ANALYSIS OF SYNTHETIC POLYMERS BY MASS SPECTROMETRY AND TANDEM MASS SPECTROMETRY

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ANALYSIS OF SYNTHETIC POLYMERS BY MASS SPECTROMETRY AND TANDEM MASS SPECTROMETRY

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Dissertation

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The utilization of MS and MS/MS techniques have resulted in the complete characterization of chain-end, in-chain and cyclic polystyrene and polybutadiene as well as an analytical method which allows the rapid determination of the location of functionality as well as determining if the material is linear or cyclic.

The characterization of in-chain polystyrene is described and compared to chain-end polymers comprised with similar functionality. This allowed the differentiation of fragment ions resulting from the CAD fragmentation between the two types of functionalization. Additionally, the MS/MS spectra of in-chain functional polymers allow the determination of average chain length on either side of the functional group.

Further expansion of polystyrene understanding was accomplished by characterizing macrocycle polystyrene which also contained a functional group. The CAD spectrum provided conclusive proof that the material was in fact cyclic due to the observed monomer losses as a result of CAD induced ring opening. After ring opening the macrocycle behaves similarly to an in-chain functional polymer and produces a mid- mass range Poisson distribution corresponding to the chain length on each side of the functional group, however, in this case it
does not directly correlate to average chain length. This cyclic fragmentation pattern was confirmed when cyclic non-functionalized polybutadiene was characterized. Here the mid-range Poisson distribution was absent due to no functionality being present. However, the same monomer loss was observed which further confirmed that the monomer loss was indeed a function of the ring opening rather than a spectral feature induced by the ToF/ToF mechanism being akin to PSD. This was further confirmed by using a Q/ToF to verify the monomer loss after ring opening.

Characterization of polybutadiene without pyrolysis was also conducted. While the adherence to free radical degradation was maintained it was discovered that unlike polystyrene, polybutadiene preferentially fragments by internal rearrangements.

Finally, by comparing the different MS/MS fragmentation patterns of the various materials utilized for this work the ability to determine where the functional group is and whether or not the material is cyclic and further if the macrocycle contains functionalization is possible by simply observing the MS/MS fragmentation pattern.
DEDICATION

To my wife Sally and my children Zachary and Elizabeth whose love, support and sacrifice made this possible and to my parents James and Nancy Dabney who gave me the will to never give up and always strive for my goals.
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CHAPTER I
POLYMER BACKGROUND

Synthetic polymers continue to be utilized in ever more increasingly technical applications either as standalone polymers or in conjunction with one or more other polymer types as blends or co-polymers to tailor desired end use properties. Various synthetic methods are utilized to create these polymers, with living polymerization techniques, in particular living anionic methods being most suitable to prepare well defined structures. Synthesis and characterization of polymers continues to be a developing field in part due to the continued systematic improvements of synthetic methods and characterization techniques. These improvements have spurred rapid growth over the past several decades. As a result of the growing use of synthetic polymers, the methods of identifying and characterizing these systems have become an important field of science. Mass spectrometry (MS) is one of the techniques utilized for this purpose and its application to polymer analysis is the central topic of this work.

Living polymerization techniques are of current interest due to their ability to deliver controlled molecular weights with narrow polydispersities. Further, unlike traditional techniques, living methods are free of chain transfer and termination limitations. Living anionic polymerization is a type of addition
polymerization but unlike traditional methods it is free of a formal termination step which allows for the ability to tailor its molecular weight, chain-end functionality as well as a prime candidate for block co-polymer building. Living anionic polymerizations provide several desirable traits to the synthetic chemist. In addition to the aforementioned freedom of chain transfer and termination, this synthetic technique allows for the creation of chain-end and in-chain functionalized polymers, cyclic polymers with functionalization incorporated into the cyclic structure as well as block and branched (co) polymers. Living anionic polymerization generally occurs with complete monomer consumption which results in polymeric organolithiums compounds that can react with electrophiles to form ω-chain-end functionalized polymers. Utilizing a single methodology to vary the functionality without protecting groups is a relatively new improvement to this synthetic technique; this area is being currently researched by Quirk et al. who use living anionic polymerization, specifically alkylolithium polymerization, in conjunction with hydrosilylation chemistry to yield polymers with both chain-end and in-chain functionalization, see Scheme 1.1 for representation of chain-end functionalization.\textsuperscript{2-10} This approach utilizes a living poly(X)lithium, where X is the monomer of interest, most commonly styrene or butadiene. This living polymer is then terminated by incorporating chlorodimethylsilane which results in a chain-end, silyl hydride-functionalized polymer. The use of Karstedt’s catalyst seen in Scheme 1.1 is a typical catalyst used in these types of hydrosilylation reactions due to it ability to react with the vinyl bonds and facilitate the addition to the Si. The resulting polymer can then be exposed to various substituted alkenes to
obtain the desired chain-end functionality including the addition of a second polymer chain of either the same or differing composition as the starting polymer. The living anionic chain-end is terminated prior to exposure to the functionalizing agent which eliminates the need for protecting groups in most cases. This methodology has been successfully applied to the synthesis of amine-, epoxy-, and perfluoroalkyl-functionalized polymers. 2-10 Polymers created by these techniques have been evaluated and characterized in this dissertation by mass spectrometry (MS) and tandem mass spectrometry (MS/MS) experiments, as will be discussed in further sections.

Scheme 1.1. General schematic for chain-end functionalization, showing the use of chlorosilane to introduce a hydrosilane end group and subsequent addition of the latter group to an alkene using Karstedt’s catalyst.3

Another type of widely used living polymerization is carbocationic polymerization and its Natural Living Carbocationic Polymerizations (NCLP)
variant. NCLP is a methodology developed by Kennedy/Puskas et al. to mimic the biosynthesis of naturally occurring polymers such as polyisoprene (PI), commonly known as rubber, and polyisobutylene (PIB), see Scheme 1.2.\textsuperscript{11-14} NCLP utilizes a monomer/initiator system such as isoprenyl alcohol/dimethylallyl alcohol (IPOH/DMAOH).\textsuperscript{15, 16} A Lewis acid (LA) is added to the system to act as the enzymatic catalyst found in naturally occurring rubber. The purpose of the LA is to activate the initiator creating an allylic carbocation which then sets the polymerization in progress, resulting in monomer addition and rearrangements accompanied by water losses. Initiation takes place with or without the DMAOH, if the DMAOH is not present the polymerization is initiated by protic initiation. This process is further influenced by the polarity of the solvent system. A solvent ratio which provides for the continued solvation of the polymer components as well as initiators, etc. is necessary to control and drive the polymerization to create desired functionalities and molecular weights.\textsuperscript{15, 16}

\textbf{Scheme 1.2. Biomimetic initiation of IP polymerization.}\textsuperscript{11}
The characterization of polymers has traditionally focused on their physical properties derived by traditional techniques like, DSC, tensile testing and TGA to name a few; today more information is required by the synthetic chemist to better tailor the polymer to a specific need. One of the most common characterization techniques associated with polymers is size exclusion chromatography (SEC), specifically, gel permeation chromatography (GPC).\(^{17}\) This method provides a quick tool for molar mass characterization. In GPC, a polymer sample is dissolved in a suitable solvent and separated according to hydrodynamic volume through a set of columns with the highest molecular weight eluting first as a result of no interaction with the interstitial volume of the columns. The detection of eluting species is generally accomplished by one or a combination of detectors, the two most common being refractive index and light scattering detectors, the discussions of which are outside the scope of this work. GPC provides information about the number average molecular weight \((M_n)\), weight average molecular weight \((M_w)\) and therefore, polydispersity index \((PDI)\) of the molecular weight distribution. This is accomplished by comparison to a calibration curve conducted prior to analysis using a set of standard materials with varying molecular weights associated with the detection range of the column set.\(^{17}\) This method has several disadvantages: external calibration is necessary and a material which closely matches the polymer of interest may not be available; methods have been developed to minimize this but the process is time consuming and tedious. GPC also does not provide absolute molar mass information, due to the reliance on an external calibration.\(^{17}\) Finally, due to the
limited resolution, information about the heterogeneity of the sample is limited, an attribute MS is well suited for. However, GPC has found additional value as a hyphenation technique with MS. Due to the separation based on hydrodynamic volume this technique allows the mass spectrometrist to fractionate either a polydisperse sample thus artificially creating a set of narrow PDI samples from which the molecular weight range more suited to a specific MS technique can be selected or a material of high molecular weight to obtain a low mass fraction, which is more suitable for MS analysis.\textsuperscript{18} Thus, the GPC-MS combination capitalizes on the strengths and minimizes the weaknesses of both techniques.

Two additional characterization methods utilized in polymer analysis are Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. FTIR is routinely used for synthesis monitoring and validation of the data collected by other techniques. FTIR provides the ability to observe the presence of monomer/precursor functionality and monitor its consumption as well as the appearance of desired end functionalities which is invaluable for process manipulation and verification of product structure. However, it lacks the ability to provide information about the presence or absence of multiple terminal groups, the degree of polymerization or the presence on side reactions.\textsuperscript{1,19-23} NMR provides the capability to fill in many of the gaps which FTIR lacks.

NMR, like MS, has become a valuable tool to the synthetic chemist and provides valuable insights into the polymer structure. NMR allows for the identification of stereochemistry as well as the presence of certain functionalities
which may not be easily observed by MS techniques; for example, in certain cases a halogen at the terminus of a polymer may be removed during the ionization process but will be detected by NMR. NMR is also able to distinguish between isobaric and isomeric structures whereas MS is not; however, this limitation is being addressed for isobaric species through hyphenated techniques, and MS\(^n\) techniques as well as ion mobility and mass accuracy improvements. MS is able to provide compositional information as well as evidence as to the presence or exclusion of multiple functionalities within the sample, provided the structures are not isobaric or isomeric; nevertheless, as previously stated, this limitation is overcome by high mass accuracy and by taking advantage of ion mobility differences between the isomeric species.

The availability of techniques that allow for the ionization of synthetic polymers has made mass spectrometry a niche area in the field of polymer characterization. The ability to separate on the basis of mass-to-charge (m/z) and the low detection limit (pico \([10^{-12}]\) to femtomole \([10^{-15}]\)) provide information to the synthetic chemist that other methods can not currently render as easily or as repeatably. Additionally, the invention and widespread use of matrix assisted laser desorption ionization (MALDI) and electrospray ionization (ESI) in conjunction with various analyzers and detectors has allowed for the ability to identify end groups, elucidate structures, provide mechanism information, determine degradation and fragmentation products, and the presence of side reactions and contaminants. All of this information has proven invaluable to the synthetic chemist for purposes of method refinement and property improvement.
MALDI which was developed by Karas and Hillenkamp\textsuperscript{24} has become a standard for the characterization of polymers. MALDI is distinguished from other laser desorption techniques by the application of a matrix which serves several functions in the MS process, as will be discussed in Chapter II. Mass spectra derived using MALDI as the ionization method generally result in singly charged quasi-molecular ions, and due to the ability to attenuate the laser energy, little to no fragmentation. Typically MALDI is interfaced with a time-of-flight (ToF) mass analyzer which is ideally suited due for mass analysis of ions produced by pulsed ionization like MALDI. Improvements in lasers, ToF analyzers and detectors have resulted in a steady increase in mass resolution and accuracy allowing greater identification capabilities. Additionally, the advent of ToF/ToF systems has enabled true tandem MS experiments; in contrast simple MALDI-ToF systems only allow for post source decay which generally results in poorly resolved spectra. It is further noteworthy that the ToF/ToF arrangement does not cut off the low mass part of tandem mass spectra as do ion trap type instruments. This allows a more complete view of the fragmentation products and thus a more complete picture of structures within a sample.

ESI is the other major ionization method utilized today, invented by Fenn et al.\textsuperscript{25} Unlike MALDI, it is a continuous ionization method. It has traditionally been applied to biomolecules due to its ability to generate multiple charged ions. Multiple charging brings the mass-to-charge ratio of a large molecule to a range that can be easily measured with conventional instruments. ESI of a biomolecule results in spectra with multiple peaks of the same species differing only in the
number of charges. For a synthetic polymer the added charge distributions often result in overlapping products and an inability to easily discern major from minor components. Utilizing ESI with a high resolution instrument, for example a Fourier transform cyclotron resonance (FT-ICR) mass spectrometer can minimize these issues. Coupling ESI to ion trap mass analyzers allows for MS\textsuperscript{n} studies which also help to interpret complex spectra.\textsuperscript{26-28} ESI most efficiently ionizes polymers which contain heteroatoms in their repeat unit.

As previously mentioned MALDI and ESI can be coupled to multiple mass analyzers, ToF and ion-traps being the most common. Ion traps come in a variety of configurations. Their main common feature is that ions of interest can be selected and retained in the trap for a defined length of time. This property provides MS\textsuperscript{n} capability which has extensive applications for structure elucidation, sequencing and block length determination. Ion traps and quadrupoles may skew molecular weight distributions; in contrast ToF analyzers provide true distributions. Utilization of a MALDI-ToF mass spectrometer in conjunction with a narrow polydispersity reproduces the true distribution of products, from which accurate molecular weight properties can be defined without the aide of an externally generated calibration curve.\textsuperscript{18, 26, 29-37}

A high resolution MS method that was not utilized in this work is Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) which was developed by Marshall et al.\textsuperscript{38-40} However, ion cyclotron resonance (ICR) was invented decades earlier by Ernest Orlando Lawrence who was awarded a patent\textsuperscript{41} and the Nobel Prize for the technology he developed.
beginning in 1929. Lawrence and others applied the technology to gas phase ion chemistry. One notable study was conducted by Hipple et al. who used ICR technology to determine the Faraday constant.42, 43

Early ICR experiments were limited to low mass resolution, low mass ranges and slow scanning speeds until two major adjustments occurred; the application of Fourier transform techniques and the use of a Penning type ion trap. These two changes resulted in ICR MS instruments that can quickly scan a large mass range as well as carry out fragmentation studies. Additionally, the ever increasing magnet size has provided increasing mass resolution which allows the differentiation of isobaric species. Finally, the ability to couple soft ionization techniques, i.e. (ESI) and (MALDI), and chromatographic separation methods, i.e. size exclusion chromatography (SEC), to FT-ICR MS allows today’s scientists to utilize this method in the analysis of ever more complex systems such as proteins and polymers.

FT-ICR MS is based on the motion of an ion in a spatially uniform static magnetic field. The motion is made coherent by applying a uniform radio frequency (rf) electric field at the same frequency as the ion cyclotron frequency. Using frequency generators, all ions trapped can be excited to such motion. This results in a digitized time-domain ICR signal which is converted to a frequency-domain spectrum (i.e., a mass spectrum) by Fourier Transform techniques.44

MS applications to polymer analysis are of current interest for several reasons; it is believed that mass spectrometry provides a “whole” picture of the polymer composition. This includes the ability to quickly derive information in
regards to chain length, monomer composition, end group architecture, etc. This information is essential the chemists developing new products and fine-tuning their end use and physical properties.

This dissertation will show that the use of MALDI in conjunction with various ToF configurations provides important details of a polymer’s architecture, and composition. Further the usefulness of tandem MS studies will be demonstrated for identifying where functional groups are located in the polymer matrix. Since confident interpretation of tandem mass spectra requires knowledge of the fragmentation mechanisms of polymer ions, this subject is also discussed.
CHAPTER II

SCIENTIFIC BACKGROUND

2.1. Mass Spectrometry.

Mass spectrometry is used to determine the composition and structure of analytes containing a single substance or a complex mixture. This is accomplished by creating gas phase ions from the analyte and then measuring the mass to charge ratio (m/z) of these ions. Mass spectra can be obtained in a number of ways depending on the MS system selected. All mass spectrometers contain an ionization source, a mass analyzer and a detector. The types and combinations of these components vary based on the desired application and available technology. In this work, the focus will be on matrix assisted laser desorption ionization (MALDI). This ionization method and ESI along with quadrupole and time-of-flight based mass analyzers are utilized for the majority of mass spectrometry analysis performed today.

2.2. Ionization Methods.

To create ions an appropriate ionization method must first be selected. This process takes into account the type of material being analyzed; volatile,
non-volatile, liquid, solid, etc. Traditionally, these methods are categorized as being “hard” or “soft”.\textsuperscript{45} Hard techniques generally result in higher levels of internal energy causing higher incidences of fragmentation where the molecular ion peak (M) may or may not be observed.\textsuperscript{46} Soft techniques result in lower internal energy and little to no fragmentation allowing the molecular ion to be observed. MALDI and ESI are considered soft techniques and are well suited for polymer analysis.

2.2.1. MALDI.

Mass spectrometry employing MALDI requires that the analyte be dissolved in a matrix. With UV lasers, the matrix consists generally of a small aromatic organic molecule containing oxo, hydroxyl, and/or carboxyl groups.\textsuperscript{46} However, other materials have also been utilized including graphite and inorganic substances, such as metallic oxides (titanium, barium, etc.).\textsuperscript{47, 48} Regardless of the choice, it must have strong absorbance at the wavelength of light emitted by the laser. In addition, many synthetic polymers do not contain a group or functionality which will easily ionize by protonation, deprotonation or electron exchange; therefore, it is necessary to “spike” the matrix/analyte solution with an ionizing agent, usually a metal ion, which will result in cationization of the analyte to create a quasi-molecular ion (M\textsuperscript{+}).\textsuperscript{46} An additional condition is that the matrix not form cluster ions, either by itself or with the cationizing agent, as such ions could overlap with those from the analyte. As a result some trial and error may be necessary to achieve the right combination/ratio of materials in conjunction
with determining threshold laser intensity. The threshold laser intensity is the amount of laser energy required to observe fully resolved isotopic clusters while minimizing laser induced fragmentation and/or matrix/salt clustering.\textsuperscript{45}

Typically, either the “dried-droplet” or “layered/sandwich” methods are employed to deposit the analyte onto a sample plate.\textsuperscript{44} In the dried-droplet method matrix/analyte solutions are mixed at the appropriate ratio with ionizing agent if necessary and deposited onto the sample plate and the solvent is allowed to evaporate leaving a dried solution of the components. The layered method differs from the dried-droplet method in that each component is deposited independently onto the sample plate with the solvent being allowed to evaporate prior to the addition of the next component. Both methods are utilized and are capable of producing quality spectra. The deposition can be conducted by hand, usually with pipettes or by mechanical systems which have become more common in the past few years, especially due to hyphenating of techniques (GPC/MALDI, LC/MALDI, etc.).\textsuperscript{45, 46, 49, 50}

The process of ionization occurs when the laser is fired and a packet of molecules is ejected from the solid solution (in this context solid solution is a convention used in the mass spectrometry community to describe a mixture of component materials necessary to conduct MALDI experiments). This irradiation causes the matrix to absorb energy from the light which results in vaporization and ionization of the matrix. The matrix then transfers its energy to the analyte. This occurs when the crystalline matrix structure is broken down to become a super compressed gas. In this state charge transfer to the analyte can take
place either by protonation \((H^+)\), by metal ion transfer (if an auxiliary salt is added to the sample) or by creation of a negative ion, usually due to an acidic proton (i.e. OH functionality in the analyte). As the matrix expands it transports analyte ions into the gas phase where additional charge transfer reactions may occur.\cite{45,46,50} See Figure 2.1 for schematic of MALDI process.

![Figure 2.1. Scheme of the MALDI ionization process.](image)

2.3. **Mass Analyzer.**

The purpose of a mass analyzer is to separate ions according to their \(m/z\). Depending on the type of analyzer this occurs either simultaneously for the mass range of interest or the mass is scanned across the range of interest and narrow \(m/z\) segments are transmitted one at a time to the detector. Several factors are important for any given analyzer; they are: the upper mass limit, transmission, resolving power, mass accuracy, dynamic range and operating
The first three are considered key variants; the mass limit determines how large of a m/z and, hence, a molecule one can process. The transmission is the ratio of the amount of ions reaching the detector versus the number of ions produced in the source. Resolution is the ability of the detector to distinguish the signals from two or more ions which have a small mass difference. Two signals are considered resolved if the valley is equal to 10% of the least intense peak for sector or ICR instruments and 50% for quadrupoles and quadrupole ion traps, or according to Equation 1, where $R$ equals resolution, $m$ equals mass, and $\Delta m$ is the smallest mass difference between two peaks.

$$R = \frac{m}{\Delta m}$$  \hspace{1cm} (1)

Another way of defining resolution is by full width at half the maximum height of an isolated peak (FWHM). For this work two types of analyzers were utilized a quadrupole and a ToF analyzer. The instruments utilized were equipped with either a single ToF analyzer, a coupled quadrupole/ToF (Q/ToF) or two ToF (ToF/ToF) mass analyzers in series.

2.3.1. Time-of-Flight (ToF) Analyzers

When ions are produced in the MALDI source they are accelerated through a potential $V$ to gain kinetic energy $K = zeV = \frac{1}{2} mv^2$, in the keV range. The ions then travel a field free distance $d$ to reach the detector at a time $t$ which is acquired as a signal. The flight time is dependant on the velocity $v$ of the ions (Equation 2) which is dependant on m/z, see Equation 3.

$$t = \frac{d}{v}$$  \hspace{1cm} (2)
Equation 3 demonstrates how \( \frac{m}{z} \) can be calculated for a measured \( t \).

Theoretically, a ToF mass analyzer has no mass limit, which makes it suitable for the analysis of high molecular weights, and the desired analyzer for synthetic polymers. Figure 2.2a illustrates the principle of a linear ToF analyzer.\(^{45}\)

Ion formation is affected by the temporal, spatial and kinetic energy distributions of the ions. The temporal distribution is determined by the length of the formation pulse; the spatial distribution depends on the volume within the source where ions are formed and the kinetic energy distribution is determined by the variations in kinetic energy as a result of the ions being formed at different times and locations. These factors cause poor resolution in linear time-of-flight instruments: different kinetic energies for ions of the same \( \frac{m}{z} \) result in ions arriving at the detector at different times. Several options have been discussed and evaluated for improving the resolution in linear ToF instruments; the flight tube can be lengthened or the acceleration voltages can be lowered, but this reduces the sensitivity. The optimum conditions determined are a flight tube of 1 m and an acceleration voltage of at least 20 kV.\(^{46}\) Another option is delayed extraction (DE); for this, the ions are allowed to drift in a field-free region before acceleration.\(^{50}\) This narrows significantly their initial kinetic energy distributions. DE is also known as time lag focusing and pulsed ion extraction (PIE).\(^{50}\)

Additional improvement in resolution and sensitivity occurred with the advent of the reflectron which is an electrostatic analyzer at the end of the field free drift tube.\(^{50}\) As shown in Figure 2.2 b, as ions of the same \( \frac{m}{z} \) but differing
kinetic energy enter the field free drift tube, the ion with the greatest kinetic energy moves faster and is separated from the ions with lower kinetic energy. As the ions reach the end of the drift tube a set of deceleration lenses are activated which allows the ions of greater kinetic energy to penetrate deeper before they stop while the ions with lower kinetic energy do not penetrate as deep. After stopping the ions are re-accelerated by the reflector along a curved path in the opposite direction and are ejected from the reflector toward a detector with the faster ions being delayed the longest such that now all ions of the same m/z reach the detector at the same time. This has a dramatic increase in resolution but causes a reduction is sensitivity and mass limit.\textsuperscript{45} Performance can be enhanced further by the utilization of a two-stage reflectron. This type of reflectron uses two successive homogeneous fields which results in resolutions greater than 20,000.\textsuperscript{46}
Figure 2.2. Schematic diagram of (a) linear ToF instrument and (b) a reflectron ToF instrument. The white and black boxes represent ions of the same m/z but different initial kinetic energies.
ToF instruments can also be utilized to conduct (MS/MS) experiments. This can be conducted in several ways; in a single ToF instrument, post source decay (PSD) is utilized. In this method, the linear and reflectron capabilities are combined. Ions fragment in the field-free region in front of the reflectron (by increasing the laser power) and the fragments are subsequently dispersed by m/z inside the reflectron. PSD analysis is possible because fragment ions and their parent ion have the same velocity prior to entering the reflectron. They move together, as a packet, until they reach the reflectron. Installing an ion gate somewhere in the field-free region en route to the reflectron permits the selection of one velocity, i.e. one parent ion and its fragments (see Figure 2.3). This parent ion and its fragments are separated by m/z inside the reflectron, because of their different kinetic energies (see Figure 2.3).

With newer instruments, MS/MS can be accomplished using various configurations, for example, Q/ToF or ToF/ToF. In the Q/ToF combination, a quadrupole is utilized to isolate the parent ion, which travels into a collision cell, pressurized with a collision gas (usually argon), where collisionally activated dissociation (CAD) takes place (see Figure 2.4). The collision cell is floated to give the entering parent ions sufficient kinetic energy ($\leq 200$ eV), so that they decompose upon colliding with the collision gas. After fragmentation in the collision cell, the resulting ions are collimated by another hexapole, before being pushed orthogonally into a ToF tube to be mass-separated and; see Figure 2.4 for a schematic of a Q/ToF instrument.
Alternatively, a ToF/ToF configuration can be utilized. In this coupling, MS/MS is accomplished as in PSD, the difference being the use of a LIFT cell where precursor ions formed at high laser power undergo CAD to create fragment ions. The LIFT cell also post-accelerates the parent and fragment ions together to a level where the kinetic energy differences do not exceed 30%. The fragments are dispersed and detected, along with the parent ion based on their flight times; see Figure 2.5 for schematic representation.

Figure 2.3. Schematic showing how PSD analysis using a two-stage reflector works. The target is at potential IS1. The extraction grid is held at IS1 during the delay time and is pulsed to IS2 (< IS1) afterwards to extract the ions into the field-free drift region. The parent or precursor ion selector (PCIS) allows only one parent and its fragments to reach the reflectron for mass dispersion. (reproduced with permission from ref. 51).
Figure 2.4. Schematic of a Q-ToF mass spectrometer. (reproduced with permission from ref. 52).
2.3.2. Quadrupole Analyzers.

Quadrupole analyzers are made of four equally spaced and parallel rods, see Figure 2.6; hexapoles, octapoles, etc. work similarly, but the discussion here will focus on the quadrupole. The rods are divided into two sets, each consisting of two opposite rods that are connected. Each set is supplied with voltages of the same magnitude but different polarity. Ions traveling in the z-direction (beam direction) are subjected to and influenced by the electric field composed of a
alternating or radio frequency (RF) and a direct current (DC) which result from the application of potentials on the rods, see Equations 4 and 5.

\[ \Phi_0^+ = + (U - V \cos \omega t) \] (4)

\[ \Phi_0^- = - (U - V \cos \omega t) \] (5)

Where \( \Phi_0 \) equals the potentials applied to the rods, \( \omega \) is the angular frequency \([(rad/s) = 2\pi \nu]\), and \( \nu \) equals the RF. \( U \) is the direct potential and \( V \) is the “zero to peak” amplitude of the RF voltage. Typical ranges for \( U \) are 500 to 2000 volts and for \( V \) 0 to 3000 volts or -3000 to 3000 volts peak to peak.\(^{45, 46}\)

As the ions are accelerated along the z-axis they move between the rods and are exposed to accelerations along both the x and y-axis which are produced by the electric fields (RF and DC). This is represented by the equations of motion; Equations 6 and 7 give the forces induced by the applied electric fields; Equation 8 demonstrates the relationship of \( \Phi \) as a function of \( \Phi_0 \). Derivatizing and rearranging leads to Equations 9 and 10 known as the equations of motion.

\[ F_x = m (d^2x/dt^2) = -ze (\delta \Phi/ \delta x) \] (6)

\[ F_y = m (d^2y/ dt^2) = -ze (\delta \Phi/ \delta y) \] (7)

\[ \Phi(x,y) = \Phi_0 (x^2 - y^2)/ r_0^2 = (x^2 - y^2)(U - V \cos \omega t) / r_0^2 \] (8)

\[ d^2x/ dt^2 + 2ze/mr_0^2, \quad (U - V \cos \omega t)x = 0 \] (9)

\[ d^2y/ dt^2 + 2ze/ mr_0^2, \quad (U - V \cos \omega t)y = 0 \] (10)

So long as \( x \) and \( y \) never reach \( r_0 \) the trajectory of the ion will remain stable and not come into contact with any of the rods. If \( r_0 \) is reached the ion with touch the rods and be ejected and thus not detected. The values for \( x \) and \( y \) are
determined by Equations 9 and 10, which are also known as Mathieu equations. Their solution gives Equations 11-13,\textsuperscript{45, 46, 50}

\begin{equation}
\xi = \omega t/2 \tag{11}
\end{equation}

\begin{equation}
a_u = a_x = -a_y = 8zeU / m\omega^2 r_0^2 \tag{12}
\end{equation}

\begin{equation}
q_u = q_x = -q_y = 4zeV / m\omega^2 r_0^2 \tag{13}
\end{equation}

where \( u \) represents \( x \) or \( y \). For a given system, \( r_0 \) and \( \omega \) are kept constant while \( U \) and \( V \) are varied. By plotting \( a_u \) versus \( q_u \) stability areas can be generated, from which one can determine what the effective mass range is for the quadrupole and what settings need to be maintained to achieve detection for a given mass. Figure 2.7 shows the stability diagrams for three masses (solid, dotted and dot/dashed curves). The straight line is a linear relationship between \( U \) and \( V \) and is called the scanning line. Increasing \( U \) and \( V \), while keeping their ratio constant, successively transmits \( m_1 \), \( m_2 \) and \( m_3 \) through the quadrupole. Ions maintain a stable trajectory for values of \( U \) and \( V \) within the stability area of their mass. Quadrupoles maintain unit resolution and are considered low-resolution instruments.\textsuperscript{45, 46} In this work a quadrupole is utilized as a mass selection device in a Q/ToF instrument.
Figure 2.6. Schematic representation of a quadrupole mass analyzer (reproduced with permission from ref 45).

Figure 2.7. Stability area as a function of U and V. As long as U and V are within the triangle for the mass of interest and below the stability line the ion will be detected. If the values are outside the area the ion will be deflected. (reproduced with permission from ref 45).
2.4. Detectors.

The purpose of the detector is to convert the ions of a given m/z into an electrical signal which can be measured and provide an output which is proportional to the intensity of the ion current. Today commonly used detectors are electron multipliers, array detectors and photon multipliers; however, the first mass spectrometers utilized photographic plates and faraday cylinders, which today only find use in specialized isotope studies. Here only the microchannel plate detector will be discussed as it is the most commonly used detector for ToF instruments.45, 46, 50

2.4.1. Microchannel Plate Detector.

A microchannel plate detector (MCP) is a type of array detector used in most MALDI-ToF instruments. It is ideally suitable for the detection of ion pulses, such as those generated by MALDI. The MCP is a plate with drilled parallel cylindrical channels. The diameter of the channels ranges from 4 to 25 μm with a center-to-center distance form 6 to 32 μm, see Figure 2.8. The plate is connected to opposite potentials, with the input side being negative and the output side being positive. The coating in each channel provides the electron multiplication by giving off secondary electrons when impacted by the primary electrons generated by the ions. Parallel plates can be used for increased signal magnification. The multiplication effect increases the number of electrons by $10^5$ to $10^8$ depending on how many plates are used. At the output side a metal
anode collimates the secondary electrons and the signal is transferred to a processor. The geometry enables ions of differing m/z to hit different channels and thus be detected at the same time.\textsuperscript{45, 46, 50}

Figure 2.8. Schematic of a multichannel plate detector. (reproduced with permission from ref. \textsuperscript{45}).
CHAPTER III
EXPERIMENTAL PROCEDURE

3.1. Chain-End and In-Chain Functionalized Polymers.

Living anionic polymerization (LAP) and LAP-based general functionalization methods (GFM) were utilized for the synthesis of the functionalized and non-functionalized polymers used in this dissertation. A GFM uses the same chemistry to introduce a variety of functional groups into a polymer. The syntheses were performed by Jon Janowski in the Department of Polymer Science at The University of Akron under the direction of R. P. Quirk. Polymerizations were conducted in sealed, all-glass reactors under high-vacuum conditions, generally using benzene as the solvent. After consumption of the monomer and prior to functionalization an aliquot of the poly(styryl)lithium or poly(butadienyl)lithium was collected as a base sample according to reported conditions.5,52

3.1.1. Polystyrenes.

The poly(styryl)lithium was terminated with either chlorodimethylsilane or dichloromethylsilane for chain-end or in-chain functionalization, respectively. The
chain-end material was then reacted with an alkene carrying the desired functional group in dry benzene that contained Karstedt’s catalyst. After the prescribed reaction time silica gel was added and the mixture separated via column chromatography to isolate the non-functional polystyrene from the functional polystyrene. For in-chain functionalized materials the break-seal was broken under ambient conditions and an excess of the poly(styryl)lithium was added to dichlorodimethylsilane. After the prescribed reaction time the mixture was reacted with ethylene oxide to add a functional group to the residual poly(styryl)lithium to aide in separation by silica-gel chromatography. The material with the in-chain silane group was then reacted with the appropriate substituted alkene in the presence of Karstedt’s catalyst. After this reaction, the polar and nonpolar products were separated by column chromatography using a 3:1 mixture of toluene : cyclohexane or toluene : ethyl acetate as eluent.5, 52

3.1.2. Polybutadiene.

Polybutadienes were prepared in a similar manner as the polystyrenes. Butadiene was polymerized using Sec-butyllithium in cyclohexane and functionalized with the proper silane, before the reaction was terminated with ethylene oxide followed by methanol. The solution was then precipitated into methanol and dried under high vacuum. Standard polybutadiene was prepared the same way except it was terminated with just methanol. Triethoxysilyl-functional polybutadiene was prepared by hydrosilation of a triethoxysilane substituted alkene with silane-functionalized polybutadiene in the presence of
Karstedts catalyst. For this material the poly(butadienyl)lithium was quenched with to provide the C$_2$H$_4$OH end group and then purified by column chromatography to separate the polar and non-polar components.

3.1.3. Cyclic Synthetic Polymers.

Two types of cyclic polymers were looked at: cyclic functionalized polystyrene and cyclic non-functionalized polybutadiene. The functionalized cyclic polystyrene was produced by reacting 5-litho-1-pentene with styrene monomer to produce poly(styryl)lithium. The poly(styryl)lithium was terminated with a reagent such that the new product contained a double bond at both the initiating and terminating chain ends. This linear polymer was then mixed with Grubb’s 1$^{\text{st}}$ generation catalyst to yield the cyclic product. Grubb’s catalyst is a ruthenium based catalyst used in metathesis reaction whereby the vinyl bonds are preferentially attacked allowing for either ring opening or in this case ring closing. The cyclization reactions cause loss of ethylene and result in centrally substituted polystyrene.

3.1.4. Cyclic Functionalized Polystyrene.

Cyclic functionalized polystyrene was synthesized by Shi-Fang Wang see Scheme 3.1. α,ω-diethenylpolystyrene was combined with Grubb’s 1$^{\text{st}}$ generation catalyst in dichloromethane under high vacuum and allowed to react for 24 hours. Using silica gel column chromatography the residual catalyst was then removed and samples used for MS and MS/MS studies.
The precursor to the cyclic functionalized polystyrene described here is α,ω-diethenylpolystyrene. This material was produced according to the schemes and descriptions provided by Wang. α-Pentenyl(polystyrlyl)lithium was produced by adding 5-lith. opentene to styrene monomer. The α-Pentenyl(polystyrlyl) lithium was then added to ethylenechlorobenzene in THF at -78°C, which resulted in the α,ω-diethenylpolystyrene.

3.1.5. Cyclic Polybutadiene.

The cyclic polybutadiene was prepared Vijay Chavan using 1st generation Grubb’s catalyst. Potassium t-butoxide was mixed with imidazolium salt and toluene under inert conditions, then Grubb’s catalyst was added. Cyclization was conducted in hexane and then exposed to flash chromatography to yield the cyclic catalyst. This material was mixed with appropriate solvents and reacted with the alkene-telechelic chain to form the cyclic polymer which was precipitated in methanol and dried under vacuum. The polymers were analyzed as received.
Scheme 3.1. Synthetic Scheme for α,ω-diethylenepolystyrene followed by the ring closing metathesis reaction with Grubb’s catalyst.


Two materials were utilized as matrices: 1, 8, 9-dihydroxy-9,10-dihydroanthracen-9-one (dithranol) (AlfaAesar, Ward Hill, MA) or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) (Fluka, St. Louis, MO). Selection was based on available lots, molecular weight of the sample of interest as well as the instrument utilized. DCTB was utilized for polymers having low molecular tails around the 500 Da otherwise Dithranol was utilized on all instruments with all polymers and salts until the lot of material was exhausted at that point DCTB was utilized due to the higher level of matrix
clustering observed when using the new lot of dithranol. Three cationizing salts were utilized; silver trifluoroacetate (AgTFA), (Sigma, St. Louis. MO), sodium iodide (NaI), (Sigma) and lithium trifluoroacetate (LiTFA), (Sigma). Selection of salt was based on the polymer being analyzed as well as whether or not MS/MS experiments were to run. When heteroatoms or an Si-H functionality was present NaI or LiTFA was utilized for MS experiments but AgTFA was used for Q-ToF MS/MS analysis due to binding affinities. LiTFA was utilized for ToF/ToF due to its higher binding affinity versus NaI and the ability to perform both MS and MS/MS experiments on the Ultraflex without the need for further sample preparation. All materials were dissolved in tetrahydrofuran (THF) (Sigma). Materials were used as received with no modifications. For the matrix, 20 mg/mL solutions were prepared, and for the salt and the samples, 10 mg/mL solutions were prepared. These solutions were mixed in a 10:2:1 ratio (matrix:sample:salt). For Reflex III experiments ~ 0.5μL was deposited per target spot and for the Q-ToF and Ultraflex ToF/ToF ~ 1.0μL was deposited per target spot. Additional details will be provided in the following sections as the instrument conditions are described.

3.3. Experimental Methods.

Three MALDI instruments were utilized. Where possible the same sample was analyzed by multiple instruments to verify results and compare instrument capabilities. The instruments will be described individually in the following sections and the comparative data will be discussed in the proceeding chapters.
MALDI-ToF instruments were selected due to the mass range of the analyzed polymers. An ESI quadrupole ion trap was also available for this work, but was not used because ESI does not ionize polystyrenes and polydienes as efficiently as MALDI.\textsuperscript{17, 45, 50}

3.3.1. Use of the Bruker Reflex III Mass Spectrometer.\textsuperscript{54}

A Bruker Reflex III MALDI-ToF mass spectrometer was utilized in a large part of this dissertation. This instrument is equipped with an attenuated nitrogen laser (337 nm) with a pulse width of approximately 3 nanoseconds. Excitation occurs over an area of $10^4 \ \mu\text{m}^2$ and irradiances are typically in the range of $10^6$ to $10^7 \ \text{W/cm}^2$. Figure 3.1 shows a diagram of this reflector-type time-of-flight mass spectrometer.

The ions are created at the ion source after ablation by the laser. They are then accelerated into the field-free region at 20 kV; from there, they strike the linear detector or penetrate the reflector depending on which mode is selected. The purpose of the reflector is to allow ions with the same m/z but different kinetic energies to reach the reflectron detector at the same time, thus increasing resolution, sensitivity and mass accuracy.

The instrument is equipped with a SCOUT ion source which automates the sample loading and spot selection. The target used was a round stainless steel target with 26 sample positions. A video camera and monitor were utilized to view the sample being irradiated as well as monitoring proper loading and unloading of the target.
Figure 3.1. Diagram of a reflectron MALDI-ToF mass spectrometer (reproduced with permission from ref 54).

An ion deflector is used to deflect low mass ions and increase the sensitivity for higher mass ions by avoiding saturation effects at the detector. The low mass ions often originate from the matrix, a contamination, or an irrelevant sample which is lower in mass than the compound of interest. Ion detection is based on the fast measurement of an electrode voltage which drops over a 50 Ω resistor as a result of ion impact. The instrument utilized a dual microchannel plate detector (MCP-detector). It consists of an array of fused lead glass tubes which are cut at a bias angle and machined to an optical finish. The wafers are chemically processed to create a uniform porous structure referred to as microchannels. The microchannels act as electron multipliers with gains of $10^6$ possible. The reflector is a two-stage gridless reflector. The lack of
grids allows for an increase in ion transmission and resolution. Data acquisition and instrument control are managed by a UNIX SUN work station.

The instrument was run in reflectron mode (unless otherwise stated) at +20 kV setting for all experiments. The time delay varied between 1.00 and 2.00 ns depending on the mass range of interest. The laser attenuation varied between 28% and 18% depending on the concentration of the sample and signal to noise ratio (S/N) for the sample being evaluated. For a given day and set of experiments the attenuation was optimized and held constant for that time period. The optimum setting changed over long time periods due to machine variability and modification of sample preparation during the course of this study. The mass range scanned was dependent on the sample being analyzed but was generally below 5000 Da. A set of samples was analyzed using a low mass cut appropriate for minimizing matrix clusters and increasing the S/N ratio. Between 400 and 1000 laser shots were collected per sample, again depending on the S/N ratio observed during the run. This instrument was used to collect mass spectra only (single stage MS experiments).

3.3.2. Waters Micromass Q/ToF Ultima Mass Spectrometer.

A Waters Micromass Q/ToF Ultima mass spectrometer (Milford, MA) was also utilized for sample analysis. The Q/ToF instrument was primarily employed for MS/MS studies after mass spectra had been collected by the Reflex III. The Q/ToF mass spectrometer is a tandem mass analyzer, in which a quadrupole is coupled with a ToF device in an orthogonal configuration. Two hexapoles are
also used, one as a collision cell to perform parent ion fragmentation with the assistance of argon (Ar) and the other as a lens to transfer the fragment and parent ions to the ToF part, see Figure 2.4. The quadrupole is used to isolate the parent ion for MS/MS studies. This instrument contained no operator controlled laser attenuation and as such 100% of the focused laser power was utilized. In MS mode, the quadrupole was used as an RF-only focusing lens to transmit all ions to the ToF part.46 Mass analysis was performed by the ToF analyzer in both MS as well as MS/MS modes.

In MS/MS mode, all ions except for the parent ion are deflected by the quadrupole, with the parent ion being transferred to the hexapole collision cell. In the collision cell, Ar is added and the parent ion collision energy (CE) is adjusted to observe the desired level of fragmentation. The CE was generally set between 60-130 eV to obtain fragmentation of the various samples tested. The appropriate amount was determined by selecting a CE such that the parent ion could still be observed in the spectra while the major fragmentation series was present with a satisfactory S/N and was resolved. Another feature available was the ability to isolate either the complete isotope cluster of a parent ion or its all \(^{12}\text{C}\) peak. Selection of one peak, the all \(^{12}\text{C}\) isotope, only is very useful for assigning structures to fragments that differ by only ~ 1-2 Da in mass and whole isotopes would, therefore overlap. The isolation was controlled by adjusting the high mass (hm) and low mass (lm) filters to adjust the quadrupole to transmit the entire oligomeric cluster or just the all \(^{12}\text{C}\) peak. Generally, the values are default set to 5 eV and 5 eV, respectively; and to isolate the all \(^{12}\text{C}\) peak, the hm was set
to around 7 eV and the Im was set to around 14 eV. Not all samples were amenable to this operation and where monoisotopic isolation could be obtained will be noted in the discussion of the results.

This instrument utilizes a non-attenuated nitrogen laser (337 nm) with a pulse width of approximately 3 nanoseconds. Excitation occurs over a region of $10^4 \mu m^2$ and irradiances are typically in the range of $10^6$ to $10^7 W/cm^2$. The Q/ToF mass spectrometer is equipped with a 96-well sample target. A video camera and in screen monitor were utilized to view the sample being targeted as well as monitoring proper loading and unloading of the target. Enough shots are taken to collect enough signal to obtain resolved peaks in the spectra. Due to the nature of the instrument, a shot count was not available. The flight tube operates on the same principle as that of the Reflex III. A significant difference is that the Q/ToF flight tube is capable of operating in a W mode which was designed to increase the resolution by lengthening the time the ions need to reach the reflectron detector; this is achieved by applying two additional sets of reflectron lens, such that the ions traverse the flight tube in a W pattern rather than the V pattern in normal reflectron mode. This function was not utilized for any of the experiments reported in this work. Data acquisition, instrument control and data analysis are managed by a PC-based Waters MassLynx workstation.

The sample preparation led to the formation of abundant $[M + Ag]^+$ or $[M + Li]^+$ ions for the polystyrenes and polybutadienes studied. The ions exiting the MALDI source were directed toward the quadrupole mass filter, which was set to transmit one oligomer only (mass-selective mode). As explained above, the
precursor ion resolution was adjusted to select one isotope or the complete isotopic cluster of an oligomer; both options were used as needed and permitted by the precursor ion identity. The RF-only hexapole collision cell was pressurized with Ar at ~0.9-1.0 bar. The fragment and undissociated precursor ions resulting after CAD in the collision cell were focused by the following RF-only hexapole lens, and the focused ion packet was accelerated orthogonally by ~10 kV into the ToF region for mass analysis. Single stage mass spectra were measured with the ToF mass analyzer by setting the quadrupole mass filter to rf-only mode, so that it transmitted all ions produced in the MALDI source (see above). The ion abundances of several ToF MS or MS/MS scans were summed to obtain spectra with good S/N ratio.

3.3.3. Ultraflex III ToF/ToF mass spectrometer.

The third instrument utilized for this work was the Bruker Ultraflex III ToF/ToF mass spectrometer (Billerica, MA), see Figure 2.5. Several differences exist between the Ultraflex and the two previously described mass spectrometers. The Ultraflex is equipped with an attenuated Smartbeam 200 Hz laser operating at 354 nm. The laser is usually set to operate at 100 Hz. This laser technology allows one to collect 1-2 orders of magnitude more shots than the Reflex III in the same time frame. This function allows for rapid spectra collection. A second difference is the coupled flight tubes. In MS mode, the ions are transferred through the first (shorter) flight tube and pushed into the second 1 m flight tube for detection in either linear or reflectron modes. The second flight
tube is similar to the Reflex III flight tube, but uses newer technology for the
gridless deflectors and MCP detectors, which enable it to keep up with the faster
laser. This resulted in resolved isotopic clusters at higher m/z values as well as
faster collection times. The ions were accelerated into the flight tubes at 25 kV
(IS1) with the IS2 and lens potentials set to 21.65 and 9.60 kV, respectively, and
were adjusted as necessary to achieve maximum resolution for the sample being
analyzed. The reflectron 1 and 2 lenses were set to 26.30 and 13.70 kV,
respectively, and the detector gain, sample rate and laser attenuation were
adjusted as needed to further maximize the resolution based on the desired
range of observation.

In MS/MS mode, the LIFT cell was set to have the following potentials:
IS1 and IS2 equaled 8 and 7.15 kV respectively with the lens potential set at 3.6
kV. The reflectron 1 and 2 lenses were set at 29.50 and 13.85 kV, respectively,
and the LIFT 1 and 2 were set at 19.00 and 2.90 kV, respectively. Additionally,
the ability to add Ar gas to the LIFT cell was available but was not utilized as no
increase in ion intensities was observed for the synthetic polymers analyzed.
The major differences between the Q/ToF and Ultraflex MS/MS modes were (a)
in total resolution, with overall resolution being superior in the Q/ToF
arrangement, and (b) in fragment ion intensities, with all fragments observed in
the Ultraflex where the CAD products do not pass RF lenses which can cause
mass discrimination.

The Ultraflex is equipped with a 384 micro-well plate. The plate is
automatically inserted and monitored by a camera and in screen monitor. The
system is controlled by the Bruker Flex-Control software with a Windows-based computer system which also contains the Bruker Flex-Analysis software for data analysis.

3.4. Data Analysis.

Data analysis involves rationalization of the spectra obtained from the various experiments conducted. Several pieces of data can be obtained by evaluating the mass spectra; what monomer or monomers were used, the initiating and terminating groups, existence of un-reacted products, side reactions, etc. When MS/MS is applied, definitive structure information is obtained for the selected oligomer based on the fragmentation pieces observed. Whenever possible the all $^{12}$C peak is selected for MS/MS analysis. Selection of this peak allows the utilization of monoisotopic masses which in turn provides the most accurate information about the exact molecular weight and composition of the observed species. The difference in parts per million (ppm) between theoretical weight of an assumed structure and the observed weight provides a measure for the confidence that the observed peak corresponds to the structure assumed. Whenever possible, this information is corroborated with information provided with the sample which allows for a high degree of confidence in the interpretation. By calculating the nominal mass difference between two adjacent oligomers, one can determine the repeat mass of the polymer and thus determine the type of polymer or dominant component in a copolymer.
If the all $^{12}\text{C}$ isotopic peak is resolved the following logic is applied to determine the end groups. First, we take the observed mass of the all $^{12}\text{C}$ isotope and subtract the monoisotopic mass of the ionizing cation which gives the mass of the oligomer. Next, we divide that value by the monoisotopic mass of the previously determined monomer repeat unit (see above), to obtain a value representative of the number of potential repeat units and the size of the ends groups. Next, we subtract the whole number, which is less than or equal to the number of monomer repeat units ($n$), leaving a fraction which in then multiplied by the mass of the monoisotopic repeat unit. This value is the lowest value possible for the mass of the combined ends groups (plus any in-chain substituents). If this value is not large enough for the expected initiating and terminating groups, we can take monomer units away from the whole number we subtracted previously until a mass value is reached that is representative of the initiating and terminating groups. Monoisotopic values can be obtained by using a reliable source, for example the NIST website: http://physics.nist.gov/PhysRefData/Compositions/index.html. See Scheme 3.2 for an example of such a calculation.

If this methodology is not sufficient to determine the structure of the observed distributions, MS/MS can then be applied and the observed peaks will be treated similarity as indicated in Scheme 3.1. Now, the masses of the fragments and their end groups are determined. Knowledge of the fragmentation mechanism is essential for assuming fragment structures to compare their theoretical masses.
to the observed fragment masses. For this reason, this dissertation elucidates in
detail such fragmentation mechanisms.

Observed m/z = 1205.5 of a PS standard \([C_4H_9-(C_8H_8)_n-H]^{Ag^+}\), \(n = ?\)

\[
\begin{align*}
1205.5 & \quad \text{(Observed all }^{12}\text{C, }^{107}\text{Ag peak)} \\
- 106.9045 & \quad \text{(Theoretical monoisotopic value of }^{107}\text{Ag minus an}\n & \quad \text{electron)} \\
1098.5955 & \quad \text{(Product mass of the all }^{12}\text{C isotope of the oligomer}\n & \quad \text{after the removal of the }^{107}\text{Ag cation)} \\
\div 104.0626 & \quad \text{(Calculated monoisotopic value for }C_8H_8) \\
10.5571 & \\
- 10 & \quad (n \leq 10 \text{ for this oligomer)} \\
x 104.0626 & \\
57.9695 & \rightarrow 58 \quad \text{(Nominal mass of the combined end groups)}
\end{align*}
\]

Nominal mass of \(C_4H_9 + H = 58\)

Therefore, we have \([C_4H_9-(C_8H_8)_{10}-H]^{Ag^+}\)

Scheme 3.2. Determination of initiator and end groups from observed m/z data.
CHAPTER IV

IN-CHAIN FUNCTIONALIZED POLYSTYRENE ANALYSIS BY MALDI-TOF MS
AND MS/MS MASS SPECTROMETRY

4.1. In-Chain Polystyrene versus Chain-End Polystyrene.

A detailed nomenclature scheme which describes the fragmentation of chain-end functionalized polystyrenes was previously described by Wesdemiotis et al, see Figure 4.1(a). Here the nomenclature scheme was amended to account for fragment ions retaining the in-chain functionality between two polymer pieces of varying lengths, see Figure 4.1(b). The placement of the functionalization between two chains necessitated the addition of a designator to distinguish between fragments lacking and fragments containing the in-chain functionalization. The lower case letter i was selected to designate fragments containing the in-chain functionality; for example $b_{ni}$ indicates a fragment retaining the initiator, the in-chain functional group and $n(CH_2-CHPh)$ groups terminated with an unsaturation. If the end groups of an in-chain functionalized polystyrene are identical, as in Figure 4.1 (b), $b_{ni}$ and $z_{ni}$ type ions are indistinguishable, as are $a_{ni}$ and $y_{ni}$ type ions.
Unlike chain-end functionalized polystyrenes with a generic structure $\alpha$-PS-$\omega$, the in-chain functionalized polystyrenes synthesized by R. P. Quirk and co-workers have the generic structure $\alpha$-PS-$\omega$-PS-$\alpha$, where $\alpha$ is the same for each end, generally sec-butyl, and $\omega$ is a silane group with various functionalities attached. This describes the MS and MS/MS characteristics of in-chain functionalized polystyrene produced by living anionic polymerization with silyl chloride linking and hydrosilylation chemistry, emphasizing the similarities and differences in relation to chain-end functionalized polymers having the same functional groups. Using the nomenclature previously described by Wesdemiotis...
et al., with additions to designate the in-chain functionalized fragments, structural assignments will be made based on the MS and MS/MS data and fragmentation mechanisms will be presented that account for the different fragmentation patterns in the MS/MS spectra of in-chain versus chain-end functionalized polymers. It will be shown that, unlike chain-end functionalized polymers, polymers functionalized in-chain with silane groups yield MS/MS spectra that reveal the length of chains on each side of the central functional group. The ability to determine the location and composition of the in-chain functional group as well as the length of the attached chains provides valuable information to the synthetic chemist in regards to degree of polymerization, monomer consumption and distribution, verification of experimental objectives, and characterization necessary for end use testing, etc.

4.2. Cyano Chain-End Functionalized Polystyrene.

First, the chain-end functionalized polymers prepared using the anionic polymerization also utilized to make the in-chain functionalized polymers were characterized. The discussion will focus on polystyrene which was prepared with cyano-functionalization at the ω terminus. The mass spectrum of this polymer showed a Poisson molecular weight distribution as a result of the narrow polydispersity, \( M_w/M_n = 1.05 \) by SEC, see Figure 4.2. A single distribution is observed corresponding to sodiated oligomers of the cyano functionalized polystyrene expected from the synthetic scheme. Sodiation was utilized to minimize oxidation of any residual Si-H to Si-OH as previously reported.
Figure 4.2. Partial MALDI-ToF mass spectrum chain-end cyano-functionalized polystyrene, showing the m/z 1870-1990 region where the 16- and 17-mers are detected with isotopic resolution. The full spectrum is shown in insert (a). Insert (b) shows the calculated isotope pattern for the 17-mer. Na+ was used for cationization.
The 17-mer (1975.0 m/z) was used to determine the initiating and terminating end groups for the distribution, which agree well with C₄H₉ (nominal mass 57) and C₃H₆Si(CH₃)₂CN (nominal mass 126), respectively. This material and the in-chain functionalized polymer were prepared using similar reaction sequences. Therefore, characterizing the chain-end functionalized polymer was necessary to validate the polymerization protocol and to differentiate fragment ions generated during the tandem MS studies. Tandem MS studies were conducted using the Ultraflex III ToF/ToF mass spectrometer and resulted in a similar pattern as previously reported for chain-end functionalized polystyrenes, where, the low mass region is dominated by abundant internal fragment ions and bₙ⁻ radical ions and the medium and high mass regions by a set of fragment ions decreasing in intensity as the mass range increases; and consisting predominantly of aₙ⁻ (a₅ through a₂₀) and yₙ⁻ (y₄ through y₁₉) type ions, see Figure 4.3. The fragmentation mechanism for this system follows free radical degradation initiated by CAD and involving random homolytic cleavages along the PS backbone. The closed-shell aₙ⁻ and yₙ⁻ series arise mainly by 1,5-H rearrangements via backbiting and consecutive β-scissions in the benzylic radicals formed by the random C-C bond homolyses. Their dissociations coproduce the internal fragments J₂⁻ and K₃⁻ (Figure 4.3). The other abundant low-mass fragments result from the extensive depolymerization via successive monomer evaporation caused by CAD. This mechanism accounts fully for all MS/MS fragments observed from the chain-end cyano functionalized polystyrene. Figure 4.4 and Scheme 4.1 summarize the pathways to these fragments and their structures.
Scheme 4.1. Internal ($J_2^*$, $K_3$) and terminal (series $a_n$ and $y_n$) fragments formed from lithated $C_4H_9$-$\{C_8H_8\}_n$-$Si(CH_3)_2$-$C_3H_6$CN by backbiting and subsequent $\beta$ C-C bond scissions in the benzylic radical ions ($b_n^*$, $z_n^*$) arising via random homolytic C-C bond cleavages along the polymer chain.
Figure 4.3. MALDI-CAD spectrum of the lithated 21-mer from C$_4$H$_9$-(C$_8$H$_8$)$_{21}$-SiC$_3$H$_6$CN (m/z 2375.5), acquired with the Ultraflex ToF/ToF mass spectrometer. The inset shows an expanded trace of the m/z 100-860 region. The precursor ion was mass-selected for CID with no collision gas at 19 kV in the LIFT cell. Monoisotopic m/z values are given on top of select peaks.
4.3. Cyano In-Chain Functionalized Polystyrene.

The in-chain cyano functionalized polystyrene synthesized by Quirk et al.\textsuperscript{5} maintained the same type of cyano functionalization as the chain-end functionalized polymer. One of the main differences in the synthesis of the two products was the utilization of dichloromethylsilane for the in-chain functionalized polystyrene instead of dimethyldichlorosilane for the chain-end functionalized polystyrene; the dichloro reagent allowed two polystyrene chains to attach to the silyl group to create the in-chain functionalized polymer. The MALDI mass
spectrum showed a Poisson distribution of resolved sodiated oligomers of in-chain cyano-functionalized polystyrene, maximized on ~1900 m/z (16-mer), see Figure 4.5. The 15-mer was selected for fragmentation on the Q/ToF Ultima mass spectrometer. The MS/MS spectrum displayed a different fragmentation pattern from that observed from chain-end functionalized polymers, compare Figures 4.5 and 4.3. Similar to the chain-end functionalized polymer the in-chain functional species leads to abundant low-mass internal and terminal fragment ions, but also a unique central region with a Gaussian distribution of quite abundant fragment peaks, see Figures 4.6 and 4.7.

The major peaks in the central region are labeled by \( a_n \), \( b_n \) and \( b_{ni}^{\prime\prime} \) and correspond to closed-shell fragments. The subscripted \( \prime \) indicates inclusion of the in-chain substituent, whereas the double prime points to a fragment with a saturated chain end. The \( b_n \) and \( b_{ni}^{\prime\prime} \) fragments are not observed from chain-end functionalized systems. The lack of \( y_n \) and \( z_n \) ions is due to the identical chain end groups, which are the \( \text{C}_4\text{H}_9 \) substituents provided by the initiator.

The new fragmentation pattern is rationalized by considering that the \( \text{Si-C}^\alpha \) bonds are weak due to the formation of well stabilized benzylic and trialkylsilyl radicals upon their cleavages and the increased crowding around the Si atom. Additionally, cleavage of the \( \text{C}^\alpha-\text{C}^\beta \) bonds is promoted by the ability of silicon to stabilize carbon centered radicals in the alpha position.\(^{58, 59}\) Preferential scission of these bonds during CAD explains the new spectral features.
Figure 4.5. MALDI-ToF MS spectrum of C₄H₉-(C₈H₈)ₙ-CH₃SiC₃H₆CN-(C₈H₈)ₘ-C₄H₉. The most abundant ion (m/z 1913.2) corresponds to the 16-mer. Na⁺ was used for cationization. Insets (a) and (b) show the experimental and calculated isotope patterns, respectively, of the 16-mer.
Figure 4.6. MALDI-CAD spectrum of silverated C$_4$H$_9$-(C$_8$H$_8$)$_n$-CH$_3$SiC$_3$H$_6$CN-(C$_8$H$_8$)$_m$-C$_4$H$_9$, where n + m = 15 (m/z = 1829.8), acquired with the Ultima Q/ToF mass spectrometer. The 15-mer precursor ion was subjected to CAD with Ar at $E_{lab} = 110$ eV.
Figure 4.7. Expanded trace of the m/z 995-1120 region in the MALDI-CAD spectrum of silverated $C_4H_9-(C_8H_8)_n-CH_3SiC_6H_6CN-(C_8H_8)_m-C_4H_9$, where $n + m = 15$. 
The observation of $b_{ni}^{II}$ fragments, which as mentioned above contain the in-chain functionality and saturated chain ends, strongly suggests that the incipient radical ions emerging from the Si-C$_{\alpha}$ bond scission are held together in a Ag$^+$-bound complex, in which H atom transfer can take place to generate $b_n$ and $b_{ni}^{II}$, depending on which piece retains the metal ion charge after dissociation, see Scheme 4.2. The stability of such an intermediate complex must result from the availability of phenyl groups at either site of the Si functionality, which can bind Ag$^+$ to keep the nascent fragments long enough together for an intermolecular H atom transfer to occur. Note, the H$^*$ transfer in the reverse direction, i.e. to form $b_{ni} + b_n^{II}$ (now the latter ion accepts the transferred H atom), is unlikely because of the low stability of C=Si double bonds.$^{58}$

Conversely, scission of the C$_{\alpha}$-C$_{\beta}$ bond creates a benzylic radical carrying the linker, i.e. $b_{ni}^*$, and a primary radical without it, i.e. $a_n^*$. The latter can dissociate consecutively by $\beta$-scissions of H$^*$, Ph$^*$, or monomer to yield $a_n$, $a_{nb}$, or $K_1$ fragments, respectively, Scheme 4.3. The benzylic radical with the linker, $b_{ni}^*$, can undergo backbiting, as shown in Scheme 4.1, to yield the internal fragments $K_{3i}$ (m/z 516), $J_{2i}^*$ (m/z 399), and smaller $a_n$ fragments, Scheme 4.3, left. It is noteworthy that the $b_n$ as well as the $b_{ni}^{II}$ distributions peak at $n \approx 7$-8, which is the average size of the PS chains added to the linker in the synthesis of this centrally functionalized polymer. Thus, such MS/MS fragmentation patterns can be used to deduce unknown chain length distributions when the polymer in question is centrally functionalized.
Scheme 4.2. Fragments formed from a silverated PS, functionalized in-chain with a Si-containing substituent after initial Si-C α bond homolyses. 

R = CH₂CH₂CH₂CN.
Scheme 4.3. Fragments formed from a silverated PS, functionalized in-chain with a Si-containing substituent after initial Cα-Cβ bond homolyses.

\[ R = \text{CH}_2\text{CH}_2\text{CH}_2\text{CN}. \]

The pathways in Schemes 4.2-4.3, which yield important signature ions for the in-chain substituent, are accompanied by random C-C bond scission, as discussed for chain-end functionalized polystyrene. The random reactions are a major source of \( b_1^\bullet, b_2^\bullet, J_2^\bullet \), and \( K_1-K_3 \) and also contribute to the \( a_n \) and \( a_{nb} \) series. Further, backbiting rearrangements in randomly formed \( b_{ni}^\bullet \) radical ions generate, according to Scheme 4.1, \( a_{ni} \) fragments, shown in Figure 4.8 (a).
Figure 4.8. Minor fragments from the silverated, in-chain functionalized PS studied. (a) Fragments $a_{ni}$ formed by backbiting and subsequent $\beta$ C-C bond scission in $b_{ni}^*$ radicals (benzylic radicals containing the in-chain substituent; (a-c) fragments $a_{ni}$, $a_{nib}$, and $b_{nix}$ formed by $\beta$ scissions from $a_{ni}^*$ or $b_{ni}^*$ radicals; (d) possible structures of the fragments observed at the indicated m/z ratios. $R = \text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$.

These fragments appear 2 m/z units (2 Da) below the $b_{ni}^{ii}$ series with approximately 2-3 times lower relative abundances (see Figure 4.7).

The randomly produced $b_{ni}^*$ radical ions may also undergo $\beta$-$\text{H}^*$ loss to yield the fragments in Figure 4.8 (c). As with all polystyrenes studied thus far, such b-type fragments have low relative intensities.$^{55,56}$ Randomly formed $a_{ni}^*$ radicals are the most likely source of the weak $a_{nib}$ series and also contribute to the $a_{ni}$ series;
the former, Figure 4.8 (b), results by $\beta$-Ph$^\bullet$ loss and the latter, Figure 4.8 (a), by $\beta$-H$^\bullet$ loss. Finally, a few other minor fragments could not be identified with confidence. Plausible structures are given in Figure 4.8 (d).

Multiple in-chain substituted polystyrenes were produced varying in the substituent attached to Si. In these compounds, the CH$_2$CH$_2$CH$_2$CN substituent was replaced by $R = H$, OH, CH$_2$CH$_2$CH$_3$, or CH$_2$CH$_2$CH$_2$COOCH$_3$. Regardless of what $R$ was the fragmentation pattern was consistent with that shown in Figures 4.6-4.7. Select MS and MS/MS spectra of these compounds are attached in appendix A.

An important benefit provided by the fragmentation patterns, as alluded to previously, is the ability to determine the average chain length of the polystyrene oligomers on either side of the functional group. This is important as the single-stage MS experiment only determines total monomer repeat units per oligomer; in contrast the Poisson distribution of the fragment ions in the MS/MS spectrum reveals the average length of the two oligomer pieces joined by the central silyl functional group. As shown in Figure 4.6, the most abundant $a_n$ fragment ion is at $n = 7$; this indicates that for this selected 15-mer the most abundant distribution corresponds to $x = 7$ and $y = 8$ for the 15-mer, indicating approximately equal chain lengths on either side of the functional group, as expected from the synthetic procedure used.
CHAPTER V

CYCLIC FUNCTIONALIZED POLYSTYRENE ANALYSIS BY MALDI-ToF AND ToF/ToF MASS SPECTROMETRY

5.1. Cyclic Polystyrene.

The ability to differentiate linear polymers from cyclics has been a challenge because isomeric cyclic and linear structures, the latter terminated by unsaturation are possible. Structural analysis may be complicated by the presence of impurities. MS/MS can be employed in such cases to ascertain the correct structure. Macrocyclic polystyrenes with a well defined connectivity can be prepared via anionic polymerization. Here, the combination of MS and MS/MS is used to conclusively determine the structure of the cyclic products resulting from such synthesis by measuring the product mass (MS mode) as well as the product fragmentation pattern (MS/MS mode).

5.2. \( \alpha, \omega \)-diethenylpolystyrene.

This material was characterized using MALDI-ToF and MALDI-ToF/ToF MS techniques, see Figures 5.1 and 5.2. The mass spectrum indicated a Poisson distribution, consistent with the narrow polydispersity (1.17) measured by SEC.
Figure 5.1. MALDI-ToF mass spectrum of the α,ω-dieneylepopolystyrene \( \text{CH}_2=\text{CH-(CH}_2\text{)}_3-(\text{C}_8\text{H}_8)_n\text{C}_6\text{H}_4-(p)\text{CH=CH}_2 \). The main trace shows the m/z 2270-2380 region and the inset the entire mass spectrum. \( \text{Ag}^+ \) was used for cationization. The minor distributions B and C are likely ω-functionalized PS with a \( n\text{-C}_3\text{H}_7 \) group at the initiating chain end (from and impurity in the initiator) and ω-unfunctionalized PS (from incomplete functionalization), respectively.
Figure 5.2. MALDI-ToF/ToF mass spectrum of the silverated 19-mer (m/z 2270) from the α,ω-diethenylpolystyrene depicted in Figure 5.1.
The spectrum contains a distribution corresponding to the $\alpha,\omega$-diethenylpolystyrene and two minor series of low intensity corresponding to unidentified products which are likely $\omega$-unfunctionalized PS and $\omega$-functionalized PS from an impurity in the initiator. The intensity of the minor series was too low to perform tandem MS studies for more definitive structural assignments. The identity of the major distribution was confirmed by comparing calculated the monoisotopic m/z value of the $\alpha,\omega$-diethenylpolystyrene 20-mer with that observed. The calculated value, 2374.293, matches the observed value 2374.298, within 50 ppm difference which is well within the 200 ppm tolerance range for an externally calibrated spectrum on the Ultraflex ToF/ToF mass spectrometer.

Additionally, a MS/MS experiment was also conducted using the Ultraflex ToF/ToF tandem mass spectrometer in order to obtain a reference spectrum of the linear architecture for later comparison with the macrocycle, see Figure 5.2. The oligomer ion at m/z 2270 (19-mer) was selected for fragmentation. The resulting spectrum replicates the characteristics observed with chain-end functionalized polymers, which were discussed in the preceding chapter (see Figure 4.3). These include abundant radical ions and internal fragments of low mass ($b_1^\bullet$, $b_2^\bullet$, $b_3^\bullet$, $b_4^\bullet$, $z_1^\bullet$, $z_2^\bullet$, $J_2^\bullet$, $K_3$) and a series of terminal $a_n/y_n$ fragments at medium and high mass. A noticeable difference, the markedly lower relative abundances of the $y_n$ series, pointing out that the $\omega$ substituted is cleaved easily. The $\omega$ end group is attached to the polymer through a bond connecting two benzylic C atoms. Preferential cleavage of this bond upon CAD leads to the
largest possible \( b_n^* \) radical ion, which can yield \( a_n \) fragments by a combination of unzipping and backbiting steps (Scheme 4.1); however, the \( \omega \) end group has been lost in this process, justifying the low relative intensities of \( y_n \). It is also interesting to note that MS/MS spectra measured with ToF/ToF instrumentation, such as the ones in Figures 4.3 and 5.2, have poorer resolution than MS/MS spectra measured with Q/ToF instrumentation, such as Figure 4.6; however, high mass fragments have greater intensities in the former than the latter spectra.

5.3. Cyclic Functionalized Polystyrene.

The mass spectrum of the cyclic centrally substituted polystyrene, see Figure 5.3, displays a Poisson distribution centered around \( m/z \) 2500. The single major series agrees well with the expected silverated PS macrocycles; however as stated previously, it is difficult to determine unequivocally that the product is cyclic purely from the mass spectrum as an isomeric linear architecture with an extra double bond would also be consistent with the observed \( m/z \) values. The synthetic scheme employed involved cyclization using Grubbs 1\textsuperscript{st} generation catalyst. Based on the mechanism of this reaction, a cyclic product missing and ethylene (C\(_2\)H\(_4\)) unit should be formed.\textsuperscript{53} Indeed, the ions of the reaction product appear 28 \( m/z \) units lower than those in the main distribution of the starting material. For example, the 21-mer of the \( \alpha,\omega \)-diethenylpolystyrene is observed at \( m/z \) 2478.4 (Figure 5.1), whereas the 21-mer of the cyclized product is observed at \( m/z \) 2450.4 (Figure 5.3).
Figure 5.3. MALDI-ToF MS spectrum of the cyclic substituted polystyrene formed by cyclization of the α,ω-diethenylpolystyrene shown in Figure 5.1. The expected cyclic structure is shown in Figure 5.4. Ag⁺ was used for cationization. The main trace shows the m/z 2440-2570 region and the inset the entire mass spectrum.
In order to verify that the observed product was indeed cyclic an MS/MS experiment was conducted using MALDI-ToF/ToF mass spectrometry. In contrast to linear structures, cyclic architectures require the cleavage of at least two bonds for fragment formation. It is therefore not surprising that the CAD spectrum acquired from the cyclic polystyrene ion is markedly different from those of chain-end or in-chain functionalized linear ions; see Figures 4.3 and 4.6 versus Figure 5.4. The silverated 23-mer of the cyclic functionalized polystyrene depicted in Figure 5.4 generates two major fragment ion series upon CAD, arising from the losses of n times the monomer, \((C_8H_8)_n\), or n times the monomer plus an additional CH\(_2\) unit, which have been labeled ◊ and ‡, respectively. Such reactions strongly suggest that fragmentation starts with random CH\(_2\)-CH(Ph) bond cleavages within the PS segment of the macrocycle to create a linear Ag\(^+\) -cationized diradical with one primary and one benzylic PS radical at its termini, as shown in Scheme 5.1. Unzipping (i.e. successive monomer losses) is facile at the primary radical site based on the behavior of the primary radical ions formed from linear polystyrenes. Consecutive intramolecular \(\beta\)-H\(^\ast\) abstraction from one radical by the other leads to fragment ions with one saturated and one olefinic chain end. Scheme 5.1 shows H\(^\ast\) abstraction from the benzylic carbon atom, which should be energetically favorable. The resulting fragment series has been termed (ab\(_n\))\(^n\), because one chain end contains a methylene carbon atom (as in \(a_n\)), the other a benzylic carbon atom (as in \(b_n\)), and one of them is saturated (indicated by \(^n\)).
\[ \diamond = (ab)_n \]

\[ \ddagger = (bb)_n \]

Figure 5.4. MALDI-CAD mass spectrum of the silverated 23-mer from the cyclic centrally substituted polystyrene shown (m/z 2658.5), acquired with the Ultraflex ToF/ToF mass spectrometer.
Scheme 5.1. Major fragmentation pathways of silverated cyclic centrally substituted polystyrene; 1,2-phenyl shift takes place immediately after ring-opening, as shown, or it may occur after one or more monomer units (C₈H₈) have been unzipped.

The second major series can be explained by a 1,2-phenyl migration at the primary radical to form a more stable secondary radical that can undergo β C-C bond scission to lose phenyl propene (118 Da). The latter molecule contains one CH₂ unit more than the monomer. A series of monomer losses may accompany this rearrangement, ultimately leading to a distribution of ring-opened diradical chains with benzylic radicals at both chain ends. Consecutive intramolecular β-H⁺ transfer between the radical sites again yields fragment ions with one saturated and one olefinic chain-end; since now both chain ends carry
benzylic carbons, this series has been named \((bb)_n\). In addition to these major
dissociation pathways, backbiting at the benzylic radicals also takes place, as
revealed by the internal ions observed at m/z 302 \((J_2^*)\) and 419 \((K_3)\). The extent
of this rearrangement is, however, diminished compared to that in linear
polystyrenes.\(^{55,56}\)

In addition to the major series there are several minor series observed as
seen in Figure 5.5. The fragment at m/z 1213.0 is the result of both initial radical
sites dissociating independently, as shown in Scheme 5.2. This process results
in the \((aa)_n\) fragment series. Other minor series that can arise by \(\beta\)-scission of \(H^*\)
or \(Ph^*\) radicals from the initial diradical emerging after ring-opening or the
diradical which has lost phenyl propene via 1,2-phenyl shift, include \((ab)_n\), \((bb)_n\),
\((a_ba)_n\), and \((a_bb)_n\), see Figure 5.5 and Scheme 5.2. All these minor dissociation
pathways are accompanied by a varying number of monomer losses (unzipping),
thereby giving rise to distributions stretching over a wide mass range. The few
remaining minor in Figure 5.5 cannot be identified with confidence and may be
internal fragments.

An important result of the MS/MS experiment is that the fragmentation
pattern of the product obtained by cyclization of the \(\alpha,\omega\)-diethenylpolystyrene is
unique and consistent with a macrocyclic architecture. Such fragmentation can
thus be used as a signature for cyclic PS structures.
Figure 5.5. Expanded trace of the MALDI-CAD spectrum of the silverated PS macrocycle, showing the m/z 1180-1300 region to document the generation of several minor series fragmentation of the 23-mer. Monoisotopic values are given upon top of the isotope clusters.

◊ = \((ab)_n\)
‡ = \((bb)_n\)
\(\Delta = (aa)_n\)
Scheme 5.2. Minor fragmentation pathway for silverated cyclic centrally substituted polystyrene. The backbiting step coproduces J$_2^*$ (m/z 303) and K$_3$ (m/z 419). A β-Ph$^*$ loss may also occur at the primary radical site, leading to (aa)$_n$ fragments. On the other hand, if both initial radicals undergo β-H$^*$ loss, series (ab)$_n$ arises, which gives rise to the satellite at the low mass side of (ab)$_n$". Similarly, β-H$^*$ losses after the CH$_2$=CH-CH$_2$-Ph loss shown in Scheme 5.1 give rise to the (bb)$_n$ satellites at the low mass side of (bb)$_n$".

Polybutadiene (PB) was prepared with two terminating (ω) end groups, H and C₂H₄OH, in order to probe in detail the fragmentation mechanism and elucidate whether cationized polybutadiene preferentially retains or loses the chain-ends during fragmentation. It was determined that polybutadiene fragmentation under MS/MS conditions follows free radical degradation mechanisms as previously reported by Lattimer et al.⁴⁹, ⁶⁰ for the thermal degradation of this polymer. The most abundant fragment ions generated by CAD are internal fragments lacking the original end groups. PB has been studied extensively by pyrolysis methods and some work has also been conducted using secondary ion mass spectrometry (SIMS); however, this work focused on the low molecular weight products formed by radical rearrangements resulting in cyclic structures with molecular ions at < m/z 150.⁴⁹, ⁶⁰-⁶⁹ Here, we focus on fragments > m/z 200 produced by CAD, which are also consistent with free radical degradation mechanisms, and result not in cyclic but
rather internal linear fragment ions, as is demonstrated by the dissociations of the functionalized chain-end PB.

6.2. Polybutadiene Nomenclature.

Polybutadiene has a different monomer repeat unit versus polystyrene which requires it to have a different naming scheme for its fragment ions. Figure 6.1 demonstrates the different designations for polybutadiene; as with polystyrene, α and ω represent the initiating and terminating groups. Differing from polystyrene is the presence of four potential cleavage sites rather than two (see in Figure 4.1). Fragment ions retaining the initiator are represented by lower case a-d and fragment ions retaining the terminator by lower case w-z. Although the preferential cleavages are between CH₂-CH₂ bonds, the nomenclature had to account for all possible cleavages. As with the PS nomenclature, upper case mid-alphabet letters are utilized for internal fragment ions, and all other rules are maintained in regards to radicals and degree of saturation.

Figure 6.1. Nomenclature scheme for chain-end functionalized polybutadiene showing two monomer units to demonstrate the repeat pattern in the naming scheme.
6.3. C₂H₄OH Terminated Polybutadiene.

Figure 6.2 shows the MALDI mass spectrum of a polybutadiene terminated by a C₂H₄OH group. This spectrum contains a Poisson distribution comprised of one major series consistent with the desired product. By terminating the PB with a functional group rather than H, one can distinguish internal fragment ions from fragment ions retaining the terminus, which are indistinguishable if the PB is terminated by H. MS/MS was conducted using a Q/ToF mass spectrometer, see Figures 6.3-6.6. For an unambiguous rationalization of the fragment ions, the all ¹²C isotope was isolated prior to fragmentation. Such isolation the eliminates ¹³C and ¹⁰⁹Ag isotopes and permits the identification of fragments differing in mass by 1-2 Da, which would overlap within an isotopic cluster.

The major fragments from PB result by CH₂-CH₂ bond scissions, Scheme 6.1, which form two resonance-stabilized allylic radicals (dₙ• and wₙ•). In turn these radicals can undergo H• loss to form dₙ and wₙ fragment ions. Alternatively, these radicals can undergo backbiting rearrangements, which move the terminal radical site to an internal position. The migrating H atom originates from an allylic CH₂ group. Since two types of allylic CH₂ groups exist in the interior of the chain, two types of internal radicals may be formed, carrying the unpaired electron in proximal or remote position relative to the original radical site (see Scheme 6.1).
Figure 6.2. MALDI-ToF mass spectrum of the polybutadiene $C_4H_9-(C_4H_6)_n-C_2H_4OH$, showing a Poisson molecular weight distribution, centered at m/z = 1778. A minor series consisting of an unknown product of synthesis denoted at m/z 1874 is observed. Ag$^+$ was used for cationization.
Figure 6.3. MALDI-CAD spectrum of the silverated 25-mer of $C_4H_9(C_4H_6)_nC_2H_4OH$. Closed-shell $J_n$ type ions dominate. Monoisotopic m/z values are given on top of selected peaks. The monoisotopic precursor ion was selected to obtain this spectrum.
Figure 6.4. Expanded trace of the MALDI-CAD spectrum of silverated \( \text{C}_4\text{H}_9(\text{C}_4\text{H}_6)_n\text{C}_2\text{H}_4\text{OH} \), showing the m/z 200–275 region. Monoisotopic m/z values are given on top of selected peaks.
Figure 6.5. Expanded trace of the MALDI-CAD spectrum of silverated C$_4$H$_9$-(C$_4$H$_6$)$_n$-C$_2$H$_4$OH, showing the m/z 430-490 region. Monoisotopic m/z values are given on top of selected peaks.
Figure 6.6. Expanded trace of the MALDI-CAD spectrum of silverated $\text{C}_4\text{H}_9(\text{C}_4\text{H}_6)_n\text{C}_2\text{H}_4\text{OH}$, showing the m/z 630-725 region. This expansion proves that fragment ions differing by 2 m/z units are differentiated if the all $^{12}\text{C}$ precursor ion is selected. Monoisotopic m/z values are given on top of selected peaks.
Consecutive β C-C bond scissions in the rearranged radicals lead to $d_n$, $w_n$, and $J_n$ fragments (from the “proximal” radical) or to $d_n^\bullet$, $w_n^\bullet$, and $J_n^\bullet$ fragments (from the “remote” radical). The radical fragments $d_n^\bullet$, $w_n^\bullet$, and $J_n^\bullet$, can undergo β-H$^\bullet$ loss to ultimately form the corresponding closed-shell products ($d_n$, $w_n$, and $J_n$).

Inspection of the MS/MS spectra in Figures 6.3-6.6 reveals that only relatively small radical ions ($\le 5$ repeat units) survive intact in considerable intensities; the larger ones mainly dissociate by β-H$^\bullet$ loss to the corresponding closed-shell species (or depolymerize by monomer losses).

The less abundant terminal fragment ions $a_n$, $a_n''$, $x_n$ and $z_n$ and internal fragment ions $K_n^\bullet/K_n$ and $L_n^\bullet/L_n$ are rationalized in Schemes 6.2 – 6.4. These fragments are ascribed to cleavages at monomer units incorporated by 1,2-addition. Even under the most favorable conditions for 1,4-addition, ~10% of the monomer units are added in 1,2-fashion.$^1$ Allylic C-C bond cleavage within such a repeat unit (Scheme 6.2) yields $a_n^\bullet$ and $x_n^\bullet$ radical fragment ions, from which closed shell $a_n$ and $x_n$ fragment ions are formed by sequential β-H$^\bullet$ loss. In addition to $a_n/x_n$ which carry double bonds at their chain ends $a_n''/x_n''$ fragments with saturated chain ends are observed (Figures 6.5 and 6.6). Their appearance suggests that the initial radical ions emerging from allylic bond cleavage are held together in Ag$^+$-bound dimers, in which inter-fragment H$^\bullet$ transfer can take place, giving rise to fragments with saturated or unsaturated chain ends, depending on which one retains the Ag$^+$ ion (see Scheme 6.2). The radical ions $a_n^\bullet/x_n^\bullet$ arising by allylic C-C bond cleavage at a 1,2-added monomer may also undergo backbiting rearrangements, as shown in Scheme 6.3.
Scheme 6.1. Fragmentation pathways of the allylic radical ions formed by random homolytic cleavages of the CH$_2$-CH$_2$ bonds in the polybutadiene (PB) chain. All species are ionized by Ag$^+$ (omitted for brevity).
Scheme 6.2. Fragmentation pathways ensuing by allylic C-C bond cleavage at a repeat unit added to the PB chain in 1,2-fashion. All species are ionized by Ag⁺.
Scheme 6.3. Backbiting rearrangements in the radical ions formed by C-C bond cleavage at a PB unit added in a 1,2-fashion (Scheme 6.2). All species are ionized by Ag⁺.
Scheme 6.4. Alternative fragmentation pathways of the $x_n^*$ radical ions formed by allylic C-C bond cleavage at a repeat unit added to the PB chain in 1,2-fashion. All species are ionized by Ag$^+$. 

$\beta$ - H$^*$ loss
Scheme 6.5. Elimination of the vinyl cyclohexane from radical ions $d_n^\bullet$/$w_n^\bullet$ to form shorter radical ions of the same type. All species are ionized by Ag$^+$. 
Such backbiting and sequential β C-C bond scissions provide an additional pathway to the major $d_n^*/d_n$ and $w_n^*/w_n$ series and coproduce four new internal fragment ions series, viz. $K_n^*$, $K_n$, $L_n^*$ and $L_n$. Scheme 6.4, shows an alternative dissociation pathway for the $x_n^*$ radical ions. Here, $x_n^*$ undergoes cyclization which, after β C-C bond scission, results in $z_n^*$ radical ions; the latter may form $z_n$ fragments via β-H* loss or react via a backbiting rearrangement, as shown in Scheme 6.1, to ultimately yield terminal $w_n^*/w_n$ and internal $K_n^*/K_n$ fragment ions. The cyclization of $x_n^*$ via the mechanism of Scheme 6.4 is in competition with the β-H* loss $x_n^* \rightarrow x_n$ (Scheme 6.3), explaining the minuscule relative intensity of $x_n$ and $x_n^*$; a similar pathway is unlikely for $a_n^*$, because it cannot cyclized to an energetically favorable six-membered ring. Note that cyclization is possible also in the major radical ion fragments $d_n^*/w_n^*$ (Scheme 6.5); however, now subsequent β C-C bond scission regenerates the same radicals. This type of mechanism is also observed during metathesis rearrangements, as discussed by Wagener et al.70

The mechanisms proposed to explain the observed fragmentations assume that the cleavage of double bonds and vinylic bonds are not competitive. Dissociation of the central CH$_2$-CH$_2$ bond of 1,4-polymerized PB creates two allylic radicals and should be the lowest energy process. Even at the units incorporated in 1,2-fashion, allylic cleavages are possible, now creating only one allylic radical (consistent with the low abundance of the fragments arising by dissociations at these units).

In addition to the CH$_2$CH$_2$OH terminated PB an H terminated PB was also evaluated by MS and MS/MS to further examine the fragmentation of PB. The mass spectrum of C$_4$H$_9$-(C$_4$H$_6$)$_n$-H showed one distribution corresponding to the desired product as evidenced by the excellent agreement between experimental and calculated m/z values of the monoisotopic silverated 30-mer, Figure 6.7: the calculated monoisotopic m/z is 1786.4 and the observed m/z is 1786.2; these match within ~ 200 ppm which is within the error range for the Reflex III MALDI-ToF mass spectrometer for externally calibrated spectra.

Tandem MS studies were then conducted using the Q/ToF mass spectrometer. As with the previous PB, the all $^{12}$C peak of the parent ion containing $^{107}$Ag$^+$ was isolated for fragmentation. Figure 6.8 shows the full MS/MS spectrum, with Figures 6.9 – 6.11 showing expansions similar to those in Figures 6.4 – 6.6. The MS/MS spectrum shows the distributions determined for C$_4$H$_9$-(C$_4$H$_6$)-CH$_2$CH$_2$OH. Here, the $w_n/J_n$ fragment ions are isomeric due to the terminal group being a hydrogen atom. Similarly, the $x_n$ and $L_n$ series overlap. Further, the $a_n$" and $x_n"$ series are barely above noise level, pointing out that a CH$_2$CH$_2$OH end group is essential for forming Ag$^+$-bound dimmers and, via them, fragments with saturated chain ends.
Figure 6.7. MALDI-ToF mass spectrum expansion of silverated $\text{C}_4\text{H}_9(\text{C}_4\text{H}_6)_n\text{H}$. The inset shows the entire distribution and the main trace an expansion of the m/z 1780 – 1850 range, with the isotopic clusters of the 30- and 31-mers. Ag$^+$ was used for ionization.
Figure 6.8. MALDI-CAD spectrum of silverated C$_4$H$_9$·(C$_4$H$_6$)$_{26}$·H. The monoisotopic [C$_4$H$_9$·(C$_4$H$_6$)$_{26}$·H + Ag]$^+$ ion was mass-selected. Monoisotopic m/z values are given on top of select peaks.
Figure 6.9. Expanded trace of the MALDI-CAD spectrum in Figure 6.8 (region m/z 200-275).
Figure 6.10. Expanded trace of the MALDI-CAD spectrum in Figure 6.8 (region m/z 420-500).
Figure 6.11. Expanded trace of the MALDI-CAD spectrum in Figure 6.8 (region m/z 620-730).
CHAPTER VII

ANALYSIS OF CYCLIC POLYBUTADIENE BY MALDI-ToF and ToF/ToF MASS SPECTROMETRY

7.1. Cyclic Polybutadiene.

Cyclic non-functionalized polybutadiene was analyzed by MS and MS/MS in order to further evaluate the ability of these techniques to differentiate and identify specific polymer architectures. Unlike the linear polybutadiene which contained initiating and terminating groups, the cyclic polybutadiene examined contained neither. The macrocycle was prepared similarly to the cyclic polystyrene discussed in Chapter V, using a starting material that introduced no functionality or substitution in the cyclized product.

MS of the cyclic polybutadiene resulted in a spectrum with a Shulz molecular weight distribution due to the wider polydispersity of the cyclic PB, see Figure 7.1. One major series is observed, which agrees with the cyclic polybutadiene structure expected from the synthetic method used. However, a linear polybutadiene with an additional (for example terminal) double bond would give an indistinguishable spectrum. The spectrum also contains a second, minor distribution which partly overlaps with the main distribution and has very low intensity.
Figure 7.1. MALDI-ToF mass spectrum of the cyclic polybutadiene included in the inset. The main trace shows the entire mass spectrum and the inset an expanded trace of the m/z 1120-1250 range. Monoisotopic masses are given on the expanded trace. Ag+ was used for ionization.
It corresponds to a trace of the pre-cyclic material, viz. sec-C₄H₉-PB-H, whose end groups add up to 58 Da. The ionized oligomers of such a PB would appear 4 Da higher than those of the cyclized product which matches well the low intensity peaks observed at the high mass side of the main series. To ascertain the structure of the main product, an MS/MS experiment was conducted.

The MS/MS experiment was performed with the Ultraflex ToF/ToF mass configuration and resulted in a similar spectrum as that seen for cyclic polystyrene, cf. Figures 7.2 and Figure 5.4. In both cases, intense high mass fragments are observed due to monomer loses; their intensity decreases toward the low mass region, while a low mass distribution increases rapidly in abundance as the mass decreases.

The all $^{12}$C peak of the precursor ion was isolated for CAD as in the previous polybutadiene study. The weakest bond in the macrocycle is the CH₂-CH₂ single bond. Preferential dissociation at such a bond yields a Ag⁺-cationized linear, symmetric diradical, see Scheme 7.1. Monomer loss(es) from this intermediate and sequential intramolecular H-atom transfer ("disproportionation") between the radical sites leads to fragments with the nominal composition (C₄H₉)ₙ and C₄H₇ (methyl terminus) / C₄H₅ (methylene terminus) end groups, as shown in Scheme 7.1. This series has been termed (dd)ₙ according to the nomenclature of PB fragments (Figure 6.1), because both chain ends are terminated with methylene carbons; the double prime denotes that one of the terminal methylene groups is saturated.
\* = (dd)_n^{\text{II}} \quad n = 4-16

Figure 7.2. MALDI-ToF/ToF mass spectrum of the silverated 17-mer (m/z 1025.7), from the cyclic PB shown in Figure 7.1. The fragments labeled by \* and named (dd)_n^{\text{II}} are generated by sequential monomer evaporation of Scheme 7.1. Monoisotopic masses are given next to select peaks.
In the low mass region, quite abundant radical ions are observed ($J_n^\bullet$, $J_n^\bullet-$ 2, $J_n^\bullet+2$ series); this can be seen more clearly in the partial, expanded MS/MS spectrum of Figure 7.3, which also attests that the radical ions are coproduced with closed-shell species ($J_n$, $J_n''$ series). There low mass products are attributed to backbiting rearrangements of the radicals, as summarized in Scheme 7.2. Note that the series $J_n$ from backbiting is indistinguishable from the major fragment ion series ($dd)_n''$. Expectedly, the fragments from backbiting decline in abundance with mass (cf. Figure 7.2). Finally, Figures 7.2 and 7.3 contain a few additional, very minor fragments, which are most clearly discerned in the expanded spectrum. These can be rationalized by cleavages at monomer units added in 1,2-fashion, see Scheme 7.3.

The observation of fragment groups with a range of saturation/unsaturation strongly suggests that the dissociating pieces can be held together by the silver ion sufficiently long for inter-fragment H-atom transfers to occur. This behavior is more pronounced for PB than PS, in agreement with the lower degree of crowding in the former polymer, which makes it easier for the reacting sites to approach each other.
Scheme 7.1. Major fragmentation pathway of silverated cyclic polybutadiene (PB). H\(^*\) loss from the diradical intermediate to form a PB chain that carries double bonds at both chain ends is not competitive.
Scheme 7.2. Backbiting rearrangements at the radical centers created by CH$_2$-CH$_2$ bond cleavage in silverated cyclic PB. The internal J$_n$ series produced this way is identical to the major (dd)$_n^{\text{II}}$ series for the symmetric unsubstituted PB studied.
Figure 7.3. Expansion of the m/z 210-275 region of the MALDI-ToF/ToF spectrum in Figure 7.3 showing more clearly the minor low mass fragments generated from the silverated PB macrocycle.
Scheme 7.3. Internal fragment series resulting from backbiting rearrangements after ring opening of a cyclic PB at a unit added in 1,2-fashion; 1,2- and 2,1-addition are indistinguishable in the symmetric macrocycle studied. Dissociation through ion-molecule complexes will coproduce fragments with more or less H atoms.
CHAPTER VIII

ANALYTICAL METHOD FOR DIFFERENTIATION OF CHAIN-END, IN-CHAIN AND CYCLIC SYNTHETIC POLYMERS.

The ability to quickly and accurately determine compositional and architectural characteristics for a given synthetic polymer is of great value to the synthetic chemist. Here through observation and replication, a method to quickly determine two important characteristics of a polymer, viz. architecture and location of functionality, has been developed.

Three main types of polymeric architecture are chain-end and in-chain functionalized linear polymers and macrocyclic (with or without functionalization) polymers. As was demonstrated in this work, MS and MS/MS techniques are quite efficient at fully providing key compositional features of these three types of polymers. Through the course of this dissertation it was observed that key differences in MS/MS patterns existed. As a result of this observation, additional samples were tested and compared to determine the applicability and repeatability of the initial observations.

For each one of the three architectures mentioned, the corresponding MS/MS patterns differ significantly enough such that one can easily detect the type of functionality present without a through interpretation of the fragment ion
peaks. This chapter will detail the major differences in the MS/MS spectra of the mentioned architectures and compare them with the spectra of appropriately structured polymers.

Figures 4.3, 5.2 and 6.3 show the MS/MS spectra of three different chain-end functionalized polymers. Regardless of initiator, monomer or termination reagent used in the corresponding synthesis, all spectra display very similar fragmentation patterns consistently, a high intensity low mass set of fragment ion peaks is accompanied by less abundant peaks at medium and high masses which decrease in intensity as they approach the parent ion.

Figures 4.6 and 4.7 and Appendix A show the MS/MS spectra of in-chain functionalized polymers. These spectra contain some of the same high intensity low mass fragment ion peaks observed for chain-end functionalized polymers; but now, an additional feature is evident, namely a near Gaussian distribution of mid mass range fragment ions resulting from the dissociations at the internal functional group of the polymer chain.

Figures 5.4 and 7.2 show the MS/MS of a cyclic centrally substituted polystyrene and a cyclic polybutadiene, respectively. The cyclic polymers consistently yield a high intensity high mass set of fragment ion peaks in addition to a lower intensity set of low mass fragment ions. The PS macrocycle leads to a larger number of fragments, because essentially all bonds in the PS frame are cleaved with equal probability. In contrast, vinylic and double bond cleavages are not competitive in the PB frame, restricting the number of available dissociation channels. A unique feature of the cyclic polymers is the sequential
elimination of the monomer units, which is not observed to any significant extent from the linear architectures.

Due to the very limited availability of cyclic polymers, MS/MS characteristics of cyclic polystyrene were examined on both the Q/ToF and the ToF/ToF instruments to verify their reproducibility. As described previously, these two instruments employ different ion activation mechanisms which might influence the resulting fragmentation patterns. For the chain-end and in-chain substituted polymers, essentially identical patterns are observed regardless of instrument. This is confirmed in Figure 8.1 which contrasts MS/MS spectra of chain-end PS acquired using these two instruments. The MS/MS spectrum of the cyclic PS acquired with Q/ToF instrumentation shows the same patterns as observed with the ToF/ToF configuration cf. Figures 8.2 and 5.4. The MS/MS spectra of various in-chain functionalized polymers (Appendix A) show a consistent pattern for these architectures as well. The high mass high intensity set of fragment ions which are not observed from any linear polymer configuration are observed in both spectra and can now be considered the key indicator of whether a polymer is a macrocycle. The fragments from sequential monomer evaporation are more intense in the ToF/ToF spectrum due to overlapping post-source decay, which is significant only within the μs time scale of the ToF/ToF experiments.68

Figure 8.3 shows a stacked comparison of the different architectures to illustrate the unique MS/MS features presented here.
Figure 8.1. Comparison of chain-end polymers of PS having the composition C$_4$H$_9$-(C$_8$H$_8$)$_n$-H showing the same pattern resulting from MS/MS experiments on both the Q/ToF (top, 25-mer), using an $E_{\text{lab}} = 120$ eV, and the ToF/ToF (bottom, 22-mer). Ag$^+$ was used as the cation in both experiments. Both spectra show the described pattern of high mass low intensity radical fragment ions followed by a set of $a_n$ and $y_n$ fragment ions of decreasing intensity as the m/z increases. Fragment nomenclature was omitted for clarity.
Figure 8.2. MALDI-CAD mass spectrum of cyclic functionalized polystyrene, indicating the same pattern observed by MALDI-ToF/ToF mass spectra. The silverated 21-mer (m/z 2449.9, observed) with the Ultima Q/ToF mass spectrometer using Ar as the collision gas at $E_{\text{lab}} = 155$ eV.
Figure 8.3. Comparison of MS/MS spectra of synthetic with different architectures. (a) chain-end functionalized PS, (b) in-chain functionalized PS, (c) macrocyclic PS, centrally substituted and (d) macrocyclic PB. Spectra (a) and (b) were acquired on the Ultima Q/ToF and spectra (c) and (d) on the Ultraflex ToF/ToF mass spectrometer. The collision energies in parts (a) and (b) were 120 eV and 125 eV, respectively. These spectra concern homopolymers; analogous differences are expected for copolymers whose spectra should be more complex, but following the same architectural trends.
CHAPTER IX
CONCLUSION

9.1. In-Chain Functionalized Polystyrene.

The tandem MS spectra of chain-end functionalized polymers and in-chain functionalized polymers allow one to ascertain the corresponding chain architecture. Tandem MS of in-chain functionalized polymers not only confirms the location of the functional group but also unveils the average chain lengths on either of its sides because of preferential backbone cleavage at or near the central functional group.

9.2. Cyclic Functionalized Polystyrene.

The differences between the fragmentation patterns of linear chain-end functionalized polystyrenes, linear in-chain functionalized polystyrene, and macrocyclic functionalized polystyrene are substantial and permit conclusive differentiation of these structures. Intramolecular H-atom migrations are found to be more pronounced in the cyclic PS architecture. This must be the result of the two radicals emerging after initial C-C bond cleavage being on the same chain, not on different chain segments.
9.3. Chain-End Functionalized Polybutadiene.

By performing tandem MS studies on H and C\textsubscript{2}H\textsubscript{4}OH terminated polybutadiene, the dissociation mechanisms and major dissociation pathways have been indentified. There fragments originate largely by cleavages of the allylic CH\textsubscript{2}-CH\textsubscript{2} bonds between repeat units connected in 1,4-fashion; however, the MS/MS spectra also contain fragments indicative of 1,2- or 2,1-additon of the monomer. Internal ions are found to dominate, especially in the medium m/z range. End group information is best obtained from very small d\textsubscript{n}\textsuperscript{*} and w\textsubscript{n}\textsuperscript{*} radical ions (1,2 repeat units) carrying one of the end groups, or at the high mass end where d\textsubscript{n} or w\textsubscript{n} terminal ions have higher relative abundances than the internal fragments.

9.4. Cyclic Polybutadiene.

Due to the absence of internal substituents the MS/MS fragmentation of the cyclic polybutadiene studied yields fewer fragment ions versus either the linear polybutadiene or substituted cyclic polystyrene studied. The degree of backbiting rearrangements in the radicals arising from initial C-C bond cleavage is substantially larger for cyclic PB than cyclic PS. Also for the corresponding linear polymers, backbiting rearrangements are more pronounced with the PB than the PS frame. The combination of MS and MS/MS conclusively characterized cyclic polybutadiene.
9.5. Differentiation of Chain-End, In-Chain and Cyclic Synthetic Polymers.

From the MS/MS fragmentation pattern one can ascertain the general architecture for a given synthetic homopolymer and differentiate whether the material is chain-end, in-chain, cyclic (functionalized or nonfunctionalized). Together with the compositional information which can be derived from the single-stage mass spectrum, this capability can provide immediate feedback to the synthetic chemist. It is noteworthy, that the synthesized architecture can be assessed by virtual inspection of the MS/MS fragmentation pattern without the need to fully assign the fragment ion peaks.


While this work has shown how MS and MS/MS studies have advanced the understanding of polymer characterization there are still areas which require further study and experimentation. A set of experiments designed to investigate the effect of CE on the fragmentation of centrally functionalized polymers to allow the conclusive determination of the lowest energy fragmentation products will allow for a better understanding of the initial cleavages and there long range effects on overall fragmentation. Another area of interest is an additional set of samples comparing higher molecular weight materials to their lower molecular weight analogs. This will provide further information for dielectric relaxation studies as well as the effect of the higher anticipated CE necessary to fragment the higher order materials and the resultant similarities and differences in the
observed fragments. As seen in lower molecular weight polymer studies, as the amount of CE increases the occurrence of more abundant low molecular weight fragment ions also increase while at the same time the larger fragment ions closer in mass to the parent ions are decreased due to the rapid decomposition of the polymer at the higher CE. Higher order polymers may or may not act in the same manner and thus provide larger intact fragment ions allowing for a better understanding of the initial bond cleavages. While there are certainly many additional paths which will allow for further understanding of the various polymers these are just a few observations based on the current work discussed here.


41. Lawrence, E. O. Method And Apparatus For The Acceleration Of Ions. 1934.


Figure A.1. MALDI-ToF mass spectrum chain-end propyl-functionalized polystyrene, showing the m/z 1870-2000 region where the 16- and 17-mers are detected with isotopic resolution. The full spectrum is shown in insert. Na$^+$ was used for cationization.
Figure A.2. MALDI-CAD spectrum of silverated C₄H₉-(C₈H₈)ₙ-CH₃SiC₃H₇-(C₈H₈)ₘ-C₄H₉, where n + m = 13 (m/z = 1658.8), acquired with the Ultima Q/ToF mass spectrometer. The 13-mer precursor ion was subjected to CAD with Ar at $E_{\text{lab}} = 110$ eV.
Figure A.3. Expanded trace of the m/z 780 - 900 region in the MALDI-CAD spectrum of silverated C₄H₉-(C₈H₈)ₙ-CH₃SiC₃H₇-(C₈H₈)ₘ-C₄H₉, where n + m = 13.
APPENDIX B

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