Observations in Solid Polyethylenes by Carbon-13 Nuclear Magnetic Resonance with Magic Angle Sample Spinning

William L. Earl*

Center for Fire Research, National Bureau of Standards, Washington, D.C. 20234

D. L. VanderHart

Center for Materials Science, National Bureau of Standards, Washington, D.C. 20234. *Received January 25, 1979*

ABSTRACT: It is shown that the ^{13}C NMR resonance lines of the crystalline component (CC) and the noncrystalline component (NCC) in polyethylene (PE) are chemically shifted from one another. This usually produces an upfield shoulder on the CC resonance line in a "cross-polarization with magic angle sample spinning" (CPMASS) experiment. Two peaks were resolved in a low crystallinity, high molecular weight sample, the NCC peak being 2.36 ± 0.1 ppm upfield from the CC peak. The chemical shift of the CC peak was measured against external Me_4Si to be 34.06 ± 0.26 ppm. Measurements of the chemical shifts of liquid n-$C_{17}H_{36}$ and cyclohexane relative to external Me_4Si were also made, and the chemical shift trends are discussed in terms of trans and gauche conformational effects on the chemical shift. Transverse relaxation times, T_{2C}, were measured for various samples; the natural T_{2C} broadened full width at half-height for the CC peak ranged from 1.00 to 2.6 Hz with a resonant proton decoupling field, ν_{1H}, of 64 kHz. The corresponding natural line width for the NCC peak was measured to be 14 ± 4 Hz, and it is presumed that this width is determined by molecular motion. The NCC peak has a substantial line width contribution from isotropic chemical shift dispersion. The capability of the CPMASS technique for resolving closely spaced, weak resonances was tested using a branched and a radiation cross-linked linear PE. Only methyl groups are completely resolved with a second resonance partially resolved in the cross-linked sample. It is noted that the CPMASS technique does not yield true relative intensities for the NCC and CC resonances.

The combined techniques of high power proton decoupling and cross-polarization between ^{13}C nuclei and protons[1] accompanied by "magic angle" sample spinning[2-5] offer the promise that solid state ^{13}C NMR spectra can approach liquid spectra in resolution. Examples for polymers are already in the literature,[3,6-9] particularly for glassy polymers,[3,6-8] where solid spectra resolve most of the chemically distinct carbons and, in some cases,[6,7] resolve different conformations present in the solid but motionally averaged in solution.

We report here results of magic angle sample spinning (MASS) experiments performed on various polyethylenes. The topics to be discussed include conformationally dependent chemical shifts, separation of crystalline and noncrystalline carbon resonances, correspondence between morphology or crystallinity and line widths, and observed distortion in cross-polarization line shapes. These spinning results augment other, more extensive, nonspinning NMR studies of solid polyethylenes which have been underway in our laboratory for the last few years and will be reported elsewhere.[10]

Experimental Section

The ^{13}C NMR spectrometer operates at 15.08 MHz. Many of the spectra reported herein employ cross-polarization (CP) from the proton spin-locked state[11] in order to generate the ^{13}C magnetization; these spectra will be referred to as CPMASS spectra. Typical cross-polarization times were 2 ms. The Hartmann–Hahn condition,[12] $\nu_{1C} = \nu_{1H}$, was satisfied during the CP time where ν_{1C} and ν_{1H} are respectively the radiofrequency field strengths, in hertz, applied to the carbons and protons. Unless otherwise indicated, ν_{1H} = 64 kHz at the magic angle; furthermore, ν_{1H} remains on during the signal acquisition period to eliminate proton–carbon dipolar couplings.[1] The MASS feature, i.e., rapidly spinning a sample about an axis inclined at 54.74° with respect to the static field, eliminates anisotropic ^{13}C chemical shift line broadening[2] so that the ^{13}C resonances appear at their isotropic chemical shift positions.

Six polyethylene (PE) samples were used in this study, one branched, low-density PE (LDPE) and five high-density, linear PE's (LPE's). The LDPE, designated sample A, is a melt-crystallized, air-cooled polycrystalline sample of an NBS standard reference material (SRM), SRM 1476. Sample B was machined as a cylinder from a high molecular weight ($M_w > 1000000$) LPE block which was molded under mild pressure. Sample C is Phillip's Marlex 6001 LPE ($M_w = 192000$), melt crystallized under mild pressure and air cooled. Sample D is NBS SRM 1475, a LPE which was pressure crystallized at 4.86 GPa and 210 °C; crystallinity is estimated to be 95%. Sample E is pressure extruded, DuPont 7026 LPE ($M_w = 161000$); this sample of so-called ultraoriented PE was fabricated elsewhere[13] and has a draw ratio of 11.8:1 based on the ram to exit port area ratio. This sample was loaded into the rotor with the draw direction parallel to the spinning axis. Sample F was also obtained elsewhere[14] and is a thick film LPE which has been radiation cross-linked with an ionizing radiation dosage of 624 MRad.

The pulse sequence used to obtain one of the spectra discussed in this paper is a $(180°–10\text{ s}–90°–10\text{ s})_x$ sequence. This pulse sequence, consisting of alternate 90 and 180° ^{13}C pulses each separated by 10 s, yields signals at full equilibrium intensity from those carbons whose longitudinal relaxation times, T_{1C}, are less than 2 s while suppressing signals from carbons with T_{1C}'s greater than 10 s. Carbons in the intermediate situation where $2s < T_{1C} < 10$ s will contribute signals strongly dependent on the particular T_{1C}. Identical proton decoupling pulses are applied following both the 90 and 180° pulses in order to eliminate transient Overhauser contributions[15] to the magnetization from those carbons with long T_{1C}'s.

A variation of the foregoing experiment, namely $(180°–\tau–90°–10\text{ s})_x$, was used in order to follow the rate of recovery of the rapidly relaxing magnetization. This carbon pulse sequence differs from that just discussed in that a variable time τ instead of 10 s is inserted between the 180 and 90° pulses; furthermore, continuous low-level irradiation is applied to the protons between the decoupling pulses so that transient Overhauser effects are eliminated.[15] Of course this yields intensities appropriate to the steady state Overhauser enhancement. If one assumes that the 90° pulse is ideal, the magnetization following the 180° pulse is independent of τ, so that line shapes for different τ's may be compared. In these experiments, line shape distortions due to pulse nonideality are expected to be small.

Transverse relaxation times, T_{2C}, were measured by applying a single 180° ^{13}C pulse at a variable time τ following the CP period. An echo forms at a time τ following the 180° pulse. The second

Published 1979 by the American Chemical Society

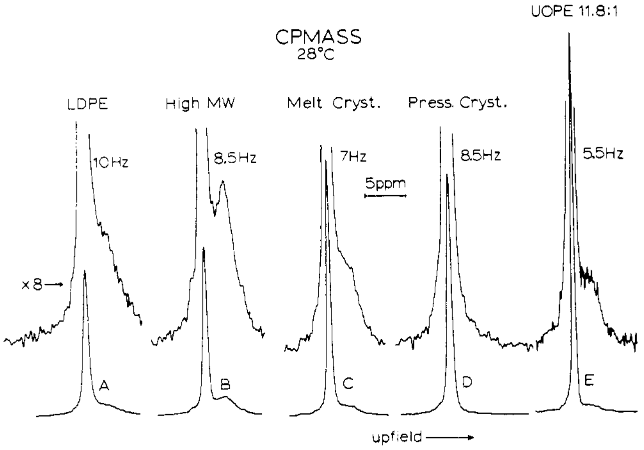

Figure 1. CPMASS ^{13}C spectra of five polyethylenes taken at 28 °C, with a 2 ms cross-polarization time, 64 kHz radiofrequency fields, and 1.4 kHz sample rotation frequency. The preparations of samples A–E are described in the Experimental Section. The upper spectra are amplified eight times compared with the lower; all spectra are normalized to the same intensity. Full widths at half-height are given for the narrow, crystalline peak; no digital broadening has been applied. The noncrystalline peak upfield from the crystalline peak is partially resolved in sample B, the high molecular weight PE.

half-echo is Fourier transformed,[16] and the logarithms of the signal intensities are plotted as a function of 2τ. High-power proton decoupling is applied continuously from the beginning of the CP period through the signal collection period. The τ's are chosen to be integral numbers of rotor revolutions in order to ensure an effective time reversal at the 180° pulse for all inhomogeneous ^{13}C interactions. The more conventional method of measuring T_{2C} using the Carr–Purcell[17] sequence of equally spaced 180° pulses does not work in solids because there is a slight cross-polarization which occurs at each 180° pulse. The cumulative effects of several of these 180° pulses renders this Carr–Purcell T_{2C} measurement meaningless.

Results

The CPMASS spectra of samples A–E taken at 28 °C are displayed in Figure 1; each spectrum is normalized to the same total intensity and is plotted at two amplification levels (×1 and ×8). No digital broadening has been applied prior to Fourier transformation of the free induction decay. The regions at the base of all of the lines except for sample D are asymmetric. This asymmetric wing is identified with the noncrystalline component[9] (NCC) since the wing intensities correlate with the expected rankings of these samples in order of increasing NCC, i.e., $D < E \lesssim C < A \lesssim B$. Further evidence that this wing is associated with the NCC is the set of line shapes, Figure 2, observed in sample B at 28 °C using the $(180°\text{–}\tau\text{–}90°\text{–}10\ \text{s})_x$ pulse sequence. These spectra show an upfield peak separated from a smaller peak, 2.36 ± 0.1 downfield. The intensity ratios of the downfield to upfield resonances are much smaller than for the CPMASS spectra indicating that the downfield resonance is nearly saturated by the choice of the 10 s interval. This near saturation is expected for the CC resonance since CC T_{1C}'s approaching 1000 s in PE have been observed.[10] Since the CC intensity reflects nonequilibrium populations, no information about CC carbon relaxation has been deduced. In contrast, the upfield resonances in Figure 2 have regained their Overhauser enhanced equilibrium population by the time $\tau = 1.6$ s. The change in NCC peak height with τ gives a T_{1C} of 175 ± 25 ms indicating that there is substantial spectral density of molecular motion in the megahertz range.[18] These observations strongly support the assignment of the downfield resonance to the CC and the upfield resonance to the NCC.

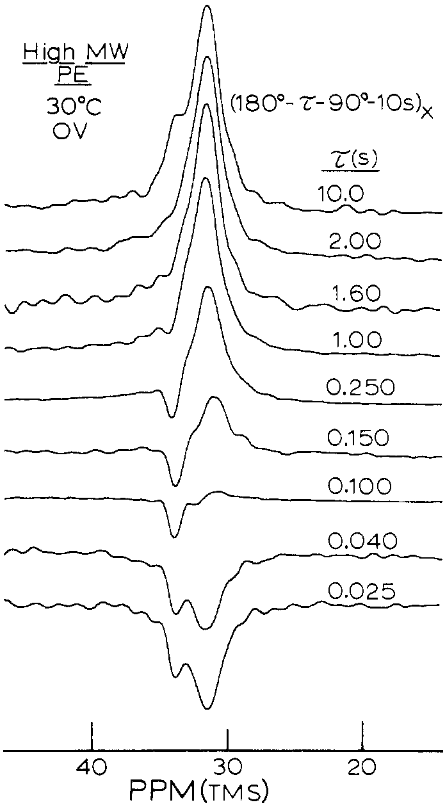

Figure 2. ^{13}C spectra at 30 °C displaying the rapid recovery of the noncrystalline component (NCC) resonance centered at 31.7 ppm. The pulse sequence on the carbons is $(180°\text{–}\tau\text{–}90°\text{–}10\ \text{s})_x$; values of τ are indicated. The protons are continuously irradiated at a low level producing Overhaused (OV) enhancement of the carbon signals to avoid transient Overhauser effects. The weaker crystalline resonance at 34.1 ppm is much attenuated in all of these spectra due to a very long T_{1C}. The T_{1C} of the NCC carbons is 175 ± 25 ms.

We note in passing that the CPMASS technique for PE generally attenuates the signal arising from the NCC relative to the CC. This conclusion is based on a measurement in sample B of the ratio, R, of the total integral of the intensity in a $(180°\text{–}10\ \text{s–}90°\text{–}10\ \text{s})_x$ compared with a $(90°\text{–}5000\ \text{s})_x$ experiment; the former experiment should yield a lower limit for the equilibrated NCC wing intensity while the latter experiment should produce an integral representing the thermally equilibrated ^{13}C magnetization arising from both the NCC and the CC. (Incidentally, the NCC line shape in the (180°–10 s–90°–10 s) experiment has no average Overhauser[15] intensity distortion because, for sample B, the proton T_1 is less than 1 s.) When the CPMASS line shape is compared to the $(180°\text{–}10\ \text{s–}90°\text{–}10\ \text{s})_x$ line shape where the integral of the latter is adjusted to be equal to the fraction R of the CPMASS spectrum integral, then the intensity of the wing in the CPMASS spectrum is 1.5–2.0 times smaller than in the $(180°\text{–}10\ \text{s–}90°\text{–}10\ \text{s})_x$ experiment. Therefore, we conclude that the relative NCC and CC intensities are not quantitatively correct; nevertheless, it is reasonable to assume that intensities in the wings of different PE's may be compared semiquantitatively. Reasons for this line shape distortion in the CPMASS spectrum are probably a longer cross-polarization time and/or a shorter proton rotating frame relaxation time for the NCC relative to the CC. Both of these effects can result from the increased molecular mobility of the NCC chain compared with the CC.

The spectra in Figure 1 indicate that there is strong overlap between the CC and NCC resonances, and only in sample B, where the NCC is largest, is the NCC peak resolvable from the CC peak. The question arises, then, whether one can experimentally improve the resolution of these components. Our approach to this question was to determine the natural width of each of the two components by measuring the corresponding transverse relaxation times, T_{2C}, and converting them to line width contributions, $\Delta\nu(T_{2C})$, through the formula $\Delta\nu(T_{2C}) = (\pi T_{2C})^{-1}$.

The observed decays in the T_{2C} measurements were not strictly exponential; some decays had a slightly faster initial rate. Nevertheless, approximate T_{2C}'s were obtained, whose corresponding CC natural line widths, $\Delta\nu(T_{2C})$, are 2.6, 1.8, 1.5, and 1.0 Hz for samples A, B, D, and E, respectively, at a rotation frequency of 2.0 kHz. In all cases where the NCC resonance appears, NCC natural line widths, $\Delta\nu(T_{2C})$, were significantly greater than those for the CC; however, it was only convenient to measure $\Delta\nu_{NC}(T_{2C})$ quantitatively for sample B. A value of 14 ± 4 Hz was obtained. The experimental width of the NCC resonance, $\Delta\nu^*_{NC}$, is not easy to determine because of overlap with the CC resonance; nevertheless, $\Delta\nu^*_{NC} = 39$ Hz was estimated for sample B based on the line width observed at $\tau = 1.0$ s in Figure 2.

An effort was made to measure solid state chemical shifts accurately so that they could be related to liquid state measurements. We hoped that chemical shift trends might yield information, particularly about molecular conformation, since the CC carbons represent an all-trans conformation, and a PE melt or solution has an equilibrium distribution of trans and gauche bonding.

The only feasible chemical shift reference for a solid is an external reference. A sealed capillary of neat ethylene glycol was prepared and inserted in the hollow bore of a PE cylinder; this cylinder was then loaded into the rotor. In order to measure the chemical shift difference between the CC peak of PE and neat ethylene glycol, it was deemed necessary, due to small magnetic field drift (external ^{2}D lock) and Block–Siegert shifts[20] associated with large decoupling fields, to collect both liquid and solid signals at the same time. Placement of a 90° carbon pulse, phase shifted by 90° from the cross-polarizing pulse and immediately preceding it, spin-locked the liquid signal while the PE signal was cross-polarizing. Both the liquid and solid signals appeared in phase with one another following the CP period. The ethylene glycol resonance was found to be 30.19 ± 0.15 ppm downfield from the CC resonance of LPE. It can be shown that the effect of spinning an infinitely long cylinder at the magic angle is to reduce the bulk susceptibility correction to zero, thus the above measurement is theoretically equivalent to using an internal shift standard. To the extent that the cylinders were not infinitely long, there could be an error due to the bulk susceptibilities, which is estimated to be less than 0.2 ppm in the worst case. This chemical shift was then converted to an equivalent measurement with tetramethylsilane (Me_4Si) as the external reference by alternately placing a 5-mm tube containing either neat ethylene glycol or neat Me_4Si inside a 10-mm tube containing acetone. Since both reference compounds could be measured with respect to acetone, the increment for converting the chemical shifts from an external ethylene glycol reference to an external Me_4Si reference, rotating at the magic angle, was determined to be 64.55 ± 0.2 ppm when corrected for bulk susceptibility effects. Therefore, relative to *external* Me_4Si, at the magic angle, the CC resonance of LPE, δ(CC), is 34.36 ± 0.55 ppm downfield from Me_4Si, and the NCC resonance of sample B, δ(NCC), becomes 32.00 ± 0.65 ppm.

Since we also wished to compare the above chemical shifts with PE solutions or melts using a similar external reference, and since LPE is difficult to dissolve at room temperature, the normal alkaline, n-$C_{17}H_{36}$, was used as a chemical shift model for "liquid-like" LPE chains at room temperature. With Me_4Si as an external reference, the chemical shift, $\delta(C_{17}{}^{i})$, of the interior methylene resonances, C_5 to C_{13}, was found to be 30.96 ± 0.10 ppm. Finally, the chemical shift of neat cyclohexane, $\delta(C_6H_{12})$, which is constrained in all-gauche conformation, was measured to be 27.84 ± 0.10 ppm relative to external Me_4Si. These latter two chemical shifts have been corrected for bulk susceptibility effects.

Discussion

It is tempting to explain most of the decrease in chemical shifts, $\delta(CC) \rightarrow \delta(C_{17}{}^{i}) \rightarrow \delta(C_6H_{12})$, as originating from conformational differences since the CC of LPE has an all-trans conformation, the internal methylenes of heptadecane have equilibrium populations of trans and gauche bonding, and cyclohexane is all-gauche (g^+g^-). If the shift, $\delta(CC) - \delta(C_6H_{12}) = 6.52 \pm 0.65$ ppm, is attributed entirely to the trans to gauche change, then one can predict the chemical shift, $\delta(C_{17}{}^{i})$, by simply calculating the equilibrium fraction f_g of gauche bonds. The chemical shift, $\delta(C_{17}{}^{i})$, should then be

$$\delta(C_{17}{}^{i}) = \delta(CC) - 6.52 f_g \tag{1}$$

Assuming a 600 cal difference between the gauche and trans states,[21,22] and including the effect of the pentane exclusion principle,[23] f_g becomes 0.37 at 300 K, and $\delta(C_{17}{}^{i})$ is predicted to be 31.95 ± 0.77 instead of 30.96 ± 0.10 ppm. This 1.0 ppm discrepancy could arise from ignoring the effects of changes in density or molecular packing in going from the crystal to the neat liquid. On the other hand, the 2.36 ± 0.1 ppm upfield shift observed in sample B between δ(CC) and δ(NCC) is within experimental error of what one would expect if one calculated δ(NCC) instead of $\delta(C_{17}{}^{i})$ in eq 1 with $f_g = 0.37$. This agreement is found in spite of the fact that there are accompanying changes in density and crystal packing in going from the crystalline to the noncrystalline region of PE. A possible resolution of these inconsistencies is that there is an upfield shift of about 1.0 ppm in replacing the crystal by a less-structured noncrystalline molecular environment and that the observed chemical shift difference, $\delta(CC) - \delta(NCC)$, is then not larger because there are constraints on the NCC chains biasing the equilibrium populations of trans and gauche conformations toward the trans. It is also conceivable that chemical shift dispersion in the NCC resonance might be attributed to variations in trans/gauche population ratios. Unfortunately, we must view this interesting possibility as speculative at this point.

Recently, Tonelli has successfully predicted the dependence of the 9-methyl ^{13}C resonance in 3,5,7,9,11,13,15-heptamethylheptadecane isomeric stereosequencing of the neighboring groups.[23,24] He used a rotational isomeric state model to calculate conformational probabilities and then predicted the chemical shift of each stereosequence based on the idea that the methyl resonance was shifted solely by the position of the carbons three bonds on either side of the one being considered. This so-called "γ effect" is such that the methyl resonance is shifted by −5.4 ppm (upfield) if either carbon three bonds away is in a gauche rather than a trans conformation and 10.8 ppm if both of these carbons are gauche. Tonelli also predicted the stereosequence dependence of the chemical shifts of CH_2 and CH carbons based on this γ effect of −5.4 ppm, but these predictions await experimental verification. The solid state chemical shifts reported here, taken in conjunction with the liquid chemical shifts for $C_{17}{}^{i}$ and for cyclohexane, are ambiguous relative to this γ effect of −5.4 ppm. If one assumes that the γ effect alone controls the methylene chemical shift, then at least two points of view can be taken: (1) Assuming that the γ effect is −5.4 ppm and operates through space rather than through the bonding electrons, then, relative to δ(CC), $\delta(C_{17}{}^{i})$ and $\delta(C_6H_{12})$ are fairly consistent with these assumptions. (Note that C_6H_{12} has only one, rather than two, γ carbons for each carbon position.) On the other hand, the small value of δ(NCC) would then imply that the fraction of gauche bonds is only 0.22 in the NCC at 28 °C. (2) Assuming that the γ effect operates through the bonding electrons and not through space, then $\delta(C_6H_{12}) - \delta$(CC) represents two γ effects per carbon so that the γ effect for two methylenes interacting would be half −6.52 or −3.3 ppm. With a −3.3 ppm γ effect, the observed δ(CC) − δ(NCC) is exactly what one would expect for a liquid-like distribution of gauche and trans bonds. But $\delta(C_{17}{}^{i})$ is then shifted too far upfield and would point to a fraction of gauche bonds of 0.52 which is excessively high.

We do not feel justified in choosing either of these two points of view; indeed, the implicit neglect of the influence of crystal packing and density changes on the chemical shift is not very satisfying. There is some recent evidence,[25] however, that the γ effect is in the range of −3 to −4 ppm instead of −5.4 ppm.

We turn now to the question of line widths and their origins, a question closely associated with expectations for and optimization of resolution in CPMASS spectra. For purposes of this discussion, we assume the simple equation for the observed full width at half-height, $\Delta\nu^*$ expressed in hertz:

$$\Delta\nu^* = \Delta\nu(B_0) + \Delta\nu(\sigma) + \Delta\nu(T_{2C}) \qquad (2)$$

where $\Delta\nu(B_0)$ is the line width contribution from magnetic field inhomogeneity across the sample, $\Delta\nu(\sigma)$ arises from isotropic chemical shift dispersion, and $\Delta\nu(T_{2C})$ is the transverse relaxation contribution discussed earlier. Equation 2 is only exact when each contribution gives rise to a Lorentzian line shape. Since there is no compelling reason for any of the contributions to be Lorentzian, eq 2 must be considered very approximate.

In our spectrometer, $\Delta\nu(B_0)$ is estimated to be 4–5 Hz judging by the line width, both spinning and nonspinning, of the ethylne glycol capillary sample under conditions of high-power proton decoupling. The effects of any precessional motion of the rotor (assumed small) are included in $\Delta\nu(B_0)$. The chemical shift dispersion contribution, $\Delta\nu(\sigma)$, arises from variations in molecular packing, in average conformation[6,7] as just discussed, and/or in local magnetic susceptibility. The natural line width, $\Delta\nu(T_{2C})$, has a complex origin. There are relaxation contributions to T_{2C} from molecular motions at the frequency ν_{1H},[6,7] from low-frequency motions which modulate the ^{13}C resonance frequency via ^{13}C anisotropic chemical shifts,[26] from cross-polarization to the spin-locked protons under conditions of large radiofrequency mismatch,[27] from off-resonance proton irradiation,[27] from weak ^{13}C–^{13}C dipolar interactions between pairs of nuclei whose chemical shift principal axes are not colinear,[26] and from molecular motion at the same rotation frequency contributing via the ^{13}C–^{13}C dipolar interaction. Due to the method chosen for determining T_{2C}, instabilities in B_0 over the period τ also contribute to T_{2C}. Although the relative importance of theses effects will be examined in more detail elsewhere,[28] a few qualitative remarks are given here.

Since the chemical shift tensor of the protons is generally anisotropic, the protons will usually have an instantaneous resonance offset. Since experiments performed in our laboratory have indicated a rather strong and roughly quadratic dependence of line width on resonance offset, there will be an "on-resonance" line width contribution associated with the mean-squared proton-resonance offset, which, in turn, can be related to chemical shift anisotropy. For PE, the proton anisotropy is approximately 5 ppm.[29] Static magnetic field inhomogeneity for a nonspinning sample (13–15 Hz full width at half-height in our case) also must be included in the resonance offset contribution to $\Delta\nu(T_{2C})$ since the instantaneous resonance offset for a given ^{13}C nucleus is the sum of contributions from proton chemical shift anisotropy and magnetic field inhomogeneities, both effects being periodic at the sample rotation frequency. Similar interplay between chemical shift anisotropy and magnetic field inhomogeneity has also been noted in a discussion of ^{13}C side band intensities in slow-spinning experiments.[26]

The variation in $\Delta\nu(T_{2C})$ for samples A–E is limited to a factor of 2.5 in total range which would suggest that at least for samples D and E molecular motion at ν_{1H} is not the dominant influence. If it were, a larger difference would probably be seen between the $\Delta\nu_C(T_{2C})$ values for samples A and D. Our current thinking is that there is negligible contribution of these small $\Delta\nu_C(T_{2C})$ values from cross-polarization, molecular motion at ν_{1H}, molecular motion at the sample rotation frequency, and slow motions modulating the ^{13}C resonance positions via the anisotropic chemical shift. We reach the latter conclusion by assuming that there are only two potential minima for a crystalline chain which are related by a 180° chain rotation and a translation by one methylene unit.[30] This so-called flip–flop motion preserves the chemical shift; furthermore, if such a flip–flop occurs, the methylene group is expected to have a negligibly small transition time compared to its residence time. Our best estimates for the contribution to $\Delta\nu_C(T_{2C})$ from mean-squared proton-resonance offset combined with magnetic-field inhomogeneities is about 0.1 Hz in sample E. Instabilities in B_0 contribute a maximum of 0.2 Hz based on a liquid echo attenuation. The contribution from a network of weakly interacting ^{13}C–^{13}C dipolar pairs whose chemical shift principal axes are not colinear cannot be eliminated as a possibility since ^{13}C–^{13}C pairs on adjacent chains in the crystallographic 110 direction have chemical shift principal axes (normal to the chain axis) which are not colinear. This contribution is very tedious to calculate, but contributions could be on the order of 1 Hz. A signature for the dominance of this line-width contribution is that it should depend inversely on the rotation frequency, ν_r.[26] While investigating the ν_r dependence of $\Delta\nu_C(T_{2C})$, we found that T_{2C} depended quite strongly on how quietly the rotor was spinning. In a separate series of experiments, we have changed ν_r and readjusted the magic angle. We obtain values for $\Delta\nu_C(T_{2C})$ for sample E of 5.0, 3.9, 3.2, and 3.2 Hz at rotational frequencies of 576, 1000, 1500, and 2000 Hz, respectively. We attribute the difference between the value of 3.2 Hz in this experiment and the 1.0 Hz reported above at rotational speeds of 2000 Hz to the fact that there was an audible hum emitted by the rotor during the experiment when 3.2 Hz was obtained that was absent during the 1.0 Hz determination. This leads us to conclude that mechanical instabilities in the rotation may be a sizable contribution to $\Delta\nu_C(T_{2C})$. In this context, the differences in $\Delta\nu_C(T_{2C})$ between samples A, B, D, and E are not necessarily significant, and the values reported should be considered as upper limits. For an ideally stable rotor at

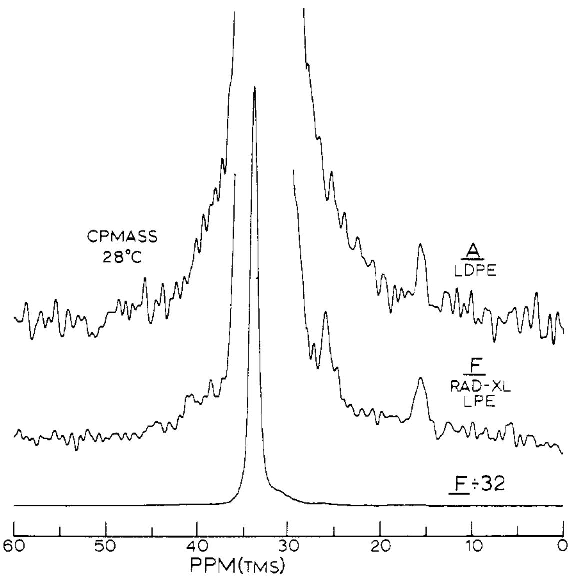

Figure 3. CPMASS ^{13}C spectra at 28 °C of sample A, a branched, low-density PE (upper), and sample F, radiation cross-linked linear PE (middle and lower). The upper and middle spectra are normalized to the same total intensity, and the lower spectrum is attenuated by a factor of 32. The number of scans for samples A and F are respectively 12 800 and 27 000. Methyl resonances in both spectra are visible near 16 ppm, and a second peak at 26 ppm is partially resolved for sample F; this latter resonance is probably the methylene adjacent to the methyl (see ref 32 and 33). Full widths at half-height for the main peak are 18 and 14 Hz, respectively, for samples A and F.

the magic angle in PE, $\Delta\nu_C(T_{2C})$ might be significantly less than 1.0 Hz, although, in support of the significance of the reported $\Delta\nu_C(T_{2C})$ values, all samples except for sample D spun very quietly.

The observed NCC line width of 39 Hz in sample B is similar to the 50–100-Hz line widths observed in other noncrystalline, glassy polymers.[6,7] The $\Delta\nu_{NC}(T_{2C})$ contribution of 14 ± 4 Hz is very likely determined by molecular motion. The contribution $\Delta\nu_{NC}(B_0)$ is again expected to be 4–5 Hz which implies that $\Delta\nu_{NC}(\sigma)$ is about 20 Hz. The possibility that this chemical shift dispersion arises primarily from differences in gauche to trans population ratios has already been mentioned.

The fact that the observed CC LPE resonances are very narrow is encouraging when one considers the capability of the CPMASS technique for obtaining good, high-resolution spectra of narrowly spaced lines. The chances for good resolution in NCC resonances are not nearly as good[9] since one must contend with both $\Delta\nu_{NC}(\sigma)$ and $\Delta\nu_{NC}(T_{2C})$. With $\Delta\nu_{NC}(\sigma)$ primarily determined by conformational and molecular packing variations and $\Delta\nu_{NC}(T_{2C})$ having a strong contribution from molecular motion, one would expect that $\Delta\nu_{NC}(\sigma)$ would decrease due to motional averaging as temperature increases, whereas $\Delta\nu_{NC}(T_{2C})$ would depend rather strongly on the correlation time for molecular motion. Narrowing of $\Delta\nu(\sigma)$ has already been noted in epoxies.[7] Unfortunately, the dependence of $\Delta\nu_{NC}(\sigma)$ and $\Delta\nu_{NC}(T_{2C})$ on experimental parameters such as ν_{1H} is not large so that one might have to search for conditions, mainly temperatures, offering the best resolution for the NCC resonance.

In a rather rigorous test of resolution capability, extended accumulations were taken on samples A and F; the spectra are displayed in Figure 3 where the lower spectrum of sample F is shown at two amplifications (×1 and ×32). Both spectra are normalized to the same total intensity. Both samples A and F should exhibit low-intensity resonances (~1%) corresponding to branches in sample A and resonances in the vicinity of cross-links or chain ends in sample F. For cross-links or branch points incorporated in crystalline regions, a question arises as to whether the resolution expected for these resonances will be narrow, like crystalline resonances, or broad, like noncrystalline resonances. Arguments in support of the latter point of view include notions that branches or cross-links represent a disruption of regular crystalline packing implying a greater molecular mobility; therefore, $\Delta\nu(\sigma)$ and $\Delta\nu(T_{2C})$ could both be important broadening mechanisms for these weak resonances.

The CPMASS spectrum of sample A only resolves the methyl resonance at about 16 ppm. This spectrum stands in rather sharp contrast to the rich detail of the ^{13}C spectra of the same material[31] at 110 °C in a 15% trichlorobenzene solution. Resonances upfield from the CC peak are simply obscured by the NCC peak in the CPMASS spectrum of sample A. The CC line width in sample A is 18 Hz for this long accumulation due to a drift in the fields at the sample relative to the external lock. Elimination of this drift is not likely to improve resolution significantly due to the presence of the wide NCC resonance.

Sample F has a higher crystallinity than sample A. The observed CC line width is 14 Hz, and one can observe not only a methyl resonance at about 16 ppm but also a peak at 26 ppm which could be associated with the position α to a long-chain methyl, in analogy with solution assignments.[32,33] The methyl and α-methylene resonances are displaced approximately 1 and 2 ppm, respectively, downfield from their positions in $C_{17}H_{36}$. On the low-field side of the CC resonance, signal to noise is not sufficient to claim the existence of other resonances.

It appears that the utility of CPMASS ^{13}C NMR spectra for determining low-intensity resonances near the strong CC PE line is limited as much by the shifted, broad resonance of the NCC as by the width of the CC resonance. Whether going to higher external magnetic fields will mitigate this problem remains to be seen. In view of the quadratic dependence of $\Delta\nu_C(T_{2C})$ on the mean-squared proton-resonance offset, one expects that for an ideal rotor and a given ν^{1H}, $\Delta\nu_C(T_{2C})$ in hertz will increase at higher magnetic fields since the proton mean-squared resonance offset contribution, expressed in hertz, is proportional to B_0^2. Whether resolution improves at high field will then depend on how dominant this contribution to $\Delta\nu_C(T_{2C})$ is. In samples containing protons of differing isotropic chemical shifts, the contribution to $\Delta\nu_C(T_{2C})$ from resonance offset may become dominant at large B_0, since the proton frequency cannot be chosen to coincide with the isotropic resonance positions of all the nuclei.

Acknowledgment. We are indebted to A. N. Garroway for helpful discussions concerning natural line widths and to M. Maricq and J. S. Waugh for making ref 26 available to us prior to publication. One of the authors (W.L.E.) acknowledges the support of the National Research Council in the form of a postdoctoral fellowship.

References and Notes

(1) A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **59**, 569 (1973), and references cited therein.
(2) E. R. Andrew, *Progr. Nucl. Magn. Reson. Spectrosc.*, **8**, 1 (1971).
(3) J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, **8**, 291 (1975).
(4) E. Lippmaa, M. Alla, and T. Tuherm, XIX Congress Ampere, Proceedings, Heidelberg, 1976, p 113.
(5) A. N. Garroway, W. B. Moniz, and H. A. Resing, Organic Coatings and Plastics, Preprints, Vol. 36, p 133, 1976; 172nd Meeting of the American Chemical Society, San Francisco, Calif., 1976.
(6) J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, **10**, 384 (1977).

(7) A. N. Garroway, W. B. Moniz, and H. A. Resing, *ACS Symp. Ser.*, No. 103 (1978).

(8) A. N. Garroway, W. B. Moniz, and H. A. Resing, *Faraday Symp. Chem. Soc.*, **13** (1979).

(9) C. A. Fyfe, J. R. Lyerla, W. Volksen, and C. S. Yannoni, *Macromolecules*, preceeding paper in this issue. This reference contains work on PE, done independently, which overlaps some of the work reported in this paper. The conclusions reached by these authors agree with our findings.

(10) D. L. VanderHart, in preparation.

(11) I. Solomon, *C. R. Hebd. Seances Acad. Sci.*, **248**, 92 (1959).

(12) S. R. Hartmann and E. L. Hahn, *Phys. Rev.*, **128**, 2042 (1962).

(13) Sample E has been kindly supplied by R. S. Porter of the University of Massachusetts. Descriptions of the fabrication may be found in (a) N. E. Weeks, S. Mori, and R. S. Porter, *J. Polym., Sci., Part B*, **13**, 2031 (1975); and (b) N. E. Weeks and R. S. Porter, *ibid.*, **13**, 2049 (1975).

(14) Sample F was kindly given to us by Professor A. Keller of the University of Bristol, U.K.

(15) J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect", Academic Press, New York, 1971.

(16) R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968).

(17) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).

(18) A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, Oxford, England, 1961, Chapter VIII.

(19) Much shorter $T_{1\rho}$ values were measured for the NCC protons in LPE relative to the CC protons at room temperature by D. W. McCall and D. C. Douglass, *Appl. Phys. Lett.*, **7**, 12 (1965).

(20) F. Bloch and A. Siegert, *Phys. Rev.*, **57**, 552 (1940).

(21) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neil, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

(22) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, 1969, Chapters III and V.

(23) A. E. Tonelli, *Macromolecules*, **11**, 565 (1978).

(24) A. E. Tonelli, *Macromolecules*, **11**, 634 (1978).

(25) A. E. Tonelli, private communication.

(26) M. M. Maricq and J. S. Waugh, *J. Chem. Phys.*, in press.

(27) M. Mehring, "High Resolution NMR Spectroscopy in Solids, NMR: Basic Principles and Progress", Vol. 11, Springer-Verlag, Berlin, 1976, Chapter IV.

(28) D. L. VanderHart, William L. Earl, and A. N. Garroway, to be published.

(29) B. C. Gerstein, private communication.

(30) H. G. Olf and A. Peterlin, *J. Polym. Sci., Part A-2*, **8**, 771 (1970).

(31) F. A. Bovey, F. C. Schilling, F. L. McCrackin, and H. L. Wagner, *Macromolecules*, **9**, 76 (1976).

(32) D. E. Dorman, E. P. Otocka, and F. A. Bovey, *Macromolecules*, **5**, 574 (1972).

(33) J. C. Randall, *J. Polym. Sci., Part B*, **11**, 275 (1973).

Carbon-13 Nuclear Magnetic Resonance of Phenolic Resins. Positional Isomers of Bis(hydroxybenzyl)phenols and Bis(hydroxyphenyl)methanes[1]

Stanley A. Sojka,[*,‡] Roger A. Wolfe,[‡] Edward A. Dietz, Jr.,[‡] and Bobby F. Dannels[§]

Hooker Chemical and Plastics Corporation, Research Center and Durez Division, Grand Island Complex, Niagara Falls, New York 14302. Received March 28, 1979

ABSTRACT: The ^{13}C NMR chemical shifts of positional isomers of bis(hydroxybenzyl) phenols and bis(hydroxyphenyl) methanes are reported. The ^{13}C NMR chemical shifts of these oligomers are assigned and grouped into classes. These data are useful for the understanding of more complex resin systems.

We wish to report the ^{13}C NMR chemical shifts of all seven possible positional isomers of bis(hydroxybenzyl)phenols and the three positional isomers of bis(hydroxyphenyl)methanes. The study of these small oligomers is necessary for the complete understanding of more complex phenolic resin systems. Recent interest in the utilization of ^{13}C NMR spectroscopy to study the structure and composition of phenolic resins has prompted us to disclose some of our initial results.[2-6]

A low molecular weight phenolic resin was made by dropwise addition of 600 g (7.4 mol) of 37% aqueous formaldehyde into 3500 g (37.2 mol) of phenol and 17 g (0.2 mol) of oxalic acid at 100 °C. The temperature was maintained at 100–110 °C for 1 h after the addition. The reaction mixture was vacuum distilled and a fraction of bis(hydroxybenzyl)phenols (12 g) was collected (bath temperature was 340–360 °C (0.02–0.03 mm)). Purified bis(hydroxybenzyl)phenol isomers were obtained by separating this fraction by LC using a E.S. Industries Chromegaprep^{TM} bonded diol column (50 cm × 9.6 mm i.d.). A 2% $CH_3OH/CHCl_3$ (vv) elution solvent was used at a flow of 5.5 mL/min. Component detection was at 254 nm. Purified bis(hydroxyphenyl)methane isomers were obtained by column chromatography of an isomeric mixture (Bisphenol F, Rhodia, Inc., Chemicals Division) on silica gel (Baker, 60/200 chromatographic grade) using 1.5% $CH_3OH/CHCl_3$ (vv) as elution solvent. The purity of isomers was found to be >90% in all cases by reinjection on the chromatographic column.

Carbon-13 chemical shifts were measured at ambient temperature using a Varian XL-100 spectrometer equipped with a Nicolet TT-100 pulse apparatus. Quadrature phase detection was used, and free induction decays were collected over 8K points. The time between 30° pulses was 25 s, and the number of scans varied between 1000 and 4000. Gated decoupling was used to suppress the Nuclear Overhauser effect. Samples were ~5% in THF-d_8 which also served as an internal field-frequency lock signal and an internal chemical shift standard. The chemical shifts were converted to the Me_4Si scale using the relationship: $\delta(Me_4Si) = \delta THF\text{-}d_8 + 25.3$. The measurements of these materials in dilute solution will reduce solvent and concentration effects upon the chemical shifts.

The ^{13}C chemical shifts and assignments are compiled in Table I for phenol (1), 2,2′-bis(hydroxyphenyl)methane (2), 2,4′-bis(hydroxyphenyl)methane (3), 4,4′-bis(hydroxyphenyl)methane (4), and all the bis(hydroxybenzyl)phenol isomers 5–11. Figure 1 shows the structures of isomers 5–11. Assignments were based upon chemical shift analogy to methyl-substituted phenols, integrated peak areas, and internal consistency. In some cases, proton

---

[‡] Research Center.

[§] Durez Division.

0024-9297/79/2212-0767$01.00/0