High-Resolution Carbon-13 Nuclear Magnetic Resonance Study of Some Solid, Glassy Polymers

Jacob Schaefer,* E. O. Stejskal, and R. Buchdahl

Monsanto Company, Corporate Research Department, St. Louis, Missouri 63166.

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ABSTRACT: Natural abundance, dipolar-decoupled ^{13}C NMR spectra have been obtained of solid poly(methyl methacrylate) and solid polystyrene at room temperature. The spectra of poly(methyl methacrylate) are well enough resolved to permit the measurement of individual spin–lattice, nuclear Overhauser, and rotating-frame cross-relaxation parameters for individual carbons. These relaxation parameters are interpreted in terms of a distribution of correlation times associated with the segmental motions of the perhaps surprisingly mobile polymer main chain in the solid state. Because of the smaller range of average chemical shifts involved, the dipolar-decoupled spectra of polystyrene are not as well resolved as those of poly(methyl methacrylate). However, the removal of chemical shift anisotropy and some residual dipolar broadening by magic-angle spinning at 2 kHz improves the resolution of the ^{13}C NMR spectrum of solid polystyrene to the point where the C$_1$-phenyl carbon, the C$_2$–C$_4$-phenyl carbons, and the main-chain carbons can all be distinguished from one another, thereby making feasible detailed relaxation experiments.

The natural abundance ^{13}C line widths of solid polymers well below the glass transition temperature are on the order of tens of kilohertz, and so virtually impossible to observe. In these systems, however, much of the line broadening is due to ^{13}C–^{1}H dipolar interactions associated with long correlation times. This broadening can be removed by *strong* proton decoupling[1] (referred to here as dipolar decoupling). Experimentally, dipolar decoupling requires a radiofrequency field comparable to the ^{1}H line width, which for most solid polymers below T_g is on the order of 5–15 G. This means that about 100 times more power must be used for dipolar decoupling than is used in routine scalar decoupling. The strong decoupling removes near static dipolar interactions in the same way conventional weaker decoupling removes weaker scalar interactions, by rapid radiofrequency stirring of the ^{1}H spins,[1] thereby producing what amounts to a high-resolution spectrum of a solid.[2] In certain situations, the resolution provided by the dipolar decoupling can be further enhanced by high-speed mechanical sample spinning.[3] With individual lines resolved for individual carbons, a wide variety[2] of spin–lattice, rotating-frame, and cross-polarization relaxation experiments can be performed and interpreted in terms of the microscopic details of polymeric segmental motion in the solid state. In this paper, we will illustrate the kind of information available from these natural abundance ^{13}C NMR experiments with results from solid-state studies of poly(methyl methacrylate) and of polystyrene.

Experimental Section

Carbon-13 spin–lattice relaxation times and nuclear Overhauser enhancements were measured by standard transient techniques[4] using a modified Bruker HFX-90 spectrometer operating at 22.6 MHz.[5] The spectrometer is equipped with a time-shared external ^{19}F field-frequency stabilization system, a quadrature ^{13}C detector, and a ^{13}C–^{1}H probe capable of accepting simultaneous high-power, long bursts of radiofrequency power at both ^{13}C and ^{1}H Larmor frequencies without breakdown or cross talk. The last feature, achieved with appropriate radiofrequency filters and traps,[2] is essential during cross-polarization relaxation experiments.

Cross-polarization experiments were performed using a four-part procedure.[2,6,7] First, the proton spins were polarized in H$_0$. Then, they were placed in the rotating frame by a 90° pulse followed by a 90° phase shift and continuous application of strong ^{1}H radiofrequency. The third part of the experiment was to establish ^{13}C–^{1}H contact for some variable time by placing the ^{13}C spins into the rotating frame by continuous rf irradiation of the carbon spins such that $\gamma_{\text{carbon}}(H_1)_{\text{carbon}} = \gamma_{\text{proton}}(H_1)_{\text{proton}}$. The final step was to sample the ^{13}C magnetization by turning off $(H_1)_{\text{carbon}}$, but still with dipolar decoupling of the ^{1}H spins.

The cross-polarization experiments were performed using a 10-mm ^{13}C insert with the ^{13}C coil wound on the inside of the glass insert, and the ^{1}H coil wound on the outside, approximately orthogonal to both H$_0$ and the ^{13}C coil. Power amplifiers capable of 100 W continuous wave were used for both ^{13}C and ^{1}H channels, producing a maximum $(H_1)_{\text{proton}}$ of 8 G, and an $(H_1)_{\text{carbon}}$ four times that. Proton decoupling fields of about 15 G (which are necessary in the study of some polymers) can be achieved with the same power amplifier by using a smaller insert. However, 8-G decoupling fields are sufficient for studies of glassy polymers at room temperature and the larger diameter insert is desirable for magic-angle spinning experiments, since this insert will accept a reasonably large rotor.

Magic-angle rotor geometry and spinning procedures have been described in detail before.[8] The only significant change for these experiments was that the rotor was constructed of polystyrene, and was itself the analytical sample. Magic-angle experiments were performed only on polystyrene.

Commercial samples of atactic polystyrene, a polystyrene copolymer, and poly(methyl methacrylate) were used for all experiments.

Results and Discussion

1. Spin–Lattice Relaxation Times and Nuclear Overhauser Enhancements.

Some dipolar-decoupled spectra of solid poly(methyl methacrylate) at 30° are shown in Figure 1. As the strength of the decoupling field approaches the ^{1}H line width of poly(methyl methacrylate) of about 4.5 G,[9] three lines are observed. (We will discuss somewhat later improvement in the resolution and characterization of these lines made possible by cross-polarization experiments.) The three lines are assigned[10] to the three protonated carbons of the repeating unit, the methylene carbon, the ester-methyl carbon, and the α-methyl carbon, in order of increasing magnetic field, respectively. The nonprotonated carbons have much longer spin–lattice relaxation times and so are not observed in an experiment with a pulse repetition period of only a few seconds. The shape and width of the three lines are unchanged (that is, there is no substantial additional narrowing) as the dipolar decoupling field is increased from 5 G to about 8 G.

The removal of dipolar broadening from ^{13}C NMR spectra often reveals the chemical shift anisotropy which characterizes the electron density distribution about various kinds of carbons.[2] The observation of a chemical shift anisotropy is unmistakable since the experimental line shape has a unique asymmetry.[2,11] The most commonly observed line shape for amorphous or polycrystalline materials is approximately triangular, with the apex of the triangle near one of the extremes of the resonance for those carbons having axial symmetry. The fact that none of the three proton-

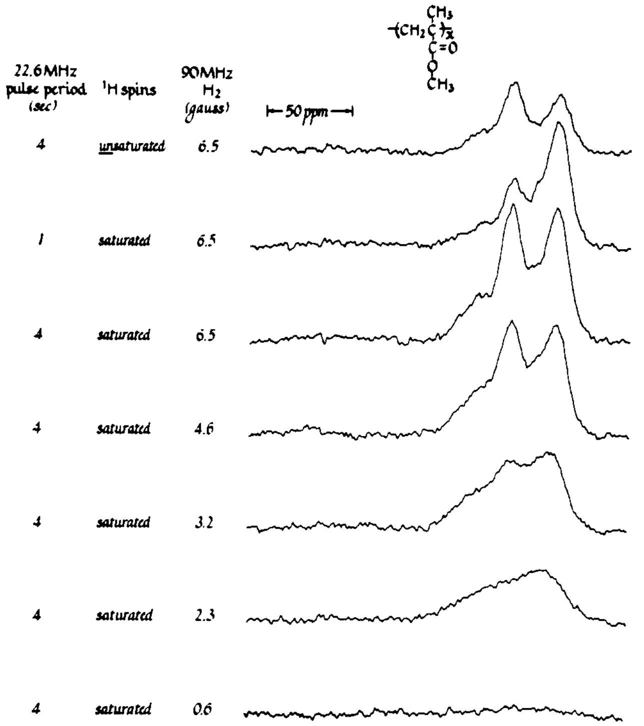

Figure 1. Dipolar-decoupled ^{13}C NMR spectra of solid atactic poly(methyl methacrylate) at room temperature under a variety of pulse and decoupling conditions. Saturation of the ^1H spin system was achieved with an 0.1-G cw decoupling field. The dipolar decoupling was gated. In all spectra, the magnetic field increases from left to right.

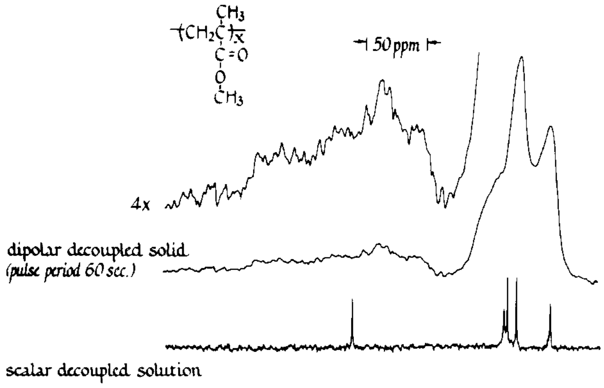

Figure 2. The dipolar-decoupled ^{13}C NMR spectrum of solid atactic poly(methyl methacrylate) compared to the scalar-decoupled spectrum of a solution of highly syndiotactic poly(methyl methacrylate). The solution spectrum is actually a composite of spectra of the polymer in methylene chloride and in ethylene chloride, with the solvent lines omitted for clarity of presentation.

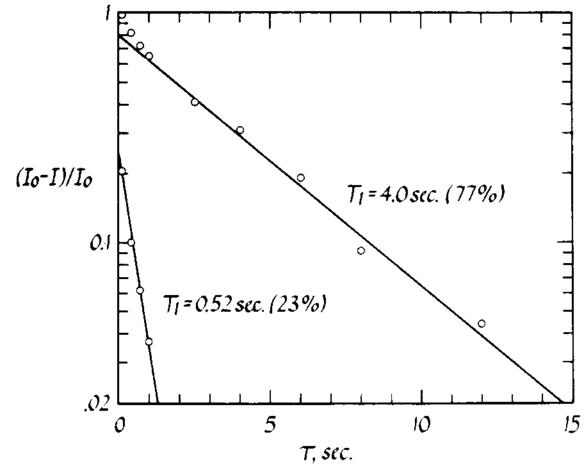

Figure 3. The T_1 behavior of the central line of the high-field grouping of the solid polymer spectrum of Figure 2.

ated-carbon lines in poly(methyl methacrylate) are clearly asymmetric can be attributed, for the most part, to the small inherent anisotropy of the chemical bonding around methyl and methylene carbons.[12]

When the pulse repetition period is lengthened to about a minute, the spectrum of solid poly(methyl methacrylate) shows the resonances due to the slowly relaxing carbonyl and quaternary carbons. The carbonyl-carbon resonance, with its pronounced chemical shift anisotropy, appears at low field, while the quaternary-carbon resonance is apparent in the change in intensity of the line 30 ppm from the α-methyl carbon line. Thirty parts per million is approximately equal to the known chemical shift between the quaternary and α-methyl carbons.[10] The dipolar-decoupled spectrum is compared to a scalar-decoupled high-resolution spectrum of a solution of a stereoregular poly(methyl methacrylate) in Figure 2. The carbonyl-carbon resonance of the polymer in solution appears at what amounts to the center of gravity of the asymmetric carbonyl-carbon resonance in the solid. There are no significant net shifts between the average values of carbon resonances in the solid compared to those in solution. Information about the tacticity of the polymer is not available in the spectrum of the solid. The presence of the approximately full chemical shift anisotropy, and general polycrystalline asymmetric line shape,[2] for the carbonyl carbon of poly(methyl methacrylate) at room temperature is a direct proof that the ester side group as a whole does not engage in extensive internal rotational reorientations, comparable to the internal motions of the ester-methyl and α-methyl carbons.[13-15] This conclusion had been suspected on the basis of proton NMR relaxation experiments,[13-15] and from dielectric relaxation measurements,[16] but direct evidence one way or the other had been lacking.

Since the observed relative intensities of the methyl- and methylene-carbon lines depend upon the pulse repetition time (compare the second and third spectra from the top in Figure 1), each line is clearly associated with its own characteristic spin-lattice relaxation time (T_1). There is no loss of information due to the averaging of spin-lattice relaxation times by spin diffusion as is the situation for ^1H NMR experiments on the same polymer.[13] (However, spin diffusion between dilute ^{13}C spins may have some influence on the very long ^{13}C T_1's.) In addition, the ^{13}C relaxation experiment is not confused by the presence of relatively minor impurities (such as residual monomer or absorbed solvent) dominating the observed signal, since all carbon lines can be identified by their characteristic chemical shifts. From Figure 1, it is obvious that the shortest T_1, which is much less than a second, belongs to the high-field α-methyl carbon line, while the ester-methyl and main-chain methylene-carbon T_1's are substantially longer, having values on the order of a second. The very short T_1 for the α-methyl carbon is consistent with ^1H relaxation data which show that, at room temperature, poly(methyl methacrylate) is near a T_1 minimum (which had been assumed to be associated with the internal motion of the α-methyl group), but far to the high-temperature side of the minimum associated with the relative unhindered internal rotation of the ester-methyl group.[15]

The strongest line in the spectrum of Figure 2 is a composite line, and is, as mentioned above, the sum of the lower field ester-methyl carbon and the slightly higher field[10] quaternary-carbon line. The results of a two-pulse

(90°–τ–90°) T_1 experiment, shown in Figure 3, are consistent with the presence of at least two T_1's, one of about half a second, and the other about an order of magnitude longer. The short T_1 component can unambiguously be assigned to the low-field ester-methyl carbon because of a small, but easily detectable, shift of the center of the composite line from low field to high field, as the delay time, τ, is increased thereby permitting more of the long-T_1 component to contribute. We suspect that the observed inequality in relative contributions of the two components to the full T_1 plot (despite equal numbers of ester-methyl and quaternary carbons) is due to distributions of T_1's for each of the two chemically different types of carbons. These distributions arise because of different local geometrical orientations with respect to nearby protons relative to H_0, and are observable because of the inherent isolation of the rare ^{13}C spins. Such T_1 distributions are common in the ^{13}C NMR spectra of solids.[17] Presumably, the distributions for the two carbons are not identical, with that of the protonated carbon being more sensitive to local orientation relative to the static magnetic field, and hence somewhat broader thereby producing the apparent 23:77 ratio of Figure 3.

The 4-sec T_1 of the main-chain quaternary carbon is about a factor of 5 longer than the T_1 of the main-chain methylene carbon. Since the methylene-carbon T_1 is so much shorter than the quaternary-carbon T_1, it is likely determined predominantly by dipolar interactions of the methylene carbon with its directly bonded protons, rather than with nonbonded methyl protons. If the latter determined T_1, one would expect a much longer relaxation time, reflecting the several Å internuclear distances involved, and the inverse sixth-power dependence on internuclear separations of these dipolar interactions.[4] Although it is true that each methylene carbon has two nearby α-methyl groups, while a quaternary carbon has only one, an unrealistically large contribution to spin–lattice relaxation from inter-chain dipolar interactions must still be assumed in order to account for the factor of 5 difference in T_1's for the two kinds of main-chain carbons if only the methyl protons influenced relaxation. Such interactions are unlikely in view of the necessarily loose packing of chains in a glassy polymer such as poly(methyl methacrylate) characterized by a relatively large mechanical loss factor.[16] In addition, we have observed proton-determined main-chain carbon, room-temperature T_1's on the order of a second for other solid polymers, such as polyacrylonitrile and poly(vinyl chloride), where there is no possibility of contributions to spin–lattice relaxation by nearby mobile side groups. Thus, the importance of main-chain protons seems clear in the spin–lattice relaxation of directly bonded carbons in solid, glassy polymers in general, and in poly(methyl methacrylate) in particular.

The nuclear Overhauser enhancement (NOE) for all three protonated carbons (including the main-chain methylene carbon) is about 2.0, less than the theoretical maximum but still far from the minimum value.[18] The NOE is readily determined by comparison of the intensities of the fully decoupled spectra obtained with and without presaturation of the ^{1}H spins (first and third spectra of Figure 1).

We attribute the observation of substantial, approximately equal NOE's for both main-chain and side-chain carbons (each relaxed predominantly by its own directly bonded protons) to the presence of a broad distribution of correlation times associated with a variety of segmental rotational and torsional motions. The presence of a distribution of correlation times tends to level the NOE's of most carbons to about the same value,[19] even though these carbons may still have significantly different T_1's. Thus, the ester-methyl and methylene carbons have the same NOE. Unlike the situation[19] for polymer systems well above T_g, however, the distribution of correlation times for solid poly(methyl methacrylate) probably has a tail in the direction of short correlation times. In other words, below the glass transition temperature, long-range cooperative motions (necessarily associated with long correlation times) are discriminated against, while many one- and two-carbon, short-range, high-frequency torsional motions can still persist, even for the main chain, and even well below T_g. Thus, deviations from a symmetrical, narrow distribution of correlation times are most likely to be toward the short-correlation time region. The net result is that a substantial NOE can still exist for main-chain carbons in a solid, glassy polymer. Naturally the high-frequency motions resulting in the substantial NOE are also effective contributors to the spin–lattice relaxation times of the various carbons. This is the reason for a methylene-carbon T_1 in the glassy polymer as short as a second, rather than the longer values one might expect for such ^{13}C T_1's in highly crystalline materials.[2]

The presence of a variety of relatively large-amplitude, torsional, segmental motions of the poly(methyl methacrylate) main chain in the solid state is consistent with prevailing intuitive physical notions about glassy polymers having substantial secondary mechanical loss characteristics.[16] The characterization of this segmental freedom of the glassy polymer by ^{13}C relaxation parameters is, as discussed above, reasonably convincing. Comparable ^{1}H T_1 data (where T_1 is averaged over all types of protons in the polymer by spin diffusion) do not, however, suggest the presence of main-chain segmental mobility for poly(methyl methacrylate) at room temperature.[13–15] This is undoubtedly due to the low activation energy associated with the main-chain motions of loosely packed chains, and, therefore, the failure of these motions to have much of an effect on a proton T_1 versus temperature plot, even though they have observable effects on the ^{13}C relaxation parameters. Previously, the connection between mechanical loss measurements and ^{1}H relaxation measurements (in particular of the T_1 minimum due to the free rotation of the α-methyl group) had been somewhat obscure because of the failure of the ^{1}H measurements to detect the presence of any substantial main-chain segmental motions. In fact, motion of the α-methyl group in highly asymmetric rotational potentials had been suggested in order to explain how the rotations of a methyl group could give rise to a mechanical loss.[16] The analysis of the ^{13}C relaxation data, however, strongly suggests segmental mobility of the main chain and so points to an explanation in terms of local cooperative motions of the main chain accompanying the onset of the α-methyl group rotation.

The presence of a variety of substantial main-chain segmental motions in poly(methyl methacrylate) has an additional influence on the ^{13}C spectra. Whatever chemical shift anisotropies are present will tend to be obscured by residual dipolar broadening. This broadening is associated with those motions having correlation frequencies relatively large compared to the dipolar decoupling field, $\gamma H_2/2\pi$, and so is not removed by the usual strong decoupling techniques. Of course, the motions responsible for broadening need not be as fast as those determining the spin–lattice relaxation in order to have correlation frequencies greater than $\gamma H_2/2\pi$. In fact, intermediate-frequency motions will have the most substantial influence since their broadening is the least averaged by the motion itself. In part, the presence of such motions explains why the small, but significant, chemical shift anisotropies of the methyl and methylene carbons are not apparent in Figures 1 and 2. The chemical shift anisotropy of the carbonyl carbon, on the other hand, is on the order of several kilohertz, which is

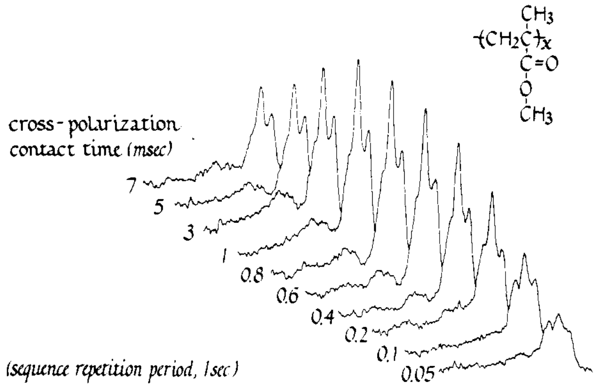

Figure 4. Dipolar-decoupled ^{13}C NMR spectra of solid atactic poly(methyl methacrylate) obtained following a single Hartmann–Hahn cross-polarization contact of variable length. The ^{1}H and ^{13}C radiofrequency fields were approximately 4.5 and 18 G, respectively.

sufficiently large to ensure that the anisotropy remains visible despite the presence of some dipolar broadening associated with intermediate-frequency segmental motions. Naturally the fact that the carbonyl carbon has no directly bonded proton tends to reduce any such broadening, relative to that experienced by the methyl and methylene carbons.

2. Cross Polarization. While a resonance from the carbonyl carbon in poly(methyl methacrylate) can be observed, the experiment is made difficult by the long carbonyl–carbon T_1 and necessary delays between sampling pulses. By using cross polarization,[2,6,7] however, we can eliminate waiting the usual several ^{13}C T_1's between samplings of the ^{13}C magnetization, and instead are required to wait only for the repolarization of the protons (which for most solid polymers is relatively efficient and occurs in substantially less than a second). The repolarization of the carbon spins then also occurs rapidly because in a solid, the cross polarization of the carbons by the protons is through a rapid spin–spin process, rather than by a slow spin–lattice process.[2]

One version of cross polarization involves producing two strong rotating magnetic fields $(H_1)_{\text{carbon}}$ and $(H_1)_{\text{proton}}$ tuned to resonance such that $\gamma_{\text{carbon}}(H_1)_{\text{carbon}} \times \gamma_{\text{proton}} \cdot (H_1)_{\text{proton}}$. When this condition (called the Hartmann–Hahn condition[6]) is satisfied, the carbon and proton spin systems are strongly coupled, even though in the static field, H_0, they are not coupled because of their widely different frequencies. The coupling occurs at the Hartmann–Hahn condition since the precession of the proton spins about their H_1 causes the component of the dipolar field along the direction of the static field H_0 to oscillate at an angular frequency $\gamma_{\text{proton}}(H_1)_{\text{proton}}$. This frequency is just right to induce transitions of the carbon spins relative to their rotating field.[7] Under optimum conditions, the two-rotating field method of cross polarization generates a carbon polarization which is approximately four times (arising from the ratio $\gamma_{\text{proton}}/\gamma_{\text{carbon}}$) the polarization obtained by ordinary magnetization of the ^{13}C spins.[2,20]

The results of a series of some two-rotating field, cross-relaxation experiments performed on solid poly(methyl methacrylate) are shown in Figure 4. The single contact time between the ^{13}C and ^{1}H spins has been varied from 7 msec to 50 μsec, with the most favorable contact time appearing to be about 1 msec. The optimum contact time depends upon the cross relaxation times in the rotating frame, the T_{CH}'s (not to be confused with the cross relaxation time in the laboratory frame T_1^{CH}). The T_{CH}'s are related to the strengths of the static dipolar interactions between carbons and protons. In addition, the optimum contact time also depends on the length of time the proton magnetization can be held in the rotating frame and so contribute to the polarization of the carbon spins.[2,6] The latter time is called the proton $T_{1\rho}$, and for poly(methyl methacrylate) around room temperature it is on the order of 5 msec.[14] The enormous advantage of performing a cross polarization, relative to a simple dipolar decoupling experiment, is made clear by the observation of strong signals from both of the nonprotonated carbons of poly(methyl methacrylate), even with sampling of the ^{13}C magnetization as rapidly as once a second (Figure 4). In a standard dipolar decoupling experiment with a ^{13}C pulse repetition period of 1 sec, no signal is observed for either the carbonyl or quaternary carbons (Figure 1).

A cross-polarization experiment also provides new information contained in the differences between cross-relaxation rates. For example, in poly(methyl methacrylate) it is clear from Figure 4 that the methylene-carbon line (the lowest field line in the high-field grouping) has the fastest cross-relaxation rate. The methylene-carbon line remains intense even for very short contact times. (Since the other lines are substantially reduced in intensity for contact times on the order of 100 μsec, cross polarization can obviously serve as a resolution enhancing technique, thereby revealing the shape and position of some lines more clearly than in a standard dipolar decoupling experiment.) The short methylene-carbon T_{CH} is undoubtedly due to near static dipolar interactions between the methylene carbon and its two directly bonded protons. Since these protons are also engaged in high-frequency motions responsible for the sizable NOE and short T_1 of the methylene carbon, and in intermediate-frequency motions responsible for residual dipolar broadening effects, this information about low-frequency motions of the methylene protons from the cross-polarization experiment supports the idea of a *broad* distribution of correlation times associated with the segmental motions of the polymer main chain in the solid state.

3. Magic-Angle Spinning. The dipolar-decoupled ^{13}C NMR spectra of most solid polymers are not as easy to deal with as that of poly(methyl methacrylate), mostly because the dispersions of isotropic chemical shifts are generally not as great. For these polymers, chemical shift anisotropy and residual dipolar broadening of carbon resonances having relatively small average chemical shift differences result in disappointingly broad and poorly resolved lines. Such spectra are not well suited for the determination of the various kinds of relaxation parameters discussed above. In order to simplify these spectra, the broadening can be removed by high-speed mechanical sample rotation at the magic angle.[3]

In this experiment, the solid polymer is fashioned into a rotor[8] which is placed in the static magnetic field in such a way that the spinning axis of the rotor makes an angle of 54.7° with the field. (A polymer powder can also be placed inside of a hollow rotor made of a suitable material such as a rigid fluoropolymer.[8]) The rotor is then spun by means of a gas jet impinging upon small vanes which are a part of the rotor body. The magic angle of 54.7° reduces to zero the $(3\cos^2\theta - 1)$ dependence of some kinds of residual static dipolar interactions, as well as the angular dependence of the chemical shift anisotropy. The net result can be a genuine high-resolution spectrum of a solid. The magic-angle spinning experiment becomes useful for ^{13}C studies, however, only when used in conjunction with dipolar decoupling. The reason for this limitation is that it is not experimentally feasible to mechanically spin a rotor at speeds high enough to remove the full static ^{13}C–^{1}H dipolar interaction encountered in solids. Mechanical spinning speeds of 2–4 kHz are relatively simple to achieve, but narrowing of the complete static dipolar interaction would require speeds at least five times as great, which we have been unable to achieve. By removing the bulk of the dipolar interactions by dipolar decoupling, however, the magic-angle spinning need only cope with line broadening effects of a few kilohertz.

This line broadening arises from at least three major sources. The most important source is chemical shift anisotropy, which for carbonyl and olefinic carbons produces a chemical shift dispersion which can be as large as 3 kHz. The pronounced asymmetry of the line shape associated with a large chemical shift anisotropy, so obvious in the ^{13}C NMR spectra of small molecules at low temperatures,[2] may, however, be obscured in polymer systems due to the overlapping of many chemical shift dispersions. As mentioned above, broadening due to chemical shift anisotropy is readily removed by magic-angle spinning. The second source of line broadening is dipolar in origin, but associated with intermediate frequencies, that is, dipolar interactions arising from torsional motions characterized by correlation frequencies which are comparable or large compared to $\gamma H_2/2\pi$. This source of line broadening cannot be removed by spinning, since the dipolar correlation frequencies involved are also large compared to any realistically achievable spinning frequency.

The third source of line broadening is again dipolar in origin, but is now associated with near static interactions which are not removed because of an inadequate decoupling field strength. Considering the variations in inter- and intramolecular distances possible in the proton–proton dipolar interactions of solid polymers, it is reasonable to suppose the existence of a sizable distribution of strengths of these static dipolar interactions. This kind of an assumption is usually made to explain the generally complex polymer proton line shapes observed.[21] Those carbons which are near protons engaged in proton–proton dipolar interactions of strengths substantially greater than that of the decoupling field will experience a static dipolar interaction unchanged by the decoupling. The broad lines arising from these carbons will not be observed above the noise, and magic-angle spinning will have no effect on their line width. (When, in fact, the decoupling field is substantially less than the average proton line width, the majority of carbons fall into this class.) When the decoupling field is comparable to the average proton line width, some carbons may still have line widths substantially unaffected, although most of them undergo dramatic narrowing. Some relatively minor broadening of the narrowed lines can still remain, however, due to long-range, intermolecular dipolar interactions between carbons and those distant protons in the polymer sample which are themselves engaged with other protons in dipolar interactions of strengths substantially greater than the decoupling field. Since this residual broading is due to static or near static dipolar interactions, and since its size is generally less than ordinary spinning frequencies, magic-angle experiments are capable of removing the broadening from the spectrum. This result is of practical importance since it is difficult to achieve very strong decoupling fields in the large coils required to perform spinning experiments. Polymer spectra resulting from the use of marginal decoupling fields inevitably show residual dipolar broadening. Fortunately, however, much of this broadening will be removed by the spinning right along with broadening due to the chemical shift anisotropy.

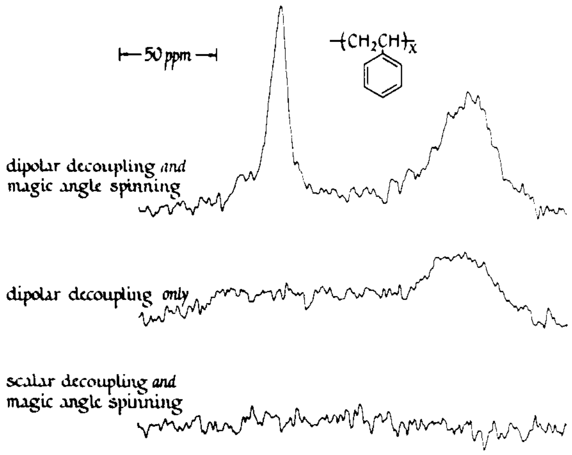

Figure 5. Some ^{13}C NMR spectra of a magic-angle rotor made of polystyrene. A pulse repetition period of 4 sec was used for all spectra.

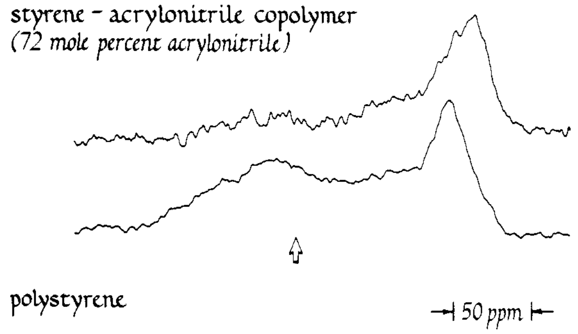

Figure 6. Dipolar-decoupled ^{13}C NMR spectra of polystyrene and of a copolymer of polystyrene. A pulse repetition period of 10 sec was used for both spectra. The arrow in the spectrum of polystyrene shows the location of the major phenyl-carbon line in a combination dipolar-decoupling magic-angle spinning experiment.

In short, magic-angle spinning will fail to remove that dipolar broadening in which either the magnitude (in hertz) or the correlation frequency of the carbon–proton dipolar interaction are much greater than the spinning frequency. It will remove chemical shift anisotropy and weak, near static dipolar broadening. One additional point should be considered. In the event that the undecoupled carbon line width, the H_2-modulated carbon–proton dipolar interaction, and the magic-angle spinning frequency are all comparable (or that the first quantity is small and the latter two equal), spinning will not further narrow partially decoupled (or decoupled) carbon lines, and may, in fact, lead to anomalous broadening. This broadening, involving two kinds of mutually defeating narrowing schemes, has been discussed in detail elsewhere, in connection with a combination spinning and multiple-pulse ^{1}H line-narrowing experiment.[22]

The results of a combination dipolar-decoupling and magic-angle spinning experiment performed on a rotor made from atactic polystyrene are shown in Figure 5. The aromatic-carbon resonances are separated from the high-field main-chain carbon resonance and are, in addition, well enough resolved by spinning at 2 kHz that the low-field C_1 quaternary-carbon line is distinguishable, as a shoulder, from the remaining aromatic-carbon lines. (Unfortunately, a direct comparison of relative intensities of aromatic- and main-chain carbon lines in this spectrum is complicated by the fact that the methylene carbons of the nylon support for the magic-angle rotor contribute to the high-field resonance.) The broadening of the aromatic-carbon lines in the simple dipolar decoupling experiment is primarily, but not exclusively, due to chemical shift anisotropy. A long-term time-averaging experiment performed on nonspinning polystyrene by itself, in fact, reveals the aromatic-carbon line shape as asymmetric (Figure 6), but not displaying a clear chemical shift anisotropy. Since the T_1's of the phenyl carbons can be shown to be less than a few seconds, we feel that substantial torsional motion of the phenyl side group must be occurring, although nothing like free rotation. This torsional motion results in dipolar broadening of the residual chemical shift anisotropy of the phenyl carbons as discussed above. In addition, some further dipolar broadening can be expected since the 8-G decoupling field used in these experiments is only comparable to the polystyrene proton line width.[23] Nevertheless, as seen in Figure 5, a large part of the line broadening is removed by magic-angle spinning thereby producing a spectrum with which one can readily perform T_1, $T_{1\rho}$, and cross-relaxation T_{CH} experiments.

It should be stressed, however, that a *combination* cross-relaxation and magic-angle spinning experiment could be complicated by the presence of either of two problems. First, if the static ^{13}C–^{1}H dipolar interaction is not particularly large for a given carbon (such as, for example, the nonprotonated quaternary carbon of polystyrene), and only static dipolar interactions are present (which is probably not the case for any carbon in polystyrene), magic-angle spinning at 2–4 kHz will remove all the heteronuclear dipolar interactions thereby short circuiting the spin–spin coupling necessary for the effective cross relaxation of that carbon.[2] Second, if, for some reason, the proton line width of a given polymer is not too large, say, on the order of 5–10 kHz, then magic-angle spinning at 2 kHz, while not substantially affecting the proton line width, may still make difficult establishing the Hartmann–Hahn condition. This occurs since the narrowed carbon lines cover a chemical-shift range comparable to the proton line width. Thus, a match of resonance frequencies in the rotating frame is not possible for all carbons at the same time, thereby confusing the results of a cross-polarization contact. We are presently in the process of evaluating these potential problems.

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Conformational Isomorphism. A General 2_1 Helical Conformation for Poly(β-alkanoates)

J. Cornibert and R. H. Marchessault*

Département de chimie, Université de Montréal, Montreal, Quebec H3C 3V1, Canada.
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ABSTRACT: Poly(β-hydroxyalkanoates) are found as endogenous carbon reserves in bacteria (e.g., poly(β-hydroxy butyrate, PHB) and as synthetic materials. In the former the β carbon is asymmetric due to a single substituent while in the latter (e.g., poly(pivalolactone), PVL) there are α and α' substituents. X-Ray diffraction analysis of crystalline oriented fibers of PHB and PVL has revealed near identical fiber repeats, and 2_1 chain symmetries. Conformational analysis of these two polyesters shows that of the possible conformations for each macromolecule the two of minimum energy are quasi-identical in terms of backbone dihedral angles, hence conformationally isomorphous. The general class of polyesters based on the substituted poly(β-propriolactone) backbone are predicted to have nearly identical crystalline conformations; in this respect they resemble the polypeptides which have the tendency to assume the Pauling helix in the crystalline state. In these poly(β-alkanoates) there are no intramolecular hydrogen bonds; van der Waals and electrostatic interactions are the main stabilizing forces. In the crystalline conformations the ester dipoles along a chain are perpendicular to the helix axis and contiguous dipoles are antiparallel with 3 Å between them.

From fiber diagrams it was shown that polyesters of the general formula $[\mathrm{COOR_1{-}OOCR_2}]_n$ (Carrothers' type) with alternating polarity of the ester groups present near planar conformations[1–6] in the crystalline state. Careful examination[6] of the homopolyesters based on ethylene glycol and the diacids (adipic and suberic, six and eight carbons, respectively) confirmed that the departure from planarity of the extended repeating unit was in the glycol moiety.

On the other hand a recent study[7] of the polyester based on butane-1,4-diol and adipic acid (poly(tetramethylene adipate)) showed that the skeleton was indeed completely extended in this case. It would appear that a more uniform spacing of the ester groups along the aliphatic chain, as would obtain in poly(tetramethylene adipate), removes the factor which produced the observed 0.5 Å shortening of the chain.[5]

By ring opening polymerization of lactones,[8–11] glycollides,[12,13] lactides,[14,15] and anhydro sulfites,[16,17] it is possi-