53. *Nuclear Magnetic Resonance in Polymethylene and Polyethylene.*

By M. J. Herring and J. A. S. Smith.

Nuclear magnetic resonance spectra have been recorded between 90° and 400° K for two samples of polymethylene of differing crystallinity and a sample of a linear polyethylene crystallised from trichloroethylene. It is shown that the α-, β-, and γ-transitions previously observed in mechanical- and dielectric-loss experiments can also be detected in the nuclear resonance spectra of these polymers, and probably of most polyethylenes, to a degree which depends on the linearity of the polymer and its previous thermal treatment. Measurements of line shape and spin-lattice relaxation time can be explained in these terms, although there is some evidence that two other transitions may be occurring. The transitions are associated with different regions of the polymer and it is tentatively suggested that the principal distinction on a molecular scale between the low-temperature transitions observed in polyethylene lies in a difference in the number of CH_2 groups in the disordered lengths of the chain.

In a previous article, one of us [1] has reviewed the work recently published by several authors on proton magnetic resonance in polyethylene. In this paper, we present fuller details of our nuclear resonance work and a more detailed discussion of the information that may be obtained from studies of line width and line shape.

Experimental

The apparatus used has been described previously,[2] except for the coil assembly and temperature-control devices which were specially developed for this work.

The coil consisted of 11 turns of 22 s.w.g. copper wire and was about ½″ long. The turns were fixed together by winding the wire sleeved with polytetrafluoroethylene round a layer of polytetrafluoroethylene tape which covered a glass tube of the same diameter as the sample, and heating the assembly in an oven at 360° c for ½ hr. The polymer fused slightly, and the coils when cooled were rigidly held together and could be slipped off the glass. The samples were cylinders, 3/8″ in diameter and 5/8″ long, which fitted closely into the coil. The coil holder and Dewar container are illustrated in Fig. 1. The coil was connected to the bridge by two German-silver tubes and was shielded by a cylindrical copper sleeve made from sheet 0·001″ thick which slipped over the outside of the Dewar delivery tube (unsilvered in this region). The whole assembly, including the shield and leads, had a Q-factor of 85 at 16 megacycles per second.

Temperatures between 90° and 290° K were obtained in a stream of nitrogen from the boiling liquid, and an electrical heater was placed in the Dewar delivery tube to provide additional control of the temperature. Between 290° and 400° K the coil was placed in a glass tube lagged with asbestos through which warmed and filtered air was passed. Sample temperatures were measured by two thermocouples, placed at either end of the sample; they were calibrated at the sublimation point of carbon dioxide and the boiling point of water. During a run it was necessary to disconnect them in order to avoid excessive pick-up in the coil.

In both types of apparatus, the sample temperature became constant after 30—40 min., although in general there was a difference in temperature between the ends of the sample. In the high-temperature apparatus, the gradient increased from 0° to 5° between 290° and 400° K, but the drift in mean temperature was small. In the low-temperature apparatus, the gradient was between 1° and 5° and tended to increase as the sample approached room temperature. Unfortunately, the mean temperature tended to drift slightly, owing possibly to the changing level of liquid nitrogen, and this would upset the balance of the bridge; with care, the drift could be reduced to less than 2° in ½ hr. and the time taken to record one spectrum was about 10 min. With a second type of Dewar vessel in which the delivery tube emerged from the

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[1] Smith, *Chem. Soc. Special Publ.*, No. 12, 1958, p. 199.
[2] Smith, *Discuss. Faraday Soc.*, 1956, **22**, 79.

base rather than the side, temperatures as low as 85° K could be reached, but the samples were less accessible.

Spectra were recorded with modulation amplitudes of about 0·7 gauss, so that the modulation correction to the second moment [3] is 0·03 gauss^2 and can be neglected. The field homogeneity over the sample was about 0·3 gauss, but in practice, because of the slow recorder response and the high time constants in the recorder channel, line widths less than 1 gauss could not be measured. The standard deviation of the line-width measurements is about 0·8 gauss, but this figure excludes systematic errors due to non-linear sweep rates and distortion by the time constant circuits. The standard deviation of the second-moment measurements depends to some extent on the line shape. The probable reason for this dependence is that at high temperatures the spectra have an intense central peak and the broad wings become more difficult to record accurately; the standard deviation is then 1·3 gauss ^{2}. At lower temperatures, this figure drops to 0·8 gauss ^{2}. All the spectra were recorded at rf levels of 100 and 200 mv to the bridge; using the equations quoted by Anderson,[4] we estimate that these figures correspond to rf fields of 2 and 4 milligauss.

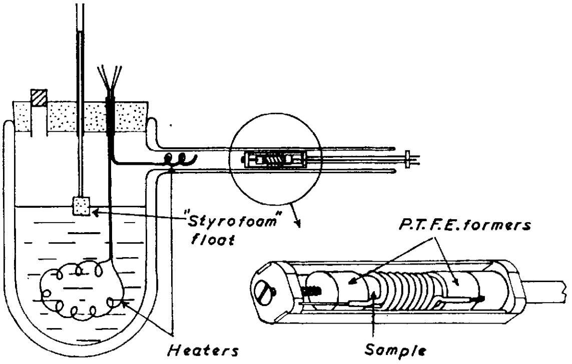


FIG. 1. *Coil assembly and Dewar vessel* (PTFE = polytetrafluoroethylene).

The samples of polymethylene (made by polymerisation of diazomethane) differed only in their heat treatment before the measurements. Sample A (PM-A) was made by gentle compression of the powder and had *d* 0·965. Sample B (PM-B) was made from the same material but had been moulded and then quenched; it had *d* 0·925. The weight average of the molecular weight was estimated to be 2·5 × 10^5, and the m. p.s lay between 411° and 413° K.

RESULTS

The temperature variation of the line width $\Delta H_{\text{m.sl.}}$ (the separation in gauss of the maxima on the derivative curve) of the two polymethylene samples is shown in Figs. 2 and 3. In the regions in which the derivative curve can be resolved into two components [1] two values of the line width at any one temperature are given; the larger value is ascribed to the so-called broad components, and the smaller to the narrow components, although neither term refers specifically to any particular region of the polymer.

Changes in the absorption line first appear around 140° K. For example, the line width of PM-B has a mean value of 15·6 gauss between 90° and 110° and 14·4 gauss between 140° and 170°, and small changes in this temperature range have been observed by other authors, *e.g.*, in PE-C[5] and an unspecified polyethylene.[6] The line shape of both polymethylene samples also undergoes a small but definite change early in the temperature range. Fig. 4 shows two derivative curves of proton resonance in PM-B taken at different temperatures. The broken line, recorded at 94°, shows the characteristic inflexion at the centre noted by previous workers,[7] and is typical of a two-spin system with a high intermolecular broadening term. When the temperature is raised to 158° this inflexion disappears and the peak curvature of the absorption line increases by about 60%; unfortunately the amount of material producing this change is

[3] Andrew, *Phys. Rev.*, 1953, **91**, 425.
[4] Anderson, *ibid.*, 1949, **76**, 1460.
[5] Varian Associates, Technical Information Bulletin, Vol. II, No. 2, 1958.
[6] Nishioka, Komatsu, and Kakiuchi, *J. Phys. Soc. Japan*, 1957, **12**, 283.
[7] Rempel, Weaver, Sands, and Miller, *J. Appl. Phys.*, 1957, **28**, 1082.

small, so that little quantitative information concerning its width and shape can be obtained by subtraction of the two curves. If we superpose two absorption curves recorded for PM-A at 94° and 194° so that they coincide as nearly as possible at displacements of more than 6 gauss from the centre, subtraction of the two gives a narrow component whose area ratio is about 10%.

For other polyethylenes of both the high-pressure and the " Marlex-50 " variety, several authors [5,8,9] have shown that a narrow component is first resolved with a width of about 5 gauss between 200° and 210°, a value which is retained up to about 240°. Not all samples show a 5 gauss component, *e.g.*, DYNK [10] shows no narrow component until 240° is reached, but this may be due to its small concentration or possibly to overlap effects which produce flat-topped derivative curves whose true widths are difficult to estimate.[11] In a cold-drawn polyethylene [9] the 5 gauss component is visible right up to 350°, although by then its width has dropped to about 3 gauss; in fact, between 310° and 350° three components of differing widths are recorded. Spin-echo studies at room temperature of Wilson and Pake's sample [12] reveal two T_2 values, of 10 and 90 μsec. Assuming a Lorentzian line shape, we derive corresponding $\Delta H_{\text{m.sl.}}$ values of 4·3 and 0·48 gauss. The former is too small to be identified with the broad component (even a Gaussian line shape gives 9·4 gauss) and is therefore attributed to the 5 gauss component.

FIG. 2. *Temperature variation of the line width of* PM-A.

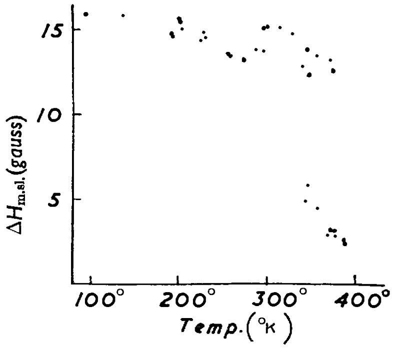


FIG. 3. *Temperature variation of the line width of* PM-B.

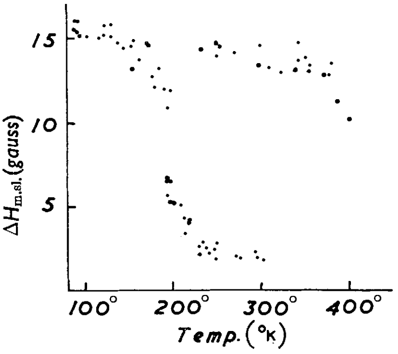


FIG. 4. *Derivative curves for* PM-B.
—— 158° K; - - - 94° K.

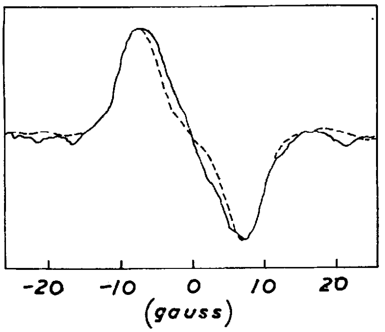
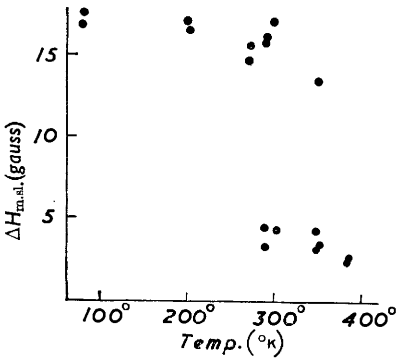


FIG. 5. *Temperature variation of the line width of a sample of " Marlex-*50 *" crystallised from trichloroethylene.*



One distinction, therefore, between PM-B and the majority of other polyethylenes is that for the former the line width appears to drop fairly continuously from 15 to 2·5 gauss between 150°

[8] Fuschillo and Sauer, *J. Appl. Phys.*, 1957, **28**, 1073.

[9] Slichter, " Growth and Perfection of Crystals " (ed. Doremus, Roberts, and Turnbull), Wiley, 1958, p. 558.

[10] McCall and Slichter, *J. Polymer Sci.*, 1957, **26**, 1.

[11] McCall and Slichter, personal communication.

[12] Norberg and co-workers, quoted by Wilson and Pake (ref. 14).

and 230°; the curve shows only a small inflexion near 5 gauss between 200° and 210°. but since the temperature gradient across the sample was about 4° its significance is difficult to assess. However, one point in connection with Fig. 3 is worth noting. This diagram represents nearly 150 independent measurements of the line width over the whole temperature range and it is very noticeable when the data are tabulated that it is practically impossible to measure the line width of the broad component between 200° and 230° (16 observations), mainly because no corresponding maximum in the derivative curve can be resolved. In fact, between 170° and 230° the derivative curve undergoes several minor changes in shape. Above 170° the line begins to narrow; at 192° a shoulder appears at about 11 gauss width which persists in all six measurements made between 193° and 195°; above 196° the shoulder disappears and does not reappear until 230°, as though another transition were occurring. At 292°, a T_2 of 60 μsec. ($\Delta H_{\text{m.sl.}}$ = 0·72 gauss) is found.[13]

The next group of line-width and line-shape changes occurs above 240° and continues to at least 320° K. Some of the changes observed are summarised below. For PM-A the line width drops by about 2 gauss to a minimum at about 270° and then rises again to 15·2 gauss, although no narrow line appears. A broad depression in the line width of one sample of " Marlex-50 " also covers this temperature region, although the change is too small to be considered highly significant.[11] With other polymers [6,7,8,10,14] a rapid temperature variation of the line width of the narrow component is observed between 260° and 300°, the variations being greatest in branched polyethylenes. The temperature at which the transition begins varies slightly from sample to sample, but the principal difference is in the temperature variation of the line width which depends on the degree of branching. With linear polymers the variation is fairly uniform, whereas with highly branched samples there is a sudden drop in the line width near 270° as a consequence of which at all higher temperatures the line widths of branched polyethylenes are much narrower than those of linear samples. Above 320° there is some evidence that the curve of $\Delta H_{\text{m.sl.}}$ against temperature flattens again, but at values which differ according to the type of polymer, *e.g.*, 0·2 gauss for DYNK [10] and 0·02 gauss for DYNH.[15] The results for the linear polyethylenes can be compared with the line-width data in Fig. 5 which refer to a sample of " Marlex-50 " that has been crystallised from trichloroethylene [16,17] at 341° K. The polymer was studied most closely between 273° and 400°. A minimum appears in the broad component curve near 270°, and the narrow component is first resolved with a width of 4 gauss which diminishes by very little right up to the m. p. After the sample had been melted and cooled to room temperature, it gave a typical " Marlex-50 " spectrum [15] with a much more intense narrow component of width 3·3 gauss.

FIG. 6. *Temperature variation of the second moment of* PM-A.

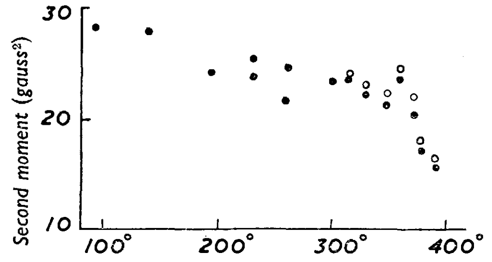
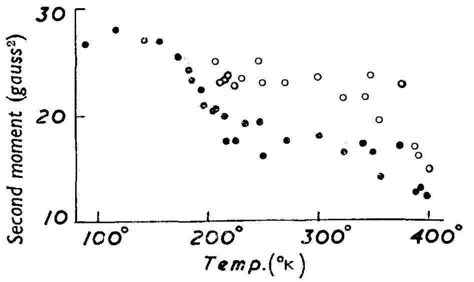


FIG. 7. *Temperature variation of the second moment of* PM-B.



● *Total curve*; ○ *broad component only.*

For PM-A the narrow component first appears in the spectrum near 340° and diminishes continuously in width as the temperature is raised. No exact parallel to this transition has yet

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[13] Unpublished work by Dr. K. Luszczynski, communicated by Dr. J. G. Powles.
[14] Wilson and Pake, *J. Chem. Phys.*, 1957, **27**, 115.
[14a] Wilson and Pake, *J. Polymer Sci.*, 1953, **10**, 503.
[15] Collins, *J. Polymer Sci.*, 1958, **27**, 67.
[16] Fischer, *Z. Naturforsch.*, 1957, **12**, a, 753.
[17] Keller and O'Connor, *Discuss. Faraday Soc.*, 1958, **25**, 114.

been observed for other polyethylenes. Samples of " Marlex-50 " above 350° [5] and DYNH above 360 [15] show a further diminution in the line width, but this transition occurs at higher temperatures than for PM-A and with much smaller line widths.

Finally, in all those samples of polyethylene in which a broad and a narrow component are observed, the line width of the former undergoes a rapid transition above 360°. For PM-B, the line width of the broad component begins to drop sharply above 380°; for PM-A, no broad component can be resolved above this temperature, but the total second moment, which is governed largely by the broad component, begins to diminish above 370°.

Figs. 6 and 7 show the temperature variation of the second moment of the two polymethylenes; the filled circles refer to the total curve and the open circles to the broad component (according to Wilson and Pake's method [14a] of decomposition). Above 360°, for both samples, the second moment drops continuously, although measurements on the polymethylenes were not carried sufficiently far to show whether the drop is continuous with the m. p. or whether a constant value is reached before this as in some long-chain molecules.[18,19] The spin-echo and line-width data [15,20] for two branched polyethylenes show practically no discontinuity at the m. p. in the short T_2 component.

DISCUSSION

Some features of the experimental results have been discussed by other authors. In particular, Wilson and Pake [14] have suggested that the narrow component is produced as a result of a transition in only part of the polymer, identified as the amorphous regions (here the word transition refers to a change in the nuclear resonance spectrum, generally detected by a diminution in the line width). The minima observed in the line width of the broad component may also be explained as follows.[1]

If at low temperatures the two components have approximately the same line width, as we pass through the transition the contraction in width of part of the signal should cause a small diminution in the apparent width of the broad component. This is because the nuclear resonance spectrum is always a superposition of these two curves and therefore the value of the field at which we observe the maximum of the broad component is affected by the intensity of the narrow component in this region. As one component narrows, the maximum moves in; as the intensity of the narrow component at the maximum of the broad component falls to zero, the line width of the latter increases to its original value. There is no evidence that the line shape of the broad component changes markedly with temperature; near 140° K the value of $\Delta H_{\frac{1}{2}}$ (the half-width in gauss of the absorption curve) for the total spectrum of PM-A is 15·8, and at 315° and 330° the resolved broad component has a half-width of 14·8 gauss. This change is too small to account for the drop, and it does not explain why the line width subsequently rises to almost its original value. If this explanation is correct, then any minimum in the broad component must denote a nuclear resonance transition in only part of the polymer. Below the transition the signal from this region will either be masked by that from the broad component or missing altogether if the spin-lattice relaxation time becomes too high.

The striking feature of the minimum in $\Delta H_{\text{m.sl.}}$ of PM-A at 270° K is that it almost coincides in temperature with the transition in branched polyethylenes which first produces the very narrow component,[8] suggesting that this transition is common to both types of polymer and does not produce a narrow component in the former because the concentration of the regions responsible for the narrow line is lower and their line width above the transition broader. The transitions observed in polyethylenes cover a large range of temperature; they can be detected near 135° K in PM-B, and PM-A shows a transition at 330°. It is possible that such relaxation phenomena are only explicable in terms of a range of correlation times, as has been proposed recently for polyisobutene.[21] An alternative explanation which is possibly more appropriate to crystalline polymers is that the

[18] Andrew, *J. Chem. Phys.*, 1950, **18**, 607.
[19] Komatsu, *J. Phys. Soc. Japan*, 1956, **11**, 755.
[20] McCall, Douglass, and Anderson, *J. Chem. Phys.*, 1959, **30**, 1272.
[21] Luszczynski, *Arch. Sci.* (*Geneva*), in the press.

changes observed in the line width really consist of a number of separate transitions each characteristic of a different region of the polymer and defined by an approximate temperature. In principle, all polyethylenes should show some, if not all, of these transitions, but the intensity and possibly the fractional reduction of the line width may vary from one polymer to another so that the narrow component may first appear as a separate peak at quite different temperatures. A minimum of four of these transitions can explain much of the published work on polyethylene; they are listed below and named after similar transitions observed in mechanical-loss experiments. The temperature range indicates the region in which the transition is first detected. Multiple T_2 values have also been observed in molten polyethylene.[20]

Transition	γ	β	PM-A	α
Temp. range (K)	140—170°	240—270°	330°	360—370°

The γ-transition produces the 5 gauss component above 200° K; it is identified with the γ-process observed in the mechanical loss experiments,[22] which occurs at a slightly lower temperature because of the difference in characteristic frequency. The fact that the 5 gauss line is detected by T_2 measurements at room temperature (where the apparent width of the line measured by steady-state experiments is 0·4 gauss) shows that the transition is unaffected by subsequent transitions (at least up to room temperature), and is therefore an independent process; its presence may also explain the large " tails " that the narrow component sometimes appears to have.[7] The differences observed in PM-B and cold-drawn polyethylene might be explained if there were another transition between 210° and 230° which reduced the line width of the narrow component to between 2 and 3 gauss and was absent in the other samples. Unfortunately the evidence for such a transition in other polymers is inconclusive, and if it occurs it will follow so closely on the γ-transition that we have little evidence either that it involves new regions of the polymer or is really part of the γ-transition.

The nuclear resonance β-transition is named after the β-process in the mechanical loss since they both appear in the temperature range 240—300° K. However, both linear and branched polyethylenes appear to show a β-transition whereas linear polyethylenes show a β-process only in dielectric-loss [19] and not in mechanical-loss experiments. In nuclear resonance, it usually gives rise to much smaller line widths than the γ-transition, so that once it has commenced the γ-line may be completely masked. An exception is the previously mentioned sample of a cold-drawn polyethylene, in which the β- is resolved from the α- and the γ-spectrum between 310° and 350° K. According to this interpretation, the narrowest line arises from the β- and the intermediate line from the γ-transition. Similarly the T_2 component of 90 μsec. ($\Delta H_{\text{m.sl.}} = 0{\cdot}48$ gauss) found in the spin-echo studies of a branched polyethylene [12] is also attributed to the β-transition. In linear polymers, we can use the Gutowsky–Pake equation in the form:

$$\nu_c = 767\,.\,\Delta H/\tan\left\{\frac{\pi}{2}\left(\frac{\Delta H^2 - B^2}{C^2}\right)\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

with $B = 0{\cdot}22$ and $C = 16$ gauss (the line widths at temperatures above and below the transition) and $\nu_c = 1/2\pi\tau_c$ the correlation frequency appropriate to a line-width measurement of ΔH; thus we evaluate ν_c at different temperatures. If the results are fitted to an equation of the form:

$$\nu_c = \nu_0 \exp - (E^*/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

we find rather variable values of ν_0 and E^*, *e.g.*, for PE-A [5] values of 10^{15} and 13 kcal./mole, for one sample of " Marlex-50 " [5] values of 10^{12} and 9 kcal./mole, and for another [10] values of 10^{10} and 7 kcal./mole. It is difficult to assess the accuracy of these figures, particularly as these transitions should really be discussed in terms of a distribution of correlation

[22] Willbourn, *Trans. Faraday Soc.*, 1958, **54**, 717.

times rather than a single value. However, the orders of magnitude are probably correct, since it has been shown recently [20] that for at least one simple form of distribution function T_2 is largely unaffected by the width of the distribution although the minimum in T_1 is broadened and raised. This may partly account for the appearance of the β-process in linear polymers in nuclear resonance but not in mechanical-loss experiments, which may be more sensitive to broad distributions. If we apply equations (1) and (2) to the line-width data of highly branched polymers, the graphs of log ν_c against T^{-1} in two samples [7,10] are found to have similar shapes, namely, a steep initial portion flattening out at lower values of T^{-1} as in Fig. 8. Again we find very variable values of ν_c and E^*, as in similar measurements of the β-process in the mechanical loss (which approach the line-width frequency near 270° K).

The nuclear resonance results suggest that the branch points are responsible for the sudden change in line width, and one point of interest is therefore whether the β-transition observed in branched polymers is related to the transition occurring at the same temperature in linear polymers. If both types show this transition with different intensities, the sharper line-width change in branched polymers could be attributed to a new transition added to that observed in linear polymers and giving rise to two regions in the log ν_c–T^{-1} curve. In the mechanical loss, the β-process occurs at nearly the same temperature whatever the length of the side chain and so has been associated with the branch points themselves.[22] A possible interpretation of the nuclear resonance results is therefore that both linear and branched polyethylenes contain regions responsible for the β-transition which in the latter also contain the branch points. It is possible that at least some of the CH_2 groups in the chain branches may have undergone a nuclear resonance transition at a lower temperature; however, as soon as the regions which contain the branch points approach a new transition, the adjacent CH_2 groups in the chain branches will begin to move at the same frequency about new axes which have a much wider spatial distribution. The increased flexibility of these groups which can now participate in the thermal motions of the two chains may produce the very narrow line characteristic of branched polymers.

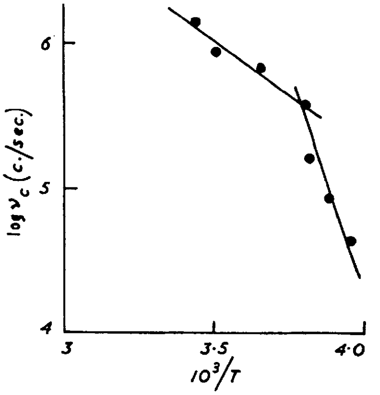

FIG. 8. *Correlation frequency* v. *temperature for* PE-C^5 *near* 270° K (*derived by assuming* B = 0 and C = 16 *gauss*).

If we classify these transitions according to the temperature at which they first appear, the transition in crystallised " Marlex-50 " can be regarded as a β-transition. However, the fact that the line width drops little below 4 gauss right up to the melting point shows that the motions available to the CH_2 groups are more spatially restricted than in normal " Marlex-50 " samples, as would be expected from the structure suggested by Keller and O'Connor.[17]

The PM-A transition also appears to be unique, although there is some evidence [22] for two mechanical-loss transitions between 250° and 340° and the second of these may be a PM-A process. Also in branched polyethylenes a maximum in the damping factor for sound waves is observed[23] near 320° at frequencies of about 5 kc./sec., although such a maximum does not occur in an unbranched, highly crystalline, Ziegler-type polymer. Without more information it is difficult to classify this transition further, although it seems to be a major process for PM-A. The temperature variation of its line width above 340° in conjunction with equation 1 gives us:

$$\nu_c = 7 \times 10^7 \exp(-5500/\boldsymbol{R}T) \quad . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

The magnitudes of ν_0 and E^* suggest that the transition is caused by chain-twisting rather than chain-rotation; E^* is close to the value of 4·1 kcal./mole attributed to the energy barrier hindering reorientation of the CH_2 groups of a paraffin chain.[24]

The α-transition has been discussed by several authors,[1,8] who attribute it to the crystalline regions of the polymer. It is identified with the so-called α-process observed in the dielectric loss of polyethylene and is associated[25] with ν_0 and E^* values of about 10^{20} and 25 kcal./mole. If the same values govern the temperature variation of ν_c, then above 360° T_1 is less than one minute if it is determined by this process and the broad component can be identified with the crystalline regions of the polymer.

More indirect evidence for the existence of these multiple transitions comes from the T_1 measurements on a branched polymer.[14] According to the Bloembergen, Purcell, and Pound theory[26] for a single correlation time, the minimum in T_1 should occur when $\nu_c = \sqrt{2}\,\nu_L$, where ν_L is the Larmor precession frequency; at temperatures above this minimum, T_1 should be of the same order as T_2. However, for polyethylene at the minimum of T_1 the ratio $T_1 : T_2$ (the latter derived from $\Delta H_{\text{m.sl.}}$ for a Lorentzian line shape) is approximately 340.[1] This discrepancy seems too large to be accounted for by a distribution of correlation times; for example, with the intensity distribution used by McCall, Douglass, and Anderson[20] and a range of correlation times large enough to remove the minimum in T_1, the ratio $T_1 : T_2$ at the value of τ_c at which the curve for T_1 rises to meet the T_2 curve is about 7. Since a minimum is observed and a ratio of 340, this type of explanation seems unlikely. The discrepancy can be accounted for if T_1 and T_2 are governed by entirely different transitions. The minimum in T_1 occurs near 280° and at this temperature T_2 as deduced from the line width is governed almost entirely by the β-transition. T_1 as measured, however, is governed by the regions with the minimum value of T_1; all others will saturate before these, so that the γ-transition is most likely to determine its value.

Since the existence of a minimum in T_1 appears to preclude a broad range of correlation times,[20] we have applied Bloembergen, Purcell, and Pound's equations with one correlation frequency, assuming that T_1 is governed by the γ-transition. The method was to deduce a plausible relation between ν_c and the temperature from equation (1) and the line-width measurements on PM-B between 170° and 200° (assuming $B = 5$ and $C = 16$ gauss), and to use this to predict T_1 values from the equation

$$\frac{1}{T_1} = A\left[\frac{(\nu_L/\nu_c)}{1 + (\nu_L/\nu_c)^2} + \frac{(2\nu_L/\nu_c)}{1 + (2\nu_L/\nu_c)^2}\right] \quad . \ . \ . \ . \ . \quad (4)$$

which has a minimum value of T_1 given by:

$$(T_1)_{\text{min.}} = 1{\cdot}06/A \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

Fig. 9 shows log ν_c as deduced from the line width plotted against T^{-1}, and the straight line is taken as a reasonable fit to the data, considering the inevitable distortion due to overlapping spectra; it follows the equation

$$\nu_c = 10^{13} \exp(-7500/\boldsymbol{R}T) \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (6)$$

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[23] Butta, *J. Polymer Sci.*, 1957, **25**, 239.
[24] Temperley, *J. Res. Nat. Bur. Stand.*, 1956, **56**, 55.
[25] Okamoto and Takeuchi, *J. Phys. Soc. Japan*, 1959, **14**, 378.
[26] Bloembergen, Purcell, and Pound, *Phys. Rev.*, 1948, **73**, 679.

If this is substituted into equation (4) with $\nu_L = 3 \times 10^7$ and $A = 76$ (from the value of T_1 at the minimum), we get the T_1 curve shown in Fig. 10, which is a reasonable fit to both Wilson and Pake's data above 260° (filled circles) and the spin-echo values [12,13] (filled triangles) at room temperature. There is no evidence for any effects of the β-transition at high temperatures; in fact, it is noteworthy that T_1 values from the spin-echo data for liquid " Marlex-50 " [20] (open circles) lie close to the extrapolated curve for the solid. If we exclude Wilson and Pake's result at 385°, the values of log ν_c for solid and liquid above 280° (with $A = 76$) lie on an excellent straight line when plotted againt T^{-1} and give the equation:

$$\nu_c = 1{\cdot}5 \times 10^{12} \exp(-5200/\boldsymbol{R}T) \quad . . . . \quad (7)$$

which is in fair agreement with equation (6) considering the large errors of this type of calculation.

FIG. 9. *Correlation frequency* v. *temperature for the γ-transition in* PM-B.

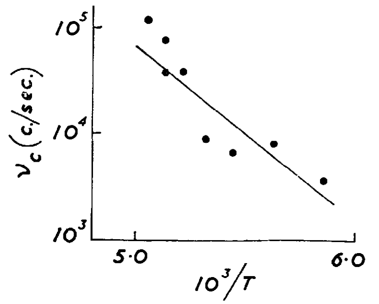
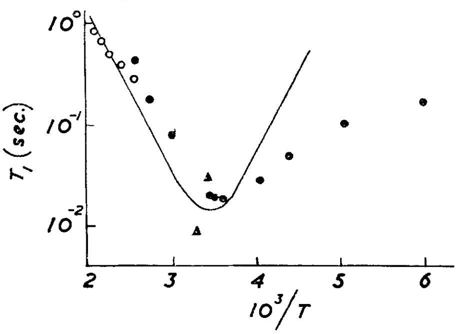


FIG. 10. *Experimental and theoretical* T_1 *values.*



Calc. from Fig. 9. ● *Wilson and Pake's values.* ▲ *Spin-echo values.* ○ *Molten " Marlex*-50."

Below 250° ($T^{-1} > 4 \times 10^{-3}$) the agreement is poor and relaxation phenomena in this region are not understood. Part of the problem is the low value recorded for T_1 below 160° K, where only the broad component is observed, and its unusually small temperature-dependence. The values range from 0·2 sec. at 170° to 2 sec. near 83°, and ν_c follows the equation

$$\nu_c = 10^7 \exp(-600/\boldsymbol{R}T) \quad . . . . \quad (8)$$

reasonably closely. Relaxation here cannot be governed by the α-transition since equation (4) and ν_0 and E^* from the dielectric-loss experiments [25] predict too large a temperature variation and impossibly long values of T_1 at low temperatures. Paramagnetic impurities may partly account for the effect, but their concentration is too low (except in irradiated samples) and presumably very variable, whereas experience shows that broad lines with good signal-to-noise ratios are obtained from all types of polyethylene so far examined at low temperatures. However, until we are reasonably certain of the origin of these T_1 values, it is not entirely correct to attribute the broad component to the crystalline regions except in the immediate vicinity of the α-transition, which itself will ensure a low value of T_1.

A possible relaxation mechanism is by spin exchange [27] with methyl groups at the chain ends, or any other disordered site within the crystalline regions where the molecular mobility is unusually high. Despite the low concentration of such sites, their influence may extend over a considerable distance. For example, in order to maintain a T_1 value in the crystalline CH_2 groups of 0·2 sec., the intermolecular dipolar coupling between them and the reorienting CH_3 groups must be at least 5 c./sec., which brings in all those CH_2

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[27] Woessner and Gutowsky, *J. Chem. Phys.*, 1958, **29**, 804.

groups within about 35 Å, namely 8000. If each chain of average molecular weight $2{\cdot}5 \times 10^5$ is assumed to contribute two freely moving CH_3 groups, then we find one such group per 9000 CH_2 groups, so that within the approximations of the calculation an appreciable part of the crystalline regions could be influenced, possibly down to quite low temperatures. The low E^* value of 600 cal./mole might be partly due to reorientation of the CH_3 groups by tunnelling.

Two other factors which may be calculated from the nuclear resonance spectra, namely, the intensity ratio and second moment, also require discussion in terms of multiple transitions. The intensity ratio is the percentage of the area under the broad component to the total area under the absorption curve. Two methods of dividing the curves are in common use; that first used by Wilson and Pake[28] in which a straight line is drawn between the maxima of the broad component, and a later method[5] in which the resonance curve below 120° is taken as reference. It has been customary to relate the intensity ratio to the so-called crystallinity of the sample as measured, for example, by X-ray methods, although comparison between the two results is not uniformly successful.[1] Part of the reason for the discrepancy may be that at least two factors must be taken into consideration.

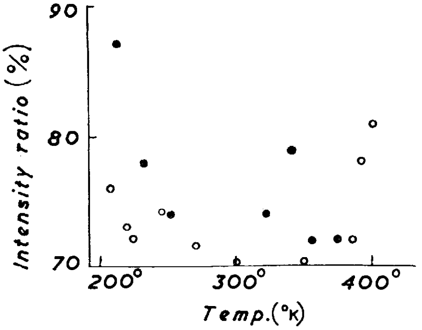

FIG. 11. *Intensity ratio of* PM-B *at different rf voltages.*
● 200 mv.; ○ 100 mv.

First, since we can only guess at the relaxation mechanism in the crystalline regions, it is difficult to establish whether all parts contribute to the broad component except in the immediate vicinity of the α-transition. In order to investigate whether different parts of the crystalline regions had different values of T_1, the intensity ratio for PM-B was measured, Wilson and Pake's method being used at different temperatures with two rf levels; in Fig. 11 the filled circles refer to spectra recorded at an rf voltage of 200 mv to the bridge, and the open circles at a value of 100 mv. The estimated standard deviation of the values is 5, and the crystallinity derived from the density[29] (0·925) is 63%. It is clear that the scatter of the results is too large for us to establish significant differences at these rf levels, except possibly at 210° and near the melting point. We must assume that between these two temperatures, at least in this sample, all parts of the crystalline regions are contributing to the broad component.

Secondly, with regard to the narrow component, the difficulty is again one of relaxation times. The γ- and the β-transition should each have a characteristic temperature-dependence on T_1, and if these relations were known it would be possible to predict which of the regions contributes, either to the broad or narrow component according to the magnitude of the line width. Although the temperature-dependence of the correlation frequency, from which we could deduce T_1 and T_2 at a given temperature, is known approximately for the two transitions, application of the equations depends on a knowledge of the rf field at which the measurements were made. At values below saturation, the intensity should vary with temperature as we pass through the two transitions.

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[28] Wilson and Pake, *J. Polymer Sci.*, 1953, **10**, 503.
[29] Nichols, *J. Appl. Phys.*, 1954, **25**, 840.

Experimentally, we find that in PM-B the difference between the mean nuclear resonance value above 230° and the density value of 63% is not large enough to be taken as significant, so that in this polymer the γ-transition is the important process. In PE-A and " Marlex-50 " [5] the intensity ratio falls continuously from 170° until near 310°, presumably as a consequence of γ- and β-transitions; between 310° and 340° it appears to vary little with temperature and in this range the stationary values of 72% and 79% are in good agreement with the density values [29] of 75% and 80%, although in poor agreement with the *X*-ray values quoted in the earlier paper.[5] Hence it is possible that in some reasonably linear polyethylenes the intensity ratio near 320° measured at a low rf level might be a good estimate of the crystallinity of the sample, and that the factors we have been discussing can be neglected. In branched polyethylenes the ratio falls continuously with rise in temperature until the broad component is no longer detected.[8] This may be a question of signal-to-noise ratio,[1] since these polymers still show the α-process in the mechanical-loss studies as the melting point is approached.

As regards the second moment, all the factors we have mentioned previously, particularly saturation effects, may affect its value and no complete discussion can be given. It may be pointed out, however, that the fairly constant value of the second moment between 250° and 330° cannot be said to be significantly different from the values of 24, 26, 27, and 28 gauss [2] computed for various polyethylenes with the probably incorrect assumption of tetrahedral CCC and HCH angles; [10,18,30] and this is especially evident if we bear in mind that no corrections have been applied for the vibrational motion of the chains, which may be large in view of the high temperature factor observed for motions perpendicular to the chains in some long-chain molecules.[31] The reason for the rise in second moment below 200° is not clear. It may be partly due to a decreased amplitude of torsional oscillation of the chains and partly to a rather high second-moment contribution from the frozen disordered regions, as has been found to occur in Terylene.[32]

We may conclude that there is some evidence for supposing that α-, β-, and γ-processes revealed by mechanical-loss experiments can also be detected in the nuclear resonance spectra of many polyethylenes; there may be an additional transition near 210° in some samples, and unique transitions are observed in crystallised " Marlex-50 " and an untreated polymethylene. At present, the limited extent of the experimental results (especially spin-echo work) implies that the following remarks on the nature of the transitions must be regarded as tentative.

It seems fairly well established that the α-transition is explained by hindered rotation of the chains as a whole in the crystalline regions of the polymer with an E^* value of about 25 kcal./mole and a favourable frequency factor (about 10^{20}). However, the β- and the γ-transition have much lower activation energies and lower frequency factors (10^{15} and less), within the limited accuracy of our evaluation of these quantities. The value of E^* for the PM-A transition is close to that characteristic of the twisting of a hydrocarbon chain, so that this and the β- and γ-transitions (which also have low values of E^*) may be attributed to chain twisting in the amorphous or disordered regions. One distinction between β- and γ-transitions (and any intermediate) in linear polyethylenes is the difference in line width observed after the transition; the value for the γ-transition is between 2 and 5 gauss, and for the β-transition is of the order of 0·2 gauss or less. The chain twisting in the latter can clearly occur about many more directions in space than in the former, so that the principal difference between the two regions from the molecular viewpoint may be that those which show the β-transition contain longer chains of disordered CH_2 groups. Twisting motions in such chains may require a fairly low E^* but a considerable degree of correlation between the motions of neighbouring CH_2 groups and therefore unfavourable frequency factors.

[30] Newman, *J. Chem. Phys.*, 1950, **18**, 1303.

[31] Welsh, *Acta Cryst.*, 1956, **9**, 89.

[32] Land, Richards, and Ward, *Trans. Faraday Soc.*, 1959, **55**, 225.

An interesting analogy can be drawn between the nuclear resonance data for polyethylene and the mechanical-loss behaviour of Nylon-6 : 6; [22] this polymer contains chains of 4 and 6 CH_2 groups and the loss curve has maxima at 160° (187 c./sec.) and 245° (157 c./sec.). They occur at the beginning of the temperature ranges proposed in a previous section for the γ- and the β-transition, suggesting the possibility that the numbers of CH_2 groups in the disordered lengths of the chains are 4 and 6 respectively. Unfortunately there is no strong evidence from the proton resonance experiments on Nylon-6 : 6 [33] for this conclusion; the line width diminishes continuously from 90° K and no separate resonance lines appropriate to the γ- and the β-transition have yet been resolved. The line-width transition in crystallised "Marlex-50" has been tentatively identified as a β-transition with restricted freedom of chain twisting, and the proposed figure of 6 for the number of CH_2 groups in the disordered lengths of the chains of this polymer is in reasonable agreement with the proposed structure.[17] The PM-A transition would then appear to be associated with at least 7 CH_2 groups and any transition intermediate between β and γ with 5, but there are no means of testing these proposals from the present results. Any transition preceding the γ must presumably be associated with 3 CH_2 groups; such a transition may be indicated in the mechanical loss curves of some polyethylenes [22] as a shoulder near 120° K, but the present nuclear resonance evidence is insufficient to confirm its existence.

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Leeds, 2.

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[33] Slichter, *J. Appl. Phys.*, 1955, **26**, 1099.