THE SADTLER GUIDE TO THE NMR SPECTRA OF POLYMERS

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INTRODUCTION

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY has firmly established itself as one of the primary analytical tools available to chemists today. Its analytical potential has not, as yet, been fully realized and new applications of the method are still being uncovered. NMR is primarily a structure-determining tool and nowhere has it found greater utility than in the elucidation of complex organic molecules. One class of compounds where its impact has been impressive is in the study of polymers.

NMR can be used to study polymers in three basic ways:

    (1)   It can be used for qualitatively identifying polymeric types.

    (2)   It can be used to identify polymer mixtures and give a reasonable estimate of the per cent composition of the individual components.

    (3)   It can be used to determine the microtacticity of portions of the polymer chain; that is, it can be used to identify the configurational sequence of short segments of the polymer backbone.

The main purpose of this book is to enable the user to readily characterize specific polymers. At first, this might appear to be an easy task, but due to the wide variety of polymers extant and the large number of variations of the basic polymer types, the problem is found to be complex. Other analytical methods (e.g. Infrared Spec., Thermal Gravimetric Analysis, etc.) also provide useful information about polymers but of a type unlike that provided by NMR. Used in conjunction with NMR, these other methods provide a broad analytical capability for the elucidation of the molecular structure of polymers, copolymers and resins.

A second objective of this volume is to illustrate the analysis of copolymers and polymer mixtures with an approach to quantitation. In many cases, it will be seen, a fairly accurate quantitative analysis may be carried out in a matter of minutes. The last application of the NMR method, the determination of tacticity, will be discussed only briefly since the fine structure of polymers is best studied with instruments of higher resolution (e.g. 220 MHz). Tacticity will, however, be mentioned in the text wherever its effects can be observed in a specific spectrum.

In this volume we seek mainly to illustrate the spectra of a variety of common polymers and copolymers and to indicate the features which make them unique. We will attempt to do this in a systematic fashion, using a minimum of organic and polymer chemistry, so that those whose background is mainly analytical, can utilize this book in its entirety.

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NMR THEORY AND DEFINITIONS

It is not the intent of this volume to give a complete description of the NMR method, its theory and applications. This has already been done in a variety of other texts. Rather, the usefulness of this text is in its specialized approach to the description and analysis of the NMR spectra of Polymers.

These spectra may be utilized for identification purposes by individuals with a minimum of training just as infrared spectra are used by the majority of chemists.

It would be useful at this point to describe briefly some of the terms and concepts which are important to the application of this method to the analysis of polymers.

I. **NMR THEORY:** Certain atomic nuclei behave as if they are small magnets. When these nuclei are placed between the poles of a magnet, they will align themselves either with or against the applied magnetic field (H_o). The nuclei now exist in two (or more) orientations and it is possible to observe energy transitions between these high and low energy states. This is done by irradiating the sample with energy in the radio-frequency range. In order for the low energy nuclei to absorb energy, the fundamental NMR equation (Eq. 1) must be obeyed:

$$\nu / H_o = \gamma / 2\pi$$

Equation 1

where: ν = irradiating frequency
H_o = strength of applied field
γ = magnetogyric constant

Briefly, this equation states that for every value of the applied field, there is only one frequency at which the nuclei can absorb energy. When this absorption of energy occurs, the nuclei are said to have been brought into resonance, hence the origin of the term NUCLEAR MAGNETIC RESONANCE. This absorption of energy can be detected and displayed on an oscilloscope or chart recorder as a "peak".

Although many nuclei possess magnetic properties, for a variety of reasons only certain of them are susceptible to the NMR method. Among the nuclei which are best studied by this technique are ^1H, ^{19}F, ^{13}C and ^{31}P. Because the magnetogyric constant (γ) for each nucleus is unique, each will resonate at a different frequency (ν) at a constant applied field (H_o). Conversely, if the frequency is kept constant, each nucleus will require a different applied field in order to satisfy the equation. Ordinarily, only one type of nucleus can be studied at one time. Since protons are by far the most commonly observed nuclei, especially in polymer NMR, no further mention of heteronuclear magnetic resonance will be made.

II. THE CHEMICAL SHIFT: Originally it was believed that all protons regardless of their chemical environment would resonate at the same frequency. In actuality it was observed that protons in different structural positions in a molecule came into resonance at different frequencies. The difference between the frequencies (or fields) at which two different nuclei come into resonance is termed the CHEMICAL SHIFT.

The chemical shift arises because protons in different structural environments are shielded to differing extents by the extranuclear electrons. Thus individual protons may experience local magnetic fields which are somewhat less than the total applied magnetic field. This SHIELDING effect also varies according to certain time dependent effects such as the proximity of other molecules in the sample solution or their orientation in the magnetic field. These effects can often be averaged out by using non-viscous solutions and by spinning the sample. What cannot be averaged out is the relative position in a molecule in which a proton is situated. Thus the chemical shift may be regarded as a sensitive measure of the electron density around each type of proton.

An NMR spectrometer is capable of "seeing" different proton groups based mainly on differences in their chemical shifts. Because the protons in tetramethylsilane (TMS) are among the most shielded protons found in organic molecules, a small amount of TMS is incorporated in all sample solutions as an internal reference and chemical shifts are measured in relation to the resonance of this material. Such measurements are usually expressed in the (δ) delta scale in units of parts per million (ppm). TMS is arbitrarily designated as 0.0 ppm. and most other proton groups occur DOWNFIELD from TMS. On a 60 MHz instrument, each 60 Hz of separation from the TMS band is designated as 1.0 ppm. The typical maximum range for protons is about 12 - 15 ppm. The NMR spectroscopist identifies proton groups, with designations such as methyl (CH_3-), methylene ($-CH_2-$), methine ($-CH-$), olefinic ($C=C-H$), aromatic ($\emptyset-H$), aldehydic ($-C(=O)-H$), etc. With a little practice, the chemist will soon learn the range of chemical shifts for each proton type but for more accurate assignments and for predicting the shifts of the protons in a specific molecule, many good CHEMICAL SHIFT TABLES are available (see page 7). In a spectrum display, TMS (0.0 ppm.) is arbitrarily positioned at the far right of the chart and all common peaks occur at varying distances to the left. NMR terminology defines a peak which is at the far left or to the left of another peak as DESHIELDED, DOWN-FIELD or at LOW FIELD. Peaks at or toward the right (near TMS) are termed SHIELDED, UPFIELD, or at HIGH FIELD.

The same substituent may have a different effect on aliphatic protons than it has on aromatic protons. A methoxy group, for instance, is a strongly deshielding group when attached to an aliphatic molecule (inductive effect) but is a strongly shielding group when attached to an aromatic ring (resonance effect).

When two or more protons have identical chemical shifts they are said to be EQUIVALENT. This equivalence may be of three types, CHEMICAL, MAGNETIC or ACCIDENTAL EQUIVALENCE. For this discussion we need not distinguish between these types but an understanding of the differences between these forms is vital to most detailed structure determinations.

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Commercial NMR spectrometers are capable of scanning a spectrum from 0.0 ppm to either 8.33 or 10.0 ppm. Since some protons may appear outside this range, most instruments are capable of "offsetting" the whole spectrum until the missing peaks are displayed. An OFFSET peak in a spectrum is usually recorded above the normal spectrum baseline and the extent of the offset (e.g. 300 Hz, 5 ppm., etc.) is indicated.

All protons which are attached to carbon atoms possess chemical shifts within fairly narrow ranges. However, those protons which are attached to the heteroatoms, nitrogen, oxygen and sulfur, do not have fixed chemical shift ranges and are called EXCHANGEABLE PROTONS. The chemical shifts of exchangeable protons are very susceptible to changes in solvent, temperature, concentration, and pH. In addition, the appearance of these peaks can vary from a sharp spike to such a broad diffuse band that it can be lost in the baseline. The main reason for the unpredictability of these peaks is that they are very labile and can exchange quite easily with other labile protons (e.g. those in H_2O). This type of proton exchange can readily be demonstrated by adding a drop of deuterium oxide (D_2O) to a water immisible solution of a compound possessing exchangeable protons. Exchange at the liquid-liquid interface is usually rapid enough to replace all of the exchangeable protons by deuterium. Since the resonance of deuterium does not appear in a proton spectrum, the result will be the loss of the signal originally produced by the exchangeable protons.

III. INTEGRATION: An important feature of NMR spectra is that the area of each band is proportional to the relative number of hydrogens contained in it. When the instrument is operated in the integral mode, the spectrum appears as a series of steps rather than peaks, and the amplitude of each step is proportional to the peak area.

The integral can thus be used to accurately determine the relative number of the various types of protons within a molecule (e.g. CH_3-CH_2-OH, 3:2:1 ratio). It can also be used to quantitatively analyze mixtures of compounds. If a separate peak in the NMR spectrum can be assigned solely to each of the components, then by measuring the integrals of these peaks, it is possible to calculate the relative number of moles of each component. Both of these applications of the integration find enormous utility in the analysis of polymers.

IV. SPIN-SPIN COUPLING: Those nuclei which can be studied by NMR can themselves act like small magnets and therefore can either add or subtract the small magnetic field which they generate, to the overall field which is experienced by a neighboring nucleus (proton). The effect of these contributions is that the signal generated by an individual proton group is split into a MULTIPLET. This phenomenon is termed spin-spin coupling or "splitting". In the case of aliphatic groups, the resulting multiplicity can often be predicted by application of the (N + 1) RULE. Simply stated, this rule predicts that the band produced by a given proton group (methyl, methylene, methine, etc.) will be split into (N + 1) peaks, where (N) represents the number of protons on adjacent carbon atoms. Applying this rule allows the chemist to rapidly and unambiguously identify various structural fragments such as ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl and tertiary butyl groups, all of which appear as unique splitting patterns.

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The separation in Hertz between the peaks of a spin-spin coupling multiplet is termed the <u>COUPLING CONSTANT</u> and is represented by the letter (J). The magnitude of J is often indicative of certain structural features in the molecule (e.g. conformation, cis/trans isomerism, etc.) Tables of coupling constants are available which can provide much useful information for the spectroscopist.

The following list contains some of the multiplets which are commonly encountered in polymer NMR spectra.

<u>Singlet:</u> A single resonance peak arises from an isolated, uncoupled proton group. Isolated methyl groups, disubstituted methanes and t-butyl groups appear as sharp singlets.

<u>Doublet:</u> A doublet consists of a pair of peaks of approximately the same height. The presence of a doublet indicates that the band arises from a proton group which is coupled to one other proton (or other nucleus with a spin of 1). The separation between the peaks of the doublet (J value) is not significantly affected by solvent changes.

<u>Triplet:</u> Triplet multiplicity is observed as three equally spaced peaks with intensities in the ratio of 1:2:1. A triplet originates from the coupling of a proton group with two other nuclei. Each proton produces a doublet and the doublets overlap to produce the center peak of the triplet.

<u>Quartet:</u> A quartet arises from coupling to three other nuclei by the same coupling constant. The three doublets overlap to form four evenly spaced peaks with relative intensities of 1:3:3:1.

<u>Pentent, Sextet, Heptet:</u> These multiplets arise from coupling with four, five and six nuclei respectively. The outer peaks become progressively smaller in comparison to those in the center of the pattern and are often lost in the baseline noise. The relative intensities of a pentet are 1:4:6:4:1, a sextet are 1:5:10:10:5:1 and those of a heptet are 1:6:15:20:15:6:1.

Multiplets which clearly exhibit predictable splitting behavior such as this, are termed <u>FIRST ORDER.</u> In aliphatic compounds, if the chemical shift differences between coupled proton groups become very small, the spectrum may lose its first order appearance and become <u>SECOND ORDER</u> or <u>HIGHER ORDER.</u> When this occurs, simple, analyzable multiplets are no longer observed.

In aromatic multiplets, several different coupling constants may be observed (J_{ortho}, J_{meta}, J_{para}) which may produce more complex (but still analyzable) multiplets. In cases such as this, the (N + 1) rule is no longer valid but an expanded version of this relationship can be used.

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Because of the large size of polymer molecules, a certain amount of band broadening occurs. This loss in resolution is due to the fact that the chemical shifts of the proton groups of each polymer unit are not exactly the same and, as a result, only the most obvious multiplets can be recognized.

In well-resolved NMR spectra, spin-spin coupling provides at least as much, if not more, information than the chemical shifts. In polymer NMR analysis, this is not the case and coupling is generally less important than shift positions.

V. POLYMER NMR: In the analysis of polymer NMR spectra the basic principles of the method are still employed, namely:
   a.   The chemical shift of the various bands.
   b.   The relative intensities of these bands.
   c.   The overall appearance of the bands.
   d.   To a lesser extent, the multiplicities of the bands.

It should be emphasized here that, save for a loss in resolution, the analysis of polymer NMR spectra is no different from that of other types of spectra. Admittedly, there are some difficulties which are unique to polymers. The main sampling problem is that of low solubility and/or high viscosity resulting in weak or poorly resolved spectra. The use of dilute solutions and/or running the spectrum at higher temperatures does much to alleviate these problems. On the other hand, once the spectroscopist is aware that he is dealing with a polymer, the structural possibilities become sharply limited and analysis is somewhat simplified. The following table has been found helpful in identifying the structural "fragments" which are found in many common, commercial polymers. Being able to recognize the appearance and chemical shifts of these "fragments", will enable the analyst to make a rapid, qualitative identification of many of the less exotic polymer types.

VI. PREPARING POLYMER SOLUTIONS: The analysis of polymers and resins by NMR requires the preparation of a non-viscous, 20% solution of the sample in a suitable solvent. Although a great deal of solubility information is available for most types of polymers, the solvents suggested are usually not appropriate for preparing NMR solutions. Solvents such as dioxane, cyclohexane, petroleum ether, xylene, tetrahydrofuran, etc., when available in deuterated form, are often quite expensive. During the preparation of the spectra for this volume, the following solvents were employed: carbon tetrachloride, deuterochloroform, acetone-d6, orthodichlorobenzene, deuterium oxide, dimethylsulfoxide-d6, a mixture of deuterochloroform and dimethylsulfoxide-d6 (Polysol-d), trifluoroacetic acid and formic acid.

Trifluoroacetic acid (TFA) was found to be an effective substitute for formic acid in the preparation of solutions of many polyamides and polyesters. Caution in the use of TFA should be employed since decomposition of the sample was observed to occur during its use in the solution of polyoxymethylenes and certain sulfide rubbers. Orthodichlorobenzene used in conjunction with heat was found to be an effective solvent for many of the high molecular weight polyethylene samples.

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