^{13}C n.m.r. and X-ray diffraction studies of the morphology of alkanes and linear polyethylenes

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^{13}C n.m.r. spin-lattice relaxation times have been determined for carbons in a number of solid alkanes and in two linear polyethylenes. ^{13}C spin-lattice relaxation times, T_1s, for the internal methylene carbons of the linear alkanes depend upon structure and chain length. There is almost a 100-fold increase in T_1 in going from orthorhombic $C_{21}H_{44}$ to $C_{60}H_{122}$. The central methylene carbons in the two polyethylenes give rise to two exponential decays. Analysis of the methyl resonances in one of these polyethylenes suggests that 60% of the methyl ends are in a crystalline environment. Low molecular weight orthorhombic alkanes are more mobile than expected from the $1/T_1$ *versus* a dimension of the unit cell relationship observed for linear and branched polyethylenes.

(Keywords: ^{13}C n.m.r.; X-ray diffraction; morphology; alkanes; linear and branched polyethylenes)

INTRODUCTION

In spite of intense investigation over many years, significant advances in our understanding of the phase structure of solid polyethylenes continue to be made. Morphologies can be studied by a wide variety of experimental techniques[1–6]. Recently, the application of solid state n.m.r. has given considerable insight into the nature of phases present in linear and branched polyethylenes[7–12]. The use of linear alkanes and low molecular weight polyethylenes as model compounds has also been of great value[13–18]. In this paper, ^{13}C spin-lattice relaxation times, T_1, are reported for such model systems and are used as a basis for discussion of the phase structures of branched polyethylenes.

In a general study of crystallinities of random copolymers of ethylene and 1-alkenes[19], it was found that numerical estimates of crystalline content varied with the experimental method being used. Density measurements gave higher values than those provided by X-ray and d.s.c., which in turn were higher than those estimated by Raman analysis and ^{13}C n.m.r. spectroscopy. The spectroscopic methods were used to estimate the amounts of a third 'interfacial' phase[3,7]. It was found, in keeping with the results of earlier workers[5], that the degree of crystallinity estimated from density is slightly greater than the sum of the crystalline and interfacial contents obtained from Raman analysis. The interfacial material appears to consist of *trans*-methylene sequences which are not packed in a sufficiently tight and ordered fashion to contribute significantly to Raman and n.m.r. estimates of crystallinity. These sequences do, however, make some contribution to estimates from X-ray, calorimetry and density methods.

X-ray diffraction studies show that increasing comonomer content causes a decrease in average crystallite breadth[19]. There is a simultaneous decrease in crystallite thickness[20], resulting in a drop of average crystallite volume by a factor of 20 or so when the comonomer content is increased from 2 to 10 mol%. At the same time the a dimension of the orthorhombic unit cell becomes larger; the increase is as much as 4% for a copolymer containing 8 mol% 1-octadecene. A second crystalline form is also present in some high comonomer content samples.

The increase in unit cell dimensions results in smaller T_1 values for the methylene carbons in crystalline regions of the copolymer. The average T_1 for a 2 mol% copolymer is 220 ($\pm$20) s but this decreases to 80 s for an 8 mol% 1-butene copolymer and to 30 s for a 10 mol% 1-octadecene copolymer. The slow decay assigned to relaxation of carbons in crystalline regions is almost single exponential in character but the slight curvature in some of the natural log of intensity *versus* time plots probably results from a distribution of T_1 values. Backbone carbons in an amorphous environment have a T_1 close to 0.3 s. The third section of the relaxation decay, intermediate between the fast decay of amorphous carbons and the slow decay of crystalline carbons, has been analysed by the method of Axelson *et al.*[8]. The T_1 values are of the order of 10 s and the corresponding methylene carbons are generally thought to be at the interface between crystalline and amorphous regions[3,5,12].

The ethylene copolymers of this earlier study make available a random distribution of sequence lengths for the production of ordered crystallites. In order to obtain information on the effect of sequence length and sequence distribution on phase structure, we have made ^{13}C n.m.r. and X-ray diffraction studies of a number of linear alkanes and linear low molecular weight polyethylenes. The n.m.r. relaxation data provide T_1 values for main chain carbons and for methyl and methylene carbons at the ends of the chains. X-ray diffraction data provide

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information on crystal structure and packing. The effect of chain length was examined for the n-alkanes $C_{21}H_{44}$, $C_{23}H_{48}$, $C_{25}H_{52}$, $C_{29}H_{60}$, $C_{50}H_{102}$ and $C_{60}H_{122}$ which are all orthorhombic at room temperature. Other hydrocarbons investigated include $C_{20}H_{42}$ and $C_{24}H_{50}$ (triclinic at 300 K) and $C_{28}H_{58}$ and $C_{30}H_{62}$ which are monoclinic. The effect of polydispersity was investigated using linear polyethylenes of low dispersity with molecular weights of ~740 and 2155. The results of these studies are then used to discuss the phase structures of the more complex copolymer systems.

EXPERIMENTAL

The n-alkanes $C_{20}H_{42}$, $C_{21}H_{44}$, $C_{23}H_{48}$, $C_{24}H_{50}$, $C_{25}H_{52}$, $C_{28}H_{58}$, $C_{29}H_{60}$, $C_{30}H_{62}$, $C_{36}H_{74}$ (Aldrich Chemical), $C_{50}H_{102}$ and $C_{60}H_{122}$ (Fluka Chemical) were used as received. The linear polyethylenes (Polymer Laboratories) were of low dispersity ($M_w/M_n = 1.15$) and their peak molecular weights were given as 740 (PE740) and 2155 (PE2155). Samples were normally crystallized from the melt.

^{13}C spin-lattice relaxation studies were made at 50.31 MHz with a Bruker CXP-200 spectrometer. The data were obtained using the cross-polarization method of Torchia[21]. The spinning speed was 1800 Hz and the contact time was 1 ms. The data for the main chain carbons in the alkanes normally followed a single exponential decay. The results for the polyethylenes were analysed by the method of Axelson *et al.*[8], since it was clear that the carbons were grouped in at least two main environments of widely differing T_1 values.

In variable temperature experiments, samples were left for 3–4 h to reach thermal equilibrium because of their poor heat conductivity. Quantitative spectra were obtained by a 90°–acq–10 s sequence and line fitting was performed by the GLINFIT program (Bruker, Canada).

The wide-angle X-ray diffraction patterns for the n-alkanes were registered by a CSS/STOE 2P/L two circle diffractometer using Cu Kα radiation[22]. Specimens were prepared by drawing the molten sample into a glass capillary for Debye-Scherrer patterns. The temperature was controlled with a resistance heater. Data were collected for 0.05° 2θ steps from 1.5° 2θ to as high as 70° 2θ when appropriate. For the polyethylenes, data were collected from 10° to 34° 2θ and the crystallinities estimated using a profile fit WAXS program[22].

D.s.c. data were obtained by means of Du Pont 990 and Mettler instruments. Samples were first melted and cooled at a rate of 10°C min^{-1}; the final heating rate was 20°C min^{-1}.

RESULTS AND DISCUSSION

The alkanes used were typically 99% pure and their melting points and phase transition temperatures were generally within 1°C of those given by Broadhurst[23]. The only exceptions were $C_{50}H_{102}$ and $C_{60}H_{122}$ which gave X-ray diffraction patterns of relatively poor quality at room temperature and melt halos at temperatures below their melting points suggesting the presence of homologues. X-ray diffraction studies[22] confirm that the samples are highly crystalline at room temperature and that the structures are as given in the literature[22,23].

The low molecular weight polyethylenes melt over relatively wide temperature ranges. At a heating rate of 20°C min^{-1}, the endotherm for PE740 begins below 325 K, reaches a maximum at 366 K and is complete at 380 K; that for PE2155 begins below 380 K, is a maximum at 400 K and is complete at 405 K. The maxima are at temperatures lower than the melting points of pure alkanes of comparable molecular weight. X-ray diffraction data show that the Bunn primitive orthorhombic subcell is present in these polyethylenes at all temperatures up to the melting point. The X-ray estimates of crystallinity at room temperature are 83% for PE740 and 86% for PE2155.

Low molecular weight alkanes: influence of crystalline structure

Tetracosane, $C_{24}H_{50}$, is typical of the low molecular weight alkanes with a triclinic structure at room temperature. Its ^{13}C n.m.r. spectrum is shown in *Figure 1*. The chemical shifts, referenced to adamantane at 29.5, 38.5 ppm, are 15.6 (CH_3), 25.6 (2-CH_2), 35.4 (3-CH_2) and 34.0 ppm (internal-CH_2). These compare with values of 16.0, 26.6, 36.4 and 34.9 ppm reported by VanderHart[24] for triclinic $C_{20}H_{42}$. The T_1 values for the end methyl and adjacent C2 are 2 and 37 s, respectively. The C3 resonance at 35.4 ppm is not well resolved but the estimated T_1 of 140 s approaches that of the internal methylenic carbons whose average value is 166 s.

Tricosane, $C_{23}H_{48}$, is typical of the low molecular weight alkanes with an orthorhombic structure at 300 K. Chemical shifts of 14.95 (CH_3), 24.9 (2-CH_2), 34.35 (3-CH_2) and 32.9 ppm (internal-CH_2) are similar to those observed by VanderHart[24]. Relaxation plots for these resonances are shown in *Figure 2*. All the decays are close to exponential in character. The slight curvature in the decay plot for the internal carbons C4 to C20 may be real but the distribution of T_1 values for these carbons is fairly narrow. The T_1 for the end methyls at 300 K is 1.4 s and for the adjacent C2 it is 16 s. The T_1 for C3 is ~24 s, i.e. close to the average value for the internal methylene carbons which is estimated to be 28 s.

The results of ^{13}C spin-lattice relaxation studies of a number of representative alkanes are given in *Table 1*. The T_1 values are for the interior methylene carbons which have a chemical shift of 32.9 ppm. At 300 K, the triclinic hydrocarbons $C_{20}H_{42}$ and $C_{24}H_{50}$ have T_1 values of the order of 160 s. This T_1 is much higher than that of the comparable orthorhombic alkane, $C_{23}H_{48}$, which has a T_1 at 300 K of 28 s. As Broadhurst has

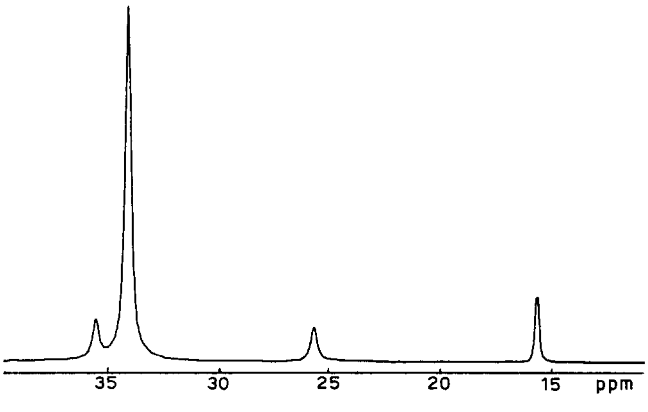

Figure 1 ^{13}C n.m.r. spectrum of tetracosane at 300 K

pointed out[23], the relative stabilities of these low molecular weight hydrocarbons are determined largely by end group packing. The even hydrocarbons, $C_{24}H_{50}$ and below, can assume a relatively tightly packed triclinic structure with molecular planes parallel to one another. The tight packing of the central methylenes accounts for the relatively high T_1 for the triclinic structure.

The monoclinic hydrocarbon $C_{28}H_{58}$ has a T_1 of 226 s at 300 K. This value is slightly higher than that of $C_{29}H_{60}$ which has an orthorhombic structure and for which the T_1 is 186 s. The mobility of the internal methylene groups is thus not significantly affected by a change from monoclinic to orthorhombic crystalline form. The Bunn orthorhombic subcell is present in both modifications and the influence of end groups decreases as the size of the alkane is increased.

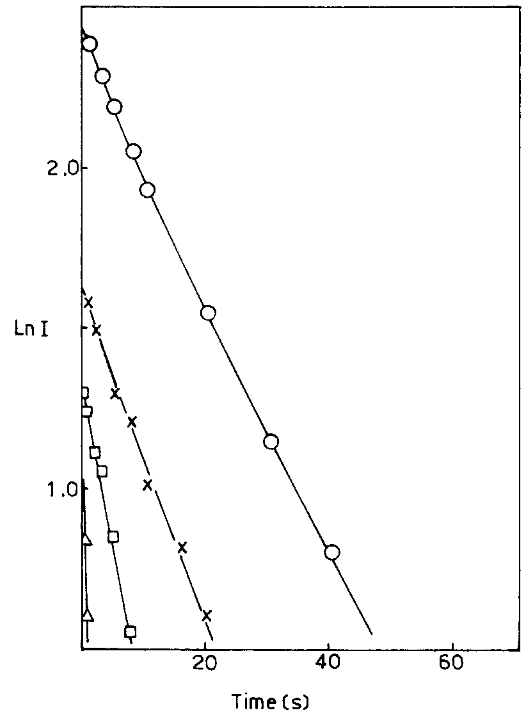

Figure 2 Relaxation plots for various carbons of tricosane at 300 K: (○) int-CH_2; (×) C_3; (□) C_2; (△) CH_3

Increase of temperature causes an expansion of a crystalline lattice and a steady decrease in T_1 when there is no phase change. With some alkanes there is a transition to a rotator phase, usually face centred orthorhombic[22], and a more abrupt change in T_1. $C_{23}H_{48}$, for example, undergoes a phase transition at 314 K and at 316 K the T_1 of the internal methylene carbons is 2.4 s while the value estimated for CH_3, C2 and C3 is 3.1 s. The high degree of rotational freedom of the molecules about their chain axes has long been recognized[23], and all carbons have approximately the same T_1 when $C_{23}H_{48}$ adopts the rotator form.

The transitions to the rotator phase for $C_{21}H_{44}$ and $C_{25}H_{52}$ take place at 305 and 320 K, respectively. At 308 K, T_1 for the central methylene carbons in $C_{21}H_{44}$ becomes 2.3 s; at 321 K, T_1 for the corresponding carbon atoms in $C_{25}H_{52}$ is 3.1 s. As with $C_{23}H_{48}$, all carbons along the chain have comparable values. The chain cross-sectional area increases significantly at the transition temperature[22], and this is accompanied by an increased mobility in the rotator phase.

Effect of molecular size and dispersity on T_1 *values for orthorhombic systems*

For orthorhombic structures, T_1 values show a strong dependence on the size of the hydrocarbon chain (*Table 2*). T_1 for the internal methylenes in $C_{21}H_{44}$ is 19 s and this rises to 186 s for $C_{29}H_{60}$ and to ~1600 s for $C_{50}H_{102}$ and $C_{60}H_{122}$. The effect of a three-fold increase in the length of the chain from $C_{21}H_{44}$ to $C_{60}H_{122}$ is thus almost a 100-fold increase in T_1 for the central carbons of the chain.

With each of the polydisperse linear polyethylenes, the change of M_w/M_n from 1.0 to 1.15 leads to two overlapping decays for the main chain methylene carbons (*Figure 3*). For PE740, which corresponds roughly to a C_{50} hydrocarbon, the larger T_1 is 510 s and for PE2155 (roughly C_{150}) it is 1500 s. The T_1 values for the more rapid decays are 53 and 90 s, respectively, at room temperature. Quantitative studies by the method of Axelson *et al.*[8] lead to estimates of 54% for the fraction

Table 1 T_1 values for internal methylene carbons of crystalline alkanes

Alkane	Structure	T_{trans} (K)	T_m (K)	T_{exp} (K)	T_1 (s)
$C_{20}H_{42}$	Triclinic	–	310	300	160
$C_{24}H_{50}$	Triclinic	321	324	300 315	166 113
$C_{28}H_{58}$	Monoclinic	331	334	300	226
$C_{30}H_{62}$	Monoclinic	332	338	300	292
$C_{36}H_{74}$	Monoclinic	345, 347	349	300	460
$C_{21}H_{44}$	Orthorhombic	305	314	300	19
$C_{23}H_{48}$	Orthorhombic	314	321	300 308	28 13
$C_{25}H_{52}$	Orthorhombic	320	327	300 314	76 14
$C_{29}H_{60}$	Orthorhombic	331	337	300	186
$C_{50}H_{102}$	Orthorhombic	–	367	300	1620
$C_{60}H_{122}$	Orthorhombic	(339)	372	300	1660
$C_{21}H_{44}$	FCO, Rotator	305	314	308	2.3
$C_{23}H_{48}$	FCO, Rotator	314	321	316	2.4
$C_{25}H_{52}$	FCO, Rotator	320	327	321	3.1

Table 2 T_1 values for individual carbons in orthorhombic hydrocarbons and polyethylenes

		T_1 (s)			
Hydrocarbon	T_{exp} (K)	int-CH_2	3-CH_2	2-CH_2	CH_3
$C_{21}H_{44}$	300	19	17	11	1.3
$C_{23}H_{48}$	300	28	24	16	1.4
$C_{25}H_{52}$	300	76	38	20	1.6
$C_{29}H_{60}$	300	186	–	–	1.9
$C_{50}H_{102}$	300	1620	–	–	–
$C_{60}H_{122}$	300	1660	–	–	–
PE740	300	510	–	4.8	1.9 (14.6 ppm)
	323	180	–	–	–
	343	79	–	–	–
PE2155	300	1500	–	7.1	1.7 (15.2 ppm) 3.0 (14.6 ppm)
	353	340	–	–	–
	373	96	–	–	–

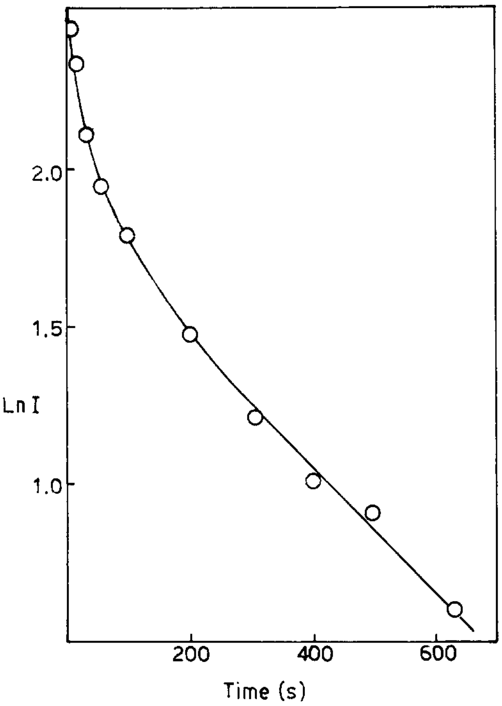

Figure 3 Relaxation plot for internal methylene carbons of PE740 at 300 K

of *trans*-methylenic carbons associated with the slow decay in PE740 at 300 K and 78% for the corresponding material in PE2155. The percentages for the carbons in the somewhat more mobile crystalline environment are 38 and 16%, respectively. The effect of polydispersity on carbon spin-lattice relaxation of the central methylene carbons is thus two-fold. First, it leads to two almost exponential decays rather than one as with the central methylene carbons of linear alkanes. Second, the larger T_1 is lower than that anticipated for an alkane of comparable chain length. Since this larger T_1 is assigned to methylene carbons in highly ordered environments comparable to those of the internal carbons of alkanes, the smaller T_1 must be associated with *trans*-methylene chains in regions which also contain end groups. X-ray diffraction data show that the total amount of orthorhombic material is >80% at room temperature. The second more mobile region is thus also orthorhombic and its lower T_1 is due to poorer packing of methylenes because of the proximity of end groups as defects.

An alternative approach is to obtain a quantitative n.m.r. spectrum of the polyethylene sample and to follow the decay of the *trans* material at 32.9 ppm separately from that of the amorphous material at 31.0 ppm (under conditions of reduced line broadening). The quantitative spectrum gives the total percentage of *trans* material in the sample and the T_1 decay analysis the fractions of *trans* material with high, intermediate and low T_1 values. The results for PE740 and PE2155 are given in *Table 3*. It is seen that a small amount of *trans* material, ~5%, with a very low T_1 is present in both linear polyethylenes. The T_1 of 0.6 s is only about twice that of methylene carbons in an amorphous environment, i.e. with a chemical shift of 31.0 ppm. In each case, the total amount of material with high and intermediate T_1s is close to the estimate of crystallinity obtained from X-ray diffraction studies. The *trans* methylene carbons with the low T_1 probably do not contribute to the X-ray crystallinity. They are presumably much less tightly packed than the methylenes in typical crystalline environments.

Environments of the end groups in polyethylenes

In the previous section it was concluded that the methyl end groups cause a slight decrease in the average T_1 of the methylene carbons which are at some distance from them and a somewhat larger decrease in the T_1 of the ordered *trans* methylenes which are closer to them. The carbons with intermediate T_1 constitute ~45% of the crystalline material in PE740 and ~20% in PE2155. When the temperature is raised to 20°C below the melting point, the total crystallinity drops and the T_1 values associated with the various crystalline regions become smaller. The fraction of crystalline material with the intermediate T_1 is, however, almost temperature independent. This suggests that restricted methyl ends are mainly randomly distributed in crystalline regions rather than being concentrated in more mobile regions which melt well below the melting point.

The methyl groups in these polyethylene samples are probably at the ends of extended chains. Chain folding has been observed with $C_{150}H_{302}$ when crystallized from solution but it is less likely in polymers crystallized from the melt[25]. Indeed, Leung *et al.*[26] observed little or no chain folding with a polyethylene of $\bar{M}_n = 2900$, $\bar{M}_w/\bar{M}_n = 1.07$, even after crystallization from dilute solution over a period of 1 week. Again, Stack *et al.*[27,28] found no evidence for chain folding in a sample of molecular weight close to 2000 but for one with $\bar{M}_n = 3800$ crystallites having a thickness smaller than the extended length could be formed under some crystallization conditions. Thus chain folding may well be a factor in polyethylenes of molecular weight of >3000 but not for the samples PE740 and PE2155 used in this study.

More direct evidence is provided by a study of the

Table 3 Crystallinities of linear polyethylenes determined by X-ray diffraction and quantitative n.m.r. analysis

		Crystalline components at 32.9 ppm (%)		
Polyethylene	X-ray (%)	High T_1	Intermediate T_1	Low T_1
PE740	82	39	44	4
PE2155	86	73	16	5

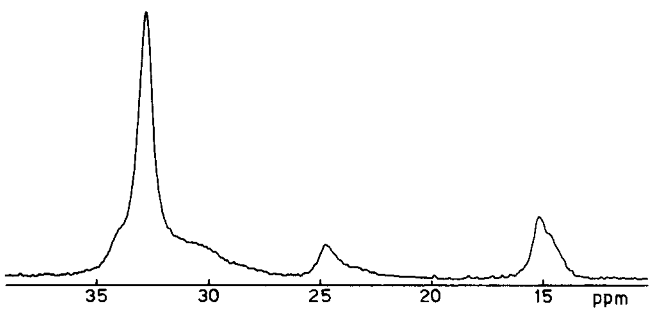

Figure 4 ^{13}C n.m.r. spectrum of linear polyethylene PE2155 at 300 K

methyl resonance in the PE2155 sample. The spectrum (*Figure 4*) shows two overlapping resonances centred on 14.6 and 15.2 ppm. The peak at 14.6 ppm has been assigned by Perez and VanderHart[29] to methyls in a non-crystalline environment and the peak at 15.2 ppm to methyls in a crystalline environment. As expected, the 15.2 ppm resonance polarizes more efficiently than the 14.6 ppm resonance. Values of T_1 for the crystalline and non-crystalline resonances are 1.7 and 3.0 s, respectively. The peak at 15.2 ppm exhibits only a single exponential decay curve, indicating that there exists only one crystalline environment for methyl ends. Analysis of a quantitative (90°–10 s) spectrum by means of the GLINFIT program gave an estimate of 60% for methyl ends in the crystalline region. VanderHart[29] observed chemical shifts of 15.3 and 14.9 ppm for methyls in a linear polyethylene of molecular weight 7400 and estimated that 75% of the methyls were in a crystalline environment at room temperature. In this case chain folding was expected to occur but it is not clear whether it influenced the fraction of methyls in a crystalline environment. Möller *et al.*[18] gave an estimate of 66% for this fraction when working with a polyethylene of molecular weight 1600. In contrast to the behaviour of these higher molecular weight polyethylenes, PE740 showed a resonance at 14.6 ppm and only slight evidence for a second resonance to lower field. Either the chemical shift difference for the methyls in the two types of environment has now become too small to be readily observed or the fraction of methyls in a well-packed crystalline environment has dropped to a low value. The average T_1 for methylene carbons in the region of methyl end groups decreases to 53 s for PE740 and this may allow significantly greater mobility for the methyl groups that are surrounded by these *trans*-methylene chains. With PE2155, increase of temperature causes a rapid drop in the percentage of methyl carbons with the 15.2 ppm shift; at 373 K, ~20°C below the melting point, it is only 6%. The *a* dimension of the unit cell increases from 7.42 Å at 300 K to 7.60 Å at 373 K while the *b* dimension is almost unaffected. The intensity of the 15.3 ppm resonance thus appears to be very dependent on the tightness of packing in the vicinity of the methyl group. A similar conclusion was reached by Möller *et al.*[18] who pointed out that considerable conformational disordering of terminal chain segments occurs in polydisperse low molecular weight polyethylenes as the melting point is approached. With their sample of molecular weight 1600, the crystallinity of the internal methylenes dropped from 86% at 300 K to 54% at 360 K but the methyl ends and adjacent methylenes gave only the melt signal.

Relationship between the crystalline T_1 *and the* a *dimension of the unit cell*

Increase in temperature causes a considerable reduction in the T_1 value of backbone carbons. For example PE740 has T_1 values for its most tightly packed methylene carbons of 510 s at 300 K, 180 s at 323 K and 79 s at 343 K. The dependence of $1/T_1$ for the slow crystalline decays of PE740 and PE2155 on the *a* dimension of the unit cell determined by X-ray diffraction is shown in *Figure 5*. Data are also plotted for the crystalline T_1 values of branched polyethylenes obtained at room temperature[19]. The presence of ethyl, hexyl and hexadecyl branches leads to a reduction in T_1 and an increase in *a*. Thus for linear polyethylenes at various temperatures where the defects are end groups and for ethylene copolymers where the defects are branches, there is a fairly good correlation between the T_1 for the most tightly packed carbons and the *a* dimension of the unit cell.

Alkanes which crystallize with orthorhombic symmetry also follow the $1/T_1$ *versus* *a* relationship if they are of sufficiently high molecular weight. For example, $C_{50}H_{102}$ has a T_1 of 1600 s and an *a* value of 7.425 Å at room temperature and the resulting point is close to that plotted for PE2155. However, as the molecular weight of the linear alkane decreases, the T_1 for the central methylenes drops rapidly while *a* increases at a relatively low rate. $C_{23}H_{48}$, for example, has a T_1 of 28 s (corresponding to $10^3/T_1 = 35$) while the *a* value has increased only to 7.455 Å. The mobility of the central carbons of these low molecular weight alkanes is highly dependent on chain length; tightness of packing of the methylene chains is only one of the factors influencing the magnitude of T_1. Davis *et al.*[30] found a similar difference in the behaviour of melt crystallized polyethylene and n-paraffins when they examined the dependence of cell dimensions on lamella thickness. They suggested that it was caused by differences in the lamella surfaces.

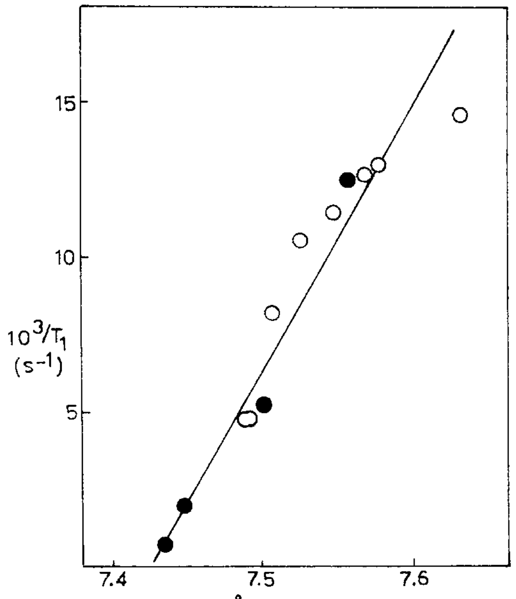

Figure 5 Plot of $10^3/T_1$ *versus* the *a* dimension of the orthorhombic unit cell for various polyethylenes: (●) linear polyethylenes; (○) branched polyethylenes

Amorphous and interfacial regions in linear and branched polyethylenes

Pure solid alkanes with orthorhombic structures are crystalline at room temperature and their main chain carbons (at 32.9 ppm) follow a single exponential decay. Methyl carbons, C2 and to a lesser extent C3 have different spin-relaxation times but they can be distinguished from the central carbons through their different chemical shifts.

When the dispersity is increased, the n.m.r. spectrum shows the presence of a small amount of material with a chemical shift centred at 31.0 ppm. It is generally agreed that this arises from conformationally disordered methylene carbons and it can be simply described as amorphous. The spectrum of PE2155 (*Figure 4*) shows only a shoulder at 31 ppm and the fraction of amorphous material at 300 K is estimated to be ~3%. The decay of the main chain carbons at 32.9 ppm is now approximated by two exponentials. One of these decays proceeds at a rate only slightly lower than that of an alkane and is associated with *trans* methylene chains which are largely undisturbed by end group defects. The other has a significantly lower T_1 and this is ascribed to the looser packing of the *trans* methylene chains in the region of the defects. X-ray diffraction patterns of PE2155 and PE740 contain a halo in addition to the two reflections associated with the (1 1 0) and (2 0 0) planes of orthorhombic material. Quantitative analysis indicates that 14% or so of PE2155 contributes to the halo. Some of this material may be truly liquid-like but the position of the maximum in the halo indicates that the remainder is packed more efficiently than in the liquid.

Branching in an ethylene copolymer has a more profound effect on the phase structure than the end groups of the linear polyethylenes PE740 and PE2155[29,31,32]. An ethylene–butene copolymer containing 2 mol% comonomer (10 branches per thousand carbons) gives a larger peak at 31 ppm in keeping with estimates that >50% of the polymer is amorphous[19]. The resonance at 32.9 ppm is made up of three components. The first consists of crystalline material with a T_1 of ~200 s, the second, usually described as interfacial, has a T_1 of ~10 s and the third has a T_1 of 0.6 s. The total amount of crystalline and 'interfacial' material estimated by n.m.r. is somewhat greater than the orthorhombic content determined by X-ray diffraction. The crystalline material of high T_1 is presumably all observed by the X-ray method together with a large part of the material of intermediate T_1. The 'interfacial' phase thus has the following characteristics: it is largely orthorhombic with unit cell dimensions close to those of the main crystalline phase; it is all-*trans* and it has an average T_1 of only 10 s or so; it may include some all-*trans* material which is not part of the orthorhombic phase but while packed more efficiently than the liquid contributes to the amorphous halo in the X-ray diffraction pattern. Such a phase may be truly interfacial connecting the main crystalline and amorphous regions. If so, it might be expected to give a wider range of T_1 values than is observed for a typical copolymer. The 'interfacial' phase might also include the very thin crystallites observed by Voigt-Martin *et al.*[20] which would be expected to have a low T_1 value. A third possibility is the ordered *trans* material which is in the vicinity of a branch when it is incorporated in a crystalline region. Such branches are not likely to be evenly distributed through the crystalline phase but to be concentrated in small crystallites or near the surfaces of larger crystallites. In the present work it was shown that incorporation of a minor defect, a methyl end group, leads to two exponential decays for the crystalline fraction of a linear polyethylene. An ethyl branch causes far more disruption to the formation of crystallites and it is perhaps not surprising that two exponential decays are observed for the crystalline fraction of a copolymer with significantly lower values of T_1. The extent to which the ordered material with low T_1 is associated with larger crystallites formed early in the cooling process and with the small thin crystallites formed at a later stage is still unresolved.

The resonance at 32.9 ppm undergoes a fast initial decay with a T_1 of only 0.6 s. The small amount of *trans* material which gives rise to this section of the decay has a mobility comparable to that of methylenes in the liquid-like amorphous phase. Presumably it is a link between amorphous and crystalline polymer with the latter having the intermediate T_1 associated with true interfacial material or small crystallites. In X-ray diffraction analysis, this mobile *trans* methylene link would contribute to the amorphous halo.

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