PE(2,4). For example, in the oligomer series of PE(2,4) for M = Na, the mass difference between peaks for n = 6 at m/z = 1117 and n = 7 at m/z = 1289 is equal to $\Delta m/z$ = 172, the mass of the repeat unit of PE(2,4). The mass difference between oligomer and fragment peaks of the repeat unit series, both consisting of the same number of repeat units and involving the same metal cation, corresponds to the combined masses of the terminal groups of PE(2,4). For example, the mass difference between the A_E peak at m/z = 857 and 859 (n = 4, M = Ag) and the B_E peak at m/z = 795 and 797 (n = 4, M = Ag) is equal to $\Delta m/z$ = 62, the combined masses of H and $O(CH_2)_2OH$.

B. PUR-II's. The oligomer, repeat unit, and fragmentation series appear in the spectra of PUR-II's up to m/z = 2500. The oligomer series consists of peaks due to intact oligomers of PUR-II and the corresponding PE, both cationized with Ag^+ and Na^+. Fragments in the repeat unit series are characteristic of the ester and ester–

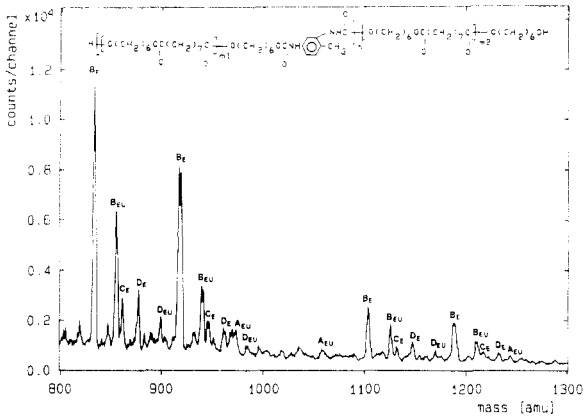


Figure 4. TOF-SIMS spectrum of PUR(6,7,4) in the mass range m/z = 800–1300. The oligomer series is identified by A_{EU}, the repeat unit by B_E and B_{EU}, and the fragmentation series by C_E, D_E, and D_{EU}.

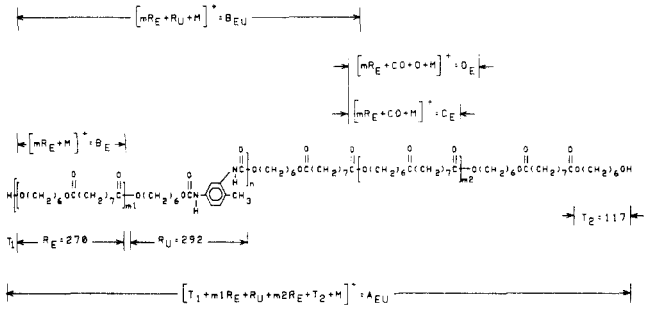


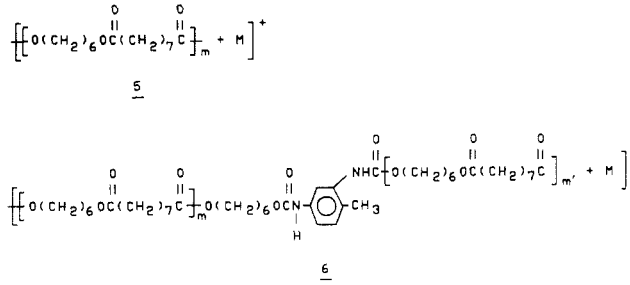
Figure 5. Structures of oligomers A_{EU} and fragments B_E, B_{EU}, C_E, D_E, and D_{EU} observed in the TOF-SIMS spectrum of PUR-(6,7,4).

urethane blocks. The fragmentation series of PUR-II's is due to fragments that consist of an integral number of PE repeat units, plus part of an additional PE repeat unit, with or without a urethane repeat unit.

Figure 4 shows a section of a TOF-SIMS spectrum for PUR(6,7,4) in the mass range m/z = 800–1300. Figure 5 shows structures of PUR(6,7,4) oligomers or fragments associated with peaks in the spectrum. The oligomer series is identified by A_{EU}. The repeat unit series are labeled B_E and B_{EU} for fragments characteristic of the ester and ester–urethane blocks of PUR(6,7,4), respectively. Peaks labeled C_E, D_E, and D_{EU} identify the fragmentation series characteristic of the ester and ester–urethane blocks of PUR(6,7,4), respectively. The structure of the PUR-(6,7,4) oligomer, bonds at which cleavage occurs, and resulting fragments of the repeat unit and fragmentation series are shown in Figure 5. Detailed listings of the oligomer, repeat unit, and fragmentation series, along with their relative intensities, are available as supplementary material.

1. Oligomer Series. In general, for PUR-II's the repeat unit and fragmentation series are more intense than the oligomer series, indicating that fragmentation for PUR-II's is more pronounced than desorption of intact oligomers. Peaks in the oligomer series correspond to oligomers of PUR-II's; in some cases oligomers of unreacted PE's were observed. PUR-II oligomers observed are characteristic of the low end of the molecular weight distribution. Presence of low molecular weight oligomers was expected from synthetic considerations, and it was verified by GPC as described in the Experimental Section. An oligomer series was not observed for all PUR-II's studied. The number of PE repeat units (i.e., m_1 + m_2 in **1**) in PUR-II oligomers can be determined for those PUR-II's for which an oligomer series is observed. The value of $m_1 + m_2$ (see Figure 5) is indicative of the size of the PE blocks in PUR-II oligomers.

2. Repeat Unit Series. In PE blocks of PUR-II's cleavages occur at every other ester bond, such that B_E fragments consist of an integral number of PE repeat units. The B_{EU} fragments could be produced by cleavages either at an ester and a urethane bond or at two ester bonds; both will produce fragments that consist of an integral number of PE repeat units, plus one urethane repeat unit. Considering the abundance of ester vs urethane bonds in PUR-II's, it is more likely that B_{EU} fragments are produced from cleavage at two ester bonds on either side of a urethane (see Figure 5). The structures of B_E and B_{EU} fragments for PUR(6,7,4) are given in **5** and **6**, respectively.



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The repeat unit series is observed for all PUR-II's studied and is the most intense series in TOF-SIMS spectra of PUR-II's. The B_E peaks are more intense than the B_{EU} peaks, reflecting the relative abundance of ester vs urethane repeat units in the PUR-II backbone. In general, intensities of Ag^+- or Na^+-cationized fragments decrease with increasing m/z values; their relative intensities vary, depending on the availability of Ag^+ and Na^+ and the stability of cationized species. Intensities of the repeat unit peaks for PUR-II(4,4,1) at ca. m/z = 400 are as much as 8760 times higher than corresponding peaks at m/z = 2400. The noise level at m/z = 2400 is approximately 10 counts/channel; thus, even at high m/z values, because of the low noise level, relatively weak peaks (e.g., 30 counts/channel) can be distinguished. Some peak overlap occurs at high m/z values; typical resolution of the instrument is approximately $m/\Delta m$ = 700. This problem is solved with the new reflector type TOF-SIMS instrument having a resolution up to $m/\Delta m$ = 13 000.[15]

Both B_E and B_{EU} repeat unit fragments consist of an integral number of PE repeat units; therefore, the spacing between consecutive peaks in repeat unit series, involving the same metal cation, is equal to the mass of one PE repeat unit. For example, for **5** and M = Na the mass difference between m = 4 at m/z = 1103 and m = 3 at m/z = 833 is 270 amu, the mass of the repeat unit of PE(6,7). The mass of the urethane repeat unit can be obtained from m/z values of B_{EU} peaks by subtracting the masses of PE repeat units and metal cation. The mass difference between B_{EU} and B_E fragments consisting of the same number of PE repeat units, after subtraction of the mass of metal cation, corresponds also to the mass of the urethane repeat unit. For example, the mass difference between **6** ($m1$ + $m2$ = 2 and M = Ag at m/z = 939 and 941) and **5** (m = 2 and M = Na at m/z = 563), afer subtraction of the masses of the metal cations, is equal to 292 amu, the mass of the urethane repeat unit of PUR-(6,7,4).

3. Fragmentation Series. Fragments of the fragmentation series are produced by bond cleavages occurring in PE blocks of PUR-II's and consist of an integral number of PE repeat units, with or without a

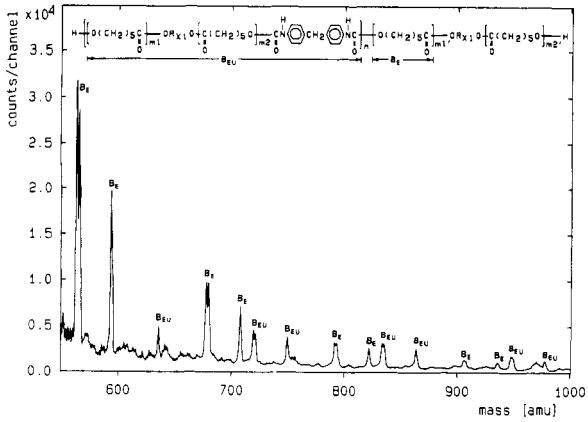

Figure 6. TOF-SIMS spectrum of unknown PUR(x_1,1) in the mass range m/z = 550–1000. Peaks of the repeat unit series characteristic of polycaprolactone and polycaprolactone–urethane blocks of PUR(x_1,1) are identified by B_E and B_{EU}, respectively.

urethane repeat unit, plus a smaller part of an additional PE repeat unit, which allows distinction between them. This type of fragmentation is shown for PUR(6,7,4) in Figure 5. Specifically, this smaller part of a PE repeat unit is CO in C_E fragments, CO and O in D_E, and O in E_E. The D_{EU} and E_{EU} fragments consist of an integral number of PE repeat units plus one urethane repeat unit and CO + O or O, respectively. Therefore, C_E, D_E, and E_E, and D_{EU} and E_{EU} fragments differ from their corresponding B_E and B_{EU} fragments by CO, CO + O, and O, and CO + O and O, respectively (see Figure 5).

II. Unknown PUR-II's. Two sets of four PUR-II's based on two polycaprolactones having unknown extender alcohols and different number-average molecular weights were examined. The unknown PUR-II's were prepared from polycaprolactones and diisocyanates, as described in the Experimental Section. The extender alcohols were known to the synthetic chemist but unknown to the analyst of TOF-SIMS data. Masses of the unknown extender alcohols were determined from TOF-SIMS spectra.

A TOF-SIMS spectrum of unknown PUR(x_1,1) in the mass range m/z = 550–1000 is shown in Figure 6. The repeat unit series is the most prominent in the spectra of unknown PUR-II's. Peaks due to B_E fragments, 7, characteristic of the ester part of polycaprolactone, are more intense than peaks due to B_{EU} fragments, 8, which are characteristic of the polycaprolactone–urethane parts of PUR(x_1,1). Data obtained for eight unknown PUR-II's are available as supplementary material.

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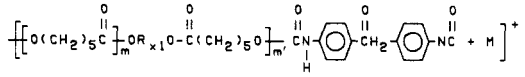

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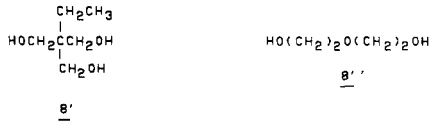
Spacings between consecutive B_E or B_{EU} peaks, involving the same metal cation, correspond to the mass of the repeat unit of polycaprolactone. Therefore, determination of the masses of the unknown extender alcohols from spacings between consecutive B_E or B_{EU} peaks is not possible. Unknown alcohols, however, are parts of B_{EU} fragments, and their masses can be obtained from m/z values of B_{EU} peaks, after accounting for the masses of known parts in the B_{EU} fragments. For example, 8 of PUR(x_1,1), for m + m' = 3 and M = Na, gives rise to a peak at m/z = 749. After the masses of the urethane (i.e., 252), caprolactone repeat units (i.e., 114), and Na^+ (i.e., 23) are subtracted, the remainder $\Delta m/z$ = 132 amu is equal to the mass of the extender alcohol minus two hydrogens. The extender alcohol could be identified from a set of possible structures provided. The extender of PUR(x_1,1) is based on trimethylolpropane (8′). The same extender triol is found



8′ 8″

in PUR(x_1,2), PUR(x_1,3), and PUR(x_1,4). A similar procedure was followed to identify the extender alcohol in PUR(x_2,j)'s. For example, for PUR(x_2,2) the B_{EU} fragments with m + m' = 4 and M = Na give a peak at m/z = 753. Accounting for the masses of known caprolactone repeat units (i.e., 114), urethane (i.e., 170), and Na^+ (i.e., 23), the remainder at m/z = 104 corresponds to the mass of diethylene glycol (8″) minus two hydrogens.

To identify a PUR-II having a totally unknown structure would have been more difficult but not impossible. The mass of the ester repeat unit could be identified from the spacings between consecutive B_E and B_{EU} peaks. The mass difference between B_{EU} and B_E fragments consisting of the same number of ester repeat units and cationized with the same metal cation would correspond to the combined masses of urethane and extender alcohol. Identification of both the urethane and extender alcohol could be achieved if a limited set of possible structures was considered.

III. Transesterification of PUR-II's in Trifluoroacetic Acid. TOF-SIMS spectra of polymers are obtained from thin polymer films cast from polymer solutions on silver substrates. This approach is useful for polymers that are easy to dissolve, but it cannot be applied to insoluble polymers. TOF-SIMS spectra of neat polymers in the medium to high mass range, although difficult to obtain because of problems due to charging, have been reported.[16] A different way to deal with polymer insolubility is to use chemical reactions to break apart the backbone into smaller, soluble polymer segments, preferably greater than one repeat unit. The progress of such reactions can be monitored, and reaction products can be characterized by using TOF-SIMS.

Transesterification of PUR-I's in TFA produces diesters of TFA and diols in PUR-I's.[10] Transesterification of PUR-II's was carried out in TFA overnight. Products were identified from TOF-SIMS spectra of PUR-II thin films cast from TFA solutions to be diesters of TFA and diols of the PE's in PUR-II's. The diesters are characteristic of the ester and the ester–urethane blocks of PUR-II's and consist of an integral number of PE, or PE and urethane repeat units, and an additional diol.

Figure 7 shows a spectrum of the transesterification products of PUR(4,4,3) and TFA in the mass range m/z = 500–2500. Diester ions characteristic of ester blocks of PUR(4,4,3) are labeled T_E, while those characteristic of the ester–urethane blocks are labeled T_{EU}. Figure 8 shows the transesterification reaction of PUR(4,4,3) with TFA. The T_E ions are diesters of 1,4-butanediol and TFA and consist of an integral number of PE repeat units plus an additional 1,4-butanediol and two trifluoroacetates at the diol ends of the PE segments (see Figure 8a, T1). The T_{EU} ions are diesters of 1,4-butanediol and TFA and consist of an integral number of PE repeat units, a urethane repeat

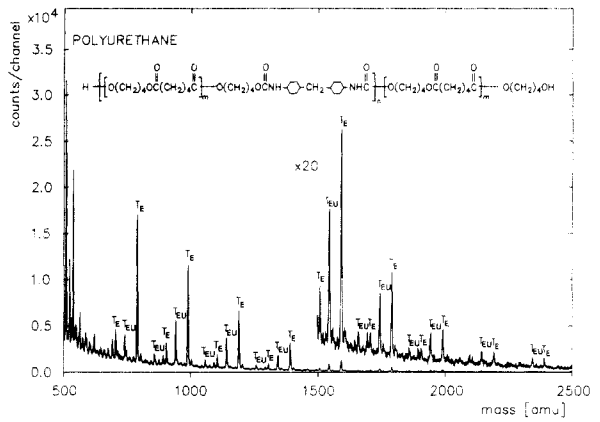


Figure 7. TOF-SIMS spectrum of PUR(4,4,3) in trifluoroacetic acid in the mass range m/z = 500–2500. Peaks correspond to Ag^+- and Na^+-cationized diesters of trifluoroacetic acid and diols of PUR(4,4,3) characteristic of ester (T_E) and ester–urethane (T_{EU}) parts of PUR(4,4,3).

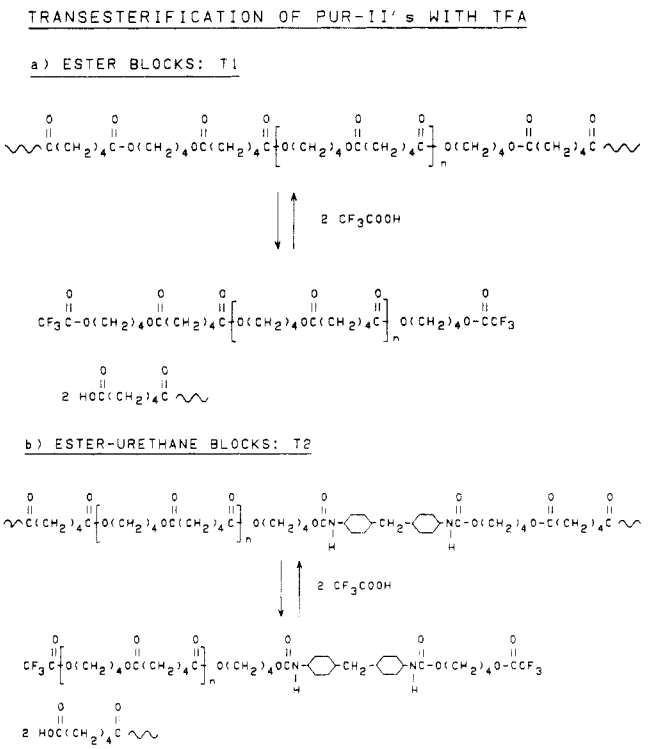
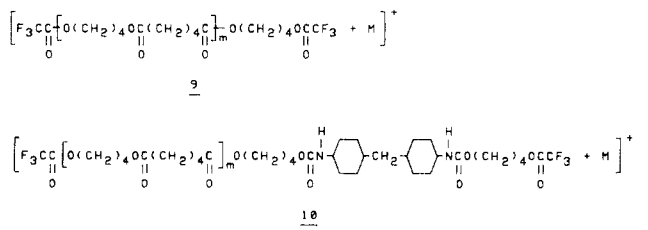


Figure 8. Transesterification of PUR(4,4,3) with trifluoroacetic acid: (a) ester blocks and (b) ester–urethane blocks.

unit, an additional diol, and two trifluoroacetates at the diol ends of PE segments of PUR(4,4,3) (see Figure 8b, T2). Both T_E and T_{EU} are cationized with Ag^+ and Na^+; their structures are given by **9** and **10**, respectively. A



9

10

listing of peaks in the transesterification spectra of PUR(4,4,1), PUR(4,4,2), PUR(4,4,3), and PUR(4,4,4) can be obtained from the supplementary material. The T_E peaks are more intense in the spectra than T_{EU}, indicating a greater abundance of ester repeat units than urethane repeat units in the PUR-II backbone. A prominent peak due to the diester of TFA and 1,4-butanediol appears at m/z = 282 in the spectra of all four PUR-II's.

Both T_E and T_{EU} consist of an integral number of PE repeat units. Therefore, the spacing between consecutive T_E or T_{EU} peaks involving the same cation corresponds to the mass of the repeat unit of PE. For example, for **9**, M = Na, the difference between m = 4 at m/z = 1105 and m = 3 at m/z = 905 is equal to $\Delta m/z$ = 200, the mass of the repeat unit of PE(4,4). The spacing between consecutive T_E and T_{EU} peaks, consisting of the same number of PE repeat units and involving the same cation, corresponds to the mass of the urethane repeat unit. For example, the difference between peaks for **10** (M = Ag, m = 2 at m/z = 1141 and 1143) and **9** (M = Ag, m = 2 at m/z = 789 and 791) is equal to $\Delta m/z$ = 352 amu, the mass of the repeat unit of the urethane, based on 1,4-butanediol and RMDI.

Transesterification of PUR's in TFA occurs at ester bonds and becomes evident from diesters detected in TOF-SIMS spectra. Transesterification can be used to selectively cleave ester bonds of insoluble PUR's, making them soluble and thus accessible to TOF-SIMS characterization. Similarly, other reactions can be used to cleave specific bonds of intractable polymers or modify polymers by incorporating desirable chemical functions in the backbone. The feasibility and progress of such reactions can be monitored by using TOF-SIMS.

IV. Comparison between PUR-II's. Structural information obtained from TOF-SIMS spectra of individual PUR-II's can be used to assess similarities and differences between them. Depending on which polymer fragments are compared, structural characteristics of the ester or urethane parts of PUR-II's can be obtained. If the spacings between consecutive B_E peaks involving the same metal cation are the same for two or more PUR-II's, then the esters of the PUR-II's must be the same. The spacing corresponds to the mass of the PE repeat unit. Similarly, for two or more PUR-II's, if peaks due to B_E fragments consisting of the same number of PE repeat units and involving the same metal cation appear at the same m/z values, then the esters of PUR-II's must be the same. For example, B_E peaks of PUR(4,4,1), PUR(4,4,2), PUR(4,4,3), and PUR(4,4,4) (Na^+-cationized) appear at m/z = 423, 623, 823, ..., etc., with a spacing equal to $\Delta m/z$ = 200. Therefore, these four PUR-II's are based on the same PE, namely PE(4,4). The B_E peaks of PUR(6,7,4) (Na^+-cationized) appear at m/z = 563, 833, 1103, ..., etc., with a spacing equal to $\Delta m/z$ = 270. PUR(4,4,4) and PUR(6,7,4) have different spacings between consecutive B_E peaks; therefore, PUR(4,4,4) and PUR(6,7,4) are not based on the same PE. Specifically, PUR(6,7,4) is based on PE(6,7).

The mass difference between B_{EU} and B_E fragments consisting of the same number of PE repeat units corresponds to the mass of the urethane in PUR-II's. If for two or more PUR-II's mass differences between B_{EU} and B_E fragments consisting of the same number of PE repeat units are the same, then the urethanes of the PUR-II's must be the same. For example, the difference between **6** ($m + m'$ = 3, M = Na) at m/z = 1125 and **5** (m = 3, M = Na) at m/z = 833 is 292 amu, which corresponds to the mass of the urethane of PUR(6,7,4). The reverse is true also; that is, if mass differences between B_{EU} and B_E fragments consisting of the same number of PE repeat units are not the same for two or more PUR-II's, then the urethanes in the PUR-II's must differ.

The mass difference between T_E diesters and B_E fragments consisting of the same number of PE repeat units, after accounting for the two trifluoroacetates in T_E, is equal to the mass of the diol in the ester, minus two hydrogens. Therefore, if for two or more PUR-II's the mass differences between T_E diesters minus the masses of two trifluoroacetates and B_E fragments consisting of the same number of PE repeat units are the same, then the diol in the ester parts of PUR-II's must be the same. The mass differences correspond to the mass of the diol minus two hydrogens. For example, the differences between m/z = 905 and m/z = 623 for PUR(4,4,3) T_E and B_E peaks, respectively, where m = 3 and M = Na, and the corresponding peaks of PUR(4,4,4) are equal to $\Delta m/z$ = 88, after subtraction of the masses of two trifluoroacetates from T_E. This means that the diols of the esters in PUR(4,4,3) and PUR(4,4,4) are the same, namely 1,4-butanediol. The same also holds true for mass differences between T_{EU} and B_{EU}. The reverse is true for mass differences between both T_E and B_E and T_{EU} and B_{EU} of PUR-II's.

The mass difference between B_{EU} fragments and T_E diesters, consisting of the same number of repeat units after accounting for the two trifluoroacetates in T_E, is equal to the mass of the diisocyanate in the urethane parts of PUR-II's plus two hydrogens. If for two or more PUR-II's the mass differences between T_E diesters minus the masses of two trifluoroacetates and B_{EU} fragments consisting of the same number of repeat units are the same, then the diisocyanates of the PUR-II's must be the same. The mass difference between B_{EU} and T_E, after subtraction of the masses of trifluoroacetates from T_E, corresponds to the mass of diisocyanate plus two hydrogens. The reverse is true also. For example, for PUR(4,4,2) the difference between B_{EU} ($m + m'$ = 2, M = Ag at m/z = 765 and 767) and T_E (m = 2, M = Ag at m/z = 789 and 791) is equal to $\Delta m/z$ = 170, after subtraction of the masses of the trifluoroacetates from T_E. Similarly, for PUR(4,4,4) the difference between B_{EU} ($m + m'$ = 2, M = Ag at m/z = 771 and 773) and T_E (m = 2, M = Ag at m/z = 789 and 791) is equal to $\Delta m/z$ = 176, after subtraction of the masses of the trifluoroacetates from T_E. The mass differences between B_{EU} and T_E for PUR(4,4,2) and PUR(4,4,4) are not the same; therefore, their diisocyanates differ. Specifically, for PUR(4,4,2) the difference of 170 amu corresponds to the mass of HX plus two hydrogens, while for PUR(4,4,4) the difference of 176 amu corresponds to the mass of TDI plus two hydrogens.

Conclusions

TOF-SIMS is a viable technique for rapid and detailed structural characterization of PUR-II's based on polyesters and diisocyanates. TOF-SIMS spectra of PUR-II's are obtained in a matter of a few minutes and extend over a wide mass range (e.g., m/z = 0–3500) in which intact oligomers and fragments, consisting of a large number of repeat units, are observed. The structural characteristics of polymer backbone are retained, and, therefore, accurate information about the repeat unit and its sequence in the backbone can be obtained. The mass of the ester repeat unit in PUR-II's is determined from spacings between consecutive oligomer or fragment peaks. Comparison of fragmentation patterns in a spectrum allows determination of the masses of the urethane repeat unit and terminal groups. The structures of unknown extender diols in PUR-II's based on polycaprolactones and diisocyanates were determined from m/z values of fragment peaks and the structure of the fragments.

Transesterification products of PUR-II's in TFA were identified from TOF-SIMS spectra to be diesters of TFA and PUR-II diols. Diesters produced from transesterification of PUR-II's with TFA consist of a large number of PE repeat units with or without a urethane repeat unit, an additional diol, and two trifluoroacetates. Comparisons between diesters and fragments of the same PUR-II allow determination of the diol and diisocyanate of the ester and urethane parts. Comparisons between fragments of different fragmentation patterns and transesterification products for various PUR-II's allow assessment of similarities and differences between them.

In summary, TOF-SIMS is a powerful new technique for definitive structural characterization of PUR-II's, comparisons between various PUR-II's to assess structural similarities or differences, and monitoring of specific polymer reactions such as transesterification with identification of the reaction products.

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Supplementary Material Available: Tables of oligomer, repeat unit, and fragmentation series of various polyester polyurethanes (30 pages). Ordering information is given on any current masthead page.

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Registry No. TFA, 76-05-1; PUR(6,7,4), 128709-74-0; PUR(4,4,3) (copolymer), 32875-03-9; poly(ethylene adipate), 24938-37-2; poly(ethylene adipate) (SRU), 24937-05-1.