Mass spectrometry (MS) of polymers represents a growing area of materials science research. This paper surveys the history of mass spectrometric methods used to characterize polymers. Several methods have historically been available for the characterization of polymers, including size exclusion chromatography (SEC), vapor phase osmometry (VPO), nuclear magnetic resonance (NMR), light scattering, infrared spectroscopy, and ultraviolet–visible spectroscopy. These methods have proven successful for polymer analysis; what advantages could MS offer relative to these “classical” methods?

The classical techniques are averaging techniques, providing information about a mixture of polymer oligomers instead of individual oligomers. These averaging methods often do not provide information about different types of oligomers or some impurities that may be present. In addition, most of the classical methods are relative methods that rely on calibration standards that may not be available for the polymer being studied. Alternatively, MS can be used to examine individual oligomers, components, and contaminants in polymer systems. In cases of polymers with a low polydispersity index, MS can give an absolute, direct molecular weight distribution. No outside polymer standards are needed to calibrate the molecular weight measurements, an important advantage when standards do not exist for the polymer of interest. Qualitative and sometimes quantitative analysis of polymer mixtures can be accomplished with MS. Mass spectrometry can also provide information on the sequencing and the microstructure (tacticity, branching) of polymers.

The history of polymer MS can be divided into three distinct time periods: the small molecule MS era (1950s–1960s), the “macromass” era (1970s–1980s), and the modern era (late 1980s to present). After briefly reviewing the chemical structure of polymers, we present a synopsis of the history of polymer MS in each era, including the development and application of related techniques.

### Polymer Chemistry Overview

At the molecular level, polymers are macromolecules produced by the chemical bonding of small molecules (monomers) to form chains. The chains of monomers (oligomers) from a sequential reaction can vary in length, yielding a distribution of oligomers with varying numbers of monomers. Besides oligomer length, a polymer can have various chemical functionalities at the ends of the chains—end-groups—and polymer chains may be composed of different monomer units in various relative amounts—copolymers.

Synthetic polymers are typically characterized by determination of the chemical structure of the repeat units and the end-groups. In addition, polymers are characterized by measuring the molecular weight distribution (MWD), typically determined as the number-average molecular weight, $M_n$, or the weight-average molecular weight, $M_w$. The polydispersity index (PD) is determined from $M_n$ and $M_w$. The following formulas describe $M_n$, $M_w$, and PD:

$$M_n = \frac{\sum NiMi}{\sum Ni}$$

$$M_w = \frac{\sum NiMi^2}{\sum NiMi}$$

$$PD = \frac{M_w}{M_n}$$

where $M_i$ is the mass of an observed polymer oligomer, and $N_i$ is the number of polymer oligomers with a mass $M_i$. A polymer with a distribution of oligomers over a broad mass range would have a high PD value (2–5); polymers with oligomers distributed over a narrow mass range typically have low PD values (1.05–2.00). In principle, mass spectral methods can directly determine $M_i$ (from the observed mass value) and $N_i$ (from the peak intensity) for each oligomer in the polymer. It is important to distinguish between “technical polymers” and biopolymers; the latter have a single mass instead of a mass distribution. The properties of technical polymers depend on the PD index, so measurement of PD by mass spectrometry is an important goal.

### Small Molecule Mass Spectrometry Era (1950s–1960s)

**Advances in Mass Analyzers**

Mass spectrometry involves the formation of gaseous ions from an analyte and subsequently measuring the mass-to-charge ratios of the ions produced. Mass spectrometers contain a source to produce the ions from the analyte, a mass analyzer to separate ions based on mass, and a detector to convert a beam of ions into an electrical signal for recording or processing. For analysis, the desired species must be charged and in the gas phase. Most conventional mass analyzers use electric and/or magnetic fields to control the path of the ions to a detector and to disperse the ions according to mass-to-charge ($m/z$) ratios.

During the small molecule era, two types of mass analyzers were developed and used extensively: sector analyzers and quadrupole analyzers. Both of these are still in wide use today. Sector mass analyzers, utilized in the earliest commercial mass spectrometers, use a magnetic and/or electrostatic sector to change the ion trajectory within the analyzer. The field of the magnetic sector is scanned sequentially to transmit ions with different $m/z$ values into a collector where...
Ionization Source Techniques

Ionization sources used during the small molecule era of polymer mass spectrometry include electron impact (EI) and chemical ionization (CI). EI was the earliest ionization technique used in commercial instruments and the earliest used for polymer mass spectrometry. In EI–MS, the sample is thermally vaporized, and sample gas molecules enter the ion source and collide with an electron beam of ~70 eV kinetic energy. Collisions of the analyte molecules with the electron beam cause analyte molecules to eject an electron forming intact molecular radical cations, \( M^+ \).

\[
M + e^- \rightarrow M^+ + 2e^-
\]

This process has a low yield (0.01%) and leaves the newly created molecular radical cations with a range of internal energies; therefore, the molecular radical cations with high energies break apart and form a number of fragment ions through decomposition reactions. As a result of this ionization, the EI mass spectrum usually consists of a molecular ion peak and a number of fragment ion peaks. The degree of fragmentation can be lowered by reducing the electron energy.

CI, introduced in 1969, is similar to EI, except a reagent gas is used to promote ionization of the analyte molecules instead of an electron beam. In addition, the source is kept at a higher pressure (0.1–2 Torr) than an EI source (10⁻⁵ Torr). The reagent gas (RH), for example, methane, is introduced into the source and is ionized by electron impact to form reactant ions \( \text{RH}_2^+ \), for example, \( \text{CH}_2^+ \) for methane) that react with analyte molecules \( M \) to form protonated analyte ions.

\[
\text{RH}^+ + \text{RH} \rightarrow \text{RH}_2^+ + \text{R} \quad \text{(reagent ion formation)}
\]

\[
\text{RH}_2^+ + M \rightarrow \text{RH} + \text{MH}^+ \quad \text{(proton transfer)}
\]

The most common CI ionization process is a proton transfer from the reagent gas to form \( \text{MH}^+ \) ions; however, the reagent gas (RH), for example, methane, is introduced into the source and is ionized by electron impact to form reactant ions \( \text{RH}_2^+ \), for example, \( \text{CH}_2^+ \) for methane) that react with analyte molecules \( M \) to form protonated analyte ions.

Pyrolysis of Polymers for Analysis

The main problem with CI and EI techniques is that the sample must be vaporized by heating, and polymers with masses greater than a few hundred daltons are not readily volatile; therefore it is difficult to introduce polymers into a mass spectrometer in the gas phase. In order to make polymers amenable to EI– or CI–MS, the polymers can be pyrolyzed— or heat-degraded—and the degradation products can be introduced into an EI or CI source for MS analysis.
the first reports of pyrolysis MS (Py–MS) of polymers were published by Madorsky and Straus (6), and Wall (7). These studies utilized offline systems in which the pyrolysis chamber was not directly interfaced to the mass spectrometer. In 1953, Bradt et al. introduced a method for online Py–MS for which the pyrolysis products were directly coupled to the mass spectrometer. Online Py–GC of polymers was introduced in 1959 (8). In the early stages of Py–MS and Py–GC, pyrolysis data lacked reproducibility and consistency. The introduction of Curie-point pyrolyzers and other advanced pyrolyzers improved the reproducibility of the results of characteristic degradation of polymeric materials. The development of GC–MS in 1965 led to the introduction of a Py–GC–MS system with a Curie-point pyrolyzer in 1966 (9). The introduction of chemically inert fused silica capillaries for GC separation in 1979 was a significant advance for the analysis of polymers for separation of polar and high boiling-point compounds as pyrolysis products. Another significant advance for Py–GC–MS (as well as direct Py–MS) in the 1970s was chemometrics, or computer pattern recognition techniques, to help identify the “fingerprint” mass spectra of pyrolysis products.

In a typical Py–GC–MS system, a microfurnace pyrolyzer, a GC, and a mass spectrometer are directly coupled in series. For pyrolysis, a small amount of polymer (10–100 µg) is rapidly pyrolyzed at about 400–600 °C with or without catalysts under a flow of a carrier gas. The degradation products flow into the GC and are separated. The products from the GC are continuously analyzed using EI–MS or CI–MS. A pyrolysis mass spectrum of a commercial sample of a household paint and a reference mass spectrum of acrylonitrile-acrylate–styrene copolymer are shown in Figure 3 (10). The mass spectrum of the paint sample has many peaks characteristic of an acrylonitrile-acrylate–styrene copolymer, indicating that the copolymer is a major component of the household paint. Additional solvents, additives, and polymers present in the paint sample were separated and identified using Py–GC–MS. Using Py–GC–MS, information about polymer composition, additives, and microstructure can be determined.

Though EI–MS, CI–MS, and Py–GC–MS are valuable techniques for studying polymers, they provide indirect analyses of polymers because they require degradation of polymer oligomers by pyrolysis. In many applications, polymer chemists would like to perform direct MS analyses of polymer systems without degrading polymers into small molecules. In direct analysis, the mass spectra would contain a distribution of oligomeric molecular ions with no or little fragmentation. The absolute molecular weight of the polymer could be determined, depending on polydispersity and other factors. Also, polymer samples could be distinguished from each other based on molecular weight. In addition, blends of polymers of different types or different end-groups could easily be distinguished. The next section describes developments in the “macromass” spectrometry era, where direct MS analysis of polymers was introduced.

“Macromass” Spectrometry Era (1970s and 1980s)

Acquiring Mass Spectra by Direct Analysis

In the macromass era, advancements in ionization techniques led to the ability to acquire mass spectra of polymer oligomer ions by direct analysis without pyrolysis. Ionization techniques that were successful for polymer analysis introduced in this era include field desorption (FD), fast atom bombardment (FAB), secondary ion (SIMS), and laser desorption (LD) mass spectrometry. These methods involved bombardment of a prepared sample with fast atoms, ions, or laser photons; or in the case of FD, a high electric field combined with gentle heating.

Field desorption mass spectrometry was introduced by Becker in 1969. The technique is derived from field ionization (FI) mass spectrometry which was originated by Inghram and Gomez in 1954 (11). FD ionization utilizes an emitter on which carbon microneedles have been grown. A polymer solution is deposited via a syringe onto the emitter, and the emitter is placed in the mass spectrometer source. The emitter is held at high positive voltage a few millimeters away from a counter electrode held at a potential about 10 kV more negative than the emitter. This setup produces high field strengths at the tips of the microneedles, causing ionization and desorption of primarily intact polymer oligomer ions. FD–MS normally has been used with a sector mass analyzer; it is considered to be a “soft” ionization method, with little fragmentation seen in FD mass spectra, an advantage when determining polymer molecular weight. A schematic of an FD source is shown in Figure 4. FD–MS has a higher mass limit for polymers than either EI– or CI–MS. The maximum mass range for FD–MS is around 10,000–15,000 kDa (2).
Figure 5 shows an example of an FD mass spectrum of polystyrene approaching the upper mass limit for FD analysis of polymers. The series of peaks in the mass spectrum represent polymer oligomers with different chain lengths. Because the intensity of each peak represents the number of molecules of a particular molecular weight, $M_w$ and $M_n$ can be calculated from the mass spectrum. Furthermore, the spacing between two peaks is the mass of the polymer repeat unit (104 $m/z$ in the case of polystyrene); each successive peak represents an oligomer with one additional repeat unit as $m/z$ values increase.

**Implementation of Additional MS Ionization Methods**

Other MS ionization methods were also introduced during this era. Static secondary ion mass spectrometry (SIMS) was introduced in 1969 by Benninghoven as a method to produce quasi-molecular ions (e.g., $M^+Ag$), as opposed to dynamic SIMS, which is used for elemental analysis and depth profiling of materials (12, 13). The first SIMS spectrum of a polymer was reported by Werner in the late 1970s (14). For one mode of static SIMS analysis, a polymer solution is placed on a metal substrate target. The solution evaporates leaving a solid, thin polymer overlayer. The target is bombarded by a primary ion beam, typically argon or cesium ions, and the primary ion beam implants primary ions and disrupts the polymer surface leading to the sputtering of secondary particles. The sputtered particles include secondary positive ions, negative ions, electrons, and neutrals. Over 99% of the sputtered particles are neutrals. Either positive or negative ions are extracted and sent to the mass analyzer. A schematic of the SIMS process is shown in Figure 6.

SIMS ionization is “harder” than FD–MS; more fragment peaks appear in SIMS mass spectra. The first static SIMS instruments used quadrupole or sector analyzers; however, the analyzers had upper mass limits of less than 1000 Da for SIMS ionization. Higher mass limits for SIMS experiments became available with time-of-flight (TOF) mass analyzers; TOF technology will be discussed below. Typically, quasi-molecular ion peaks for polymers up to 10,000 Da can be seen in SIMS mass spectra acquired with TOF mass analyzers; these results are comparable to FD–MS. Similarly to FD–MS, SIMS mass spectra of polymer oligomers with masses greater than about 12,000 Da contain only fragment ion peaks. The fragment ions from FD–MS are due to pyrolysis of the polymer from heating; however, in SIMS the fragments ions are formed from bombardment by the primary ion beam. Information such as monomer units, end-groups, and fragmentation patterns can be determined from fragment peaks (15). A second mode of SIMS operation is to ion-bombard thick films directly. This produces small fragment ions (<500 Da) that can be useful for polymer identification, impurity detection, and to study surface modification and other surface reactions.

Introduced in 1981, fast atom bombardment (FAB) is an ionization technique similar to SIMS (16). In FAB, a solution of a polymer is mixed with a liquid matrix, such as glycerol, and placed on a substrate. The sample is bombarded with neutral atoms (e.g., argon or xenon). The bombarding atoms ionize the sample, and ions are extracted and mass analyzed. The most notable difference between FAB and SIMS is the primary beam is composed of neutral atoms in FAB instead of ions. The use of neutral atoms can be an advantage because sample charging is reduced. The use of a liquid matrix continuously replenishes the sample to avoid depletion, a potential problem in SIMS when used with scanning instruments. FAB ionization is also suitable for sector instruments that can provide high peak resolution. FAB–MS is not used much anymore for polymer analysis, since newer techniques have been developed that give better results.

Another ionization technique developed in the late 1970s and early 1980s was laser desorption mass spectrometry (LD–MS). For LD ionization, a sample is deposited on a substrate, sometimes with an added salt, and is then ablated with a submicrosecond laser pulse. Ionization occurs mainly by cation attachment to the desorbed molecules. The ions are extracted into a mass analyzer.

**Progress from Coupling with TOF Analyzers**

Real advancements with LD–MS and static SIMS occurred when these methods were coupled to TOF analyzers. Unlike the sector and quadrupole analyzers, TOF analyzers separate ions simultaneously instead of scanning a mass range. Scanning mass analyzers such as sector and quadrupole analyzers is not optimal for LD–MS or SIMS because a con-
tinuous ion beam or laser quickly depletes the sample, leaving little time for scanning mass analyzers to collect mass spectra. Therefore, TOF mass analyzers in combination with a pulsed primary ion beam or laser source provide an excellent combination for SIMS or LD–MS.

TOF analyzers were developed in the 1950s; however, pinnacle advancements in TOF analyzer design occurred in the late 1970s. In a TOF analyzer, the ions produced in the ion source are accelerated with an electric potential in the keV range into a field-free flight tube (Figure 7). The time that it takes the ions to “fly” down the flight tube to the detector is measured. The flight time is dependent on the velocity of the accelerated ions, which in turn is dependent on \( m/z \) values. Smaller ions (lower \( m/z \)) travel faster in the flight tube and reach the detector before larger (heavier) ions. TOF analyzers have the highest ion transmission of any mass analyzer and a theoretically unlimited upper mass limit. Figure 8 shows a mass spectrum demonstrating the capability of the SIMS technique to detect oligomer ions in the \( m/z \) mass range of 2000–12000 using a TOF analyzer.

Several other ionization techniques were introduced in this era that had some success for polymer mass spectrometry, including desorption chemical ionization (DCI), plasma desorption (PD), electrohydrodynamic ionization (EHI), thermospray ionization (TSP), and atmospheric pressure chemical ionization (APCI). However, none of these methods readily produces oligomer ions in the high-mass range. During this era, mass analyzer technology had advanced sufficiently that the limiting factor in mass spectrometry of large molecules was the ionization technique itself. The race was on to develop mass spectrometry ionization techniques that would readily ionize molecules larger than 10,000 Da.

Modern Era of MS (Late 1980s to Present)

Developments in Ionization Methods Lead to Nobel Prize

Two ionization methods were developed in the late 1980s that increased the molecular weight range for mass spectrometry of synthetic polymers and biomolecules. The introduction of electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI) as mass spectrometry ionization methods has tremendously improved the performance of molecular weight determination for molecules larger than a few thousand daltons. Chain entanglement can be a significant limitation for obtaining polymer mass spectra. Both ESI and MALDI keep the polymer dilute, thereby minimizing this effect. The 2002 Nobel Prize in Chemistry was awarded to John Fenn and Koichi Tanaka for their contributions to the development of these ionization techniques.

For ESI, a dilute solution of polymers is forced through a needle held at high potential (0.5–5 kV) at atmospheric pressure. A schematic of an ESI source interfaced to a mass analyzer is shown in Figure 9. The high potential on the needle produces solvent droplets that are highly charged. As charged aerosol droplets of solution exit the needle, the droplets diminish in size as the solvent evaporates. The droplets continue to diminish in size to a point where the surface charge on the droplets exceeds the Rayleigh limit of instability, and, as a result, the droplets disintegrate into even smaller droplets through a series of coulombic “explosions”. The droplets continue to “explode” and reduce in size until charged polymer molecules are ejected from the droplets. The ions produced are analyzed with a mass analyzer, typically a quadrupole or ion trap. In the positive ion mode, \( M(H^+)_n \) or \( M(cation^+) \) ions are detected.

Malcolm Dole reported the electrospray ionization of polystyrene oligomers in 1968. However, Dole used a rather primitive mass analyzer and polystyrene was not the ideal
Fenn successfully demonstrated ESI–MS in 1984; Fenn based his ESI source on the general design originated in the 1960s by Dole, but added a drying gas to help evaporate solvent from the ions (18). Fenn’s ESI source was coupled to a quadrupole mass analyzer. In 1988, Fenn reported ESI mass spectra of poly(ethylene glycol) (PEG) oligomers (19). Fenn reported the presence of multiply-charged oligomer peaks for PEG samples with average masses of 400–17,000 Da. A mass spectrum of a PEG sample with an average mass of 600 Da from Fenn’s 1988 results is shown in Figure 10; note that the mass scale in this mass spectrum is reversed, running from right to left. The singly-charged oligomer ions with one Na⁺ attached have m/z values in the range of 280–600 and are labeled with I. The peaks under label II are doubly-charged and are assigned to oligomers with two Na⁺ cations attached. The doubly-charged peaks are at lower m/z values than the singly-charged peaks because they represent the molecular weight of the oligomer plus the mass of two Na⁺ ions divided by the number of charges (two). For PEG samples with a mass of 3350 Da, Fenn found peaks for ions having 3, 4, 5, and 6 Na ions attached. Fenn found that regardless of the molecular weight of the PEG oligomers, the ion peaks in the mass spectra fell in a mass range below a m/z value of 1500 due to multiple charging. Although ESI–MS of high molecular weight mass polymers produces oligomer ions, the multiply-charged ion peaks overlap in low-resolution mass spectra, making interpretation difficult.

One advantage of ESI–MS over other MS methods is the ability to directly couple liquid chromatographic methods such as SEC or HPLC to mass spectrometry. The eluant from the chromatographic column flows directly into the ESI source for online separation. Polymers can be separated according to chemical structure or molecular size by chroma-

Figure 10. Mass spectrum of PEG 600. Major peaks under I are oligomers with one Na⁺ attached. Those under II have two Na⁺ attached. Peaks labeled THA and TBA are due to tetraheptyl- and tetrabutylammonium ions. (Reprinted from ref 19 with permission of the American Chemical Society.)

Figure 11. Selected ion plots from SEC–ESI–MS for sodium-ionized GMA–BMA copolymers, the oligomers with 48, 36, 24, and 12 repeat units. (Reprinted from ref 20 with permission of the American Chemical Society.)
tography, and molecular weight information can be obtained by mass spectrometry. An example of the power of SEC–ESI–MS is shown in Figure 11 (20). The SEC chromatogram shows the separation of glycidyl methacrylate (GMA) and butyl methacrylate (BMA) copolymer oligomers with 48, 36, 24, and 12 repeat units, and selected mass spectra ion plots of sodium-ionized GMA–BMA oligomers are shown in the insets.

Using MALDI–MS Methods with Polymers

The introduction of matrix-assisted laser desorption ionization mass spectrometry was quite possibly the most significant advance in the history of polymer mass spectrometry. The principal difference between MALDI–MS and LD–MS is that sample preparation for MALDI analysis includes an organic matrix in addition to the analyte. In MALDI sample preparation, a dilute polymer solution is mixed with a more concentrated matrix solution. A small aliquot of the mixture is applied to a sample plate, and the matrix and polymer co-crystallize as the solvent evaporates, leaving the polymer dispersed in the solid sample-matrix crystals. A laser irradiates the sample-matrix crystals, the matrix molecules absorb the laser energy, vaporize, and transfer energy to polymer analyte molecules, causing them to vaporize as well. During this process, the energy absorbed is dispersed throughout the crystal and the charge is transferred to the polymer molecules—usually by proton or metal ion addition—and the newly formed polymer ions are extracted into a mass analyzer. A schematic of the MALDI desorption process is shown in Figure 12.

For MALDI sample preparation of synthetic polymers, a cationization agent (e.g., a metal salt such as sodium iodide or silver trifluoroacetate) is usually added during sample preparation to enhance ionization of the polymer during the laser desorption process. MALDI matrices that are selected for MALDI experiments have strong absorption bands at the laser wavelength, normally a pulsed UV laser of 337 nm (N2) or 355 nm (Nd:Yag). 1,8-Dihydroxy-9-anthrone (dithranol) and 2,4-dihydroxybenzoic acid (DHB), two common UV–MALDI matrices used for synthetic polymers, are shown below.

The basic idea for MALDI–MS was first reported by Tanaka in 1987 (21). In 1988, Tanaka reported molecular ions of PEG with a mass of 20,000 Da. Independently in 1988, Karas and Hillenkamp reported MALDI of proteins with masses up to 67,000 Da using an organic matrix of nicotinic acid; these workers introduced the key concept of using an organic matrix to effect desorption and ionization (22). In 1992, Karas and Hillenkamp demonstrated the ability of MALDI–MS to obtain mass spectra of synthetic polymers with masses of 70,000 Da (23). Figure 13 shows a mass spectrum of 20,000 Da polystyrene from that paper. Singly-charged oligomer ion peaks with 104 Da spacing are shown in the inset. Dimer, trimer, and tetramer oligomer ion complexes up to 80,000 Da are also present in the mass spectrum. Molecular weight distributions (MWD) for polymers with low polydispersity indices measured by MALDI were found to agree more or less with other methods, such as SEC and vapor phase osmometry (VPO).

The most common mass analyzer used for MALDI experiments is a TOF mass analyzer; the theoretically unlimited mass range of a TOF mass analyzer is necessary for MS of high mass synthetic polymers. Li reported mass spectra of narrow polydispersity polystyrene standards with nominal molecular weights of up to 1.5 million Da (24). MALDI-TOF mass spectra of polystyrene samples with nominal mo-
Molecular weights of 333,000, 600,000, and 900,000 Da are shown in Figure 14. At these high masses oligomer peaks are unresolved and the entire oligomer distribution appears as one broad peak. Multiply-charged distributions are also present; for example, in Figure 14C the peaks at m/z values of 450,000; 300,000; and 225,000 are the doubly-, triply-, and quadruply-charged oligomer distributions, respectively. The MWD values calculated from MALDI spectra of high molecular weight polystyrene agreed with those from other methods, such as SEC.

It should be noted that direct MWD determination using MALDI–TOF MS is typically limited to polymers with low polydispersity indices because of mass discrimination effects where high mass components are generally underrepresented compared to low mass components in the mass spectra. It is often quoted that MALDI MWD measurements are accurate for samples with a polydispersity index of less than 1.2 (25). High mass ions produce a lower detector response than low mass ions; therefore, molecular weight averages are typically skewed for broadly dispersed oligomers. Nevertheless, Malvagna et al. reported accurate MWD determinations for poly(vinylpyrrolidone) with masses of 40,000 and 160,000 Da and polydispersity indices of 1.8 and 2.2 using sample preparation techniques involving flash-freezing and freeze-drying of the sample preparations (26).

MWD information about polydisperse polymers can also be obtained by coupling SEC chromatography with MALDI–MS. SEC–MALDI–MS is typically an offline method; fractions of SEC column eluant are collected, followed by MALDI mass analysis of the fractions (27, 28). The individual SEC fractions contain narrow polydispersity oligomer mixtures for mass analysis. MALDI–MS of the separated samples provide important insight about the chemistry and molecular weights of the sample, including information on purity, end-groups, and repeat unit mass. The SEC fractions of polydisperse polymers mass-analyzed by MALDI can then be used as narrow polydispersity mass standards for SEC mass calibrations. One example of the coupling of SEC to MALDI is the work of Mehl et al. on SEC–MALDI of a polydisperse polyurethane (29, 30). Figure 15 shows the SEC chromatograms of ethanolamine-degraded polyurethane (PUR) fractions mass-analyzed by MALDI. The SEC–MALDI of a polydisperse polyurethane (29, 30).

![Figure 14](image1.png)

Figure 14. Mass spectra of three poly(styrene) samples with nominal molecular weights of (A) 330,000 Da; (B) 600,000 Da; and (C) 900,000 Da. (Reprinted from ref 24 with permission of the American Chemical Society.)

![Figure 15](image2.png)

Figure 15. (A) Size-exclusion chromatogram of ethanolamine-degraded polyurethane (PUR). (B) Selected fractions are marked and the corresponding MALDI spectra are shown. (C) A MALDI–SEC calibration curve for PUR degradants (squares). The points of the SEC calibration curve based on PS standards are indicated by triangles. (Reprinted from ref 30 with permission of Springer-Verlag.)
gram of polyurethane (A) along with MALDI mass spectra of selected fractions (B). The SEC calibration curve of polyurethane (PUR) SEC fractions analyzed by MALDI–MS had a different slope from the calibration curve obtained from polystyrene standards (Figure 15C).

MALDI–MS investigations are not limited only to determinations of MWD: this technique can also be used to obtain end-group information, including the presence of cyclic oligomers (31, 32). MALDI–MS is also capable of analyzing the structure of copolymers, including providing oligomer masses and composition of repeat units (33, 34). Recently, MALDI–MS quantification of polymers has been demonstrated. Yan quantified poly(dimethyl siloxane) samples with different molecular weights (35). Murgasova coupled SEC and MALDI–MS to quantify a blend of polystyrene and poly(α-methylstyrene) (36). MALDI–MS was used to characterize narrow polydispersity SEC fractions because SEC could not differentiate the two polymers.

Other Mass Analyzers

Two other mass analyzers have been widely used in polymer mass spectrometers during the modern era: the quadrupole ion trap and Fourier transform ion cyclotron resonance (FTICR or FTMS) mass analyzers. The ion trap is essentially a three-dimensional quadrupole and consists of a ring electrode and two end caps. Ions are created within the trap with an electron beam for EI, or injected into the trap from an external electrospray or desorption source. Ions are stored in the trap by biasing the ring electrode with a variable rf voltage. Ions circulate in a stable orbit within the cavity surrounded by biasing the ring electrode. Mass spectra of trapped ions are obtained by scanning the rf potential so that ions with different masses sequentially develop unstable trajectories and hit an external ion detector. Ion traps have a higher upper mass limit than quadrupoles and are commonly used with ESI sources.

The development of FTICR mass analyzers in the 1970s was inspired by Fourier transform nuclear magnetic resonance (NMR) spectroscopy (37–39). Similarly to ion traps, FTICR mass analyzers trap ions inside a cell using a combination of magnetic and electric fields. This cell is located inside a superconducting magnetic field (B) of 3–10 T. Ions are injected into the cell and move in circular trajectories perpendicular to the B-axis with an angular cyclotron frequency. The trapped ions are then subjected to a frequency sweep of an rf pulse that increases linearly in frequency during its lifetime. After the frequency sweep, the image current induced by various orbiting ion packets is amplified and stored in memory. The time domain signal is transformed to yield a frequency domain signal, which is then converted into a mass spectrum. Because frequency measurements can be made with high precision, extremely high mass resolution is possible with FTICR mass analyzers.

Figure 16 demonstrates how the high resolution of MALDI–FTICR–MS can separate ion peaks with the same nominal mass in a methyl methacrylate (MMA) and butyl methacrylate (BMA) copolymer. It should be noted that the cluster of peaks in the top mass spectrum are the isotopic peaks of a sodium-attached MMA–BMA copolymer oligomer with 11 MMA units and 10 BMA units; successive peaks represent the presence of 13C isotopes in the sodium-ionized oligomers. The bottom mass spectrum contains silver-ionized oligomers of 13 MMA and 8 BMA units in addition to the sodium-cationized oligomers of 11 MMA and 10 BMA units. The monoisotopic peak (m/z 2546.577) of silver-cationized oligomers with 13 MMA and 8 BMA repeat units is separated by a m/z value of 0.28 from the monoisotopic peak (m/z 2546.394) of sodium-cationized oligomers with 11 MMA and 10 BMA repeat units. Baseline separations of ion peaks in this mass range are not possible with TOF or quadrupole mass analyzers.

Summary

Despite the challenges of introducing polymers into the gas phase, mass spectrometry techniques have been developed to characterize polymers. EI–MS and CI–MS, combined with pyrolysis, can provide information about the identity and the presence of contaminants or additives in polymers. The introduction of soft ionization techniques, such as FD and SIMS, allowed polymer chemists to analyze molecular ions of polymers with masses lower than 10,000 Da. The subsequent development of MALDI and ESI techniques shattered the 10,000 Da ceiling. Continued improvements in methods and instrumentation will offer new and better ways for the mass spectral characterization of polymers. Mass spectroscopy should now be recognized as a complementary polymer characterization technique along with SEC and NMR.

Literature Cited
