# PART IV

# POLYMER CHARACTERIZATION

# 16

# POLYMER SPECTROSCOPY AND COMPOSITIONAL ANALYSIS

GLADYS DE LOS SANTOS-VILLARREAL AND LUIS E. ELIZALDE

## 16.1 INTRODUCTION

The molecular structure plays an important role in determining the characteristics, properties, and behavior of any polymer during its end use. The elucidation of a polymer structure can be conducted in several ways. Since many years ago, several characterization techniques have been used to analyze basically aspects such as the composition, configuration, and conformation of the chemical groups within the polymer.

By analyzing the composition of a polymer molecule, the nature of the atoms in the polymer chain and the type of bonding can be inferred. Then, the configuration gives an idea about the chemical state of the polymer, the spatial order of the chemical groups, and the optical characteristics and possible behavior of the whole molecule. The conformation characterizes the geometrical state of a polymer.

Polymer chains are made up of sequences of chemical repeating units that may be arranged regularly or irregularly along the backbone conforming the microstructure and morphology of the polymer molecule. Chain alignments, orientation, and entanglements in the molecule play an important role in providing valuable information during qualitative and quantitative analyses.

Ideally, a polymer chain can be represented as in Figure 16.1.

From the composition, the polymer structure can also be inferred if detected differences between two structural elements in the polymer are used. For example, signals for an initiator fraction can be compared with the monomer structure or the functionalizing end group; that is, it is possible to measure the individual number of any component in the polymer chain [1].

Characterization of polymers can be conducted in several ways, from the oldest and simplest techniques to the most sophisticated and complete spectroscopic characterization techniques.

The older methods of noninstrumental chemistry, which still possess high informational value, are those dealing with the chemical analysis of polymers based on searching the number and kind of elements that can occur in a given sample of an unknown polymer.

This chapter is a brief summary of spectroscopic characterization techniques that can be used to identify the polymer structure.

## 16.2 ELEMENTAL ANALYSIS

### 16.2.1 General Principles

Combustion techniques, such as pyrolysis, are one of the most common analytical methods of identification of the constituents of any sample; the structure of the monomers or any other added molecules used during the polymer synthesis can then be subsequently confirmed by spectroscopic techniques.

Analytical methods usually involve, for example, burning of a sample in an oxygen-containing atmosphere, in order to determine amounts of carbon, hydrogen, nitrogen, sulfur, halogens, and oxygen (the last one by difference). Also, dry-ashing, fusion, bomb, and acid digestion can be used to remove organic material and trace metal

*Handbook of Polymer Synthesis, Characterization, and Processing*, First Edition. Edited by Enrique Saldívar-Guerra and Eduardo Vivaldo-Lima.

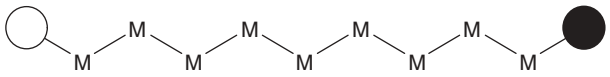


**Figure 16.1** Representation of a linear polymer chain. M represents the repeating unit or the monomer that will be repeated *n* number of times. Clear and black circles can both be either the initiator fragment remaining on each side of the molecule or an end group deliberately added to functionalize the polymer.

**TABLE 16.1 Elemental Composition of Some Common Polymers**

| Polymer | C | H | O | N |
|---|---|---|---|---|
| Polyethylene | 85.63 | 14.37 | — | — |
| Polypropylene | 85.63 | 14.37 | — | — |
| Polyisoprene | 86.88 | 13.12 | — | — |
| Polybutadiene | 88.82 | 11.18 | — | — |
| Poly(vinylmethylketone) | 68.55 | 8.63 | 22.83 | — |
| Poly(ethyleneterephthalate) | 64.90 | 6.30 | 28.00 | — |
| Poly(methyl methacrylate) | 59.98 | 8.05 | 31.96 | — |
| Poly(vinyl acetate) | 55.81 | 7.02 | 37.17 | — |
| Nylon 6, 10 | 68.04 | 10.71 | 11.33 | 9.92 |
| Nylon 6, 6 | 63.69 | 9.80 | 14.14 | 12.38 |
| Polyacrylamide | 50.69 | 7.09 | 22.51 | 19.71 |

residues, which can be further analyzed by spectroscopic techniques.

Elemental composition of some common polymers used to manufacture several products is presented in Table 16.1.

Elemental composition and content of some specific elements is an important analytical tool for polymer characterization, mainly for the characterization of copolymers and polymer blends and the determination of molecular weight of homopolymers [2, 3].

The knowledge of the elemental composition of a polymer can be a useful indicator of the identity of the polymer.

***16.2.1.1 Determination of Copolymer Composition*** Elemental analysis (EA) is a convenient method for determination of copolymer and blend composition if one homopolymer contains an element not present in the second one. For example, EA can be properly used to quantify nitrogen in copolymers containing acrylonitrile units and oxygen in polymeric surfactants such as poly(oxyalkylene). Therefore, for a binary system, every element can be balanced according to the following equation:

$$f_1 + f_2 = 1 \tag{16.1}$$

$$W_{X1} f_1 + W_{X2} f_2 = W_{Xm} \tag{16.2}$$

where $f_1$ and $f_2$ are the weight fractions of components 1 and 2, respectively; $W_X$ is the weight fraction of a given element in the copolymer or polymer blend; and 1, 2, and m denote component 1, component 2, and their mixture, respectively. For every element X,

$$f_2 = \frac{W_{Xm} - W_{X1}}{W_{X2} - W_{X1}} \tag{16.3}$$

If only one of the homopolymers in the copolymer of polymer blend contains the element X, then

$$f_2 = \frac{W_{Xm}}{W_{X2}} \tag{16.4}$$

The values of $W_{Xm}$ are obtained by EA, while those of $W_{X1}$ and $W_{X2}$ are calculated according to the chemical formula of the respective component in the mixture or copolymer.

In this way, EA can be applied to determine monomer composition in copolymers and polymer blends and any other composite material. Although results from EA are comparable to those obtained from spectroscopic techniques such as IR and NMR (nuclear magnetic resonance) spectroscopies, developments in EA are needed to improve the accuracy and precision of the method.

***16.2.1.2 Determination of Molecular Weight*** Commonly used techniques to determine molecular weight of polymers are osmometry, viscosimetry, light scattering, gel permeation chromatography, NMR, etc. (Chapter 17). In all of them, the sample must be soluble in organic solvents or water. However, several kinds of polymers, such as the new and intelligent materials, especially highly thermostable or conductive polymers such as poly(phenylene sulfides), poly(*p*-xylylidene), or polypyrrole, are barely soluble or even insoluble in typical solvents. In such cases, EA is a promising and useful method.

The molecular weight of polymers could be obtained from the analysis of some elements present in the polymer chain; for example, heavy metal salts from the analysis of the metal content.

For polymers with high molecular weight, the results obtained from EA should be consistent with the formula of the repeating unit; however, also for oligomers, molecular weight must be calculated from the formula:

$$M = K1 - (\mathrm{AaBb}\cdots\mathrm{Yy}\cdots) - nK2 \tag{16.5}$$

where $M$ represents the molecular weight and $K1$ and $K2$ denote atoms or groups of atoms at the ends of the macromolecules; therefore, the equation for calculation of degree of polymerization is derived from the simple percentage formula of a given element Y, that is, from the ratio of the weight of element Y contained in a polymer to the total molecular weight, $M$, of a polymer.

The calculation of $M$ depends on structural factors of a given polymer, and the result depends on the correct

estimation of the type of end groups as well as on the choice of the analyzed element Y. Then, the content of the element Y is taken directly from the EA value; hence, the result depends on the precision in the analysis of Y.

## 16.3 INFRARED SPECTROSCOPY

### 16.3.1 General Principles

Infrared spectroscopy is a technique based on the vibrations of atoms of a molecule. In order to get a spectrum, the sample is placed in a sample holder and then an infrared ray is passed through the sample. The signals or peaks that can be appreciated in an IR spectrum correspond to the energy absorbed by the sample at specific frequencies that depend on the molecule's structure. To detect a signal, molecules must change their electric dipole during irradiation, which implies the generation of specific movements between atoms and chemical bonds [4].

Interactions between IR radiation and molecules involve changes in molecular dipoles associated with vibrations and rotations. The atoms in molecules can move and bond lengths can vary; also, one atom can move out of its present plane in stretching and bending movements. Vibrations can involve a change in either bond length (stretching) or bond angle (bending). Depending on the type of movement, there are also symmetric and asymmetric stretchings; each of them is represented as an individual absorption signal in Figure 16.2.

Even for simple molecules, there will be many vibrational signals. A simple molecule can generate a complex spectrum. In a polymer, the repeating unit represents the simple molecule that will be generating a pool of signals or bands. Bands of vibrations associated with the presence of characteristic functional groups are called *skeletal vibrations*, and these skeletal vibrations are likely to constitute a pattern or fingerprint of the molecule as a whole.

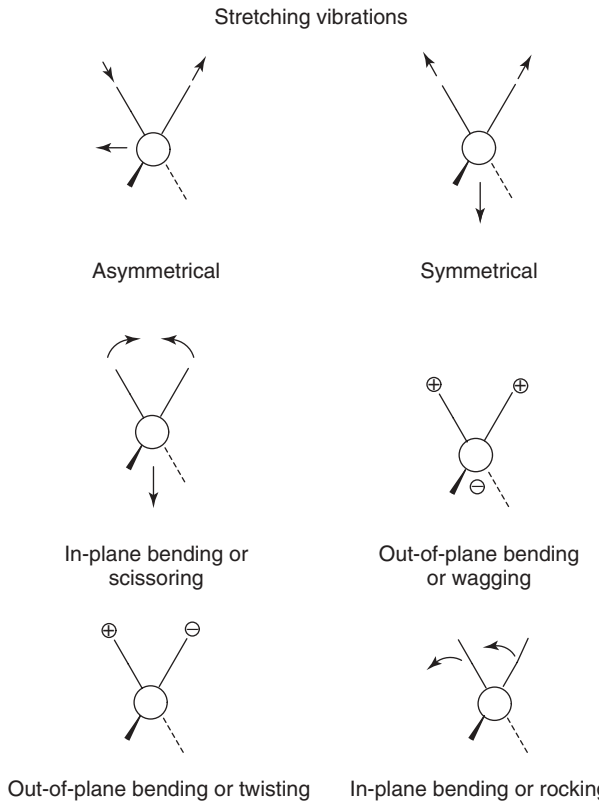


**Figure 16.2** Symmetrical and asymmetrical stretching and bending movements in chemical bonds.

### 16.3.2 Instrumentation

During the 1940s, the first IR spectrometers were commercially available and they relied on prisms to achieve the dispersion of IR irradiation. After 1950, the most significant advances in IR spectroscopy were related to the appearance of Fourier transform (FT) spectrometers. This type of equipment processes the obtained results with an interferometer using the well-established mathematical equation of the FT. Once FT-IR spectroscopy was developed, it was possible to get high quality spectra with minimal data acquisition time. To get spectra, an interferogram is generated. This is a collection of the signals produced by the change of path length between two beams by the use of a moving mirror in the apparatus.

In practice, the radiation emerging from a source is passed through an interferometer and then through the sample before reaching the detector. On amplification of the signal, in which high frequency contributions have been eliminated by a filter, the data are converted and processed by FT. The most common interferometer used in FT-IR is the Michelson interferometer, which consists of two perpendicularly plane mirrors, one of which can travel in a direction perpendicular to the plane. A semireflecting film, the beam splitter, bisects the planes of these two mirrors. The beam splitter material has to be chosen according to the infrared region to be examined.

### 16.3.3 Qualitative Analysis of Polymers

Most organic molecules (including polymers) show absorption bands from the interaction between the IR radiation and the atoms in a chemical bond in the mid-IR region. Most IR studies are related to the analysis of vibrations in the mid-IR region, but near- and far-IR regions also provide important information about certain materials.

Figure 16.3 represents the whole infrared region and its divisions into near-, mid-, and far-infrared spectroscopy.

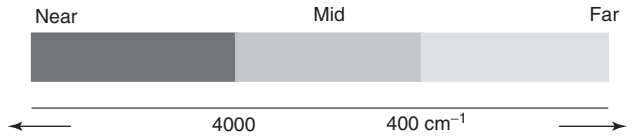


**Figure 16.3** Regions for the study of IR: near, middle, and far. (*See insert for the color representation of the figure*.)

The mid-IR spectrum (4000–400 $cm^{-1}$) can be divided into four main regions, and the nature of a group frequency may generally be determined by the region in which it is located. In Table 16.2, the fundamental vibrations of some common chemical bonds in the mid region are presented and the wavelength and region for each vibration are included.

More details are given in Table 16.3 for each region to identify the main functional groups attached to the polymer backbone.

Each band in an IR spectrum can be assigned to a particular movement in a molecule or group of atoms in a chemical bond. If this is applied to any bond in a molecule, there will be multiple bands even for similar molecules. A spectrum may have a hundred or more absorption bands and there is no need to assign the vast majority; this can be regarded as the "fingerprint" of the molecule.

**TABLE 16.2 Fundamental Vibrations for the Four Major Regions in the Mid-IR**

| Chemical Bond | Wavelength Region ($cm^{-1}$) | Region Name |
|---|---|---|
| X–H | 4000–2500 | Stretching |
| C≡X | 2500–2000 | Triple bond |
| C═X | 2000–1500 | Double bond |
| C–X | 1500–600 | Fingerprint |

**TABLE 16.3 Comments for the Most Common Chemical Transitions during IR Analysis**

| Wavelength ($cm^{-1}$) | Chemical Bond | Comments |
|---|---|---|
| 3700–3600 | O–H | Broad band |
| 3400–3300 | N–H | Sharp band |
| 3000–2850 | C–H | Several stretching bands |
| 2300–2050 | C≡C | Sharp but weak band |
| 2300–2200 | C≡N | Sharp band with medium intensity |
| 2400–2200 | P–H, Si–H | — |
| 2000–1500 | C=C, C=O, C=N | Carbonyl stretching is one of the easiest absorptions to recognize in an IR spectrum |
| 3000–1700 | C–H, N–H, O–H | Stretching bands usually weak in intensity |

### 16.3.4 Quantitative Analysis of Polymers

The Lambert–Beer law is used to relate the amount of light transmitted by a sample to the thickness of the sample. The absorbance of a solution is proportional to the sample concentration:

$$A = lc\varepsilon \tag{16.6}$$

where $A$ is the absorbance; $c$, the sample concentration; $l$, the length of the cell; and $\varepsilon$, the constant of proportionality, which is referred as the molar absorptivity. The absorbance can be defined as

$$A = \log_{10}\left(\frac{I_0}{I}\right) \tag{16.7}$$

where $I_0$ corresponds to the light entering the sample and $I$ is the light transmitted by the sample. Since the absorbance is dimensionless, the transmittance $T$ can be defined as

$$T = \frac{I}{I_0} \tag{16.8}$$

In order to quantify the amount of an analyte or molecule in a given sample, absorbance against concentration must be plotted and the resulting graph should be linear. To analyze a solution of unknown concentration, a calibration procedure must be followed. Solutions of known concentration need to be prepared, a suitable band must be chosen, and the absorbance at this wavenumber can be measured. Then, a calibration graph must be prepared that relates the measured absorbance of an unknown sample to its concentration.

For quantification of a functional group present in a sample or a polymer, several factors need to be considered. The first factor relates to the absorbance value of the band to be quantified, this must be neither too weak nor too intense. The second one refers to the choice of a suitable absorption peak that does not overlap any other peak. Another problem can be the presence of asymmetric shapes of the bands; in this case, peak heights cannot be used because the baseline will vary from sample to sample and peak area measurements must be used instead. Quantitative measurements need to be carried out on absorbance spectra.

IR spectroscopy can be used to measure the number of functional groups in a molecule or polymer backbone since absorptivity of the bands corresponding to the groups is proportional to the number of groups that are present in the sample. This approach can be used, for example, to measure the number of methylene groups in polyethylene (PE), determining molecular weight by measuring the stretching in the C–H bond at 1467 $cm^{-1}$. Quantification usually is

performed for samples in solution because analysis of solid samples results in more errors due to scattering of radiation.

### 16.3.5 Sampling Methods

There are several types of methods to obtain an IR spectrum depending on the nature of the sample to be analyzed. Transmission spectroscopy is based on the absorption of IR radiation at specific wavelengths as the radiation passes through a sample. With this technique, it is possible to analyze liquids, solids, or gaseous samples. This is the most common method; the samples can be placed in a cell in solution, dispersed in NaCl, KBr, $CaF_2$ (for water-soluble samples), or CsBr. Liquid thin films can also be analyzed using a drop of the sample, which will be sandwiched between two IR KBr cells and placed in a holder. When samples are analyzed in a solvent solution, several factors must be considered: the solvent has to dissolve the whole sample with a minimum of solvent–solute chemical interactions and it should not strongly absorb IR radiation.

### 16.3.6 Attenuated Total Reflectance (ATR)

When the sample to be analyzed is a solid or liquid, the intensity of the spectral features is determined by the thickness of the sample, which cannot be more than a few tens of micrometers. An attenuated total reflection accessory operates by measuring the changes occurring in a totally reflected IR beam when it comes into contact with a sample. An IR beam is directed onto an optically dense crystal with high refractive index at a certain angle, creating an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. This evanescent wave protrudes only a few micrometers (0.5–5 μm) beyond the crystal surface and into the sample. Consequently, there must be good contact between the sample and the crystal surface. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits at the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an IR spectrum as shown in Figure 16.4.

### 16.3.7 Diffuse Reflection IR Fourier Transform Spectroscopy (DRIFT)

As a nondestructive method, DRIFT has been used to map the millimeter-scale of some surfaces, giving some mapping data that require geometric corrections for quantitative interpretation [5].

### 16.3.8 FT-IR Microscopy

To study very small samples, it is possible to pass an IR beam through a sample holder where the sample has been fixed by a microscope. This technique can be used to characterize samples with particle size less than 10 μm. IR radiation is focused onto a sample placed in a microscope and then collected by an objective that produces an image within the barrel of the microscope. In addition, by switching mirrors in the optical train, the microscope can be converted from transmission mode to reflectance mode.

### 16.3.9 Real-Time IR Spectroscopy

The final IR spectrum observed by a user for any sample (organic molecule or polymer) consists of a series of scans. An IR spectrum is composed generally of at least 20 scans. However, the combination of multiple scans with FT-IR provides a powerful real-time (RT) method for monitoring chemical changes, such as an in situ polymerization reaction. The rate of UV curing and photopolymerization, for example, can be easily calculated by analyzing the quantitative appearance or disappearance of a specific absorption band.

RT-FTIR spectroscopy has been a valuable technique to monitor reaction yields during UV curing processes, since IR spectra can be acquired before, during, and after exposure to the light without moving or changing the sample. In cases where an infrared feature corresponds to a chemical bond involved in the photopolymerization process, obtaining multiple spectra each second during the curing process can provide an accurate measure of the kinetics involved in the reaction and the extent of conversion [6].

RT-FTIR is used most of the times for photopolymerization reactions as a well-suited methodology to follow the

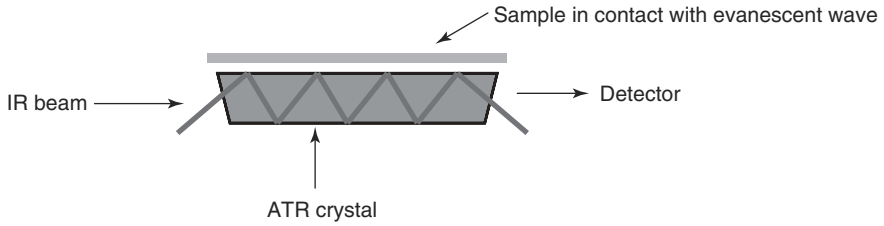


**Figure 16.4** Mechanism of IR analysis by attenuated total reflectance. (*See insert for the color representation of the figure*.)

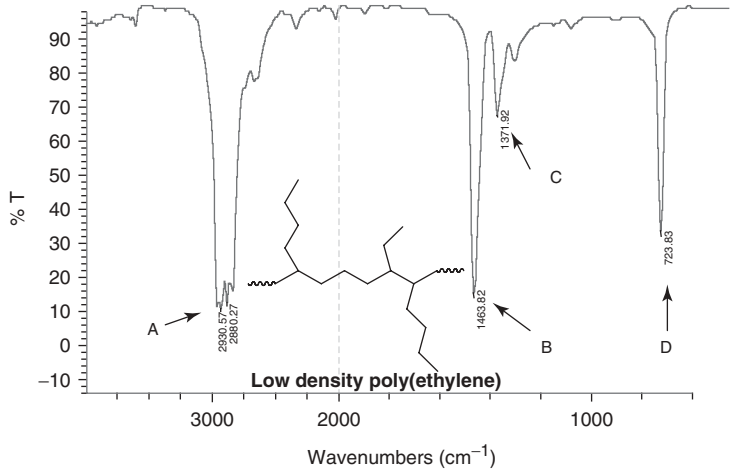


**Figure 16.5** IR spectrum for low density polyethylene.

polymerization of monomer mixtures leading to the formation of either crosslinked copolymers or interpenetrating polymer networks. Analysis can be performed following the disappearance of a specific band on UV light exposure [7]. This technique provides RT analysis with high sensitivity, short response time, and versatility, giving as a result a powerful tool of investigation [8].

### 16.3.10 Discussion of IR Spectra for Polyethylene

The IR spectrum for low density PE in Figure 16.5 shows four high intensity absorption bands. The first band (A) corresponds to the symmetric and asymmetric stretchings of methyl and methylene groups. Then, symmetrical bending of methyl (B) and methylene (C) groups of the polymer is observed, and the last band (D) corresponds to the stretching movement of the methylene groups in the backbone of the polymer chain.

However, the IR spectrum for high density PE in Figure 16.6 shows some differences, since there are three main signals for a molecule having the same chemical composition. Band (A) represents the symmetrical stretching for methyl and methylene groups, and band (B) corresponds to the symmetric methylene bending. The last one (C) is ascribed to the absorption of the methylene groups.

### 16.3.11 Conclusions

FT-IR spectrometry is an instrumental technique of analysis that presents significant advantages over other analytical

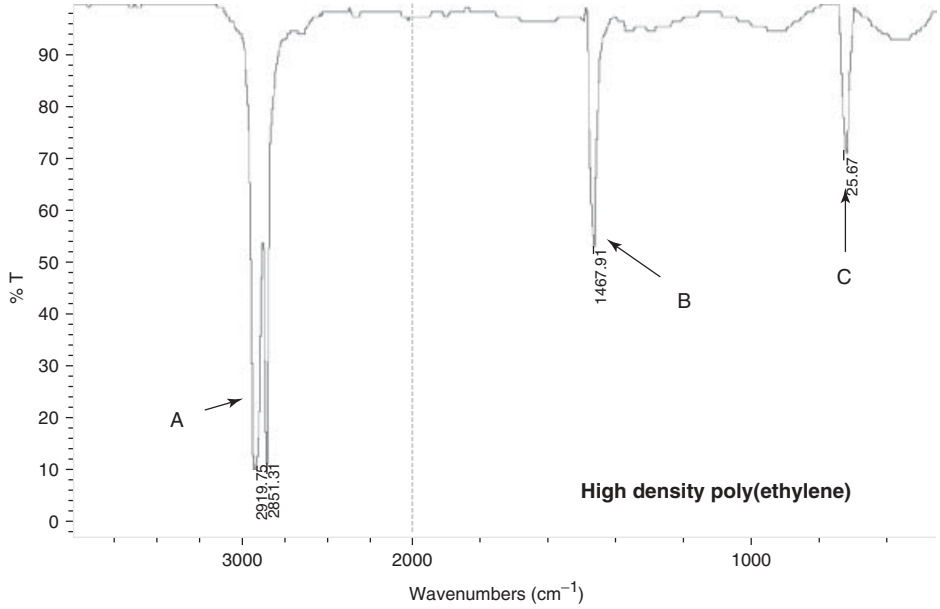


**Figure 16.6** IR spectrum for high density polyethylene.

techniques; it has good signal-to-noise ratio, good capacity of obtaining absorption spectra of low energy, and, therefore, also bands of absorption of weak intensity.

IR has been used in addition to many other techniques to analyze polymer and copolymer compositions, either by itself or in addition to other techniques. Recently, the characterization by spatial differentiation of submicrometer domains in poly(hydroxyalkanoate) copolymer by the combination of atomic force microscopy (AFM) and IR spectroscopy was reported [9, 10]. This new capability resulting from the combination of two single instruments enables the spectroscopic characterization of microdomain-forming polymers at levels not previously possible.

## 16.4 NUCLEAR MAGNETIC RESONANCE OF POLYMERS IN SOLUTION

NMR is now a powerful analytical technique that has widespread applications in all areas of chemistry, including polymer characterization. Using NMR for elucidating the molecular structure of an unknown sample of polymer, accurate information can be obtained for qualitative and quantitative analyses of polymeric materials.

NMR is basically another form of absorption spectrometry that can be used in addition to IR, or UV, spectrometries. It is based on the absorption of electromagnetic radiation under appropriate conditions in the radio-frequency region at frequencies defined by the nature of the sample. Absorption is a function of each nucleus in the molecule. The main purpose of this technique is to provide information for the identification of organic molecules by studying the magnetic properties of nuclei.

All nuclei carry a charge. In some nuclei, this charge spins on the nuclear axis, and this circulation of nuclear charge generates a magnetic dipole along the axis (Fig. 16.7).

The angular momentum of the spinning charge can be described in terms of spin numbers, having the values of 0, 1/2, 1, 3/2, etc., where 0 denotes "no spin" like in $^{12}C$, $^{16}O$, $^{32}S$, etc. For these elements, NMR experiments cannot be conducted since there is no spin angular moment and thus no magnetic moment to be analyzed. Several nuclei, however, such as $^{1}H$, $^{3}H$, $^{13}C$, $^{15}N$, $^{19}F$, $^{29}Si$, and $^{31}P$ have spin numbers $I$ of 1/2 and a uniform spherical charge distribution, so all of them can be studied by NMR. Because of the abundance of the $^{1}H$ isotope (of about 100%) in all types of organic molecules, $^{1}H$ is obviously the most studied nucleus, resulting in relevant information for the proper determination of molecular structures. In quantum mechanical terms, the spin number $I$ determines the number of orientations that a nucleus may assume in an external uniform magnetic field in accordance to the formula $2I + 1$. For example, considering the proton whose spin number

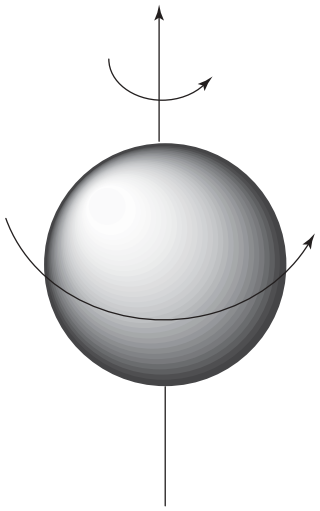

**Figure 16.7** Magnetic dipole generated by the spinning charge of a proton nucleus.

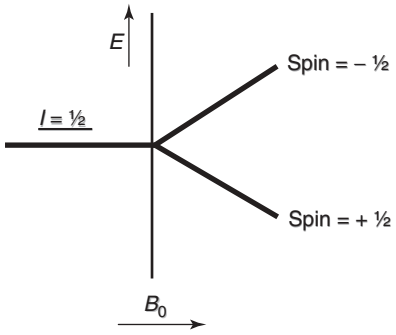


**Figure 16.8** Two energy levels for a proton in a magnetic field $B_0$.

$I$ is 1/2, there are two energy levels as can be seen in Figure 16.8.

The nuclear magnetic moment, $\mu$, is given as

$$\mu = \frac{\gamma I h}{2\pi} \tag{16.9}$$

where $h$ is the Planck's constant and $\gamma$ is the gyromagnetic ratio, which is a constant for each particular nucleus.

The most observed nuclei by NMR are $^{1}H$ and $^{13}C$, both of them having spin number $I = 1/2$ and two magnetic states, characterized by a set of magnetic quantum numbers.

An irradiation with a frequency of 100 MHz is needed at a magnetic field $B_0$ of 2.33 tesla (T) for the proton to be excited from the lower energy state to the higher energy state.

### 16.4.1 Chemical Shift

Considering the hydrogen atom as an example, the electron shielding process, when the nucleus of the observed atom is placed in a magnetic field, can be analyzed.

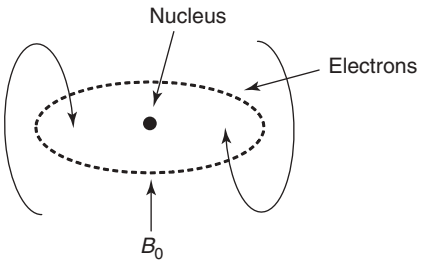


**Figure 16.9** Motion of electrons by a magnetic field and around a nucleus.

In the presence of the magnetic field, the electron circulates in anticlockwise direction to $B_0$. The motion of the electron is similar to an electric current flowing in a closed loop, and as such, it is associated with a secondary magnetic field that opposes the applied field $B_0$. Thus, the observed resonance frequency of a proton appears to be slightly less than that predicted from the value of $B_0$ and the gyromagnetic ratio of a proton (Fig. 16.9).

Therefore the chemical shift, $\delta$, is defined as the nuclear shielding divided by the applied field, and thus is only a function of the nucleus and its environment. It is always measured from a suitable reference compound:

$$\delta = \frac{B_{\text{ref}} - B_{\text{sample}}}{B_{\text{ref}}} \times 10^6 (\text{ppm}) \qquad (16.10)$$

where $B_{\text{ref}}$ is the magnetic field at the reference nuclei and $B_{\text{sample}}$ is the field at the sample nuclei. Chemical shift $\delta$ in parts per million (ppm) is a molecular parameter depending only on the measurement conditions and not on the magnetic field or frequency applied for the determination.

According to the previously described equation, tetramethylsilane (TMS) is usually the recommended reference compound for analyses of $^1$H and $^{13}$C NMR. This has several advantages: it is chemically inert, symmetrical, and soluble in most organic solvents; it gives a single sharp signal and absorbs at higher field than almost all protons from organic molecules. Usually, the absorption peak of TMS is fixed at 0.00 Hz or ppm.

The methyl protons of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS), acetonitrile, and dioxane have been sometimes used as external standards.

Extensive tables and charts of chemical shifts have been published in the literature, providing useful information about the region where specific groups of protons appear in the spectrum. Figure 16.10 shows the chemical shifts observed for the most common functional groups in organic molecules.

As previously mentioned, $^{12}$C nucleus is not magnetically active for NMR analyses, but $^{13}$C with $I = 1/2$ can be detected by this technique. However, since the natural abundance of $^{13}$C is about 1.1% that of $^{12}$C, and its sensitivity is only about 1.6% that of $^1$H, the overall sensitivity of $^{13}$C compared with $^1$H is about 1/5700. Even when this characteristic can be considered as a disadvantage in comparison to $^1$H NMR, $^{13}$C NMR is being extensively used with excellent results for characterization of plenty of samples and their molecular arrangement.

The same transient and local magnetic fields affect both nuclei in the same way with respect to chemical shift: carbon as well as proton. The presence of equivalent carbon atoms in a molecule results in a discrepancy between the number of peaks and the actual number of carbon atoms in the molecule. $^{13}$C shifts are related to the hybridization and substituent electronegativity and are affected by substitutions as far removed as the $\delta$ position. In the benzene ring, for example, pronounced shifts for $^{13}$C are caused by substituents in the ortho, meta, and para positions.

The range of shifts generally encountered in routine $^{13}$C studies is about 240 ppm, and, as mentioned for $^1$H NMR, the location of regions for particular absorption

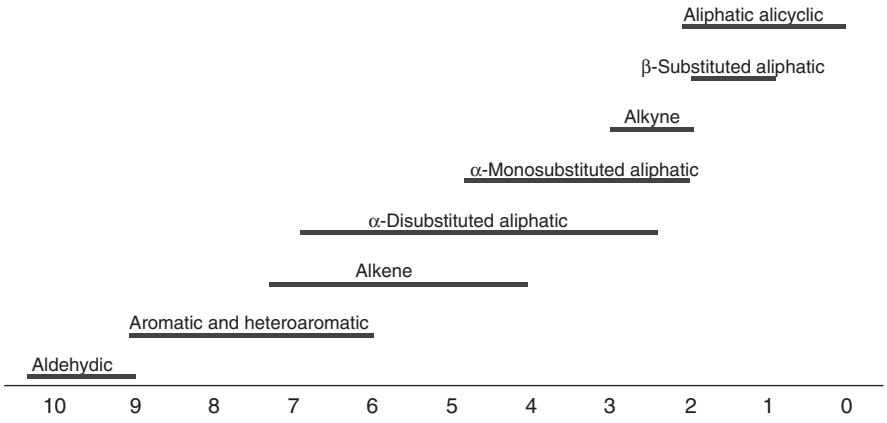


**Figure 16.10** $^1$H NMR, general regions of chemical shifts in organic molecules.

peaks depend on the type of substituents and adjacent carbon atoms in the studied molecule.

The chemical shift for usual polymers lies in the range of 0–200 ppm and provides the possibility of observing detailed structural differences.

### 16.4.2 Spin-Spin Coupling

NMR spectra consist not only of individual lines but also of groups of lines termed *multiplets*. The splitting of a peak into a multiplet arises from nuclear interactions called *spin-spin coupling*.

It has been suggested that the mechanism involves the bonding electrons. The discussion about two adjacent atoms can be centered in the spin state of the nucleus of atom A, which is coupled to the nucleus of spin state of atom B, via the bonding electrons. The energy level of spin A depends on the orientation of spin B, so two spectral lines are generated. The magnitude of the interaction is given by the spin-spin coupling constant $J_{AB}$, which is expressed in hertz and is independent of the applied field.

$^{13}C$ NMR spectra are usually obtained under $^{1}H$ decoupling conditions because in this way the spectra become much simpler. The low abundance of $^{13}C$ nuclei results in a low possibility of observing $^{13}C$–$^{13}C$ spin-spin coupling. This makes the spectra simpler, but information on C–C connectivity in the chains is scarcely obtainable.

Besides $^{1}H$ and $^{13}C$ nuclei, several other NMR observable nuclei have been utilized in polymer analysis, because $^{15}N$, $^{19}F$, $^{29}Si$, and $^{31}P$ nuclei are found in some important polymers.

### 16.4.3 Instrumentation

High resolution NMR spectrometers can be categorized into continuous wave (CW) and pulsed FT, both of them requiring a radio-frequency source and a magnetic field. As illustrated in Figure 16.11, which shows an FT-NMR spectrometer, the tube containing the sample solution is placed in a probe that is set in the magnetic field. Then, the sample tube is rotated about its axis using an airflow. The radio-frequency radiation is transmitted by a coil on the probe and detected either by the same coil or by a separate one. When the resonance condition has been achieved, the sample absorbs energy from the radio-frequency radiation and the resulting signal is detected on the receiver coil, amplified, and recorded. Using this procedure, the spectrum is obtained.

After the excitation pulse is turned off, the spin system emits the energy, returning to thermal equilibrium of the spin states. The signal observed in this process is called the *FID* (*Free Induction Decay*) *signal*, which is a spectrum recorded in the time domain.

### 16.4.4 Sample Preparation

Analysis of polymers involves dissolving a polymer sample in a suitable solvent and introducing the polymer solution in an NMR sample tube. The sample solution must be clear and free of suspended dust and impurities.

For $^{1}H$ and $^{13}C$ NMR experiments, the samples must be prepared in totally or partially deuterated solvents to avoid the interference created by solvent signals. In most of the modern NMR instruments, the deuterium signal from the solvent is used by an NMR lock system to avoid fluctuation of the magnetic field strength. Recent advances in NMR provide spectra with high resolution and high signal-to-noise ratio. This enables one to take the spectrum of the sample solution at very low concentrations.

A routine sample for proton NMR consists of about 5–20 mg of the sample in 0.4 ml of deuterated solvent in a 5 mm o.d. NMR test tube. $^{13}C$ NMR spectra are obtained under the same experimental conditions than proton analyses, but with a sample amount of 100–200 mg.

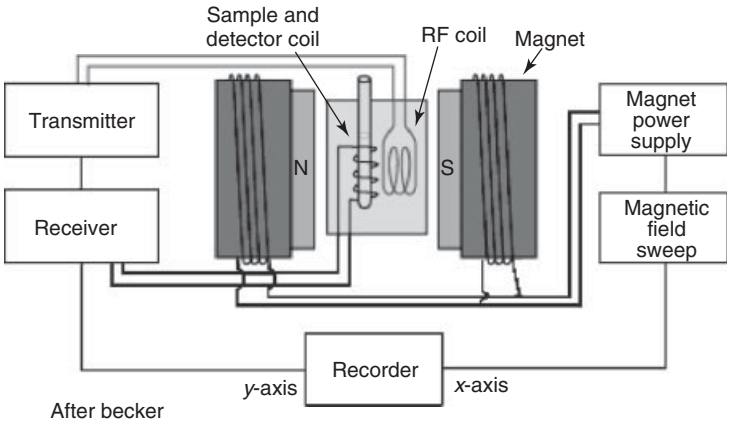


**Figure 16.11** Diagram of an FT-NMR spectrometer. (*See insert for the color representation of the figure*.)

### 16.4.5 Qualitative Analysis of Polymers

NMR spectroscopy is an analytical tool extremely useful to follow the synthesis of polymers or supramolecular systems, from starting materials, intermediates, to products, and their three-dimensional conformation. The rapid development of advanced techniques has substantially broadened the application of NMR to the study of polymers [11–13].

Examples of $^1$H NMR spectra of polystyrene (PS) and its monomer styrene (S) are shown in Figure 16.12a and b, respectively. The faster decay of the signal from PS than that from the monomer is due to faster relaxation of the spins or shorter relaxation times. The difference is reflected as a difference in peak width.

Several characteristic signals appear in the $^1$H NMR spectra for styrene: the doublet at 5.25 ppm corresponding to one of the methylene protons from the vinyl fraction of the molecule and the doublet at 5.8 ppm for the other proton of the same group. Then, a pair of doublets is also observed at 6.65–6.75 ppm, corresponding to the proton of the carbon atom directly attached to the aromatic ring. The signals at 7.2–7.4 ppm can be attributed to the five aromatic protons in the monomer molecule.

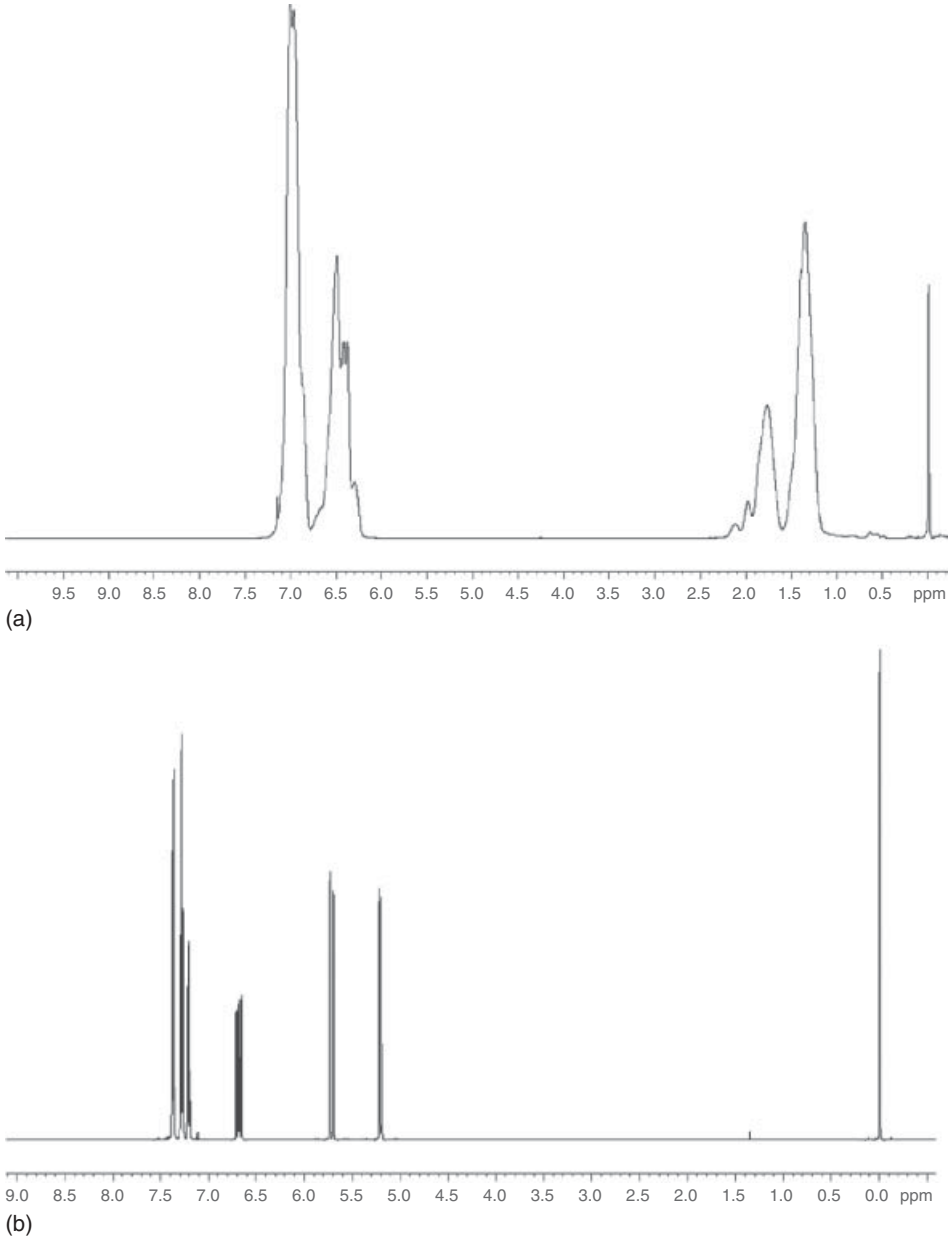


**Figure 16.12** (a) $^1$H NMR spectrum for polystyrene. (b) $^1$H NMR spectrum for styrene.

By comparing this spectrum with that of the corresponding polymer, in the PS spectrum, the disappearance of the signals for the vinylic protons can be clearly detected and a new broad band for aliphatic protons is observed. As mentioned, broad peaks can be attributed to the relaxation time of the atoms in the molecule and the high concentration of protons in the observed region of the polymer chain.

As an additional example, for the structure in Figure 16.13, Figure 16.14 shows the $^1$H NMR spectrum for a sample of poly(dimethylsiloxane) (PDMS-H) obtained by anionic polymerization of hexadimethyltrisiloxane ($D_3$) initiated by butyl-lithium in the presence of chlorodimethylsilane [14].

In Figure 16.13, the chemical structure of the obtained polymer can be appreciated, while Figure 16.14 shows the $^1$H NMR spectrum for PDMS-H.

For this polymer, a complex broad peak corresponding to the methyl protons (d) placed over the silicon atom in the polymer chain is observed at 0–0.2 ppm. Then, at approximately 0.5 ppm, there is a peak assigned to the methylene group (c) belonging to the butyl fraction from the initiator and next to the first silicon atom in the polymer chain. Protons (b), represented as a multiplet, have been assigned to the methylene groups from the butyl fraction. The last signal (a) is a triplet that corresponds to the methyl group, also from the initiator fraction, in the PDMS-H chain. Since the PDMS-H synthesized in this experiment has low molecular weight (<10,000 g/mol), the proton from the silane functionalizing group (e) placed at the end of the polymer chain can be easily detected.

Plenty of applications of NMR in polymer structure elucidation research can be found in the literature; the

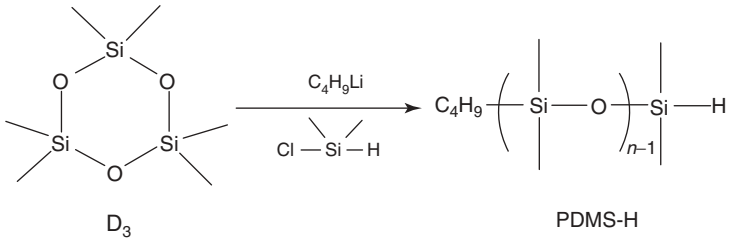


**Figure 16.13** Chemical structure representation of the synthesized poly(dimethylsiloxane) (PDMS-H).

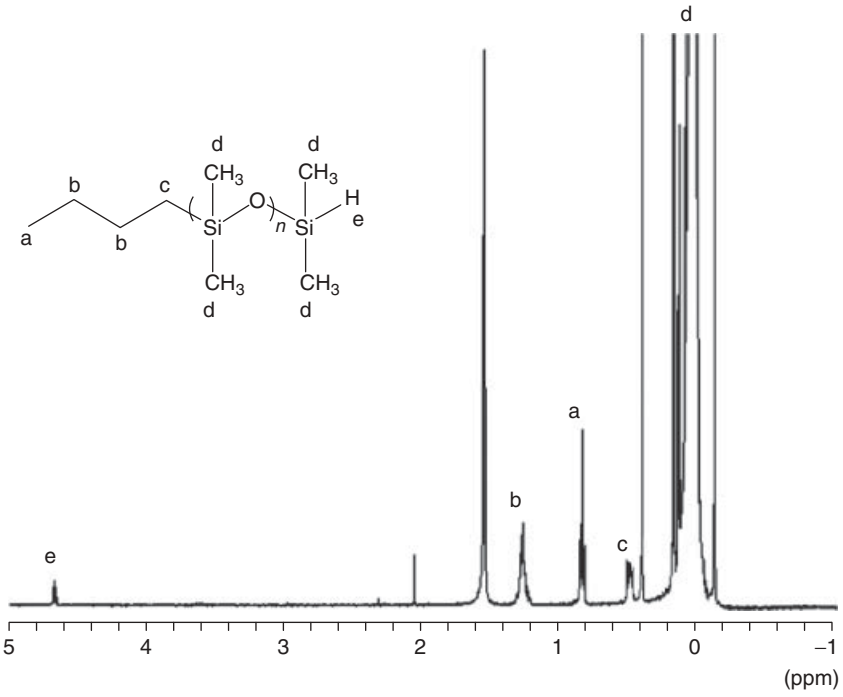


**Figure 16.14** $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ in ppm) for synthetic poly(dimethylsiloxane) (PDMS-H).

reports cover a broad range of polymeric systems, including copolymers [15].

There are three sources of interference with sample analysis via $^{1}H$ NMR: residual protons in deuterated solvents, water solubilized in the sample solution, and any other impurity present at the moment of the analysis. Sometimes the content of water represents an important problem to solve, particularly in the case of diluted samples in which the absorption peaks will have low intensity.

Deuterated chloroform is one of the most commonly used NMR solvents since it is the cheapest one due to the presence of only one deuterium atom in its molecule. However, besides water, some impurities dissolved in chloroform can sometimes occur, such as trichloroethane, dichloromethane, dibromomethane, acetonitrile, acetone. Water can also be introduced in the solvent during storage and its content increases gradually with time.

Solutions of polymer samples sometimes contain small amounts of low molecular weight impurities, including unreacted monomer and the solvent used for polymerization or purification.

Elucidation of the polymer structure depends on the nature of the chemical bonds between the atoms in the polymer chain. Sometimes, bonding can be inferred from the $^{1}H$ and $^{13}C$ chemical shifts and from the spin-spin coupling between nuclei. The first step in an NMR study of a polymer is to assign NMR to specific structural features of the polymer. Observing the following clues, it is possible to get the exact or the most approximate molecular structure of an unknown polymer via NMR analysis.

- Whenever possible, chemical shifts of low and high molecular weight of the same polymer must be compared.
- It is important to estimate the polymer chemical shifts using additivity relationships.
- It is easier to assign a structural model when the synthesized polymer has known structural or compositional features that establish chemical shift resonance–structure relationships.
- To highlight specific sites on the polymer chain, the polymer can be enriched with $^{13}C$ or with deuterium sites instead of protons.
- Computer simulation and comparison with spectra reported in the literature can be done in order to predict chemical shifts and multiplicity of some peaks, calculated on the basis of assumed polymerization kinetics and statistical models.
- Two-dimensional techniques revealing correlations between nuclei can be employed.

Two-dimensional NMR techniques can be satisfactorily used to determine the coupling between nuclei and to reveal the chemical shifts of these nuclei.

### 16.4.6 Two-Dimensional NMR Analysis

For many years, researchers have been using NMR in addition to other analytical techniques, such as IR or MS (mass spectrometry), to characterize and to quantitate organic molecules. In that sense, an NMR spectrum is normally obtained under standard conditions. In science, molecular complexity in organic synthesis has increased and normal experiments have been run at an increasingly higher magnetic field strength, resulting in the overlapping of signals.

Multidimensional NMR experiments offer a new way to resolve even highly overlapping resonances into readily interpretable multiplets and permits chemical shift assignments to be made in a simple manner [16–18].

Homonuclear correlation spectroscopy (COSY) offers a way to identify spin-coupled pairs of nuclei, even when structural information for the specific molecule under study is completely lacking. Correlation is established using homonuclear coupling, so the technique essentially shows the same information in one plot as in 1D homonuclear decoupling experiments. A potentially useful application for this class of analysis is the spin-spin correlation of $^{13}C–^{13}C$, but there are two main problems with this approach. The first one is related to the need of the presence of $^{13}C$ nuclei in two adjacent atoms. In natural abundance, this probability is too low, so the experiment is highly insensitive and suitable only for concentrated samples rich in carbon content. The second one relates to the relative weakness of the spin-coupled peaks from $^{13}C–^{13}C$ pairs when compared with the peaks from isolated $^{13}C$ nuclei.

It is also possible through selective heteronuclear single-frequency decoupling to correlate bonded carbons and protons (HETCOR, Heteronuclear Correlated Spectroscopy) as an alternative to identify all directly bonded and long-distance carbon-proton pairs in a molecule.

In addition, a common experiment in NMR is the study of the relaxation behavior of nuclei, such as the nuclear Overhauser effect (NOE), to identify the local neighborhood of the nucleus and to infer information about the distances between atoms. From this, NOESY (nuclear Overhauser and exchange spectroscopy) and ROESY (rotating-frame Overhauser spectroscopy) methods are derived. The NOESY experiment correlates peaks by means of the nuclear Overhauser enhancement and identifies pairs of nuclei that are sufficiently close together in space to relax by their dipole–dipole interaction. This technique is not applicable in determining stereochemical assignments but may be extremely useful in determining the chain conformation in a study of an alternating copolymer such as that formed by styrene and methyl methacrylate [19].

Multidimensional NMR techniques, such as 2D-INADEQUATE, can allow the direct tracing out of carbon

skeletons of molecules, even without any prior partial knowledge of the structure of the molecule [20].

### 16.4.7 Quantitative and Compositional Analyses

NMR is a very useful technique in organic synthesis, not only as a method for characterization but also as an analytical tool that offers the capability of providing information about molecular architecture particular of each polymer, which cannot be obtained by any other technique [21].

Using NMR, it is possible to quantify the following.

***16.4.7.1 Functional Groups and Compositions in Polymers, Copolymers, or Polymer Blends*** The chemical shifts observed in an NMR spectrum characterize the environment of the nucleus under observation. The identification and quantification of functional groups such as pendant groups can be performed following the ratio between a characteristic peak for a proton or a carbon of that group and the proton or carbon of a known group in the polymer [22].

A specific example illustrates this point [23, 24]. The composition of the product copolymer in Figure 16.15 was determined by the relationship between the integrals of the two hydrogen atoms having a chemical shift of 8.0 ppm, which corresponds to the photochromic monomer, and the three hydrogen atoms at 3.25, 2.93, and 2.78 ppm of the oxyrane ring (Fig. 16.16).

In addition, NMR can be used to determine the composition of a mixture by measuring the intensities of peaks belonging to each component in it. The components

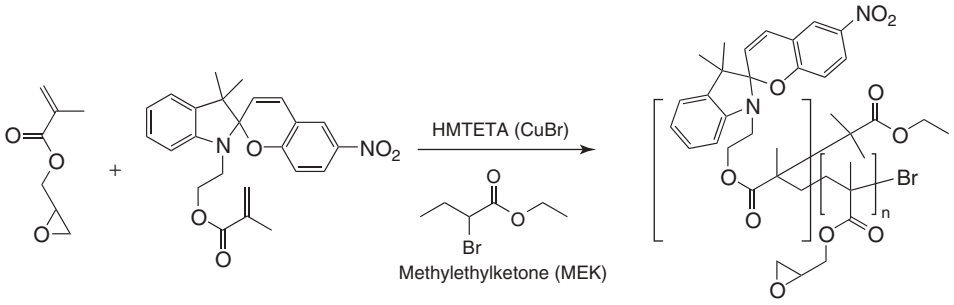


**Figure 16.15** Chemical structure of poly(glycidyl methacrylate-*r*-1′-(2-methacryloxyethyl)-6-nitro-3′,3′-dimethylspiro-[2*H*-1]-benzopyran-2,2′-indoline). HMTETA: 1,1,4,7,10,10-Hexamethyltriethylenetetramine; MEK: Methyl ethyl ketone.

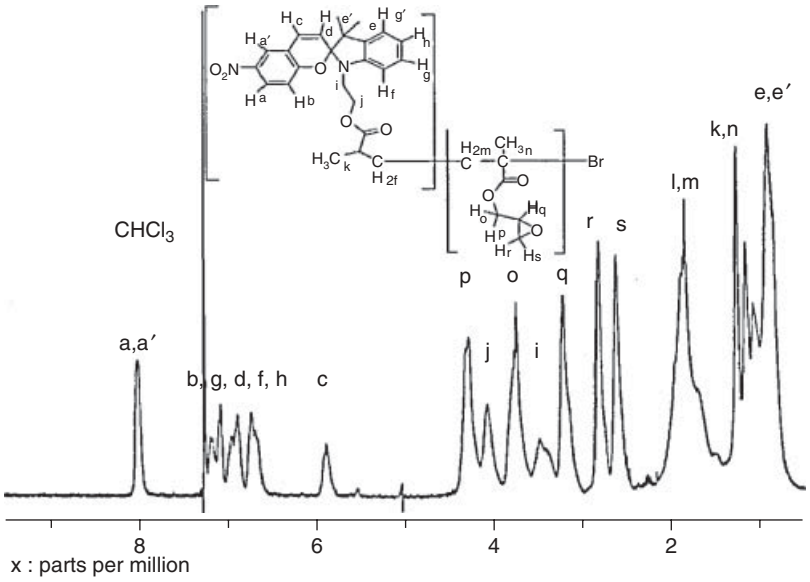


**Figure 16.16** $^{1}$H NMR of the copolymer poly(glycidyl methacrylate-*r*-1′-(2-methacryloxyethyl)-6-nitro-3′,3′-dimethylspiro-[2*H*-1]-benzopyran-2,2′-indoline). *Source*: Reprinted with permission from Flores M, Elizalde LE, de los Santos G. *J Macromol Sci Pure Appl Chem* 2009;46:223 [23]. Copyright 2009 Taylor & Francis.

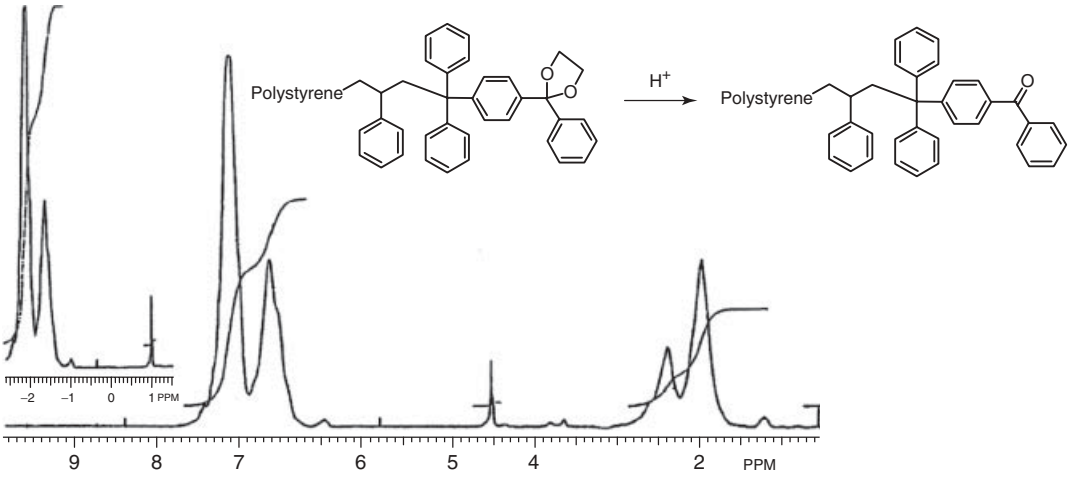


**Figure 16.17** $^{1}$H NMR for benzophenone (before deprotection) end-functionalized polystyrene synthesized by anionic polymerization. *Source*: Reprinted with permission from Kalyuzhnaya E, de los Santos G, Elizalde LE, Guerrero R. *J Appl Polym Sci* 1996;61:1055 [25]. Copyright 1996 John Wiley and Sons.

may be different chains in a polymer blend, different monomer units in a copolymer, or a polymer included in small amounts as an additive.

***16.4.7.2 End Groups*** The end groups of a chain are determined by all the chemical steps in a polymerization reaction. The determination of the end-group structures is often extremely valuable in studying those processes. As an example, Figure 16.17 shows the resulting polymer from the anionic polymerization of styrene. During this addition polymerization, the growth of the PS chain was conducted as a living process, which was then terminated by a benzophenone derivative [25]. Monofunctional PSs were prepared by this anionic polymerization. The $^{1}$H NMR spectra of the prepared polymers contain, besides ordinary signals of PS, a signal at 4.03 ppm belonging to the methylene of the 1,3-dioxolane ring. The amount of the end group was calculated from the ratio between these two signals [26].

Quantitatively, the end-group intensity relative to the main-chain intensity gives the number-average degree of polymerization directly.

***16.4.7.3 Stereochemistry (Tacticity)*** Vinyl polymers were the first to be classified stereochemically and studied by NMR. When the relative configuration of neighboring units among carbons in a polymer chain is considered, several stereochemically different diastereomers are possible. The first two diastereomers shown in Figure 16.18 are termed (i) *isotactic* and (ii) *syndiotactic*.

In isotactic polymers, all the groups have the same configuration, while in the second one, the syndiotactic stereoisomer, the pending groups in the polymer chain are alternating.

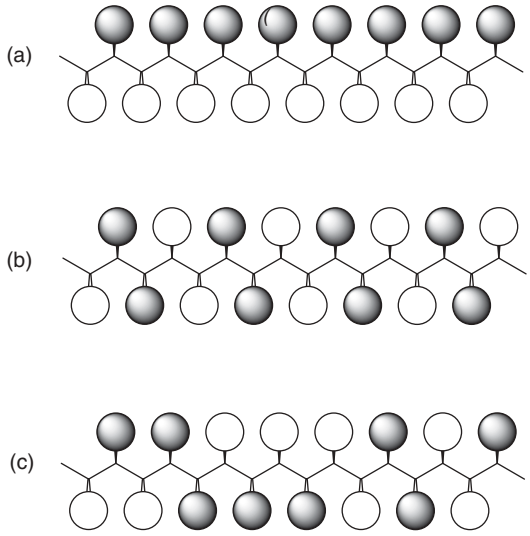


**Figure 16.18** Schematic representation of (a) isotactic, (b) syndiotactic, and (c) atactic polymers.

There also exists the possibility of having a polymer with an irregular arrangement of the pending groups, which is termed *atactic*.

Examples of these three types of structural arrangements are known; in general, stereoregular polymers are synthesized by the use of coordination catalysts, whereas atactic polymers are formed by uncoordinated catalysts such as free radicals or free ions. Stereoregular polymers are often partially crystalline, and usually, even the isotactic and syndiotactic isomers have different properties. For example, isotactic poly(methyl methacrylate) (PMMA) has a glass-transition temperature of 35 °C, while that of the syndiotactic polymer is 105 °C.

In most NMR spectra of stereoregular polymers, the key factor for the analysis is the methylene group in the polymer chain. In an isotactic molecule, the two methylene protons are not identical, and therefore, two resonances must be observed. For a syndiotactic chain, the two protons in the methylene group are identical by symmetry, so only one resonance is observed [27].

The $^{13}C$ spectra of stereoregular polymers show a single sharp line for each chemically distinct carbon because, within each type of chain, each monomer residue is identical. However, the chemical shifts for isotactic and syndiotactic chains are not the same.

## 16.5 MASS SPECTROMETRY

### 16.5.1 General Principles

MS is a useful analytical technique to analyze and determine the molecular structure of an organic compound by observing its fragmentation pattern. This can be applied to qualitative or quantitative analysis.

In a common experimental routine, an organic sample is introduced to the instrument through the gas phase of a gas chromatograph that is kept in contact with an ion source resulting in the ionization of the sample molecules. At this point, positive ions are selected by particle size and conducted to the mass analyzer. Then, the resulting fragments are analyzed and the data processed. Finally, through the analysis of the sharp lines observed in the spectrum, there will be enough information to determine the molecular structure.

A mass spectrum is a two-dimensional representation of signal intensity of a fragment and the ratio between mass ($m$) and charge ($z$) of the fragment ($m/z$). The intensity of the peak correlates with the abundance of the corresponding ion.

Often but not always, the molecular ion peak can be appreciated in the mass spectrum, resulting from the detection of the intact ionized molecule. It is usually accompanied by several peaks at lower $m/z$ caused by fragmentation of the molecular ion to yield fragment ions.

The peak showing the highest intensity in a mass spectrum is called the *base peak*. In most cases, this signal is normalized to 100% relative intensity.

There are several aspects about the performance of the mass spectrometer that must be considered:

*Sensitivity* This term refers to the overall response of the instrument to the investigated analyte when the apparatus is operated under well-defined methods. The sensitivity is defined as the slope of a plot of analyte concentration versus signal strength.

*Detection Limit* This term is often confused with sensitivity since it defines the smallest flow or the lowest amount of analyte necessary to obtain a signal that can be distinguished from the background noise.

*Signal-to-Noise Ratio* This parameter describes the uncertainty of an intensity measurement and provides a quantitative measure of a signal's quality by quantifying the ratio of the intensity of a signal relative to noise. Noise can be obtained from different sources: impurities due to sample handling, impurities from previous samples run by gas chromatography, column bleed, and the electronics in the instrument. Consequently, signals and their intensities can be influenced by noise.

### 16.5.2 Electron Ionization

The fundamental principle of MS is based on the impact of electrons onto neutral gaseous molecules that are usually obtained from the transfer line placed at the end of a gas chromatograph. These neutral gaseous molecules undergo ionization (electron ionization (EI)), generating positive, negative, and neutral charged fragments. Electron impact ionization or electron impact is still an important technique to analyze molecules with low to medium polarity and also organic nonionic compounds.

### 16.5.3 Sample Introduction

There are different types of instruments that can be attached to the EI source for MS analysis. The most commonly used technique consists of the analysis of a gaseous sample obtained from the gas chromatograph. However, other introduction systems, such as reservoir inlets and direct insertion probes, are also frequently used.

Table 16.4 summarizes existing sample introduction systems for EI-MS.

### 16.5.4 Other Ionization Processes

As mentioned before, MS is a useful technique to analyze unknown organic molecules by studying their fragmentation pattern. However, since there are several requirements for samples to be analyzed, when an organic molecule is unsuitable to be studied by gas chromatography, another suitable analytical technique can be chosen, for example, liquid chromatography (LC), direct injection probe (DIP), and direct exposure probe (DEP).

A specific problem in MS analysis of polymers, which can make it difficult to be performed by normal techniques, is related to the fact that the most common procedure to introduce the sample in the ionization chamber is to take it from the gaseous stream at the end of a gas chromatograph; however, the usually high molecular weight and covalent

**TABLE 16.4 Sample Introduction Systems for EI-MS**

| Inlet System | Principle | Types of Analytes |
|---|---|---|
| Reservoir inlet | Sample is vaporized in a heated reservoir | Liquids with low to medium boiling points |
| Direct insertion probe (DIP) | Sample is heated directly into the ionization chamber without the use of GC | Solids, waxes, thermally unstable molecules, liquids with high boiling temperature |
| Direct exposure probe (DEP) | Sample particles are heated on a metal filament | Solids of extremely low volatility and that are thermally unstable |
| Gas chromatograph (GC) | Sample is obtained from the eluent gas stream and injected directly into the ion source | Most volatile organic compounds and volatile mixtures of organic molecules |
| Liquid chromatograph (LC) | Connected via particle beam interface | Used for analytes that cannot be separated by GC due to its high polarity |

bonding in the polymer makes the material prone to be degraded before entering the ionization chamber. This translates into clogging of the chromatographic column. To avoid such circumstances, several techniques associated to MS, which also analyze the fragmentation pattern, have been developed and some of them are described in the following sections.

***16.5.4.1 Matrix-Assisted Laser Desorption/Ionization (MALDI)*** This topic has received much attention since several years ago, especially with regard to its application to polymer analysis.

In MALDI (matrix-assisted laser desorption/ionization), the ionization process occurs in two steps: an initial primary ionization followed by a secondary reaction [28]. During primary ionization, the ions are formed after the sample has absorbed the energy from the laser beam, and then, upon continuing laser beam irradiation, the analyte undergoes secondary neutralization reactions with free electrons until they become singly charged. Meanwhile, neutral analyte molecules evaporate and are charged by secondary protonation reaction. In this way, they can be detected.

Since its introduction by Karas and coworkers in 1987 [29], MALDI has become a powerful analytical technique for the study of thermolabile or unstable molecules and nonvolatile samples such as polymers.

A MALDI mass spectrum can be very useful when applied to polymers, because important structural information can be obtained, such as the nature of the repeating unit; the presence of end groups; molecular weights; molecular weight distributions; some information about branching; information on the nature of random, ordered, and block copolymers; and the presence and nature of some additives in the polymer [30].

From 1987 up to now, there are many reports in the literature related to the satisfactory use of MALDI to characterize polymer chains [31]. The first reports of polymer characterization by MALDI were published by Tanaka et al. [32] in 1988 describing the characterization of poly(propylene) and poly(ethylene glycol) (PEG) using MALDI.

The mass spectrometer most widely used with MALDI is the TOF-type (time of flight) mass spectrometer, mainly due to its large mass range. MALDI-TOF is equipped with an ion mirror to reflect ions, which uses an electric field, doubling the ion flight path and increasing thus the resolution [33, 34].

In the field of living radical polymerization, MALDI-TOF has been highly useful for characterization of polymers prepared by nitroxide-mediated radical polymerization (NMRP) [35, 36], atom transfer radical polymerization (ATRP) [37], and reversible addition-fragmentation chain transfer polymerization (RAFT) [38, 39]. The modern MALDI-TOF-MS permits fast and accurate determination of a variety of polymer characteristics [40].

***16.5.4.2 Analysis of Nonpolar Polymers*** MALDI analysis of hydrocarbon polymers is a challenging task since they are chemically inert due to the absence of functional groups in their chains, making their characterization somewhat difficult. In that sense, PS is one of the most common synthetic polymers analyzed by MALDI-MS due to the presence of the phenyl functionality in PS that facilitates its easier ionization compared to other nonpolar nonfunctional polymers such as poly(butadiene), poly(isoprene), polyethylene, or poly(propylene).

***16.5.4.3 Tandem Mass Spectrometry*** Tandem MS is an early technique that involves the isolation of a specific ion followed by its fragmentation, which occurs in a collision cell, resulting in a fragment ion spectrum. This technique has been satisfactorily used for the study of peptide sequences [41], but it can also be used for the analysis of synthetic polymers.

In 2009, Crecelius et al. [42] reported the characterization of homopolymers, copolymers, and star-shaped polymers by tandem MS. The main aim of the work was the analysis of end-group functionalization, which can be determined faster by this technique.

In polymer analysis by MALDI-related techniques (such as tandem MS), there are two possibilities to obtain fragment ion spectra. The first one uses the traditional MALDI

instrument equipped with a reflector to collect metastable fragments that are formed during ion acceleration out of the ion source in the field-free region. This fragmentation is termed *postsource decay* (PSD). The main disadvantage of a PSD spectrum is the long acquisition times, since recording a mass spectrum can take up to 1 h, after which unresolved peaks still remain. The other possibility is the collision-induced dissociation (CID), which requires the placement of a collision cell in the field-free region of the analyzer. This last technique has been successfully used in polymer characterization in recent years. There are many published works related to the investigation of structural features and end-group determination for a variety of polymers. Homopolymers such as PMMA, linear and branched [43]; PEGs [44, 45]; and PSs [46] have been characterized by MALDI-CID analysis.

## REFERENCES


1. Koenig JL. *Spectroscopy of Polymers*. 2nd ed. New York: Elsevier Science Inc.; 1999. p 12.
2. Dobkowski Z. Appl Polym Anal Charact 1992;2:363.
3. Rabindranath M, Sukumar M. J Polymer Mater 1993; 10(3):183.
4. Silverstein RM, Bassler GC, Morrill TC. *Spectrometric Identification of Organic Compounds*. 5th ed. New York: John Wiley & Sons, Inc.; 1991. p 91.
5. Leue M, Gerke H, Ellerbrock R. Soil Sci Soc Am J 2011;75(5):1626.
6. Lowry S, Weesner F. *Spectroscopy Solutions for Materials Analysis*. Special Issue, Aug 1, 2011 (e-journal). http://www.spectroscopyonline.com/spectroscopy/FT-IR+Spectroscopy/Using-Real-Time-FT-IR-to-Characterize-UV-Curable-O/ArticleStandard/Article/detail/735157.
7. Decker C. Polymer News 2005;30(2):34.
8. Pereira HL, Machado F, Lima LE, Pinto JC. Macromol Symp 2011;299/300:1.
9. Curtis M, Lo M, Kjoller K, Prater C, Noda I. Appl Spectros 2011;65(10):1145.
10. Prater C, Kjoller K, Shetty R, Dazzi A. Laser Focus World 2011;47(3):52.
11. Matyjaszewski K, Gnanou Y, Leibler L. Macromolecular engineering. In: Matyjaszewski K, Gnanou Y, Leibler L, editors. *Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications*, Volume 3. Weinheim, Germany: Wiley VCH; 2007. p 1937.
12. Ibett RN. *NMR Spectroscopy of Polymers*. 1st ed. Glasgow, UK: Blackie Academic & Professional; 1993.
13. Hatada K, Kitayama T. *NMR Spectroscopy of Polymers*. Berlin, Germany: Springer; 2004.
14. González M, Elizalde LE, Saldívar E. Synthesis of block copolymer poly(dimethylsiloxane-b-methylmethacrylate) by anionic ring opening polymerization and ATRP. 2nd US – México Meeting Advanced Polymer Science and XXIV SPM National Congress; 2011 Dec 7–11: Cancún, Q. Roo.
15. Shu J, Li P, Chen Q, Zhang S. Macromolecules 2010; 43(21):8993.
16. Croasmun WR, Carlson RMK. *Two-Dimensional NMR Spectroscopy*. 2nd ed. Hoboken NJ: John Wiley & Sons; 1994.
17. Hatcher P, Bialk H, Sleighter R, McKee G, Liu Z, Byrne C. 234th American Chemical Society National Meeting, David J. Clifford Memorial Symposium; 2007 Aug 19–23; Boston, MA, USA.
18. Webb G. Int J Plast Technol 2004;8(2):371.
19. Mirau PA, Bovey FA, Tonelli AE, Heffner SA. Macromolecules 1987;20:1701.
20. Webb G. Macromolecules 2005;38(7):2775.
21. Webb G. J Polym Sci A Polym Chem 2005;43(5):1100.
22. Webb G. Polym J 2007;39(2):118.
23. Flores M, Elizalde LE, de los Santos G. J Macromol Sci Pure Appl Chem 2009;46:223.
24. Webb G. MACRO 2004, International Conference on Polymers for Advanced Technologies; 2004 Dec 15–17, Thiruvananthapuram, India.
25. Kalyuzhnaya E, de los Santos G, Elizalde LE, Guerrero R. J Appl Polym Sci 1996;61:1055.
26. Webb G. Eur Polym J 2006;42(6):1455.
27. Webb G, editor. *Modern Magnetic Resonance*. Volume 1. Heidelberg: Springer; 2006. p 553.
28. Batoy SMAB, Akhmetova E, Miladinovic S, Smeal J, Wilkins CL. Appl Spectros Rev 2008;43:485.
29. Karas M, Bachman D, Bahr U, Hillenkamp F. Int J Mass Spectrom Ion Process 1987;78:53.
30. Hercules DM. Anal Bioanal Chem 2008;392:571.
31. Pasch H. Polymer Preprint 1996;37(1):319.
32. Tanaka K, Waki H, Ido Y, Akita S, Yoshida Y, Yoshida T, Matsuo T. Rapid Comm Mass Spectrom 1988;2:151.
33. Ladaviere C, Lacroix-Desmazes P, Delolme F. Macromolecules 2009;42(1):70.
34. Nonaka H, Ouchi M, Kamigaito M, Sawamoto M. Macromolecules 2001;34(7):2083.
35. Farcet C, Belleney J, Charleux B, Pirri R. Macromolecules 2002;35(13):4912.
36. Dourges M, Charleux B, Vairon J, Blais J, Bolbach G, Tabet J. Macromolecules 1999;32(8):2495.
37. Shen X, He X, Chen G, Zhou P, Huang L. Macromol Rapid Comm 2000;21(16):1162.
38. England RM, Rimmer S. 238th American Chemical Society National Meeting, Stimuli-Responsive Polymer Materials and Composites; 2009 Aug 16–20; Washington, DC, USA.
39. Wang D, Zhou Q, Pu H, Yang G. J Polym Sci A Polym Chem 2008;46(11):3756.
40. Dempwolf W, Flakus S, Schmidt-Naake G. Macromol Symp 2009;275–276:166.
41. Nesvizhskii AI, Vitek O, Aebersold R. Nat Methods 2007;4:787.

42. Crecelius AC, Baumgaertel A, Schubert US. J Mass Spectrom 2009;44:1277.
43. Jackson AT, Bunn A, Chisholm MS. Polymer 2008;49:5254.
44. Miladinovic S, Robotham SA, Wilkins CL. Anal Bioanal Chem 2008;392:585.
45. Jackson AT, Slade SE, Thalassinos K, Scrivens JH. Anal Bioanal Chem 2008;392:643.
46. Polce MJ, Ocampo M, Quirk RP, Leigh AM, Wesdemiotis C. Anal Chem 2008;80:355.