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Nature of the Proton NMR Transverse Relaxation Function of Polyethylene Melts. 1. Monodispersed Polyethylenes

M. G. Brereton, I. M. Ward,* N. Boden,[†] and P. Wright[‡]

Interdisciplinary Research Centre in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, United Kingdom

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ABSTRACT: Results are presented for NMR measurements on a series of samples of linear polyethylene with low polydispersity over a range of molecular weights. In general terms, the experimental data are consistent with results of previous workers. The main thrust of the present investigation is to show that the transverse relaxation function can be accurately described by a recent theoretical model due to Brereton. This theory is based on a scale-invariant model of the dipolar interactions assumed responsible for the relaxation of transverse magnetization. It incorporates a rather general hierarchy of chain dynamics which can be used to accommodate the Rouse model at small space and time scales and a variety of other models, e.g., the reptation model, at larger space and time scales. The model is shown to account for the complex shape of the transverse relaxation function observed for high molecular weight samples of low polydispersity, showing that this has its origin in the restrictions on molecular mobility imposed by the entangled nature of the polymer melt.

1. Introduction

It has long been known that pulsed nuclear magnetic resonance (NMR) is a useful tool for the study of the dynamics of polymer melts.[1-5] Early studies on polyethylene by McCall et al.[1] have been followed by more recent investigations by Charlesby,[6] Cohen-Addad,[7] and Kimmich.[8,9] Despite these studies and the interest in polyethylene melts as model molecular liquids[10] and the consequent theoretical work on them, the interpretation of the NMR data, particularly at high molecular weights, has remained inconclusive and uncertain. In this work we confirm that the transverse relaxation function is more sensitive to structural changes than the spin–lattice relaxation and self-diffusion measurements. It is also relatively easy to obtain and has therefore been used to characterize a series of well-defined monodispersed polyethylene melts. By eliminating the complication of polydispersity, side chains, and the role of differing functional groups, it has been possible to obtain some unambiguous data which we have used as a reliable basis for some theoretical modeling.

At low molecular weights the situation is relatively simple since the transverse relaxation function shows a single-exponential behavior for which the relaxation time T_2 can be assigned. From the observed molecular weight dependence of T_2 we show in section 5 that the Rouse model of polymer chain dynamics is applicable and determine from the data the relaxation spectrum of the polyethylene chains, the molecular weight of a Rouse subunit, and the NMR coupling constant.

At higher molecular weights the NMR transverse relaxation function is decidedly nonexponential and clearly reflects a more complex dynamics. In line with the approach of other groups[5,8,9] two parameters are used initially to characterize the shape of these curves: T_2^*, the time for the relaxation to decay to $1/e$ of its original value, and T_2', a characteristic time constant obtained by fitting the tail of the relaxation function. The values of T_2^* and T_2' are in agreement with those of other workers.

In contrast to this previous simplistic parameterization, we have successfully fitted the actual shape of the transverse relaxation function to a theoretical calculation given by one of us.[11,12] The calculation was based on a scale-invariant model of the dipolar interactions assumed responsible for the relaxation of transverse magnetization. The model also incorporates a rather general hierarchy of chain dynamics which can be used to accommodate the Rouse model at small space and time scales and a variety of other models, e.g., the reptation model, at larger space and time scales. The actual fit and model parameters obtained are given in section 5.

Finally we show that at high molecular weights, where the chains are fully entangled, the initial decay of the relaxation function can be fitted by a one-parameter function. The parameter used is directly related to the molecular weight of the chain between entanglements and has more physical significance than the phenomenological parameter T_2^*.

2. Experimental Section

NMR Measurements. The NMR measurements were performed with an extensively modified Bruker SXP pulsed NMR spectrometer operating at 100 MHz.

The longitudinal relaxation times, T_1, were determined by using a simple inversion–recovery technique with logarithmically varied pulse separations.[13,14]

The transverse relaxation functions were obtained with the Levitt–Freeman modification of the Carr–Purcell echo train technique.[15] This is a self-compensating sequence which ensures that every second echo is correct, providing that diffusional processes are not significant. The sequence is

$$90°x\text{–}\tau\text{–}(90°x\ 180°y\ 90°x\text{–}\tau)_n$$

where the composite pulse produces an equivalent transformation of the magnetization to a single 180° pulse.

Accurate timing of the echo measurements was ensured by using the triggered data collection mode of a Datalab DL9225 transient recorder and a Fluke frequency synthesizer referenced pulse programmer clock to control the application of both the refocusing the data collection pulses; this limited the time between data points to a maximum of 180 μs and collected a maximum of 4096 points, with 1 in 256 amplitude resolution, leading to a maximum time duration of ~0.75 s. Typically 16 sweeps would be averaged.

As the free induction decay and the transverse relaxation function should be the same at short times or in the absence of

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[†] School of Chemistry, University of Leeds.

[‡] ICI Chemicals & Polymer Group, Research & Technology Department, Propathene Group, Room D313, Wilton Centre, P.O. Box 90, Wilton, U.K.

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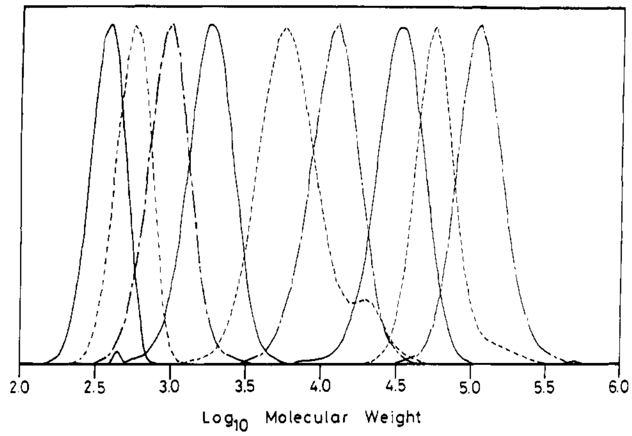

Figure 1. GPC traces for monodispersed polyethylenes.

Table I
Summary of DSC and GPC Results for Monodispersed Polyethylenes

M_n	M_w/M_n	T_{mp}, K (±1 K)
342	<1.07	328.5 ± 2
525	<1.07	356.5
900	1.12	381.0
1700	1.13	396.0
5700	1.41	405.0
11400	1.16	403.5
30600	1.14	404.0
55700	1.14	
107000	1.15	404.0

inhomogeneities, the initial amplitude of the transverse relaxation function was obtained by fitting the front of the free induction decay to a polynomial function and determining the amplitude at time zero.

The temperature of the samples during experiments was controlled by a unit based on an Oxford Instruments DTC2 temperature controller using a gold/iron(III) with chromel thermocouple placed near the sample (~15 mm). This was calibrated before each experiment with a thermocouple in a sample holder at the sample temperature in the probe head. Accuracy of temperature determination and stability during experiments were both better than 1 K.

All samples were evacuated for at least 24 h before study, with heating to aid the release of trapped gases, and then sealed at a vacuum of $\sim 10^{-4}$ Torr; this helped prevent degradation by oxidation at high temperatures.

Locking, flux stabilization, and shimming of the main magnetic field were all achieved by using collinear coils on the main pole pieces and controlled by Varian units. Field changes during experiments were typically <4 Hz.

Sample Characterization. A series of narrow molecular weight (monodispersed) polyethylene fractions were obtained and characterized with a Perkin-Elmer DSC-2 differential scanning calorimeter and a Waters 150C gel permeation chromatograph (by Mr. C. J. Frye of BP Chemicals Ltd). It was found that they have low polydispersity ($M_w/M_n < 1.2$) and similarly shaped molecular weight distributions (see Figure 1 and Table I). All the samples have a melting point at or below 404 ± 1 K; above this temperature they are translucent.

All the samples with an average molecular weight M_n of 900 or more were obtained from the National Bureau of Standards, Washington, DC, and our results confirm their specifications to within a few percent; their molecular weight values have been used throughout this study.

The two lowest molecular weights were obtained from Fluka AG Buchs SG, Switzerland. Both are specified as 98% pure.

3. Results

Longitudinal Relaxation. For all the molecular weights at all temperatures studied (in the melt) a single-exponential longitudinal relaxation, characterized by a time T_1, was recorded. For each molecular weight T_1 followed an Arrhenius temperature dependence with a single activation energy of 17.5 ± 1.0 kJ K^{-1}. No attempt was made to find the T_1 minimum, but these results indicated that the materials are on the high-temperature side of the T_1 minimum at 422 K, the BPP motional narrowing region.[13,16]

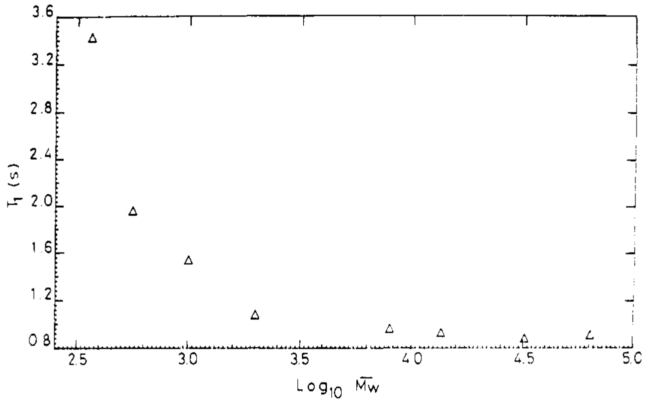

Figure 2. Molecular weight dependence of T_1.

The variation of T_1 with molecular weight at 422 K is shown in Figure 2. It can be seen that T_1 decreases with increasing molecular weight down to a limiting value of ~0.9 s for $M_n > 5700$. It was not possible to discern any explicit relationship between T_1 and molecular weight apart from this plateau.

These results are similar to those obtained by other groups and to those obtained on similar polymers such as polystyrene and poly(ethylene glycol);[3,17] McCall et al.[1] observed a plateau at MW ~ 10 000. Kimmich et al.[8] suggested that their data showed three molecular weight regions for T_1 (and similar dependencies for T_2) and that instead of a plateau $T_1 \propto M^{-0.14}$ for MW > 13 000; these findings are not substantiated by the results in this study. Studies of other polymers[17] seem to suggest that the plateau region starts at molecular weights just above the (viscoelastically determined) critical molecular weight for the onset of entanglements, M_c; as M_c for polyethylene[18] is 3800, this behavior agrees with our results.

Transverse Relaxation Parameters. In solids it is customary to make measurements of the second moment of the resonance, and this can be used to relate quantitatively to the structure and molecular motion. In melts and liquids, on the other hand, it is difficult to obtain accurate values of the second moment, and a similar theoretical approach is not appropriate. We have therefore attempted to obtain information directly from the transverse relaxation function. In the first instance there are three simple ways in which this can be parameterized. First, if the decay is exponential we can define T_2, the transverse relaxation time. At low molecular weights the transverse relaxation functions of polyethylenes of molecular weight 1700 or less were found to be exponential and are shown in Figure 3. It was found that there was a simple relationship between T_2 and the number-average molecular weight M_n: i.e., $T_2 \propto \ln M_n$ as shown in Figure 8 and discussed later.

At higher molecular weights the transverse relaxation function was a complex function, which was not possible to characterize by a simple time constant (see Figure 4). In the first instance, following the approach of other groups we have considered T_2^*, the time for the transverse relaxation function to decay to e^{-1} (for an exponential decay this is equivalent to T_2), and T_2', the characteristic time constant obtained by fitting the tail of the transverse relaxation function to an exponential function (see Figure

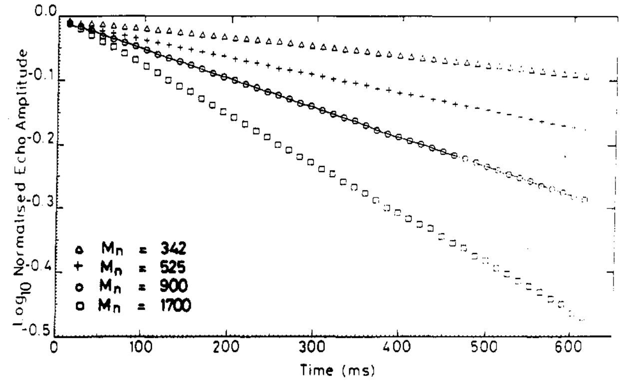

Figure 3. Transverse relaxation functions of low molecular weight monodispersed polyethylenes at 422 K.

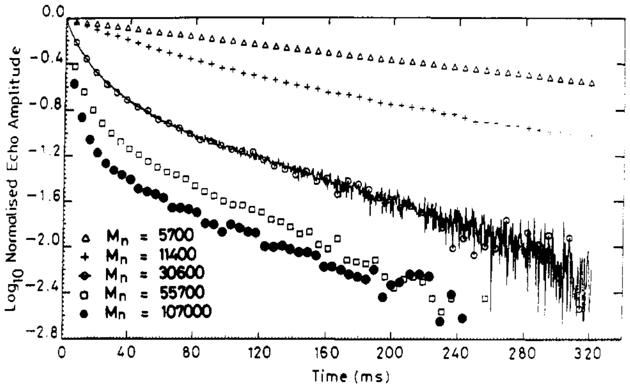

Figure 4. Transverse relaxation functions of higher molecule weight monodispersed polyethylenes at 422 K.

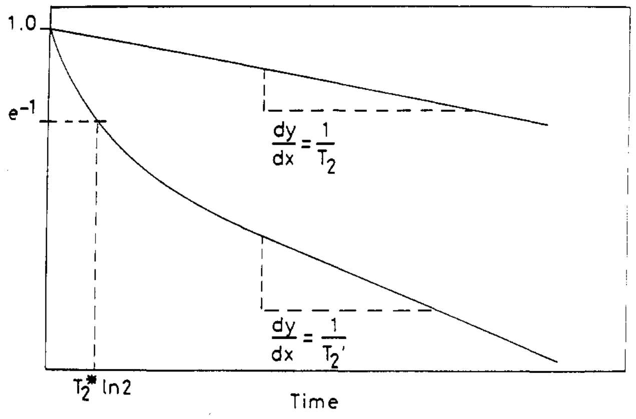

Figure 5. Schematic diagram showing the evaluation of the transverse relaxation function parameters T_2, T_2', and T_2^*.

Table II
T_1, T_2, T_2', and T_2^* Values for Monodispersed Polyethylenes at 422 K

M_n	T_1, s	T_2, s	T_2', s	T_2^*, s
342	3.43 ± 0.04	3.062	(3.062)	(3.062)
525	1.96 ± 0.05	1.609	(1.609)	(1.609)
900	1.54 ± 0.04	0.952	(0.952)	(0.952)
1700	1.08 ± 0.014	0.568	(0.568)	(0.568)
5700	0.963 ± 0.004		0.283	0.237
11400	0.929 ± 0.006		0.223	0.094
30600	0.881 ± 0.003		0.094	0.017
55700	0.907 ± 0.006		0.070	0.006
107000	0.901 ± 0.004		0.065	0.003

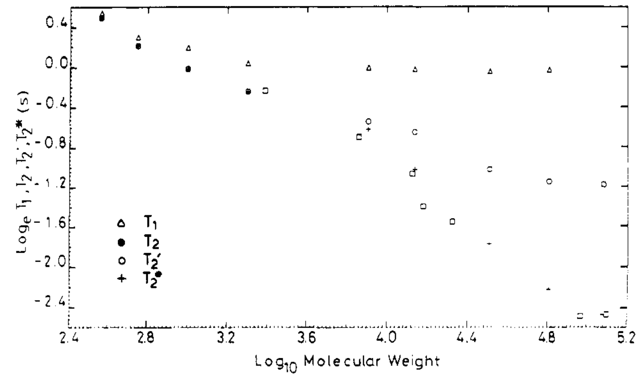

Figure 6. Relationship between T_1, T_2, T_2', T_2^*, and molecular weight.

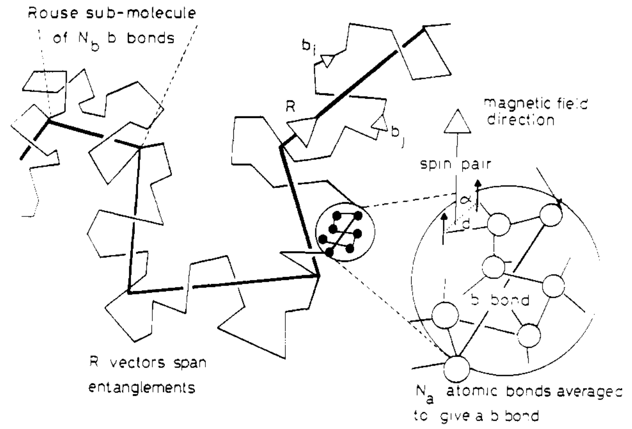

Figure 7. A hierarchical model for the NMR properties of entangled polymer melts.

5). These parameters have the advantage over studies of the second moment of being easy to calculate and can be easily compared to T_2 values, although unlike T_2 and the second moment, they have no direct simple physical significance. T_2^* is mainly dominated by the amount of unaveraged dipolar coupling, whereas T_2' is affected by many variables such as free chains, chain ends, and partially averaged dipolar coupling. The values obtained are listed in Table II.

T_2' was found to be essentially uninformative, quickly tending toward a plateau value after initially extending to molecular weights well above M_c. The dependence of T_2^* on molecular weight is similar to that observed by previous workers[5,8] and is shown in Figure 6.

At this stage, we will turn to the theoretical interpretation of the transverse relaxation time and show that it is much more informative to obtain information from this directly rather than from the simpler parameterization followed previously.

4. Theory

Scale-Invariant Model. Cohen-Addad in a series of papers[19,21] showed that by averaging over the NMR properties of a relatively small number N_a ($\simeq 10$) of monomer units, a scale-invariant model of the polymer chain could be developed. This procedure renders many of the details at the atomic level irrelevant and is particularly suited to a treatment of the dynamics at times considerably longer than the local atomic times.

The approach of Cohen-Addad was further developed and extended by one of us[12] to include a hierarchy of dynamical structures, and a novel method was presented for an exact calculation of the transverse relaxation function. The model is schematically shown in Figure 7: a small number N_a of ethylene monomer units are considered to form a submolecule described by a bond vector **b**. This forms the basic unit of our model and is associated with a rescaled dipole interaction of strength Δ, which determines the inverse basic NMR time scale of the model and is given by

$$\Delta = \gamma^2 h / 4d^3 N_a \tag{1}$$

where d is the distance apart between the protons.

In the next section we will show how N_a and hence Δ can be obtained from experimental NMR results obtained from unentangled polyethylene, by assuming that the dynamics of the chain formed by the **b** bond vector submolecules is described by the Rouse model.[22]

Entanglements. At higher molecular weights the polymer chains become entangled and the effect of the NMR relaxation function will be considered in terms of entanglement vectors $\{\mathbf{R}_i\}$ spanning subgroups of N_b of the original chain of **b** bond vectors, as shown in Figure 7. The $\{\mathbf{R}_i\}$ vectors form a larger scale and dynamically slower level in a hierarchy of structures, which could be extended indefinitely using the theoretical methods developed in ref 12.

The number N_b of Rouse **b** bond vectors spanning an entanglement vector $\mathbf{R}_i$ is a parameter that we will determine in the next section from the experimental results. Since the structure formed by the $\{\mathbf{R}_i\}$ vectors is taken to represent the entangled network, it will in general have different dynamical properties from the $\{\mathbf{b}_i\}$ chain. However, for both levels of the hierarchical structure we will assume that all the dynamical information is contained in the bond correlation function:

$$C_{ij;\mathbf{b}}(t) = \langle \mathbf{b}_i(t')\cdot\mathbf{b}_j(0)\rangle / \langle \mathbf{b}^2\rangle$$
$$C_{ij;\mathbf{R}}(t) = \langle \mathbf{R}_i(t)\cdot\mathbf{R}_j(0)\rangle / \langle \mathbf{R}^2\rangle \tag{2}$$

The technique of working out the NMR properties of these hierarchical structures was considered in detail in ref 12. The results are summarized in the Appendix. The analysis of the experimental data described in the next section is presented entirely in terms of parameters associated with the two correlation functions given in (2).

5. Data Analysis

Unentangled (Rouse) Regime. For unentangled chains in the molten state the Rouse model of chain dynamics is appropriate. In this model the bond–bond correlation function $C_{ij;\mathbf{b}}(t)$ is expressed as a sum over relaxation times τ_p for each normal mode p, where

$$\tau_p = \tau / \sin^2(\pi p/2N) \simeq 4\tau N^2/\pi^2 p^2 \tag{3}$$

N is the number of $\{\mathbf{b}\}$ bonds forming the chain, p is an integer ranging from 1 to N, and τ is the fastest relaxation time appropriate to the smallest chain length scale considered. i.e., one **b** bond. For $\Delta\tau \ll 1$ the relaxation function $G(t)$ given by (A2)–(A5) in the Appendix was evaluated in ref 11 and the result is an exponential relaxation

$$G(t) = \exp[-6\Delta^2 \tau t \ln(N)/\pi] \tag{4}$$

The experimental data shown in Figure 3 can be fitted by the form

$$G(t) = \exp(-t/T_2)$$

where

$$T_2 = \alpha \ln(M_n) + \beta \quad \text{for } M_n < 5700 \tag{5}$$

α and β are parameters that have been determined by the fit shown in Figure 8 as

$$\alpha = 0.89\ \mathrm{s}^{-1} \quad \text{and} \quad \beta = -4.94\ \mathrm{s}^{-1} \tag{6}$$

The parameters τ and N governing the Rouse model can now be determined from these data as follows: The molecular weight M_n of a polyethylene chain can be expressed as $M_n = (mN_a)N$, where m (=28) is the weight of an ethylene monomer unit, N_a is the number of monomers in an NMR submolecule (Rouse) unit, and N is the number of Rouse units in the chain formed by the $\{\mathbf{b}\}$ vectors. The term $\ln(M_n)$ can be written as

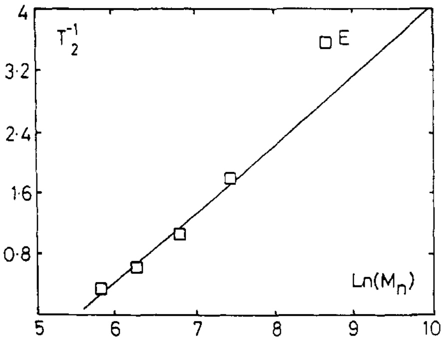

Figure 8. The fitting of the Rouse model to the measured T_2.

$$\ln(M_n) = \ln(N) + \ln(N_a m)$$

so that by comparing (4) with (5) we can identify

$$\ln(mN_a) = \beta/\alpha \quad \text{and} \quad 6\Delta^2\tau/\pi = \alpha \tag{7}$$

The first relation in (7) determines the average number of monomer units/Rouse unit as $N_a = 9.0$. This in turn determines the NMR frequency Δ from (1) as

$$\Delta = \gamma^2 h / 2N_a d^3 = 5606\ \mathrm{s}^{-1} \tag{8}$$

using $d = 1.95$ Å for the interproton distance. Finally the Rouse relaxation time τ is determined from the second relation in (7) as

$$\tau = \alpha\pi/6\Delta^2 = 1.49 \times 10^{-8}\ \mathrm{s} \tag{9}$$

The original approximation $\Delta\tau \ll 1$ is also verified by these results.

Entangled Regime. For $M_n \geq 5700$, the NMR relaxation is still approximately exponential but the rate is significantly greater than that predicted by the Rouse model. This has been indicated by the point labeled "E" on Figure 8 and is taken to indicate the onset of entanglement coupling. The number of **b** bonds or Rouse subunits comprising this molecular weight is estimated as $M_n/(mN_a) \sim 17$. For higher molecular weights the relaxation curves decay sharply and are decidedly nonexponential in shape.

We have analyzed these results by assuming that over an arc length scale of the order of approximately 20 **b** bonds the dynamics of the chain is increasingly governed by entanglements. The entanglement dynamics will be described in terms of the $\{\mathbf{R}\}$ vectors The Rouse model is retained for the $\{\mathbf{b}\}$ chain, while for the $\{\mathbf{R}\}$ chain a single relaxation time $T_\mathbf{R}$ is used for simplicity by setting

$$C_{ii;\mathbf{R}}(t) = \langle \mathbf{R}_i(t)\cdot\mathbf{R}_i(0)\rangle / \langle \mathbf{R}^2\rangle = \exp(-t/T_\mathbf{R}) \tag{10}$$

and ignoring the chain aspect of the $\{\mathbf{R}\}$ vectors.

The product formula given by (A2) in the Appendix was numerically evaluated in order to calculate the full relaxation function $G(t)$.

The other remaining parameter required to calculate $G(t)$ is N_b, the number of Rouse units between entanglements. We have already seen from the results for the $M_n = 5700$ polymer chains that this will be of the order of $\sim$20 **b** bonds; nevertheless, to produce an accurate fit to the experimental results, it is necessary to treat this as a parameter. In the actual fitting procedure adopted it

Table III
Parameters of the Hierarchical Model Derived from Fitting the Experimental Data Shown in Figures 8 and 9

	data points 1	2	3	4	5
M_n	5700	11400	30600	55700	107000
Parameters Used in the Fit					
N_R	0.9	1.2	2.6	7	19
N_f	0.3	0.5	0.7	0.6	0.7
T_R, ms	0.02	0.18	4	75	500
Number of **b** Bonds between Entanglements Calculated from N_R and N_f					
N_b	18	26	36	29	21

Summary of All the Parameters Obtained from the Experimental Results

fundamental Rouse relaxation time	$\tau = 1.49 \times 10^{-8}$ s
no. of ethylene monomers/Rouse subunit	$N_a = 9.0$
mol wt of Rouse subunit	$M_a = 252$
Rouse normal mode relaxation times	$\tau_p = \tau/\sin^2(\pi p/2N)$
no. of Rouse subunits in a chain of mol wt M_n	$N = M_n/268$
average no. of **b** bonds between entanglements	$N_b = 25$
average mol wt between entanglements	$M_R = 6300$
NMR frequency scale $\Delta = \gamma^2 h/4d^3N_a$	$\Delta = 5606$ s^{-1}

was more convenient to choose the number N_R of **R** vectors required to span the complete chain rather than N_b. The numbers N_R and N_b are related by $M_n = N_R N_b(N_a m)$, where $N_a m = 252$ is the molecular weight of a single Rouse unit and $N_b(N_a m)$ is the molecular weight between entanglements.

Finally in order to fit the experimental relaxation function at small values $G(t)/G(0) \sim 0.1$, especially for the higher molecular weights, we found it necessary to include some effect due to free chain ends. This was done by allowing a small number N_f of the **R** vectors to have a relaxation time of T_f faster than T_R. The number N_f is treated as a further parameter but T_f was taken from the data for $M_n = 11\,400$, which just begin to show the effects of entanglements. This value was then maintained as the free chain value for molecular weights greater than 11 400. For $M_n = 5700$ and 11 400 which are only just entangled then the free Rouse result T_2, predicted from (5), was used for T_f.

Detailed Fits to Relaxation Function. A fit to the relaxation function for the molecular weight $M_n = 5700$ ($\sim$23 **b** bonds), which just shows evidence of the effects of entanglements, is found for $N_R \sim 1$, $N_f = 0.3$, and $T_R = 20$ μs. The relaxation time of $T_R = 20$ μs of the "entangled" section may be compared to the slowest Rouse mode $\tau_1 = 4\tau N_b^2/\pi^2 = 2.9$ μs, necessary for a complete relaxation of a chain of 23 bonds. T_R is approximately an order of magnitude slower than the slowest Rouse mode τ_1, which further confirms the interpretation that entanglements are just beginning to play a role in the dynamics of chains of this length. The next molecular weight $M_n = 11\,400$ ($N_b = 49$ **b** bonds) is fitted in a similar manner with $\simeq$2**R** vectors spanning the entire chain and a slower relaxation time of $T_R = 0.18$ s.

The data at the higher molecular weights are well fitted by a fully developed entanglement network of **R** vectors and a small and relatively constant number N_f of more mobile end vectors. The relaxation time T_R is also considerably increased and is almost static on the NMR time scale at the very highest molecular weight. The fitting parameters are given in Table III and the corresponding theoretical fits shown in Figure 9.

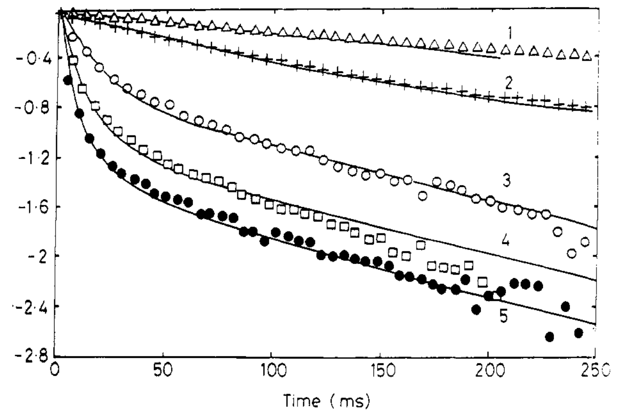

Figure 9. Model fit to the experimental data on the transverse relaxation function $G(t)$.

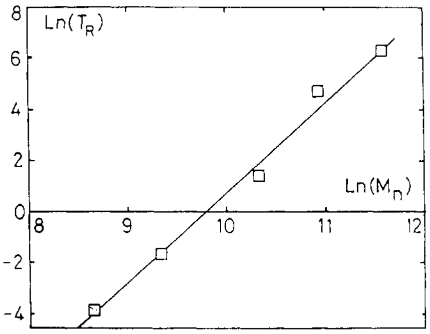

Figure 10. Molecular weight dependence of the entanglement relaxation time T_R.

Entanglement Relaxation Time. The dependence of the entanglement relaxation time T_R on the molecular weight M_n is shown in Figure 10 in the form ln (T_R) versus ln (M_n). The slope is given by 3.5; hence $T_R \sim M_n^{3.5}$. This is entirely consistent with visoelastic relaxation data on polymer melts in the entangled regime. The average number of Rouse units between entanglements also turns out to be approximately constant at 26, corresponding to a molecular weight of 6552.

6. Discussion and Conclusions

This study has confirmed that the transverse relaxation function is more sensitive to changes in molecular weight than the longitudinal relaxation and that at high molecular weights (well above M_c) the transverse relaxation functions of polymer melts are complex. The reasons for this complex shape have been discussed in previous studies by other groups; it has been suggested[8] that the polydispersity of the samples studied is the reason for the observed shape, but in view of the narrow molecular weight distributions used in this study and in studies by other groups, polydispersity can be discounted—studies using even narrower fractions of other polymers have also shown complex transverse relaxation functions.

The shape of the transverse relaxation function must therefore be due to the residual dipolar coupling resulting from the anisotropic motion of the polymer chains on the NMR time scale. By averaging over configurational changes much faster than the NMR time scale, a dynamic scale-invariant model of the dipolar coupling was obtained. Exact results can be obtained from this model for the NMR relaxation function in terms of the bond vector correlation function. For relatively small chains, below the entanglement molecular weight, the Rouse model of chain dynamics is applicable and enables the residual dipolar coupling Δ, appropriate to these scales, to be determined. From the experimental results we found $\Delta = 5606\ \text{s}^{-1}$ and the number of ethylene units comprising each Rouse subunit is determined as approximately 9.0, giving each Rouse unit a molecular weight of 252. In addition, the Rouse relaxation spectrum of a chain of molecular weight M is given by $\tau_p = \tau/\sin^2(\pi p/2N)$, where $\tau = 1.49 \times 10^{-8}$ s and $N = M/252$.

At higher molecular weights the relaxation function is more complex and reflects further anisotropies in the motion of the polymer chains which we assign to the effects of entanglements. In the studies of other groups[5,8] parameters such as $T_2{}^*$ and $T_2{}'$ have frequently been used in an ad hoc manner. This enables the comparison of our results with those of the other groups from which it is apparent and it can be seen that they are very similar. The use of a single parameter such as $T_2{}^*$ to describe the initial decay of the relaxation function is undoubtedly useful but strictly phenomenological. However, from our present work we can suggest an alternative and physically meaningful parameter to characterize the initial decay of the relaxation.

It will be recalled that we introduced a new chain structure at larger space and slower time scales given by the $\{\mathbf{R}\}$ vectors shown in Figure 7. This represents a simple attempt to describe the effect of entanglements on the NMR properties of the polymer chains along the lines of the tube model of de Gennes and Edwards. Two additional parameters were used to describe this structure: a single relaxation time $T_\mathbf{R}$ and the molecular weight $M_\mathbf{R}$ of the chain segment spanned by an $\mathbf{R}$ vector. At the higher molecular weights of 30.6×10^3, 55.7×10^3, and 107×10^3 (data points 3, 4, and 5 in Figure 9) the chains are sufficiently long to be spanned by many $\mathbf{R}$ vectors. We can now show that the initial decrease in the relaxation function is largely independent of $T_\mathbf{R}$ for $t \ll T_\mathbf{R}$ and is determined by the single parameter $M_\mathbf{R}$. In other words, for $t < T_\mathbf{R}$ we can effectively consider the $\mathbf{R}$ (entanglement) vectors as fixed in space and set $T_\mathbf{R} \to \infty$. In this limit the full relaxation function can be analytically evaluated as (e.g., Appendix (A6))

$$\text{real part of } \left[\left(1 - \frac{2i\Delta t}{N_b}\right)^{1/2}\left(1 + \frac{i\Delta t}{N_b}\right)\right]^{-1} \tag{11}$$

where N_b is the number of Rouse units in a chain segment spanned by one of the $\mathbf{R}$ vectors. $M_\mathbf{R}$ is related to N_b by $M_\mathbf{R} = 252N_b$ and essentially represents the molecular weight between entanglements as perceived by NMR techniques.

Expression (11) can be simplified to an algebraic function and is clearly governed by the single parameter N_b. Using this single parameter and (11), we have attempted to fit the initial decay ($t < 30$ ms) of the relaxation function. The results are shown in Figure 11. Attempted fits were made only for the higher molecular weights (data points 3, 4, and 5) as these, especially points 4 and 5, show evidence of a fully developed $\{\mathbf{R}\}$ structure. The lower molecular weights of 5.7×10^3 and 11.4×10^3 (data points 1 and 2) are in a crossover region between the unentangled Rouse dynamics and the slower, entangled structure described by the vectors $\mathbf{R}$.

For molecular weights where the number of entanglements per chain $\gg 1$ (data points 4 and 5), the one-parameter form (11) describing fixed $\mathbf{R}$ vectors provides a reasonable fit to the initial decay of the relation function. For the data points 1, 2, and 3 and to a lesser extent those of 4, the full dynamical (including $T_\mathbf{R}$) model is required. The fitting parameter N_b is in close agreement with those reported in Table III which were found by fitting the entire relaxation function to the two-level dynamical model. The interpretation of N_b or equivalently $M_\mathbf{R}$ is the molecular weight between entanglements. The best fit is provided by the highest molecular weight (data points 5) and gives $N_b = 21$ or $M_\mathbf{R} = 5.3 \times 10^3$. This can be compared with the critical molecular weight of 3.8×10^3 for the onset of the 3.4 power law seen in the viscosity of polyethylene melts. The higher value obtained from NMR is not unexpected as the decay of local magnetization seen in an NMR experiment is not related in any simple way to the transport of momentum. The NMR experiment is considerably less sensitive to the polymer chain structure than the viscosity experiment. For example, in the Rouse model the NMR relaxation rate depends only weakly on molecular weight as log (M), whereas the viscosity is linearly dependent on M.

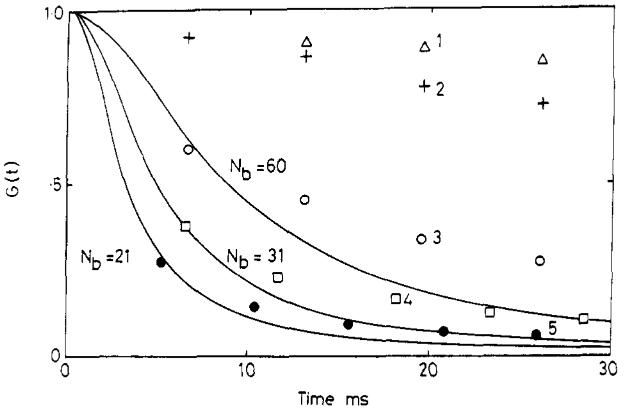

Figure 11. NMR function $G(t)$ fitted to eq 11, which describes fixed entanglement points.

In the crossover from chains of molecular weight 1700, where the Rouse model is applicable, to those of molecular weight 55 700, where there is a fully developed entangled chain described by the $\{\mathbf{R}\}$ bond vectors, the full two-level hierarchical system with dynamics is required. The values of the relaxation time $T_\mathbf{R}$ of the $\{\mathbf{R}\}$ bonds required to fit the data show the strong dependence on molecular weight of $M^{3.5}$, which is characteristic of entanglements. The number of bonds N_b between entanglements, determined as an average over all the data, is approximately constant at about 25, which further supports the entanglement picture.

Finally we may add that in order to fit the long tail of the relaxation function it was necessary to assume that some bonds were undergoing relatively fast orientational motion even in the entangled regime. We ascribed these to chain end bonds which are free to reorientate and can be described by Rouse dynamics. This picture is confirmed by the fact that the number of chain end bonds required to produce the fit remained relatively constant for all molecular weights.

Now that we have been able to assess the NMR results in terms of the Brereton theory, we are able to gain an understanding of the validity of previous research in this area. Charlesby's suggestion[6] that the transverse relaxation curves for cross-linking polymers can be analyzed into two parts, one corresponding to the gel fraction and the other to the sol fraction, although too simplistic, does contain some intuitive justification. Certainly there is a liquid-like component, and this relates to part of the structure, but it is incorrect to conclude that the sol fraction will necessarily show a simple exponential decay. It has been clearly shown that the transverse relaxation for uncross-linked polymer is not exponential at molecular weights beyond M_c, the entanglement molecular weight.

The proposed analysis has been shown to produce a much better understanding of the changes in transverse relaxation with molecular weight. The present data, when parameterized by T_2*, show similar changes with molecular weight to those observed by previous workers, e.g., three regimes of behavior, but we do not consider that this approach is more than purely phenomenological and it does not provide any basic physical insight into the behavior.

Finally we can perhaps comment that the T_1 measurements are much less informative than the transverse relaxation measurements because T_1 relates to high-frequency (and localized) molecular motions close to the Larmor frequency ω_0 (and $2\omega_0$). Further information could be probably be gained from $T_{1\rho}$ measurements, which relate to a lower frequency range.

Further work is necessary on the theoretical interpretation of the NMR results, on the effect the presence of chains of different lengths has on the transverse relaxation function, and whether other NMR techniques (e.g., $T_{1\rho}$ measurements or deuterium studies of deuterated tracer molecules in protonated matrices) might be more informative; we hope to present work in these areas at a later date.

Appendix: Theory

NMR Transverse Relaxation Function. The transverse relaxation function $G(t)$ due to dipolar interactions between proton pairs is given by[23]

$$G(t) = \cos\left[\delta \int_0^t (3\cos^2\alpha(t') - 1)\,\mathrm{d}t'\right] \tag{A1}$$

where $\alpha(t')$ is the angle that the vector distance **d** between the proton pair makes with the applied magnetic field. (This is schematically shown on the right-hand side of Figure 7.) The strength of the dipolar coupling is given by $\delta = 3\gamma^2 h/4d^3$ and the averaging is taken over all dynamically accessible configurations available in the time interval 0 to t. It is assumed that the proton pair is rigidly attached to the main chain so that the dynamical behavior of the polymer chain is monitored through the time dependence of the angle $\alpha(t)$. Unfortunately, the complexity of the local connectivity in terms of bond angles and steric hindrances makes an analytic calculation of the relaxation function $G(t)$ unfeasible. Using the scale-invariant model outlined in section 4, we can write[11] the NMR relaxation function for the scale-invariant model in the form

$$G(t) = \text{real part: } g(2\Delta,t)\, g(-\Delta,t)\, g(-\Delta,t)$$

where

$$g(\Delta,t) = \prod_\alpha (1 - 3it\Delta_\alpha(t))^{-1/2} \tag{A2}$$

α is an integer variable taking values in the range ($-\infty$ to $+\infty$), and $\Delta_\alpha(t)$ is related to the bond correlation functions by the integral relation

$$C_{ij;\mathbf{b}}(t) = \langle \mathbf{b}_i(0)\cdot\mathbf{b}_j(t)\rangle$$

$$C_{\mathbf{R}}(t) = \langle \mathbf{R}(0)\cdot\mathbf{R}(t)\rangle \tag{A3}$$

$$\Delta_\alpha(t) = \Delta \int_0^1 \mathrm{d}u\,(1-u)\cos(2\pi\alpha u)\, C^*(ut) \tag{A4}$$

where

$$\begin{aligned} C^*(t) &= C_{ii;\mathbf{b}}(t) \quad (\{\mathbf{b}\}\text{ structure alone}) \\ &= C_{ii;\mathbf{b}}(t) + C_{\mathbf{R}}(t)/N_{\mathbf{b}} - \sum_{j=1}^{N_{\mathbf{b}}} C_{ij;\mathbf{b}}(t) \\ &\qquad (\{\mathbf{b}\}\text{ and }\{\mathbf{R}\}\text{ structures}) \end{aligned} \tag{A5}$$

$N_{\mathbf{b}}$ is the number of **b** vectors spanned by one **R** vector. For static correlations $C_{\mathbf{b}}(t') = 1$; then $\Delta_\alpha(t') = \Delta\delta_{\alpha 0}$ and (A2) reduces to the known static result

$$g(\Delta,t) = (1 - 3i\delta t)^{-1/2} \tag{A6}$$

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