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MAGIC ANGLE NMR STUDIES OF POLYMERS

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Abstract - The combination of cross polarization, high-power resonant proton decoupling, and magic angle sample spinning makes possible liquid-like, high-resolution ^{13}C and ^{15}N NMR spectra in many kinds of organic solids. Such spectra can be particularly useful in the characterization of the chemical and physical structure of solids which may be difficult to analyze by other means. Many polymers fall into this category in that they are non-crystalline, opaque, and impossible to melt or dissolve without altering their structure. Cross-linking, thermal degradation, or the energetic condensation of small molecules can produce polymeric systems which are difficult to characterize for these reasons. Biological macromolecules represent another class of systems presenting demanding analytical problems. Examples are given where either ^{13}C or ^{15}N high-resolution, solid-state NMR spectra provide unique structural information about such materials.

INTRODUCTION

Many techniques can be used to determine the structures of solid polymers. However, some polymers present special problems that make them difficult to characterize. Polymers which cannot be dissolved or melted without disruption or destruction of the features of interest form a large class of such polymers, especially if they are not crystalline and are opaque to light. Many of these polymers can be profitably studied by using the combination of cross polarization followed by high-power resonant proton decoupling (Ref.1) and magic angle sample spinning (CP/MAS) to obtain liquid-like, high-resolution, rare-spin NMR spectra (Ref.2,3,4). Since it is unnecessary to alter the sample beyond making it fit the spinner, it is possible to study the material as is.

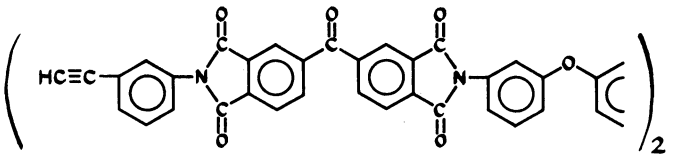
We demonstrate the kind of information that can be obtained by high-resolution NMR spectroscopy in the solid state in several intractable systems of practical importance: (a) The ^{13}C spectrum of a highly cross-linked polyimide polymer yields information about the bonds formed when the resin is cured. (b) The thermal degradation of polyacrylonitrile en route to the production of carbon fibers, in which aromatic character is first developed through cyclization, is characterized with ^{13}C spectra. (c) One theory of the development of heteropolypeptides on primitive Earth involves the polymerization of hydrogen cyanide in the presence of ammonia. Attempts to duplicate this reaction produce an extremely complex, intractable material about which natural-abundance ^{15}N NMR has something to say. (d) Lignin is a natural component of wood which can either be encountered as a large-volume by-product of paper manufacture or as a precursor of humic soils and fossil fuels. The ^{13}C spectrum of this complex material contains considerable chemical information. (e) Finally, we use ^{15}N NMR to study an entire organism labeled by feeding it with a ^{15}N-containing nitrogen source. Such organisms can be observed alive or lyophilized to examine metabolic processes.

EXAMPLES OF STRUCTURAL DETERMINATION BY CP/MAS

Cross-linked resins

Polyimide polymers formed from acetylene-terminated polyimide resins homopolymerized at elevated temperatures and pressures have excellent thermal and physical properties. This is because they polymerize without liberating volatile by-products which can cause voids to form. The mechanism of cure has been believed to be aromatization of the acetylenic end groups but this has been impossible to verify due to the intractability of the cross-linked resin.

Thermid 600 polyimide resin and cured Thermid were both obtained from Gulf Oil Co. The resin consists mostly of the structure



although some incompletely imidized prepolymer is probably also present. The 15.1-MHz ^{13}C-NMR spectra shown in Fig.1 were each obtained from the time average of approximately 50 000

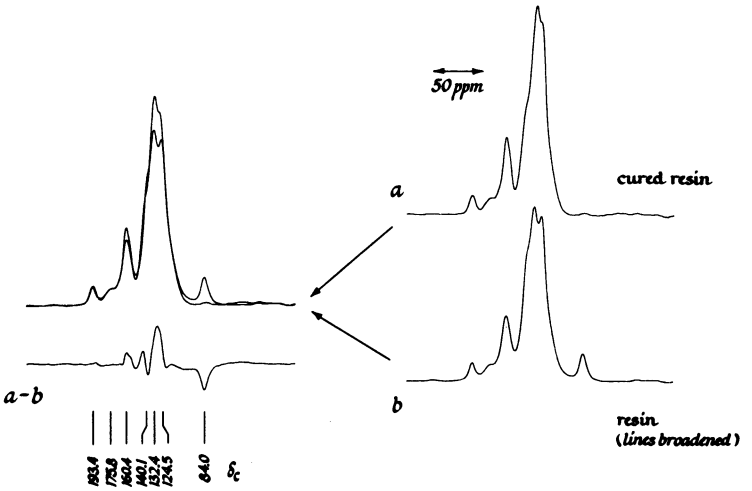
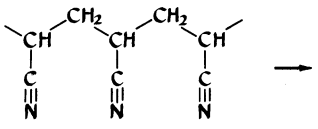


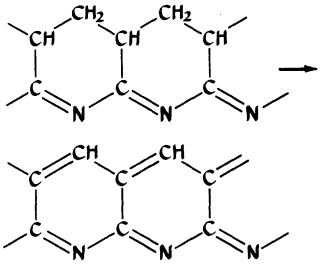
Fig.1. Cured Thermid 600 resin (a) and the resin before curing (b). The resin spectrum has been artifically broadened to facilitate comparison. The two spectra are also shown superimposed and their difference (a-b) is plotted. The net area of the difference spectrum is zero.

transients (Ref.5). Magic-angle spinning of the powdered samples was at 2.2 kHz in a 700-μL Beams-Andrew (Ref.6) Kel-F hollow rotor. Matched spin-lock cross-polarization techniques were used with 1-ms single contacts and 38 kHz H_1's. The negative-going peak in the difference spectrum at 84.0 ppm represents the loss of nearly all the acetylenic end groups during the curing process. Although some of the positive going peaks (in the regions 125-129 and 140-144 ppm) indicate the possible cyclotrimerization of the lost acetylenic end groups, at most 30% can be accounted for that way. The remainder appear to be consumed by addition reactions. These conclusions were reached using straightforward correlations between structure and isotropic carbon chemical shifts despite the fact that the resolution of the spectra is limited to resonance bands rather than well resolved lines.

Carbon-fiber precursors

One method of producing carbon fibers begins with fibers made of polyacrylonitrile homo- or copolymers. They are first subjected to a low-temperature pyrolysis in air which partially aromatizes and oxidizes them. A subsequent high-temperature carbonization is used to produce carbon fibers. The result of the first step, which may have considerable influence on the final product, is difficult to characterize by conventional spectroscopy. The aromatization may take place in the following two steps:





The effect of oxidation on Orlon 42, primarily polyacrylonitrile, is shown by the ^{13}C-NMR spectra in Fig.2 (Ref.7). The Orlon 42 spectrum reveals an aliphatic region (up-field, to

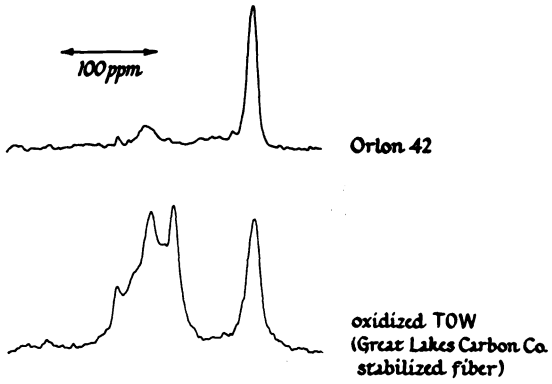


Fig. 2. 15.1-MHz ^{13}C-NMR spectra of Orlon 42 before and after low temperature pyrolysis in air. Approximately 50 000 2-ms single matched cross-polarization contacts (with 40-kHz H_1's) were used for each spectrum. Spinning was at 2 kHz.

the right) and a nitrile region (down field) somewhat broadened by higher-order ^{13}C-^{14}N couplings not removed by magic-angle spinning (Ref.8). After oxidation, the relative contribution of aliphatic carbons is much reduced and at least three aromatic-carbon lines have joined the nitrile line. Such spectra can be used either of two ways. They may be used to sort out the details of the carbonization process. They may also be used as a "fingerprint" to assist quality control in the manufacturing process.

Primitive heteropolypeptides

It has been proposed by Matthews and co-workers (9,10) that the original heteropolypeptides on primitive Earth formed directly from hydrogen cyanide polymerizing in the presence of ammonia and then reacting with water; the intermediate formation of α-amino acids is not required. They have attempted to duplicate these reactions in the laboratory under various conditions, but the resultant products are so complex that they defy straightforward analysis. Particularly, the argument hinges on the presence of peptide bonds in the intact reaction products. The choice was made to use ^{15}N NMR to examine these difficult solids since ^{13}C NMR is not exclusive in its identification of the peptide linkage (Ref.11).

The solid produced by the combination of hydrogen cyanide and anhydrous ammonia (Ref.12) was separated into a cold-water soluble form (subsequently lyophilized) and a cold-water insoluble form. These materials were provided by C. N. Mathews from his original experiments performed some 15 years ago. The natural abundance ^{15}N NMR spectra of these two materials are shown in Fig.3 (Ref.13). The cold-water soluble fraction exhibits some of the

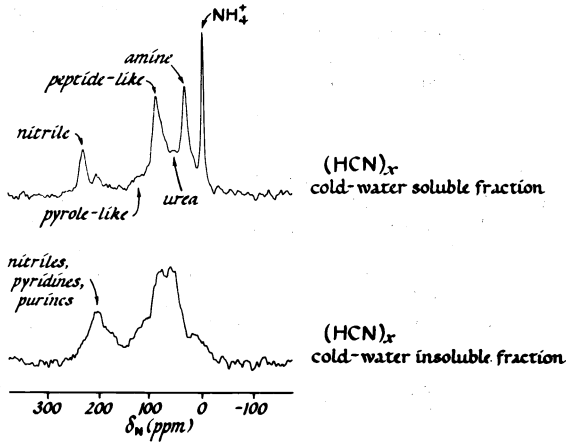


Fig.3 9.12-MHz ^{15}N-NMR spectra of two fractions of the solid product of the reaction of hydrogen cyanide and anhydrous ammonia. Several hundred thousand 3-ms single matched cross-polarization contacts (with 30-kHz H_1's) were used for each spectrum. The 300-mg samples were spun at 1.4 kHz.

variety of chemical functionality found in these materials. However, what we are looking for is relatively large molecules such as would be more likely to remain behind in the cold-water insoluble fraction. The presence of a broad resonance in the 90 ppm region (relative to ammonium sulfate) strongly suggests the occurrence of peptide-like bonds in relatively large molecules, a finding which is at least consistent with the original proposal.

Lignin

The chemistry of lignin is not so much mysterious as it is complicated. Lignin is made up of a large variety of mostly aromatic residues capable of coupling together in many different ways. The result is a ^{13}C-NMR solid spectrum as complex as most intact biological materials (Ref.4). This may be seen in Fig.4 (Ref.14). Although several relatively sharp

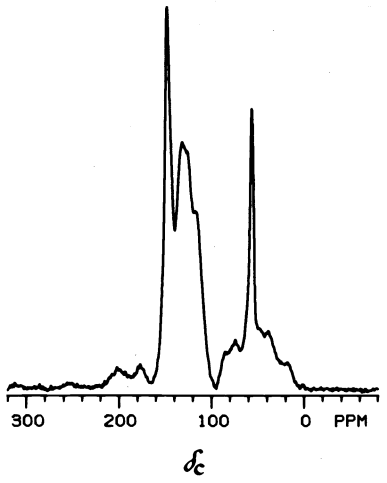


Fig.4. 15.1-MHz ^{13}C-NMR spectrum of lignin. The sample was spun at 833Hz. The resulting spinning side bands were isolated by suitable PASS sequences and the side-band intensities returned to the center bands.

lines may be observed and identified, there is some absorption over almost the entire range of carbon chemical shifts. The problem is not so much one of using such a spectrum - to see chemical changes, for instance (Ref.15) - but one of obtaining the spectrum free of spurious lines and false intensities. The difficulty lies in the spinning sidebands which may occur in magic-angle spinning spectra (Ref.16). Not only do they divert intensity from the center bands, but they also may obscure other center bands. This is a particular problem in a substance like lignin where there is no place within the spectrum to accommodate sidebands. A scheme to produce phase altered spinning sidebands (PASS) has been developed (Ref.17) which makes it possible to isolate the sideband spectra, even when they overlap center bands, and return this intensity to its proper place in the center bands. This technique is demonstrated in Fig.4 where, despite the purposely low spinning speed, sidebands have been eliminated and total center band intensity has been recovered.

Nitrate metabolism

The only convenient radioactive isotope of nitrogen ^{13}N has too short a half-life to make it usable as a label for many kinds of metabolism studies. Accordingly ^{15}N looks attractive for this purpose. NMR detection provides chemical information more easily than mass spectroscopy. Solid-state ^{15}N NMR permits observation of intact materials and also reaps a considerable signal enhancement from the cross-polarization process. By causing an organism to metabolize a specifically ^{15}N-labeled nitrogen compound, one can observe the ensuing chemistry in ^{15}N-NMR spectra. An example is shown in Fig.5 (Ref.18). These

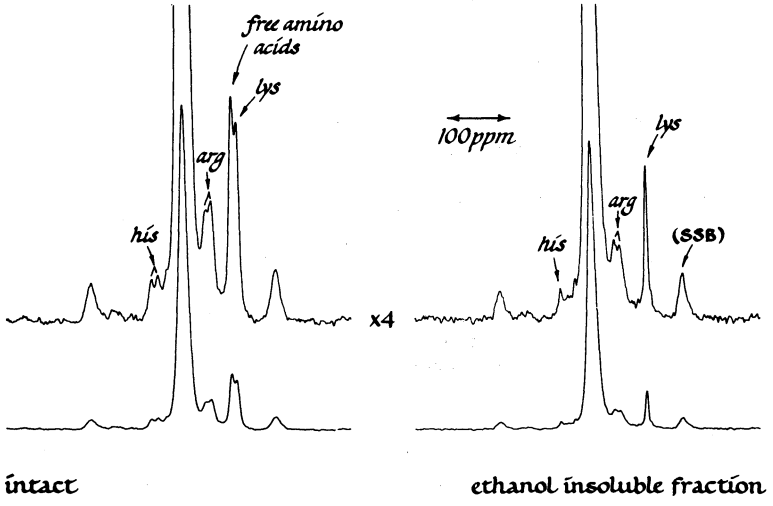


Fig.5. 9.12-MHz ^{15}N-NMR spectra of lyophilized N. crassa mycelia, harvested after 8 hours in [^{15}N] nitrate medium, intact and ethanol-extracted. Innoculating cells were grown in natural-abundance ammonia medium. Approximately 100 000 1-ms single matched cross-polarization contacts (with 32-kHz H_1's) were used for each spectrum. Spinning was at 1.3 kHz so that the spinning sidebands (SSB) can be seen.

spectra are largely the spectra of the protein in these cells. The amide nitrogens along the protein main-chain give rise to the dominant line in the center of the spectrum. Several side-chain nitrogens of different chemical functionality can also be seen, as can free amino acids. Depending on the organism, the label used, and the conditions of administering it, the pattern of intensities will be seen to change, disclosing details of the protein synthesis. The further possibility also exists of introducing both ^{15}N- and ^{13}C-labels (Ref.19,20,21).

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