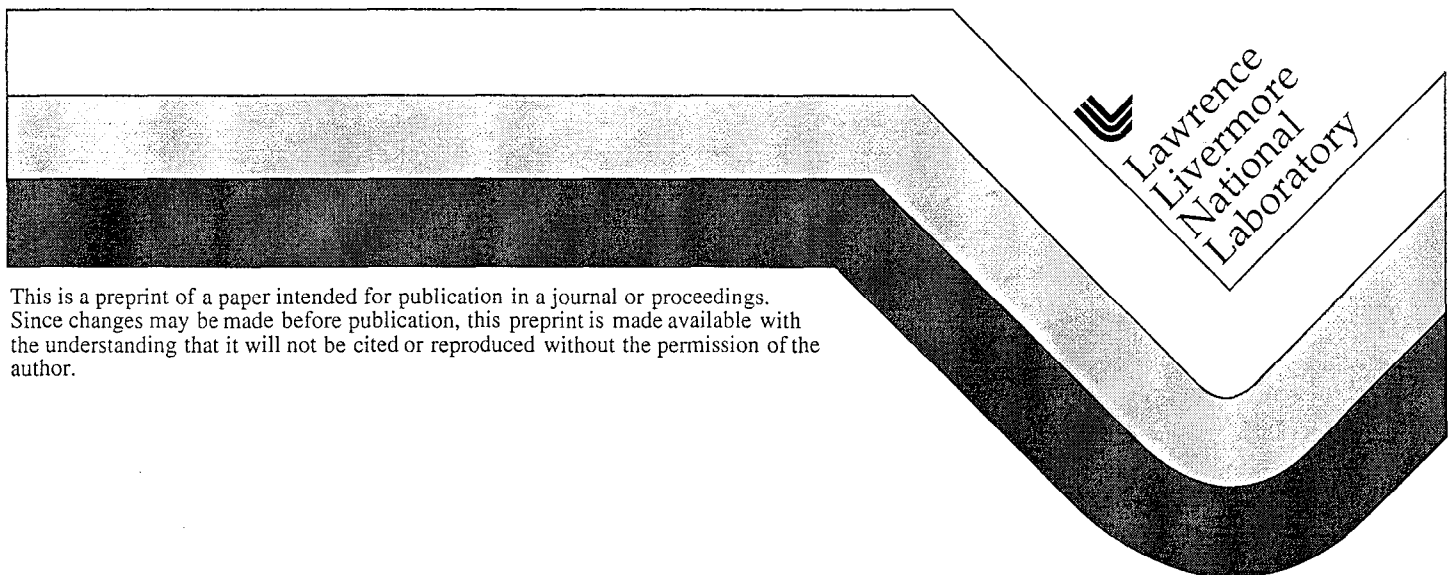# MALDI Analysis of Estane Degradation

George E. Overturf III
James D. LeMay
Bobby Russell
William Nonidez
Jimmy Mays
Helen Ji Haining
E.M. Kober

March 26, 1999

MALDI Analysis of Estane Degradation (U)

George E. Overturf III, James D. LeMay
Lawrence Livermore National Laboratory

Bobby Russell
Mason & Hangar Pantex Plant

William Nonidez, Jimmy Mays, Helen Ji Haining
University of Alabama, Birmingham

E. M. Kober
Los Alamos National Laboratory

Introduction

Estane is a polyester polyurethane used as a binder for plastic-bonded explosives (PBX). This paper examines the use of size exclusion chromatography (SEC) and matrix assisted laser desorption ionization (MALDI) to look at the low molecular weight (MW) degradation products obtained from the deliberate hydrolysis of Estane.

Estane 5703, which is manufactured by B. F. Goodrich, is used as a binder for the high explosives PBX-9501 and LX-14. Los Alamos National Laboratory's surveillance community has noted a subtle reduction in the MW of Estane in fielded PBX-9501 and significant degradation of Estane occurring in their bulk reserve PBX-9501. The structure for Estane 5703 is given in Figure 1.
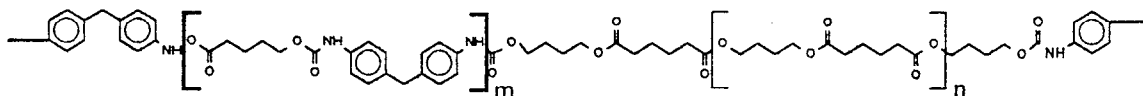
Figure 1. Chemical structure for Estane 5703.

A possible mechanism for the MW loss is through the hydrolysis of the ester "soft" segment. Pantex[1] performed a study to model MW changes due to hydrolysis of the ester segment over a range of temperatures and humidities. Molecular weights were measured SEC relative to polystyrene (PS) standards. Figure 2 shows the chromatograms for neat Estane samples exposed to high humidity for varying periods of time.

One of the goals of this study was to identify the low MW products seen in the badly-decomposed sample (far right-hand chromatogram). Unfortunately, SEC is inherently poor in accurately measuring low MW oligomers whether by light scattering or viscometry[2] detection.

Our work focuses on the use of a relatively new detection technique, MALDI, to identify these peaks. MALDI can yield m/z values within 1 amu. Used in conjunction with SEC, each eluted slice becomes a mass spectral "fingerprint" of the separated component(s).

Figure 2. SEC chromatograms (differential refractometer response vs. column retention time, mL) for Estane samples (left to right): control, 0.5 mo., 1 mo., and 2 mo. @ 90°C.
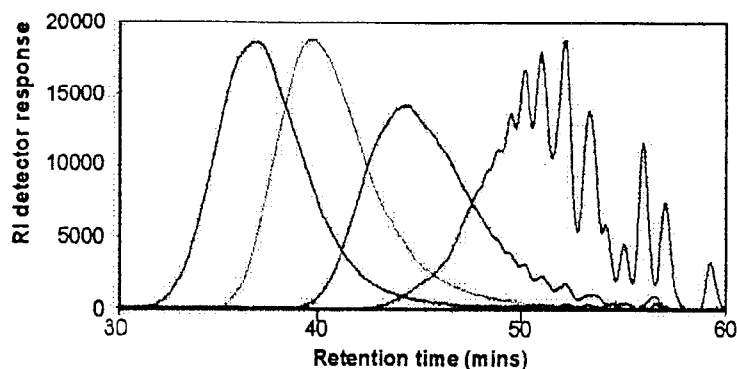
In the time-of-flight (TOF) spectrometer, ions are accelerated under fixed potential conditions from a specific point at a specific starting time. As the ions drift towards the detector they are separated according to their mass-to-charge ratios where the lighter ions are accelerated more quickly. The typical mass "window" available from the TOF detector is ~20,000 amu. The main benefit of TOF spectrometry is its ability to shift this window to much higher MWs than can be reached by quadrapole mass spectrometers.

Polymer is introduced into the TOF spectrometer by laser ablation of a matrix material that contains dilute quantities of the polymer. The matrix must be able to absorb strongly near the wavelength of the laser, share some common solvent with the polymer, and be able to impart a charge to the polymer upon laser ablation.

The resulting mass spectra allows for exact MW determination of the degradation peaks seen in Figure 2 and, due to the low fragmentation, it provides parent masses for direct speciation.

Experimental

Materials: Trans-3-indoleacrylic acid (IAA) and potassium trifluoroacetate (KTFA) were purchased from Aldrich Chemical Co. and used without further purification as the matrix. Certified Grade tetrahydrofuran (THF) from Fisher Scientific Co. was used without further purification as the mobile phase for gel permeation chromatogrpahy (GPC) separations . Certified Grade THF that was distilled over sodium metal before use was used for sample and matrix preparation.

Samples: Estane 5703P (lot # 6EE3000SK1) aged in a test matrix of time (2 and 4 mo.) and temperature (75°C and 90°C) at 100% humidity. Historical binder samples were obtained by dissolution of the PBX into THF with occasional agitation by hand over a 24-hour period. Supernatent was removed from the standing solution and filtered using a 0.2μm PTFE luer-lock into a tared vial. The mass was obtained after evaporation and sufficient solvent added to make 0.05wt% solution.

Gel-permeation Chromatography: The SEC instrument is a Waters Model 515 GPC/RI system (~30°C) with two columns (Jordi-Gel mixed bed column and a 500 Jordi-Gel column with a mean permeability of 500Å). Nominal flow rate was 1.0mL/min and all injection volumes were 200 μL of ~5 mg/mL.

MALDI sampling: An Advantec SF-2120 Microfraction Collector (Interplate, Toyo Roshi International, Inc.) was used for sampling the effluent from the columns and to deposit the sample fractions onto the PerSeptive Biosystems PLT-100 sample plate for mass spectrometry (MS) analysis. The Interplate was connected in parallel with a Waters 410 Refractive Index Detector. Four fractions per minute were collected at 15 seconds per fraction.

Results

The acquired mass spectra were related to the elute degradation peaks seen in the most severely-degraded Estane (far right-hand chromatogram in Figure 2) which allowed for direct determination of the low MW peaks shown in Figure 3.

Identification of the chemical fragments responsible for these peaks was obtained by comparison with predictions of probable hydrolysis fragments. Polyester hydrolysis is acid or base catalyzed and creates an alcohol and a carboxylic acid as is shown in the reaction shown in Figure 4.
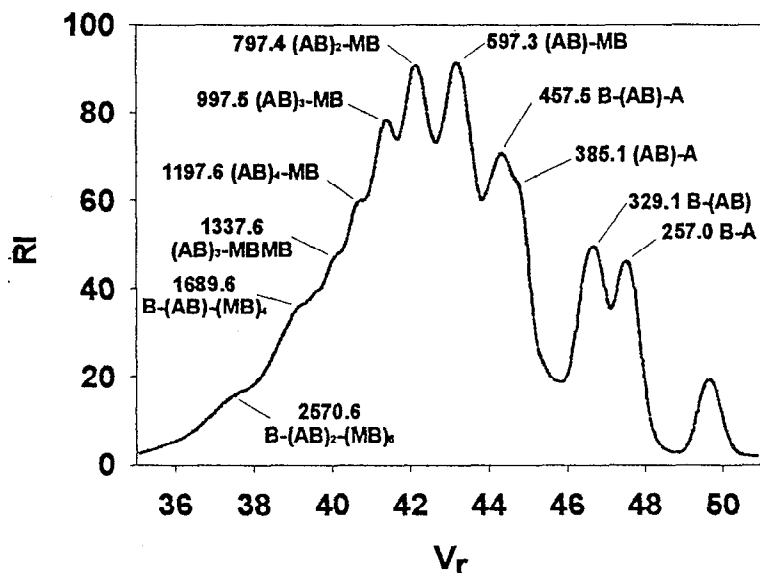

Figure 3. Chromatogram of hydrolyzed Estane (2 mos. at 75°C). Differential refractometer response versus retention volume in mL.
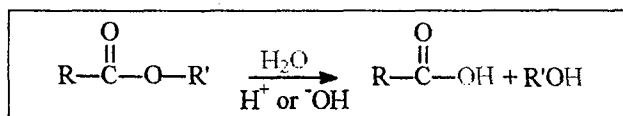

Figure 4. Hydrolysis reaction for polyesters.

To simplify the following discussion of hydrolysis fragments, we have assigned acronyms to segments of Estane based upon its synthetic precursors. Estane 5703 is a terpolymer that is formed by the addition reaction between a diisocyanate and two types of diol. The specific diisocyanate is methylenediphenyldiisocyanate (MDI or M). The first diol is simply butanediol (BDO or B) and the second is a diol terminated oligomer of polytetramethyleneadipate (A).

Upon examination of the structure of Estane 5703 in Figure 1, it is apparent the hydrolysis should occur principally in the ester "soft" segment with the production of fragments which are "butanediol-like" and "adipic acid-like". Further examination of potential structures based on decomposition fragments predicts several things. First, every "MDI-like" fragment must be attached to a "BDO-like" fragment. Second, every adipic acid-like fragment must be attached to a "BDO-like" fragment. Using the terminology defined above, the hydrolysis mechanism as well as the preceding two rules, one can suggest the probable hydrolysis fragments for Estane 5703 that are given in Table I.

Molecular masses were calculated for all the structures suggested by Table I and compared to the spectra. Matches were typically within 1 amu. These abbreviated structures have been applied to the low MW peaks in Figure 3.

The lower MW products in the chromatogram show an orderly progression towards the smallest polyester building blocks. However, the higher MW inflections cannot be described by a single species as is obvious in the broadening of the peaks at lower retention volumes. This is not surprising since SEC separates according to hydrodynamic volume, not species, and thus at higher MWs there may be several fragments which have the same hydrodynamic volume.

Closer examination of the mass spectra associated with the higher MW degradation peaks show that this retention volume is shared by MDI "hard segments" which are incrementally losing ester fragments (see Figure 5).

Table I. Predicted fragments from the hydrolysis of Estane 5703.

Not B terminated: $(AB)_n(MB)_mM_{n+m+1}$

$(AB)_n(MB)_{m-1}M$	abv. (A-M)
$(AB)_i(MB)_{m-1}M(BA)_j$	abv. (A-A)
$(MB)_i(AB)_n(MB)_jM$	abv. (M-M)

Singly B terminated: $A_nM_mB_{n+m}$

$(AB)_n(MB)_m$	abv. (A-B)
$B(AB)_n(MB)_{m-1}M$	abv. (B-M)
$B(AB)_n(MB)_mA$	abv. (B-A)

Doubly terminated: $A_nM_mB_{n+m+1}$

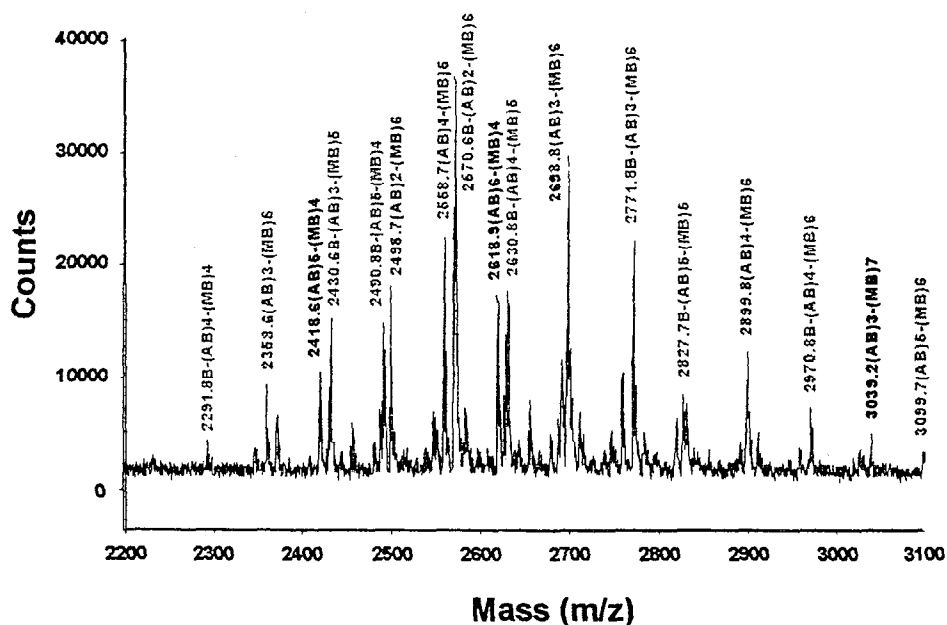|	
$B(AB)_n(MB)_m$	abv. (B-B)

Figure 5. Mass spectra of the Estane 5703 degradation peak around 2600 amu (~37.5 mL) composed of $B(AB)_n(MB)_m$ and $(AB)_n(MB)_m$ fragments where n = 4-6 and m = 4-7.

Discussion

After review of all the mass spectra, we observe that only short B-(BM)$_m$ (m$\leq$4) oligomers are found (B-B terminated). The small amount of M-B hydrolysis implies that the Estane was probably made with a shorter polyester macrodiol (MW ~1000) than previously thought. No (MB)$_m$ or (MB)$_m$M species (M-B and M-M terminated) were found, nor were simple degradation products thereof (CO$_2$ loss followed by amine oxidation). This strongly suggests that little M-B (urethane) hydrolysis is occurring although it might be followed by some reaction not yet considered. Only shorter lengths of AB oligomers were found (any termination) and these conform to the conditions where (AB)$_n$ with n $\leq$ 4; (AB)$_n$(MB)$_m$ with n$\leq$5, m=1-8. The presence of only shorter oligomers of AB is consistent with use of a shorter polyester macrodiol (MW ~1000); however, due to the severe nature of the degradation it is impossible to predict the initial chain length. Many oligomers with high hard segment content are found where (AB)$_n$-(MB)$_m$ with n=1-4 with M$\geq$4. The high concentration of hard segments may represent a preference in incorporating (MB)$_m$ at lower MWs.

Certain worthwhile lessons were learned about performing MALDI analyses. The first is that the method development time is often very long. This is because the matrix must be chosen and may not be appropriate for all MW fractions of the sample. Furthermore, the ratios of matrix to sample have to be worked out. If the ratio is too high or low, the matrix won't work. Additionally, the instrumental parameters must be correct and as these are a function of the matrix and MW, the settings may vary as MW changes.

The second is that actual analysis time is long and labor intensive. The matrix solution has to be added to the analyte after it is spotted on the sample plate. This is done by hand and is slow. Often high MW samples have to be redissolved and reapplied. Interpretation of spectra is often ambiguous due to the fact that different polymeric species may ionize in different ways. When this happens, additional experiments must be run to identify the ionization process.

Conclusions

SEC/MALDI has been successfully used to accurately measure the MW of hydrolysis degradation products from Estane 5703. Reasonable structure assignments have been made to the degradation products and several observations reported. Most of the low MW degradation peaks have been identified as ester hydrolysis fragments. The data suggest that the polyester macrodiol may be shorter than the ~2000 amu reported by the manufacturer. Experiments are ongoing to determine if hydrolysis occurs within the material's applied environment.

---

[1] Russell, B. Presented at the Enhanced Surveillance Program Annual Review, Albuquerque, NM, Mar. 1998.

[2] Chance, R. R.; Baniukiewica, S. P.; Mintz, D.; ver Strate, G.; Hadjichristidis, N. *Int. J. Polymer Analysis & Characterization*, 1995, *1*, 3-34.