INTRODUCTION

From a traditional perspective, mass spectrometry and polymer analysis appear to be incompatible. Mass spectrometry requires gas-phase ions for a successful analysis and polymers are composed of large, often entangled macromolecules that are not readily converted to gas-phase species. Despite these natural difficulties, mass spectrometry techniques have been developed to characterize the chemical structures of polymers that are of interest to the coatings community. Traditional mass spectrometry techniques developed for polymer analysis, like pyrolysis gas chromatography mass spectrometry (py-GC-MS) use thermal energy to vaporize nonvolatile samples. This thermal energy also decomposed the polymers into constituent parts. The full chemical structure information was lost.

The chemical structure of a polymer is typically characterized by determining the repeat units (composed of the monomers used to produce the polymer), the end groups that cap the repeat units, and the molecular weight (MW) distribution of the individual oligomers. Relatively new mass spectrometry techniques have been developed to measure these aspects of polymer samples. The new techniques are matrix-assisted laser desorption/ionization (MALDI), and electrospray ionization (ESI). In MALDI the material to be analyzed (the analyte) is mixed with an analysis aid (the matrix) which is easily volatilized by the appropriate laser light. In ESI the analyte is sprayed from a small orifice in a high electric field. Both techniques have been developed to introduce nonvolatile materials into a mass spectrometer. These revolutionary techniques have effectively opened polymers to mass spectrometric characterization. The importance of these new techniques were recognized by the award of half of the 2002 Nobel Prize in Chemistry to Koichi Tanaka and John Fenn for their roles in the invention of MALDI and ESI, respectively.

Mass spectrometers are instruments that measure the mass to charge ratio of charged particles. There are a variety of methods to measure mass to charge. The most common mass spectrometers used with MALDI and ESI sources for the study of polymer materials are time-of-flight (TOF) instruments. TOF mass spectrometers measure mass to charge by accurately measuring the time required for an ion to traverse the instrument after acceleration from a known voltage. Modern TOF instruments have very high mass ranges (up to $10^6 \text{ D}$), high mass resolution (up to 20,000 using full width at half maximum, FWHM), high mass accuracy (as good as 5 ppm), and have the multiplex advantage (the mass spectrometer is not scanned, all of the ions are detected). These instruments are particularly well suited to the analysis of low mass polymers.

MALDI and ESI can be applied to a variety of chemical structure problems related to coatings materials. The mass data can be important in helping solve problems such as:

- **Example Application:**
  The paper concludes with an example of how MALDI was applied to aid in the characterization of a novel polyol polymer targeted for coatings applications.
The mass spectrometry methods are particularly effective when employed as part of a multi-technique analytical approach. As with any method these methods bring both benefits and limitations. The benefits include absolute mass measurement, chemical structure information, and high sensitivity. Some of the limitations can be complex data, poor quantitation of mixtures, difficulty with polydisperse samples, and a need to control the sample preparation of analytes. Polydisperse samples are challenging to these MS techniques because, despite being related by a common repeat unit, oligomers of sufficiently different size begin to respond differently in the analysis. For samples with polydispersity (PD) greater than about 1.5, these differences can significantly impact the analysis.

MALDI

MALDI can be a very powerful method to characterize polymer materials. Figure 1 shows an example of a MALDI mass spectrum of a sample of polytetramethylene glycol (PTMEG) 1000. This experiment was done using 2,5-dihydroxybenzoic acid (DHB) as the matrix and methanol as the solvent. This experiment was done using polymer MALDI samples, wet and dry. In the wet methods, analyte and matrix solutions are made and then mixed to generate the desired matrix to analyte ratio (M/R). A small aliquot of the mixed solution is then applied to a substrate. The solvent is removed either through allowing it to evaporate or by spraying the solution on the substrate. A typical wet sample preparation method for a relatively low mass analyte involves mixing a 5 mg/ml analyte solution 1:7 with a 0.25M matrix solution using the same solvent for both solutions. For an air dry deposition, 0.5 ml of the combined solution is applied to the substrate and the solvent is allowed to evaporate under ambient conditions.

Dry MALDI sample preparation methods have recently been introduced to help address analytes with poor or no solubility. In a typical dry sample preparation 5 mg of the analyte are ground together with about 30 mg of matrix crystals using a small mortar and pestle. A small amount of the resulting mixture is applied to the substrate with a metal spatula. Any excess material on the substrate is removed leaving a gray haze on the substrate. Both sample preparation methods work. The dry methods tend to produce better data, but the wet methods tend to be less time consuming.

The key to MALDI experiments is the matrix. In each experiment the matrix has four vital roles that must be accomplished to produce ions: intimacy, absorption, desorption, and ionization. Intimate contact between the matrix and the analytes is required to produce ions. Part of the selection criteria for a matrix is that it will readily mix with the analyte. Matrices are chosen that have similar hydrophilicity or hydrophobicity to the analyte. Some common matrices used in polymer MALDI experiments include DHB for analytes soluble in methanol, ferulic acid and α-cyano-4-hydroxycinnamic acid for less polar analytes soluble in tetrahydrofuran (THF), and dithranol and trans-retinoic acid for nonpolar analytes soluble in THF or toluene.

The analyte molecules need to be in close proximity to the matrix molecules to be effectively desorbed. The only source of energy in the experiment to induce desorption is the laser light. The matrix must absorb at the wavelength of the laser. Most commercial MALDI instruments have ultraviolet nitrogen lasers with emission at 337 nm. To volatilize the analyte the matrix must enable the desorption of the analyte from the substrate. The interaction of the matrix with the laser light produces a gas pulse from the surface of the sample. The analyte molecules are desorbed from the surface in a micro-sized supersonic expansion. Finally, to be detected by mass spectrometry, the matrix must facilitate the ionization of the analyte molecules. MALDI ions are not formed by direct absorption of the laser light. Primarily we observe cationized species.

Figure 1—A typical MALDI mass spectrum of PTMEG 1000. The inset shows the partial resolution of the carbon isotopes for the n = 47 oligomer.
Since most matrices are acidic, protonation is a common mechanism for analytes with basic functional groups. Metal cationization is the other primary ionization mechanism. Analytes with oxygen functionality are readily cationized with alkali metals and analytes with unsaturated hydrocarbon functionality are readily cationized with transition metals like silver and copper. For analytes that require metal cationization, a source of the metal is a required part of the sample preparation.

MALDI is significantly challenged by chemistry that has too little chemical functionality to stabilize a cation in the gas phase. For example, saturated hydrocarbons like polyethylene and polypropylene are extremely difficult to analyze, and only very low molecular weight analytes have been analyzed by MALDI to date.

**ESI**

ESI is also developing into an important analytical technique for polymer materials. In ESI, we use a fluid flow through a narrow capillary held at high voltage to create ions. To successfully analyze a sample by ESI, the analyte must be soluble in the fluid. The interaction of the moving fluid and the high voltage forms a Taylor cone at the exit of the capillary. A Taylor cone occurs when the flow changes from large droplets falling from the capillary to a spray directed out of the capillary orifice. Tiny droplets are sprayed out of the capillary. These droplets have high charge density and coulombic forces cause them to split into successively smaller units until individual charged molecules are released. These individual charged molecules can have high charge states. Due to the fluid flow aspects of ESI, it is an ideal technique to couple with liquid chromatography (LC) experiments. The LC-ESI coupling can provide both quantitative and qualitative results.

ESI can be a very sensitive analytical technique, especially with chromatography separation prior to analysis. We find it especially important in the analysis of complex mixtures of surfactants. The improved sensitivity of the LC-ESI experiments can detect much lower amounts of individual surfactants in mixtures than MALDI and can be far more quantitative about surfactant mixtures.

One of the key challenges in applying ESI to mixture samples is the competition effects. These effects can impact the sensitivity of the analysis. A variety of competition effects occur during the ion production process in ESI. For example, competition between different analytes for the surface of the droplets can greatly impact the relative sensitivity of ESI. The production of the ions occurs primarily from the surface of the droplets. If one component of a mixture does not effectively populate the droplet surface, it will not be as readily detected as the species that do populate the surface.

Competition between different analytes for the available charges is another effect that can greatly impact sensitivity. Like MALDI, the ESI experiment must provide an ionization mechanism for the polymer analytes. Some polymers will protonate, but many need metal cationization with Na$^+$ or Ag$^+$, and these metal cations need to be provided.

One of the clear differences between MALDI and ESI is the high charge states that are common in ESI analyses. MALDI typically produces only singly charged ions, while ESI will often generate a variety of charge states. These charge state distributions are dependent on the functionality and relative size of the analyte. Figure 2 shows four ESI mass spectra of polyethylene glycol (PEG) samples with increasing average molecular weight. At low mass, we observe relatively simple mass spectra with two charge states, +1 and +2. As the average molecular weight of the PEG increases, so does the number and complexity of the charge state distributions.

---

**Figure 2**—Four ESI mass spectra of PEG polymers. The PEG 1000 and PEG 1450 mass spectra show distinct oligomers with multiple charge states. The PEG 8000 and PEG 17,500 mass spectra show unresolved distributions of oligomers and charge states. Used with permission of reference 18.

**Figure 3**—A typical MALDI mass spectrum of PS 4000 cationized with Ag$^+$. The ions of decreasing intensity at the low mass end of the distribution are silver clusters. Calculating the average molecular weights directly from the PS oligomer intensities yields the displayed values.
distribution until the combination of the oligomer distributions and the charge state distributions create only a large envelope of ions. With sufficiently high mass resolution, these charge states can be resolved and assigned, but this is relatively difficult work.19

**MOLECULAR WEIGHT DETERMINATION**

Once mass spectra have been produced, using either MALDI or ESI, several different aspects of the chemical structure can be determined. The first of these is the average molecular weight. Figure 3 shows a MALDI mass spectrum of a narrow polydispersity (PD) polystyrene (PS) sample. The main ion peaks in the spectrum are assigned as PS oligomers cationized with Ag+. The ions at the low mass edge of Figure 3, decreasing in intensity with increasing mass are assigned as sliver clusters.20 For this sample, we can calculate the average molecular weights directly from the areas of the ion peaks:

\[
M_N = \frac{\sum M_i N_i}{\sum N_i} \\
M_W = \frac{\sum (M_i)^2 N_i}{\sum M_i N_i} \\
\text{Polydispersity} = \frac{M_W}{M_N}
\]  

where \(M_i\) is the mass of an individual ion and \(N_i\) is the area under that ion peak. Once the mass spectrometer is calibrated, absolute masses are measured, not relative masses like in gel permeation chromatography (GPC). For the PS sample in Figure 3, we calculate \(M_N = 4130\) D and \(M_W = 4470\) D, with PD = 1.08.

Molecular weights measured by MALDI typically agree well with traditional measures, like GPC, for samples with narrow polydispersity. Figure 4 shows three calibration curves comparing the MALDI molecular weight compared to the GPC molecular weight for PEG, PS and polymethylmethacrylate (PMMA) standards.21 We see excellent agreement between the two techniques for these relatively simple standards. If the PD is < 1.25 MALDI can generate the correct distribution. For samples with 1.25 < PD < 1.5, MALDI will typically generate useful results with some deviation in the MW values. These deviations are due to both instrumental and chemical effects on different size molecules in the experiment. The instrumental effects concern issues such as detection efficiencies. The chemical effects include issues such as desorption and ionization efficiencies. Despite differing only in the number of repeat units, oligomers of sufficiently different size begin to behave differently by MALDI. These differences impact the ability of MALDI to quantitatively analyze these types of samples. For samples with 1.5 < PD < 1.75, MALDI can generate useful information on \(M_N\) values, but the \(M_W\) results will err low. The differences in the responses tend to discriminate against the higher molecular weight portion of the distribution. For samples with PD > 1.75, MALDI will not typically generate useful molecular weight information. For samples with PD > 2.0, MALDI will not typically generate a mass spectrum that even provides qualitative value.

**REPEAT UNITS AND END GROUPS**

Figures 1–3 show MALDI and ESI mass spectra with clearly resolved and assigned oligomers. The mass differences between the ions determines the mass of the polymer repeat units. While mass alone is not sufficient to determine the repeat units, the context of the sample often provides enough information to generate high confidence in the polymer identity.

The masses of the specific oligomer ions also generate information about the polymer end groups. If we subtract the mass of all of the repeat units from the ion mass, the residual mass includes the mass of the end groups and the cation. The chemical identity of the end groups can then be determined either from combining the mass data with some spectroscopy data (like nuclear magnetic resonance, NMR, or infrared, IR), or by measuring the accurate mass of the oligomer. The accurate mass measurement can help determine the most likely elemental composition responsible for the residual mass.

Figure 5 shows a small segment of MALDI mass spectra of two surfactants. Both the upper and lower mass spectra

![Figure 4](link)

**Figure 4**—Three calibration curves showing excellent agreement between average molecular weights determined for PEG, PS, and PMMA standards by MALDI and GPC up to about 100,000 D.
show two oligomers cationized by both Na\(^+\) and K\(^+\) resulting in ion peaks spaced by 16 D. Calculations for the end group mass can easily determine that the upper spectrum corresponds to ethoxylated octylphenol (Igepal CO 630) and that the lower spectrum corresponds to an ethoxylated nonylphenol (Triton X-100).

**COMBINING WITH CHROMATOGRAPHY**

As discussed above, ESI is regularly and easily coupled with LC techniques. Chromatography, especially GPC, can also be coupled with MALDI to help generate data for samples with broad polydispersity.\(^{17,22-23}\) We can take advantage of the key strengths of both techniques: the superior size separation capability of the GPC and the mass resolution and mass accuracy of the mass spectrometry.

*Figure 6* shows a series of MALDI mass spectra obtained from the GPC separation of a sample of PTMEG 1000.\(^{22}\) Each mass spectrum corresponds to a particular elution time from the GPC column. These GPC fractions were collected continuously using a LC Transform (Lab Connections, Northborough, MA).\(^{24}\) At each position along the transform track, we can generate a high quality MALDI mass spectrum. Comparing *Figure 6* to *Figure 1* shows the power of separating the sample prior to analysis. We see low intensity, high mass oligomers much better after separation than without separation. We can also spot impurities more effectively after separation.\(^{22}\)

Another use for GPC–MALDI data is to create calibration standards for GPC. Because GPC needs relative calibration, the mass accuracy is often limited by the chemical similarity of the analytes and the standards. In some cases, similar standards are not available. We can use the combination of MALDI and GPC to correlate absolute mass measurements with elution volumes. We can then construct a GPC calibration specific to the desired chemistry, and improve the performance of the GPC experiments.\(^{22}\)

**ION FRAGMENTATION**

Unlike more traditional mass spectrometry techniques, ESI and MALDI ions are intact, showing little or no fragmentation. In both techniques, the desorption mechanism does not involve heat, electron impact, or ion impact. The lack of fragmentation is important in the determination of average molecular weights and end groups. To solve some chemical structure questions, however, it would be advantageous to create ion fragments to look at the chemical connectivity in the ions. Both MALDI and ESI have the capability to create ion fragments. In MALDI, post source decay (PSD) experiments generate a type of MS/MS experiment.\(^{25-26}\)

In MALDI–PSD we select the ion of interest and induce fragmentation by increasing the number of collisions during the desorption process. The number of collisions is increased by greatly increasing the amount of laser light delivered to the sample. The increased amount of laser light desorbs more material from the sample, inducing more collisions with the MALDI ions. It is important to realize that the fragments are not photoinduced. We can mass measure the fragment ions by changing instrument voltage settings.

Fragmentation in ESI is also a collisional process. In the ESI experiment the ions travel through a skimmer from a relatively high pressure region of the mass spectrometer to a low pressure region. A voltage is applied to the skimmer to help guide the ESI ions through to the mass analyzer. Controlling the skimmer potential controls the degree...
of fragmentation: the lower the skimmer potential, the less fragmentation. The skimmer potential needs to be optimized because the degree of fragmentation can be different for different oligomers in a sample. Because this fragmentation is not specific, it can best be understood with chromatographic separation of the components prior to fragmentation. If multiple oligomers are present in the source simultaneously, their fragments will all be detected together. Mixtures of analytes, each with oligomer and charge state distributions, and fragmentation generally creates very difficult data sets to interpret.

**EXAMPLE**

**Characterization of a Novel Coatings Polymer**

MALDI mass spectrometry was an important tool in our characterization of a novel polyol polymer developed for use as a coatings material. The material is made using a novel synthesis involving cationic polymerization and an emulsified epoxy resin. The MALDI analysis was part of an integrated characterization involving IR, NMR, and GPC. MALDI was important in providing chemical structure information. Figure 7 shows the MALDI mass spectrum of the material. We see clusters of ions separated by 358 D, the expected repeat mass corresponding to a bisphenol–A diglycidyl ether (BADGE) resin + water. The average molecular weights calculated from this spectrum are $M_N = 2100$ D and $M_W = 2900$ D with a $PD = 1.4$. Figure 8 shows an expansion of the MALDI mass spectrum with peak labels for many of the significant ions. We can assign most of the ions in the spectrum.

Figure 9 shows the chemical structure determined for this material. The main product corresponds to a copolymerization of BADGE + water with glycol end groups (labeled A in Figure 8). The ions labeled B and C in Figure 8 are assigned as oligomers with defects in the end groups. The B ions have one epoxy end group, and the C ions have two epoxy end groups. The ions labeled D in Figure 8 incorporate an epoxy repeat unit from the starting BADGE material. This repeat unit has been carried through the polyol polymerization. The ions labeled E in Figure 8 remain unassigned.

The MALDI data provided key chemical structure for this novel material. We could verify the repeat units of the poly-
mer, measure the average molecular weights, and obtain information about a variety of end groups present in the material.

CONCLUSIONS

MALDI and ESI have become important characterization tools for polymers of interest to the coatings industry. The mass data obtained from these experiments can help determine the chemical structures of important materials by providing information on the polymer repeat units, end groups, and molecular weight distributions. By better understanding how these experiments are done and how the data can be analyzed, these techniques can find even greater incorporation into the daily characterization of materials.

ACKNOWLEDGMENTS

I would like to thank Air Products and Chemicals, Inc. for support for this article, Dr. John Sadowski for critical review of the manuscript, Dr. David Parees, Prof. Kevin Owens and Dr. Michael Liu for valuable discussion and collaboration on MALDI related projects, Mr. Dale Willcox for valuable discussion about ESI projects, and Dr. Fritz Walker and Ms. Renee Keller for the opportunity to work on the novel polyol polymer.

REFERENCES

(9) Fenn, J.B., Mann, M., Meng, K., Wong, S.F., and Whitehouse, C.M., Science, 64, 64 (1989).