HIGH RESOLUTION NMR OF POLYMERS IN THE SOLID STATE

FOURTH POLYMER DIVISION TOPICAL WORKSHOP

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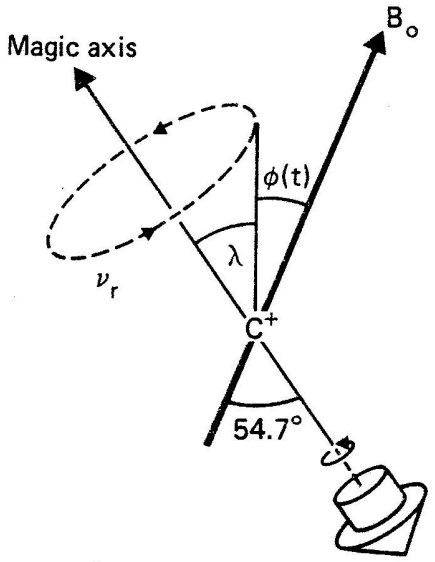

PREFACE

This workshop, High Resolution NMR of Polymers in the Solid State, represents the fourth meeting of this type sponsored by the Polymer Division of the ACS.** The workshops focus on selected, narrow areas of polymer science. They are intended to assess the current state of knowledge in an area and to provide a forum for discussion of unsolved problems. State-of-the-art overviews by experts from academia and industry and active participation by conference attendees are key features of the workshops.

The focus of this workshop is on recent high resolution NMR techniques (i.e., cross-polarization, magic-angle spinning methods (CP/MAS); multi-pulse methods; and quadrupole echo spectroscopy) developed to study materials in the solid state and the novel applications of these techniques in polymer science. Presentations in the form of lectures and posters will be given by recognized experts who have pioneered this field and by active researchers from the academic, government, and industrial communities. Topics to be covered include: introduction to high resolution NMR techniques; applications to polymer chemistry and biochemistry; applications to polymer structure, morphology and dynamics.

The intent of the Workshop is to promote open discussion on the utility of solid state NMR in polymer science. Time has been set aside after each lecture for discussion; in addition, there is ample time in the afternoons for impromptu discussions growing out of the regular sessions. In the spirit of the meeting, each attendee is encouraged to participate fully.

J. R. Lyerla, Chairman
Fourth Topical Workshop

**CONTRIBUTIONS OF FINANCIAL AND OTHER RESOURCE SUPPORT OF THE IBM SAN JOSE RESEARCH LABORATORY FOR THIS WORKSHOP ARE GRATEFULLY ACKNOWLEDGED.

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HIGH RESOLUTION NMR IN SOLIDS
OVERVIEW OF THE CP/MAS EXPERIMENT

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The cross-polarization, magic-angle spinning (CP/MAS) NMR experiment has become stock-in-trade for detailed studies of the structure and dynamics of organic solids. In this overview, the resolution and sensitivity problems inherent in attempting to obtain useful C-13 NMR spectra of bulk solids will be discussed, along with the magnetic resonance ideas underlying the solution to these problems. Specifically, proton-carbon dipolar coupling and carbon chemical shift anisotropy are the two major sources of line broadening, while C-13 sensitivity is poor for the same reason as in solution, i.e. low natural abundance and long carbon spin-lattice relaxation times. The techniques used to remedy these problems - high-power proton decoupling, magic-angle spinning and cross-polarization in the rotating frame - will be described. Examples of some recent refinements of high resolution solid state NMR methods will also be given.

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WEDNESDAY MORNING SESSION

CROSS-POLARIZATION/MAGIC-ANGLE SPINNING NMR SPECTROSCOPY RESOLUTION, QUANTITATIVE ASPECTS, AND THE ROLE OF SPIN DIFFUSION

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One of the principal reasons for doing magic-angle spinning (MAS) during acquisition of solid-state carbon-13 NMR spectra is the improved differentiation of resonances belonging to carbons in chemically or physically different environments. The factors which limit resolution are therefore important to understand and will be discussed. Moreover, since it is often the objective of high resolution NMR techniques to evaluate quantitatively the amounts of various constituents, the conditions under which quantitative relative intensities are achieved will also be examined. Intensity distortions are important to consider because C-13 magnetization is usually generated indirectly via cross-polarization from the protons; moreover, these techniques are frequently applied to systems with motional or structural heterogeneity. Finally, the concept of nuclear spin exchange will be presented because it is very useful in understanding the processes of cross-polarization and relaxation in inhomogeneous systems. In fact, it is one of the few ideas which leads to NMR experiments probing dimensions larger than a few angstroms.

WEDNESDAY MORNING SESSION

APPLICATION OF CP/MAS NMR TO POLYMER CHEMISTRY AND STRUCTURE IN THE SOLID STATE

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In general CP/MAS NMR measurements yield structural information for solids complementary to that obtained for X-ray diffraction measurements. In the case of solid polymers, the NMR results are particularly valuable as the diffraction data is very limited due to the nature of the systems. In the case of amorphous polymer systems, diffraction measurements are precluded and the NMR data provide otherwise unobtainable information on their structures and chemical reactions. These points will be illustrated using results from C-13 and N-15 NMR investigations of phenol-formaldehyde and other resin systems, their curing and thermal decomposition reactions. P-31 NMR studies of polymer immobilized catalysts and C-13 and Si-29 NMR measurements on model systems of fiber reinforcement will also be discussed.

In the case of "crystalline" polymers, X-ray diffraction measurements, although limited, when compared to single crystal studies have provided postulated solid state structures. In these cases, e.g. polyethylene, polypropylene and others, the NMR spectra may show characteristic fine structure which reflects the solid state structure directly and which complements the diffraction data. A very important application in the case of crystalline polymers is the use of the NMR measurements to bridge the gap between the high molecular weight polymer and the model oligomer whose structure may be directly determined by single crystal X-ray diffraction measurements. These points will be illustrated by C-13 NMR results obtained from cellulose and its oligomers and for other polymer systems.

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WEDENESDAY MORNING SESSION

DETERMINATION OF INTERMOLECULAR STRUCTURE WITH CARBON-13 SPIN DIFFUSION

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In carbon-13 labelled materials, spin diffusion occurs over a time period of less than one second. For samples in which the carbon spin-lattice relaxation times are much longer than this, the spin diffusion can be used as source of structural information. We have measured the rate of spin diffusion in both spinning and non-spinning samples with two-dimensional NMR. In the spinning samples, the spin diffusion gives information about the chemical nature of neighboring carbons in space. In the non-spinning samples, the spin diffusion gives information about the relative orientation of neighboring molecules. We have tested the method on polymer blends and on a model compound, C-13 labelled zinc acetate. We are testing whether spin diffusion can be used to examine local orientational structure in amorphous polymers.

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WEDNESDAY EVENING SESSION

MOLECULAR MOTIONS IN EPOXY POLYMERS AS DETERMINED BY ^{13}C NMR

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In polymers mechanical loss spectroscopy provides an overall picture of the frequency and temperature dependence of mechanically active molecular motions. But identification of the particular chemical moieties which actually participate in those motions and a detailed description of their dynamics are more difficult. ^{13}C NMR can not only suggest a polymer's chemical structure but also provide highly site-specific information about molecular motion. As illustrated, the present variable temperature (150-350K) solid state ^{13}C NMR study shows that in the four epoxy polymers examined the phenylene rings are locked into place near 150K and reorient at higher temperature. For a piperidine-cured DGEBA epoxy, parallel analyses of these NMR lineshape results and existing mechanical loss data for the secondary (β) relaxation peak suggest that the motions seen by the two spectroscopies can be described by a common distribution of correlation times. Two classes of correlation time distributions (homogeneous and inhomogeneous) are investigated. These two classes arise from fundamentally different physical processes; though they cannot be distinguished by dielectric or mechanical loss spectroscopy, they can be distinguished in principle by NMR.

THURSDAY MORNING SESSION

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POLYMER MOTION FROM ROTATIONAL DIPOLAR SPIN-ECHO ^{13}C NMR

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The reduction in the strength of the dipolar interaction of an isolated CH pair by molecular motion (of frequency greater than the interaction itself) is a measure of the amplitude of the motion. The condition that the CH pair be isolated is achieved by proton-proton (WAHUHA) decoupling. The time evolution of a carbon magnetization can then be detected under the influence of ^{1}H-^{13}C coupling alone using 2-dimensional techniques. The resulting carbon signal can be observed with magic-angle spinning for high resolution. This experiment was introduced by Munowitz, Griffin and co-workers (J. Chem. Phys. 76, 2848, 1982.)

We have used the experiment over the last 18 months to examine molecular motion in some 50 polymers and model systems. Polycarbonate and various substituted, or modified, polycarbonates are well-suited to study by this technique because of the presence of a variety of large-amplitude motions. Both restricted ring rotations and 180° flips (about the ring C_2 axis) are present, as well as more complicated low-frequency reorientations which involve the adjacent isopropylidine unit. Polystyrenes have considerably less molecular motion on average, although a small fraction of sites (the exact amount depending on the type of polystyrene and its thermal history) can exhibit large- amplitude motion. Sorting out the details of complicated distributions of motions for such dynamically heterogeneous systems is straightforward in the natural- abundance carbon experiment because total magnetization is derived reliably and quantitatively from the protons, even in systems with very little motion. In addition, selection by carbon $T_{1\rho}$'s can be used during the cross-polarization preparation so that the dipolar coupling of only a controlled fraction of the system is observed.

THURSDAY MORNING SESSION

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APPLICATION OF HIGH RESOLUTION NMR TECHNIQUES TO POLYMER COMPATIBILITY AND MORPHOLOGY

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The mechanical properties of polymers depend not only on molecular structure and mobility but also on morphology. For example, the modulus of a drawn semicrystalline polymer is sensitive to the orientation and arrangement of crystals and to the bridging network which connects the crystals to one another. Measurements of orientation or heterogeneities in relaxation behavior offer some important clues about morphology. In addition, spin diffusion experiments performed on the proton spins and "read out" via either the proton or carbon signals allow one to obtain simultaneous information about orientation and spatial proximity of one region to another. Examples of these experiments will be taken from studies on polyethyleneterephthalate and polyethylene. The presentation will emphasize studies of morphology rather than compatibility; the latter topic will be addressed briefly.

DEUTERON NMR METHODS FOR STUDYING MOLECULAR DYNAMICS OF POLYMERS

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Pulsed deuterium NMR provides especially clear-cut information about rotational motions in polymers. The techniques that have recently been developed in this area will be described, analyzing the response of the $I = 1$ spin system in the presence of motion to the solid echo two-pulse and the Jeener-Broekaert three-pulse sequence, respectively. This allows the monitoring of rotational motions in polymers over an extraordinarily wide range of characteristic frequencies (1Hz - 10MHz). Moreover, by taking partially relaxed spectra, motional heterogeneity can be detected not only in semicrystalline materials but in glassy materials as well.

The techniques will be illustrated by experimental examples including: polystyrene, where side group motion and chain reorientation in the vicinity of the glass transition can be studied seperately; polycarbonate, where the addition of plasticizer molecules causes motional heterogeneity; polyethylene, where the chain motion in the amorphous layers was investigated in both isotropic and drawn material. In addition, studies of order and mobility in side chain liquid crystalline polymers as well as their low molecular weight analogs will be described. Finally, the restriction of mobility in model membranes stabilized by polymerization will be demonstrated.

FRIDAY MORNING SESSION

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DEUTERIUM NMR STUDIES OF STRUCTURE, MORPHOLOGY, AND DYNAMICS IN SOLID POLYMERS

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Quadrupole echo deuterium NMR spectroscopy is a powerful tool for assessing structure, morphology, and dynamics in solid polymers. Polymers that bear deuterium at unique sites can be used to provide highly specific information concerning the frequency and angular range of local molecular motions. Examples will be presented, showing that this technique provides new information concerning aromatic ring flips, motions about three bonds in polymers, copolymer morphology, and polymer-water interactions.

The results show that the occurrence of aromatic ring flips in poly(butylene terephthalate) is related to the free volume available for such motions, and that there is a heterogeneous distribution of phenyl ring flip rates throughout the polymer. A mechanism for motions about three bonds has been established for the alkyl chain in poly (butylene terephthalate). It is in agreement with the calculations and mechanisms proposed by Helfand, in which counter rotation occurs about second neighbor parallel bonds. Deuterium NMR in the solid state shows that these same three-bond motions occur in copolymers containing poly(butylene terephthalate) as the hard segment. Additionally, the amount of hard segment that is dissolved in the soft segment can be assessed.

The interaction of water (D_2O) with epoxy resins can be studied using deuterium NMR in the solid state. The results show that there is no isotropically free water, but that the water molecules hop among -OH (-OD) sites with a correlation time of approximately 10^{-7}s. The interaction of water with epoxy resins appears to be one of dynamic hydrogen bonding.

FRIDAY MORNING SESSION

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MULTIPLE-PULSE LINE NARROWING TECHNIQUES AND THEIR APPLICATION TO POLYMERS

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The multiple-pulse sequences, WAHUHA, MREV-8, and BR-24, suppress the effect of homonuclear dipolar interactions in solids. When applied to proton and fluorine, these experiments enable the observation of the weaker nuclear interactions of chemical shifts and relaxation. One application to polymers makes use of the anisotropy of the chemical shift tensor. The motional narrowing of multiple-pulse lineshapes is related to the specific mode of molecular motion, much like the quadrupolar lineshapes of deuterated solids. Since the chemical shift anisotropy of fluorine is much larger than that of protons, this measurement has mainly been applied to fluorocarbon polymers.

A somewhat different application is the measurement of relaxation under multiple-pulse conditions. This relaxation time is essentially identical to spin-lattice relaxation in the rotating frame; however, because of suppression of spin diffusion, a common spin temperature is not rapidly established, so that seperate relaxation decays by seperate species can be observed. This technique is particularly useful in semi-crystalline polymers

For the identification of distinct chemical sites, i.e. chemical shift measurement, the anisotropy of the chemical shift must be removed. This is achieved by combined rotation and multiple-pulse spectroscopy (CRAMPS).

This presentation will consist of an introductory discussion of multiple-pulse NMR, average Hamiltonian theory, and stroboscopic observation. This will be followed by examples of applications to polymer systems.

FRIDAY MORNING SESSION

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HOLE BURNING TO STUDY MOLECULAR REORIENTATION CHARACTERISTICS IN SOLIDS

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C-13 NMR spectra of organic solids with proton stirring but without magic angle spinning are broad, powder pattern lines. The molecular orientation and NMR frequency are directly related through the anisotropic chemical shift. These lines are inhomogeneously broadened; holes can be burned into them, serving to tag molecules or groups at certain physical orientations to the applied magnetic field. By observing the hole at a succession of times after the hole is formed, molecular reorientation can be observed: reorientation is accompanied by a change in frequency of the saturated spins.

The first application of this technique is on glassy glycerol. By observing the diffusion of the hole in the NMR line, the reorientation time is measured to values as long as 200s. The shape of the diffusing hole indicates that the reorientation steps are through large angles (<45 degree).

The second application of the technique is on the twisting of para-terphenyl at its phase transition at 193K. The hole was burned (actually a series of holes, using the three pulse method which is the Fourier transform of hole burning) above the transition temperature and observed six seconds later and 20K below the transition! The broadening of the hole indicates the extent of molecular twisting at the phase transition. This technique holds promise for doing NMR crystallography on polycrystalline samples.

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POSTER SESSION THURSDAY EVENING

VARIABLE TEMPERATURE NMR MEASUREMENTS OF SOLID POLYMERS USING CP/MAS NMR SPECTROSCOPY

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The ability to perform variable temperature measurements using CP/MAS NMR techniques makes it possible to investigate solid state phenomena which are otherwise inaccessible using the CP/MAS technique. In particular, the ability to observe dynamic phenomena such as relaxation behavior and lineshape analysis as a function of temperature makes it possible to study fisrt and higher order phase transitions in crystalline and amorphous polymers. Several examples of these advantages are presented. Illustrative of the such data are the spin-lattice relaxation times in the laboratory and rotating frames for isotactic polypropylene over the temperature range 77 to 300 K. All carbons of the polymer repeat unit show minima that reflect methyl group rotational motions at the relevant measuring frequencies of 15MHz and 57KHz, respectively. Relaxation behavior for this 90% crystalline polymer shows a single exponential form indicative of a narrow and homogeneous distribution of correlation times. In contrast, the relaxation behavior of polymethylmethacrylate and polytetrafluoroethylene show nonexponential behavior indicative of a distribution of correlation times, which is common for glassy polymers. The CP/MAS spectra of PTFE also show the presence of the crystal-crystal phase transition at 19C by the sharp change in linewidth due to concurrent change in molecular motions.

POSTER SESSION THURSDAY EVENING

APPLICATIONS OF SOLID STATE NMR TO STRUCUTRE, MORPHOLOGY AND MOTIONAL ASPECTS OF SELECTED POLYMERS

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Since Schaefer and coworkers have demonstrated that the combination of magic-angle spinning (MAS) to reduce chemical shift anisotropy and "high power" decoupling with cross-polarization to reduce dipolar coupling and to additionally increase sensitivity could yield high resolution spectra of solids, considerable interest has developed to evaluate the potential of this technique to characterize polymers and other solids with regard to structure, morphology, and motion. During this period, considerable progress has also been achieved in the basic technique, especially MAS and dipolar decoupling. In addition, with a better understanding of the technique, a number of new pulse sequences have been used which either substantially increase the information obtained or improve the quality of the spectrum.

In addition to CP/MAS, dipolar dephasing, inversion recovery CP/MAS, gated high-power decoupling, and rotating frame relaxation measurements will be used to illustrate the study of structure, resonance isolation, morphology, and motion in polymers and organic solids. Polyoxymethylene, polyethylene, norbornene end capped polyimides, as well as epoxy and urethane polymers, and copolymers of acrylonitrile/methylmethacrylate are used as examples.

POSTER SESSION THURSDAY EVENING

PROTEIN DYNAMICS USING ^{2}H AND ^{13}C SOLID STATE NMR

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We have analyzed ^{13}C lineshape and relaxation data to elucidate backbone dynamics of a structural protein, collagen, in intact tissues. We have used ^{2}H NMR to study the mobility of collagen side chains in various connective tissues. To achieve the resolution needed to obtain detailed dynamic information, we have labeled (a) reconstituted lathyritic (uncross-linked) collagen fibrils (b) intact rat tail tendon (cross-linked) and (c) rat bone (cross-linked and mineralized) collagen with [1-^{13}C] and [2-^{13}] glycine and L-(methyl-$^{2}H_3$] methionine.

Our results indicate differences in molecular mobility of the collagen backbone in the various samples at 22°C. We interpret our results in terms of the effect of cross-linking and mineralization on collagen dynamics. Since collagen fibrils are highly ordered in the direction parallel to the helix axis we have assumed a model in which azimuthal orientation of the collagen backbone is assumed to fluctuate as a consequence of reorientation about its axis. We analyse the glycine carbonyl lineshapes and α-carbon relaxation times to obtain the root mean square fluctuation in azimuthal angle, γ_{rms}, values. From an analysis of lineshapes which are sensitive to molecular motions having correlation times, $\tau_c \leq 10^{-4}$s, we find that γ_{rms} equals 41°, 31°, and 14° for uncross-linked, cross-linked and mineralized collagens, respectively. In contrast, the corresponding values of γ_{rms} obtained from an analysis of relaxation data are 12°, 9° and 6°, respectively, as the relaxation times are sensitive to molecular motions with $\tau_c \sim 10^{-8}$s.

We have recently obtained ^{2}H NMR spectra of L-[methyl-$^{2}H_3$]-methionine labeled collagen samples. These results will be discussed in relation to the effect of cross-linking and mineralization on the motions of collagen sidechains.