Carbon-13 Spin Relaxation Parameters of Semicrystalline Polymers. Linear Polyethylene

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ABSTRACT: The carbon-13 spectra and relaxation parameters for bulk linear polyethylene were obtained at 45 °C and 67.90 MHz for a variety of different semicrystalline samples. By control of molecular weight and crystallization temperature the level of crystallinity was varied from 0.51 to 0.95, the extremes that are attainable. A variety of morphological forms were developed. The spin–lattice relaxation times, T_1, were found to be the same for all samples, independent of polydispersity, density, or morphological form. The effective correlation time was calculated to be the same as that previously reported for the interior chain atoms of pure molten *n*-alkanes. Thus the fast internal segmental motions, which determine T_1, are essentially the same in the noncrystalline regions of linear polyethylene and in the melts of low molecular weight *n*-alkanes. A full nuclear Overhauser enhancement factor is found for samples of lowest crystallinity in accord with the value reported for the pure melt. However, this factor decreases to unity as the level of crystallinity increases to 0.94. There appears to be a correlation between the observed line widths and sample morphology since the results fall into several distinct categories. However, a detailed interpretation must be reserved until all the factors which can significantly contribute to the line width are evaluated. Both T_1 and T_2 increased as the temperature was varied from 45 to 145 °C. However, contrary to expectations the ratio T_1/T_2 increased. This result suggests that either the motional properties of the polyethylene backbone are substantially different from other chains due to a change in shape in the distribution of correlation times with temperature, or that a static factor, enhanced by the high field, is contributing to the line width.

The use of carbon-13 nuclear magnetic resonance and spin relaxation techniques to study the structure of, and motions within, bulk synthetic polymers is well established.[1–7] Most of the studies to date have been concerned with completely amorphous polymers well above their glass transition temperatures. Glassy polymers have been investigated using dipolar decoupling, cross polarization, and magic angle spinning techniques.[8,9] The only semicrystalline polymer that has been reported in detail is *trans*-polyisoprene,[2,4] for which ^{13}C spin–lattice relaxation times, nuclear Overhauser enhancement factors, and line widths were obtained.[4]

The overall molecular structure of a semicrystalline polymer is very complex.[10] A lamella-like crystallite is the usual predominant feature for homopolymers. Associated with these crystallites are interfacial and interzonal or amorphous regions.[10–12] Moreover, the crystallites can be organized, under certain circumstances, into higher levels of morphology or supermolecular structure such as spherulites and related forms.[13] The level of crystallinity, the distribution between interzonal and interfacial regions, and the morphological forms that develop depend on the molecular weight and the crystallization temperature in a systematic manner that has been extensively studied.[10,11,13] Elucidation of the details of the structure of the different regions and the basis for the organization has been the subject of extensive study for several decades. Since carbon-13 spin–lattice relaxation times (T_1), spin–spin relaxation times (T_2), and nuclear Overhauser enhancements factors (NOEF) can provide detailed information concerning overall molecular and segmental motion,[1,14] it appears appropriate to apply these techniques to semicrystalline polymers when the various structural factors have been systematically controlled. With the above in mind, and to assess the usefulness of these parameters in contributing to an understanding of the molecular parameters involved, we have measured the ^{13}C T_1's, T_2's, and NOEF's at 45 °C and 67.90 MHz of a series of linear polyethylene samples of different molecular weights, densities, and morphologies. We have also investigated T_1 and T_2 as a function of temperature between 45 and 145 °C.

Experimental Section

Carbon-13 NMR. Natural abundance ^{13}C Fourier transform NMR spectra under conditions of scalar proton decoupling were recorded at 67.90 MHz and 45 °C on a Bruker HX-270 spectrometer. The samples consisted of chunks or pellets of polyethylene that were suspended in finely powdered poly(vinyl chloride) that was added to fill the remaining volume of the 10-mm NMR tube. Field-frequency locking was not used. Given the large values of the measured line widths ($\gtrsim$500 Hz) and the relatively slow drift of the magnetic field of the superconducting NMR spectrometer ($\sim$0.4 Hz/h for ^{13}C operation), the effect of no field-frequency lock was negligible. The ^{13}C spectrum of the PVC filler consisted of only an extremely broad band of very low intensity. It made no perceptible contribution to the spectra being reported.

The line wideth measurements of the different samples were obtained under identical decoupling conditions, i.e., noise modulation bandwidth and decoupling field strength. Most of the determinations were made consecutively. For the few determinations made at other times, sample a (Table I) was used as a comparative line width standard. The standard line width varied only slightly (<10%) from the original value.

The width of the proton resonance arising from the noncrystalline region of polyethylene was estimated to be about 3–4 kHz from the narrow component of a typical broadline NMR spectrum.[15,16] Hence a proton decoupling bandwidth of approximately 10 kHz was used. A substantially narrower bandwidth (3 kHz) resulted in a relatively small amount (10–90 Hz) of additional broadening, depending on the sample. This narrower bandwidth was used for the T_1 and NOEF measurements. The strength of the decoupling field used was approximately 0.8 G. This value is typical of that used for noise modulated ^{1}H decoupling in ^{13}C experiments on liquids and mobile solids.[14] Our experimental conditions are essentially the same as those used by Schaefer for similarly constituted polymers.[4] The ^{13}C line width of a test sample (sample a, Table I) was narrowed by about 10% upon increasing the decoupling field to 1.6 G. Line widths at half-height were measured directly from the printed spectra and were corrected for broadening due to sensitivity enhancement.

Spectral widths of 20 kHz were employed with 4096 or 2048 frequency domain points. In most cases quadrature detection was used. Free induction decays were multiplied by a decreasing exponential function to enhance signal to noise. The 90° rf pulse used was of 34 μs duration in most cases. Spin–lattice relaxation times were obtained using the standard inversion–recovery pulse sequence[17] with the pulse repetition rate equal to approximately three times the measured T_1. Carbon-13 nuclear Overhauser enhancements were measured using a gated decoupling technique,[18] with the period between the end of data acquisition and the next 90° pulse equal to about four times the T_1 value. Recent analyses[19] of the gated decoupling method for NOE measurement indicate that it may be necessary to employ substantially longer delay periods ($\gtrsim 8T_1$) than are used for T_1 experiments. Use of delays which are too short could result in an underestimation of the NOE. Since we observe the maximum NOE in two cases, and since all NOE's were determined under identical conditions, we conclude that the delay period used here is adequate.

The high-temperature measurements were carried out using a

Table I
Carbon-13 Spin Relaxation Parameters of Linear Polyethylene

	Degree of crystallinity (density)							
	Bulk[e]	Film[f]	M_η	T_1, ms[a]	NOEF	$W_{1/2}$, Hz[b]	Morph.	R_{sph}, μm
				(A) Unfractionated Samples				
(a)	0.51	0.53	2.0×10^6	369	2.0[c]	501	None	
(b)	0.68	0.69	1.7×10^5	356		700	Spher.	6.9
(c)	0.72	0.75	2.0×10^6	358		496	None	
(d)	0.81	0.78	1.7×10^5	348	1.5[d]	695	Spher.	16.5
				(B) Fractionated Samples				
(e)	0.54	0.55	6.1×10^6			500[g]	None	
(f)	0.70	0.68	6.1×10^6			503	None	
(g)	0.54	0.53	2.5×10^6			560	None	
(h)	0.51	0.50	2.5×10^5	355	2.0[c]	625	Spher.	4.4
(i)	0.57	0.56	8.1×10^4	343		622	Spher.	2.5
(j)	0.94	0.92	2.75×10^4	352	1.0[d]	945	Rod	

[a] Estimated accuracy ±10%. [b] Estimated accuracy ±5–10%. [c] Estimated accuracy ±0.1. [d] Estimated accuracy ±0.2. [e] For NMR. [f] For light scattering. [g] Estimated.

Bruker B-ST 100/700 variable temperature unit. At 90 °C the sample, in a 10-mm NMR tube, was covered with D_2O for locking purposes. At 116 and 145 °C, the polyethylene pieces in a 10-mm tube were not covered with liquid. However, the sample tube was concentrically placed within a 13-mm tube with tetrachloroethane-d_2 in the annulus for locking. In the 90 °C T_1 experiment for $C_{44}H_{90}$ the sample, in an 8-mm tube, was concentrically placed in a 10-mm tube with D_2O in the annulus.

Polyethylene Samples. Several different types of linear polyethylene samples were studied. The two unfractionated samples, $M_\eta = 2.0 \times 10^6$ and 1.7×10^5, were Hifax-16 and Marlex-50 and obtained from the Hercules Co. and Phillips Petroleum Co., respectively. The molecular weight fractions were obtained from several different sources. The two highest molecular weights, $M_\eta = 6.1 \times 10^6$ and 2.5×10^6, were obtained by liquid–liquid fractionation using methods previously described.[20,21] The three lowest molecular weight fractions were obtained from preparative gel permeation chromatography and supplied by Societe Nationale des Petroles D-Aquitaine (SNPA).

The variations in the level of crystallinity were obtained by methods previously developed.[11,20,21] The low levels of crystallinity (samples a, b, e, g, h, i) were obtained by rapidly quenching, under vacuum, from the melt at 165 °C to a temperature of less than −70 °C. The relatively high levels of crystallinity (samples c, d, f, and j) were obtained by transferring the molten polymers to 130 °C, where they were isothermally crystallized for 14 days. The samples were then slowly cooled to room temperature over the period of 1 day. The degree of crystallinity was obtained from density measurements in a 2-propanol–water gradient column at 23 °C using the specific volume relations of Chiang and Flory.[22] The enthalpy of fusion was determined for several samples in the conventional manner.[23,24] The relationship between the density and enthalpy of fusion followed the pattern previously established.[24]

Low-Angle Light Scattering. For these experiments thin films were prepared by melting the sample (at 165 °C) between the plates of a Carver Press. The thin films were crystallized in a manner very similar to that described above. The densities at room temperature were very similar to the samples prepared for the NMR measurements. In all cases the polymer film thicknesses were in the range of about 30 to 100 μm.

The H_v small angle scattering patterns were recorded with a photographic laser light scattering apparatus similar to that developed by Stein.[25] To reduce surface scattering, the films were placed between glass microscope slides with silicone oil as an immersion fluid. The spherulite size was calculated from the H_v pattern by the formula[26]

$$4.1 = \frac{4\pi R}{\lambda} \sin\left(\theta_{\max}/2\right)$$

where R is the radius of the spherulite, λ is the wavelength of the light in the film, and $\theta_{\max}$ is the scattering angle (measured with the film) at which the maximum scattering intensity occurs.

Results and Discussion

A summary of the results is given in Table I. Here the different samples studied, their level of crystallinity as obtained from density measurements, and the ^{13}C T_1's, NOEF's, and resonance line widths at 45 °C and 67.90 MHz are listed. The last two columns in Table I summarize the morphological characteristics that were obtained from the low angle light scattering patterns. The next-to-last column indicates the kind of morphology or supermolecular structure formed. In accord with previous reports no distinct morphology is observed for the very highest molecular weight samples.[13] This conclusion can now be extended to high molecular weight samples of much higher density than have previously been studied. Thus samples which are 70% crystalline but of high molecular weight, greater than $\sim 2 \times 10^6$, do not display any distinct morphological features. The highest level of crystallinity sample that we have produced (sample j) gives a pattern which is characteristic of large rodlike aggregations of lamellae approximately 20 μm in length. All the other samples studied here are spherulitic. Their radii, in microns, are listed in the last column of Table I. Some new aspects of the influence of molecular weight and level of crystallinity on the morphology or supermolecular structure can be seen even in these limited observations. They are clearly in need of further investigation but this subject is removed from the main theme of the present study. It suffices, for present purposes, to just note these different classes of morphology.

Figures 1 and 2 illustrate the partially relaxed FT spectra for samples a and j, respectively. These samples represent the extremes of molecular weight and density that have been studied. Figures 3 and 4 show the nuclear Overhauser enhancement measurements for the same samples. Taking into account the very large line widths observed here, compared to those normally observed for polymers in solution,[1] the quality of the spectra in Figures 1–4 can be considered quite good. It should be recognized that for the 94% crystalline sample, the observed signal arises from approximately 6% (~35 mg) of the total number of CH_2 units and has a line width of approximately 1 kHz. As is indicated in Table I, reasonably accurate T_1 and NOE values could be obtained for this sample (Figures 2 and 4). The resonances observed in the scalar proton decoupled ^{13}C spectra for these samples should arise only from the relatively mobile amorphous and interfacial noncrystalline regions.[1] This conclusion was confirmed by an unsuccessful attempt to obtain a high resolution ^{13}C NMR spectrum of polycrystalline n-tetratetracontane ($C_{44}H_{90}$) under the same operating conditions. This solid hydrocarbon, which serves as a good model for the crystalline regions of linear polyethylene, yields a spectrum which consists of only an extremely broad band many thousands of Hertz wide, and

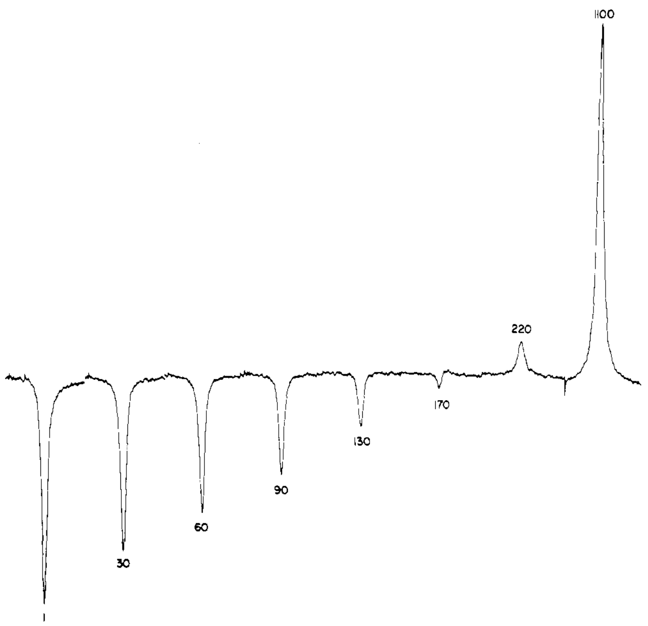

Figure 1. Set of partially relaxed ^{13}C FT NMR spectra of linear polyethylene; sample a, degree of crystallinity 0.51 (Table I); at 45 °C and 67.9 MHz. τ values are shown in ms, 2200 scans, 1.1 s pulse sequence repetition rate, 11.7 Hz artificial broadening due to exponential filtering.

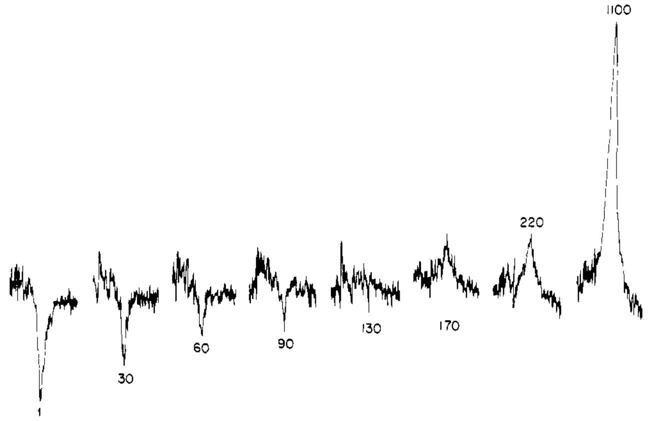

Figure 2. Set of partially relaxed ^{13}C FT NMR spectra of linear polyethylene; sample j, degree of crystallinity 0.94 (Table I); at 45 °C and 67.9 MHz. τ values are shown in ms, 12 500 scans, 1.1 s pulse sequence repetition rate, 15 Hz artificial broadening due to exponential filtering.

of very low intensity relative to the spectrum of the highest density polyethylene sample. In fact, this band cannot be distinguished from the slight baseline roll that is sometimes obtained in FT NMR spectra after the accumulation of large numbers of transients and can be easily attributed to this factor. As indicated previously, similar results were obtained for the finely powdered poly(vinyl chloride) filler.

The presence of crystallinity might be expected to influence the spectra of the noncrystalline regions and the associated ^{13}C relaxation parameters.[4] As is definitively shown in Table I, this expectation is not fulfilled for the spin–lattice relaxation time, T_1. Irrespective of the wide range in level of crystallinity and molecular weights studied and the different morphological forms and spherulite sizes that are represented by these samples, T_1 is, *within experimental error*, equal to 350 ms. Similar results have been obtained for *cis*-polyisoprene.[27] In this latter case, a comparison can be made at the same temperature between the completely amorphous, supercooled polymer and one which is about 30% crystalline. Identical T_1's were obtained at 0 °C for each carbon of completely amorphous and partially crystalline *cis*-polyisoprene.[27]

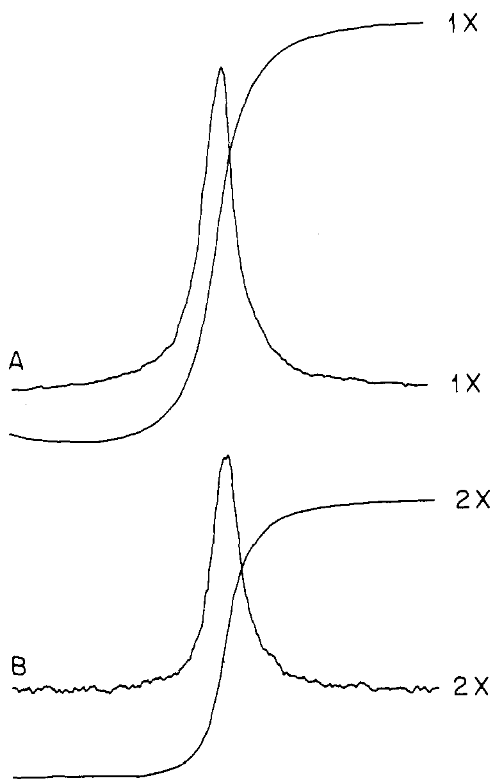

Figure 3. Carbon-13 spectra and integrals used to determine the NOE with gated decoupling for sample a (Table I); 1024 scans, 1.4 s pulse sequence repetition rate, 25 Hz artificial broadening due to exponential filtering. Scaling factors for spectra and integrals are at right: (A) with NOE; (B) without NOE.

To interpret these results we recognize that T_1 is determined by the relatively fast, and thus localized, segmental motions that occur at or near the Larmor frequency. These types of motions must then be the same for the noncrystalline regions of all the samples studied. This result might be anticipated for samples of low density which do not form spherulites since long sequences of disordered units should be present. In this connection, we note that the spin–lattice relaxation times of carbons in completely amorphous polyisobutylene are independent of molecular weight in the range 1.3×10^3 to 3.5×10^6.[7] The fact that the spherulite forming samples also have the same T_1 indicates that the fast segmental motions of the amorphous material contained within the system of organized lamellae are also the same. It is, however, quite surprising that the sample which is 94% crystalline, sample j, also has the same T_1. In this case the signal must arise almost entirely from regions that are on or in very close proximity to the crystallite surface and might be anticipated to be highly constrained. The results for linear polyethylene, and for *cis*-polyisoprene,[27] indicate that the segmental motions which are reflected in the T_1 measurements are the same for all noncrystalline regions of polymers as well as for the melt.

The NT_1 value of about 700 ms found for the linear polyethylene samples indicates that the internal rotations about the carbon–carbon bond are relatively fast. This conclusion is reached because of the full NOEF values found for the samples of lowest density so that the extreme narrowing condition appears to be satisfied for T_1 and NOEF.[14] However, the line widths are much broader than required to fulfill

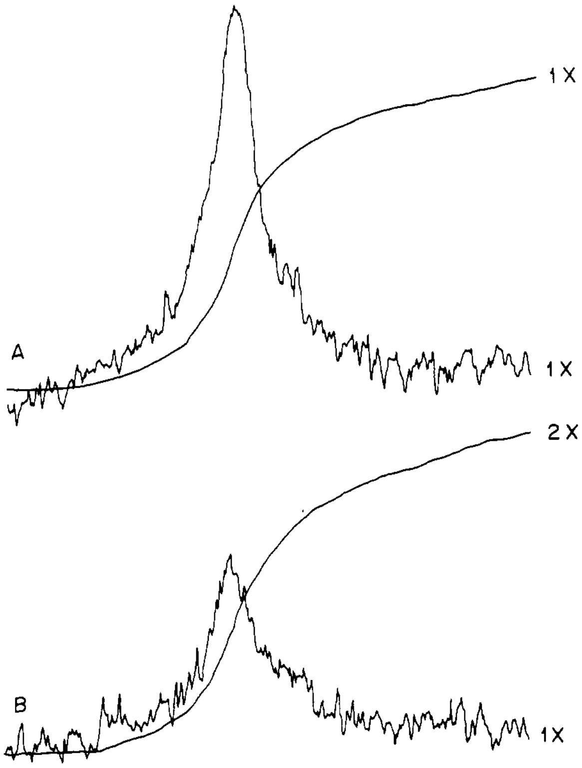

Figure 4. Carbon-13 spectra and integrals used to determine the NOE with gated decoupling for sample j (Table I); 11 000 scans, 1.4 s pulse repetition rate, 31 Hz broadening due to exponential filtering. Scaling factors for spectra and integrals are at right: (A) with NOE; (B) without NOE.

this condition (see below).

In examining the segmental motions of the noncrystalline regions of linear polyethylene, as monitored by ^{13}C T_1's, it is of interest to compare them with the properties of molten, low molecular weight n-alkanes. The T_1 for linear polyethylene is about ⅓ to ½ the value found at a comparable temperature for the interior chain atoms of pure, molten n-alkanes containing 18–20 carbon atoms.[28,29] Lyerla, McIntyre, and Torchia[29] used a self-consistent analysis to determine correlation times for internal motion. The effective correlation time, τ_{eff}, is expressed as

$$\tau_{\text{eff}} = \frac{r_{\text{CH}}^6}{N\hbar^2\gamma_{\text{C}}^2\gamma_{\text{H}}^2}\frac{1}{T_1} \tag{1}$$

Here r_{CH} is the carbon-hydrogen bond distance, γ_{C} and γ_{H} are the gyromagnetic ratios of carbon and hydrogen, respectively, and N is the number of directly attached protons. The value of τ_{eff} for the jth carbon within the chain was considered to have contributions from both the overall and internal motions and could be expressed as

$$({}^j\tau_{\text{eff}})^{-1} = ({}^j\tau_{\text{i}})^{-1} + (\tau_{\text{o}})^{-1} \tag{2}$$

Here τ_{o} is the correlation time for isotropic overall rotation (the same for all carbons) and ${}^j\tau_{\text{i}}$ is the correlation time due to internal motions for the jth carbon. The difference in the rates of segmental motion between carbons j and k is thus given as (ref 29)

$$\tau(j,k)^{-1} = ({}^j\tau_{\text{eff}})^{-1} - ({}^k\tau_{\text{eff}})^{-1} = ({}^j\tau_{\text{i}})^{-1} - ({}^k\tau_{\text{i}})^{-1} \tag{3}$$

The highest molecular weight n-alkane that has been studied to date is n-eicosane ($C_{20}H_{42}$).[29] At 39 °C and 15.08 MHz, carbons up to four from the chain end could be resolved and distinguished from the internal CH_2 resonance. Using this treatment, the best available estimate for the correlation time for internal motion of the backbone would be τ(4,internal) which represents the value farthest away from the chain end that can be measured. From the data given in Table II of ref 29 and eq 1 and 3 presented here, we find that for n-eicosane $\tau(4,\text{internal}) = 6.6 \times 10^{-11}$ s. For polyethylene, if one identifies τ_{eff} with τ_{seg}, then from eq 1 and the experimental NT_1 value of 700 ms we obtain the same value of the correlation time at 45 °C. While the exact quantitative agreement obtained between τ(4,internal) of n-eicosane and τ_{seg} of polyethylene is probably fortuitous, and the use of an isotropic model for polyethylene is admittedly approximate, these calculations very strongly suggest that the segmental motions are identical in the two cases.

Table II
Temperature Dependence of the ^{13}C Spin-Lattice Relaxation Times and Resonance Line Widths of Linear Polyethylene[a]

T, °C	T_1, ms[b]	$W_{1/2}$, Hz[b]	Apparent T_2,[c] ms	T_1/T_2
45	350	503	0.63	550
90	770	338	0.94	820
116	1050	245	1.3	810
145	1590	183	1.7	870

[a] Sample f. [b] Estimated accuracy ±10%. [c] Apparent $T_2 = 1/\pi W_{1/2}$.

A more rigorous analysis has been used by Levine et al.[30] These authors calculate ^{13}C dipolar relaxation times for molecules rotating anisotropically and with multiple internal rotations.[30] They apply the theory to a number of n-alkanes, treating the overall rotation of the molecules as being that of axially symmetric prolate ellipsoids (all-trans configuration assumed). It was found that the diffusion coefficient about the ith bond, $D_i \equiv 1/(6\tau_{\text{i}})$, was the same for all bonds except the one adjacent to the terminal methyl. The value of D_i decreases almost linearly, from 2.0×10^{10} to 0.8×10^{10} s^{-1}, as n goes from 6 to 18. As in the previous analysis, individual D_i's could be obtained only up to four bonds away from the chain end to the limitations of spectral resolution. The D_i value for the longest chain length corresponds to a τ_{i} value of 2.2×10^{-11} s, which is very close to the value obtained from the treatment of Lyerla, et al.[29] A linear extrapolation of the plot of D_i against n from Figure 9 of ref 30 indicates that a τ_{i} value of the order of 6.6×10^{-11} would be obtained for an alkane chain of about 22 carbons assuming a constant D_i for all bonds except that adjacent to the terminal methyl. These analyses strongly support the concept that the fast segmental motions, which determine T_1, are essentially the same in the noncrystalline regions of linear polyethylene and in the melts of low molecular weight n-alkanes. Moreover, neither the level of crystallinity nor the major differences in the morphological forms that have been developed influence this type of motion in the polymer.

The temperature variations of the ^{13}C T_1's for sample f ($M_\eta = 6.1 \times 10^6$, $1 - \lambda = 0.70$) over the range 45 to 145 °C are given in Table II and Figure 5. T_1 is a smoothly increasing function of temperature which again confirms the "fast solution" for τ_{eff} at 45 °C. The value of 1.59 s at 145 °C reported here is in agreement with the value of 1.37 s obtained by Inoué et al.[31] at 155 °C for the pure melt.

The plot in Figure 5 does not reveal any major discontinuity in T_1 as the melting temperature is traversed. This result is in apparent contradiction to a recent report on proton spin-lattice relaxation[32] for a high molecular weight linear polyethylene sample. The proton T_1 for the mobile fraction of an annealed sample increased from 0.8 to about 1.1 s between 45 and 120 °C then dropped sharply to about 0.6 s at T_{m}.[32] Above

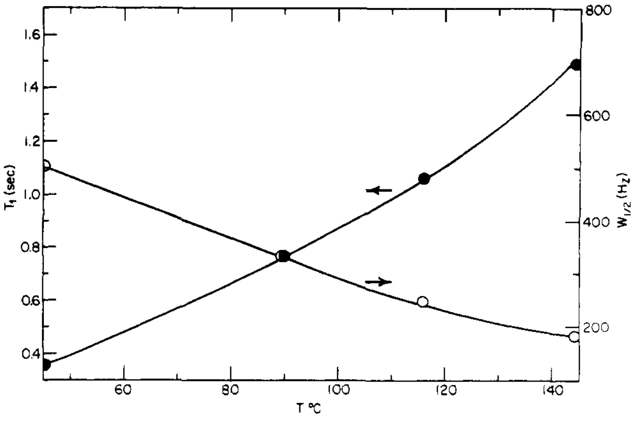

Figure 5. Plot of T_1 (●) and $W_{1/2}$ (○) as a function of temperature for linear polyethylene. Sample f ($M_\eta = 6.1 \times 10^6$; $1 - \lambda = 0.70$; nonspherulitic).

T_m, the proton T_1 rose again, but at a faster rate than in the lower temperature range. The ^{13}C data, on the other hand, can exhibit, at most, only a very small discontinuity in this temperature range.

The smooth increase in the ^{13}C T_1 with increasing temperature through the melting point is not surprising since there are several reasons that the ^{13}C T_1's are more reliable indicators of molecular mobility than proton T_1's.[1] Most important, spin–lattice relaxation of protonated carbons at natural abundance is dominated by the intramolecular dipolar mechanism with the attached protons. It is not subject to the complication of spin diffusion.[1] Thus, the fast segmental motions, which are independent of degree of crystallinity and morphology and are the same as in the totally amorphous polymer, would not be expected to be significantly influenced by the melting of crystalline regions.

The T_1 value obtained for linear polyethylene at 90 °C can be compared with that of the *n*-alkane *n*-tetratetracontane ($C_{44}H_{90}$), which is a pure liquid at this temperature. The interior carbons of $C_{44}H_{90}$ exhibit a T_1 of 1.23 s at 90 °C, compared to the value of 0.77 s for polyethylene. Recalling the previous comparison of T_1 values of polyethylene with *n*-eicosane at 45 °C and the subsequent analysis in terms of overall and segmental motions (eq 1 and 3), we conclude that overall molecular rotation still makes a significant contribution to the interior carbon T_1 of $C_{44}H_{90}$. However, this T_1 is closer to that for polyethylene at 90 °C than was found for *n*-eicosane at 45 °C relative to the polymer at the same temperature. Hence overall rotation makes a reduced contribution to the T_1 of $C_{44}H_{90}$ at 90 °C. A direct comparison of segmental motions, as was given for *n*-eicosane and polyethylene, was not readily possible for $C_{44}H_{90}$ because of the difficulty of resolving the relatively weak C-4 resonance from the interior methylene resonances.

In contrast to the spin–lattice relaxation times, the NOEF values (measured NOE-1) given in Table I are not the same for all samples. The two samples of lowest crystallinity, samples a and h, respectively, have the maximum NOEF of 2.0. Inoué and collaborators[31] found the full NOE value for molten polyethylene at 155 °C. Thus a full NOE can be considered to be characteristic of the completely molten state of polyethylene. This state would then be characteristic of the noncrystalline regions of samples a and h. For samples with the highest crystallinity, d and j, the NOEF is significantly reduced. From the data that are presently available the NOEF appears to depend on the level of crystallinity and not specifically on the morphological form. These first reported observations, with varying crystallinity and morphology, suggest the possibility that, when reduced values are observed, the nuclear Overhauser enhancement factor may be a sensitive probe of the noncrystalline structure.

Reduced NOEF values have been previously reported for carbons in pure amorphous polymers[4] and in solution.[33] In general the same NOEF was found for all backbone carbons. The measured value did not correspond to that predicted from the measured T_1 for an isotropic, one correlation time model.[3,4,33] The measured T_1 was such that the extreme narrowing condition should be fulfilled, and hence a maximum value of NOEF was expected. This apparent discrepancy was explained by introducing a broad distribution of correlation times.[1,3] With this postulate it was possible to simultaneously explain the observed T_1, T_2, and NOEF values.[1,3] However, for bulk polyisobutylene, where reduced NOEF's were also observed,[7] the ^{13}C spin-relaxation parameters could be interpreted, to a reasonable approximation, by a single correlation time model (or at most a narrow distribution) but with a "slow" solution, not in extreme narrowing, for τ_{eff}. The validity of the "slow" solution in this case was confirmed by the frequency dependence of T_1.

In the present case a distribution of correlation times is not required to solely explain the T_1 and NOEF results by themselves for the lowest crystallinity samples. The "fast" solution for τ_{eff} is confirmed for the samples having full NOEF and indirectly for the remaining samples, since T_1 does not change. For the "slow" solution of τ_{eff} to apply to the other samples, essentially the minimum NOEF of 0.15 is necessary. This requirement is not compatible with the experimental observations. The reduced NOEF's observed for the higher crystallinity samples could arise from some phenomenon involving a distribution of correlation times imposed by the crystalline regions. However, the detailed nature of such a distribution is not clear. Evidently the noncrystalline regions of these high crystallinity samples experience chain motions that reduce the NOEF substantially but do not affect the line widths or T_1's to a degree expected on the basis of previous studies.[1,3,4] The possibility also exists that the observed NOEF, particularly for the higher crystallinity samples, arises from the CH_2 units being located in more than one motional environment, as for example from the interfacial and interzonal regions. Hence the NOEF would represent a weighted average value.

The experimentally observed ^{13}C line widths are not the same for all the polyethylene samples and are in the range of about 500–900 Hz at 67.90 MHz. For other polymers that have been studied to date, both in bulk and in moderately concentrated solution,[1,4,33] T_2 is not generally equal to T_1. The polyethylene line widths are about two or three orders of magnitude broader than would be expected if $T_1 = T_2$. As has been indicated in the Experimental Section, the ^{13}C line width of a test sample narrowed by only about 10% upon doubling the decoupling power. Hence incomplete decoupling is not a major factor in determining the large line widths observed with polyethylene. These results have, in a general way, been attributed to the fact that, for polymers, the segmental motions which contribute to T_1 and the NOEF are not necessarily the same motions that determine T_2 and hence the line width. Slower modes of polymer motion, characterized by long correlation times, do not effectively contribute to T_1 and the NOEF but can contribute to T_2. However, for elastomers with effective correlation times, calculated on the basis of T_1, comparable to that of polyethylene, much reduced NOEF's and line widths of the order of 20–50 Hz were observed.[3,4] These are very narrow compared to those found for polyethylene.

There is evidence that suggests that the resonance lines become broader with crystallinity. A study of *trans*-polyisoprene, which is about 40% crystalline at 40 °C, indicated a broadening of all the ^{13}C resonances which could be due to this cause.[4] However, a direct comparison was not made with the completely amorphous polymer to firmly establish this point. A comparison of the ^{13}C spectra of completely amorphous and partially crystalline (about 30%) *cis*-polyisoprene at 0 °C indicates that the line width increases by about 50% with crystallization.[27] Though there is clear evidence that crystallinity does cause a broader spectral line than would otherwise be expected, the polyethylene line widths are substantially larger than have been observed for the other semicrystalline polymers. For the semicrystalline polyethylenes a rather unusual set of ^{13}C spin-relaxation data are found, namely very large line widths accompanied by long T_1's and substantial NOEF's. A major problem thus arises in having to simultaneously account for the T_1's and substantial or full NOEF values which suggest fulfillment for samples (a and h) of the extreme narrowing conditions with the apparently contradicting feature of line widths which are an order of magnitude larger than is observed for *trans*-polyisoprene.[4]

There are several possible reasons that can be offered for the abnormally large line widths that are observed. One is that the ^{13}C spin-relaxation behavior is due to a distribution of correlation times (for isotropic rotation). However, in view of the T_1 values, their temperature dependence, and the full NOEF's, a distribution resembling that used previously by Schaefer for amorphous elastomers[1,3] cannot simultaneously explain the data. In fact, we have found that such a distribution cannot explain the data for crystalline *trans*-polyisoprene at 40 °C.[4,27] Phenomologically, it should be possible to construct a modified distribution which would simultaneously explain all these ^{13}C spin-relaxation parameters. Essentially a bimodal form would be required, with one portion having the bulk of its spectral density at or near the Larmor frequency (for T_1 and NOEF). The spectral density of the other portion would be concentrated in the low-frequency region (for T_2). The high-frequency portion of this distribution could be adjusted to account for reduced NOEF's as observed for samples d and j. This construction would represent a formal analysis without any direct connection, at present, to molecular interpretation.

Another possible explanation is that the large line widths arise from incomplete motional narrowing. Restrictions of the segmental motion due to the presence of crystallites, the further influence of higher morphological forms, and the presence of chain entanglements in the amorphous regions could restrict the CH vectors from rotating at a fast enough rate through all solid angles of space. As has been pointed out by Schaefer this possibility is distinguished from broadening due to slow but isotropic rotation, as characterized by the "intermediate" and "slow" regions of correlation time distributions used previously.[3,34] If this explanation is accepted, there is still the need to explain the major differences observed between *trans*-polyisoprene and at least the low-level crystallinity polyethylene at the same temperature. These polymers have approximately the same degree of crystallinity, and both exhibit fast segmental mobility on the basis of their T_1 values. Yet the line width observed for polyethylene is about an order of magnitude larger than that found for the comparable carbons of *trans*-polyisoprene. With this explanation there must be a major influence of the chemical structure of the repeating unit.

Contributions of nonmotional or static phenomena to the line widths need also to be given some consideration. One such possibility would be that differences in bulk magnetic susceptibility exist within the sample volume. Change in nuclear screening would result[35,36] and give rise to a broadening of the resonance. Such broadening could occur from the irregular macroscopic sample configuration used here or possibly from microscopic differences within the sample. Broadening from this cause will vary linearly with the applied field[36] and hence will be approximately three times more severe in the present work at 63.4 kG as compared to all previous studies of this type which were carried out at lower field strengths.[4] Further studies are obviously required to ascertain and separate the different contributions to the observed line widths. Some of these are currently in progress.

The third column of Table II gives the ^{13}C line width of polyethylene, sample f, as a function of temperature through the melting region. As expected the line narrows with the increased segmental mobility introduced at higher temperatures. The crystalline content also decreases to zero as the temperature increases to 145 °C.[20] However, despite the observed narrowing, the line is still substantially larger than expected at the higher temperatures when compared with other polymers. For example, the polyethylene line width of 183 Hz at 145 °C is about an order of magnitude greater than is observed for *cis*- or *trans*-polyisoprene at 40 °C and 22.6 MHz.[4] We have also found that the methylene resonance of bulk polyisobutylene ($M = 3.5 \times 10^6$) at 145 °C and 22.6 MHz has a width of about 55 Hz[37] although its average segmental mobility at 45 °C is over two orders of magnitude slower than polyethylene at the same temperature.[7] In view of the slight dependence of the line width at 45 °C on decoupling power, the relatively large value observed for polyethylene at 145 °C cannot be due to incomplete decoupling. The proton line being decoupled is much narrower at 145 °C than at 45 °C. Moreover, at 116 °C and certainly in the pure melt at 145 °C the presence of crystalline regions cannot be making a substantial contribution to the line widths.

Also listed in Table II are the apparent T_2's calculated from the line widths (apparent $T_2 = 1/\pi W_{1/2}$) and the ratio T_1/T_2 at each temperature. For amorphous polymers, T_1 is generally greater than T_2.[4,38] This behavior has been attributed to the presence of slow modes of polymer motion which contribute to T_2 but not to T_1. As the temperature increases, polymer chain segments will experience increased motional freedom and hence the average correlation time will decrease. Moreover, if a distribution of correlation times is invoked to describe the motion, the width of such a distribution should be narrower (i.e., the motion is more liquid-like) at high temperatures.[1] Such narrowing of the correlation–time distribution with increased temperature has been observed for several polymers in solution.[34] Hence it is expected that with increasing temperature the ratio T_1/T_2 will decrease and approach unity.[38]

The opposite behavior is, however, found for polyethylene (Table II) where the T_1/T_2 ratio essentially increases with increasing temperature. It is difficult to explain this behavior if only motional factors are responsible for the line width at 145 °C. At this temperature all restraints on chain mobility arising from the presence of crystalline regions must be removed. The influence of factors responsible for incomplete motional narrowing of the lines at 45 °C should be greatly reduced. Even though chain entanglements will still be present, the motional behavior of a CH vector in polyethylene at 145 °C should approach that in a low molecular weight *n*-alkane in the liquid state. There could, therefore, be a large static factor contributing to the line widths or a change in the shape of the distribution of correlation times with temperature.

It was recently found that there was essentially no change in T_1/T_2 with temperature for bulk *cis*-1,4-polybutadiene.[39] However, in this study the temperature range was only 19 °C, which is not very decisive for analytical studies. Moreover, the values of T_1/T_2 for polyethylene are about one and a half orders of magnitude larger than for *cis*-polybutadiene.[39]

Detailed correlations between the line width of ^{13}C resonances arising from the amorphous and interfacial regions of semicrystalline polymers, in particular polyethylene, and morphology cannot be made with certainty until the major factors contributing to such line widths have been delineated. The results reported here point to the possibility that ^{13}C line widths could serve as a sensitive probe of semicrystalline polymer morphology. For example, the data in Table I do not show any obvious relation between the observed line widths and degree of crystallinity or polydispersity of the different samples. There does, however, appear to be a correlation between the line widths, as directly measured, and the morphology or supermolecular structure. The line widths can be divided into essentially three categories. All samples, irrespective of molecular weight, polydispersity, or density, which do not show any definite morphology samples (a, c, e, f) have the narrowest lines all of which have a width of about 500 Hz. The line widths of the samples which display a definite spherulitic morphology are greater. They range over about 100 Hz. They may also be dependent on the spherulitic radius, but a larger range in sizes needs to be developed to more definitely establish such a pattern. The third category, with a much broader resonance line width, is associated with the rodlike morphology of the sample of highest density. In this connection we should note that we have recently obtained a ^{13}C spectrum for a polyethylene fraction crystallized from dilute solution. This sample, with a degree of crystallinity, from density of 0.80 has an observed line width of about 2000 Hz.

In summary, the detailed study of the carbon-13 relaxation parameters for linear polyethylene has indicated that the fast internal segmental motions, as manifested in T_1, are independent of the level of crystallinity and the different supermolecular morphological forms that have been developed. The motions in the noncrystalline regions are essentially the same as those in the melts of low molecular weight *n*-alkanes. The apparent values of T_2, as determined from the observed line widths, are very small reflecting abnormally broad resonance lines for polyethylene in both the partially crystalline and completely amorphous states. The different possibilities that could be contributing to this observation have to be sorted out so that any relationship that may exist between T_2 and morphology can be established.

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