Mass Spectrometry of Polymers and Polymer Surfaces

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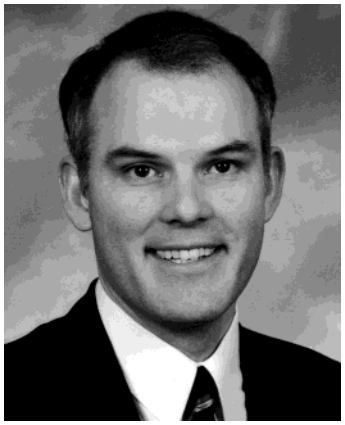
Contents



Scott D. Hanton was born in 1963 in Saginaw, MI. He received his B.S. degree in Chemistry from the Honors College at Michigan State University in 1985. He received his Ph.D. degree in Physical Chemistry from the University of Wisconsin—Madison in 1990 after completing his thesis work in gas-phase ion–molecule reaction chemistry with Professor James Weisshaar. In 1990 Scott joined Air Products and Chemicals, Inc., as the technical expert in the Laser Applications Laboratory. By 1995, Scott was deeply involved with research and applications in matrix-assisted laser desorption/ionization (MALDI) and moved to the Mass Spectrometry Laboratory. In 1998, Scott became Lab Supervisor for Mass Spectrometry, and in 2000, Scott became the Group Head for the Organic Materials Analysis group, which is comprised of the Nuclear Magnetic Resonance, Mass Spectrometry, and Chromatography Laboratories. Scott enjoys technical problem-solving using MALDI, gel permeation chromatography, and time-of-flight secondary-ion mass spectrometry. Away from work, Scott is very happy with his wife of 15 years, Helen, and their young son, Brian.

I. Introduction

Mass spectrometry of polymers and polymeric surfaces represents a very broad field of active research. There are many different experimental techniques used to probe polymers and polymeric surfaces as well as numerous polymer compositions and surfaces that invite careful study. In this paper we will survey some of the more important contributions with the aim to cover a wide variety of techniques and systems. The examples discussed will provide an overview of using mass spectrometry to solve interesting and important issues involving polymers and their surfaces. For the most part, the paper is organized primarily by mass spectrometry technique with the analysis of bulk polymers addressed first and the analysis of polymer surfaces addressed second.

From a traditional point of view mass spectrometry of polymers or surfaces appears to be rather incompatible. Mass spectrometry techniques require gas-phase ions for a successful analysis, while polymers are composed of large, entangled macromolecules that are not readily converted to gas-phase species. Despite this inherent incompatibility, mass spectrometry researchers have used significant creativity to develop ingenuous methods to use mass spectrometry to investigate many different aspects of polymer and surface chemistry.

For the purposes of this paper, a polymer is any material that is composed of related oligomeric

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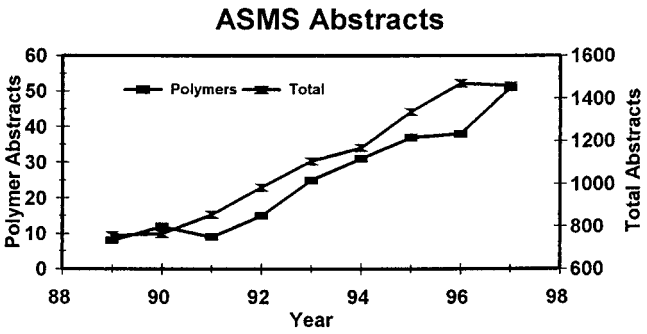


Figure 1. Number of polymer abstracts and number of total abstracts per year for the period 1989−1997. The number of polymer abstracts has increased by over 600% over that period. (Reprinted with permission from ref 1. Copyright 1998 American Society for Mass Spectrometry.)

molecules. Polymers have repeat units composed of the monomers used to produce them. They also have end groups that cap the repeat units. The polymer is characterized by the chemical composition of the repeat units, the end groups, and the molecular weight distribution of the individual oligomers. Mass spectrometry techniques have been developed to characterize all of these aspects of the bulk polymer, as well as characterization of the polymer sample for undesired contaminants and side reactions.

A surface is the interface at the site of a phase change. Many different surfaces can be observed: air−solid, air−liquid, and liquid−solid are common interfaces. Most of the surfaces studied by mass spectrometry are either air−solid or air−liquid interfaces. Secondary-ion mass spectrometry (SIMS) is the primary mass spectrometry technique used to analyze polymer surfaces, and this discussion of surfaces will concentrate on that technique. A large body of recent literature reviews and discusses the more general mass spectrometry of surfaces.

As new mass spectrometric techniques have been invented, many of the key developments have been driven by the desire to analyze larger and more complex biomolecules. For attendees of the annual American Society of Mass Spectrometry (ASMS) Conference on Mass Spectrometry and Allied Topics, this has been quite clear. The number of papers presented on bioanalysis has increased hugely over the past 10 years. As these new techniques are introduced, they are also recognized as having important applications on polymer systems as well. The number of polymer abstracts to the annual ASMS conference has grown at an even faster pace than the overall rate.[1] Figure 1 shows the growth of total abstracts and the growth of polymer abstracts over the period from 1989 to 1997. For more information on the mass spectrometry of polymers, several general reviews are available.[2−6]

II. Polymer Chemistry

Polymers are produced from the sequential reaction of monomer units to form distributions of related molecules, oligomers, that can vary in the number of reacted monomer units, or chain length, the chemical species at the ends of the chains, end groups, and if the oligomer has multiple monomer units the relative amounts of the different units. Polymer materials are typically characterized by measuring the chemical structure of the repeat units and the end groups and by measuring the molecular weight distribution of the series of oligomers. The molecular weight distribution is determined by the number-average molecular weight, M_N, the weight-average molecular weight, M_W, and the polydispersity. The two average molecular weights are the first two moments of the distribution of oligomer molecules

$$M_N = \Sigma M_i N_i / \Sigma N_i \quad (1)$$

$$M_W = \Sigma (M_i)^2 N_i / \Sigma M_i N_i \quad (2)$$

$$\text{polydispersity} = \text{PD} = M_W / M_N \quad (3)$$

where M_i is the mass of an observed ion and N_i is the number of ions observed.

Traditionally, polymer materials are analyzed by different techniques to obtain the chemical structure and molecular weight information. Techniques such as gel permeation chromatography (GPC, also known as size-exclusion chromatography, SEC), light scattering, osmometry, nuclear magnetic resonance (NMR) spectroscopy, and end group titration are used to measure the average molecular weights. Spectroscopy techniques such as NMR, infrared (IR), and X-ray photoelectron spectroscopy (XPS) are used to determine the chemical functionality of the repeat units and sometimes the end groups. The development of mass spectrometry techniques capable of analyzing polymer materials has added complementary methods to characterizing polymer samples.

III. Mass Spectrometry Basics

A mass spectrometer is an instrument designed to measure the mass-to-charge ratio (m/z) of analyte ions. To be analyzed by a mass spectrometer, the desired species must be charged and in the gas phase. In this article we will discuss a number of different methods to create charged species from polymers and surfaces. Once the charged particle is in the gas phase, mass spectrometers use electric and/or magnetic fields to control the paths of the ions. In general, the details of the different kinds of mass spectrometers will not be discussed here.

The most common types of mass spectrometers used to analyze polymers and surfaces are quadrupole, magnetic sector, time-of-flight (TOF), and Fourier transform (FT, also known as ion cyclotron resonance, ICR) instruments. One of the exciting recent mass spectrometer innovations has been the introduction of orthogonal TOF instruments for electrospray ionization (ESI) experiments.[7−8]

Table 1. Types of Mass Spectrometers

type	separation	resolution
quadrupole	rf and dc fields	low
magnetic sector	magnetic fields	high
time-of-flight	velocity	high
Fourier transform	magnetic field	very high

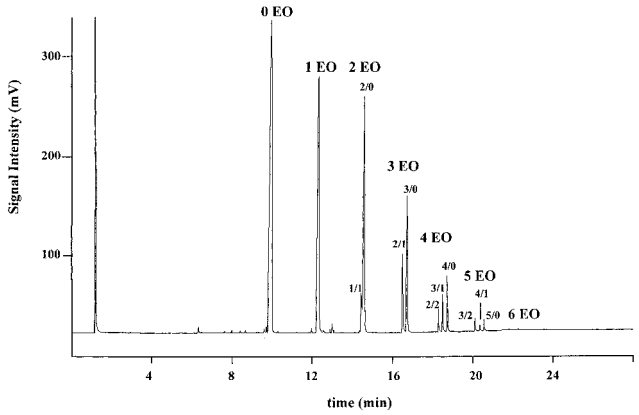


Figure 2. GC-MS EI TIC of S420. Each of the peaks is assigned as an individual oligomer of the ethoxylated surfactant.

More information on the basics of mass spectrometry and mass spectrometers can be found in a number of books and articles.[9−13]

IV. Mass Spectrometry of Polymers

A. GC-MS

Traditional gas chromatography−mass spectrometry (GC-MS) with electron ionization (EI) or chemical ionization (CI) is still used to probe polymer chemistry. GC-MS is a very valuable technique to identify and characterize small volatile components of polymer materials, residual monomers, and unwanted contaminants. GC-MS is a two-dimensional analysis combining the power of gas chromatography and mass spectrometry. GC-MS can resolve and completely characterize a vast number of volatile compounds. The limitation of the technique is that to be analyzed the compound must be sufficiently volatile to elute from the chromatograph.

In polymer analysis, GC-MS has long been used to identify and characterize volatile components and contaminants.[14] One example of this application is the identification of odor problems in commercial products. Maeno and co-workers used sniff port GC-MS to characterize an odor problem in a wet polyacrylate superabsorbent polymer.[15−16] The use of a human observer as a GC detector must be done very carefully to protect the observer from any hazardous materials that could be in the column effluent. In their experiments, Maeno and co-workers discovered that compounds with a vinyl ketone-like structure caused the odor problems and 5-methylhex-1-en-3-one (isobutyl vinyl ketone) was especially malodorous.

We use GC-MS to characterize very low molecular weight oligomeric materials.[17] These low molecular weight oligomers are not efficiently metal cationized and are not effectively analyzed by some of the other mass spectrometry techniques, such as matrix-assisted laser desorption/ionization (MALDI), ESI, fast atom bombardment (FAB), or secondary-ion mass spectrometry (SIMS). For example, we can completely characterize the lowest molecular weight commercial ethoxylated Surfynol surfactant (2,4,7,9-tetramethyl-5-decyne-4,7-diol) named S420 by GC-MS. Figure 2

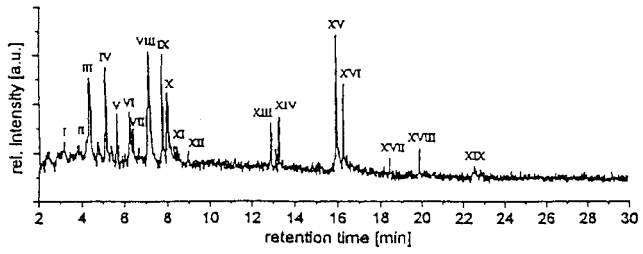


Figure 3. GC-MS EI TIC of photodegradation products of solid PPE. (Reprinted with permission from ref 18. Copyright 1999 Elsevier Science Inc.)

shows the total ion chromatogram (TIC) obtained from EI of S420. Each of the intense peaks is assigned as an individual oligomer of S420. The fine structure observed for the higher peak clusters is assigned as the resolution of the ethoxylated chain length isomers. Because the Surfynol surfactants are diols, each alcohol can be ethoxylated. From the distribution of the oligomer peaks we can calculate the average molecular weights of $M_N = 281$ u and $M_W = 292$ u with PD = 1.04. In addition to the molecular weight distribution information, we also obtain chemical structure information from the individual EI mass spectra.

GC-MS can also be used to characterize the degradation products of polymers. Pyrolysis followed by GC-MS will be discussed separately in the next section. Other methods to degrade the polymer material include photolysis and thermochemolysis.[18−19] Richter and co-workers used GC-MS and liquid chromatography (LC)-MS techniques to characterize the photodegradation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPE) polymers.[18] Understanding the photodegradation processes are important to improving the light stability of PPE. The photodegradation was done using radiation from a Hg/Xe arc lamp. Figure 3 shows a EI TIC of photodegraded PPE. The chromatogram of the photodegradation products shows 19 primary peaks. These peaks were assigned with the help of the Wiley fragmentation database and a series of low molecular weight standards. The photodegradation products can be identified as sets of homologous series and are characteristic of the repeat units of the PPE polymer. The authors propose that the primary photoprocess involves the cleavage of the hydroxyl end group.

GC-MS can also be combined with solid-phase microextraction (SPME) to characterize degradation products in polymers.[20] Hakkarainen and co-workers show that SPME followed by GC-MS can be more effective than headspace GC-MS to identify degradation products from low-density polyethylene (LDPE) films.[21] The LDPE films were treated with ultraviolet (UV) radiation for 100 h followed by mild thermal aging at 80 °C for 5 weeks. SPME was done with silicon-based fibers coated with both poly(dimethylsiloxane) (PDMS) and polar carbowax (divinylbenzene). Figure 4 shows three GC-MS TIC from (a) SPME using the PDMS-coated fibers, (b) SPME using the carbowax-coated fibers, and (c) headspace GC-MS. Several different degradation species are detected. They are primarily ketones, carboxylic acids, ketoacids, and furanones. Clearly, both of the SPME

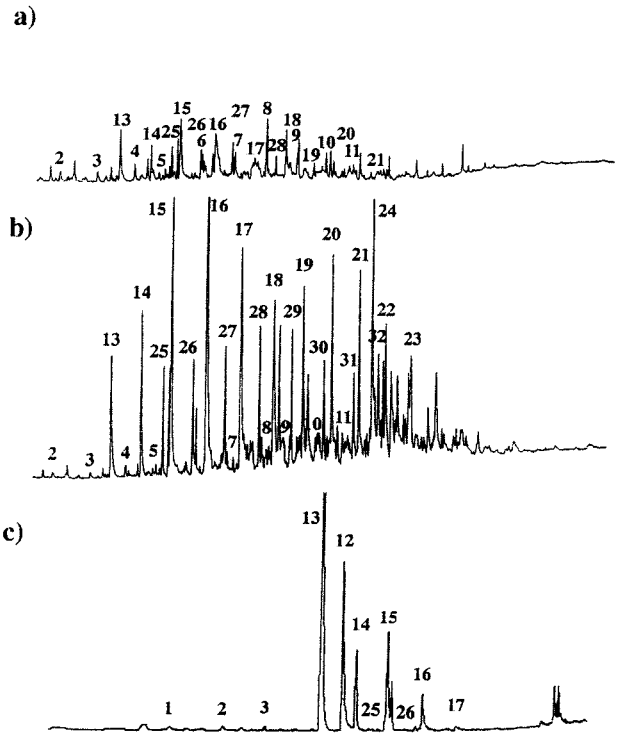


Figure 4. GC-MS EI TIC of UV degradation products from LDPE films from (a) SPME using the PDMS-coated fibers, (b) SPME using the carbowax-coated fibers, and (c) headspace GC-MS. (Reprinted with permission from ref 21. Copyright 1997 Plenum Publishing Corp.)

experiments identify many more degradation products than the headspace GC-MS. Hakkarainen and co-workers used the GC-MS data to evaluate the relative thermal stability of different LDPE films.

B. Pyrolysis

Pyrolysis mass spectrometry is a technique that uses heat to produce volatile ions for mass spectrometric analysis.[22−24] The heat necessary to produce useful fragments depends on the thermal stability of the polymer but usually ranges from about 250 to 1000 °C. Typically, this heating causes damage to the polymer and only relatively low mass fragments of the polymer can be analyzed. These fragments often contain sufficient information to identify the chemistry of the original polymer but the average molecular weight information will be lost. Table 2 shows some common polymer degradation products observed by pyrolysis mass spectrometry.[25] This is a relatively straightforward method to establish the chemical structure of an unknown polymer material.

The heating for pyrolysis may take place directly in a mass spectrometer where the pyrolates are ionized by EI, CI, or direct laser ionization, or the heating may be separate from the mass spectrometer, and other mass spectrometry experiments can be applied to the pyrolates, such as GC-MS, ESI, or MALDI. The pyrolysis process can also be characterized by thermogravimetric−mass spectrometry (TG-MS) methods[26] and by combined TG-MS and GC-MS.[27] The key advantage of pyrolysis mass spectrometry is that it is a relatively simple experiment that yields direct measurements of the bulk polymer

Table 2. Degradation Products Encountered in Studying Polymers by Pyrolysis[a]

pyrolysis products	likely source
decane, decene, etc.	polyethylene (PE)
dimethyl heptene	polypropylene (PP)
isoprene, limonene	polyisoprene (PI)
HCl, benzene, naphthalene	poly(vinyl chloride) (PVC)
HCl, trichlorobenzene	PVC
acetic acid, benzene	poly(vinyl acetate)
styrene	polystyrene (PS)
acrylonitrile	polyacrylonitrile
methyl methacrylate	poly(methyl methacrylate) (PMMA)
butyl methacrylate	poly(butyl methacrylate (PBA)
ethyl acrylate	poly(ethyl acrylate)
butyl acrylate	poly(butyl acrylate) (PBA)
tetrafluoroethylene	poly(tetrafluoroethylene) (PTFE)
furans, levoglucosan	cellulose, paper

[a] Reprinted with permission from *Am. Lab.* **1999**, *31* (19), 30. Copyright 1999 International Scientific Communications, Inc.

chemistry. In some well behaved cases, quantitative results can be achieved.[28−29]

Direct pyrolysis mass spectrometry experiments can be used to establish both the chemical structure of the polymer and to investigate the thermal degradation pathways.[30] A good example of this work is the investigation of polyetherimide (PEI) by Carroccio and co-workers.[31] In these experiments, PEI is gradually heated from 50 to 700 °C at 10 °C/min. The pyrolates are then ionized by EI. Figure 5 shows examples of the mass spectra obtained. About 57 different pyrolate ions are identified in the mass spectra. The mass spectral information is combined with the pyrolysis temperature information to create thermal profiles. Figure 6 shows a series of thermal profiles for crude and purified PEI for some of the more important ions observed in the mass spectra. The chemical assignments and the thermal profiles of the ions yield important information about the structure and the development of mechanisms involved in the thermal degradation of PEI.

Direct pyrolysis mass spectrometry can also be used to characterize random and block sytrene−butadiene copolymers.[32] These experiments showed that in the block copolymer, each block pyrolyzed similarly to the corresponding homopolymer. The random styrene−butadiene rubber, however, produced pyrolysis data that showed a shared nature between the two homopolymers.

Pyrolysis field ionization mass spectrometry (FIMS) can be used as a direct technique to obtain mass-analyzed data on higher mass pyrolysis products.[33] Lattimer showed that pyrolysis FIMS can characterize diene rubbers. An example of a pyrolysis FIMS mass spectrum of polybutadiene at 300−325 °C is shown in Figure 7. The pyrolysis FIMS data provide insight into the low-temperature pyrolysis mechanisms of the diene rubbers. The data can be interpreted in terms of free radical degradation mechanisms.

The development of direct laser photoionization techniques to pyrolysis mass spectrometry provides the advantage of a "soft" ionization technique. Zoller and co-workers developed pyrolysis−photoionization−mass spectrometry methods to identify and

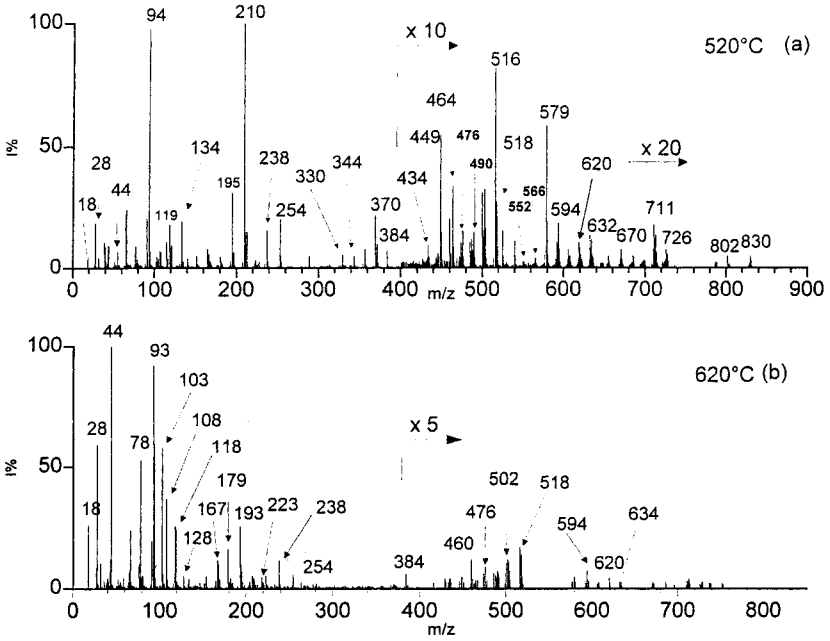


Figure 5. EI mass spectra of pyrolysis products evolved from purified PEI samples at (a) 520 and (b) 620 °C. (Reprinted with permission from ref 31. Copyright 1999 Wiley-VCH, Verlag, GmbH.)

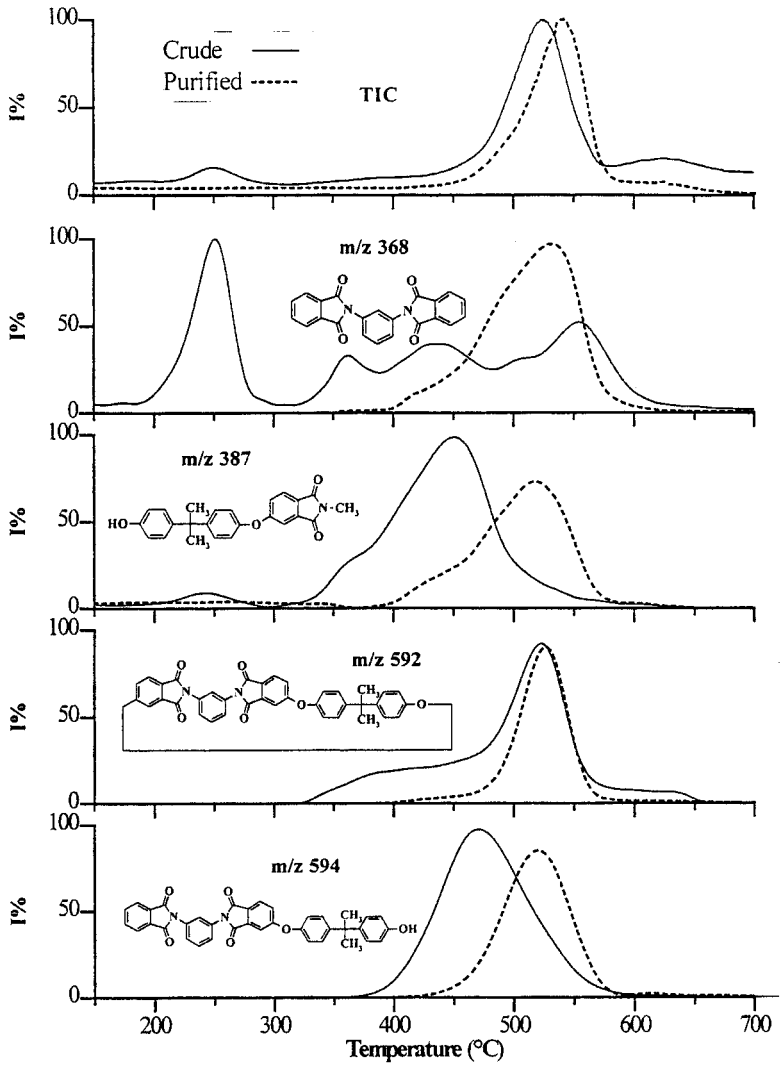


Figure 6. TIC and temperature-resolved evolution profiles of the ions detected at 368, 387, 592, and 594 u observed in the direct pyrolysis mass spectra of the crude (—) and purified (···) PEI samples. (Reprinted with permission from ref 31. Copyright 1999 Wiley-VCH, Verlag, GmbH).

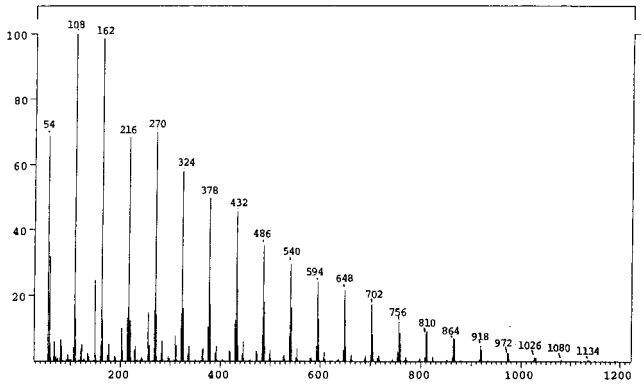


Figure 7. Pyrolysis field ionization mass spectrum of PBD. (Reprinted with permission from ref 33. Copyright 1997 Elsevier Science B.V.)

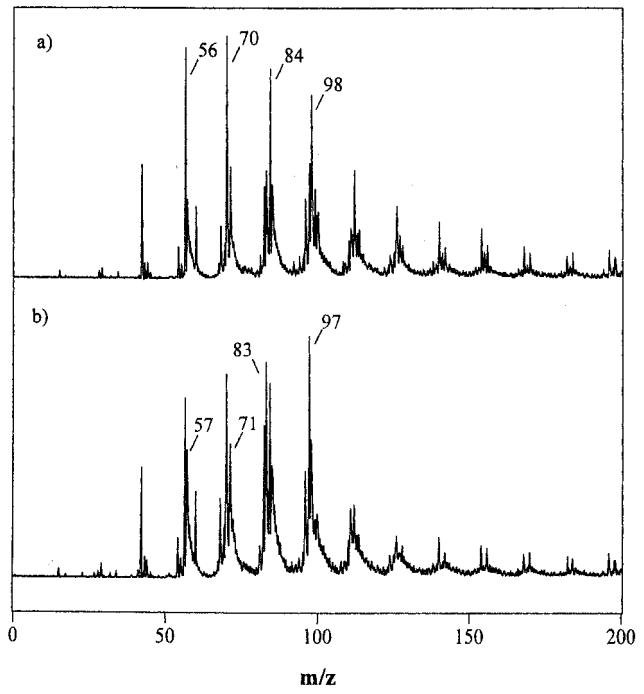


Figure 8. Pyrolysis−photoionization mass spectra of (a) low- and (b) high-density polyethylene. (Reprinted with permission from ref 34. Copyright 1999 American Chemical Society.)

quantitate polyethylene and acrylonitrile−butadiene polymer materials.[34−35] In these experiments, pyrolates were created in the source of a reflectron time-of-flight mass spectrometer (TOFMS) and ions created by photoionization with vacuum ultraviolet laser radiation of 118.2 nm. The VUV laser is created by frequency-tripling the 355 nm third harmonic of an Nd:YAG laser. Figure 8 shows pyrolysis−photoionization mass spectra of low- and high-density polyethylene produced by this technique. The mass spectra are clearly different, and the differences can be related to the degree of branching in the samples. Using principal-component analysis and linear discriminant analysis, the different polyolefin samples are properly classified.

While direct pyrolysis mass spectrometry can be a very powerful tool to characterize polymer materials, the mass spectra can be very complex and difficult to interpret. Both computer modeling and the use of chromatography prior to mass analysis can be used

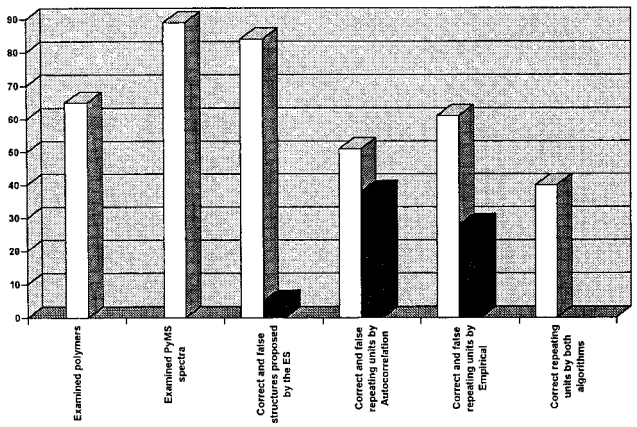


Figure 9. Results of testing expert system to aid in the interpretation of direct pyrolysis mass spectra. (Reprinted with permission from ref 36. Copyright 1998 Elsevier Science B.V.)

to simplify the interpretation process. Georgakopoulos and co-workers developed an expert system (ES) to aid in the interpretation of direct pyrolysis mass spectra.[36] Their expert system contains reference spectra for a variety of condensation polymers, including polyamides, polycarbonates, polyethers, polyesters, polyureas, polyurethanes, polyimides, polysulfides, polysulfones, polyschiff bases, polysiloxanes, and polyphosphagenes. The system also contains data acquired using EI, CI, and desorption chemical ionization (DCI). The system was tested using 89 mass spectra belonging to 65 polymers. Figure 9 shows the results of the testing. Using the expert system interfaced with a human user determined the best choice of the repeating unit in 84 (94.4%) cases. In an automatic mode, autocorrelation determined the best choice for the repeating unit in 51 cases and the empirical algorithm determined the best choice for the repeating unit in 61 cases.

The pyrolysis can also be done remote from the mass spectrometer. In some cases, experiments can be done that cannot be accomplished with direct ionization inside the mass spectrometer, using GC to simplify the individual mass spectra, for example. Figure 10 shows pyrolysis GC-MS elution chromatograms, also called pyrograms, for a polyethylene standard and a clear food wrap.[25] In this case, the pyrolates were separated via GC prior to MS analysis. The addition of GC separation can be very useful to separate the various EI fragment mass spectra.[37] The individual ion fragmentation patterns can be used to properly assign the various pyrolates. In Figure 10a we can clearly see ion peaks assigned as different chain length segments of polyethylene. These hydrocarbon segments clearly show the chemical structure of polyethylene, but the average molecular weights of the original polyethylene sample have been lost. In Figure 10b we can clearly see that the clear food wrap has the same chemical structure pyrolates as the polyethylene standard.

Pyrolysis GC-MS can also be used to monitor the polymerization of a thermally cured polymer.[38] Galipo and co-workers were able to follow the progress of polymerization of a polyimide (Ciba-Geigy Matrimid 5292) by identifying characteristic pyrolates of both

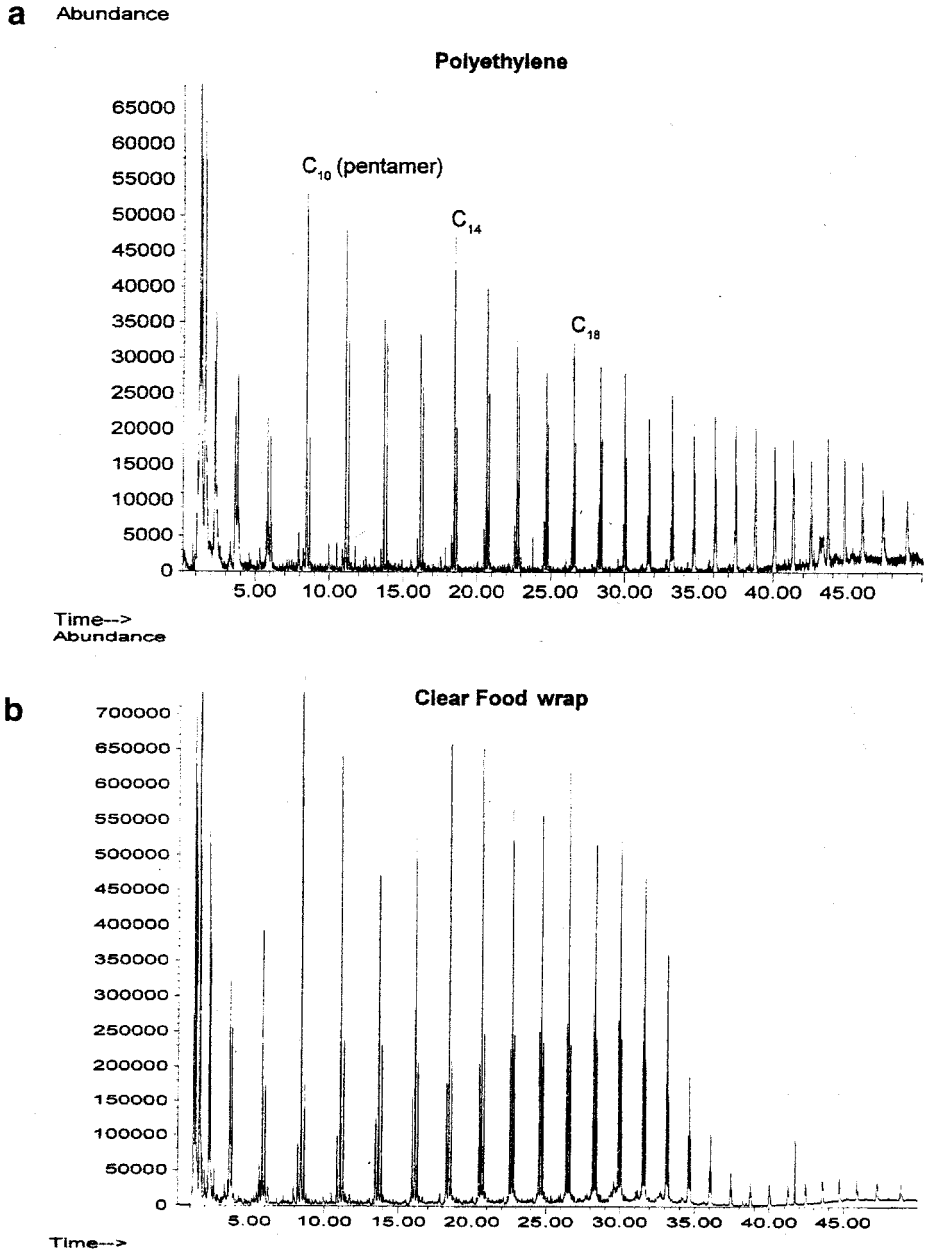


Figure 10. Pyrolysis−GC-MS chromatograms of (a) reference PE pyrolyzed at 750 °C, and (b) sample of clear food wrap (polyethylene film). (Reprinted with permission from *Am. Lab.* **1999**, *31* (19), 30. Copyright 1999 International Scientific Communications, Inc.)

the reactants and the products. More information on the pyrolysis GC of coating materials is in the recent review by Haken.[39]

Controlling the heat delivered to a pyrolysis mass spectrometry experiment can also create higher mass pyrolates. These higher mass pyrolates can then be analyzed by techniques such as MALDI or ESI (both MALDI and ESI will be discussed below).[40−41] Lattimer and co-workers use low-temperature pyrolysis, in the range of 250−325 °C, followed by MALDI to study polyurethane materials.[40] There have been many different investigations of the pyrolysis of polyurethanes, but this work provides additional insight by characterizing higher molecular weight products. The use of MALDI to analyze the low-temperature pyrolysis products allows the characterization of much higher mass pyrolates than the use of direct pyrolysis or pyrolysis GC-MS experiments. Figure 11 shows a MALDI mass spectrum of polyurethane pyrolyzed at 300 °C for 30 min. In Figure 11, Lattimer and co-workers identified five different oligomeric series (shown in the figure as series A, B, D, E, and K). The series are assigned as A, linear diol; B, cyclic polyester; D and E, terminally unsaturated polyesters; and K, dehydration of B series cyclic polyesters. The pyrolysis−MALDI data indicates that the polyurethane degradation follows two pathways: dissociation of the urethane linkage and ester exchange.

ESI can also be used to mass spectrally analyze pyrolysis products. Barton and co-workers used pyrolysis−ESI and MALDI to characterize degradation pathways in poly(propylene oxide) (PPO) polymers.[41] Figure 12 shows a pyrolysis−ESI mass spectrum for

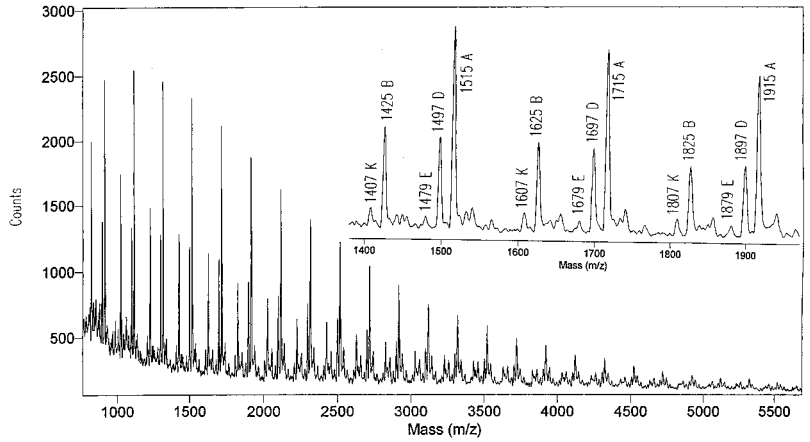


Figure 11. MALDI mass spectrum of polyurethane pyrolyzed for 30 min at 300 °C. (Reprinted with permission from ref 40. Copyright 1999 Elsevier Science B.V.)

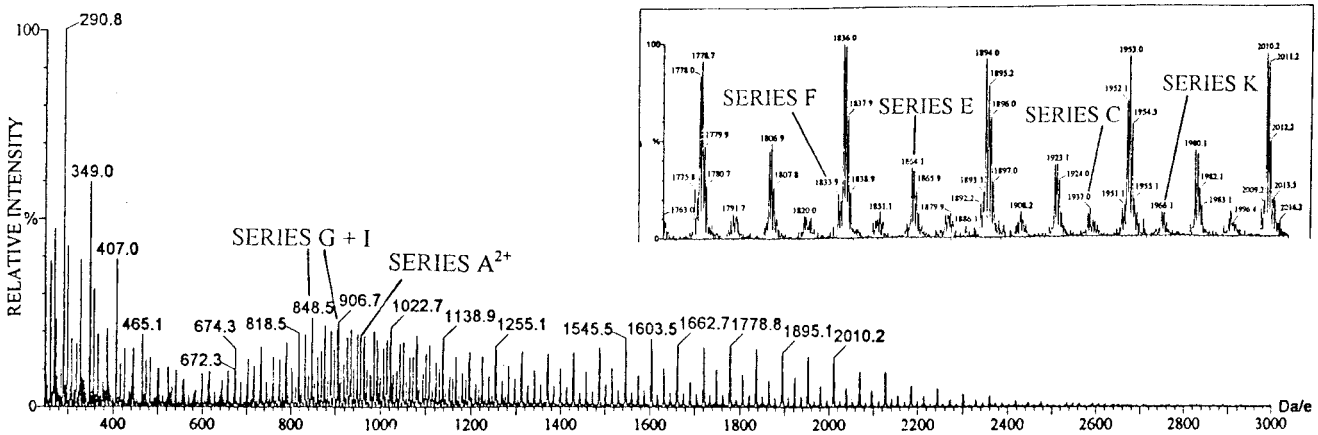


Figure 12. ESI mass spectrum of pyrolyzed PPO (ESI conditions, THF/MeOH (50/50) mobile phase containing 0.5% aqueous NH_4Cl. Inset contains expansion from 1763 to 2016 u. (Reprinted with permission from ref 41. Copyright 1995 Elsevier Science Ltd.)

a sample of linear PPO with a nominal molecular weight of 2000 u. The authors observed and identified several different series in the mass spectrum. These results suggest that C−C and C−O cleavage adjacent to the alkoxy radical are key degradation pathways for PPO. In addition, the authors point out that the pyrolysis−ESI data also support a major role for the secondary alkoxy radical in the degradation pathway.

C. GDMS

Glow discharge mass spectrometry is another technique capable of fingerprinting different polymer materials.[42] Glow discharge techniques have become well established for elemental analysis. GDMS techniques are now being developed for polymer analysis. One specific advantage of GDMS in polymer analysis is the ability to analyze bulk samples. Very little sample preparation is required, and relatively large pieces of different materials can be directly analyzed. This could be particularly valuable for materials that are not soluble, such as some thermoplastics and complex copolymers. In GDMS, the analyte behaves as the cathode in a low-pressure discharge. To enable the technique to analyze nonconducting samples such as polymers, a secondary cathode is used to create a direct current (dc) discharge at the surface of the sample.[43] Both radio frequency (rf) and dc GDMS techniques have been developed.[44−45] A good example of spectral fringerprint data obtained by GDMS is from Shick and co-workers on poly(tetrafluoroethylene) (PTFE).[44] A GDMS fingerprint mass spectrum of a 1.5 mm thick PTFE sample is shown in Figure 13. Atomic and molecular ions typical of PTFE are clearly observed. All of the ions can be assigned as $C_xF_y^+$. Further development of GDMS methods for polymers includes a cryogenically cooled sample holder to aid in the analysis of thermally labile polymers.[46]

D. FD and FAB

Field desorption (FD)[47−48] and fast atom bombardment (FAB)[49] mass spectrometry are techniques that were developed to provide mass specificity to compounds that are insufficiently volatile to analyze by traditional mass spectrometry techniques. FD and FAB were widely practiced at one time and often used in conjunction with magnetic sector instruments to provide high mass accuracy data for materials up to a few thousand mass units (u). While still important techniques, FD and FAB have been widely replaced by MALDI and ESI techniques, which will be discussed below.

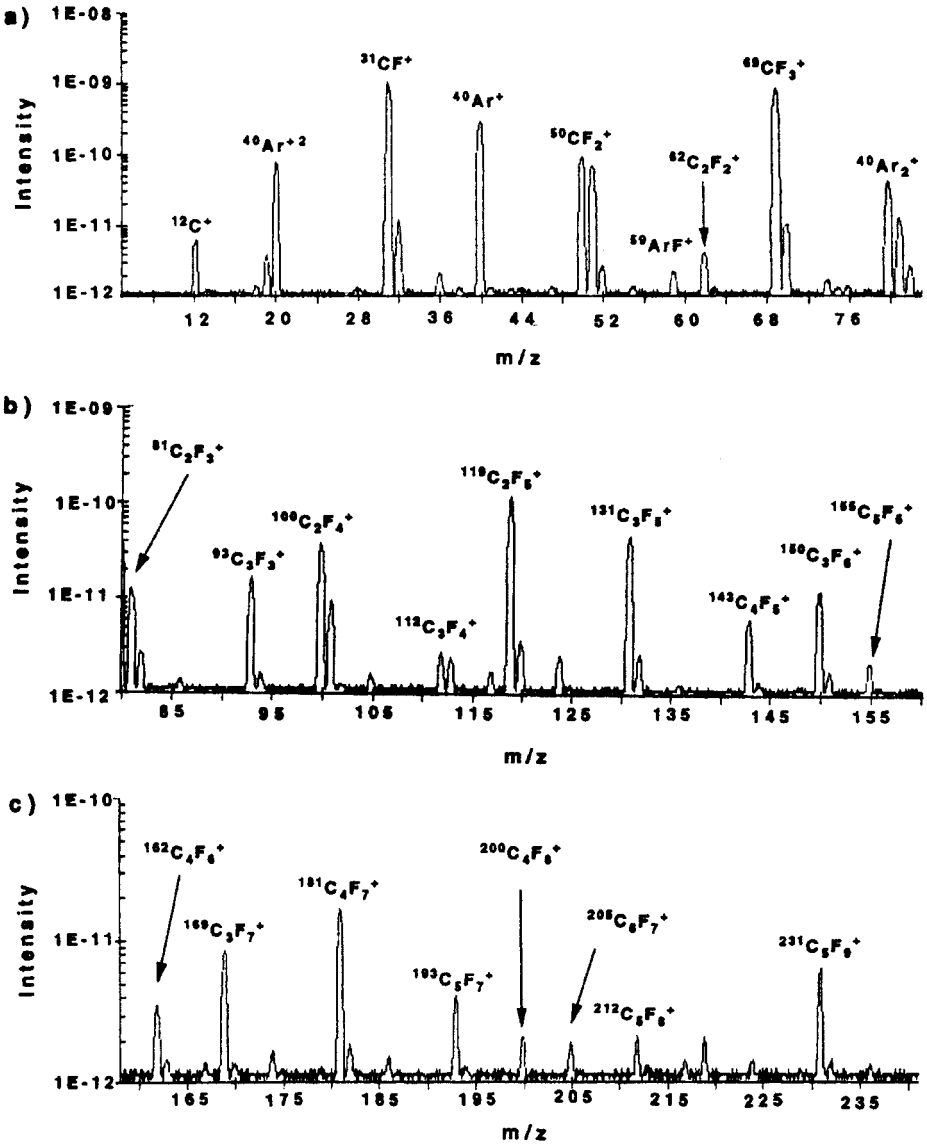


Figure 13. GDMS mass spectrum of a 1.5 mm thick PTFE sample: (a) 4−80, (b) 81−160, (c) 161−240 u acquired with 20 W rf power and an Ar pressure of 0.075 mbar. (Reprinted with permission from ref 44. Copyright 1996 American Chemical Society.)

In FD, a dilute solution of the polymer is applied directly to a filament on which pyrolitic carbon microneedles have been grown.[50] This emitter is held at high voltage and placed close to the counter electrode creating the very high field potentials required for field ionization. FD is a soft ionization technique, producing primarily intact oligomer ions, and has been shown to be effective in analyzing low molecular weight polymers, such as polystyrene.[51] FD with multiple cationization charges is being explored to help extend the mass range of magnetic sector instruments.[52] FD is a time-consuming and experimentally challenging technique but it still practiced and has particular utility in analyzing polymers which lack sufficient functionality to be ionized by MALDI. Evans and co-workers showed that FD can characterize low molecular weight polyethylene standards, as shown in Figure 14.[50] FD is also used to analyze prepolymers and polymer additives in cases where techniques such as MALDI or liquid secondary-ion mass spectrometry (LSIMS) have added complications due to matrix interference.[53−54]

In FAB, a dilute solution of the polymer is mixed with a liquid matrix, such as glycerol, and applied to a probe tip. The probe is bombarded with a fast atom beam. FAB and LSIMS are closely related techniques. The main difference between the techniques is that a neutral primary beam is used for FAB and a charged primary beam is used for LSIMS. The liquid matrix serves to keep individual oligomer molecules separated and to constantly refresh the surface of the sample, allowing long analysis times. One key disadvantage of FAB is that the surface of the liquid matrix is the only part of the sample analyzed. FAB can have distinct problems with discrimination based on relative surface activity of different analytes. Figure 15 shows a FAB mass spectrum of an ethoxylated Surfynol surfactant, S465.[17] The mass spectrum clearly shows the oligomers of the surfactant sample. While the popularity of FAB has declined with the rise of MALDI and ESI, FAB experiments are still done on materials such as poly(methyl methacrylate peroxide),[55] epoxy−amine addition polymers,[56] and polyester copolymers.[57]

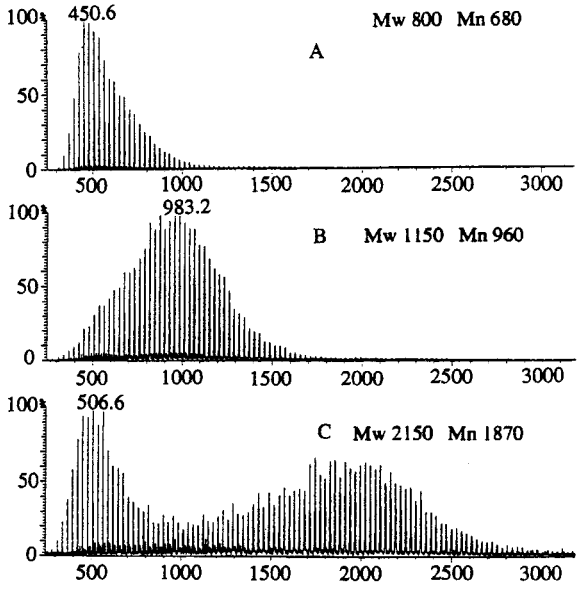


Figure 14. FD mass spectra of low molecular weight PE standards. (Reprinted with permission from ref 50. Copyright 1996 American Society for Mass Spectrometry.)

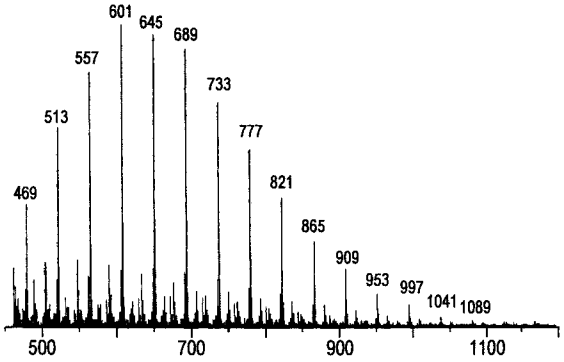


Figure 15. FAB mass spectrum of the S465 ethoxylated surfactant. The ion at 513 u is assigned as the six ethoxylate oligomer. (Reprinted with permission from ref 17. Copyright 1998 American Society for Mass Spectrometry.)

E. LDMS

Laser desorption mass spectrometry (LDMS) is a technique that was developed to analyze materials by focusing high-power laser beams on the surface and mass analyzing the ablated species. Ions could be formed coincident with the ablation laser or postionized with either another laser or with an electron beam. Laser-ablated atoms can also be analyzed by inductively coupled plasma mass spectrometry to characterize trace levels of atomic species.[58] The development of MALDI (discussed below) as a special case of LDMS has greatly reduced the amount of LDMS still used, although LDMS techniques in FTMS instruments can produce a significant amount of information on polymer materials.[59−60] Recent examples of LDMS for polymer analysis are the detection of polymer additives,[61−62] characterization of perfluorinated polyethers,[63] characterization of polymer end groups,[64] characterization of nylon 6.6 ablation,[65] and characterization of C_{60} materials.[66]

Wright and co-workers used LDMS with nonresonant, ultraviolet (UV) laser postionization to detect phenolic antioxidants and UV stabilizers (Tinuvin) in polymer samples.[61] Figure 16 shows LDMS mass spectra of Tinuvin 320 and Santo White Powder observed in samples of poly(oxymethylene) (POM). The detection limit for the Santo White Powder was determined to be 28 ppm. Subsequent depth profiling experiments by Zhan and co-workers showed that the additives were depleted from the surface of the sample relative to the bulk. The intensity of the Santo White Powder was 40% lower in the near surface region than in the bulk.

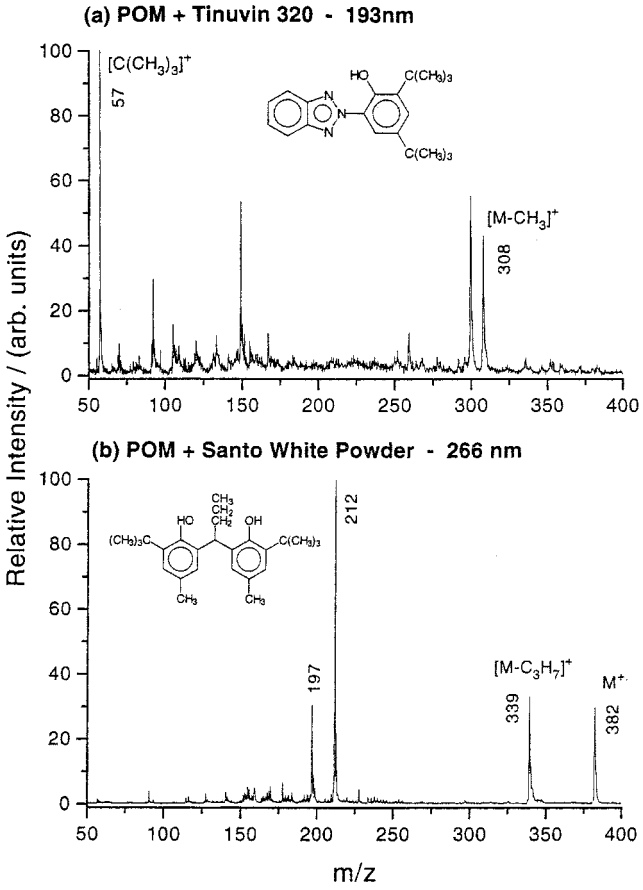


Figure 16. LDMS mass spectra of injection-molded samples of POM (a) containing 0.3 wt % Tinuvin 320 using 193 nm photoionization and (b) containing 0.1 wt % Santo White antioxidant using 266 nm photoionization. (Reprinted from ref 61. Copyright 1998 American Chemical Society.)

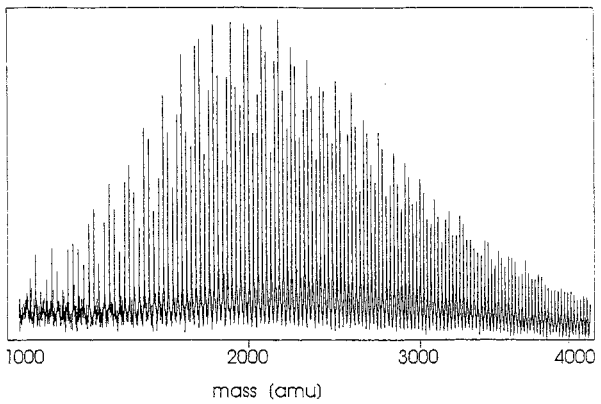


Figure 17. LD REMPI mass spectrum of Z-Dol with esterified end groups. The sample was desorbed with 532 nm and postionized with 193 nm. (Reprinted with permission from ref 63. Copyright 1996 American Chemical Society.)

De Vries and co-workers used LDMS with resonant-enhanced multiphoton ionization (REMPI) to characterize films of perfluorinated polyethers.[63] The polymers either contain or are modified to contain aromatic chromophore end groups. Figure 17 shows the LDMS mass spectrum of Z-Dol with esterified end groups. From mass spectra like Figure 17, de Vries and co-workers can calculate average molecular weights, end group distributions, and repeat unit distributions in copolymers.

F. MALDI

MALDI is a special case of LDMS using specific sample preparation methods and low fluence laser desorption to create the analyte ions. It is perhaps the most important mass spectrometry technique currently being used to analyze polymer systems. Since its introduction by the Tanaka and Hillenkamp laboratories,[67−69] MALDI has rapidly grown in applications ranging from sequencing peptides to measuring the average molecular weights of complex synthetic polymer materials. With the recent developments of delayed extraction and post-source decay (PSD), MALDI can address a wide variety of analytical issues.

In MALDI, a dilute solution of the analyte polymer is mixed with a more concentrated matrix solution. Typical MALDI matrices are aromatic organic acids. A small aliquot of the mixture is applied to the MALDI target and crystallizes as the solvent evaporates. After the target is placed in the source of the mass spectrometer, a laser irradiates the target, vaporizing the matrix, and desorbing polymer oligomers into the gas phase. Neutral gas-phase oligomers are cationized by protons or metal cations. The ions are extracted into the mass spectrometer, mass analyzed, and detected.

Many different laboratories have recently investigated MALDI measurements on a large variety of polymer chemistry, both standards and unknown samples. This body of work has contributed significantly to the overall understanding of MALDI of polymers. Table 3 lists some of the important contributions to this work. Table 3 is not meant to be all-inclusive, but rather a place to start an investigation of a variety of polymer MALDI experiments. Additional information can be found in recent review articles on polymer MALDI by Raeder and Schrepp[70] and by Nielen.[71]

1. Sample Preparation

The MALDI experiment is dominated by sample preparation issues. The sample preparation method is vital to the success of polymer MALDI experiments. Professor Kevin Owens of Drexel University says that a MALDI mass spectrometer is an instrument designed to determine if the sample preparation was done correctly. For some materials, there may be several different sample preparation methods that produce essentially the same results. Unfortunately, significant errors in the sample preparation can lead to completely erroneous results.[134,135]

The sample preparation for polymer MALDI must accomplish five different roles, one for the solvent and four for the matrix. The roles are as follows. (1) Separate the individual oligomers—the solvent must effectively separate the molecules of the sample. We need to minimize interactions between the analyte molecules and generate individual molecules for the MALDI experiment to analyze. (2) Isolate the oligomers—the matrix must maintain the separation of the oligomers accomplished by dissolving the sample in a good solvent. Most of the matrices used in polymer MALDI are small aromatic organic acids that readily form crystals as the solvent evaporates. (3) Absorb energy—the matrix must absorb the energy delivered to the sample, usually by a 337 nm laser. New experiments have also started to investigate infrared (IR) laser desorption for MALDI of polymers.[136] (4) Desorb the analyte—the matrix must convert the energy delivered by the laser to eject the analyte molecules into the gas phase. (5) Ionize the analyte—the matrix must provide an ionization path to the analyte molecules.

Several different strategies for sample preparation have been demonstrated for polymer MALDI. The simplest is the dried droplet method. In the dried droplet method, a dilute solution of analyte is prepared in a good solvent. This analyte solution is then mixed with a more concentrated matrix solution in the same solvent. The solvent must be selected carefully to be a good solvent for both the analyte and the matrix. Almost any relatively volatile solvent can be used. The mix ratio of the two solutions should result in a matrix-to-analyte ratio of between 100 and 10 000 depending on the chemistry and molecular weight of the polymer. For low molecular weight polymers, we typically use 5 mg/mL polymer solutions and mix them 1:7 with 0.25 M matrix solutions.[17,137] About 1 μL of the resulting solution is then simply spotted on the target substrate and allowed to dry. For many of the simpler polymer MALDI experiments, this method is adequate to produce good data.

Another popular method is the layer method. In the layer method, the matrix solution is applied to the target surface first and allowed to dry. The sample solution is then applied to the dry matrix crystals. In some cases, the sample preparation can be aided by the addition of a surfactant.[138]

Some samples require more control over the evaporation process to achieve successful sample preparation. In these cases, the evaporation can be controlled by either electrospraying[139] or pneumatically spraying[140,141] the sample onto the target. While these two techniques have different mechanics, the results are similar. The spraying techniques control the evaporation of the solvent to obtain improved mixing of the analyte and the matrix. This is especially important for analytes that have relatively poor solubility in the matrix and for experiments where quantitation is important.[139]

The spraying experiments generate very flat, homogeneous samples for the MALDI experiment. Figure 18 shows total ion, time-of-flight (TOF) secondary-ion mass spectrometry (SIMS) images of dried droplet and electrosprayed PMMA 2900 samples.[137] The image in Figure 18a shows definite crystal structure of the matrix. The image in Figure 18b is

Table 3. Representative MALDI References by Chemistry[a]

chemistry	comment	group
alkylthiophenes		Liu et al.[72]
anhydride and epoxy	copolymer	Leukel et al.[73]
aromatic polyether	dendritic	Hayes et al.[74]
aryl ether ketones	synthesis products	Wang et al.[75]
aryl esters	dendrimers	Mowat et al.[76]
butyleneadipate and butyleneterephthlate	copolymers	Montaudo et al.[77]
cellulose	low molecular weight	Francotte et al.[78]
coal derivatives	soft pitch	Johnson et al.[79]
ethoxylated materials	commercial products	Berchter et al.[80]
ethoxylated surfactants	commercial products	Bartsch et al.[81]
fluorinated polymers		Latourte et al.[82]
hydrocarbon	rigid rod	Raeder et al.[83]
metallo-supermolecules	synthesis product	Schubert et al.[84]
methacrylate	copolymer	Suddaby et al.[85]
methylphenylsilane	synthesis product	Montaudo et al[86]
methylstyrene and vinylpyridine	copolymers	Wilczek-Vera et al.[87]
Novalac resins	synthesis products	Mandal et al.[88]
Novalacs, polyesters		Pasch et al.[89]
Nylon 6	end group analysis	Montaudo et al.[90]
PBD, PI	narrow standards	Yalcin et al.[91]
PDMS	narrow standards	Montaudo et al.[92]
PDMS	copolymers	Servaty et al.[93]
PDMS	copolymers	Yoshida et al.[94]
PEG	narrow standards	Montaudo et al.[95]
PEG	narrow standards	Dey et al.[96]
PEG	end group derivatization	Weidner et al.[97]
PEG, PMMA, polyester	narrow standards	Blais et al.[98]
PEG, PMMA, PS	narrow standards	Montaudo et al.[99]
PEG, PS	narrow standards	Whittal et al.[100]
PET	degradation products	Weidner et al.[101]
PET, PMMA, PS	narrow standards	Jackson et al.[102]
PMMA	narrow standards	Jackson et al.[103]
PMMA	chain transfer agents	Kapfenstein et al.[104]
PMMA	individual oligomers	Larsen et al.[105]
PMMA	end groups	Maloney et al.[106]
PMMA	narrow standards	Spickermann et al.[107]
PMMA	emulsion polymerization	Thomson et al.[108]
PMMA, PEG, PS	narrow standards	Thomson et al.[109]
PMMA, PS	narrow standards	Belu et al.[110]
PMMA, PS	narrow standards	Lloyd et al.[111]
poly(amidoamines)	hyperbranched	Hobson et al.[112]
poly(butyl methacrylate)		Danis et al.[113]
poly(hydroxy butanoate)		Buerger et al.[114]
poly(methacrylic acid)	degradation product	Burkoth et al.[115]
polyacrylonitrile, PS, PEG, PMMA	narrow standards	Linnemayr et al.[116]
polyester	hyperbranched	Feast et al.[117]
polyester	dendrimer	Sahota et al.[118]
polyesters	copolymers	Montaudo et al.[119]
polyesters	commercial products	Williams et al.[120]
polyesters	synthesis products	Guittard et al.[121]
polyimides	synthesis products	Kottner et al.[122]
polyols	commercial products	Schreimer et al.[123]
polyols	copolymers	van Rooij et al.[124]
poly(styrene sulfonic acid)		Danis et al.[125]
PS	High MW	Schreimer et al.[126]
PS	narrow standards	Zhu et al.[127]
PS, PBD, PI	narrow standards	Danis et al.[128]
PS, PBD, PI	narrow standards	Pastor et al.[129]
PS, PBA, polyester, polycarbonate	broad standards	Nielen et al.[130]
Silicone polymers		Krueger et al.[131]
silsesquioxanes		Wallace et al.[132]
styrenes	copolymers	Wilczek-Vera et al.[133]
surfynol surfactants	ethoxylated	Parees et al.[17]

[a] Where PBD is polybutadiene, PI is polyisoprene, PDMS is polymethylsiloxane, PEG is poly(ethylene glycol), PMMA is poly(methyl methacrylate), PS is polysterene, PET is poly(eteylene terephahalate), PBA is poly(butyl acrylate).

completely homogeneous on the lateral resolution scale of the experiment, about 1 μm. Individual ion images (for the matrix, Na^+ cationization agent, and the polymer) all show the same effect. Ion imaging will be discussed in greater detail below in the polymer surface section.

The choice of solvent is critical to the success of a polymer MALDI experiment.[72,142,143] If the polymer sample is not fully soluble in the solvent, only the dissolved portion of the sample will be observed by MALDI. Yalcin and co-workers show how the choice of solvent can dramatically effect the calculated

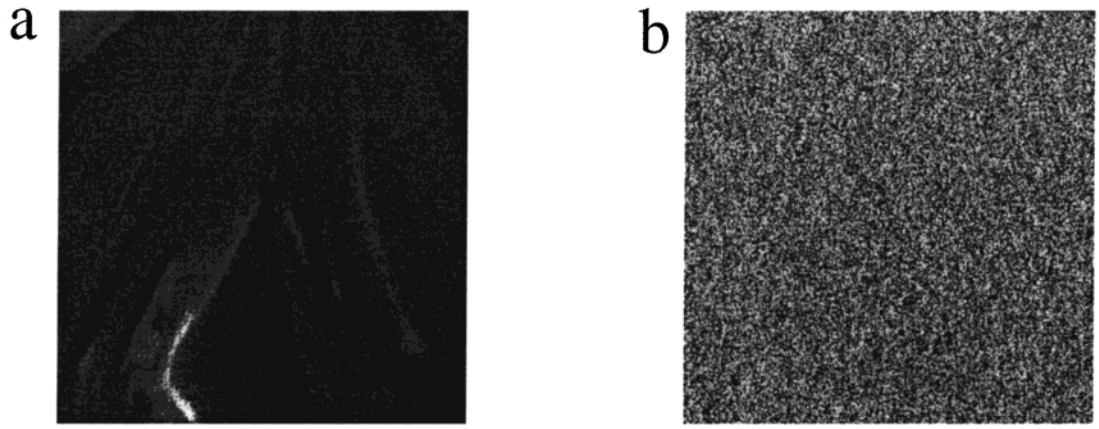


Figure 18. SIMS total ion images from PMMA MALDI sample preparations using acetone and DHB: (a) air-dry deposition and (b) electrospray deposition. (Reprinted with permission from ref 137. Copyright 1999 American Society for Mass Spectrometry.)

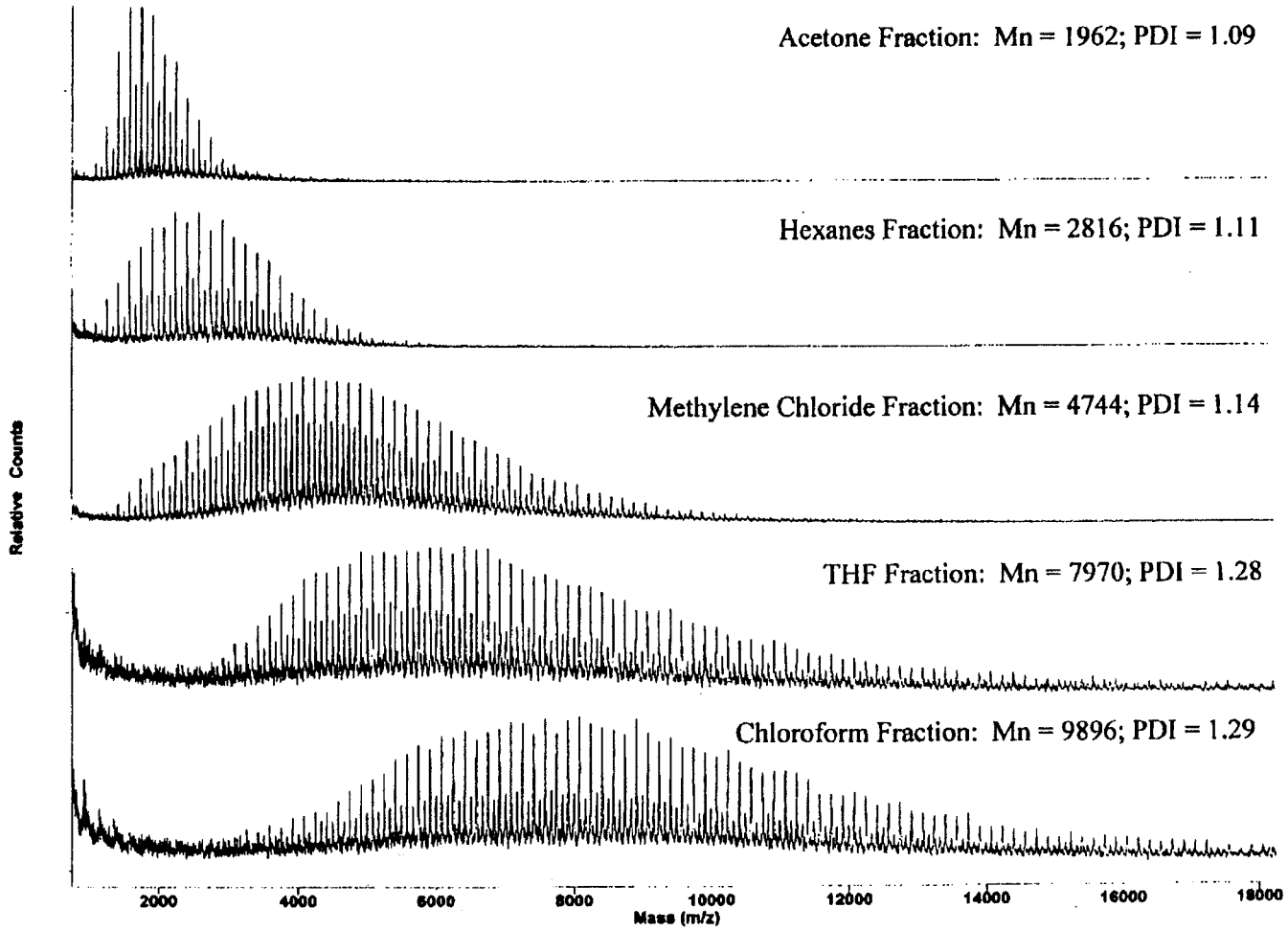


Figure 19. MALDI mass spectra of a poly(alkylthiophene) fractionated with acetone, hexanes, methylene chloride, THF, and chloroform, from top to bottom. (Reprinted with permission from ref 72. Copyright 1999 American Chemical Society.)

average molecular weights for polystyrene.[142] An interesting example of using changes in sample solubility to affect the MALDI measurements in a positive way is shown by Liu and co-workers in their work with poly(alkylthiophenes).[72] They use changes in the sample solubility in different solvents to create narrow polydispersity samples (PD range from 1.09 to 1.29) from a relatively broad polydispersity polymer (PD = 1.94). Figure 19 shows five different solvent extractions of the poly(alkylthiophene) using acetone, hexane, methylene chloride, tetrahydrofuran (THF), and chloroform. The solvent extractions provide narrow samples that are ideal for MALDI analysis. Figure 19 is an important reminder that

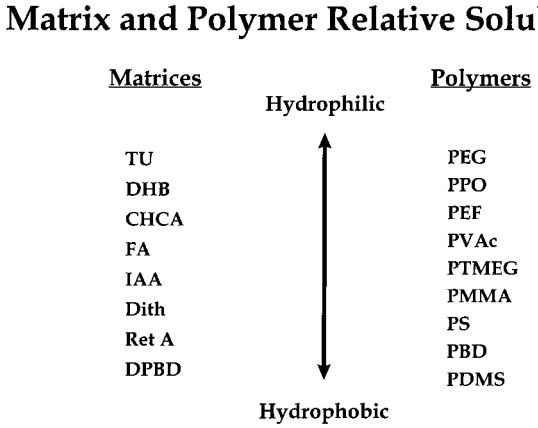


Figure 20. Relative hydrophobicity/hydrophilicity of some common polymer MALDI matrices and standard polymers, as determined by complementary MALDI and MESIMS experiments. Abbreviations: TU = thiourea, DHB = 2,5-dihydroxybenzoic acid, CHCA = α-cyano-hydroxy-cinnamic acid, FA = ferulic acid, IAA = indole acrylic acid, Dith = dithranol, Ret A = retinoic acid, DPDB = diphenyl butadiene, PEG = poly(ethylene glycol), PPO = poly(propylene oxide), PEF = poly(ethynl formamide, PVAc = poly(vinyl acetate), PTMEG = poly(tetramethylene glycol), PMMA = poly(methyl methacrylate), PS = polystyrene, PBD = polybutadiene, and PDMS = poly(dimethyl siloxane).

the choice of solvent for a particular sample will be a key step in determining the appearance of the MALDI mass spectrum.

The choice of matrix is also critical to the success of polymer MALDI experiments.[116] A wide variety of polymers have been analyzed, and a variety of matrices have been successfully used (see Table 3). Using a combination of MALDI and surface analysis (Matrix-enhanced secondary ion mass spectrometry, MESIMS), we developed a simple figure showing the relative hydrophilicity/hydrophobicity of several common matrices compared to common polymers, shown in Figure 20.[144] Using the relative hydrophilicity/hydrophobicity data shown in Figure 20 aids in reducing the time to develop a suitable sample preparation method for polymer MALDI.

The final role of the matrix is to provide a suitable ionization pathway for the polymer oligomers. Polymer samples observed in MALDI are cationized: amine functions tend to protonate,[145] oxygen functions tend to alkali cationize, and unsaturated hydrocarbons tend to copper or silver cationize.[91,128,129,146,147] Since most of the matrices are organic acids they can readily supply a proton. If metal cationization is required, then a source of the appropriate metal must be included in the sample preparation method. While the mechanisms of ionization in MALDI are not yet well understood, a combination of preformed ions and gas-phase cationization reactions probably explains most of the observed ionization.[148−151] Zenobi and co-workers wrote a review article on this topic.[152] It has been observed for some polymers, especially poly(ethylene terephthalate), that the choice of the cation can significantly impact average molecular weight measurements.[104,153] New cationizing agents are still being developed and investigated.[154] Metallocenes have been shown to improve signal intensity for higher molecular weight polymers.[155]

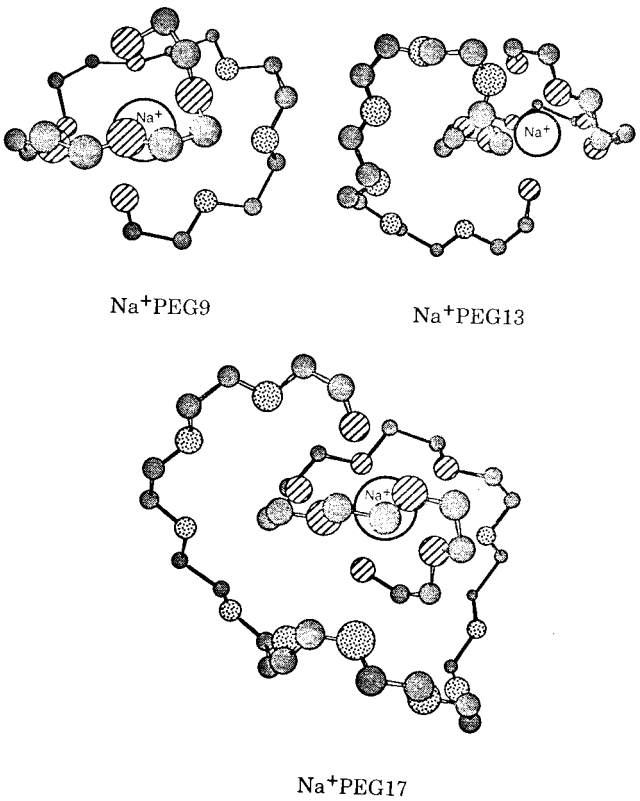


Figure 21. Lowest energy structures found for Na^+ cationized PEG_9, PEG_{13}, and PEG_{17}. Hydrogen atoms are omitted for clarity. Carbon atoms are gray. Oxygen atoms within 0.3 nm of an Na^+ are striped, and all other oxygen atoms are dotted. (Reprinted with permission from ref 162. Copyright 1995 Elsevier Science.)

Theoretical methods are being used to better understand the issues of cationization in MALDI. Marino and co-workers show how theory and experiment can be used to complement each other to aid the understanding of ionization in mass spectrometry.[156] For some small ether complexes, Hartree−Fock and perturbation theory are used to characterize the ether−alkali metal interaction.[157−160] Molecular modeling studies of an ethoxylated surfactant show increasing cation stability with increasing oligomer chain length.[17,161] These results complement the mass spectrometric data.

Bowers and co-workers used ion chromatography/ion mobility experiments combined with molecular mechanics to extract the conformations of cationized oligomers.[162−164] Their results indicate that alkali-cationized PEG oligomers prefer a near planar 5-fold coordination sphere capped on top and bottom leading to an 8-fold coordination for Na^+ cationization. Figure 21 shows the lowest energy structures found for $PEG_n + Na^+$, with $n = 9$, 13, and 17.[162] Li^+, a smaller cation than Na^+, a prefers a lower coordination of seven, and Cs^+, a larger cation than Na^+, prefers a larger coordination of 11. These structures help us to better understand alkali cationization in MALDI, including the effects of cationization on average molecular weight.

The success of a variety of MALDI experiments indicates that if a particular polymer material can be ionized, a sample preparation method can probably be developed to analyze it by MALDI. The

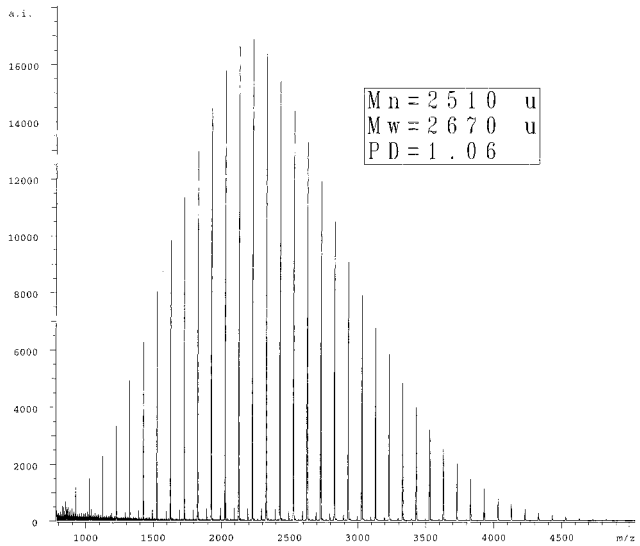


Figure 22. MALDI mass spectrum of PMMA 2900.

problem of finding a suitable cationizing agent is the key to adding polyolefins to the list of materials that can be successfully analyzed by MALDI.[165]

2. Molecular Weight Measurement

One of the key experiments for polymer MALDI is to measure the average molecular weights of polymer materials. Figure 22 shows a MALDI mass spectrum of a relatively simple poly(methyl methacrylate) (PMMA) standard. This mass spectrum was obtained using a dried droplet sample preparation with THF as the solvent and IAA as the matrix on a Bruker Biflex instrument (Billerica, MA). In the mass spectrum we can clearly see individual oligomers spaced by 100 u from 800 to 4900 u. These ions can be assigned as Na^+-cationized PMMA oligomers. The average molecular weights are calculated directly from the ion intensity and ion masses in the mass spectrum using eqs 1−3. The ion masses are corrected for the mass of the cation, subtracting 23 u in this case for Na^+ cationization. For the spectrum shown in Figure 22, we calculate average molecular weights of $M_N = 2510$ u and $M_W = 2670$ u, with PD = 1.06.

The methods to calculate the average molecular weights from the mass spectral data have been developed by several instrument vendors and laboratories. In its simplest form, the average molecular weights are the first two moments of the distribution of oligomer intensity. The algorithms for these moments can be written and coded for computation relatively simply.[166] The most complicated issue in calculating the average molecular weights is the fact that the time-of-flight mass spectral data most commonly used in MALDI is not collected linear in mass but linear in time. Li and co-workers describe an important correction factor for the signal intensity that needs to be made during the mass calibration process, before the average molecular weights are calculated[167]

$$q(m) \propto D(t)/(\mathrm{d}m/\mathrm{d}t) \qquad (4)$$

where $D(t)$ is the MALDI detector response as a function of time, t, $q(m)$ is the corrected number molecular weight distribution as a function of mass, m, and $\mathrm{d}m/\mathrm{d}t$ is the derivative of the calibration equation.

Table 4. Molecular Weight Data for PS Standards[a]

polymer standard	molecular weight and polydispersity: by classical methods[b]	by MALDI[c]
polystyrene 5050	M_n = 4755 (GPC) M_w = 4992 (GPC) M_n = 4720 (VPO) M_v = 4950 (IV) PD = 1.05 (GPC)	M_n = 5189 (0.5% RSD) M_w = 5329 (0.5% RSD) PD = 1.027 ± 0.001
polystyrene 7000	M_n = 6770 (GPC) M_w = 6962 (GPC) M_w = 7170 (LLS) M_v = 6943 (IV) PD = 1.03 (GPC)	M_n = 6998 (0.5% RSD) M_w = 7132 (0.5% RSD) PD = 1.019 ± 0.001
polystyrene 11600	M_n = 11356 (GPC) M_w = 11687 (GPC) M_w = 11000 (LLS) M_v = 10720 (IV) PD = 1.03 (GPC)	M_n = 11074 (0.5% ± RSD) M_w = 11187 (0.5% RSD) PD = 1.010 ± 0.001

[a] Reprinted with permission from ref 127. Copyright 1998 American Society for Mass Spectrometry. [b] These results are provided by the suppliers; GPC, gel permeation chromatography; VPO, vapor-phase osmometry; IV, intrinsic viscosity; LLS, laser light scattering. [c] From five trials.

The MALDI average molecular weights are most often compared to GPC average molecular weights. Some care must be taken to ensure a fair comparison.[168] Jackson and co-workers showed that comparing the peak molecular weight, or M_P, values from GPC and MALDI is problematic without first plotting both data sets on the same x-axis.[169] The M_P value should be recorded only for weight fraction versus log mass plots to reduce the confusion. The usual moments, M_N and M_W, are a better way to compare MALDI and GPC data.

The accuracy of MALDI average molecular weights has always been a good source of debate. There is general agreement that MALDI average molecular weights are accurate for low polydispersity samples. There have been many investigations into the accuracy of polymer MALDI, and most of the papers listed in Table 3 compare MALDI average molecular weights against another technique, usually GPC. Zhu and co-workers provide a good examination of the details of understanding the issues involved in measuring polymer average molecular weights by MALDI.[127] Their data is reproduced here as Table 4. The data show relative standard deviations of 0.3−0.5% for nominal masses between 5050 and 11 600 u.

The National Institute of Science and Technology (NIST) has sponsored investigations into the accuracy of polymer MALDI average molecular weights.[170,171] Guttman and co-workers prepared well-characterized narrow polydispersity PMMA 6300 and PS 7000 materials. The PMMA 6300 sample compared well in their in-house study to GPC. The PS 7000 sample was distributed to 18 interested laboratories for a round-robin experiment. Each laboratory was asked to analyze the sample both by a prescribed sample preparation method (using all *trans*-retinoic acid as

the matrix and THF as the solvent) and their favorite sample preparation method for PS. Most of the laboratories used dithranol as their second choice of matrix. The results of the round-robin experiment were $M_N = 6600 \pm 100$ u and $M_W = 6700 \pm 90$ u. The low uncertainty in the molecular weights shows extremely good reproducibility from lab to lab.

As discussed above, MALDI molecular weight measurements have been very successful for narrow polydispersity samples. The oft quoted statement about MALDI average molecular weight measurements is that they are accurate for samples with a PD less than about 1.2.[172] This is certainly true, but for samples with PD between 1.2 and ca. 1.6, there are few well characterized standards. For samples with PD above about 1.6, MALDI clearly has problems accurately measuring the average molecular weight distributions. Issues that effect the measurement of accurate molecular weights for broad polydisperse polymers include sample preparation, laser fluence, instrument dynamic range, delayed extraction time,[173] fragmentation, multimer formation, multiple charging, detector saturation, and relative detector response.[105,153,174−177] The issues involved in measuring broader polydisperse samples have often been investigated by creating broad samples by blending narrow standards. These studies show the problems inherent in quantifying polymer blends by MALDI.[175] Some of the problems associated with measuring average molecular weights of broad polydisperse samples can be alleviated by using GPC to simplify the samples prior to MALDI analysis. These experiments will be discussed below in the Chromatography−Mass Spectrometry section. There is also work underway to correct the MALDI mass spectra of wide polydisperse samples to obtain accurate average molecular weights.[178,179]

MALDI techniques have been developed by Schreimer and co-workers to measure average molecular weights of very high mass polymers.[126] Figure 23 shows MALDI mass spectra for narrow PD PS standards having nominal molecular weights of (A) 330 000, (B) 600 000, and (C) 900 000 u. On the basis of their techniques and instrument, Schreimer and co-workers established the current record for highest molecular weight measured by polymer MALDI. They successfully analyzed a 1.5 million u polystyrene (PS)!

While measuring accurate molecular weights for very high mass polymers by MALDI can be quite challenging, so can measuring accurate molecular weights for very low mass polymers. It is clear that very low mass polymers do not cationize well by MALDI. It seems that about five ethoxy repeat units are required before cationization-related discrimination effects are no longer observed.[180] Parees and co-workers show that for a very low molecular weight ethoxylated surfactant, S420, the cationized mass spectrometry data results in significantly higher average molecular weight values due to poor ionization of the less ethoxylated oligomers.[17]

One method to avoid cationization discrimination for very low molecular weight materials is to derivatize the end groups. Barry and co-workers derivatized

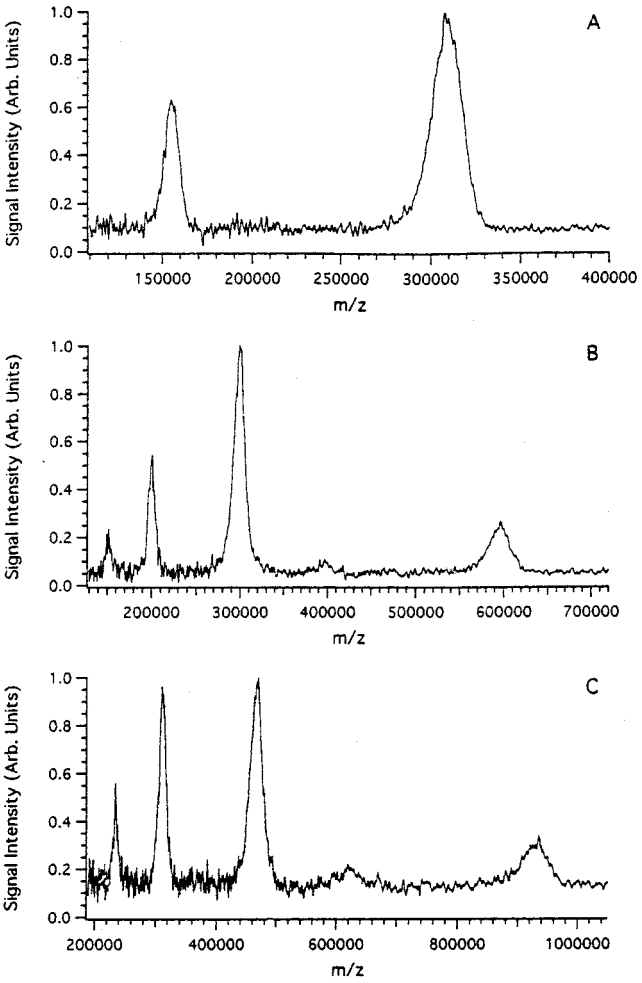


Figure 23. MALDI mass spectra of three PS samples with nominal molecular weights of (a) 330 000, (b) 600 000, and (c) 900 000 u. The lower mass-to-charge ratio ions are due to multiply charged ions. (Reprinted with permission from ref 126. Copyright 1996 American Chemical Society.)

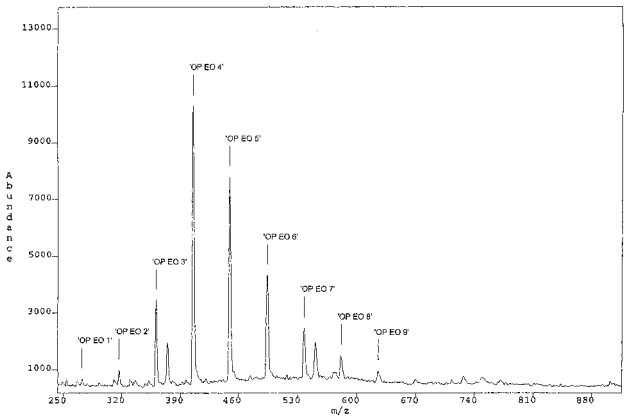


Figure 24. MALDI mass spectrum of a low molecular weight octyl phenol ethoxylate. (Reprinted with permission from ref 181. Copyright 1997 John Wiley & Sons, Ltd.)

ethoxylate polymers with phthalate anhydride to significantly increase the oxygen functionality of the analytes.[181] Figures 24 and 25 show the difference between MALDI mass spectra for a low molecular weight octyl phenol ethoxylate before (Figure 24) and after (Figure 25) derivatization. The derivatization of the analyte clearly leads to more intense short ethoxy chain oligomers. The difference can readily

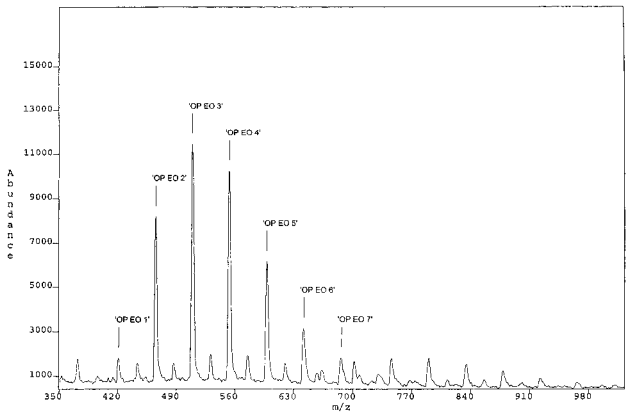


Figure 25. MALDI mass spectrum of a low molecular weight octyl phenol ethoxylate derivatized with phthalic anhydride. (Reprinted with permission from ref 181. Copyright 1997 John Wiley & Sons, Ltd.)

Table 5. Molecular Weight Data vs Derivatization

sample	M_N	M_W	PD
before derivatization	416	425	1.02
after derivatization	332	338	1.02

be seen in the calculated average molecular weights for the two samples, as shown in Table 5.

The results from the derivatized samples more closely match molecular weight measurements from other techniques, like NMR and titration.

Most polymer MALDI experiments are done on time-of-flight (TOF) instruments. We have not discussed many instrument issues with respect to measuring accurate average molecular weights; however, one case that requires special mention is the use of a Fourier transform mass spectrometer (FTMS). FTMS instruments have the advantage of very high mass resolution, but care must be taken when measuring polymer average molecular weights. The frequency nature of the data collection can lead to isotope beating effects that can cause errors in average molecular weights acquired on an FTMS instrument. Easterling and co-workers show that they can be reduced by collecting longer transients or by ejecting the isotope-containing ions.[182] Wilkins and co-workers show that the FTMS instrument can show a time-of-flight effect during ion trapping.[96,129] Figure 26 shows the effect of changing the gated trapping time on the apparent molecular weight distribution of a PBD 1350 sample.[129] The TOF effect on the molecular weight distribution can be reduced by acquiring and combining spectra with different trapping times[96,183] or by the implementation of an open-ended cylindrical analyzer cell.[184]

3. End Group Determination

While the bulk of the mass in a typical polymer is composed of the repeat units, the chemical structure of the end groups can be extremely important to the performance properties of any polymer material. Determining the end groups can be vital to understanding the polymer chemical structure. Polymer MALDI mass spectra can be used to determine the mass of the end groups of the oligomers if acquired at sufficient mass resolution. Many of the experiments listed in Table 3 used the mass spectral data to characterize the oligomer end groups. The development of higher mass resolution mass spectrometers for MALDI has greatly improved our ability to characterize oligomer end groups. Delayed extraction has been the key technical development to improving the mass resolution of the TOF instruments commonly used for MALDI.[185] Whittal and co-workers show the effect of delayed extraction on mass spectra

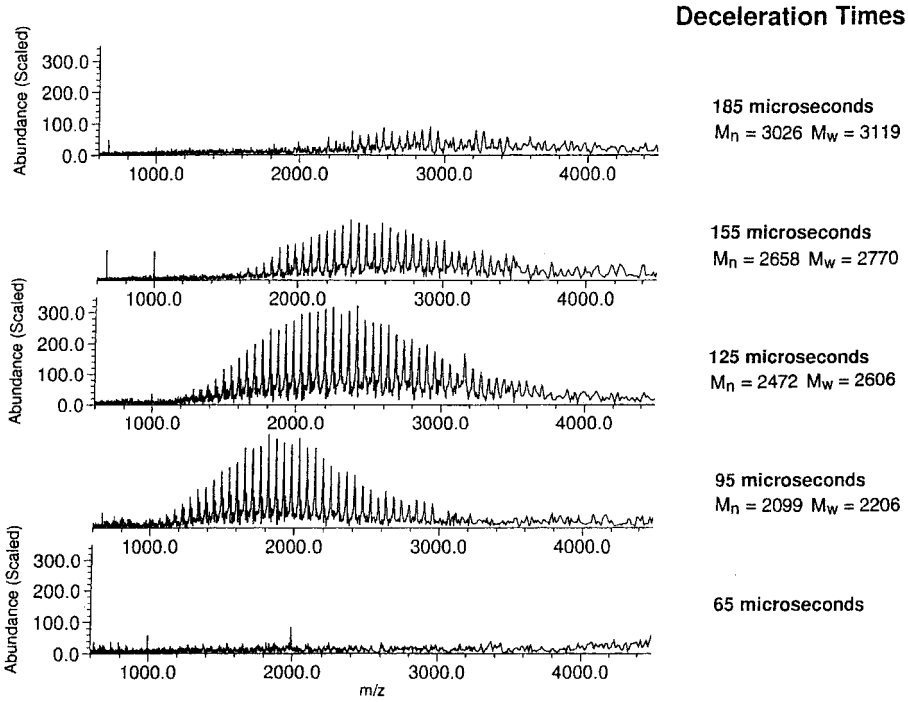


Figure 26. MALDI−FTMS mass spectra of hydroxyl terminated PBD 1350 taken at different gated trapping deceleration times following the laser pulse. The spectra clearly show a TOF effect on the ion distributions.(Reprinted with permission from ref 129. Copyright 1997 American Society for Mass Spectrometry.)

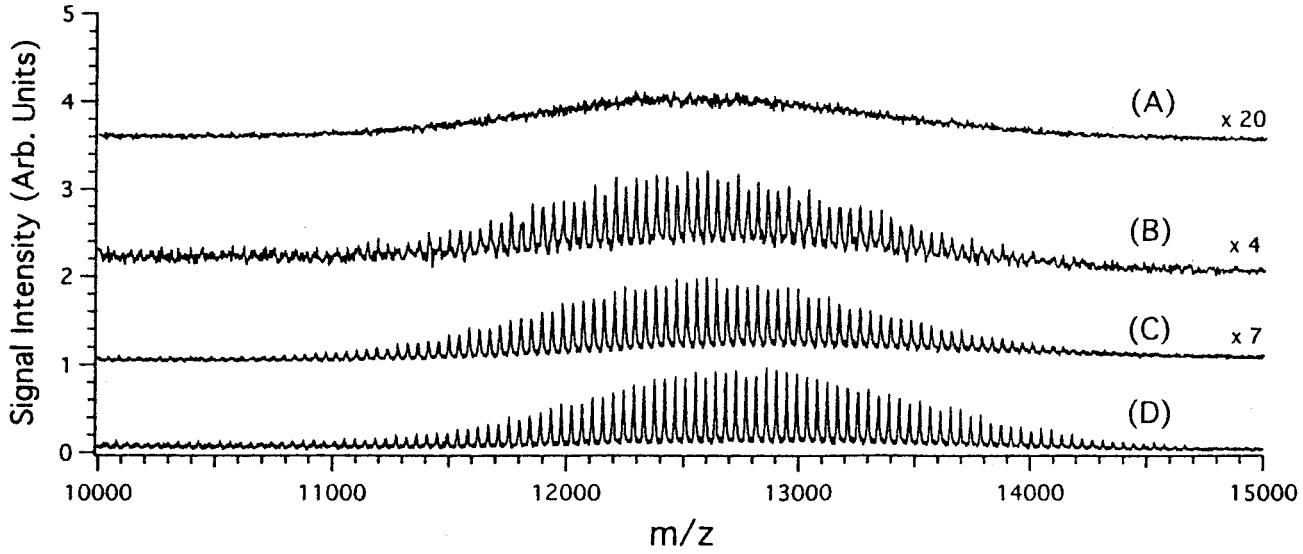


Figure 27. MALDI mass spectra of PEG 15 000: (a) continuous extraction with HABA, (b) delayed extraction with DHB, (c) delayed extraction with IAA, (d) delayed extraction with HABA. (Reprinted with permission from ref 186. Copyright 1997 American Chemical Society.)

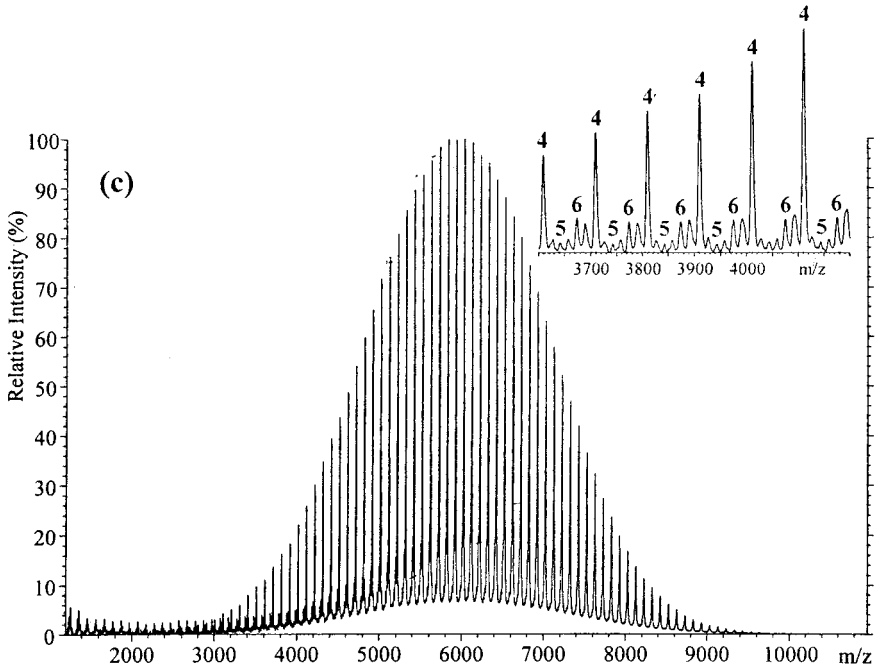


Figure 28. MALDI mass spectrum of a PMMA sample with three different end groups. (Reprinted from ref 103. Copyright 1997 John Wiley & Sons, Ltd.)

of PEG 15,000 in Figure 27.[186] In Figure 27, the A and D trace are both acquired in linear mode with 2-(4-hydroxyphenylazo) benzoic acid (HABA) as the matrix. Without delayed extraction the PEG oligomers are not resolved. Only a broad hump is seen. With delayed extraction the individual oligomers are resolved.

Maloney and co-workers used MALDI mass spectra to determine the end groups of PMMA produced from a variety of different synthetic methods.[106] Jackson and co-workers also used MALDI to determine the end groups of a variety of different PMMA samples.[103] Figure 28 shows a MALDI mass spectrum and expansion of one of the samples. The resolution of these experiments was sufficient to identify the masses of eight different end groups on the PMMA samples. Single MS experiments can only measure the residual mass after the mass of the repeat units are accounted for. Without other information, such as knowledge of the synthesis or spectroscopic data (like NMR, IR or XPS) indicating the chemical functionality, the mass spectral data cannot specify the chemical structure of the end groups. In conjunction with NMR spectroscopy, these chemical structures were determined.

Montaudo and co-workers used MALDI mass spectra to characterize the end groups of Nylon 6 polymers following selective degradation under different conditions.[90] Figure 29 shows one example of this work with a sample of Nylon 6 reacted with adipic acid. In Figure 29, we see cyclic species and oligomers with acid/acid and acid/amine end groups.

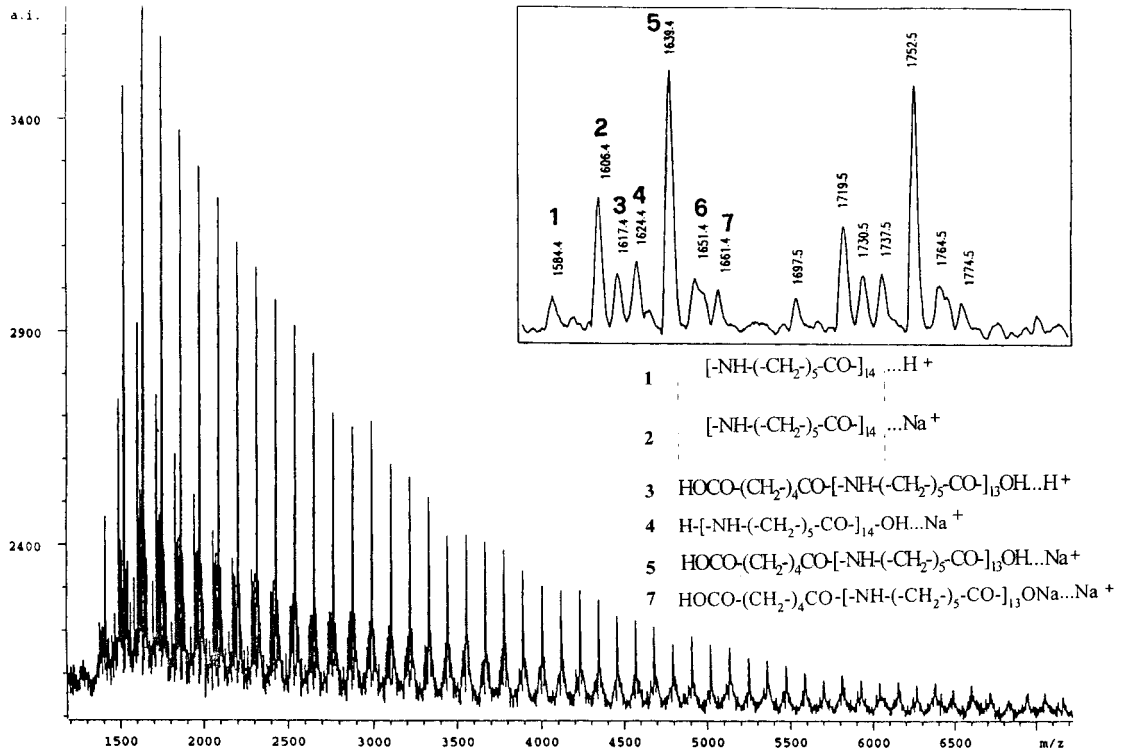


Figure 29. MALDI mass spectrum of Nylon 6 reacted with adipic acid. The expansion shows the seven different species identified. (Reprinted with permission from ref 90. Copyright 1996 John Wiley & Sons, Ltd.)

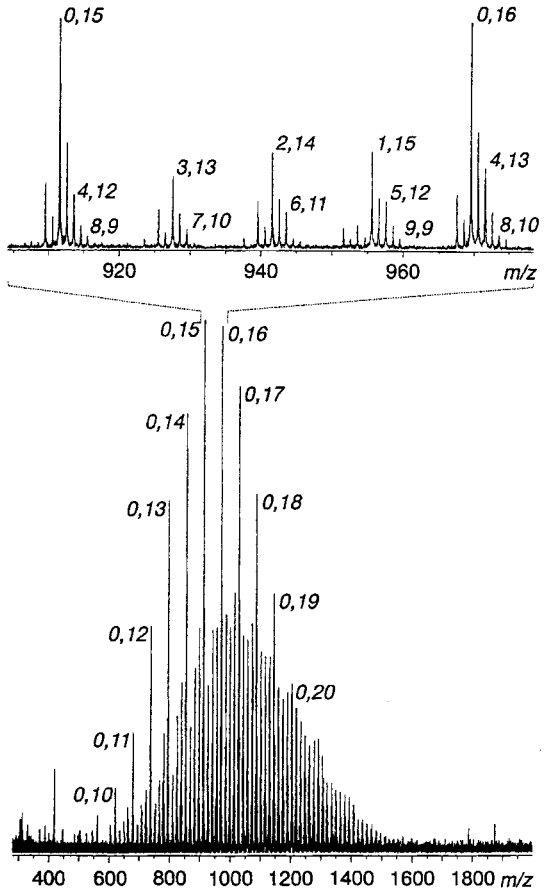
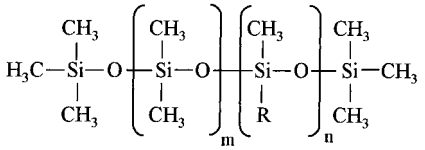


Figure 30. MALDI mass spectrum obtained on an FTMS instrument of a common EO/PO copolymer. The expansion shows a series of copolymer ion assigned (number of EO units, number of PO units). (Reprinted with permission from ref 124. Copyright 1998 American Chemical Society.)



R1: $(CH_2)_3O(CH_2CH_2O)_aH$

R2: $CH_2CH_2C_bF_{2b+1}$

b = 1, 4, or 8

Figure 31. Structures of two silicone copolymers modified with R1 = EO or R2 = perfluoroalkyl chains. (Reprinted with permission from ref 94. Copyright 1998 John Wiley & Sons, Ltd.)

4. Copolymer Analysis

Most of the work to date in polymer MALDI has been done on homopolymers, materials created from a single monomer species. Materials created from two or more monomer species are copolymers. There has been relatively little MALDI work done on copolymers due to the problems in developing suitable sample preparation methods for them. The different components of a copolymer must still be soluble to create a successful MALDI sample. MALDI techniques are now being developed to analyze copolymers in conjunction with other analytical techniques, such as GPC, NMR, and other mass spectral methods.[187] Often the MALDI data is too complex or too ambiguous due to multiple assignments to conclusively specify the material with the mass spectral

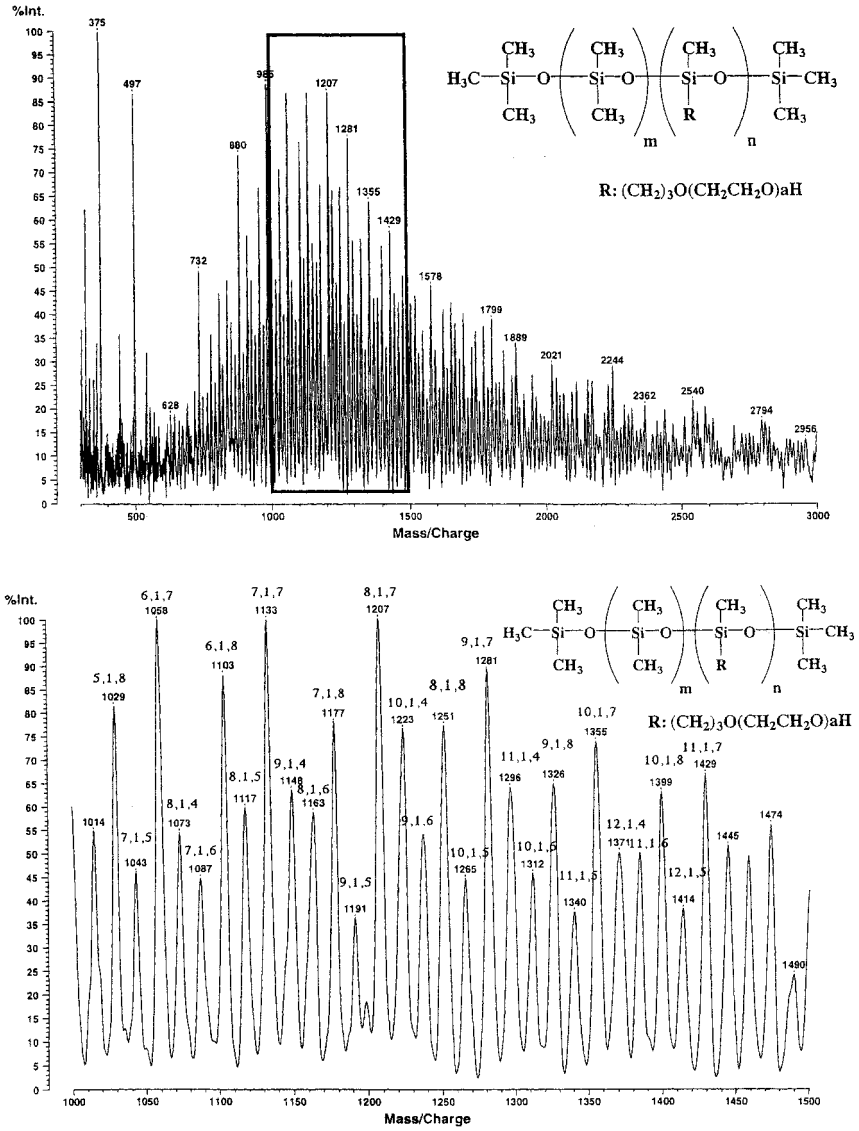


Figure 32. MALDI mass spectrum of a silicone copolymer modified with EO: (top) full spectrum and (bottom) expansion from 1000 to 1500 u. The expansion mass spectrum shows the assignments based on the structure shown in Figure 31. The peaks are labeled both by mass and with the number of each type of repeat unit (m, n, b), where b = a × n. (Reprinted with permission from ref 94. Copyright 1998 John Wiley & Sons, Ltd.)

data alone. Figure 30 shows a MALDI mass spectrum of a common copolymer surfactant composed of both ethylene oxide (EO) and propylene oxide (PO) monomer units obtained by van Rooij and co-workers on an FTMS instrument.[124] The expansion in Figure 30 shows the ion assignments as the number of EO segments, number of PO segments for the monoisotopic ions. This is the most straightforward type of copolymer to analyze by MALDI because of the similarity in solubility and cationization stability between the EO and PO units.

MALDI has also been applied to characterize the chemical structures of silicone surfactants.[93] Yoshida and co-workers used MALDI to characterize EO or perfluoroalkyl-modified PDMS.[94] Modified PDMS surfactants are important components of many products in the cosmetics industry. The basic structures of the modified PDMS polymers are shown in Figure 31. Figure 32 shows an example of a MALDI mass spectrum of an EO-modified PDMS. The upper mass spectrum in Figure 32 is quite complex, with many ions near in mass. The lower mass spectrum is an expansion of the boxed region of the upper mass spectrum. It shows the assignments based on the structure shown in Figure 31. The peaks are labeled both by mass and with the number of each type of repeat unit (*m*, *n*, *b*), where $b = a \times n$. Some of the ions can be assigned to more than one possible combination of monomer units. In this case ^{1}H NMR data was used to help choose the most probable ion assignments.

Comprehensive studies of the chemical structures of diblock methylstyrene−styrene and methylstyrene−vinylpyridine copolymers were recently completed by Wilczek-Vera and co-workers.[87,133] These experiments were done using a method referred to as method of analysis of copolymers (MAC) MALDI. Figure 33 shows MALDI mass spectra of methylstyrene−vinylpyridine copolymers of increasing complexity. The data are assigned using the pattern of

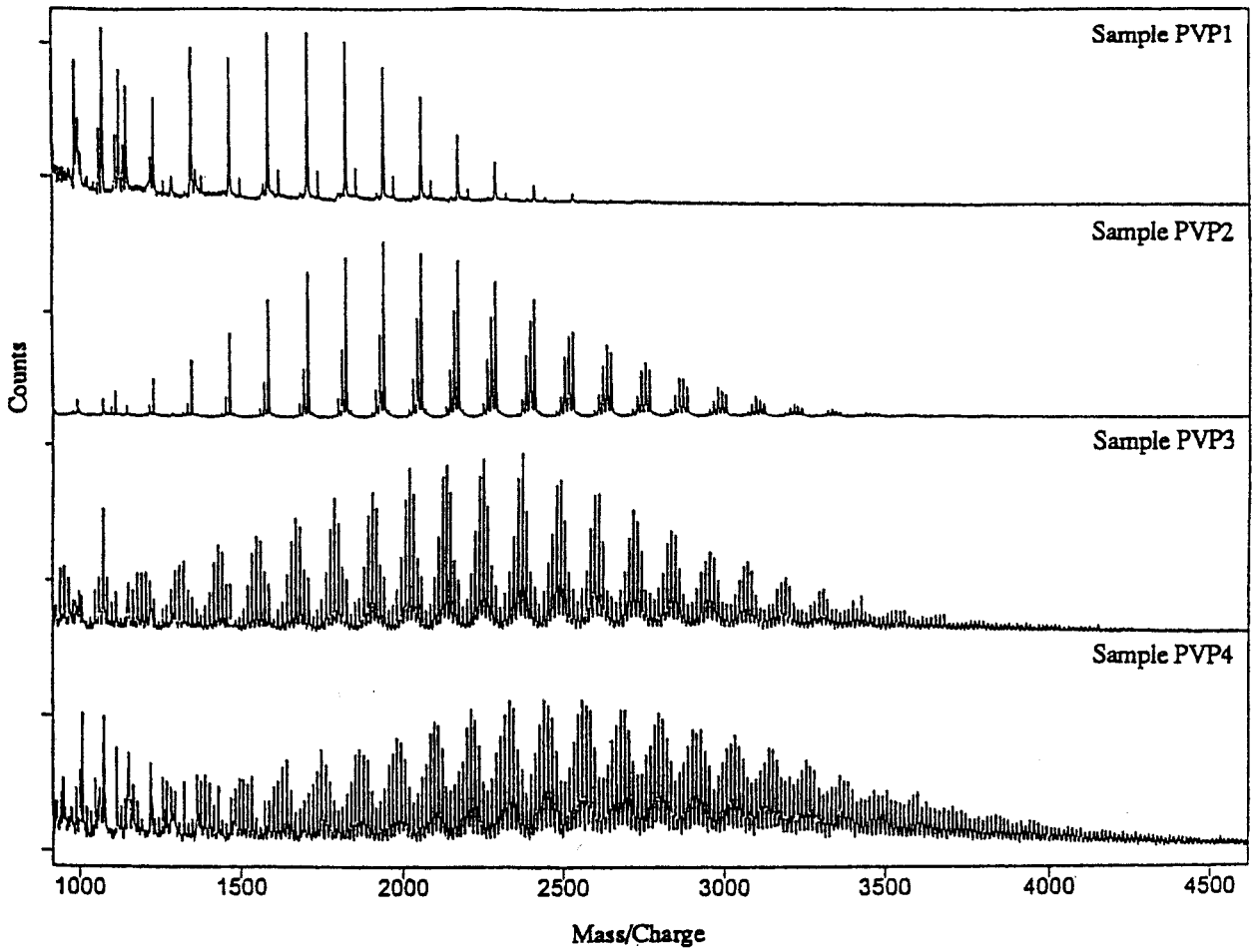


Figure 33. MALDI mass spectra of poly(α-methylstyrene)-*b*-poly(4-vinyl pyridine) diblock copolymers of increasing complexity. (Reprinted with permission from ref 87. Copyright 1999 John Wiley & Sons, Ltd.)

peak clusters and a statistical random coupling hypothesis test. Once a consistent assignment has been produced, the data can be plotted as three-dimensional surfaces of the length distributions of the blocks in each sample. Figure 34 shows four such arrays.

In an example of a more complex copolymer, Montaudo and co-workers used MALDI to characterize a three-component copolymer, or terpolymer, composed of poly(butylene succinate), poly(butylene adipate), and poly(butylene sebacate).[119] Using a program based on chain statistics, MACO4,[188] the most likely composition converged at 32/34/34 (succinate/adipate/sebacate).

5. Application to Synthesis Products

As polymer MALDI methods become better developed, the technique is being applied to monitor and characterize polymerization reactions.[189] MALDI data can be used to characterize both the chemical structures of the products and the rate coefficients of the polymerizations. Wang and co-workers characterized macrocyclic aryl ether ketone oligomers using MALDI and GPC.[75] The polymerization is accomplished by reacting bisphenol A with 1,2-bis(4-fluorobenzoyl)-benzene under pseudo-high dilution conditions. Figure 35 shows the MALDI mass spectrum of the cyclic oligomer products. The spectrum shows a series of low molecular weight oligomers and the assigned structure. Two different ions are observed for each oligomer. The extra peak is assigned as $(M - O)^+$, the result of an intramolecular cyclization that forms an isobenzofuran.[190]

Schweer and co-workers used MALDI and GPC data to measure the free-radical propagation rate coefficients for pulsed-laser polymerizations of methyl methacrylate and styrene.[191] The key to these experiments is measuring accurate average molecular weights. The use of both MALDI and GPC enables the authors to use the relative strengths of both techniques. These experiments show that MALDI brings the advantage an absolute mass scale and the absence of broadening errors compared to GPC in determining the average molecular weights for the narrow polydispersity samples prepared in this study.

G. ESI

Electrospray ionization (ESI) is a relatively new ionization method that along with MALDI has significantly changed the field of mass spectrometry.[192−194] In ESI, a dilute solution of the analyte is injected at a constant flow to a small diameter capillary or needle held at high voltage (0.5−5 kV). As the solution passes through the needle, the accumulation of excess charge due to the high potential creates a Taylor cone at the exit. As the solution is sprayed

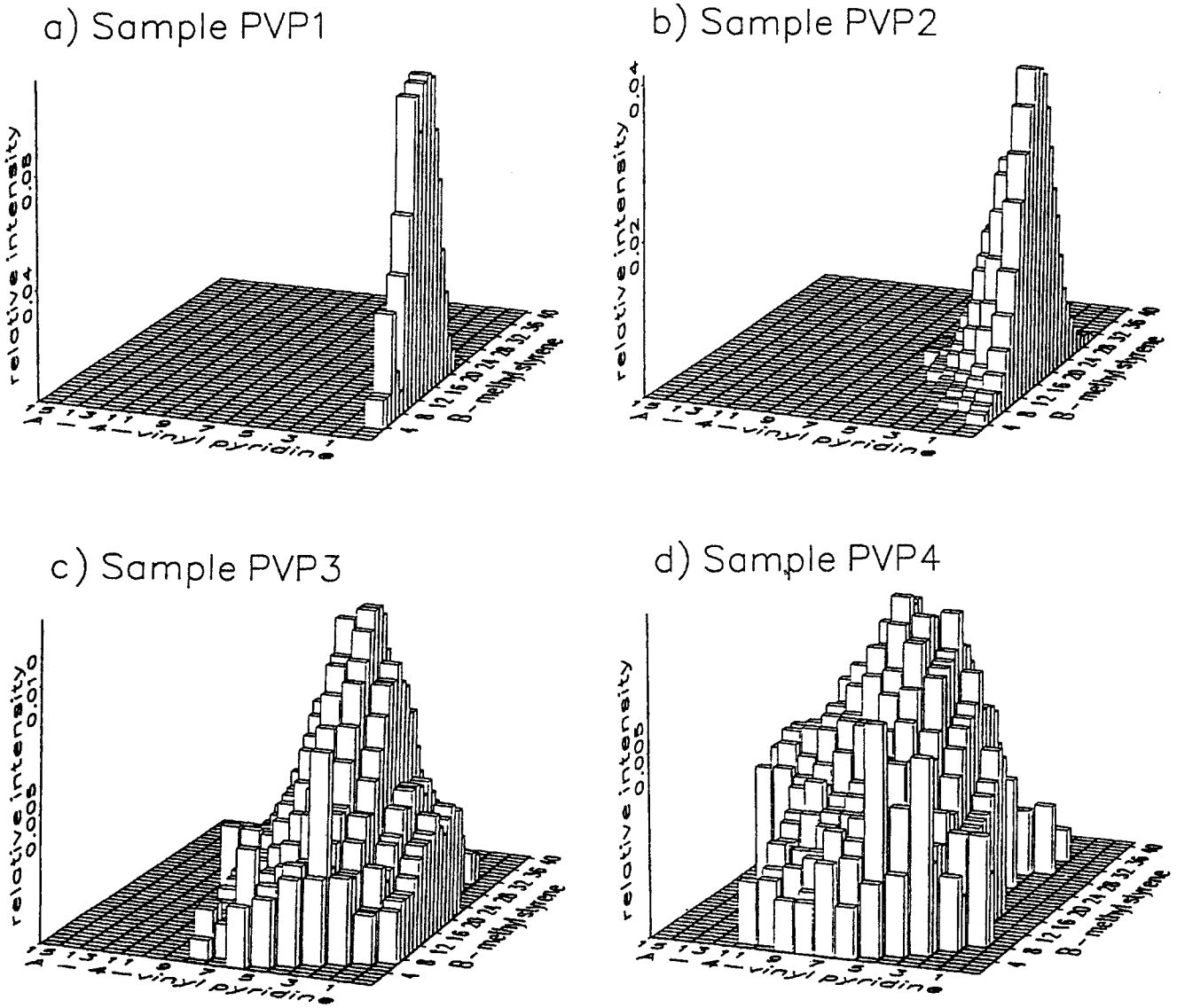


Figure 34. Experimental normalized distribution of units for poly(α-methylstyrene)-*b*-poly(4-vinyl pyridine) diblock copolymers of increasing complexity. (Reprinted with permission from ref 87. Copyright 1999 John Wiley & Sons, Ltd.)

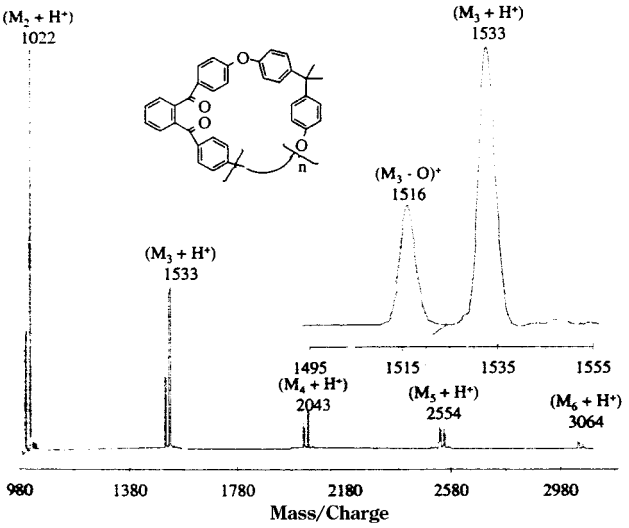


Figure 35. MALDI mass spectrum of cyclic aryl ether ketone oligomers. (Reprinted with permission from ref 75. Copyright 1996 John Wiley & Sons, Ltd.)

from the exit, the solvent begins to evaporate creating an aerosol of highly charged droplets. The high charge density on the surface of the aerosol droplets leads to droplet fission, which leads ultimately to droplets capable of producing detectable ions.[195] While ESI has found tremendous success in analyzing biomolecular species, it has proven difficult to optimize for polymer applications. One of the key advantages of ESI is the additional charges on the detected ions. The increased charge decreases the mass-to-charge ratio (*m*/*z*) and enables the detection of higher mass species in mass spectrometers with limited *m*/*z* range. Unfortunately, the higher charge is not a single charge state, but it is a distribution of charge states. When this charge state distribution is created with an oligomer chain length distribution, very complex mass spectra can arise.[196] Figure 36 shows an ESI mass spectrum obtained on an FTMS instrument for PEG 4500.[197] In Figure 36, we can see the complexity of oligomer chain length and charge state distributions, even for a moderate size polymer

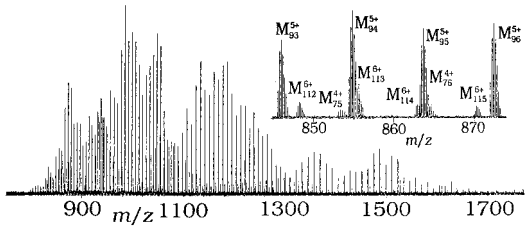


Figure 36. ESI mass spectrum of PEG 4500 obtained on an FTMS instrument. The resolving power is about 10^5. (Reprinted with permission from ref 197. Copyright 1995 American Chemical Society.)

Table 6. Representative ESI References by Chemistry

chemistry	comment	group
fluorinated polymers	commercial materials	Latoute et al.[82]
methacrylates	coploymers	Shi et al.[200]
PDMS	narrow standards	Maziarz et al.[201]
PEG	narrow standards	Maziarz et al.[202]
PEG, PDMS	narrow standards	Yan et al.[203]
PEG, polyester	narrow standards	Hunt et al.[204]
PMMA	narrow standards	McEwen et al.[205]
PMMA & acrylic	copolymers	Haddleton et al.[206]
polyester	from paint resins	Hunt et al.[207]
polyesters	sythesis products	Guittard et al.[121]
polyesters	commercial products	Williams et al.[120]
polyesters		Hunt et al.[208]
polysulfides		Mahon et al.[209]
PPO	synthesis products	Stolarzewicz et al.[210]
PS	narrow standards	Deery et al.[211]
surfactants	ethoxylated	Castillo et al.[213]
surfactants	ethoxylated	Crescenzi et al.[214]
surfactants	consumer products	Ogura et al.[215]
surfactants	ethoxylated	Prokai et al.[216]
surfynol surfactants	ethoxylated	Parees et al.[17]

sample. O'Connor and co-workers[197] and Maekawa and co-workers[196] also showed the enormous complexity observed for higher mass polymers. With the high mass resolution of the FTMS instrument, these spectra can be deconvoluted and assigned, but this is much too difficult for routine analyses.

Despite the problems of spectral complexity, ESI is used successfully to solve problems in polymer mass spectrometry. Some representative examples of polymer ESI analyses are listed in Table 6. Additional information can be found in recent review articles by Saf, Mirtl, and Hummel[198] and Lorenz, Maziarz, and Wood.[199]

ESI data can be used for all of the same analyses described above for MALDI. Average molecular weight determinations can be complicated by differences in charge state distributions for different chain length oligomers.[217] This can lead to significantly different measurements of the polymer average molecular weights for different charge states. ESI mass spectra also depend on the cone voltage and the ion accumulation time.[202,206] The cone voltage has been shown to have a focusing effect dependent on the mass-to-charge ratio which impacts the average molecular weight measurements.[204] Unfortunately, increased cone voltage can also increase the intensity of in-source collision-induced dissociation (CID) creating fragment ions. While these fragment ions can be very useful in chemical structure determination, they can skew average molecular weight measurements.

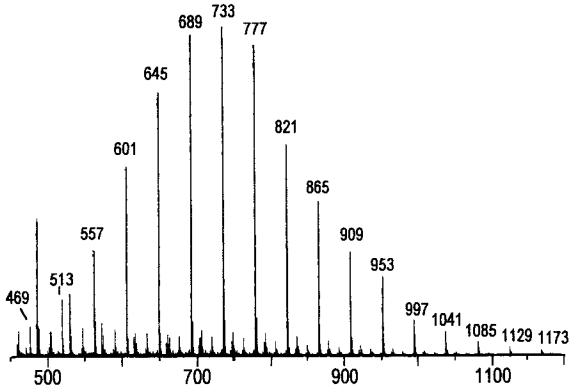


Figure 37. ESI mass spectrum of the S465 ethoxylated surfactant. The ion at 513 u is assigned as the six ethoxylate oligomer. (Reprinted with permission from ref 17. Copyright 1998 American Society for Mass Spectrometry.)

Due to the complexity of oligomer and charge state distributions, ESI appears to be most often used to analyze low molecular weight, ethoxylated surfactants. In many of these experiments, the charge state distribution can be controlled to be essentially singly charged. Figure 37 shows an example of an ESI mass spectrum of an ethoxylated Surfynol surfactant.[17] All of the ions observed in Figure 37 are singly charged and Na^+ cationized. The calculated average molecular weights agree well with MALDI, SIMS, FAB, and FD.

Hunt and co-workers used ESI to measure average molecular weights of polyester resins.[208] They found that the average molecular weights for narrow polydisperse samples agreed well with MALDI and GPC results. In these experiments, ESI had similar problems analyzing broad polydisperse samples to MALDI. They also noted that MALDI and ESI differed on the relative intensity of minor oligomer series. The MALDI experiments appeared to detect branched oligomers better, while the ESI experiment appeared to detect cyclic oligomers better. Judicious use of both techniques may be able to solve more difficult problems.

Average molecular weight measurements by ESI can also be affected by the solvent. As in MALDI, ESI results are sensitive to the solubility match between the solvent and the analyte. Latourte and co-workers examined the distribution of fluorinated phosphazine oligomers in different solvents.[82] Figure 38 shows the impact of solvent polarity on the observed ESI oligomer distribution. The average molecular weight goes through a maximum at a middling polarity.

Maziarz and co-workers used ESI to determine the end groups for an amine-functional PDMS polymer.[201] Figure 39 shows one of their ESI−FTMS mass spectra. Using the high mass resolution and mass accuracy of an FTMS mass spectrometer, they could readily separate and identify three different end groups (dipropylamine [△], propylamine + methoxy [φ], and propylamine + hydroxy [□]), two different cations (H^+ and Na^+), two different charge states (+1 and +2 [○]), and ion fragments. All of the assignments were made with less than 10 ppm mass error.

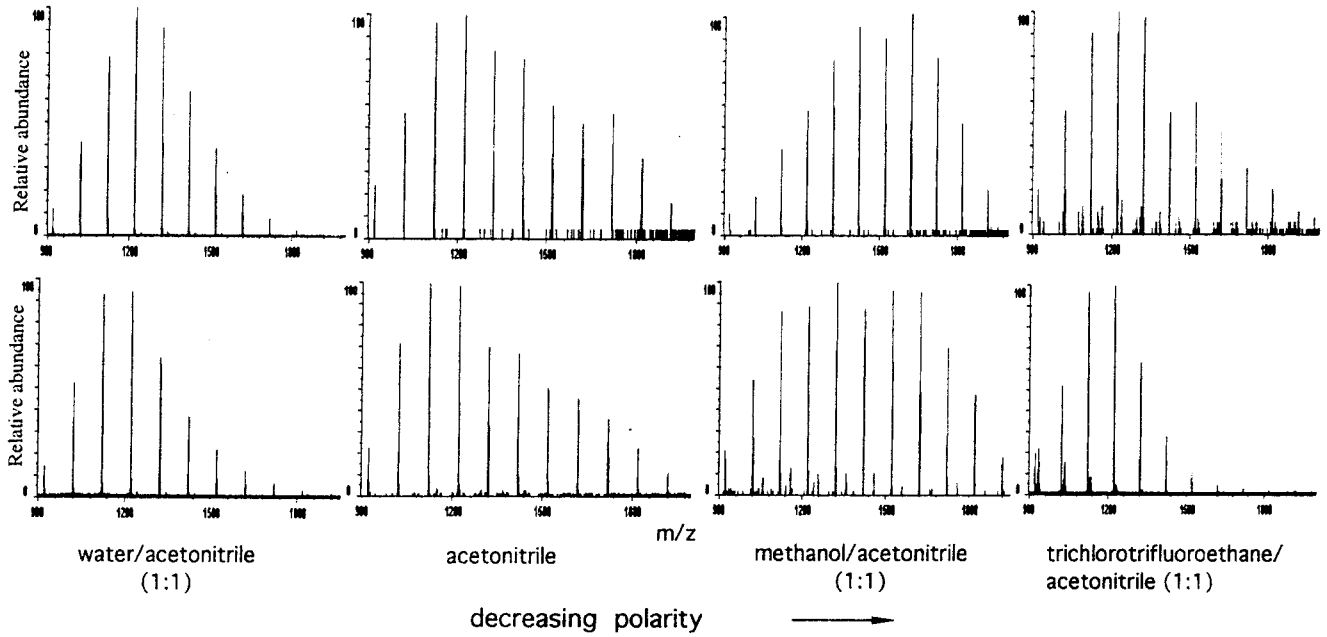


Figure 38. ESI mass spectra of fluorinated phosphazine dissolved in four different solvent systems, presented in order of decreasing polarity, left to right. The top row of spectra were collected using 5 L/min of drying gas at 90 °C. The bottom row of spectra were collected using 6 L/min of drying gas at 105 °C. (Reprinted with permission from ref 82. Copyright 1997 American Society for Mass Spectrometry.)

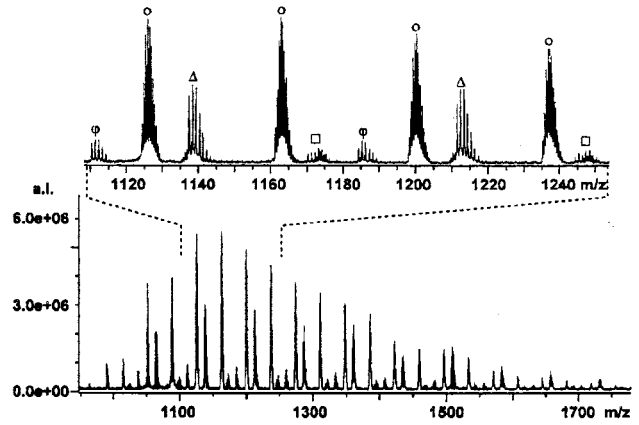


Figure 39. ESI mass spectrum obtained on an FTMS instrument for an amine functional PDMS 2500. (Reprinted with permission from ref 201. Copyright 1999 American Chemical Society.)

ESI is particularly well suited to LCMS methods. The ESI ionization source can accept the column eluant of the chromatograph. LC-ESI techniques will be discussed further in the Chromatography section below.

H. MS/MS

Multiple stages of mass analysis in a single experiment have long been used to determine the chemical structure of analyte molecules. In MS/MS experiments, the first stage of mass analysis is used to select a specific mass range to examine in a second stage of mass analysis. Between the two stages of mass analysis, additional energy is added to the system to fragment the ions of interest. These fragment ions are mass analyzed in the second stage. Multiple stages of MS, or MS^n, are possible on ion trap and FTMS instruments. MS/MS experiments have a long history, but the development of collision-induced dissociation (CID) and post-source decay (PSD) experiments have increased their utility for polymer systems.

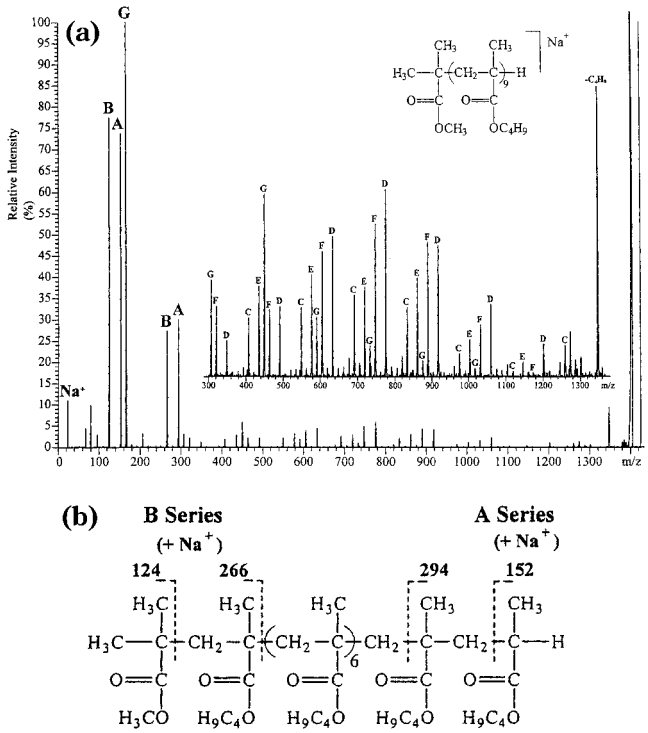


Figure 40. MALDI−CID mass spectrum of the Na^+ cationized 9-mer of a PBMA (structure shown). Also shown is the proposed fragmentation pathways for the A and B ion series. (Reprinted with permission from ref 219. Copyright 1997 American Society for Mass Spectrometry.)

A number of interesting CID experiments have recently been reported on polymers using both LSIMS[53] and MALDI to measure chemical structures for PEG,[218] polymethacrylates,[219] and PS.[220,221] These

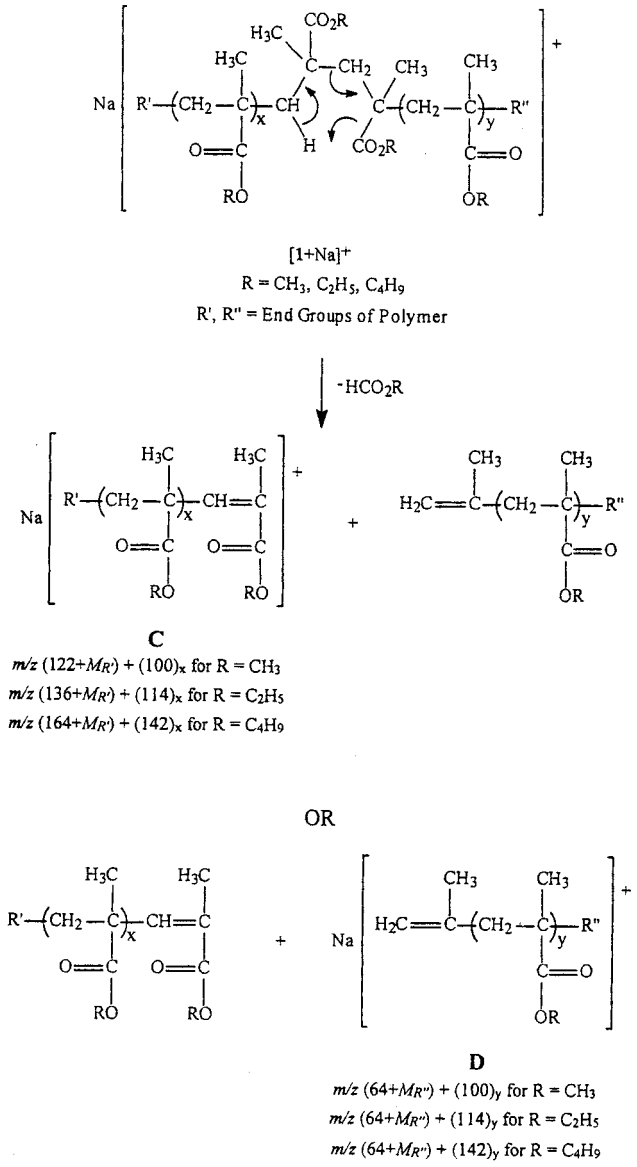


Figure 41. Proposed mechanism for generation of the C and D series. For PBMA, R = C_4H_9. (Reprinted with permission from ref 219. Copyright 1997 American Society for Mass Spectrometry.)

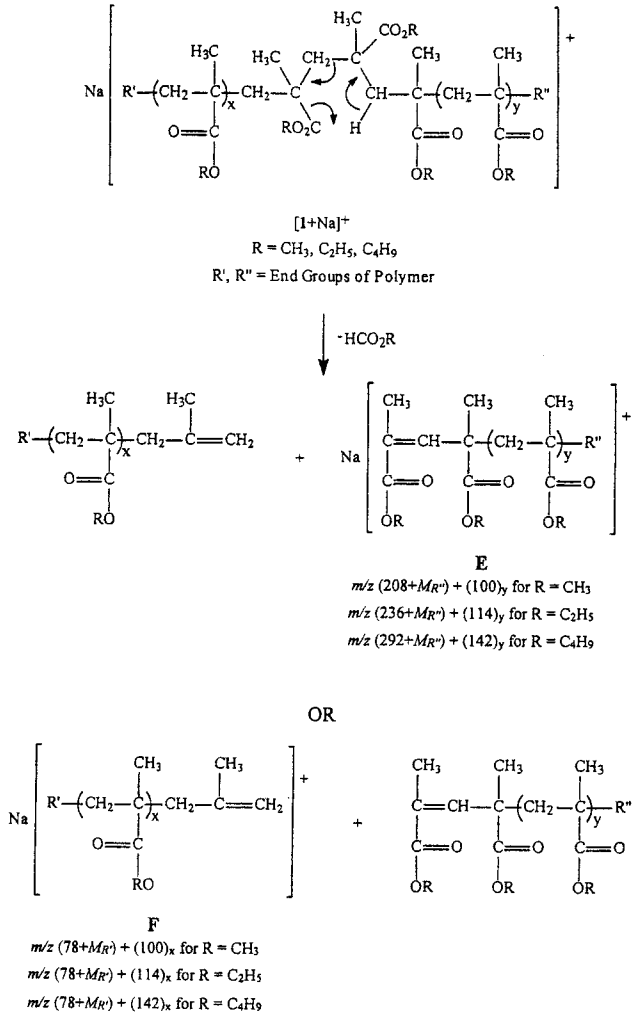


Figure 42. Proposed mechanism for generation of the E and F series. For PBMA, R = C_4H_9. (Reprinted with permission from ref 219. Copyright 1997 American Society for Mass Spectrometry.)

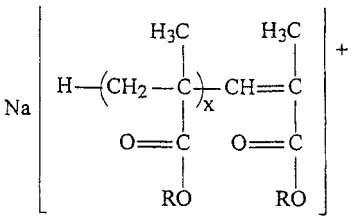


Figure 43. Proposed structure of the G series. For PBMA, R = C_4H_9. (Reprinted with permission from ref 219. Copyright 1997 American Society for Mass Spectrometry.)

experiments use CID on hybrid magnetic sector instruments[222,223] using He, Ar, or Xe as the collision gas. In each of these experiments, fragment ions were observed that aid in the determination of the polymer repeat units and end groups. For example, Jackson and co-workers studied the MALDI−CID of poly(butyl methacrylate) (PBMA) at a collision energy of 800 eV in Xe.[219] Figure 40 shows the MALDI−CID mass spectrum obtained from the $n = 9$ oligomer. The CID process produces a rich fragmentation spectrum. The fragmentation scheme shown in Figure 40 shows how the intense low mass fragment ions labeled with **A** and **B** can be used to determine the chemical structures of the oligomer end groups. The lower intensity, higher mass fragment ions derive primarily from chain rearrangements. The assigned fragmentation schemes are shown in Figures 41−43. For PBMA, R is C_4H_9.

CID experiments have also been reported on an FTMS instrument using sustained off-resonance irradiation (SORI). In these experiments, Pastor and co-workers show MALDI−CID mass spectra for PEG, PS, and PISP.[224] Since the entire polymer distribution was analyzed using SORI, the fragment ions can be calibrated against the known parent ion masses. This yields high mass accuracy for the fragment ions.

The development of MALDI PSD experiments have provided a more accessible MALDI MS/MS experi-

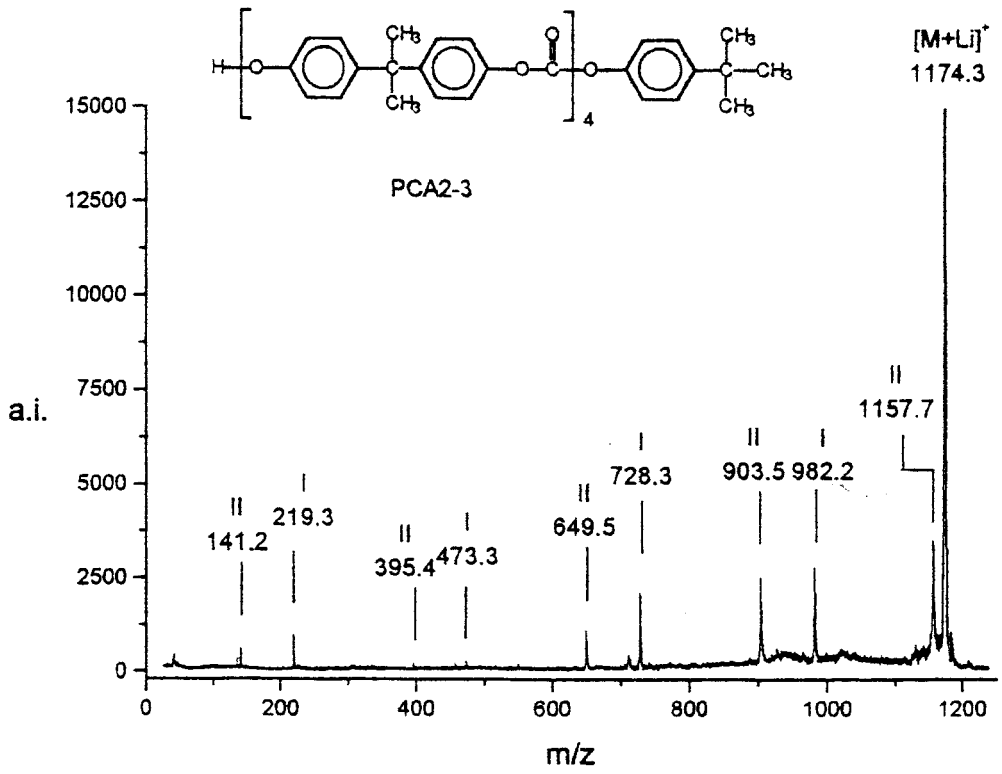


Figure 44. MALDI−PSD mass spectrum of the Li^+ cationized tetramer of the shown polycarbonate. (Reprinted with permission from ref 225. Copyright 1999 IM Publications.)

ment, as these experiments can be done on most commercial TOF reflectron instruments today and do not require the complex hybrid magnetic sector or FTMS instruments used to do the CID experiments discussed above. In PSD the desired ion is selected in the linear portion of the TOF flight tube. Since the mass resolution at this point in the experiment is not very high, a broader range of masses are selected than in the sector experiments. Fragmentation is accomplished by increasing the desorption laser fluence, presumably increasing the number of gas-phase species escaping the surface of the sample and thereby increasing the number of collisions experienced by the selected ion. PSD spectra are acquired by scanning the reflectron and collecting the fragment spectrum in several segments.

MALDI PSD has been applied to numerous biomolecules, but reports on synthetic polymers are still rare. Przybilla and co-workers investigated PSD of polycarbonates,[225] and Scrivens and co-workers investigated PSD of PMMA.[221] In both the polycarbonate and PMMA experiments, the fragment ions could be used to better understand the chemical structures of polymer the end groups. Figure 44 shows the MALDI PSD mass spectrum of a polycarbonate oligomer from Przybilla and co-workers. In Figure 44 we see the parent ion + Li^+ and a series of fragment ions marked with a I or II. The two series are spaced by 254 u, the mass of the polycarbonate repeat unit. Each series is assigned as a portion of the polymer chain with only one of the end groups. Interestingly, Li^+ cationization is used for these PSD experiments because Na^+ and K^+ cationization do not lead to fragments.

I. Liquid Chromatography and Mass Spectrometry

Combining liquid chromatography and mass spectrometry techniques can provide significant advantages. As seen above in the GC-MS section, the chromatography can significantly simplify the material delivered at a given time to the mass spectrometer. In these two-dimensional analyses, both the chromatography and the mass spectrometry can be optimized to solve the particular problem. The LC-MS area has seen a large amount of development in recent years, especially methods of interest to the pharmaceutical industry. Here only a few examples will be discussed that are more suited for the analysis of polymers. More information on analyzing polymers with various LC-MS techniques can be found in a recent review article by Pasch.[226]

1. GPC-MALDI

The combination of GPC and MALDI is a natural extension of the powerful capabilities of these techniques. GPC is a traditional method to measure the average molecular weights of polymers. GPC has the advantage that it can separate complex samples on the basis of molecular size and can readily analyze broad polydisperse samples. The disadvantages of GPC, however, are that the elution volumes must be calibrated to molecular weight for specific polymers, and it has very low mass resolution. MALDI has the advantage of high mass resolution, high mass accuracy, and high sensitivity with the disadvantages of sample discrimination and inaccurate average molecular weights for samples with broad polydispersity. There are three common methods to combine

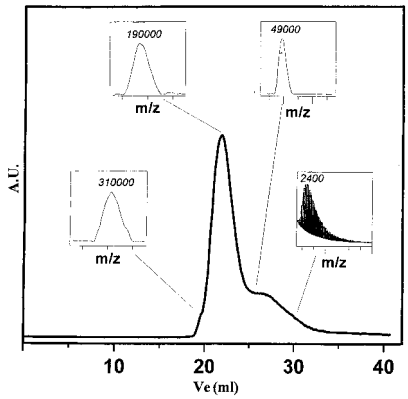


Figure 45. GPC chromatogram of a PDMS sample in THF. The insets show the MALDI mass spectra obtained from selected fractions. (Reprinted with permission from ref 230. Copyright 1998 John Wiley & Sons, Ltd.)

GPC and MALDI: collect individual GPC fractions followed by MALDI of the fractions, collect continuous GPC fractions followed by MALDI, and direct, on-line MALDI analysis of the GPC eluant.

Collecting and analyzing individual GPC elution fractions can be painstaking work generating many samples. Some examples of these experiments include characterizations of polyester copolymers,[227,228] PMMA,[229,230] PDMS,[231] coal derivatives,[79] and a series of synthetic polymers, including PS, polybutylacrylate, polycarbonate, polyester, and a methacrylate copolymer.[130] In each of these cases, the GPC separation provided narrow polydispersity samples to the MALDI experiment. These samples were readily analyzed after the separation. The MALDI data on the separated samples provide important insight into the chemistry and the molecular weights of the samples.

One example that illustrates these experiments is the work of Montaudo and co-workers on polydisperse PDMS.[230] Using GPC size separation, they collected 81 individual fractions of 0.10−0.30 mL. The fractions were analyzed by MALDI. Figure 45 shows the GPC chromatogram for a high molecular weight sample of PDMS along with the MALDI mass spectra of selected fractions.

Table 7 shows the MALDI average molecular weights and the elution volume of several fractions. It is clear from the polydispersity values that the GPC provides narrow fractions for MALDI. These data can be used to create an improved calibration for the GPC. The use of MALDI data to calibrate GPC experiments can be a significant improvement over the creation of narrow standards suitable for GPC calibration or the assumptions necessary to calibrate from other chemistry, most likely PS.

The second method of coupling GPC and MALDI is to continuously collect the eluant on an appropriate target followed by MALDI. The key to this approach is to efficiently spray the column eluant onto a target containing the MALDI matrix. This can be done with a commercially available liquid chromatography transform (LCT) from Lab Connections, Inc. (a Mocon company, Northbourough, MA),[232−235] home-built units,[141] or with a robotic interface.[236] Figure 46 shows data obtained using the Lab Connections

Table 7. Average Molecular Weight Data of GPC Fractions Analyzed by MALDI for a PDMS Material (PDMS1)[a]

fraction	M_p[b]	M_n[c]	M_w[d]	M_w/M_n	V_E[e]
15	300 000	296 000	300 000	1.01	20.71
18	275 000	267 000	274 000	1.03	21.01
21	230 000	222 000	227 000	1.02	21.32
25	190 000	198 500	206 000	1.04	21.72
29	155 000	150 000	157 000	1.05	22.12
33	140 000	142 000	151 000	1.06	22.53
35	128 000	127 500	134 000	1.05	22.73
38	100 000	100 500	106 500	1.06	23.03
44	78 000	77 000	81 500	1.06	23.64
50	49 000	51 000	54 000	1.06	24.24
54	42 000	43 000	45 000	1.05	24.64
66	16 000	16 500	18 000	1.09	26.88
70	6 300	9 000	9 800	1.09	28.10
75	3 300	5 200	5 800	1.11	29.63

[a] Reprinted with permission from ref 230. Copyright 1998 John Wiley & Sons, Ltd. [b] Most probable molecular mass. [c] $M_n = Sn_iM_i/Sn_i$. [d] $M_w = Sn_iM_i^2/Sn_iM_i$. [e] V_E = elution volume of each fraction.

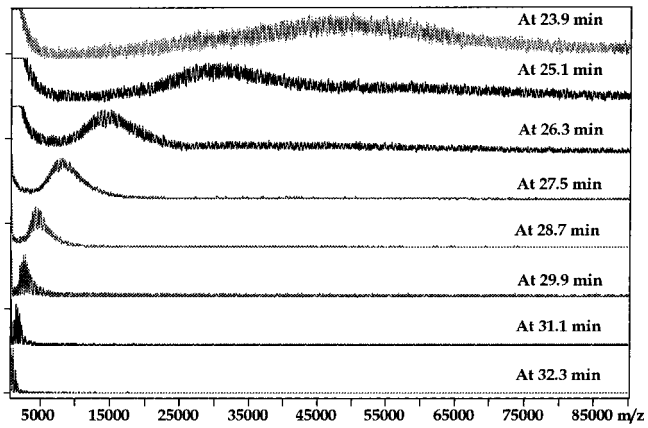


Figure 46. Individual LCT−MALDI mass spectra of GPC eluant fractions from the broad PMMA sample applied to a DHB substrate target.

equipment on a broad polydispersity sample of PMMA. Each of the MALDI mass spectra were obtained at a different elution volume. The measured molecular weights continuously decrease for every spot analyzed along the track of the elution. Using GPC to separate the sample prior to MALDI enabled the mass analysis of the sample. The broad polydispersity had made MALDI analysis alone highly problematic.

Ultimately, the GPC and MALDI experiments can be connected on-line.[158−160] These experiments have recently been done on low molecular weight PEG and PPG standards by Fei and co-workers.[240] The eluant of the GPC column is introduced to the mass spectrometer as an aerosol containing both the matrix and the analyte. While the results show promise for connecting LC and MALDI in a continuous analysis, experimental problems hinder its application to more polymer analyses. More information on coupling MALDI with LC on-line can be found in a recent review article by Murray.[241]

2. Other Chromatography–MALDI

While GPC is the most prevalent chromatography technique combined with MALDI analysis, it is not

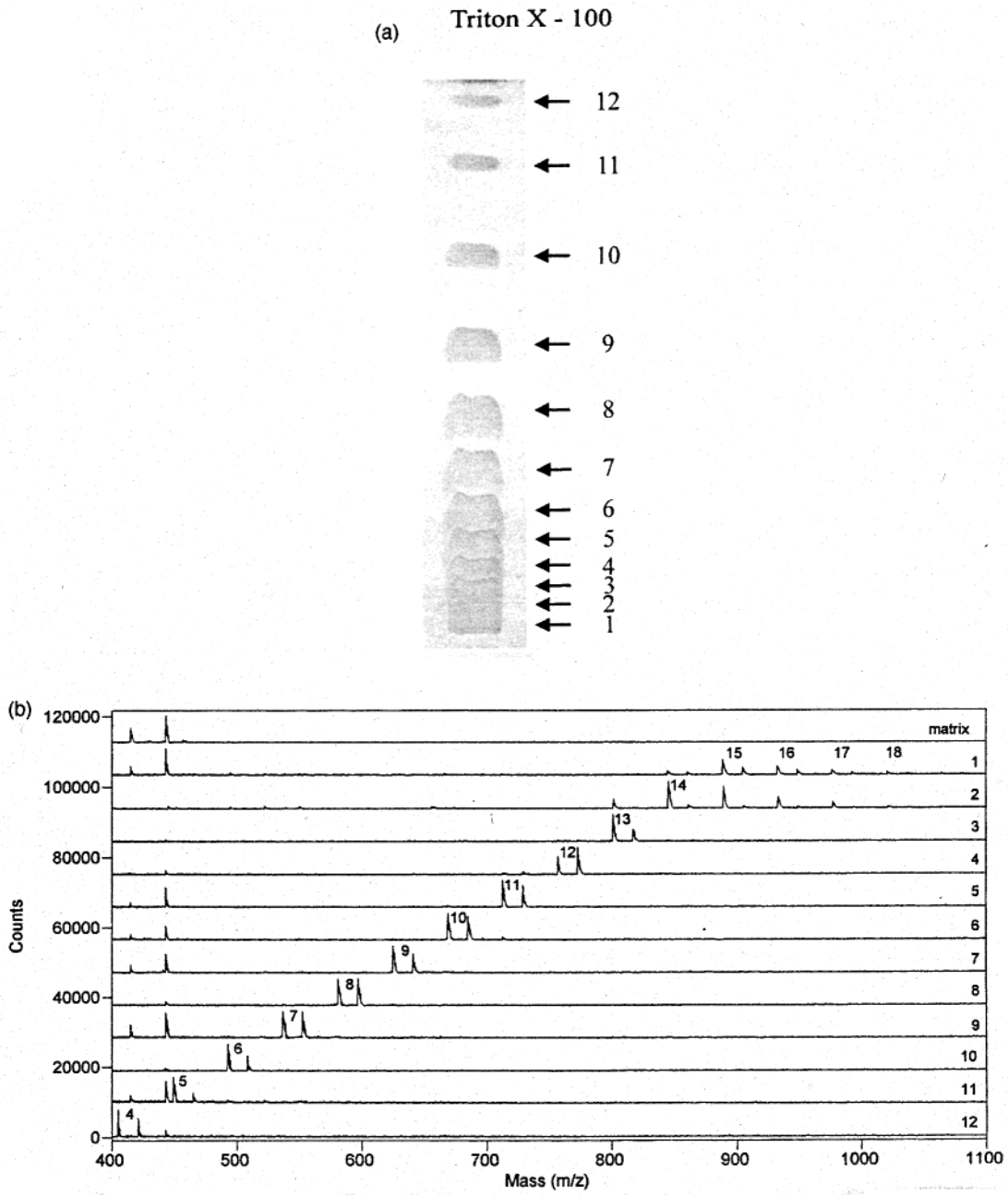


Figure 47. TLC−MALDI: (a) TLC of Triton X-100; (b) MALDI mass spectra of the individual TLC fractions. The fraction numbers are on the right. The oligomer numbers are labeled between the corresponding Na^+ and K^+ cationized peaks. (Reprinted with permission from ref 246. Copyright 1997 Elsevier Science B.V.)

the only one. Thin-layer chromatography (TLC),[242] capillary electrophoresis,[243] temperature gradient inverse chromatography,[244] and gradient reverse-phase liquid chromatography[131,245] are also used. Cumme and co-workers use TLC and gradient reverse-phase liquid chromatography to examine the composition of ethoxylated surfactants in nonionic detergents.[246] Figure 47 shows the results of TLC−MALDI experiments on a sample of Triton X-100. The upper portion of Figure 47 shows the resolved spots obtained from TLC. Each of the numbered spots was totally scraped off the TLC substrate and analyzed by MALDI. The MALDI mass spectra are shown in the lower portion of Figure 47. Most of the spots contain a single oligomer (both Na^+ and K^+ cationized).

3. LC-ESI

The combination of ESI with various LC methods is very natural. ESI requires a steady flow of liquid, perfect for connection to an LC column. Several different LC techniques have been connected to ESI, including GPC, gradient reverse-phase liquid chromatography, capillary zone electrophoresis, gradient polymer elution chromatography, supercritical fluid chromatography,[247] and liquid chromatography at the critical point of adsorption. A few examples of connecting ESI with LC include investigations of ethoxylated surfactants,[213−214,248] (methoxymethyl)melamine resin,[249] and polyesters.[121,208,250] Aaserud and co-workers used GPC−ESI−FTMS to investigate several methacrylate samples.[251] The advantages of

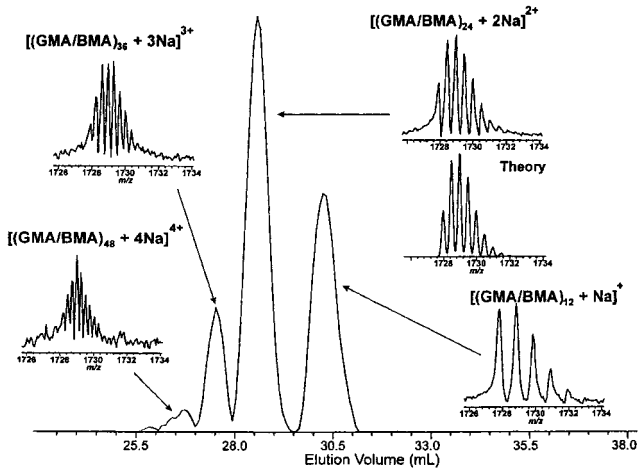


Figure 48. Selected ion plots from GPC−ESI−FTMS for Na^+-cationized GMA/BMA copolymers, the 48-, 36-, 24-, and 12-mers. (Reprinted with permission from ref 251. Copyright 1999 American Chemical Society.)

GPC−ESI−FTMS are shown in Figure 48. Figure 48 shows selected ion plots for sodium-cationized glycidyl methacrylate (GMA) and butyl methacrylate (BMA) copolymers. Since GMA and BMA have the same nominal mass of 142 u, the mass spectrum of the whole copolymer is highly complex. The chromatographic separation enables the separation of the various copolymer oligomers. Note that each of the oligomers shown in Figure 48 are observed around 1729 u.

Crescenzi and co-workers used gradient reverse-phase liquid chromatography (LC)−ESI on a quadrupole mass spectrometer to determine nonionic ethoxylated surfactants in environmental water samples.[214] They showed that the different surfactants could be readily identified and quantified by LC-ESI methods. The limit of detection was shown to be 20 pg/component injected on column. The analysis of municipal water showed the existence of surfactants in the parts-per-trillion level.

J. Static SIMS

A SIMS experiment consists of several steps: primary ion bombardment, energy transfer, particle desorption, particle mass analysis, and particle detection. In this technique, the sample is bombarded with a primary ion beam, typically Ar, Xe, Ga, or Cs ions, accelerated to 5−25 kV and focused on the surface of the sample. The primary ion strikes the sample surface and transfers energy and momentum to the sample in a process called the collision cascade. These transfers result in the desorption of neutral species, secondary electrons, and secondary ions. The secondary ions are mass analyzed and detected.[252,253] The energy transferred to the sample decreases with distance away from the primary ion impact site. Close to the impact site, atoms and electrons are desorbed; farther from the impact site whole molecules are desorbed. Because energy is only deposited in the upper layers of a sample surface, SIMS experiments are highly surface sensitive, usually only observing secondary ions from the top couple of monolayers.

SIMS experiments can be done on a variety of mass spectrometers including quadrupoles, magnetic sectors and TOF instruments. The emergence of TOF analyzers for SIMS has greatly broadened the application of SIMS for polymers. To effectively interface with the TOF mass spectrometer, the ion source is pulsed, creating the ion packets analyzed by TOF. The impact of the primary ions on the sample surface will eventually damage the surface. The dosage of the primary ion beam defines two related experiments. High-dosage experiments ($>1 \times 10^{12}$ ions/cm^2) are dynamic SIMS experiments. Dynamic SIMS is often used to measure elemental depth profiles. Low-dosage experiments ($\leq 1 \times 10^{12}$ ions/cm^2) are static SIMS (SSIMS) experiments. Static SIMS experiments provide mass spectra characteristic of the top few atomic layers. The use of SIMS to investigate a variety of surfaces will be further discussed below in the Mass Spectrometry of Surfaces sections.

Two different types of SSIMS experiments can be used effectively to obtain mass spectra of polymer samples.[254−256] SSIMS of a thin-layer sample can provide the same types of data as is obtained by MALDI, FAB, or FD. Thin-layer polymer samples are created by depositing a few microliters of a dilute (1 mg/mL) polymer solution in a good solvent on an appropriate surface. Roughened or acid-etched silver or a silicon wafer are often used. As in MALDI, a cationization agent needs to be present. The cationization agent could be from the surface (for example, Ag) or added to the sample solution (for example, Na^+). These data can be used to characterize chemical structures and measure average molecular weights.

The second common SSIMS experiment used to analyze polymer samples involves a thick-layer sample. In these experiments a solid piece of a polymer is used as the sample. These experiments have a significant advantage in sample preparation. No solvent or matrix is needed. This can be a very important method to analyze insoluble materials. These experiments provide data similar to pyrolysis and LD experiments with the generation of primarily low molecular weight fingerprint mass spectra. The data can be used to determine the repeat units, end groups, and surface contaminants in the polymer sample. Since these experiments produce primarily low molecular weight fragments, quadrupole mass spectrometers are often used. Since most thick layer polymer samples are insulators, charge compensation is required to obtain good SSIMS mass spectra.[257]

The use of ToF−SIMS to characterize polymer samples has been developed and established by the collaboration of the Benninghoven and Hercules groups. Their work has contributed a significant number of papers on a wide variety of topics concerning polymer analysis by SSIMS.[258] Table 8 shows some representative recent examples of SSIMS analyses of polymer materials.

There is a significant amount of SSIMS information currently available in the literature. More information can be found in books[252,293,294] and in recent review articles by Van Vaeck, Adriaens, and Gijbels,[295] Adriaens, VanVaeck, and Adams,[296] Wien,[297] and Bertrand and Weng.[298] Many different examples

Table 8. Representative SSIMS References by Chemistry

chemistry	comment	group
methacrylates	copolymers	Briggs et al.[259]
metacrylic acid + styrene	latex copolymers	Davies et al.[260]
PBD	narrow standards	Vanden Eynde et al.[261]
PBD	F functional end groups	Patwardhan et al.[262]
PDMS	narrow standards	Dong et al.[263]
PDMS	narrow standards	Yan et al.[203]
PDMS + polyamide	copolymers	Senshu et al.[264]
PE, PP, copolymers	commercial products	Galuska[265]
PEG	narrow standard	Keller et al.[266]
PEG	commercial products	Shard et al.[267]
PEG	functional end groups	Wen et al.[268]
PEG, PPG	narrow standards	Hittle et al.[269]
PET	bulk sample	Reichlmaier et al.[270]
Perfluoro-polyethers	commercial products	Kasai et al.[271]
phosphazene	commercial products and synthesis	Groenewold et al.[272]
PI		Xu et al.[273]
polyisobutylene	commercial products	Xu et al.[274]
PMMA, PS	tacticity	Vanden Eynde et al[275]
PMMA, PP, PS	compare to theory	Endo et al.[276]
polyesters	biodegradeable	Chen et al.[277]
polyesters	copolymers	Lang et al.[278]
polyester polyurethanes		Cohen et al.[279]
poly(lactic acid)	copolymers	Shard et al.[280]
poly(malic acid)	copolymers	Leadley et al.[281]
poly(sebacic anhydride)	copolymers	Leadley et al.[282]
PP	stereoregular	Xu et al.[283]
PS	narrow standards	Lee et al.[284]
PS	end groups	Linton et al.[285]
PS	end groups	Vanden Eynde et al.[286]
PS	end groups	Vanden Eynde et al.[287]
PS	deuterated end groups	Vanden Eynde et al.[288]
PS	F functional end groups	Affrossman et al.[289]
PS and PI	copolymers	Nicholas et al.[290]
PS, PBD, PI	narrow standards	Belu et al.[110]
PS, PIP, PBD, PIB, PE, PP	standards	Galuska[291]
siloxanes	narrow standards	Dong et al.[292]
surfynol surfactants	ethoxylated	Parees et al.[17]

of SSIMS mass spectra of polymers can be obtained from the journal *Surface Science Spectra*.[299]

1. Molecular Weight Measurements

ToF−SIMS can produce mass spectra of intact oligomer ions. As in MALDI, the average molecular weights are calculated directly from the moments of the distribution of ion peak areas. Due to the fragmentation that occurs in SSIMS experiments, average molecular weights can be measured on only relatively low molecular weight polymers. The degree of fragmentation and the highest molecular weight that can be measured by SSIMS varies with the chemical structure of the polymer. For example, much higher molecular weight PS oligomers can be detected than PEG oligomers.[137] The highest molecular weight sample for which we have produced average molecular weight data by SSIMS is PS 5400.

Lee and co-workers investigated the average molecular weights of different PS samples.[284] Figure 49 shows TOF−SIMS data for three different PS samples (nominal molecular weights 800, 2500, and 3400 u) analyzed as thin layers on silver. In Figure 49, the PS oligomers are clearly observed. By the 3400 u sample, significant fragmentation in the mass spectrum is observed. Lee's calculated M_N values for the mass spectra in Figure 49 agree well with their GPC results. The fragmentation observed in the higher molecular weight samples by SSIMS can be used to advantage. These mass spectra contain both the average molecular weight data from intact oligomers and a significant amount of chemical structure information from the various fragments.

Average molecular weight data can also be obtained by carefully analyzing the fragments produced by SSIMS. Galuska analyzed a variety of polymer thin films.[291] Looking specifically in the low molecular weight, fingerprint region, Galuska observed that the relative intensity of the protonated monomer ion is reasonably constant for samples with molecular weight above about 20 000 u but increased rapidly for samples below about 10 000 u. Galuska correlated the intensity of the protonated monomer with the average molecular weights for a wide variety of polymers, including PS, PI, PBD, polyisobutylene (PIB), polyethylene (PE), and polypropylene (PP). The correlation works well for polymers below about 20 000 u. The relationship between the protonated monomer intensity and the polymer molecular weight was fit to eq 5

$$\text{Relative (monomer} + \text{H}^+) = M(\text{MW}/1000)^E + B \quad (5)$$

where M is the slope, MW is the polymer molecular weight, E is a constant ranging from −0.5 to −0.6, and B is the ion ratio intercept. Figure 50 shows the plots of protonated monomer relative to the $C_2H_3^+$

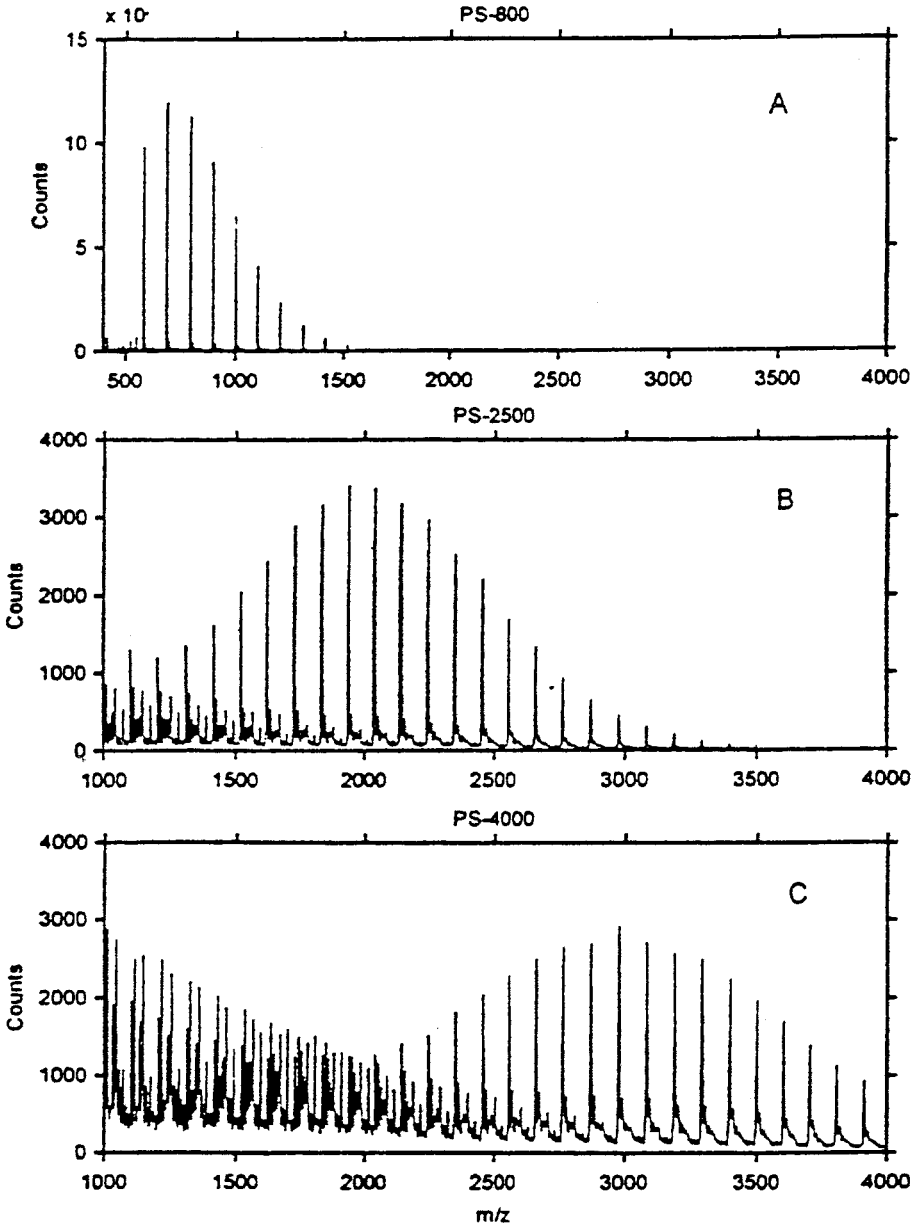


Figure 49. TOF−SIMS mass spectra of Ag^+ cationized (a) PS 800, (b) PS 2500, and (c) PS 4000. (Reprinted with permission from ref 284. Copyright 1999 Hyomen Bunseki Kenkyukai.)

fragment for (a) 1,4-polybutadiene ethylene (top) and (b) polyisoprene (bottom).

Table 9 shows the tabulated results for the polymer types studied. The table includes the polymer type, the reference ion, the parameters from eq 5, and the estimated errors in average molecular weight calculations. Similar calculations of polymer average molecular weight have also been made by Vanden Eynde and co-workers using characteristic end group fragments instead of protonated monomer fragments for PS[187] and PBD.[261]

2. Chemical Structure Analysis

The fragmentation observed in SSIMS mass spectra can be quite useful in determining the chemical structure of the polymer sample. Both end groups and repeat units can be determined. SSIMS data is used to probe many different features of polymer samples, including tacticity,[275] polymer blends (stereoregular PP,[287] PS + poly(dimethyl phenylene oxide),[301] different molecular weight PS,[302] PS + poly(vinylpyrrolidone),[303] PMMA + ethylene-tetrafluoroethylene,[304] PS + fluorine functional end-capped PS[289]), functional end groups,[262] and copolymer analysis.[259,264,282,291] Two valuable compilations of low-resolution SSIMS fragment mass spectra have also been published,[305,306] and a high-resolution library is being generated.[307] These compilations can be a great aid in identifying unknown polymers from fragment ions.

In a recent example, Dong and co-workers studied the changes in fragmentation patterns for different siloxane polymers.[292] They determined the fragmentation mechanisms for dimethyl-, hydromethyl-, and methylphenyl-substituted siloxanes. The different functional siloxanes have different fragmentation pathways which can be used to differentiate them.

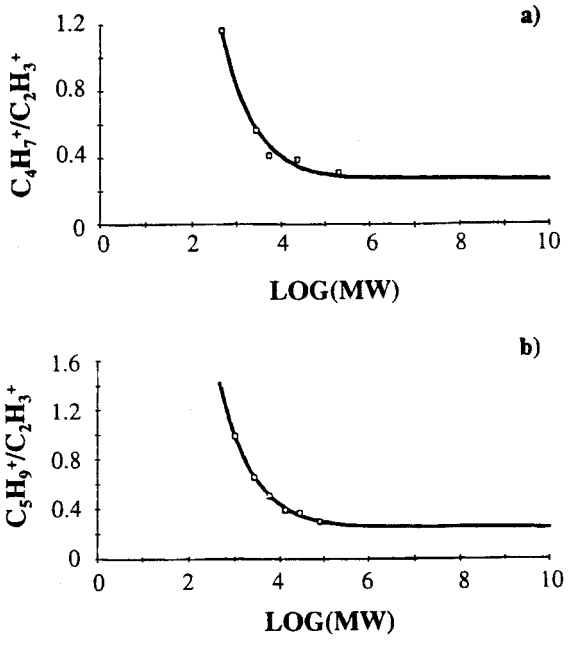


Figure 50. Plots of protonated monomer relative to the $C_2H_3^+$ fragment for (a) 1,4-polybutadiene ethylene (top) and (b) polyisoprene (bottom). (Reprinted with permission from ref 291. Copyright 1997 John Wiley & Sons, Ltd.)

Changing the end group of the polymer also can significantly change the SSIMS mass spectra. Kasai and co-workers showed that introducing −OH end groups into a series of perfluoro-polyethers (PFPE) enabled the detection of intact oligomer ions.[271] Figure 51 shows positive- and negative-ion SSIMS mass spectra for normal and −OH-terminated, commercially available Demnum PFPE. PFPE's with typical perfluorinated alkyl end groups produce only low molecular weight fragments in positive-ion mode. In negative-on mode, both materials produce fragments assigned as $R-O^-$. Combining the positive- and negative-ion experiments on both materials enables the chemical structures to be determined.

Pinto and co-workers use SSIMS data to map copolymer decomposition chemistry.[308] Their results on a methacrylic copolymer show three different ablation mechanisms: chain unzipping, chain cross-linking, and monomer fragmentation. Their results agree well with other studies using laser desorption and plasma polymerization.

Biodegradeable polymers have been the subject of several recent articles. Much of this work is motivated by finding better materials for drug delivery systems. These materials tend to be polyester polymers and copolymers of natural products. Several of these articles also show the complementary nature of SSIMS and XPS.[278,280−282] The SSIMS provides qualitative details on the chemical structures, and the XPS provides good quantitation of the surface species. Chen and co-workers studied the in-vitro hydrolytic degradation of a series of biodegradeable polymers.[277] The distribution of hydrolysis products enabled the measurement of kinetics for the degradation. The data can be used for rapid screening of new materials. SSIMS and surface analysis are becoming increasingly important to the pharmaceutical industry.[309]

3. MESIMS

Matrix-enhanced secondary-ion mass spectrometry (MESIMS) is a specific SSIMS experiment that uses MALDI-like sample preparation methods.[310,311] Matrix effects in SIMS have long been established.[312] In MESIMS, matrix effects are optimized to increase the secondary-ion signal. Typical matrices studied are the common MALDI matrices. MESIMS methods have been developed to measure low molecular weight polymers and to investigate MALDI sample preparation.[137,144] We have found that the surface of the prepared sample is highly dependent on the combination of polymer and matrix. Using MESIMS to probe the surfaces of these samples, we have determined the relative solubility of various common MALDI matrices (as discussed above in Figure 20). This work has enabled us to greatly decrease the time necessary to develop sample preparation methods for new polymer samples.

K. Comparisons of Multiple Techniques

Many of the mass spectrometry techniques discussed above can provide similar data on low molecular weight polymer samples. Several recent papers have compared the results of different techniques (Table 10).

In general, the results between the various techniques agree reasonably well. An example of the mass spectrometry technique comparisons is shown in

Table 9. Molecular Weight Calibrations: Parameters and Accuracies[a]

						% error at MW of[b]		
polymer	ion ratio	*M*	*B*	*E*	*R*	500	3000	10 000
1,4-polybutadiene	$C_4H_7^+/C_2H_3^+$	0.561	0.267	−0.6	0.993	10	14	20
polyisoprene	$C_5H_9^+/C_2H_3^+$	0.743	0.248	−0.6	0.998	9	12	18
polyisoprene	$C_5H_9^+/C_5H_7^+$	2.91	0.558	−0.6	0.998	9	10	13
polystyrene	$C_7H_7^+/C_2H_3^+$	1.38	1.067	−0.5	0.982	14	20	28
polystyrene	$C_4H_7^+/C_7H_5^+$	44.7	1.290	−0.6	0.982	8	8	9
polyethylene	$C_2H_5^+/C_2H_3^+$	0.286	0.414	−0.5	0.975	20	33	40
polyethylene	$C_3H_7^+/C_3H_5^+$	0.382	0.487	−0.5	0.964	18	23	33
polyisobutylene	$C_4H_9^+/C_2H_3^+$	1.442	1.692	−0.6	0.998	14	22	35
polyisobutylene	$C_4H_9^+/C_4H_7^+$	1.330	0.890	−0.6	0.969	13	18	24
polypropylene	$C_3H_7^+/C_3H_5^+$	0.502	0.489	−0.5	1.000	15	22	30
poly(1-butene)	$C_4H_9^+/C_2H_3^+$	1.252	0.311	−0.5	−−	12	13	16

[a] Reprinted with permission from ref 281. Copyright 1997 John Wiley & Sons, Ltd. [b] Errors were calculated by assuming a relative ion intensity precision of 5%.

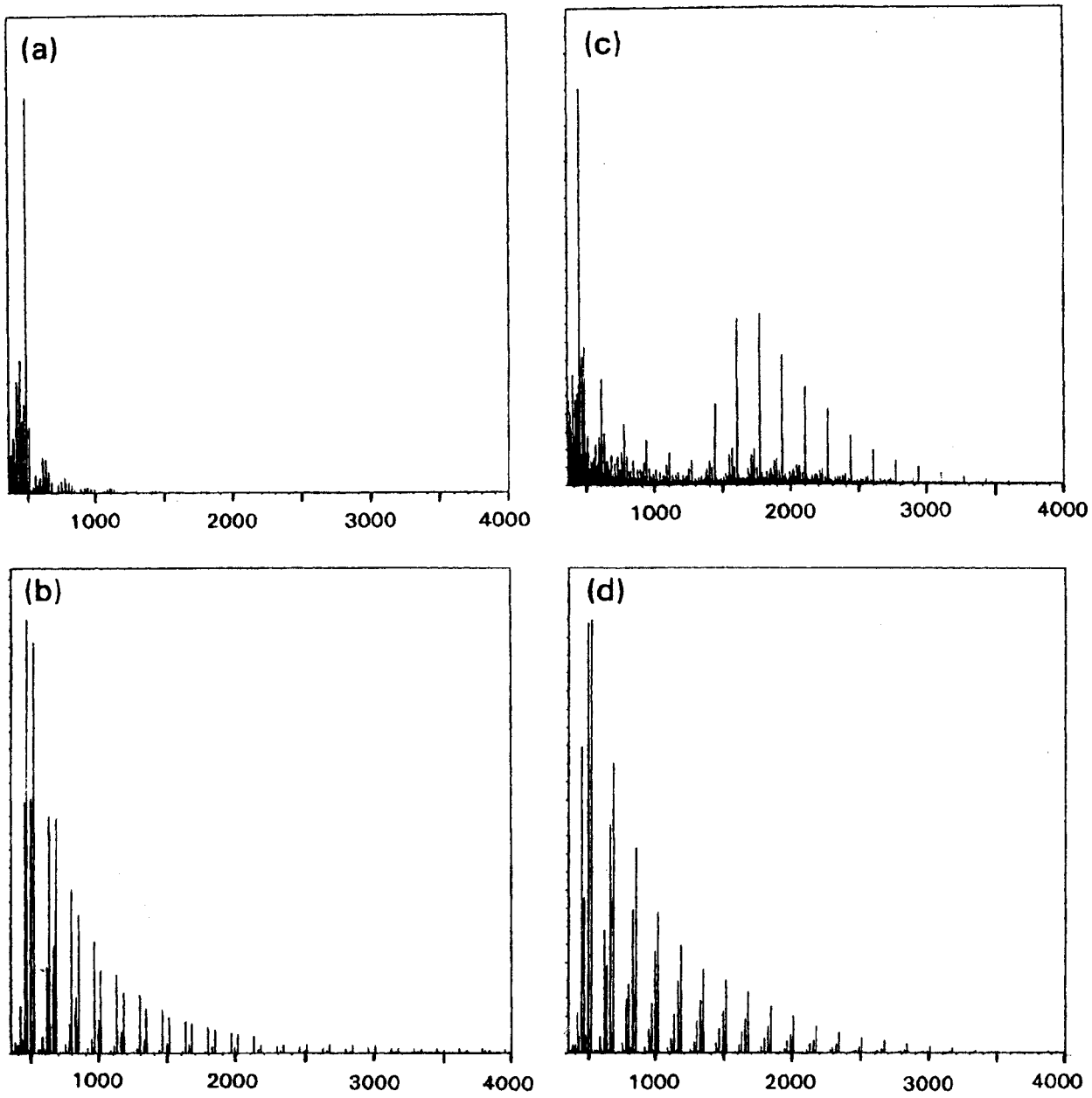


Figure 51. SSIMS mass spectra observed from a normal and a −OH-terminated PFPE: (a) normal−positive ion, (b) normal−negative ion, (c) −OH-terminated−positive ion, and (d) −OH-terminated−negative ion. The nominal average molecular weight of the −OH-terminated sample was determined to be about 2000 u by ^{19}F NMR. (Reprinted with permission from ref 271. Copyright 1998 American Chemical Society.)

Table 10. Recent Comparisons of MS Techniques

chemistry	techniques	group
fluorinated polymers	MALDI, ESI	Latourte et al.[82]
PDMS	MALDI, ESI, SSIMS, GPC	Yan et al.[203]
PS	MALDI, SSIMS, GPC	Lee et al.[284]
PS, PI, PBD	MALDI, SSIMS, GPC	Belu et al.[110]
surfynol surfactants	MALDI, GC-MS, FAB, ESI, FD, SSIMS	Parees et al.[17]
polyesters	MALDI, ESI, FAB, NMR, GPC, titration	Williams et al.[120]
polyesters	MALDI, ESI, GPC	Hunt et al.[208]

Figure 52 from Parees and co-workers.[17] Figure 52 shows mass spectra of an ethoxylated Surfynol surfactant (S465) analyzed by FAB, ESI, SSIMS, MALDI, and FD. The calculated average molecular weights for all five measurements are very similar.

Three of the studies showed that average molecular weights determined by MALDI are somewhat higher than those determined by SSIMS.[110,203,284] The increased fragmentation observed by SSIMS may impact these results, especially for the higher molecular weight samples studied. The surface sensitivity of SSIMS may also lead to a different observed oligomer distribution due to segregation of the sample by size at the vacuum−solid interface.

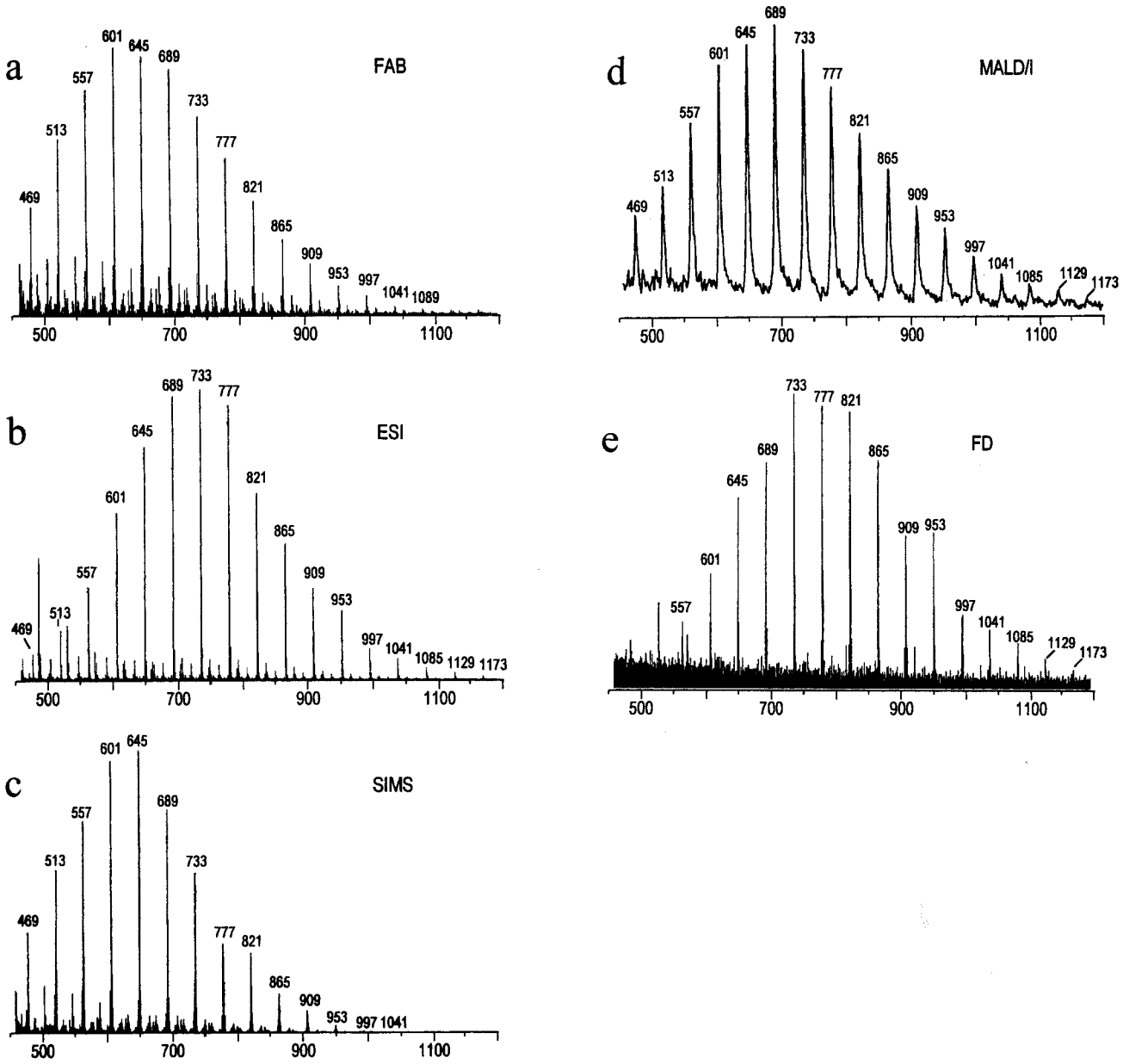


Figure 52. Mass spectra of an ethoxylated Surfynol surfactant (S465): (a) FAB, (b) ESI, (c) SSIMS, (d) MALDI, and (e) FD. (Reprinted with permission from ref 17. Copyright 1998 American Society for Mass Spectrometry.)

V. Surface Chemistry

Surfaces or interfaces are the boundaries between the different states of matter. They are the regions where one phase ends and the next begins. These regions include gas−liquid, gas−solid, liquid−liquid, liquid−solid, and solid−solid. Surfaces play an important role in many technological processes, such as catalysis, corrosion, and adhesion.[313] These processes depend on the chemical composition of the interface. The depth of the interface depends on short-range molecular forces.[314] Since the principle forces between molecules are van der Waals forces and they decrease with the seventh power of the intramolecular distance, the interaction between nearest neighbors is critical. A molecule will experience essentially symmetrical forces once it is a few molecular diameters away from the surface.

VI. Mass Spectrometry of Surfaces

Many different analytical techniques have been developed to characterize the chemical composition of surfaces.[293−294] Most of these techniques use spectroscopy or microscopy. While several mass spectrometric techniques have been developed to analyze surfaces, SIMS is by far the dominant method. In this article, we will concentrate almost exclusively on SSIMS techniques and examples on polymer surfaces. As discussed above in the SIMS section of polymer mass spectrometry, there is a significant amount of literature available on the mass spectrometry of surfaces. Primary references for more information are the recent review articles by Van Vaeck, Adriaens, and Gijbels,[295] Adriaens, Van Vaeck, and Adams,[296] Hanley, Kornienko, Ada, Fuoco, and Trevor,[315] and Vickerman,[316] the book by Benning-

hoven,[252] and the series of books containing the papers from the Secondary Ion Mass Spectrometry Conferences.[317] Due to this wealth of existing literature, we will cover the polymer surface mass spectrometry in less detail than the polymer mass spectrometry discussed above.

Since surface mass spectrometry provides information about only the top few molecular layers of a sample, it is enormously sensitive to the surface species. In some cases, like the surfactant contamination of a coating, SSIMS can be much more sensitive than bulk methods because the contaminant has been concentrated at the surface of the sample prior to the analysis. On the other hand, if a sample has been contaminated by improper sample handling, a fingerprint, for example, the underlying sample may not be detected because the contamination occupies all of the accessible surface layers.

SSIMS is the most prevalent surface mass spectrometry technique used to characterize polymer surfaces. Other techniques that are used include dynamic SIMS,[318,319] LDMS,[320] thermal desorption,[321,322] and secondary neutral mass spectrometry (SNMS).[315,323] While dynamic SIMS is most often used to measure depth profiles in semiconductor materials, Pinto and co-workers show how it can be used effectively to measure diffusion in a polymer application.[318]

A. Polymer Additives

Surface analysis of polymeric materials can provide information about both the chemical structure of the polymer and about surface active additives. The chemical characterization of the polymer materials was discussed above in the SIMS section. Polymer additives are an important part of many industrial formulations. Additives are added to products to modify the field performance in a way that the main components of the product cannot accomplish. Examples of polymer additives that can be characterized by SSIMS include lubricants,[271] surfactants,[266,324,325] antistatic agents,[326] antioxidants,[327] plasticizers,[328−330] toughening agents,[331] and adhesion promoters.[326] More information on studying adhesion by SIMS can be found in a review article by Spool.[332]

Munro and co-workers demonstrate the detection of a phthalate plasticizer on the surface of a PVC-based material.[328] Figure 53 shows the SSIMS mass spectrum of the PVC material. The ion observed at 391 u is characteristic of di-isooctyl phthalate, a common plasticizer. The presence of the plasticizer at the surface of the material can cause problems with some applications, especially adhesion.[330]

SSIMS techniques have been developed to detect additives in finished coatings. The data are used to identify additives in good coatings and to solve problems in defective coatings. Antioxidants are often added to polymer coatings to improve stability in sunlight. Walzak and co-workers showed how to characterize a light-stabilizing additive down to 0.2% (w/w).[333] Figure 54 shows SSIMS mass spectra of PE with (a) and without (b) the Chimassorb 944FD (C944) light stabilizer. The 599 u ion observed in Figure 54 (a) is assigned as the protonated repeat unit of the C944 additive.

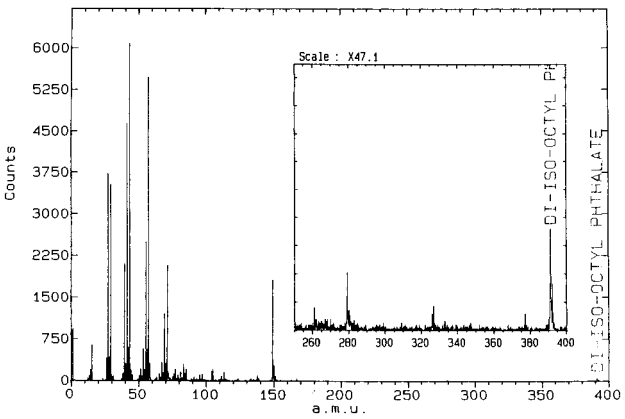


Figure 53. SSIMS mass spectrum of the surface of a PVC material showing the presence of a dioctylisophthalate. (Reprinted with permission from ref 328. Copyright 1993 Blackie, Glasgow, U.K.)

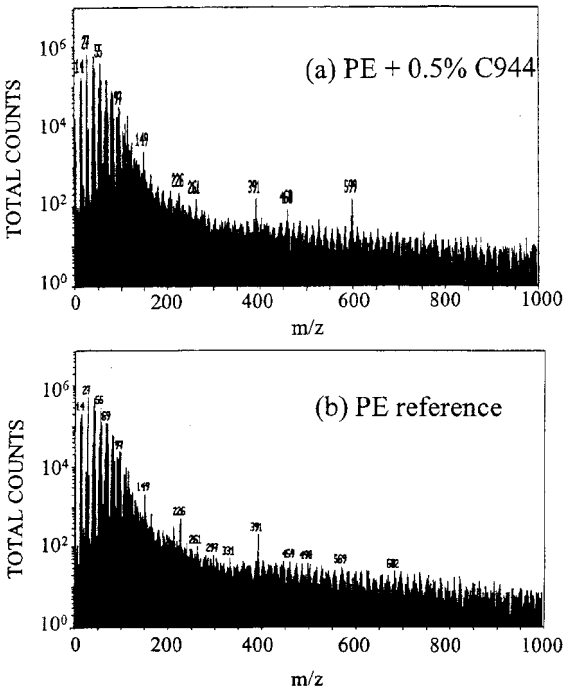


Figure 54. SSIMS mass spectra of (a) PE containing 0.5% C944 and (b) high-purity PE. The 599 u ion is assigned as the protonated repeat unit of the C944. (Reprinted with permission from ref 333. Copyright 1999 American Chemical Society.)

Andrawes and co-workers showed that SSIMS results on characterizing light stabilizers in coatings agreed well with supercritical fluid extraction chromatography.[334] Dietrich showed how SSIMS can be used to detect submonolayer levels of a lubricant additive in paint defects.[335] Sometimes a number of different additives can all be observed on the surface of a material, such as PET.[326,336] Weng and co-workers showed that the surfactants necessary to stabilize latex emulsions can be quantitatively detected by SSIMS.[324]

B. Surface Contamination

Surface contamination can impair the surface properties of many processes. For example, migration

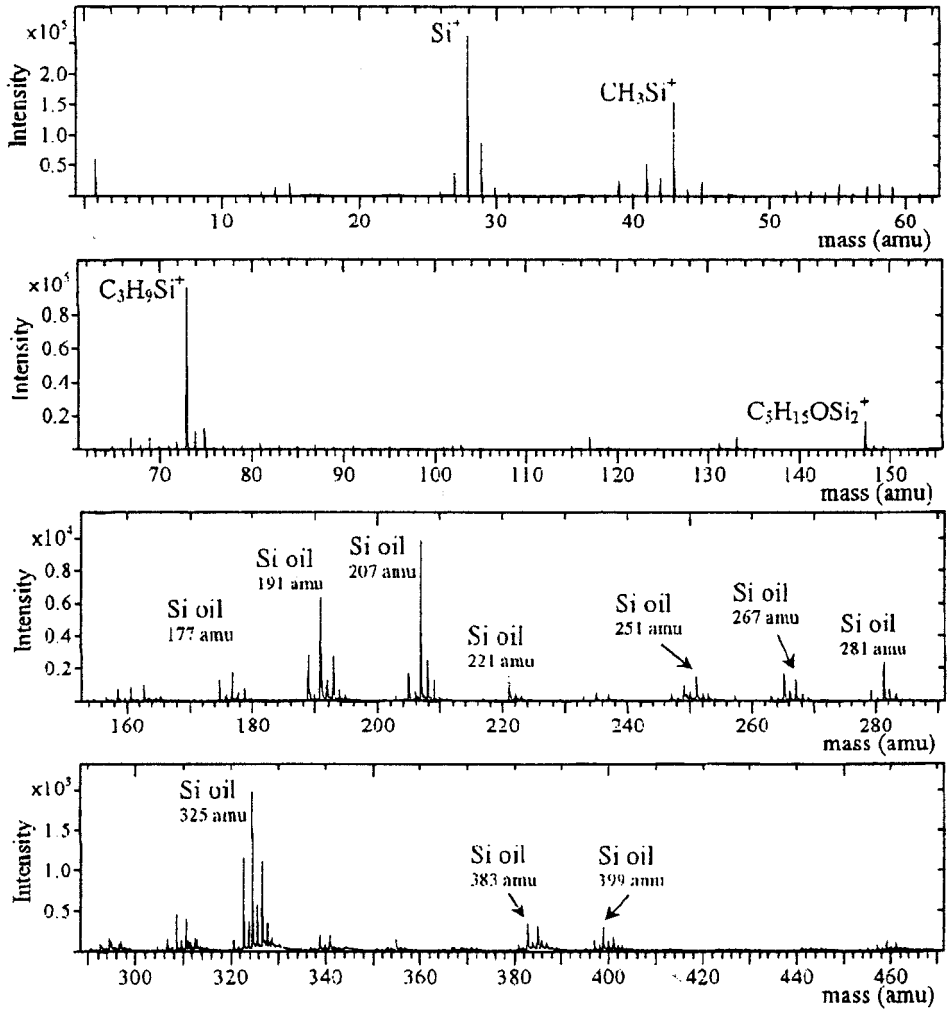


Figure 55. SSIMS of an as received AFM cantilever. Several peaks characteristic of PDMS are labeled. (Reprinted with permission from ref 337. Copyright 1999 American Chemical Society.)

of excess lubricant to the surface of a coating can impair adhesion or migration of UV-unstable components can cause color changes in coatings. A very common form of surface contamination is by siloxane surfactants. PDMS is a highly surface active lubricant that can cause adhesion failures between layers of a coating. SSIMS has characterized PDMS contamination in many different applications, including atomic force microscopy (AFM) cantilevers,[337] pharmaceutical injection vials,[266] poly(vinyl chloride) (PVC) ion-selective electrode membranes,[329] styrene-butadiene rubber,[298] automotive clearcoats,[330] epoxy adhesives,[338] and poly(vinyl acetate−ethylene) coating on PVC.[339] An example of a SSIMS spectrum showing siloxane surfactant contamination is shown in Figure 55 from Lo and co-workers on an AFM tip.[337] Detailed explanation of the siloxane fingerprint mass spectra are available.[305,306]

The other key contamination concern for surface analysis is from improper sample handling. Surface contamination from fingerprints, plastic containers, or contaminated tools can completely obscure the analytes of interest. Proper sample handling and storage must be considered an integral part of good laboratory practice.[340]

C. Surface Modification

New polymer surfaces can be created by traditional polymerization processes or by modifications of existing surfaces. Surface modifications are used to improve surface wettability and adhesion. Polymer surfaces can be modified by many different processes. Many of the modifications have been characterized by SSIMS and XPS experiments. The effects of plasma discharge have been investigated on cresol−novolak photoresists,[341] polyimide,[342] and PP.[316] Saito and co-workers showed that the oxygen plasma modification of the cresol−novolak photoresists created a balance between oxidation and vaporization in a thin surface layer.[341] Canry and co-workers showed that oxygen plasma modification of PP added oxygen functionality to the polymer surface and that the amount of oxygen functionality grew strongly with time in the plasma.[343]

Metallization of polymer surfaces is done to increase the mechanical strength and gas barrier properties of a polymer surface and have been studied by SSIMS and XPS. Wolany and co-workers show the improved adhesion of copper to a polyimide surface after heat treatment.[344] The heat treatment removes

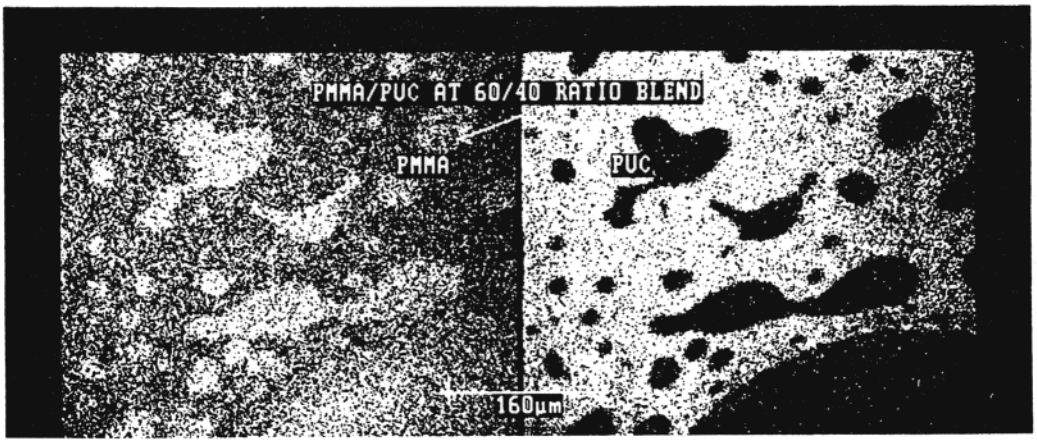


Figure 56. SSIMS chemical images of a 40:60 blend of PVC:PMMA. The image on the left is from O^- and OH^- due to PMMA and the image on the right is from Cl^- due to PVC. (Reprinted with permission from ref 328. Copyright 1993 Blackie, Glasgow, U.K.)

surface moisture and leads to better metal overlayer adhesion. Travaly and co-workers studied the use of copper and aluminum to metallize a variety of polymer surfaces.[345,346] These experiments show that aluminum binds with the oxygen functionality on the surface and forms primarily a two-dimensional array. The aluminum layer forms faster than the copper layer. The copper layer forms a weaker metal−polymer interaction and forms primarily three-dimensional growth with copper clusters observed on the surface.

Other surface modifications can be characterized. Heat treatment has been shown to eliminate oxygen from POM to form a hydrocarbon surface and to oxidize the surfaces of PBD and PS.[347] Surface reaction of poly(aryl ether ether ketone) (PEEK) films can produce a variety of oxygen, nitrogen, and sulfur functionality on the surface.[348] Also, UV irradiation can modify polymer surfaces by reducing the thioester surface functionality on wool[316] and changing the surface of chemical photoresists due to photooxidation.[349]

New surfaces can be created by plasma desposition. Almost any organic molecule can be polymerized and deposited with these techniques. Because plasma-deposited films (PDF) can create very different chemical structures than produced by traditional polymerization methods, the interpretation of the mass spectra can be problematic.[296] Leggett and co-workers used SSIMS and XPS to characterize unsaturation and the inclusion of oxygen functionality in PS PDF's.[350] Alexander and co-workers showed that the functionality of the PDF was dependent on the plasma power.[351] SIMS can also be used to monitor the ions formed during plasma deposition.[352] Much more information on the surface characterization of PDF's can be found in a recent review article by Johnston and Ratner.[353]

D. Imaging

Most commercially available TOF−SIMS instruments today are capable of collecting spatially resolved, chemically sensitive images of the surface. As the primary ion source is rastered over the surface of the sample, the software records the primary ion source position, the secondary-ion arrival times, and intensities. The ion images are reconstructed from these files by plotting the ion intensities as two-dimensional maps corresponding to the raster pattern. Total ion images or selected ion images can be created. These images can be enormously powerful tools in understanding the spatial relationships on a surface. Before ion imaging, microscopy could provide images of the surface and mass spectrometry could provide surface chemical structure information. Ion imaging allows the combination of these two powerful techniques. On our TRIFT II TOF−SIMS instrument (Physical Electronics, Eden Prairie, MN) we can image features as small as about 1 μm in diameter. The ion images shown above (Figure 18) in the MALDI section are examples of using SSIMS ion imaging to solve sample preparation problems. Ion imaging has been explored in detail in a recent review article by Pacholski and Winograd.[354]

Ion imaging is used to solve a variety of polymer surface problems. Ion images are used to monitor molecular diffusion.[355] Deimal and co-workers showed that surfactants such as PDMS and PFPE have significant surface diffusion ($10^{-7}-10^{-6}$ cm^2/s) but that typical polymers such as PMMA and PS do not. Ion imaging is also used to monitor the various layers of automotive coatings.[356,357] Bertrand and co-workers show ion images of a polymer blend of 20% PP and 80% PET.[298] The images show a smooth surface of PET with isolated nodules of PP. Munro and co-workers use imaging SIMS to show surface heterogeneity in a polymer blend of 40% PVC and 60% PMMA.[328] Figure 56 shows ion images of oxygen (left) and chlorine (right) characteristic of PMMA and PVC, respectively. Figure 56 shows that this polymer blend creates a blended surface, as well as a blend in the bulk.

Walzak and co-workers show the use of SSIMS imaging to monitor the distribution of an antioxidant additive in PE.[333] Figure 57 shows differing concentrations and distributions of the additive: (a) 2.0%, well distributed, (b) 0.25%, well distributed, and (c) 2.0% poorly distributed. The combination of mass

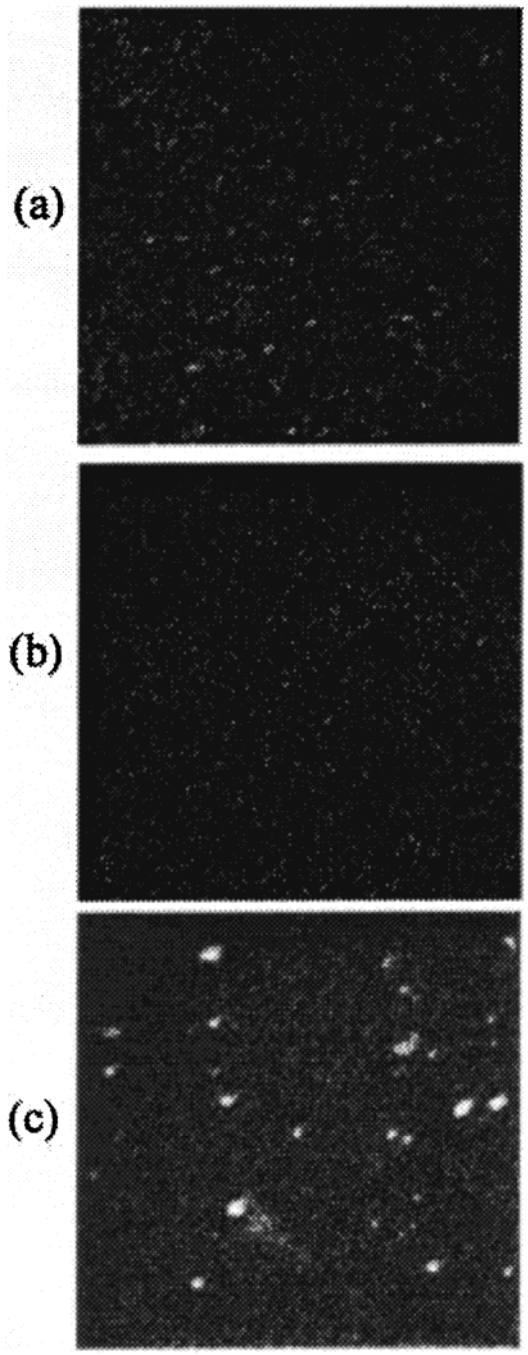


Figure 57. SSIMS images from PE films with differing amounts of C944: (a) 2.0% C944, well dispersed, (b) 0.25% C944, well dispersed, (c) 2.0% C944, poorly dispersed. (Reprinted with permission from ref 333. Copyright 1999 American Chemical Society.)

spectral data and the imaging data enables the identification of both the relative concentration of the additive and its distribution on the surface of the PE film.

In addition to imaging SSIMS, new MALDI imaging experiments may extend ion imaging methods to samples more amenable to MALDI.[358,359]

VII. Concluding Remarks

Despite the natural incongruity of gas-phase ions and polymers, mass spectrometry techniques have been developed to provide a significant amount of information about polymeric materials. Traditional mass spectrometry methods like pyrolysis and GC-MS can provide information about the repeat units, contaminants, and additives in polymer materials. The development of soft ionization techniques like FAB and FD extended the ability of mass spectrometry to analyze intact oligomers of relatively low molecular weight polymers. With the more recent developments of MALDI, ESI, and SIMS, the utilization of FAB and FD have decreased but the utilization of mass spectrometry to characterize polymer materials has greatly increased. In parallel with the development of techniques to analyze bulk polymers has been the development of surface mass spectrometry techniques, especially SIMS, and the application of these techniques to polymer surfaces. Mass spectrometry is now recognized as an important polymer characterization technique along with GPC and NMR. The future of mass spectrometry of polymers continues to be bright. The continued improvements in techniques and instrumentation will open new doors to the mass spectral characterization of polymers. The continued improvement of hyphenated techniques and improved ion imaging methods will enable even more applications for mass spectrometry of polymers and polymer surfaces.

VIII. Acronyms

AFM	atomic force microscopy
ASMS	American Society of Mass Spectrometry
BMA	butyl methacrylate
CI	chemical ionization
CID	collision-induced dissociation
dc	direct current
DCI	desorption chemical ionization
EI	electron ionization
EO	ethylene oxide
ES	expert system
ESI	electrospray ionization
FAB	fast atom bombardment
FD	field desorption
FD	field desorption
FIMS	field ionization mass spectrometry
FT	Fourier transform
GC-MS	gas chromatography-mass spectrometry
GMA	glycidyl methacrylate
GPC	gel permeation chromatography
ICP	inductively coupled plasma
ICR	ion cyclotron resonance
IR	infrared spectroscopy
LC	liquid chromatography
LCT	liquid chromatography transform
LDMS	laser desorption mass spectrometry
LDPE	low-density polyethylene
LSIMS	liquid secondary-ion mass spectrometry
m/z	mass to charge ratio
MAC	method of analysis of copolymers
MALDI	matrix-assisted laser desorption/ionization
MESIMS	matrix-enhanced secondary-ion mass spectrometry
M_N	number-average molecular weight
M_W	weight-average molecular weight
NIST	National Institute of Science and Technology
NMR	nuclear magnetic resonance spectroscopy
PBD	poly(butadiene)
PBMA	poly(butyl methacrylate)

PD	polydispersity
PDF	plasma-deposited film
PDMS	poly(dimethylsiloxane)
PE	poly(ethylene)
PEI	polyetherimide
PPEK	poly(aryl ether ether ketone)
PFPE	perfluoro-polyether
PI	poly(isoprene)
PIB	poly(isobutylene)
PMMA	poly(methyl methacrylate)
PO	propylene oxide
POM	poly(oxymethylene)
PP	poly(propylene)
PPE	poly(phenylene oxide)
ppm	parts per million
PPO	poly(propylene oxide)
PPO	poly(propylene oxide)
PS	polystyrene
PSD	post-source decay
PTFE	poly(tetrafluoroethylene)
PVC	poly(vinyl chloride)
REMPI	resonance-enhanced multiphoton ionization
rf	radio frequency
SEC	size-exclusion chromatography
SIMS	secondary-ion mass spectrometry
SORI	sustained off-resonance irradiation
SPME	solid-phase microextraction
SSIMS	static SIMS
TG-MS	thermogravimetric−mass spectrometry
TIC	total ion chromatogram
TLC	thin layer chromatography
TOF	time-of-flight
TOFMS	time-of-flight mass spectrometer
u	mass units
UV	ultraviolet
XPS	X-ray photoelectron spectroscopy

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