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Pulse and multiple pulse N. M. R. studies of crystallinity
and molecular dynamics of solid state polymers

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Pulse and multiple pulse N. M. R. studies of crystallinity
and molecular dynamics of solid state polymers

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This dissertation is primarily concerned with the application and interpretation of pulse and multiple pulse N. M. R. techniques on two solid state polymeric systems, polypropylene and polyethylene. The degree of crystallinity of two polypropylene samples was investigated by analyzing the time decays of a simple $\pi/2$ pulse and the more complex eight-pulse cycle. The single pulse experiment gives the superposition of two decays, the short component being attributed to the rigid region while the long component to the mobile region. Heating of the samples to 88°C produced a situation where the rigid and mobile regions become synonymous with the crystalline and noncrystalline regions. The eight pulse cycle will only average the homonuclear dipole-dipole interactions, H_D , only at observation times nt_c , when the criteria $t_c |H_D| \ll 1$ is met. With the selection of the appropriate cycle time, t_c , of 72 usec only the magnetization of the noncrystalline region will be monitored. The application of the eight pulse cycle, seventeen pulse cycle, $-M_x$ phase pull sequence, and $P_x - M_y$ phase pull sequence allowed for a variety of interaction Hamiltonians of polyethylene to be investigated.

I. LITERATURE REVIEW

As early as 1936 Gorter had already predicted the possibility of observing N. M. R. in macroscopic matter. By 1939 Rabi demonstrated that it was indeed possible to induce transitions of atomic nuclei between adjacent energy levels in atomic beams if the nucleus is subjected to the action of a weak alternating magnetic field of definite frequency and polarization. The frequency of the radiation that induces such a transition must coincide with the energy difference between the adjacent energy levels. This phenomenon of induced transitions of atomic nuclei between energy levels under the action of an alternating magnetic field of resonance frequency is called nuclear magnetic resonance. The practical aspects of this experiment lay dormant until 1945 when Bloch (1), Bloch et al. (2), and Purcell et al. (3) simultaneously carried out the first successful experiments to observe N. M. R. in macroscopic matter.

The remaining material will emphasize the application of N. M. R. of solid polymeric materials and the development of multiple-pulse N. M. R. as a high resolution technique. However, the purpose here is not to present a review of all previous work in these fields but rather to illustrate an overall view of the areas.

The type of problems in physics or chemistry to which N. M. R. is applicable are often either directly or indirectly related to the effect of molecular motion on the N. M. R. spectrum. The ability of N. M. R. to discern molecular motion over a wide range

of frequencies is ideal for the study of solid polymers, where both mechanical and physicochemical properties are to a certain extent determined by the character of the molecular motion. A number of reviews give detailed discussion of this particular aspect of N. M. R. (4-8). When wide line solid state N. M. R. techniques are applied to molecular motion in polymers, typically qualitative rather than quantitative results are obtained. Routinely a plot of relaxation rate versus temperature is used to make inferences pertaining to molecular motion. In a continuous wave experiment, the line width, which is equivalent to the relaxation rate, $1/T_2$, is plotted versus temperature. A maxima in the relaxation rate versus temperature curve occurs when the correlation time for a motional process corresponds to an allowed nuclear transition.

McCall and Falcone (9) studied molecular motion in natural rubber using a variety of relaxation rates, $1/T_1$, $1/T_2$, and $1/T_{1\rho}$. The changes with temperature of the various relaxation rates allowed the molecular motion to be monitored over nearly five orders of magnitude. A low temperature maxima for $1/T_1$ was ascribed to the rotation of substituent methyl groups, while the maxima at higher temperatures was associated with reorientation of segments of the main polymer chain. There were corresponding maxima for $1/T_{1\rho}$ which occurred at lower temperatures and which reflected the shift of the spectrum of molecular motions to lower frequencies. With increasing

temperature and molecular motion, dipolar interactions are partially averaged which explained the reduction in $1/T_2$ at higher temperatures.

Solid state N. M. R. has seldom been used as an analytical tool to study the structure of molecules. The reason for this lack of use is that the broad featureless lines encountered in solid state N. M. R. generally contain little information directly relatable to the fine details of the chemical structure of the material being studied (10-12). The dominant source of this broadening is nuclear dipole-dipole interactions. In some circumstances, however, line shapes of solids can assume a complex form with a more or less clearly expressed structure containing chemically useful information. This structure may be a reflection of the presence of weakly interacting groups of atoms in the solid, the effect of a chemical shift, or the presence of two phases in the system.

Isolated groups of atoms consisting of two or three nuclei have a complex N. M. R. spectrum, which may be calculated theoretically. Thus, Powles and Gutowsky (13) working with methyl chloroform in the solid state showed that the N. M. R. line of a methyl group consists of a triplet. In a solid polymer the characteristic line shape of a group of atoms will only be observed if the neighboring groups are not so near as to contribute significant broadening. Polymers which contain such isolated

methyl groups (14) are polymethyl methacrylate, polycarbonate, and butyl rubber.

The line width of the N. M. R. spectra of solid polymers can range from 10 - 100 KHz. The chemical shift for protons is not more than several hundred Hz and therefore is not observed in polymer spectra. The situation is quite different for fluorine which has a chemical shift an order of magnitude larger than protons. If the N. M. R. line is sufficiently narrow, a complex line shape may occur due to the chemical shift. This effect has been observed in crystalline copolymers of tetrafluorethylene-hexofluoropropylene (15) and of vinylidene fluoride-hexofluoropropylene (16).

Often polymers exist as a two phase system, consisting of macroscopic crystalline and noncrystalline phases. In 1953, Wilson and Pake (17, 18) showed that over a definite temperature range the N. M. R. line of protons in polyethylene had a structure which was characteristic of a two phase system. Their explanation was, that since the motional effects, and even the relative position of the nuclei, will in general be different in the two regions, one expects to obtain two signals which, however, will be superimposed, since the difference in the resonant frequencies are small compared to the linewidth. These two signals can, in favorable cases, be separated in a more or less arbitrary manner and the relative number of resonant nuclei in each region be determined, and hence the proportion of material in each

region estimated. This has been moderately successful in the case of polyethylene (17, 19, 20, 21, 22), polytetrafluoroethylene (17, 23) and the silicones (24, 25). However, attempts to extend the method of determining crystallinity to other polymers (26, 27) and to use the method over a wide range of temperatures did not give satisfactory results. Thus the extent to which these two signals can be distinguished depends on the difference in their parameters and indeed on the extent to which it is valid to speak of distinct sets of nuclei at all. Consequently one can get two superimposed broad lines which are not distinguishable. However with rising temperature the motional effects in the noncrystalline region may be more pronounced and more rapid so that the signal narrows allowing for the identification of two lines. A measure of agreement has been found between crystallinities determined in this manner and those determined by X-ray methods. It is clear however, that the two methods are sensitive to rather different parameters (21, 22, 28) namely motion and ordering, so that a complete correlation should not be expected.

During recent years a number of interesting high resolution experiments have been developed which are potentially useful for investigating a variety of nuclear spin interactions in solid materials. The application of these techniques was one of the principal subjects of the First Specialized Colloque Ampere (29) and the conference began with a review of Andrew (30) who covered all current methods of achieving resolution in the solid state.

The most prominent methods are: (1) magic angle sample rotation (31-34), (2) double resonance methods on rare spins (35-37), (3) multiple-pulse (38-43), and (4) a combination of magic angle spinning and multiple-pulse (44, 45). In the discussion to follow only the multiple-pulse experiments will be considered. An excellent theoretical account of the multiple-pulse experiments is given in a review article by Mansfield (46).

As was previously discussed much of the useful information in the N. M. R. spectrum, such as chemical shifts, Knight shifts, and electron-coupled spin-spin interactions, is obscured by strong dipolar interactions. During the past few years a variety of multiple-pulse experiments have been developed which are intended to remove or reduce the dipolar interactions, but at the same time retaining these other, often more useful interactions (47-57). Thus progressively better resolution has been accompanied by increasing complexity in both the multiple-pulse cycles and instrumentation. The necessary symmetry requirements of a line narrowing multiple-pulse cycle have been previously discussed (53, 58). The factors which limit the resolution under a multiple-pulse cycle have been the subject of intense investigation. Rhim et al. (59) considered the nature of finite pulse width, H_1 inhomogeneity, off resonance effects, phase errors, and residual dipolar effects, as important in determining the residual linewidth, with particular emphasis on the Waugh four-pulse cycle (53) and the eight-pulse cycle of Rhim et al. (57). They demonstrated

that H_1 inhomogeneity causes residual broadening both directly and indirectly, due to cross-coupling with the other Hamiltonian terms of the spin system. Rhim et al. also maintain that their eight-pulse cycle is much less dependent on the stability of the r. f. transmitter than the Waugh four-pulse cycle. The same group also illustrated (60) the application of the average Hamiltonian formulation as a method of systematically dealing with pulse imperfections. This theoretical technique allowed them to explain many features of spectra obtained with an improperly tuned spectrometer.

U. Haeberlen in Chapter III in Van Gerven (61) confined his attention to various coherent phase errors encountered in multiple-pulse experiments. He developed a general scheme for self-correcting errors, which reduces the sensitivity of the multiple-pulse response to phase control settings and drift. This is accomplished through the use of a phase-modulation r. f. carrier which automatically compensates for the systematic phase errors of the four independent r. f. pulses.

Experiments exploiting high-resolution techniques in solids have so far been largely structural investigations, rather than enquiries into the dynamic properties of materials. However, a paper which considers a number of line narrowing techniques in relation to their susceptibility to the molecular motion, is that of Müller and Willsch (62). They compute the effect of thermal motion on the relaxation function which governs the

decay of the transverse magnetization as prolonged by the line narrowing experiments.

II. INTRODUCTION

Pulse N. M. R. is basically a dynamic technique (63) in which a nuclear spin system of interest is disturbed from equilibrium and its return to equilibrium monitored. In a rigid lattice there exist a wide variety of physical interactions important in coupling the nuclei to the lattice and thus providing the mechanism for the return to equilibrium. The nuclear spin Hamiltonian, H , consists of a number of terms that describe these physically different interactions of the nuclear spins. The significant terms of the nuclear spin Hamiltonian in a solid are given by

$$H = H_Z + H_\sigma + H_Q + H_D + H_J \quad (1)$$

Where all of these interaction Hamiltonians have the general form

$$H_C = -\hbar \vec{I} \cdot \vec{T}_C \cdot \vec{O} \quad (2)$$

This equation represents the interaction of the nuclear spin $\vec{I}$ with another physical quantity, $\vec{O}$. The tensor, $\vec{T}_C$, represents the coupling interaction between the vectors $\vec{I}$ and $\vec{O}$.

The Zeeman Hamiltonian, H_Z , couples the nuclear spins with the external static magnetic fields. Taking the external field, $\vec{H}$, along the Z direction yields

$$H_Z = -\gamma \hbar \vec{H} \cdot \vec{I}_Z \quad (3)$$

A chemical shift arises when the external field induces a screening of the nuclei, which in a solid depends upon the direction of the field relative to the molecular co-ordinate

system. The chemical shift Hamiltonian, H_σ , is (64)

$$H_\sigma = \gamma \hbar \vec{I} \cdot \vec{\sigma} \cdot \vec{H}_0 \quad (4)$$

with $\vec{\sigma}$ being the chemical shift tensor.

Nuclei with spin $\vec{I}$ greater than $\frac{1}{2}$ possess an electric quadrupole moment which may interact with the gradient of an electric field at the nucleus. In a coordinate system (X, Y, Z) in which the field gradient tensor is diagonal, the quadrupole Hamiltonian is (10)

$$H_Q = \{e^2 q Q / (4I(2I - 1))\} \{3I_z^2 - \vec{I}^2 + \gamma(I_x - I_y)\} \quad (5)$$

with the principal values V_{xx} , V_{yy} , V_{zz} of the field gradient tensor and

$$eq = V_{zz} \quad (6)$$

$$\gamma = (V_{xx} - V_{yy}) / V_{zz} \quad (7)$$

The three interaction Hamiltonians which have been discussed H_Z , H_σ and H_Q are single-spin Hamiltonians. The next two terms to be presented are many-spin Hamiltonians, which in principle couple all spins in the sample.

The magnetic dipole-dipole interaction between spins $\vec{I}_i$ and $\vec{I}_K$ separated by $\vec{r}_{iK}$ is represented by the dipolar Hamiltonian (10)

$$H_D = \sum_{i \neq K} \{ (\gamma_i \gamma_K \hbar^2) / |\vec{r}_{iK}|^3 \} (\vec{I}^i \cdot \vec{I}^K) - 3 (\vec{I}^K \cdot \vec{r}_{iK}) (\vec{I}^i \cdot \vec{r}_{iK}) / |\vec{r}_{iK}|^5 \quad (8)$$

where $\gamma_i \gamma_K \hbar^2 / |\vec{r}_{iK}|^3$ is the order of magnitude of the interaction energy between two spins corresponding to a local magnetic field at the i^{th} nucleus of $\gamma_K \hbar / |\vec{r}_{iK}|^3$. The dipolar Hamiltonian of Eq. 8 is conveniently decomposed in the following fashion (11, 65)

$$H_D = \sum_{i \neq K} (\gamma_i \gamma_K \hbar^2 / |\vec{r}_{iK}|^3) (A_{iK} + B_{iK} + C_{iK} + D_{iK} + E_{iK} F_{iK}) \quad (9)$$

where only A_{iK} and B_{iK} commute with the Zeeman operator. In solid state N. M. R. the basic concern is the secular part H_D'

of the magnetic interaction energy containing

$$A_{iK} = I_z^i I_z^K (1 - 3\cos^2\theta_{iK}) \quad (10)$$

and

$$B_{iK} = -(\frac{1}{4})(I_+^i + I_-^K + I_-^i I_+^K)(1 - 3\cos^2\theta_{iK}) \quad (11)$$

where I_+ and I_- are raising and lowering operators. H_D' may then be expressed as

$$H_D' = \frac{1}{2} \sum_{i < K} F_{iK} (3I_z^i I_z^K - \vec{I}^i \cdot \vec{I}^K) \quad (12)$$

where

$$F_{iK} = (\gamma_i \gamma_K \hbar^2 / |\vec{r}_{iK}|^3) (1 - 3\cos^2\theta_{iK}) \quad (13)$$

Notice that the summand in Eq. 12 is a product which may be considered to consist of two components, F_{iK} and $3I_z^i I_z^K - \vec{I}^i \cdot \vec{I}^K$. F_{iK} depends only on the real space coordinates, while $3I_z^i I_z^K - \vec{I}^i \cdot \vec{I}^K$ depends only on spin coordinates. This is an important observation which will be used later.

The indirect spin-spin coupling Hamiltonian may be written as

$$H_J = \sum_{i < K} \vec{I}^i \cdot \vec{J}^{iK} \cdot \vec{I}^K \quad (14)$$

where J^{iK} is a tensor of rank two.

In principle, an N. M. R. experiment might be capable of independently measuring each of the above interactions separately. For many spin $\frac{1}{2}$ nuclei ($H_{Q=0}$), major difficulty is that the dipolar interaction is sufficiently large to mask any information due to the remaining interactions. I first discuss the magnitude of the dipolar interaction, and then develop the means of removing the effect of this interaction from the solid state N. M. R. spectra.

For a stationary molecule in a solid the nucleus will "see" a total magnetic field, H_{eff} , which is the sum of two parts: (1) a contribution, $\vec{H}_0$, from the laboratory magnet and (2) a contribution, $\vec{H}_{\text{loc}}$, mainly from the dipolar fields originating in the nuclear magnetic moments associated with the spins of all neighboring nuclei. If the orientation of the magnetic moments are completely random, then the sum of their contributions, $\vec{H}_{\text{loc}}$, will be a statistical parameter. Therefore, there exists a distribution of the magnitudes of the magnetic field for an ensemble of spins in a macroscopic sample. This dispersion in the local environments of the nuclei is the cause of dipolar broadening of N. M. R. spectra of solids. For N. M. R. of protons this interaction alone gives linewidths of 50 KHz.

Nature provides a clue as to a method of "removing" the dipolar interaction. It is well-known that in liquid N. M. R. the line widths can be on the order of 1 Hz. The major reason for the sharpness of N. M. R. spectra in liquids is because the spacial orientational dependence of the dipolar interaction, F_{iK} , has become an average value. In other words, in a liquid where there exists a great amount of motion the nuclei will "see" only an average $\vec{H}_{\text{loc}}$. Unfortunately, all possible anisotropic interactions, not just the dipolar interaction, are averaged out due to rapid isotropic molecular motion in liquids.

In order to experimentally access interactions smaller than H_0 in solids, a number of ingenious schemes have been used. The

particular techniques to be discussed here involve the artificial stirring of the nuclear spins, thereby providing a motional averaging in spin space.

This dissertation is primarily concerned with the application and interpretation of these techniques on two solid state polymeric systems, polypropylene and polyethylene. In the polypropylene system both the conventional free induction decay experiment and the eight-pulse cycle (60) are used in the determination of crystallinity. For the polyethylene system a series of multiple-pulse experiments examine a variety of interaction terms.

III. EXPERIMENTAL METHODS

A. The Equipment

The repertoire of pulse N. M. R. has been considerably enlarged in the past few years by a large number of new experiments (47-57, 66-68). These experiments consist of applying a long burst of strong magnetic excitation in which the r. f. amplitude and phase are programmed in periodic, but often complicated fashion. The complex nuclear response is then monitored in the windows between cycles of r. f. excitation. The response in these windows trace out the decay which the system would execute under the influence of an "average Hamiltonian."

The following consists of a brief discussion of the spectrometer used in our research group, which is capable of performing multiple-pulse experiments. As a framework the generalized block diagram of Figure 1 shall be used. A more thorough review of the spectrometer may be obtained in the literature (69-71).

The Varian Magnet provided the permanent magnetic field H_0 of 1.4T, necessary for the separation of the nuclear spins energy. Being an electromagnet required that both the power supply and magnet were kept at a constant temperature by the circulation of water at a controlled temperature. The field homogeneity over a sphere 5 mm in diameter was approximately 0.40 ppm.

Multiple-pulse line narrowing experiments require that

$$|\vec{H}_1| \gg |\vec{H}_{int}| \quad (15)$$

Figure 1. A block diagram of the N. M. R. spectrometer used in multiple-pulse experiments.

where $|\vec{H}_{int}|$ is the magnitude of the interaction Hamiltonian, which is averaged and $|\vec{H}_1|$ is the magnitude of the r. f. magnetic field strength. Since the local dipolar fields of protons in solids is of the order of 20 G, the transmitter must be capable of supplying the required power necessary to produce a sufficient $\vec{H}_1$ in a 5 mm r. f. coil. This requirement was amply met using the IFI Model 404 Broad-banded Laboratory Amplifier. The transmitter gave linear amplification of signals in the frequency range of 200 KHz to 220 MHz with pulses of 400 watts. The 400 watts of output translates into 1 usec $\pi/2$ pulses or an $\vec{H}_1$ of 62.5 G.

The probe contains an electrical coil for the coupling of the nuclear spins with the r. f. pulses. The probe, with a tapped tuned series circuit design (72), was able to cope with the high r. f. voltage and was able to quickly dissipate the power after a pulse. With a Q of 20, the recovery time of the combined transmitter-probe-receiver system was limited by probe ring down of 3.5 usec.

One of the most crucial components of a multiple pulse spectrometer is the receiving system, which consists of a preamplifier, phase detection-demodulation system, and a d. c. amplifier. The preamplifier must be able to meet several stringent requirements: (1) withstand over-voltages from radio frequency pulses (2) have a recovery time of less than 2 usec (3) linear amplification over the range of $1\mu v$ to several millivolts (4) low noise figure. This was best accomplished by constructing the

preamplifier in three stages. The first stage is an Avantek 511 which is a wide band amplifier with a frequency response from 5 to 500 MHz and a gain of 16 ± 1 db. The second and third stage are Spectrum Microwave Model SML-D10 limiting amplifiers. These wide band amplifiers responded to frequencies in the range of 40 to 380 MHz and have a gain of 30 db each. The d. c. amplifier behaves both as an amplifier and as a filter. This is accomplished by limiting the bandwidth from d. c. up to 1 MHz depending on the filter setting. The d. c. amplifier has voltage gain from 55 to 550 in five steps.

A Biomation TM805 transient recorder, with a minimum sampling time of 0.2 usec was used to accumulate all data. The memory of the unit contains 2048 eight bit words. The Biomation is interfaced with a PDP-11/10 computer for signal averaging and data manipulation.

B. Experimental Procedure

Unless otherwise specified the measurements reported here were done at room temperature on the spectrometer previously described. Measurements have involved the standard T_2^* and T_1 pulse experiments, and multiple-pulse measurements using an eight-pulse cycle (57), the $-M_x$ phase pull sequence (73), the $P_x - M_y$ phase pull sequence, and a seventeen-pulse cycle.

The net magnetization $\vec{M}$ following a $\pi/2)_x$ pulse lies entirely along the y axis. The net magnetization is then observed to

dephase in the x-y plane with the characteristic time constant T_2^* . This experiment is commonly referred to as the free induction decay experiment with the dominant interaction in solids being dipolar.

The procedure employed to determine the time constant for the spin-lattice relaxation, T_1 , was the basic $\pi)_y, \tau, \pi/2)_x$ sequence. The $\pi)_y$ pulse inverts the net magnetization along the z axis. The system returns to equilibrium at a rate of $1/T_1$ for a period τ . The $\pi/2)_x$ pulse places the net magnetization along the y axis where the initial amplitude is observed and recorded. The system is allowed to return to equilibrium and the sequence repeated for a different τ . Since $1/T_1$ determines the rate at which the system returns to equilibrium, it also determines the period between experiments, which is typically $5 T_1$. The value of T_1 is sensitive to molecular motion in the MHz region.

The multiple pulse sequence which averages the dipolar interaction to second order is referred to as an eight-pulse cycle. The pulse sequence for the eight-pulse cycle is shown in Figure 2. Sampling of the magnetization is performed in the 2τ window at the end of each eight-pulse cycle. The initial pulse is a preparation pulse which places the net magnetization along the y axis. The spectrometer was properly tuned so that the effects of instrumental artifacts were minimized (60). The eight-pulse cycle averages the dipolar interactions, at observation

Figure 2. The eight-pulse cycle used for the averaging of the homonuclear dipolar interactions. The cycle time for the pulse sequence is t_c and the pulse width is τ_w .

times nt_c , only when the criteria

$$t_c |H_D| \ll 1 \quad (16)$$

is met. Therefore, it is critical to obtain cycle times, t_c , as small as possible, consistent with best averaging. Cycle times as short as 20.4 usec were obtained in the present work. The most interesting information obtained for the eight-pulse cycle experiment are the three components, σ_x , σ_y , σ_z , of the chemical shift tensor. However, the eight-pulse cycle may also be applied to the investigate molecular motions in the 10 - 100 KHz range.

The $P_x - M_y$ phase pull sequence consists of a modified eight-pulse cycle. The modification comes in the introducing of a phase error in the x pulse. The phase is pulled until an on resonance signal is observed. The deliberate phase error averages out second order dipolar interaction $H_D^{(2)}$ and the chemical shift term, H_σ to all orders. The only relaxation available is the multiple-pulse spin-lattice relaxation.

The $-M_x$ phase pull sequence also consists of a modified eight-pulse cycle. The modification comes in the introducing of a phase error in the x pulse, the removal of the preparation pulse, and observing the signal along the x direction. The phase is pulled to observe the longest time decay. The effective relaxation mechanisms under the $-M_x$ phase pull sequence are second order dipolar and the multiple-pulse spin-lattice.

The seventeen-pulse cycle is the newest and least tested multiple-pulse technique. The pulse cycle consists of two

eight-pulse subsycles separated by a π_y pulse. Sampling is performed at the end of each seventeen-pulse cycle. The effective relaxation mechanisms under the seventeen-pulse cycle are second order dipolar and the multiple-pulse spin-lattice.

Two commercial polypropylene films, which had been treated differently, were obtained from Hercules Chemical Company Incorporated. Both films were cast from Pro-fax Polypropylene 6523 film using a Hartig extruder by Dr. Edward Tokarsky. The films are approximately 7 mm wide and showed no apparent crystalline orientation by X-ray methods. One of the films was maintained at 150 - 155°C for 15 minutes and then cooled slowly to room temperature. This process supposedly caused the diameter of the crystallites to increase from 70Å to about 140Å.

A sample of pressure-crystallized linear polyethylene was obtained from the National Bureau of Standards. This sample was composed mainly of extended-chain crystals and has a degree of crystallinity of 96 percent.

The crystallization of the sample was carried out as follows. A sample of SRM 1475 linear polyethylene was placed in a steel pressure vessel, 2.5-cm I. D. and 2.5-cm wall thickness, and then pumped down to a pressure of about 1×10^{-4} mm of Hg. After 2 h, a sealing plug was forced into the bore and the vessel was disconnected from the vacuum line. A piston was used to push the plug until the load reached 5000 lb. The whole vessel was then heated to 210°C while the position of the piston was kept

constant. To do this the load on the piston was increased to about 60,000 lb. The piston load was reduced in order to melt the polymer and then increased in 2500 lb. increments, followed by 5 minute waiting periods, to crystallize the sample under high pressure. After 20 minutes the heaters were switched off and the load on the advancing piston was kept between 60,000 and 65,000 lb. as the vessel was cooled to 100°C. After cooling to 25°C over a 15 hour period the load was 45,000 lb. The sealing plug was withdrawn and the sample removed.

IV. DETERMINATION OF DEGREE OF CRYSTALLINITY IN POLYPROPYLENE

A. The Free Induction Decay Technique

Some polymers consist of two macroscopic regions, crystalline and noncrystalline. The polymer structure in the crystalline region can be determined by X-ray diffraction. One model (74, 75) for the noncrystalline region is indicated in Figure 3. This model consists of loops hanging out of the crystals (l_1 , l_3 , and l_4), regular folds (l_2), tie molecules connecting two different crystals (t_1 and t_2), and chains with one free end (f). The type of chain which dominates the noncrystalline regions probably depends on the conditions of crystallization. An important consideration in understanding mechanical behavior of polymers is motion and partial orientation of the noncrystalline regions (76).

As a consequence of the influence of the mobility on the relaxation rate, $1/T_2$, the F. I. D. signal of a partially crystalline material above the glass transition temperature consists of two components: (1) a long component, M , caused by the chains in the noncrystalline regions which are able to perform segmental motion, and (2) a short component caused by the chains in the crystals, R_C , and by the comparatively rigid chains in the noncrystalline regions, R_{NC} , as for example chain t_1 in Figure 3. In this case the crystalline fraction, $R_C/(M + R_C + R_{NC})$, is not equal to the rigid fraction, $(R_C + R_{NC})/(M + R_C + R_{NC})$. Therefore, under these conditions, it is impossible to determine the degree

Figure 3. Representation of different types of chains in a noncrystalline region

Figure 4. The volume-temperature relations for a polymer glass

of crystallinity with a single pulse N. M. R. experiment. One possible method to circumvent the present difficulties is to heat the sample. In order to clarify the previous statement it will be necessary to discuss the various thermal transitions found in polymers.

Polymeric materials are characterized by two major types of transition temperatures--the crystalline melting temperature, T_m , and the glass transition temperature, T_g . The crystalline melting temperature is the melting temperature of the crystalline domains of a polymer sample. The glass temperature is a condition best appreciated by considering the rapid increase of viscosity which occurs when liquids are cooled and when crystallization does not take place. Some compounds e.g. NaCl will crystallize on cooling to their melt temperature. In other compounds with sufficiently complex molecular units, the rate of crystallization may become so slow that a glass is formed before a significant portion of the material has crystallized. Therefore, in those cases where the polymer is capable of crystallization, the crystallization is generally incomplete, so a substantial part of the polymer assumes a glassy state as the polymer is cooled further.

Figure 4 assumes that substances can crystallize or solidify to a glass depending upon the experimental conditions (77). If crystallization occurs, then at the melting temperature there is a discontinuous change, nearly always a decrease, in volume.

But if the melt is cooled and crystallization prevented, the transition from the highly viscous supercooled melt to the rigid glass will begin at T_e . The volume-temperature plot then joins the curve for the glass at T_{g1} , where the solidification process is terminated. The temperature at the intersection of the extrapolated curves of the melt and glass respectively is called the glass transition temperature, T_g .

The temperatures T_e , T_g , and T_{g1} depend on the rate of cooling. As shown in Figure 4, the volume-temperature course of glass 1 will approach that of glass 2 if the rate of cooling is reduced sufficiently. Thus the characteristics, in this case the volume, of the glass formed are in part determined by its previous history. Glass 1 cannot be changed to glass 2 except by heating above the freezing-in temperature, T_e . It should be noted that below T_e crystalline growth is nonexistent. Therefore, it follows that a glass is not in a state of internal equilibrium and its equilibrium properties are not fully defined by an equation of state when the temperature and pressure are fixed.

The heating of the polymer will cause a decrease in viscosity allowing for an increase in mobility. Consequently, the percent of rigid chains in the noncrystalline region, R_{NC} , decreases with increasing temperature. However, care must be taken not to alter the characteristic of the polymer by heating to a temperature greater than T_e . Hopefully, as the temperature approaches T_e ,

the value of R_{NC} will approach zero. Under this condition, the crystalline fraction and the rigid fraction are synonymous.

The two component decay of the polypropylene samples was found to fit the superposition of a Gaussian and Lorentzian decay. The relation is given by

$$M(t) = M_s^0 \exp - (t/(\sqrt{2} T_{2s}))^2 + M_l^0 \exp - (t/T_{2l}) \quad (17)$$

where M_s^0 and M_l^0 are the initial magnetizations due to the rigid and mobile regions respectively. Table I illustrates the temperature dependence of T_{2l} , T_{2s} , and the percent rigid component for the two polypropylenes. To interpret the data however, there must be evidence that the characteristics of the polymer were not changed by heating. This condition guarantees that the temperature did not exceed the freezing in temperature, T_e . This was accomplished experimentally by quenching the sample after the final run and repeating the experiment at 22°C. The four parameters for the two runs at 22°C agreed to within experimental error. Therefore the conclusion can be made that the freezing in temperature, T_e , was not exceeded. In both polymers the short decay constant, T_{2s} , remains nearly constant over the entire temperature range. This is indicative that the increasing temperature is having a negligible affect on the crystalline region. In contrast the long decay constant, T_{2l} , exhibits marked increases with increasing temperature. This increase of T_{2l} is due to the increase in segmental motion in the noncrystalline region. Also, the percent rigid component shows a decrease as the temperature is increased.

Table 1. Temperature dependence of T_{21} , T_{2s} , and percent rigid component

Sample	Conditioned Polypropylene			Unconditioned Polypropylene		
Temp(°C)	<u>T_{2s} (usec)</u>	<u>T₂₁ (usec)</u>	<u>Rigid %</u>	<u>T_{2s} (usec)</u>	<u>T₂₁ (usec)</u>	<u>Rigid %</u>
22	9.6	35	88	10	25	85
34	9.8	60	86	10	26	69
43	10	84	83	10	37	63
56	10	120	82	11	60	61
72	11	170	79	12	97	58
88	11	200	76	12	113	59

The decrease in rigid component is due to the fact that rigid noncrystalline regions become mobile noncrystalline regions with increasing temperature.

Table 2. The comparison of the degree of crystallinity of two polypropylene samples as determined by a variety of experimental techniques

Technique	Percent crystallinity of polypropylene	
	Conditioned	Unconditioned
F. I. D. at 22°C	88	85
ΔH_f	80	55
F. I. D. at 88°C	76	59
Density	72	
Eight-pulse cycle	67	65

Table 2 illustrates the various values obtained for percent crystallinity with different techniques. For the F. I. D. technique the values at both 22°C and 88°C are given. The values for 88°C clearly are in better agreement with the other techniques, than are the value at 22°C. This tends to support the belief that as

the temperature approaches the freezing in temperature, T_e , the rigid fraction will approach the value of the crystalline fraction.

B. The Eight-Pulse Cycle Technique

In the previous section we saw how a single pulse experiment made it possible to obtain two decays due to the two macroscopic phases. It was not possible to unambiguously separate the contributions due to these phases, however. One possible solution to the dilemma appears to be the eight-pulse cycle (60), which at appropriately selected cycle times allows the experimenter to see the noncrystalline region.

The eight-pulse cycle shown in Figure 5 is the multiple pulse sequence designed for the averaging of the homonuclear dipolar interaction to first order, which is the major interaction in polypropylene. During the period τ the spin systems evolve in time under homonuclear dipole-dipole interactions with the net magnetization decaying according to the relation

$$M(t) = M_s^0 \exp - (K_s T)^2 + M_l^0 \exp - (K_l T) \quad (18)$$

where K_s and K_l are the rate constants for the short and long components respectively. The eight-pulse cycle averages the homonuclear dipole-dipole interactions, H_D , only at observation times nt_c , when the criteria

$$t_c |H_D| \ll 1 \quad (19)$$

is met. If this condition is met for all dipolar interactions,

Figure 5. The r. f. pulse sequence for homonuclear decoupling is shown. P_u is a preparation pulse applied prior to the first eight-pulse cycle

the net magnetization will decay as

$$M(t) = M^0 \exp - (Kt) \quad (20)$$

where M^0 is the magnetization at initial time t_0 and the value of K is primarily related to the chemical shift anisotropy. In order to calculate the total number of protons the experiment is repeated utilizing exactly the same conditions on a standard water sample.

The utility of the eight-pulse cycle for the determination of the crystallinity in polypropylene involves the selection of a cycle time satisfying

$$t_c |K_I/\pi| \ll 1 \quad (21)$$

and

$$t_c |K_S/\pi| \geq 1 \quad (22)$$

The first condition states that the cycle time is sufficiently short to average the homonuclear dipole-dipole interactions of the mobile fraction. The second condition states that the cycle time is too long to average the dipolar interaction of the rigid component. Therefore, the rigid component will decay with the time constant K_S and will have appreciably decayed before the first data point is collected. Hence the only protons seen are in the mobile fraction. The mobile fraction will be given by

$$M. F. = (M^0 \exp(K_I \tau)) / (M_I^0 + M_S^0) \quad (23)$$

This technique was first used on polyethylene (40) where a direct interpretation of degree of crystallinity was possible under the assumption that the mobile fraction and the noncrystalline fraction were identical.

Before attempting to determine the degree of crystallinity utilizing the eight-pulse cycle, it was first necessary to determine the appropriate cycle times needed to satisfy Eq. 21, 22. Figure 6 is a plot of the percent of the number of protons observed versus cycle time. At very short cycle times the eight-pulse cycle is essentially effective in averaging the homonuclear dipolar interactions of all the protons. Hence at a cycle time of 24 usec all the protons are observed. With increasing cycle time the eight-pulse cycle does not average the homonuclear dipole interactions of all the protons as a consequence the percent of the protons observed decreases. At a cycle time of 54 usec there is an abrupt decrease in the percent of the protons observed. This abrupt change is the failure of the homonuclear dipolar interactions in the rigid regions to be averaged to zero at cycle times greater than 54 usec. Therefore at a cycle time of 72 usec only the noncrystalline protons are observed.

Table 2 allows for the comparison of the degree of crystallinity obtained with the eight-pulse cycle with other techniques. According to the eight-pulse cycle results, the degree of crystallinity for the two polypropylene samples is nearly identical. The F. I. D. technique at 22°C also indicates that the degree of crystallinity for the two samples is nearly the same. These results tend to infer that at room temperature the two samples "look" the same to solid state N. M. R.

Figure 6. The percent of protons in a sample of polypropylene detected under the eight-pulse cycle as a function of cycle time

V. STUDY OF POLYETHYLENE USING MULTIPLE-PULSE N. M. R.

When dipolar contributions are attenuated by motional averaging in spin space via appropriate multiple-pulse experiments, there remains the relatively smaller contribution to the magnetic environment of a given nucleus, arising from the surrounding electronic configuration. When a molecule is placed in a magnetic field, motion is induced in its electrons. This motion in turn induces a "shielding" field, $\vec{H}_s$, which has magnitude proportional to the external field, $\vec{H}_0$. This proportionality constant is referred to as the shielding constant and is represented by σ . One of the characteristics of crystalline substances are physical properties which are anisotropic in space. The variation of the induced magnetic moment with direction of the applied field is only one example of this phenomenon.

Suppose, in a single molecule that a magnetic field $\vec{H}_1$ in the x-direction induces a magnetic field $\vec{H}_{s1}$ in the x-direction. Similarly a magnetic field $\vec{H}_2$ in the y-direction with the same magnitude as $\vec{H}_1$, induces a magnetic field $\vec{H}_{s2}$ in the y-direction with a different magnitude from $\vec{H}_{s1}$. If both $\vec{H}_1$ and $\vec{H}_2$ are simultaneously applied, the resultant magnetic field will be the vector sum of the two individual fields. Likewise the net induced magnetic field will be the vector sum of $\vec{H}_{1s}$ and $\vec{H}_{2s}$. However, the induced magnetic field is no longer in the same direction as the applied magnetic field.

Generally the induced magnetic moment is not in the direction of the applied magnetic field. If the molecule were rotated with respect to the coordinate axis, the magnetic field $\vec{H}_2$ in the y-direction would induce a magnetic field with both x and y components. Similarly, $\vec{H}_1$ would induce a magnetic field with both x and y components. The situation is more complex, but still the magnitude of the induced magnetic field is proportional to any applied magnetic field.

Finally consider the general case of an arbitrary orientation of a molecule with respect to the coordinate axes. A magnetic field in the x-direction will induce a magnetic field with the x, y, and z components

$$\vec{H}_{s1} = \sigma_{xx} \vec{H}_x, \vec{H}_{s2} = \sigma_{xy} \vec{H}_x, \vec{H}_{s3} = \sigma_{xz} \vec{H}_x \quad (24)$$

Similarly, for a field in the y-direction

$$\vec{H}_{s1} = \sigma_{yx} \vec{H}_y, \vec{H}_{s2} = \sigma_{yy} \vec{H}_y, \vec{H}_{s3} = \sigma_{yz} \vec{H}_y \quad (25)$$

and for a field in the z-direction

$$\vec{H}_{s1} = \sigma_{zx} \vec{H}_z, \vec{H}_{s2} = \sigma_{zy} \vec{H}_z, \vec{H}_{s3} = \sigma_{zz} \vec{H}_z \quad (26)$$

Therefore, the net induced magnetic field $\vec{H}_s$ in the external field $\vec{H}_0$ is given by

$$\vec{H}_s = \overline{\sigma} \cdot \vec{H}_0 \quad (27)$$

where $\overline{\sigma}$ is the chemical shift matrix and has the form

$$\begin{array}{ccc} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{array}$$

The values of the coefficients are arbitrary in the sense that they depend upon the coordinate system selected. To avoid this

arbitrariness, the standard convention is to report the principal axis values with $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$. In reporting values of shielding in this manner implicit recognition is made of the fact that for protons, $\bar{\sigma}$ is for all practical purposes symmetric.

There are two methods for obtaining the principal axis values using N. M. R. The first method considered involves use of experiments on a single crystal, which for simplicity of discussion will have all nuclei of interest in magnetically equivalent sites. The effective magnetic field at each nucleus is given by

$$\vec{H}_{\text{eff}} = \vec{H}_0 - \vec{H}_s \quad (28)$$

and therefore the frequency of radiation that induces a transition between adjacent energy levels is

$$\nu_0 = \gamma |\vec{H}_{\text{eff}}| / 2\pi \quad (29)$$

Because all sites were selected to be magnetically equivalent, only one frequency will appear in an absorption. By rotating the crystal, $\vec{H}_{\text{eff}}$ changes, and consequently the N. M. R. frequency changes. Careful measurement of the change in frequency with rotation angle allows the determination of the principal axes of the chemical shift matrix, and the alignment of the nucleus in the crystal.

Many solid samples are difficult or impossible to obtain in single crystal forms. The experiment then must be done on powdered, randomly oriented samples. Because the N. M. R. absorption line varies with orientation of $\vec{H}_0$ relative to local

crystal axes, the resultant spectrum is smeared over a range of frequencies. Analysis of the spectrum will yield principal axes of the matrix, but not orientation. The particular chemical shift matrix considered here is an axially symmetric matrix where $\sigma_{11} = \sigma_{22} \neq \sigma_{33}$. For this case it has been shown (78) that the line shape is given by

$$N(\sigma) = K\{(\sigma_{||} - \sigma_{\perp})(\sigma - \sigma_{\perp})\}^{-\frac{1}{2}} \quad (30)$$

where K is a normalization constant, $\sigma_{||} = \sigma_{11} = \sigma_{22}$, $\sigma_{\perp} = \sigma_{33}$, and $N(\sigma)$ is a distribution over chemical shifts. An illustration of an axially symmetric chemical shift matrix is shown in Figure 7.

The point of the present work is the use of strong homonuclear decoupling to selectively remove the effects of dipolar interactions while retaining the effects of other interactions, in particular the chemical shifts including their anisotropic parts. The major objectives of the experimenter then becomes: (1) the careful selection of compounds "well suited" for powder multiple-pulse work (2) to maximize the spectral resolution (3) the actual measurement of the chemical shift tensor.

The first objective concerned with the selection of a sample compound is important if one intends to obtain interpretable results. Several of the basic criteria for a compound which is "well-suited" for powder multiple-pulse work are:

- (1) The compound itself and the space group in which it crystallizes should be such that the spectrum is not overcrowded with lines.

Figure 7. The theoretical line shape of an axially symmetric shift tensor

- (2) The compound contains a limited selection of atoms, such that heteronuclear broadening is minimized.
- (3) The compound should be preferably a rigid solid at room temperature, to avoid dynamic dipolar broadening.

An examination of Linear High Pressure Polyethylene verifies that it satisfies almost all of the above criteria.

Linear polyethylene contains predominantly one chemically distinct proton, that in the methylene group ($-\text{CH}_2-$). Methylene protons in malonic acid, succinic acid and succinic acid anhydride have been studied by Haberland (79-81) and found to exhibit a relatively small chemical shift anisotropy. To complicate matters, the methylene protons have a large dipolar interaction due to the small nearest neighbor internuclear distance of 1.7 Å. Therefore, the determination of the chemical shift anisotropy is a formidable task and requires very strong homonuclear decoupling for maximum resolution. Although several excellent papers by Rhim et al. (57, 60) provide general guidelines, the only method presently available for determining which experimental parameters yield the best resolution is ultimately parameter variation in the experiment itself.

Figures 8 and 9 give the dependence of linewidth or resolution on cycle time and offset respectively. The figures indicate that the best resolution will occur at a cycle time of 21.6 μsec and an offset of +500 Hz. Performing the experiment near the previously described conditions gave the spectrum shown in Figure 10. The

Figure 8. The resolution of Linear High Pressure Polyethylene under the eight-pulse cycle as a function of cycle time at an offset of +500 Hz

Figure 9. The resolution of Linear High Pressure Polyethylene under the eight-pulse cycle as a function of offset at a cycle time of 21.6 usec

Figure 10. The eight-pulse spectrum ($t_c = 20.4$ usec) of Linear High Pressure Polyethylene fitted to an axially symmetric tensor with an anisotropy of +4.72 ppm

crosses represent the experimental data and the solid line is obtained by computerized fitting (78) of Eq. 30. The chemical shift tensor for the CH_2 proton determined by the present work is axially symmetric and has a total anisotropy, $\sigma_{11} - \sigma_{\perp}$, of 4.72 ppm which is somewhat less than that found for protons in the neighborhood of carbonyl groups, and surprisingly almost a factor of two less than that found in succinic acid and its anhydride (Table 3).

As we have seen, a useful measurement in solid state N. M. R. is that of the line shape associated with the chemical shift anisotropy. This line shape is revealed when the dipolar Hamiltonian is attenuated under the appropriate multiple pulse sequence. However, this line shape may be distorted due to other Hamiltonians which also survive under the eight-pulse cycle and give significant contributions to the frequency spectra. It appears in cases where significant unwanted broadening was exhibited, that the majority of the broadening could be attributed to three interaction terms:

- (1) The second order dipolar term in the Magnus Expansion, $\bar{H}_D^{(2)}$, tends to become larger if the cycle time is not short enough or if there exists considerable molecular motion.
- (2) The life-time broadening term which corresponds to the spin-lattice relaxation times under the multiple-pulse experiment, and sets the limit to the narrowing. It

Table 3. The chemical shift anisotropy in ppm of the methylene protons for different compounds

Compound	Formula	$\sigma_{ } - \sigma_{\perp}$	Ref
Malonic acid	$\text{CH}_2^*(\text{COOH})_2$	5.9	80
Malonic acid	$\text{CH}_2^*(\text{COOH})_2$	4.9	80
Succinic acid	$(\text{CH}_2^*\text{COOH})_2$	8.6	81
Succinic acid Anhydride	$(\text{C}_4\text{H}_4\text{O}_3)$	10.2	81
Polyethylene	$\{\text{CH}_2\}_n$	4.7	

is important to realize that T_{1y} is in general shorter than the longitudinal relaxation time T_1 .

- (3) Finally broadening may be attributed to a wide variety of instrumental artifacts.

The discussion to follow involves the ability of the multiple pulse techniques to selectively alter the manner in which each of these Hamiltonians affects the time evolution of the spin system. Thus one may sort the various contributions and determine the quantitative effect of each Hamiltonian. As an example, four multiple pulse cycles together with the conventional free induction decay will be used to examine the contributions of the various Hamiltonians of Linear High Pressure Polyethylene.

The free induction decay and the frequency spectrum of Linear High Pressure Polyethylene are shown in Figure 11. The complex line shape in the frequency spectrum is associated with the two phases present in the polyethylene sample. The relatively large line width of 1,256 ppm indicates a rigid solid with little molecular motion. The contributions to the line shape of the

free induction decay spectrum are from the secular dipolar, chemical shift, and relaxation effects. The relaxation contribution is shown to be small from the measured value of the spin-lattice relaxation time of approximately 1 sec. The contribution of the chemical shift was previously obtained in the fitting of the powder pattern and is 4.72 ppm. Therefore, the secular dipolar term accounts for nearly all of the broadening.

In principle one should be able to experimentally estimate the magnitude of the chemical shift interaction by applying either the seventeen-pulse cycle or the $-M_x$ phase pull sequence in conjunction with the eight-pulse cycle. Since the primary interaction remaining under the seventeen-pulse cycle and the $-M_x$ phase pull sequence are residual dipolar, instrumental, and relaxation effects, it is possible to subtract the line width associated with these measurements from the normal eight-pulse spectrum and thus isolate the contribution due to the chemical shift interaction. The value obtained in such a manner should coincide with the value of 4.72 obtained in fitting the powder pattern.

A typical time spectrum of the seventeen-pulse cycle for the polyethylene sample is shown in Figure 12. This complex decay can be decomposed into at least two independent decays. A physical basis for the two decays is not yet understood. In the first column of Table 4 the seventeen-pulse cycle results are used in conjunction with the eight-pulse cycle results to

Figure 11. A time decay and a frequency spectrum of Linear High Pressure Polyethylene following a free induction decay experiment

Figure 12. The seventeen-pulse time decay of Linear High Pressure Polyethylene at a τ of 1.8 usec which corresponds to 21.6 usec/channel

Table 4. The analysis of a variety of interaction terms in ppm of Linear High Pressure Polyethylene

Evaluation Technique	8 pulse minus 17 pulse	8 pulse minus $-M_x$	$P_x - M_y$	$-M_x$ minus $P_x - M_y$
Interaction Hamiltonian	H_σ	H_σ	$H_{\text{Lifetime}} + H_{\text{inst}}$	$\sum_i H_D^{(i)}$
τ (usec)				
2.0	5.4	4.4	8×10^{-3}	6.0
2.4	0.9	3.1	44×10^{-3}	8.7
2.6	2.0	3.8		8.6
2.9	0.0	5.7	77×10^{-3}	8.2

evaluate the chemical shift interaction. At a τ of 2 usec, where the spin averaging is sufficient, the experimental determination of the chemical shift interaction yields a value of 5.4 ppm, which agrees well with the value of 4.7 ppm obtained in the fitting of the powder pattern. The evaluations of the chemical shift interaction at larger τ do not agree well with this value. The cause for the abrupt breakdown is the lack of averaging dipolar interaction at larger cycle times.

Several frequency spectra of the $-M_x$ phase pull experiment are shown in Figure 13 and Figure 14. In the second column of Table 4 the $-M_x$ phase pull results are used in conjunction with the eight-pulse cycle results to evaluate the chemical shift interaction. All the values thus obtained reflect to within experimental error the expected chemical shift anisotropy of 4.7 ppm. The average chemical shift anisotropy obtained from column 2 is 4.3 ppm. Therefore, where the seventeen-pulse cycle fails

Figure 13. The $-M_x$ phase pull spectra of Linear High Pressure Polyethylene at a τ of 2.0 usec which corresponds to 40 Hz/channel

Figure 14. The $-M_x$ phase pull spectra of Linear High Pressure Polyethylene at a τ of 2.9 usec which corresponds to 28 Hz/channel

to selectively average the second order dipolar, instrumental, and relaxation effects, the $-M_x$ phase pull is successful.

A further analysis of the various interaction terms can be obtained through the application of the $P_x - M_y$ phase pull sequence. The major interactions for this sequence are instrumental and relaxation effects. In Figure 15 and Figure 16 several phase pull time decay spectra of the polyethylene sample are illustrated. The results in column 3 of Table 4 indicate that the contribution due to instrumental broadening is less than 8×10^{-3} ppm. The residual dipolar term $\sum_i H_D^{(i)}$ is evaluated by subtracting the interaction associated with the $P_x - M_y$ phase pull sequence from the $-M_x$ phase pull sequence. This residual term appears to be the dominating interaction of the $-M_x$ phase pull sequence.

Figure 15. The $P_x - M_y$ phase pull time decay of Linear High Pressure Polyethylene at a τ of 2.4 usec which corresponds to 34.8 usec/channel

Figure 16. The $P_x - M_y$ phase pull time decay of Linear High Pressure Polyethylene at a τ of 2.9 usec which corresponds to 34.8 usec/channel

VI. REFERENCES

1. F. Bloch, Phys. Rev. 70, 460 (1964).
2. F. Bloch, W. W. Hansen, and M. Packard, Phys. Rev. 70, 474 (1964).
3. E. M. Purcell, N. Bloembergen, and R. V. Proud, Phys. Rev. 73, 679 (1948).
4. J. A. Saurer and A. E. Woodward, Rev. Mod. Phys. 32, 88 (1960).
5. C. P. Slichter, Macromolek. Chem. 34, 77 (1959).
6. D. W. McCall, Acc. Chem. Res. 4, 223 (1971).
7. A. E. Woodward, SPE Trans. 2, 86 (1962).
8. A. E. Woodward, Trans. N. Y. Acad. Sci. 24, 250 (1962).
9. D. W. McCall and D. R. Falcone, Trans. Faraday Soc. 66, 262 (1970).
10. A. Abragam, Principles of Nuclear Magnetism (Clarendon Press, Oxford, 1961).
11. C. P. Slichter, Principles of Magnetic Resonance (Harper and Row, New York, 1963).
12. T. C. Farrar and E. D. Becker, Pulse and Fourier Transform N. M. R. (Academic Press, New York, 1971).
13. J. G. Powles and H. S. Gutowsky, J. Chem. Phys. 21, 1965 (1953).
14. I. Ya Slonim and A. N. Lyubimov, The N. M. R. of Polymers (Plenum Press, New York, 1970).
15. C. W. Wilson, J. Polymer Sci. 56, 516 (1962).
16. R. C. Ferguson, J. Polymer Sci. A2, 4735 (1964).
17. C. W. Wilson and G. E. Pake, J. Polymer Sci. 10, 503 (1953).
18. C. W. Wilson and G. E. Pake, Phys. Rev. 89, 896 (1953).
19. R. L. Collins, Bull. Amer. Phys. Soc. 1, 216 (1956).
20. D. C. Smith, Industr. Engng. Chem. 48, 1161 (1956).
21. N. Fuschillo, E. Rhian, and J. A. Saurer, J. Chem. Sci. 25, 381 (1957).

22. W. P. Slichter and D. W. McCall, J. Polym. Sci. 25, 230 (1957).
23. C. W. Wilson and G. E. Pake, J. Chem. Phys. 27, 115 (1957).
24. J. G. Powles and A. Hartland, Nature, Lond. 186, 26 (1960).
25. J. G. Powles, A. Hartland, and J. A. Kail, Proc. Phys. Soc. Lond. 75, 243 (1960).
26. N. Fuschillo and J. A. Saurer, Bull. Am. Phys. Soc. 2, 125 (1957).
27. W. P. Slichter and E. R. Mandell, J. Phys. Chem. 62, 334 (1958).
28. W. P. Slichter, J. Appl. Phys. 31, 1865 (1966).
29. Proceedings of the First Specialized Colloque Ampere, ed. J. W. Hennel, Inst. Nuclear Physics, Krakow, 1973.
30. E. R. Andrew, Proc. First Specialized Colloque Ampere, ed. J. W. Hennel, Inst. of Nuclear Physics, Krakow, 1973, (1).
31. E. R. Andrew, W. S. Hinshaw, and A. Jasinski, Chem. Phys. Letters 24, 399 (1974).
32. H. Pivcova, D. Daskocilova, Z. Veksli, and B. Schneider, J. Magn. Resonance 14, 182 (1974).
33. H. Benoit and M. Rabii, Chem. Phys. Letters 21, 466 (1973).
34. M. Rabii, Compt. rend. (B) 277, 269 (1973).
35. A. Pines, M. G. Gibby, and J. S. Waugh, J. Chem. Phys. 34, 1663 (1961).
36. P. K. Grannel, P. Mansfield, and M. B. Whittaker, Phys. Rev. (B) 8, 4149 (1973).
37. B. Pansak, A. Pines, and J. S. Waugh, J. Chem. Phys. 59, 591 (1973).
38. B. C. Gerstein and R. G. Pembleton, Analytical Chem. 49, 75 (1977).
39. B. C. Gerstein, C. Chow, R. G. Pembleton, and R. C. Wilson, J. Phys. Chem. 81, 565 (1977).
40. R. G. Pembleton, R. C. Wilson, and B. C. Gerstein, J. Phys. Chem. 66, 5133 (1977).

41. L. M. Ryan, R. C. Wilson, and B. C. Gerstein, Chem. Phys. Letters 52, 341 (1977).
42. L. M. Ryan, R. C. Wilson, and B. C. Gerstein, J. Chem. Phys. 67, 4310 (1977).
43. C. R. Dybowski and R. W. Vaughan, Macromolecules 8, 50 (1975).
44. B. C. Gerstein, R. G. Pembleton, R. C. Wilson, and L. M. Ryan, J. Chem. Phys. 66, 361 (1977).
45. R. G. Pembleton, L. M. Ryan, and B. C. Gerstein, Rev. Sci. Instrum. 48, 1286 (1977).
46. P. Mansfield, Progr. N. M. R. Spect. 8, 43 (1971).
47. P. Mansfield and D. Ware, Phys. Letters 22, 133 (1966).
48. J. S. Waugh and L. M. Huber, J. Chem. Phys. 47, 1862 (1967).
49. D. Ware and P. Mansfield, Phys. Letters 25A, 651 (1967).
50. J. S. Waugh, L. M. Huber, and E. D. Ostroff, Phys. Letters 26A, 211 (1968).
51. P. Mansfield and D. Ware, Phys. Letters 27A, 160 (1968).
52. J. S. Waugh, C. H. Wang, L. M. Huber, and R. L. Vold, J. Chem. Phys. 48, 622 (1968).
53. J. S. Waugh, L. M. Huber, and U. Haeberlen, Phys. Rev. Letters 20, 180 (1968).
54. U. Haeberlen and J. S. Waugh, Phys. Rev. 175, 453 (1968).
55. W. A. B. Evans, Ann. Phys. 48, 72 (1968).
56. P. Mansfield and K. H. B. Richards, Chem. Phys. Letters 3, 169 (1969).
57. W. K. Rhim, D. D. Elleman, and R. W. Vaughan, J. Chem. Phys. 59, 566 (1973).
58. C. H. Wang, J. Chem. Phys. 59, 225 (1973).
59. W. K. Rhim, D. D. Elleman, and R. W. Vaughan, J. Chem. Phys. 59, 3740 (1973).
60. W. K. Rhim, D. D. Elleman, L. B. Schreiber, and R. W. Vaughan, J. Chem. Phys. 60, 4595 (1974).

61. L. Van Gerven, Nuclear Magnetic Resonance in Solids (Plenum Press, New York and London, 1974).
62. R. Müller and R. Willsch, J. Magn. Reson. 21, 135 (1976).
63. N. G. McGrum, B. E. Read, and G. Williams, Anelastic and Dielectric Effects in Polymeric Solids (John Wiley & Sons, London, New York, and Sidney, 1967).
64. E. R. Andrew and V. T. Wynn, Proc. Roy. Soc. 291, 257 (1966).
65. U. Haeberlen and J. S. Waugh, Phys. Rev. 185, 420 (1969).
66. P. Mansfield, J. Phys. C. 4, 1444 (1971).
67. L. M. Stacey, R. W. Vaughan, and D. D. Elleman, Phys. Rev. Lett. 26, 1153 (1971).
68. R. W. Vaughan, D. D. Elleman, W. K. Rhim, and L. M. Stacey, J. Chem. Phys. 57, 5383 (1972).
69. R. W. Vaughan, D. D. Elleman, L. M. Stacey, W. K. Rhim, and J. W. Lee, Rev. Sci. Instrum. 43, 1356 (1972).
70. B. Gerstein, C. Chow, R. Pembleton, and R. Wilson, J. Phys. Chem. 81, 565 (1977).
71. J. D. Ellett, M. G. Gibby, U. Haeberlen, L. M. Huber, A. Pines, and J. S. Waugh, Adv. Magn. Reson. 5, 117 (1971).
72. P. D. Murphy and B. C. Gerstein, Analysis and Computerized Design of N. M. R. Probe Circuits (IS-4436, Ames Lab., DOE, 1978).
73. K. F. Lau and R. W. Vaughan, Physical Rev. B 15, 2449 (1977).
74. R. F. Boyer, J. Macromol. Sci. (B) 8, 503 (1973).
75. H. G. Zachmann, J. Polym. Sci. Polym. Symp. 72, 111 (1973).
76. R. J. Samuels, Polymer Engineering and Science 16, 572 (1976).
77. G. Rehage and W. Borchard, The Physics of Glassy Polymers, (Academic Press, New York, 1973).
78. P. D. Murphy and B. C. Gerstein, Analysis and Computerized Fitting of the Lineshape of the N. M. R. Powder Pattern (IS-4516, Ames Lab., DOE, 1978).
79. U. Haeberlen, Adv. Magn. Reson. supplement 1976.

80. U. Haeberlen, U. Kohlschutter, J. Kempf, H. W. Spiess, and H. Zimmerman, Chem. Phys. 3, 248 (1974).
81. U. Haeberlen and U. Kohlschutter, Chem. Phys. 2, 76 (1973).

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