Chapter 5

A New Generation of Mass Spectrometry for Characterizing Polymers and Related Materials

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Mass spectrometry is a powerful analytical technique for characterizing polymers. New mass spectrometry ionization methods have extended the molecular weight range over which macromolecules can be ionized to millions of Daltons. And new breeds of mass spectrometer analyzers and detectors are quickly extending the absolute measurable molecular weight range into the millions. More important to polymer scientists and engineers than these high mass achievements in mass spectrometry is that today's mass spectrometers can determine structural information on oligomers quickly, directly, and routinely for several classes of compounds. In particular for polymer systems below 10,000 Daltons, few indirect analytical methods can provide the information provided directly by mass spectrometry. Some state-of-the-art mass spectrometry techniques are discussed and several examples are presented to illustrate molecular weight and structural determination by mass spectrometry.

Mass spectrometry is rapidly evolving in its scope of applications for macromolecular analysis through new ionization techniques. For example, laser desorption ionization (LDI) techniques coupled with time-of-flight mass spectrometry (TOFMS) can produce accurate molecular weight information quickly for molecular weights of a quarter million. In a single laser shot, the LDI technique coupled with Fourier Transform Mass Spectrometry (FT/MS) can provide detailed chemical information on polymeric molecular structure and provide direct determination of additives and contaminants in polymers. State-of-the-art mass spectrometry methods can be coupled with gel permeation chromatography (GPC) in an off-line mode, or directly coupled via electrospray ionization for the analysis of macromolecules. All of these mass spectrometry techniques offer new analytical capabilities to solve problems in research, development, engineering, production, technical support, competitor product analysis, and defect analysis.

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0097–6156/94/0581–0055$08.00/0

In Hyphenated Techniques in Polymer Characterization; Provder, Theodore, et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1994.

Mass Spectrometry Today

During the last 10 years, the growth in mass spectrometry applications in the biosciences has been remarkable. There have been a number of advances in mass spectrometry instrumentation that have allowed the molecular weight and structure of peptides and proteins to be determined. Today, direct protein analysis is performed by mass spectrometry with matrix-assisted laser desorption ionization (*1, 2*) and electrospray ionization [ESI] (*3*). On-line liquid chromatography mass spectrometry (LC/MS) of proteins is becoming commonplace. In addition, mass spectrometers have evolved from finicky research instruments to routine user-friendly shared spectrometers. The same advantages that mass spectrometry is providing to the biosciences may be realized in polymer science.

Laser Desorption/Ablation Ionization Methods. Matrix-assisted laser desorption ionization (MALDI) relies on the use of a solid chromophoric matrix, chosen to absorb laser light, which is co-mixed with the analyte (*4*). Typically, a solution of a few picomoles of analyte is mixed with a 100-to-5000 fold excess of the matrix in solution. A few microliters of the resulting solution are deposited on a mass spectrometer solids probe, and the solvent is allowed to evaporate before inserting the probe into the mass spectrometer. When the pulsed laser beam strikes the sample surface in the spectrometer, the sample molecules are desorbed/ionized at high efficiency. The various mechanisms for matrix and non-matrix assisted laser desorption have been discussed (*5, 6*).

A matrix is not always necessary or desirable to obtain a mass spectrum of a sample. For example, to rapidly determine if an ultraviolet (UV) absorbing additive is present in a paint sample by LDI mass spectrometry, it is not convenient to alter the sample to introduce a matrix. Instead, a paint chip could be directly analyzed by laser desorption with a UV or other type of laser.

Pulsed lasers with relatively short pulse widths (<50 ns) are typically used for laser desorption/ablation techniques because of their high peak powers and because short pulses reduce sample consumption and minimize laser-induced pyrolysis of the sample. Only mass spectrometers that can measure ions of all mass-to-charge values near simultaneously (corresponding to a single short laser pulse) or mass spectrometers that can trap all the ions produced in a single laser pulse are compatible with this pulsed ionization technique. Time-of-flight (*2,7-9*) and Fourier transform mass spectrometers (*9-14*) are commercially proven for laser desorption/ablation mass spectrometry. The TOFMS detects all ions near simultaneously, and the FT/MS is a ion trapping mass spectrometer that detects all ions simultaneously.

Other types of mass spectrometers, low, medium, or high performance, which scan by measuring one mass-to-charge ratio at a time cannot be used effectively for laser desorption (*9*). High-resolution magnetic sector mass spectrometers, fitted with array detectors to allow simultaneous ion detection, have been shown to be able to measure laser desorption mass spectra over a limited mass range and with relatively low resolving power (*15*). Quadrupole ion trap mass spectrometers (radiofrequency ion traps) capture and store all the ions formed in a single laser burst; however, they measure ions sequentially over relatively long periods of time (*16*) and produce low-resolution mass spectra. During the long measurement time the trapped ions may undergo ion chemistry and ion collisions that affect the integrity of the ions that are ultimately measured.

Electrospray Ionization. Electrospray ionization is a recent ionization technique that has been applied to large macromolecules such as proteins, although it is applicable to other large molecules including polymers. It is a method for transform-

ing ions that are present in a solution (*17*) into characteristic ions in the gas phase (mass spectrometers can only analyze ions in the gas phase). A sample solution is sprayed or nebulized under the influence of a high electric field. The resulting aerosol is desolvated by a combination of heat, gas flow, and vacuum; and by using supersonic beam methods, a beam of characteristic gas-phase ions is simply and efficiently formed for mass spectrometric analysis. The electrospray ionization method often results in the formation of multiply-charged molecules in the gas phase for high molecular weight species.

With electrospray, molecules are produced with a distribution of charge states. In other words, positively-charged macromolecules may be produced with, for example, a distribution of 10, 11, 12, etc. protons (or other cations) attached. Therefore, the mass-to-charge ratio of the multiply-charged macromolecule is some fraction of the molecular weight, for example, a tenth, eleventh, twelfth, etc., which lowers the mass-to-charge range at which the ion distribution resides. However, this complicates the determination of the true mass of the macromolecule. With conventional low-resolution mass spectrometers, the true mass of the macromolecule is determined by an indirect and iterative computational method.

With the Fourier transform mass spectrometry technique, the ^{13}C isotopes corresponding to each charge state can be easily resolved in the mass spectrum, which cannot be accomplished with lower resolution mass spectrometers. By counting the number of ^{13}C isotopic peaks in a single mass unit, or equivalently by dividing the mass difference between two adjacent ^{13}C peaks in a given charge state's isotopic cluster into unity gives the charge-state value by direct measurement (*18*). Therefore, the mass difference between the ^{13}C peaks allows the molecular weight to be directly determined. In other words, the molecular weight is calculated by multiplying the apparent mass-to-charge ratio by the charge state less the mass of the attached cations.

Electrospray ionization has three advantages for mass spectrometry. First, it allows large macromolecules to be ionized, and second, because the ions formed by ESI are typically multiply charged, the mass-to-charge ratios of ionic macromolecules are decreased into a mass regime where mass spectrometers operate most effectively. For example, polymers up to 5,000,000 have been measured by electrospray ionization mass spectrometry (*19*), and more recently single ions of several million in molecular weight have been measured by FT/MS (*20*). Third, because the input to electrospray ionization is a liquid, it serves as an interface between the mass spectrometer and liquid chromatographic techniques including gel permeation chromatography (GPC) also called size-exclusion chromatography [SEC] (*21*), and capillary electrophoresis (*22*).

Determination of Molecular Weight Distribution

Why use Mass Spectrometry? Mass spectrometry can provide the most accurate mass determination of all analytical techniques, and furthermore, the measurement is direct. Today, the strength of mass spectrometry lies in determinations below 100,000 Daltons. It allows the direct analysis of solid materials including bulk, surface and additive chemistries. Mass spectrometry has relatively high sensitivity, dynamic range and linearity. Mass spectrometry, unlike chromatography, is comparatively fast and has capabilities to provide structural information. Also, mass spectrometry has the capability to resolve or separate components of complex mixtures on the mass scale.

Why Chromatography? Gel permeation chromatography is accurate and routine for average molecular weight determinations in excess of 50,000. Chromatographic methods separate complex mixtures resolved in time. For example, in a GPC an oligomer mixture is separated by hydrodynamic size (volume).

The GPC separated mixture can be used as a direct sample input into a mass spectrometer for mass analysis. As will be discussed below, the limitation in GPC is more related to the traditional detectors than the chromatography. The mass spectrometer is a more ideal detector for liquid chromatography.

Gel Permeation Chromatography. The use of GPC in combination with viscometry and light scattering detectors for the determination of a polymer's absolute molecular weight distribution is becoming more common. However, there can be limitations of these analytical systems for the analysis of low molecular weight polymers (<50,000 Daltons). Viscometry and light scattering detectors are not as sensitive to lower molecular weight polymers under normal GPC conditions. The concentration detector is usually a refractometer that may not always give reliable concentration information below 50,000 Daltons without meticulous calibration. Yet, many industrial laboratories routinely rely on GPC measurements below 50,000 Daltons and even below 10,000 Daltons.

The viscometer sensitivity is dependent upon the specific viscosity of the sample so it is not uncommon for an analyst to compensate by using high concentrations of low molecular weight samples to get reasonable signal-to-noise. These high concentrations in turn influence the elution time (volume) of the unknown polymer sample. An accurate elution volume is critical for the molecular weight determination by using the universal GPC calibration.

A light scattering detector's sensitivity is a function of molecular weight. With polymers below 25,000 Daltons, the sensitivity is a limitation. The signal from the light scattering detector is due to the sample's excess Rayleigh factor R_θ. The excess Rayleigh factor is a function of the square of the change in refractive index with concentration [$(dn/dc)^2$]. Therefore, if the polymer exhibits a low dn/dc, less than 0.06 under normal GPC concentrations, the detector may not provide sufficient signal-to-noise to calculate the molecular weight distribution.

It is well known that the refractive indices of low molecular weight polymers in solutions are affected adversely by different end groups. In other words, at low molecular weight, the detector is more sensitive to chemical composition than it is to molecular weight. The use of a refractive index detector for low molecular weight concentration determinations can be unreliable because the dn/dc of the sample may change as a function of molecular weights below 50,000 Daltons.

Mass Spectrometry. An alternative to using GPC with viscometry and light scattering detection for the determination of low molecular weight polymer distributions is mass spectrometry. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI TOFMS) can give fast, accurate information about the degree of polymerization (molecular weight distribution).

Figure 1 compares a gel permeation chromatogram, a MALDI TOFMS mass spectrum, and a MALDI FT/MS mass spectrum of an unknown industrial polymer. The mass spectra were obtained by using 2,5-dihydroxybenzoic acid (DHBA) as the matrix and 337 nm radiation from a nitrogen laser. The MALDI TOFMS result was obtained by averaging over 50 laser shots. The MALDI FT/MS result was obtained by measuring a single laser shot, which is indicative of higher sensitivity.

The results from both MALDI TOFMS and Laser Probe FT/MS illustrate higher molecular weight and higher resolution data than that obtained by GPC. In addition, the higher resolving power achievable with the FT/MS instrument, compared to either GPC and TOFMS, demonstrates that each individual oligomer is resolved on the mass scale. Furthermore, it illustrates how molecular information can be obtained from a single mass spectrum. For example, the accurate mass FT/MS spectrum establishes unequivocally that each oligomer measured has a mass difference of 44.026 which corresponds to C_2H_4O -- the repeating unit of

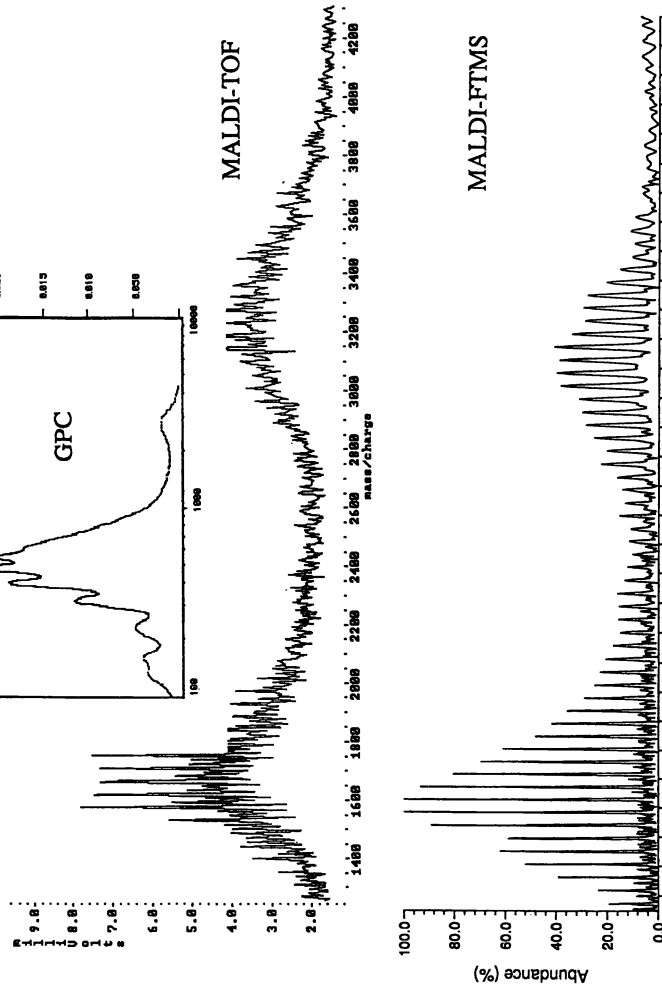

Figure 1. Comparison of analytical results obtained on an industrial polymer by gel permeation chromatography (top) and matrix-assisted laser desorption ionization mass spectrometry (linear time-of-flight mass spectrometer [center] and Fourier transform mass spectrometer [bottom]). From the FT/MS data the polymer can be identified as a substituted polyethylene glycol.

polyethylene glycol. This data establishes that the polymer is some type of polyethylene glycol, whereas the GPC and TOFMS data only give information about the molecular weight. The GPC data illustrates the problem of that method when analyzing unknown and/or low molecular weight polymers even though in this case the GPC experts in our company calibrated and acquired the data. The two mass spectrometric methods are in excellent qualitative agreement; however, the GPC data severely underestimates the molecular weight.

Figure 2 illustrates the application of Laser Probe FT/MS to monitoring a feedstock. In this example, a batch of poly(dimethylsiloxane) was specified to have an average molecular weight of approximately 2,000 Daltons. The direct analysis of the polymer by Laser Probe FT/MS reveals a bimodal distribution between 2,400 and 8,000 Daltons. These results were obtained by a traditional laser desorption ionization method by using a carbon dioxide laser operated at 10.6 μm and by doping potassium bromide into the sample. Alkali halide doping is a common method used with infrared lasers to assist ionization by alkali metal attachment. The series of ionized oligomers results from attachment of the potassium ion to each oligomer (M_n+K^+). From these data, the mass spectrometer data station extracts relative oligomer abundances and computes a weight average molecular weight of 5,300. In this example, the polymer average molecular weight was quite different than what the manufacturer had thought was produced and sold.

The first two examples illustrate bimodal distributions, which can often be characteristic of real industrial samples. The next example (Figure 3) shows the results obtained from a commercial reagent sample of polymethyphenylsiloxane. These results were obtained by matrix-assisted laser desorption ionization (MALDI) technique where ultraviolet radiation, typically from a nitrogen laser (337 nm) is used with a UV absorbing matrix (in this case, dihydroxybenzoic acid [DHBA]) that is co-mixed with the polymer sample. The mass spectrum illustrated was obtained by a single laser shot. As can be seen in the figure, a distribution centered about m/z 3,000 is observed. The molecular weight given on the bottle, which was likely determined by a traditional and indirect method, was 2,600.

Compared to other ionization methods, laser desorption data are not only fast and easy to obtain, but they also appear to yield the highest average molecular weight. This may be explained by the harshness of the other ionization techniques that tear apart the molecular entities during the ionization process. Figure 4 is a Laser Probe FT/MS spectrum of Oxypruf-20 [tetrakis(hydroxypropoxypropoxypropoxypropoxypropyl)]hydrazine obtained by direct carbon dioxide (10.6μm) laser desorption. In this case, the distribution shows an abundant series of $[M+K]^+$ peaks and to a lesser extent $[M+Na]^+$ peaks (salts were not added; the alkali metals are ubiquitous in many materials). The peaks in each series are separated by 58 Daltons, which is the mass of the repeating group. The weight average molecular weight determined in our laboratory was 1,313.3. In a separate published study (*23*), the weight average molecular weight was determined to be 1,314.6 by laser desorption FT/MS. Secondary ion mass spectrometry (SIMS) and fast atom bombardment (FAB) ionization techniques, gave values of 773.7 and 569.2 respectively, which illustrates that they may not be as generally well suited for molecular weight determinations.

Table I lists the various classes of polymers that have been studied by laser desorption ionization FT/MS techniques. Molecular weight information or structural information or both has been obtained on all of the polymers listed. In many cases, derivatives, homologous series, or different molecular weight distributions within each class listed have been reported.

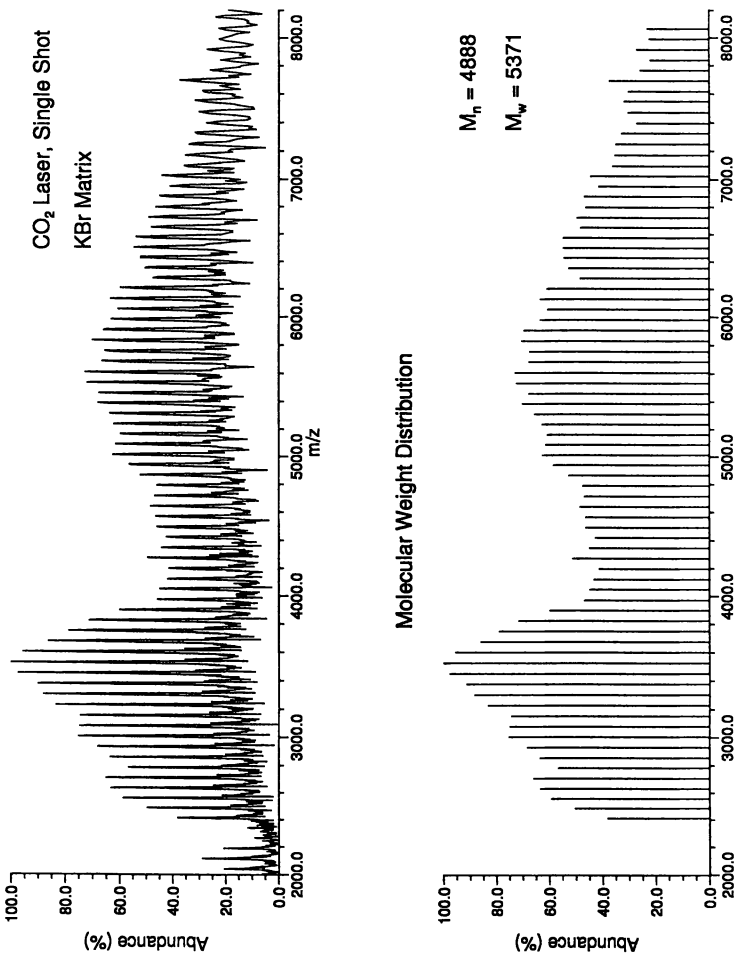

Figure 2. A Laser Probe FT/MS spectrum (top) of an industrial polymer with a theoretical molecular weight of about 3,000. The mass spectrum illustrates a bimodal molecular distribution of poly(dimethylsiloxane) oligomers. The weight average molecular weight calculated from these mass spectrometry data is 5,295 (bottom).

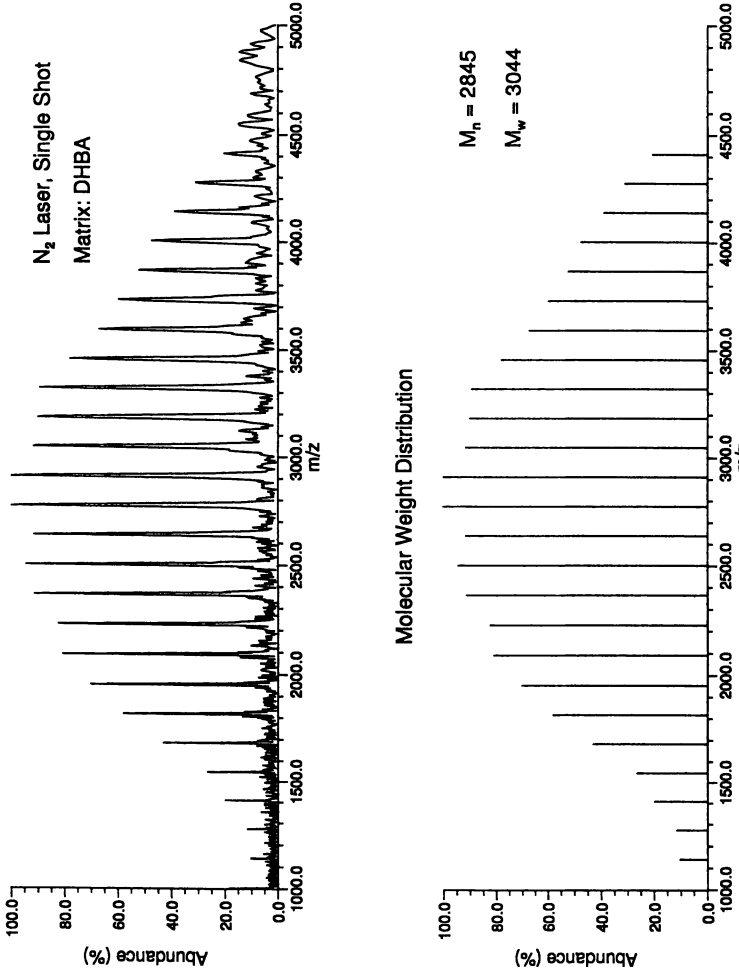

Figure 3. A Laser Probe FT/MS MALDI spectrum (top) of a commercial polymer reagent whose molecular weight is suggested to be 2,600. The weight average molecular weight (M_w = 3044) is computed directly from the mass spectrometry data (bottom).

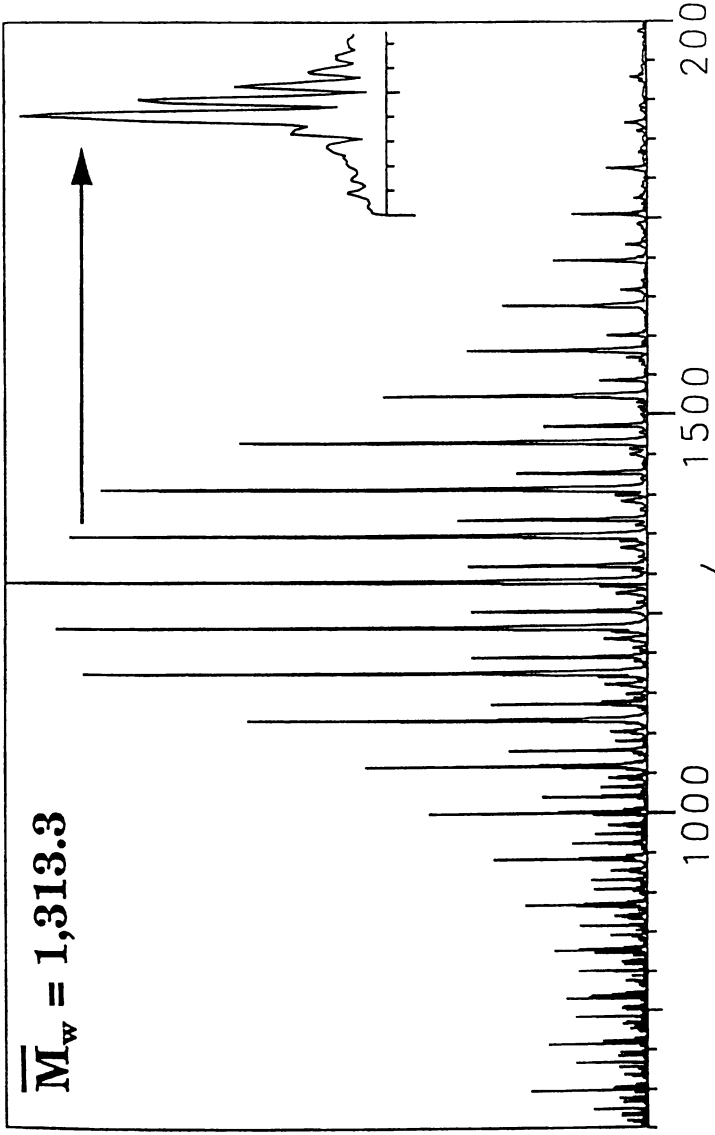

Figure 4. Laser Probe Mass Spectrum of Oxypruf-20 illustrating a weight average molecular weight of 1,313.3. These data are consistent with a published value of 1314.6 which was obtained independently by Laser Probe FT/MS (*23*).

Table I. Classes of Polymers Studied by Laser Desorption Fourier Transform Mass Spectrometry[a]

acrylic acid
acrylonitriles (*26*)
alkoxylated pyrazoles (*23*)
alkoxylated hydrazines (*23*)
amic acid (*27*)
amides
analines (*28, 29*)
brominated p-phenylenes (*30*)
butadienes (*31*)
caprolactone diols (*32*)
dimethylsiloxanes (*33*)
diols
esters
ethylene glycols (*25, 32-34*)
ethylene glycol methylethers (*32*)
ethylene imines (*32*)
ethylene terephthalates (*35*)
ethylenes (*26, 31*)
fluorocarbons (*36, 37*)
hydroxybutylic acid
hydrocarbon waxes
imides (*25, 27, 33*)
isoprenes (*31*)
kapton
methyl methacrylates (*33, 38*)
methylphenylsiloxanes
methyl-dipyrrolylenes (*28-30, 39*)
monols
nucleotides
nylons
octylphenol ethoxylates
oxypropylenediamines
p-phenylenes (*29-30, 40, 41*)
peptides
perfluoro ethers (*37, 42*)
phenyl-pyrrolylenes (*28-30, 39*)
phenylene sulfides (*25, 26, 28, 29*)
propylene glycols (*32, 34*)
pyrenes (*29*)
saccharides
selenienylenes (*28, 30, 39*)
styrenes (*26, 31, 35*)
sulfonic acids
tetrafluoroethylenes
thienylenes (*28-30, 39*)
triols
vinyl acetates (*25*)
vinyl phenols (*29*)
vinylchlorides (*26*)

copolymers
β-hydroxyalkanoates (esters)
dimethylsiloxane/ethylene oxide
ethylene glycol/propylene glycol (*43*)
ethylene/tetrafluoroethylene (*25, 26*)
methylmethacrylate/butylacrylate (*43*)
methylmethacrylate/methacrylic acid
methylmethacrylate/styrene (*43*)
pyromelletic dianhydride/ oxydianiline (*25*)

[a] Polymers (non-biological) without references are unpublished work from the authors' laboratories.

Structural Determination

As mentioned previously, FT/MS is capable of providing more detailed structural information compared to most any other analytical technique. For example, it is possible to measure the absolute mass of an oligomer or a polymer fragment ion, and from that mass measurement the most probable elemental composition can be computed by the mass spectrometer data station. A more accurate mass measurement (i.e. a lower error on the measurement) limits the chemical formulas that can be computed. Generally this elemental composition information is all that is needed to confirm a suspected molecular structure or substructure. However, if this is not sufficient, mass spectrometry/mass spectrometry (MS/MS) techniques (*24*) can be applied.

Figure 5 conceptualizes how the end groups on the industrial sample of polyethyleneglycol (PEG) discussed in Figure 1 can be determined by accurate mass measurement. The mass spectrum and expansion plot shown in Figure 5 were ob-

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tained by mixing a PEG standard with the industrial PEG. Two series of ions can be observed and measured with high mass accuracy in the mass spectrum. The series (nominal mass) of higher abundance species (1466, 1510, 1554, ...) result from potassium ion attachment to the PEG standard. The second series (nominal mass) of ions of lower abundance (1524, 1568, 1612, . . .) result from ionization of the industrial PEG. The two series differ by 14 mass units; however, because the measured mass difference is accurate to better than a few parts per million, mass differences attributed to the obvious CH_2, N, etc. can be eliminated. A further clue about the structure of the endgroup was obtained by doping the sample with KBr. It was observed that the mass of the industrial polymer shifted, compared to the mass determined by the mass spectrum obtained with only the DHBA matrix (Figure 1), corresponding to the displacement of a cation by the potassium ion. The expansion plot in Figure 5 illustrates the molecular formula for the PEG standard and the industrial polymer. It was confirmed that the industrial polymer was synthesized to have at least one anionic terminal group, and these results confirmed the presence of an anionic group by the observation that a proton was displaced and exchanged by the potassium ion after doping with KBr. With some additional information from the polymer chemist, the molecular structure of the end group could be determined by accurately measuring the mass difference between the PEG standard and the industrial PEG sample. The modified PEG end group will have a molecular substructure mass corresponding to one of the following mass differences:

$$[(C_2H_4O)_nX^-K^+]K^+ - (C_2H_4O)_nK^+ + m(C_2H_4O), \text{ where } m = 1, 2, 3, ...$$

This is simply the measured mass difference between two corresponding oligomers of the industrial and standard PEG plus the molecular mass of the repeating unit taken m times. Starting at m=1 and incrementing it, the chemical composition is computed by using the mass spectrometer data station. Choices are limited by specifying that the chemical composition only contains C, H, O, K, and X. At some value of m, a chemically-sensible elemental composition is recognized. A proposed endgroup structure can be further supported by using MS/MS techniques on one of the oligomeric ions and confirmed further by other analytical methods if warranted. (The structure of the endgroup and X cannot be revealed because of the proprietary nature of the sample).

In the MS/MS of polymers, a single oligomeric ionic species is isolated in the mass spectrometer. This is easily accomplished in an FT/MS instrument, which is a magnetic ion trap. Therefore, all the oligomeric species, except the one of interest are ejected from the FT/MS ion trap, hence leaving a population of one oligomer. After this gas-phase isolation is completed by the data station, the selected oligomer is broken down inside the mass spectrometer by using one of several common dissociation techniques. Finally, the dissociation products are measured by acquiring a product ion mass spectrum.

Figure 6 illustrates MS/MS on the n=6 oligomer of a copolymer of β-hydroxyalkanoate, which was determined to contain five C_8 and one C_6 repeating units. After dissociation of the n=6 species, a mass spectrum is measured. Four distinctive fragmentation patterns are observed depending on which end of the oligomer sequentially dissociates. The data illustrate that the oligomer dissociates by four different sequential cleavages. These correspond to sequential loss of three monomeric units:

1. C_8, C_8, C_8
2. C_8, C_8, C_6
3. C_8, C_6, C_8
4. C_6, C_8, C_8.

This illustrates that the C_6 repeating group is randomly incorporated into the n=6 copolymer. This example serves to illustrate that MS/MS is useful for the characterization and determination of the sequence of copolymers.

In Hyphenated Techniques in Polymer Characterization; Provder, Theodore, et al.;
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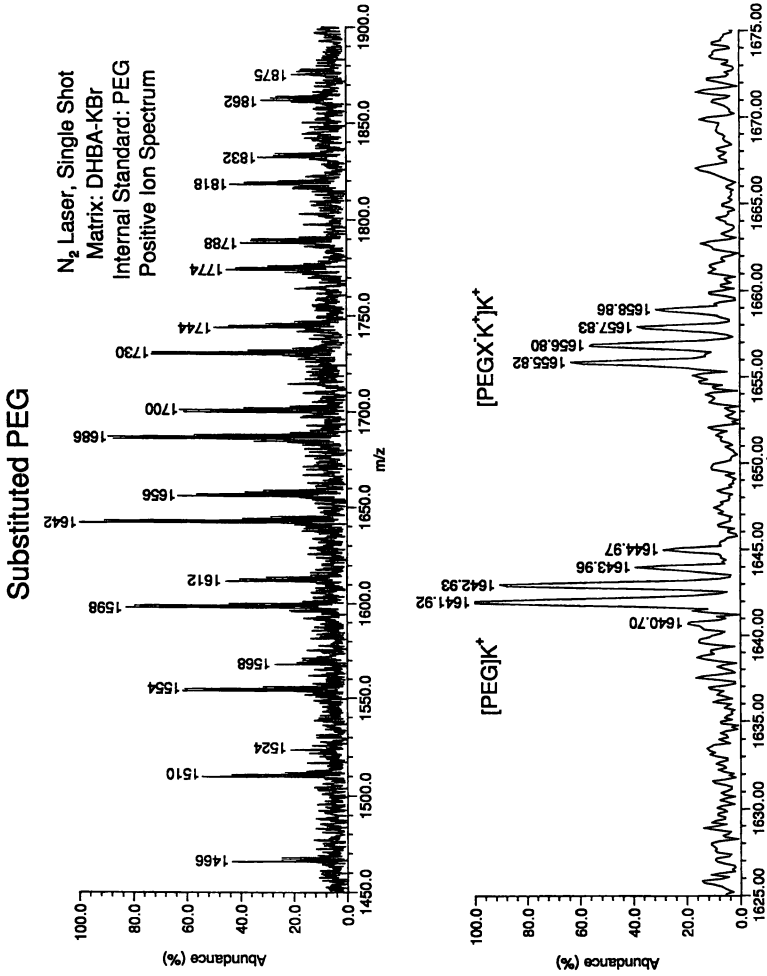


Figure 5. Exact mass comparison of oligomeric ions obtained by MALDI FT/MS on a mixture of polyethylene glycol and a substituted polyethylene glycol (Same industrial sample as represented in Figure 1. The end group composition may be determined by these data.)

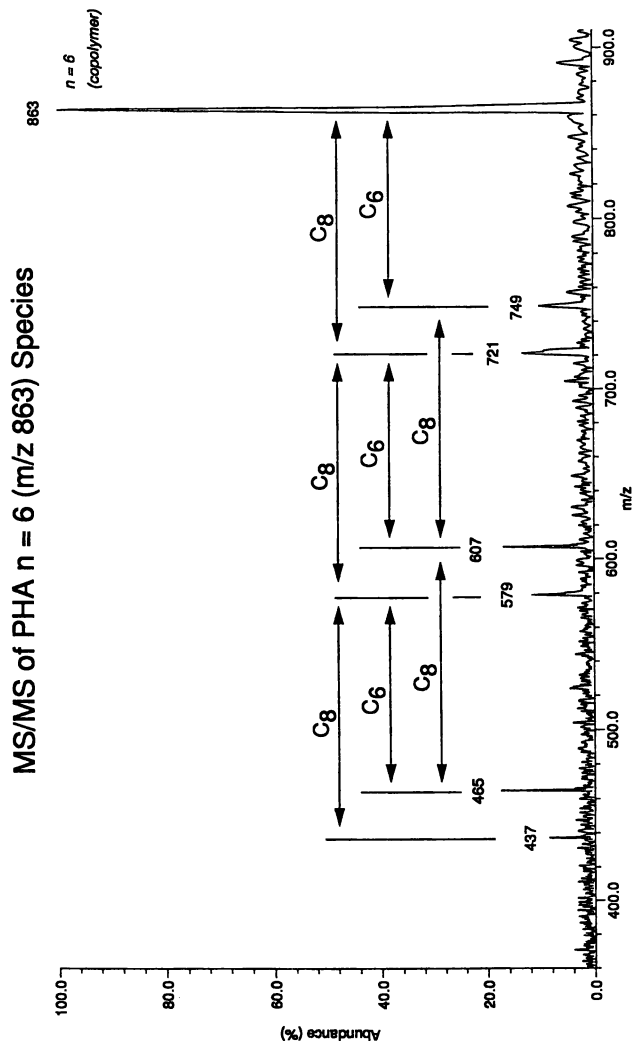
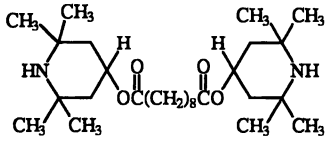


Figure 6. The mass spectrometry/mass spectrometry spectrum of an oligomer of a β-hydroxyalkanoate containing five C_8 units and one C_6 unit. The fragmentation illustrated in the mass spectrum shows that the position of the C_6 group is random.

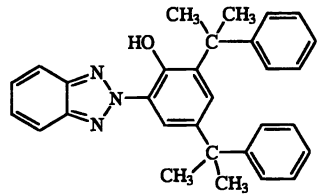
Additives and Contaminants

The laser-based methods discussed thus far can be used to probe surface and interstitial contaminants as well as for the direct determination of additives in a complex matrix. It is now common to have a CCD camera and video display that gives a microscopic view of the sample when it is in the mass spectrometer. This allows contaminants, defects, and areas of interest to be observed and manipulated while under the probing beam of the laser (*25*). A number of industrial examples have proved that direct Laser Probe FT/MS analyses can rapidly determine many additives directly, even when the combination of laborious classical wet chemical techniques with other modern instrumental methods have proved difficult and time consuming.

Figure 7 illustrates the direct determination of two antioxidants in a crosslinked polymer. The protonated molecule is observed for Tinuvin 900 and the odd-electron molecular ion is observed for Tinuvin 770. In this example, a carbon dioxide laser was used to ablate the sample, and following the ablation step an electron beam was turned on to ionize the ablated materials. Exact mass measurements confirmed the identity of the two additives present at about 2%. Each laser shot ablates very small quantities of the sample producing a mass spectrum as illustrated in Figure 7. The molecular ion signals observed correspond to the detection of about 30 picomoles of additive in each laser ablation event. In some extreme cases, we have determined detection sensitivities that are sub-attomolar; in particular when determining an UV absorbing surface species with an UV laser probe. Table II illustrates that a wide variety of additives have been determined by Laser Probe FT/MS.



Tinuvin 770



Tinuvin 900

Electrospray and Chromatography

The application of electrospray to polymer characterization is in its infancy. It can be a viable approach to analyzing high molecular weight polymers by taking advantage of the fact that the effective mass-to-charge ratio is decreased into the realm of high-performance mass spectrometry measurements because of the high charge states that are observed.

Figure 8 illustrates a simplistic example of electrospray FT/MS on poly(propylene glycol) [PPG] 720. The solution used to obtain the mass spectrum was approximately 75 micromolar PPG in 1:1 THF:MeOH with 0.5% NaCl. A few picomoles of the PPG was consumed to obtain the mass spectrum. Each oligomer is ionized by sodium ion attachment from the solution. Only the single charge state (singly-charged species) is observed for each oligomer.

As the polymer size increases, the number of charge states will increase for each oligomer. This leads to an extremely complex mass spectrum when there is a distribution of several charge states for each oligomer. Fortunately, the FT/MS is an ultrahigh resolution technique that is capable of resolving the many overlapping charge states of different oligomers. Still, this is may prove to be a formidable computational task.

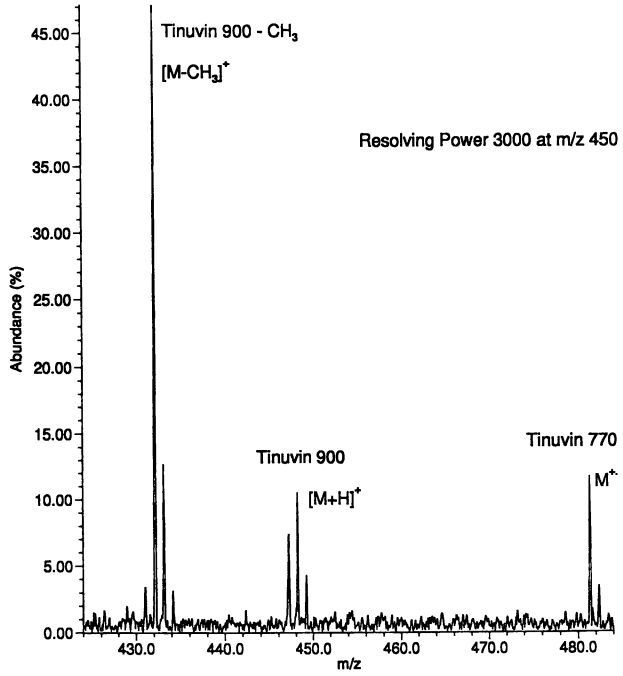


Figure 7. The Laser Probe FT/MS Spectrum of a piece of a cross-linked polymer illustrating the presence of two antioxidants.

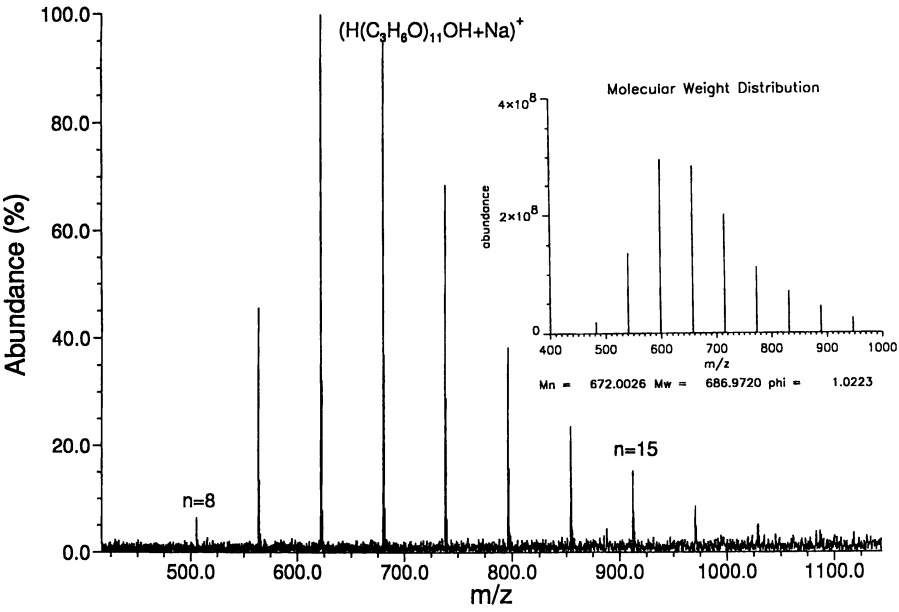


Figure 8. Electrospray ionization/Fourier transform mass spectrum of poly(propylene glycol) 720. Only the single charge state oligomeric species are observed. The weight average molecular weight calculated from the mass spectrum is 687.

Table II. Additives Studied by Laser Desorption Fourier Transform Mass Spectrometry[a]

Acrawax (*44*)	Sandostab (*47*)
Antiozonants (*45*)	PEPQ
Carbon Black	Seenox (*47*)
Chimassorb	4125
Dyes (*46*)	Spinuvex (*47*)
EBS Wax (*44*)	A36
Goodrite (*47*)	Stearamides (*44*)
3114	surfactants
Irganox (*44, 47*)	Tinuvin (*44, 47*)
245, 259, 1010, 1035, 1076,	144, 320, 326, 328, 440,
1098, 3114, MD1024	622, 770
metal stearates (*47*)	Ultranox (*44, 48*)
Naugard (*44, 47*	226, 236, 246, 626
76, 524, BHT, DLTDP, DSTDP	Weston (*44*)
Oleamides (*44*)	618, TNNP
Pigments	Wingstay (*45*)
Polygard (*44*)	100, 300
	XR 2502 (*48*)

[a] Additives without references are unpublished work from the authors' laboratories.

An alternative, and a more elegant approach to analyzing large polymers is to couple a GPC via an electrospray ionization interface to the FT/MS. Each oligomeric fraction that elutes from the GPC would be measured directly by mass spectrometry with minimal interference from the multiple charge states of adjacent oligomers.

Summary

Gel permeation chromatography can provide a cost-effective solution to most molecular weight measurements over 10,000 Daltons. Modern laser-based mass spectrometry methods have many applications to polymer characterization. The strengths of mass spectrometry are in the molecular weight regions where GPC performance tails off (<10,000 Daltons) or when detailed molecular structures are needed.

MALDI/TOF provides cost-effective measurements for low molecular weights (less than 100 Daltons) to over 250,000 Daltons. Today, the Laser Probe FT/MS technique can provide accurate molecular weight information for polymers that are less than 20,000 Daltons. Additionally, the FT/MS has features that allow molecular structures and substructures of most classes of polymers to be probed. These mass spectrometry techniques are also directly applicable to contaminant and additive analysis.

There are prospects of coupling GPC to these and other state-of-the-art mass spectrometers. For example, polymer additive analysis can now be performed

In Hyphenated Techniques in Polymer Characterization; Provder, Theodore, et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1994.

routinely by LC/MS. Furthermore, there is promise for high-molecular weight characterization (>50,000 Daltons) by using electrospray ionization, another new method for ionizing large molecules in solutions. The electrospray method is expected to allow GPC to be coupled directly to the FT/MS.

Acknowledgments

The authors thank Richard Nielson and Andy Jarrell (Waters), Trevor Havard (Precision Detectors), William Simonsick, Jr. (E.I. DuPont de Nemours & Co.), Jaap Boon (FOM Institute), James DeVries and Tom Prater (Ford Motor Company) for helpful discussions. The technical assistance of David A. Weil (3M) and Joel Covey (Extrel FTMS, Inc.) for the acquisition of some mass spectra is appreciated.

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RECEIVED August 10, 1994