

Nuclear Magnetic Resonance Studies of Molecular Relaxation Mechanisms in Polymers

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In recent years substantial progress has been made in the understanding of the structures and dynamics of high polymers. Crystal structures and chemical composition are well known for most common polymers.^{1,2} The fringed micelle model for crystalline-amorphous organization has been supplemented by the discovery and elucidation of chain folding and the relationship of chain-folded lamellae to spherulitic structures.^{2,3} Relaxation phenomena have been related to molecular motions, and qualitative and semiquantitative interpretations of diverse relaxation experiments show gratifying consistency.^{4,5} In this paper I give a summary of the contributions of nuclear magnetic relaxation to polymer science. Work on solid polymers will be emphasized. The plan of the paper is to concentrate on the interpretation of nmr parameters and molecular information derivable therefrom. Experimental methods and physical theory will not be treated.

Despite the fact that chemists are often quite sophisticated in the use of high-resolution nmr techniques, there seems to be only a limited appreciation of the physical basis and usefulness of nmr relaxation methods. For this reason I will give a qualitative discussion of nmr relaxation. In addition, nmr relaxation differs from the more familiar dielectric relaxation in ways that are commonly not understood. Consequently, I will describe both experiments in an effort to clarify the relationships between the methods.

Dielectric relaxation can be described in the following way. An electric field is applied suddenly to a dielectric material. The dielectric relaxation experiment is concerned with the time dependence of the buildup of polarization along the field. This macroscopic polarization is conceived as the partial orientation of permanent molecular dipoles. As the molecular dipole moments are rigidly coupled to the orientation of the molecules (or molecular groups), the time associated with the growth of the macroscopic polarization is about the same as the average time required for reorientation of an individual molecule (or group). The latter quantity is called the correlation time, τ_c . Thus, dielectric relaxation provides an intuitive and direct way of measuring molecular rotational freedom. Note that the

electric field does not make the rotation occur. The field only biases the average orientation so that a measurable polarization is created. Note also that there is no resonant character to the effect. Molecular reorientation occurs through random motions (jumps or gradual diffusion), with no accompanying molecular precession.

Nmr spin-lattice relaxation can be measured as follows. A magnetic field is applied suddenly to a specimen, and the time dependence of the magnetization (*i.e.*, magnetic polarization) along the field is studied. The functionality of the time dependence is usually exponential, and the time constant is called the spin-lattice relaxation time, T_1 . Macroscopically the spin-lattice relaxation experiment is analogous to the dielectric relaxation experiment. On a molecular level, however, the effects are significantly different. The nuclear magnetization is the sum over all the individual nuclear magnetic moments. The orientations of these nuclear magnets (for nuclei of interest here, *i.e.*, spin $1/2$) are only very loosely coupled to the molecular positions or orientations. Consequently, T_1 is usually a much longer time than the molecular correlation time, τ_c . Even when the molecular framework is engaged in the vigorous thermal motion of a liquid, the nuclear gyroscopes ride along maintaining the orientation of their precessional axes along the direction of the laboratory magnetic field.

The nuclear magnetization is small and most easily detected by resonance methods. Although each nucleus precesses about the field direction, the directions of the components of magnetic moment perpendicular to the field are distributed uniformly so that there is zero macroscopic normal moment. The macroscopic moment parallel to the magnetic field exists because there are more nuclei in one spin quantum state than the other (*i.e.*, $+1/2$ vs. $-1/2$). In an nmr experiment a magnetic field is applied, perpendicular to the large polarizing field, that rotates at the same frequency as the nuclear precession. This rotating field tends to tip the macroscopic magnetization, thereby creating a macroscopic precessing magnetization that is relatively easy to detect. By adjusting pulse duration and intensity, the nuclear magnetization can be tipped by any desired angle. A 90° pulse rotates the magnetization by 90° , and so on.

Another way of measuring T_1 is shown in Figure 1. A short pulse of resonant energy, indicated by the rotating magnetic field H_1 , turns the magnetization, M , over (*i.e.*, a 180° pulse). Subsequently, the magnetiza-

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(2) P. H. Geil, "Polymer Single Crystals," Interscience, New York, N. Y., 1963.

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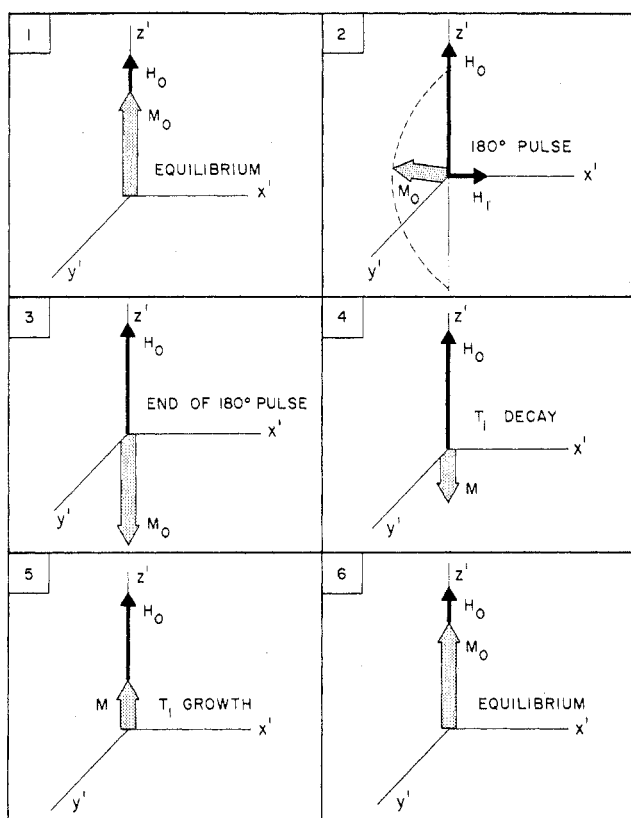


Figure 1. This sequence of diagrams illustrates relaxation of the component of nuclear magnetization parallel to the magnetic field direction. A pulse of resonant energy (2) turns the magnetization by 180° . The magnetization then returns to equilibrium as indicated. During the return to equilibrium, the magnetization can be sampled by applying a 90° pulse and observing the intensity of the resulting induction.

tion must return to its equilibrium state along the field direction. By sampling the magnitude of M as a function of time, the time constant T_1 can be determined. This sampling can be accomplished by applying a 90° pulse and observing the intensity of the resultant induction.

The return of the nuclear magnetization to equilibrium after a 90° pulse occurs in two stages (Figure 2). The transverse part decays to zero with a time constant called the spin-spin relaxation time, T_2 . This decay occurs because the spins do not precess at exactly the same rate and tend to get out of phase. This can be thought of in terms of a variation in magnetic field, and consequently in precession frequency, from one nucleus to another. If the field varies greatly across the specimen, the precession rates differ greatly and the nuclear moments get out of phase quickly. Thus, a broad resonance corresponds to a short T_2 . It is generally true that the resonance width, δH , is roughly equal to $1/\gamma T_2$. γ is the gyromagnetic ratio, a constant for a given nucleus. As discussed above, the longitudinal component of magnetization grows to its equilibrium value with the time constant T_1 .

The third nmr relaxation experiment is carried out in the rotating frame, *i.e.*, in a coordinate system rotating about the magnetic field direction. The magnetization

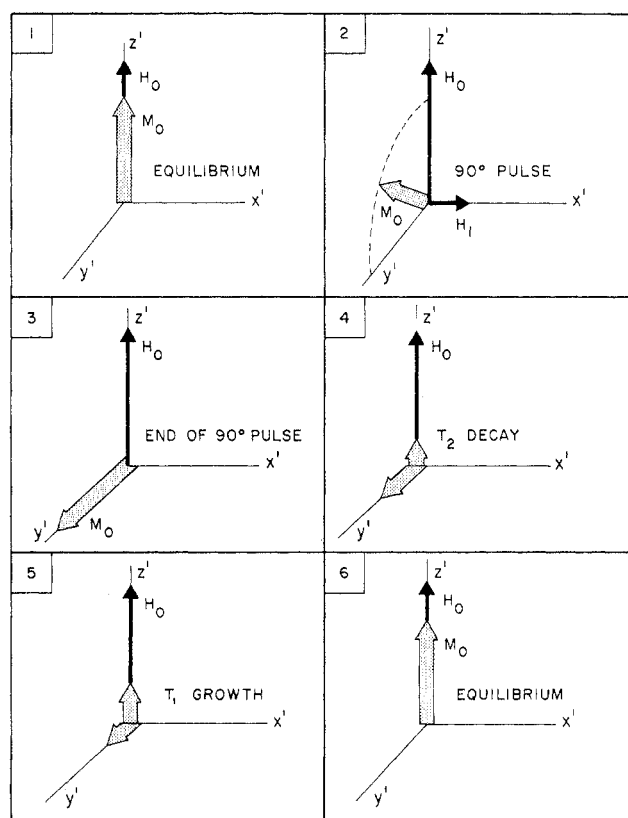


Figure 2. This sequence of diagrams illustrates relaxation following a 90° pulse. As the induction signal is proportional to the transverse component of \vec{M} , the induction decay gives a direct measure of T_2 . In solids $T_1 \gg T_2$.

is rotated through 90° by means of the resonant field H_1 (Figure 3). A 90° phase shift is applied suddenly, leaving H_1 parallel with the magnetization. In this experiment H_1 remains "on" and \vec{M} is allowed to approach equilibrium in the presence of the \vec{H}_0 and \vec{H}_1 . \vec{M} is sampled at various times. The time constant for this relaxation is labeled T_{1p} . Sampling is achieved by simply shutting off H_1 suddenly and observing the intensity of the induction decay that follows. We note that this is a relaxation of a transverse component, *i.e.*, normal to \vec{H}_0 , but it is longitudinal in the rotating frame, *i.e.*, along \vec{H}_1 .

T_1 involves changes in the energy of the spin system, $-\vec{M} \cdot \vec{H}_0$. Molecular motions induce these changes most efficiently where the correlation frequencies for molecular motion are comparable with the resonance frequency. Thus, when $\nu_c \cong \nu_0$, T_1 exhibits a minimum, $\nu_c \equiv 1/(2\pi\tau_c)$. The resonance frequency, ν_0 , is typically 10^7 to 10^8 Hz. T_2 processes involve only the decay of the transverse component of the magnetization, and there is no energy associated with this component. Therefore, this is purely an entropy relaxation. In polymer solids it turns out that T_2 is a measure of spread in the local magnetic field averaged over a time of the order of T_2 . T_2 in a typical polymer ranges from about 10^{-5} sec at the lowest temperatures to 10^{-3} sec in a rubbery region. A change in T_2 is observed when ν_c is of the order of 10^5 Hz. T_{1p} processes involve an energy $-\vec{M} \cdot \vec{H}_1$ and T_{1p} shows minima when

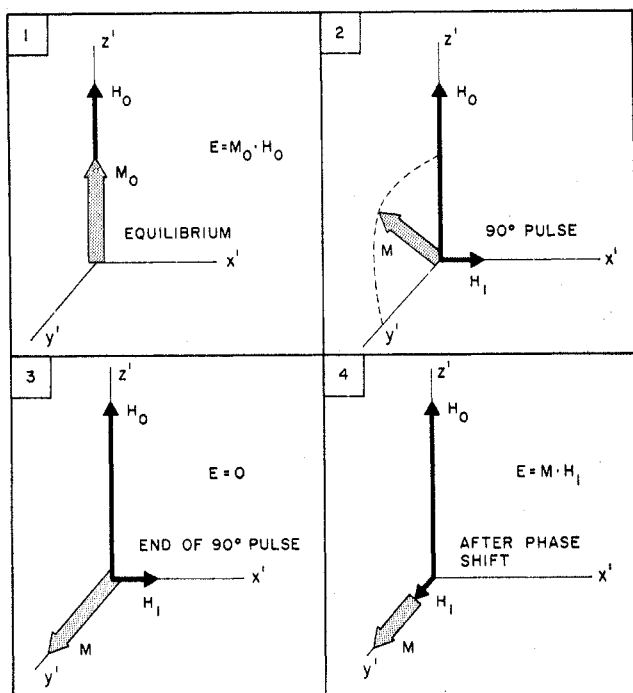


Figure 3. This sequence of diagrams illustrates relaxation in the rotating frame. By application of a 90° pulse followed by a 90° phase shift, the nuclear magnetization is made to lie along the resonant magnetic field, H_1 . M then decays in the presence of H_1 and H_0 .

motions occur near the resonant frequency in field H_1 , *i.e.*, when $\nu_c \sim \gamma H_1/2\pi$. ν_c values of 10^4 to 10^5 Hz are accessible by this method. Although it is not obvious from this discussion, $T_{1\rho}$ in certain cases can be employed to measure ν_c in the range 10 to 10^3 Hz.¹⁰ Schematic temperature dependences of T_2 and resonance width, δH , are shown in Figure 4. Schematic temperature dependences of T_1 , T_2 , and $T_{1\rho}$ are shown in Figure 5.

Nmr Theory and Interpretation

The theory for nmr relaxation is in an advanced stage of development.⁶⁻⁸ Internuclear dipolar interactions predominate. The analysis is somewhat complex and will not be repeated here. We will only discuss briefly some of the physical ideas underlying the theory and note some theoretical results that are useful in discussing nmr relaxation in polymers.

When $T_1 \gg T_2$, as is the case in all solid and rubbery polymers, the resonance width, $\delta H \sim 1/\gamma T_2$, can be thought of as the average deviation of magnetic field (from H_0) at a typical nucleus. This local field has its origin in the magnetic dipoles of the neighboring nuclei, and it can be shown that eq 1 obtains for spin $1/2$ nuclei.

$$(1/T_2)^2 = (9\gamma^4 \hbar^2/32) \sum_k \langle |f_{k0}|^2 \rangle \quad (1)$$

where $f_{k0} = (3 \cos^2 \theta_k - 1)/r_k^3$ where \vec{r}_k is the radius

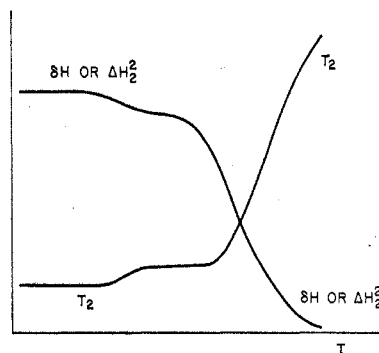


Figure 4. Temperature dependence of T_2 and resonance width, schematic.

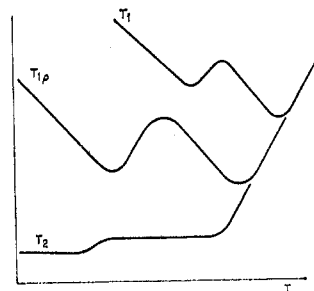


Figure 5. Temperature dependence of T_1 , T_2 , and $T_{1\rho}$, schematic.

vector from the typical nucleus to nuclear neighbor k and θ_k is the angle between \vec{r}_k and the laboratory magnetic field direction. When molecular motion occurs, θ_k and r_k become time dependent and a time-averaged f_{k0} must be employed. These motions become apparent when the correlation time for the molecular motions becomes comparable with T_2 . In this region T_2 will be temperature dependent and the theoretical situation is difficult. When the motions are much faster or much slower than T_2 , predictions of T_2 through eq 1 have been highly successful, leading to structural information and conclusions concerning mechanisms for molecular motion. The lattice sum in eq 1 converges rapidly and lends itself readily to machine computation. Molecular motions can be approximated closely by a succession of discrete structural adjustments.

Considering only the angular factor $3 \cos^2 \theta_k - 1$, it is clear that f_{k0} averages to zero when all angles become available to the internuclear vectors, *i.e.*, $\overline{\cos^2 \theta_k} = 1/3$. Thus T_2 for liquids will become very large as the local field averages to zero. A specific motion such as single axis rotation may change T_2 by about a factor of two. Vibrational motions are hardly noticeable.

For two interacting nuclei the time-average local field can be written as eq 2, where μ is the magnetic

$$H_{loc} \cong (\mu/r^3)(1/T_2) \int_0^{T_2} (3 \cos^2 \theta(t) - 1) dt \quad (2)$$

moment and the time dependence of the nuclear separation has been ignored. If $\theta(t)$ varies over its range of values rapidly (compared with T_2), then the time average can be replaced by a space average (eq 3),

(6) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **74**, 679 (1948).

(7) C. P. Slichter, "Principles of Magnetic Resonance," Harper and Row, New York, N. Y., 1963.

(8) A. Abragam, "The Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961.

$$H_{1oc} \cong (\mu/r^3) \int_0^\pi (3 \cos^2 \theta - 1) f(\theta) \sin \theta d\theta \quad (3)$$

where $f(\theta)$ is a function that contains any restrictions on the motion. For example, if $f(\theta)$ is constant, we have unrestricted motion and $H_{1oc} = 0$, $T_2 \rightarrow \infty$.

Consider now the following model⁹ of a slight motional restriction in order to get a feel for the sensitivity of T_2 . Suppose $f(\theta)$ is constant for $\theta > \theta_0$ but zero for $\theta < \theta_0$. That is, the internuclear vector samples all directions $\theta > \theta_0$ with equal probability in a time short compared with T_2 but is totally excluded from the small cone defined by $\theta = \theta_0$. It follows that

$$H_{1oc} \cong (\mu/r^3) \sin^2 \theta_0 \quad (4)$$

where the averaging is extensive, *i.e.*, when T_2 lies well above its low-temperature limit, T_{2LT} . Thus, keeping in mind $T_2 \sim 1/\gamma H_{1oc}$

$$\sin^2 \theta_0 \cong T_{2LT}/T_2 \quad (5)$$

For $T_{2LT}/T_2 \sim 10^{-2}$, commonly observed a few degrees above T_g , $\theta_0 \sim 5^\circ$, a very small cone indeed. Note that this estimate has been made in such a way as to *overestimate* θ_0 so the restrictions on motion can be expected to be less severe than our estimate.

The foregoing model calculation indicates almost no restriction on the internuclear direction. A more satisfying model would be based on the assumption that all directions are accessible but motion is not arbitrarily fast compared with T_2 . In this case the time average, eq 2, would not be replaced by the space average, eq 3. Unfortunately we do not have a simple calculation for this situation.

T_1 is governed by the fluctuations in the local field that occur near the resonance frequency. T_1 passes through a minimum at temperatures for which $\nu_c \sim \nu_0$, and the minimum value of T_1 can be shown to be given by eq 6. (If T_2 changes by only a small amount at the

$$(T_1)_{\min} = [2\pi\nu_0/(2^{1/2})](T_{2LT})^2 \quad (6)$$

corresponding relaxation, eq 6 and 7 must be modified. In this case $(1/T_{2LT})^2$ would be replaced by $(1/T_{2LT})^2 - (1/T_{2HT})^2$, where T_{2LT} and T_{2HT} are the plateau values on the low- and high-temperature sides of the relaxation in question.) Similarly, T_{1p} is governed by fluctuations in the local field that occur near the rotating frame resonance frequency, $\gamma H_1/2\pi$. The magnitude of T_{1p} at the minimum can be shown to be given by

$$(T_{1p})_{\min} = 4\gamma H_1(T_{2LT})^2 \quad (7)$$

At temperatures sufficiently low that $\nu_c \ll 1/T_2$ it has been shown¹⁰ that $\nu_c \cong 1/(2\pi T_{1p})$ when $H_1 \sim \delta H$ and no interfering relaxation processes are present. This is called the Slichter-Ailion region.¹⁰

According to eq 6 and 7, $(T_1)_{\min}$ and $(T_{1p})_{\min}$ are

estimated to be of the order of 10^{-2} and 10^{-4} sec, respectively, but experimental values for polymers are usually substantially higher. This can be interpreted in terms of a relaxation in which only a part of the specimen engages in motion but relaxes the entire spin system through spin diffusion. For example, at low temperatures the methyl protons in normal paraffins relax the stationary methylene protons and $(T_1)_{\min}$ and $(T_{1p})_{\min}$ are higher the longer the chain.¹¹ Similarly, in branched polyethylene methyl rotation provides the nmr relaxation at low temperatures. A second interpretation of the discrepancy between the computed and measured relaxation time minima involves the distribution of molecular correlation frequencies ν_c . Equations 6 and 7 were derived on the assumption of a narrow relaxation time distribution. Whereas this is often a good approximation in low molecular weight substances, it is known that polymers generally exhibit broad distributions.¹²

There have been a number of attempts to determine activation energies for molecular processes from the study of the temperature dependence of T_2 in the transition region. This procedure does not work for polymers because of the broad distribution of correlation frequencies. Attempts to analyze the temperature dependences of T_1 and T_{1p} fail for the same reason.¹³ Activation energies can be reliably deduced⁵ from the combined use of T_2 transition temperature and T_1 and T_{1p} minima (see eq 8-10).

In summary, nmr data can yield reliable information on molecular relaxation processes in the following ways: (1) At the temperature of a T_2 transition the correlation frequency is approximately

$$\nu_c \cong 1/\pi T_{2LT} \sim 10^{4.5} \text{ Hz} \quad (8)$$

(2) At the temperature of a T_1 minimum

$$\nu_c \cong 2^{1/2}\nu_0 \cong 10^8 \text{ Hz} \quad (9)$$

(3) At the temperature of a T_{1p} minimum (depending on H_1)

$$\nu_c \cong \gamma H_1/2\pi \cong 10^4\text{--}10^5 \text{ Hz} \quad (10)$$

(4) In favorable circumstances,¹⁰ $\nu_c \ll 1/T_2$, no interfering processes

$$\nu_c \cong 1/2\pi T_{1p} \cong 10\text{--}10^3 \text{ Hz} \quad (11)$$

(5) Model calculations give an indication of the generality of motions above T_g . (6) Model calculations of T_2 via eq 1 serve to confirm structures and motional mechanisms. This is particularly effective when the motion is specific enough to be analyzed readily. Methyl rotations and main-chain reorientations are good examples.

Nmr correlation frequencies have been compared with dielectric and dynamic mechanical relaxation

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(13) J. G. Powles and K. Luszczynski, *Physica*, **25**, 455 (1959).

frequencies for polymers, and the correlation is in general excellent.⁵ Figure 6 shows an Arrhenius plot for polyisobutylene (PIB) with the three types of data indicated by N, D, and M. Two loci of correlation frequencies are evident. The low-temperature process is associated with highly hindered methyl rotation and the high-temperature process is the glass transition. Activation energies are proportional to the slopes of these curves. An extensive collection of composite Arrhenius plots has been published.⁵

Site Model Theory

Molecular theories for correlation frequencies have been presented by many workers. For the purposes of interpreting relaxation processes in solid polymers, we believe that the site model theory of Hoffman^{14,15} and his coworkers is particularly well adapted. Briefly, a molecular entity is assumed to move subject to a double-well potential (Figure 7). Transitions between the wells are governed by first-order rate constants k and k' , and it is shown that the rate of approach to equilibrium is given by $2(k + k') = 2\pi\nu_c$. The activation energy for ν_c is approximately the barrier height as viewed from the higher well. The model can be generalized to more complex patterns of potential wells, and correlation frequency distributions follow naturally. The molecular entity under study can be a side group, a portion of a side group, or a section of the main chain. The theory provides a rational connection between macroscopic dielectric properties and molecular structure and interaction. In favorable cases it is possible to estimate the barrier height and shape from a knowledge of molecular geometry and van der Waals forces.¹⁶

Site model theory as it is presently developed is applicable only to the definite motions of definite molecular groups. The treatment of glass transition phenomena thus requires a different approach.

To conclude this section, it is perhaps worthwhile to distinguish between the molecular correlation frequency ν_c , a relaxation frequency, and other frequencies that describe resonant processes, *e.g.*, vibration and rotation in gases. ν_c is an inverse measure of the *average* time it takes a molecule or molecular group to move appreciably (*e.g.*, diffuse one diameter). ν_c does not describe the rate of a regular oscillatory process. The manner in which motions occur in relaxation processes (*i.e.*, many small steps *vs.* a few large steps) is usually not made evident by nmr experiments.

Side-Group Motions

Nmr studies of side-group motions in solid polymers have been quite successful. Many reports have been published, particularly by Slichter¹⁷ and Powles,¹⁸ and

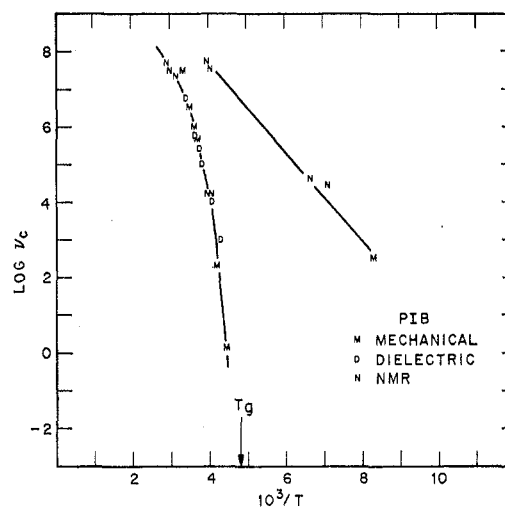


Figure 6. Arrhenius plot for polyisobutylene (PIB). N indicates nmr results. D indicates dielectric results. M indicates dynamic mechanical results.

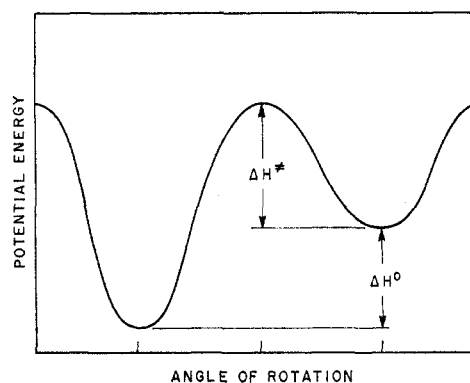


Figure 7. Potential energy barrier diagram.

we will not attempt an exhaustive review of this work here. Nearly all commercially important polymers have been studied, and a coherent general knowledge of the frequency-temperature behavior of side-group motions can be claimed.⁵ In addition, intensity comparisons in nmr studies often serve to identify the molecular group involved and the nature of the motion. Early studies of the acrylic polymers are notable in this regard.¹⁹

Methyl group reorientations have been studied by nmr methods in many polymers. Slichter¹⁷ has given a good summary of this work. Owing to the fact that these motions are inactive dielectrically, the nmr technique plays a unique role here. The nmr data²⁰ for polycarbonate are shown in Figure 8. The low-temperature T_1 and T_{1p} minima and the T_2 transition clearly indicate methyl rotation. In polycarbonate the methyls occur in pairs attached to the same carbon atom leading to steric effects that result in methyl rotations setting in at fairly high temperatures.¹⁷ In natural rubber²⁰

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(18) J. G. Powles, B. I. Hunt, and D. J. H. Sandiford, *Polymer*, **5**, 505 (1964), and earlier papers cited therein.

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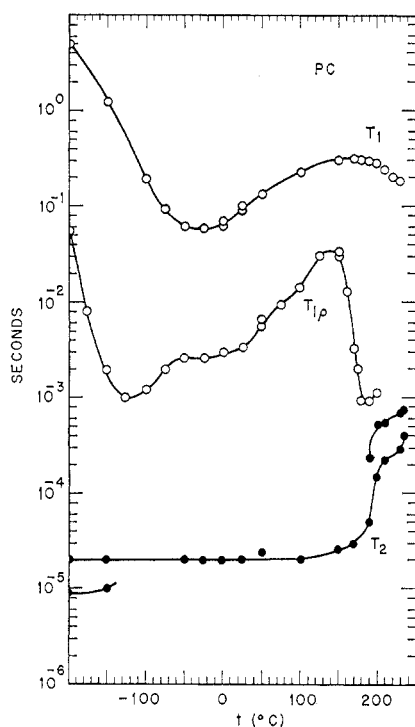


Figure 8. Nmr data for polycarbonate.

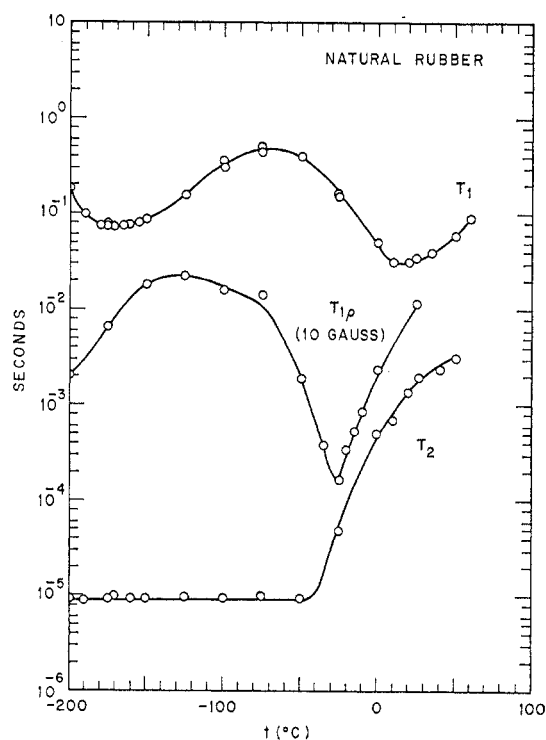


Figure 9. Nmr data for natural rubber.

(Figure 9), less hindrance prevails. In branched polyethylene^{20,21} low-temperature nmr T_1 results indicate methyl rotation (Figure 10). However, the methyl protons are present in such small concentration that the effect is not prominent in the T_2 data. The methyl protons, $\sim 5\%$ of the total population, provide T_1 relaxation to the entire spin system through spin diffusion.

Poly(methyl methacrylate) is a good example of a polymer in which various motions can be resolved^{18,19,22} (Figure 11). T_1 minima for the ester methyl, main-chain methyl, and main-chain reorientations are observed at <100 , 250 , and 490°K , respectively. The ester group rotation is not resolvable from main-chain activity in T_1 data. In general, multiple relaxations will be better resolved the lower the frequency of the experiment. This is simply a consequence of the observation that high-temperature relaxations tend to have large activation energies. Clearly, the high temperature of the α -methyl relaxation is a result of hindrance from the ester group attached to the same chain carbon.

We have carried studies²³ of poly(vinyl acetate) (Figure 12) to low temperatures and obtained an interesting type of methyl rotation. T_1 and $T_{1\rho}$ minima near 50 and 30°K are observed, but no change in T_2 is found to accompany the $T_{1\rho}$ minimum. This result is believed to be associated with quantum mechanical tunneling of the methyls, and similar results have been

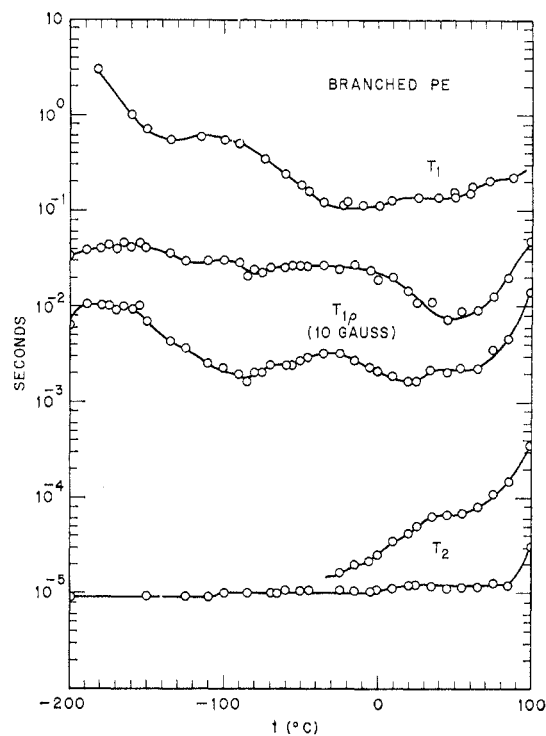


Figure 10. Nmr data for branched polyethylene.

obtained in some methylbenzenes.^{24,25} This matter is not of primary interest in the context of polymer motions, but we should be aware that the customary interpretation of the activation energy (~ 1 kcal/mole in this case) in terms of a barrier to rotation is probably not applicable here.

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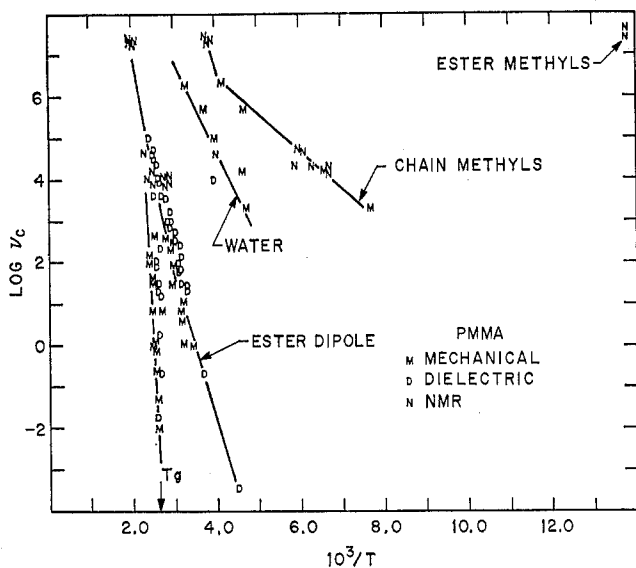


Figure 11. Arrhenius plot for poly(methyl methacrylate).

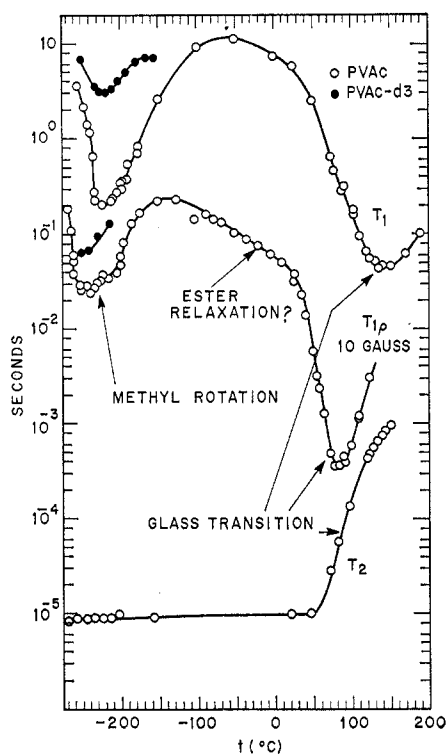
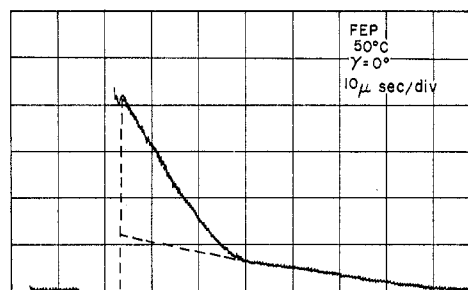


Figure 12. Nmr data for poly(vinyl acetate).

It is also interesting to note that in poly(vinyl acetate) the known⁵ motion of the acetate side group is not at all obvious in the nmr parameters (Figure 12). This is presumably due to the introduction of only weak local field modulation on acetate rotation. As the methyl groups are already in rapid rotation, this is not too surprising.

Specialized Main-Chain Motions in Crystalline Polymers

Rotation about the main-chain axis is well established in entirely crystalline paraffins and other long-chain compounds.²⁶ Similar motions are also known to occur

Figure 13. Free induction decay signal showing evidence for two T_2 's.

in high polymers, even in chain-folded crystal lamellae.^{4,5} Site model theory has been successfully applied to these motions by Hoffman and coworkers,⁴ and they have succeeded in including the effect of chain twisting in a satisfying way. Polymers that have long, linear uncross-linked chain structures usually exhibit these specialized rotations. These same structural features tend to favor crystallization and lead to complex crystalline-amorphous morphologies.

Nmr relaxation studies of partially crystalline polymers are conveniently carried out and often highly informative.^{27,28} It is commonly found that the amorphous regions pass through the glass transition at temperatures well below the temperatures at which crystalline molecular activity is observed. Thus, a range of temperature can be found in which T_2 differs significantly between the crystalline and amorphous regions. A free induction decay signal is shown in Figure 13, and two time constants are in evidence. (Broad-line (steady-state) nmr studies reveal a narrow resonance superimposed upon a broad resonance, but it is frequently more difficult to sort out the components as the modulation amplitudes are incompatible.) Generally the component with the longer T_2 corresponds to the amorphous regions, above T_g . Below T_g , T_2 is about the same for the crystalline and amorphous regions and they are unresolvable. Free induction decay intensity ratios taken from curves like Figure 13 yield crystalline:amorphous ratios directly. Degrees of crystallinity deduced by this method^{21,28} are consistent with X-ray, density, specific heat, and infrared determinations keeping in mind the approximate nature of the crystallinity parameter itself. Polyethylenes²¹ poly(tetrafluoroethylene),²⁹ and various polyamides³⁰ are examples of systems that have been studied in this way. In addition, the sorption of solvents in polymers can be studied in this manner. For example, in polyethylene⁹ it was observed that CCl_4 had no effect on the crystalline signal but increased T_2 of the amorphous signal markedly. This proves that this solvent enters only the amorphous regions under the conditions of the

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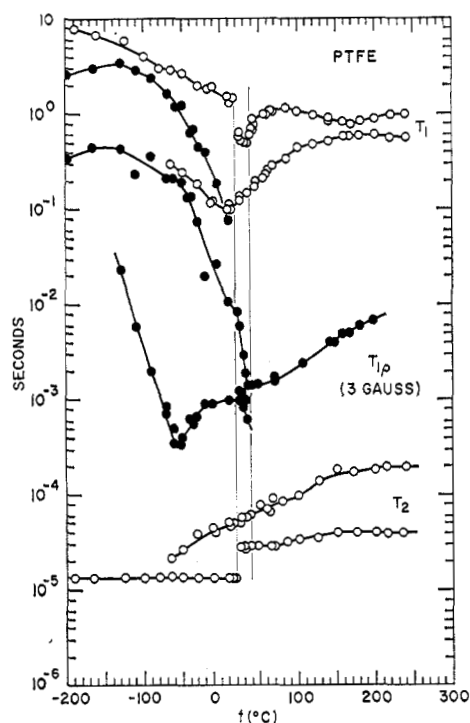


Figure 14. Nmr data for polytetrafluoroethylene.

study. This area of study has not been given much attention, and much remains to be done.

Poly(tetrafluoroethylene) is an excellent example of a polymer that exhibits specialized motions in the crystalline regions. Wilson and Pake²⁷ correctly assigned the crystalline and amorphous components in an early study. Two crystalline polymorphic transitions are well known.³¹ ¹⁹F relaxation time data²⁹ are shown in Figure 14. Two T_2 's are evident over a wide range of temperature. The change in T_2 near 20°C was assigned to main-chain rotation by Slichter³² and Hyndman and Origlio³³ on nmr evidence. The crystal structure changes from triclinic to pseudohexagonal at this point.³¹ The sharp change in the shorter T_2 at 20°C and the insensitivity of the longer T_2 leave no doubt as to the correctness of the earlier^{32,33} motional assignments. The crystalline transition above 35°C is known to be more subtle, but it is also evident in the T_2 behavior. Nmr fiber data³⁴ for FEP, a copolymer of tetrafluoroethylene and a small amount of hexafluoropropylene, are shown in Figure 15. The orientation angle, γ , is the angle between the fiber axis and the magnetic field direction. Although the transitions are less sharp and occur at lower temperatures, the molecular motions in the copolymer are evidently the same as in the homopolymer. Detailed analysis based on eq 1, the known molecular structure and crystal parameters, and the assumption of rotation about the helical axis

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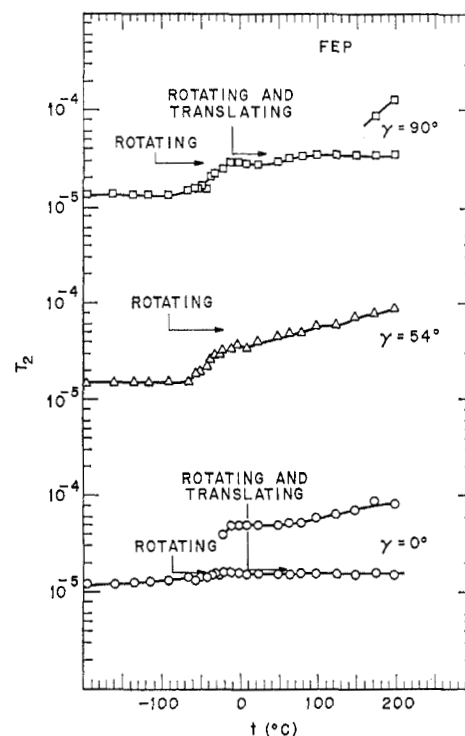


Figure 15. Nmr data for a tetrafluoroethylene-hexafluoropropylene copolymer (FEP). The arrows indicate theoretical predictions based on eq 1 and model motions. "Rotating" refers to a model motion in which the chains rotate rapidly about their long chain axes. "Rotating and Translating" refers to a model motion in which rapid translation parallel to the axis occurs in addition to rotation.

of the molecule yield quantitative agreement with the observed T_2 plateau values. Similar calculations allowing the chains the further freedom of longitudinal translation account for the changes observed above 35°C. No nmr data are used in making the predictions indicated in Figure 15. Only structural data, the model, and fundamental constants are involved. Equation 1 also accounts for the rigid lattice T_2 .

The molecular motions associated with the crystalline transitions of poly(tetrafluoroethylene) and FEP are thus well accounted for. However, owing to the first-order character of the transitions, the T_2 data do not convey information regarding the frequency of motion beyond the observation that the ν_c 's above and below the transitions bracket $1/\gamma T_2 \sim 10^5$ Hz. $T_{1\rho}$ and T_1 (Figure 14) indicate that ν_c is increasing rapidly just below the 20°C transition. Reorientations occur at frequencies below 10^4 Hz in the triclinic phase but jump to much higher frequencies when the crystal structure becomes pseudohexagonal. Similar remarks apply to the 35°C transition. We note that although the nmr results provide powerful evidence concerning the geometry of the molecular motions and average motional rate, no mechanism information is imparted. That is, the motion could be classical rotation or activated jumping between a limited number of orientations. The above discussion would be the same either way.

T_1 and $T_{1\rho}$ have not been particularly useful in the

characterization of specialized polymer motions. This is largely a consequence of the difficulty in predicting the magnitude of the T_1 and $T_{1\rho}$ minima when a distribution of correlation frequencies is present and of the sensitivity of T_1 and $T_{1\rho}$ to spin-diffusion processes. One successful study has been reported.³⁵ The α relaxation in polyethylene (linear), a high-temperature crystalline phenomenon, has been studied by means of rotating frame experiments. The crystalline and amorphous $T_{1\rho}$ signals were resolved and the ν_c deduced from the Slichter-Ailion¹⁰ relation $\nu_c \cong 1/(2\pi T_{1\rho})$. A comparison of these results with dielectric data is shown in Figure 16. The close agreement with the dielectric data suggests that the α relaxation is a bulk effect in polyethylene, *i.e.*, not a chain end or impurity effect. Rotation about the main-chain axis is the obvious mechanism.

The theory of the dependence of T_1 and $T_{1\rho}$ as a function of fiber orientation has been given.³⁶ Data for FEP were analyzed and found to be consistent with molecular mechanisms deduced from T_2 studies.

The Glass Transition

The glass transition is probably the most studied and least understood relaxation phenomenon. Certainly it is the most important. It has received a great deal of theoretical attention, but it is my opinion that all existing theories are seriously deficient. Theoretical discussions have been presented by Bueche,³⁷ Gibbs,³⁸ Ferry,³⁹ Turnbull and Cohen,^{40,41} and others from various points of view. Equations have been developed that can be fitted to many experimental measurements. Our disappointment with existing theories is not based upon numerical comparisons. Rather, we find the physical models to be unsatisfying. We will not review the theories but concentrate on the empirical results of nmr measurements and some general interpretations that would seem not to be in question.

Glass transition phenomena appear to be independent in many respects of the molecular nature of the substance involved. The "glass transition" is the normal manner in which a "solid" amorphous material becomes a viscous liquid or rubber. The behavior of inorganic glasses, low molecular weight organic glasses, and high polymer glasses is remarkably uniform. Nmr data for poly(vinyl acetate) are shown in Figure 12. Data for *o*-terphenyl⁴² are shown in Figure 17. Results for glassy $\text{Ca}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$,⁴³ glycerol,⁴³ and natural

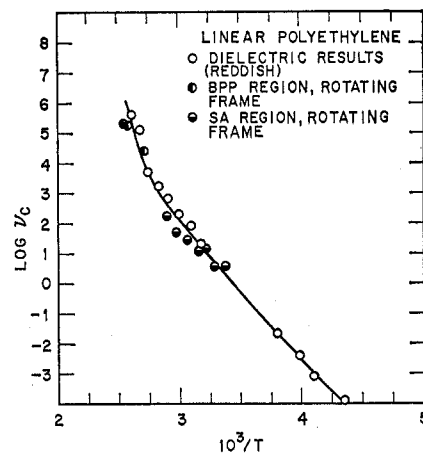


Figure 16. Correlation frequencies for the α relaxation in polyethylene. SA refers to correlation frequencies deduced from the Slichter-Ailion region¹⁰ (see text).

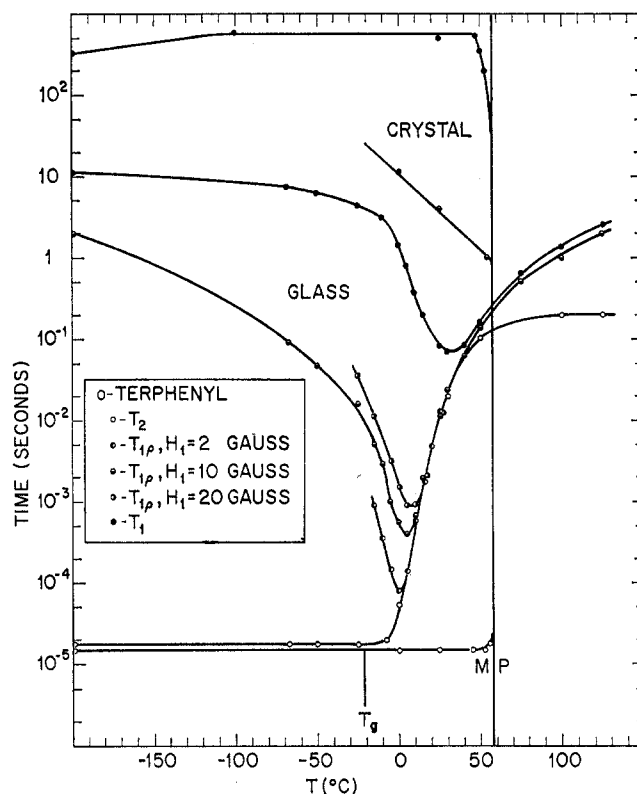


Figure 17. Nmr data for *o*-terphenyl.

rubber²⁰ (Figure 9) are similar in form. Indeed, all nmr studies of glass transitions yield results of this general form.⁴⁴

The example of *o*-terphenyl is particularly instructive because it is easy to maintain this substance in the completely crystalline or completely amorphous states. *o*-Terphenyl is available in very pure form and is not hydrogen bonded or polymeric. Thermodynamic measurements⁴⁵ have been made in both the crystalline and supercooled states, and the entropy difference at the glass transition temperature is found to amount to

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about 6 eu. This entropy implies a prodigious disorder. Any discussion^{37,38} of a state for which the configurational entropy is zero is highly hypothetical.

Furthermore, the manner in which the kinetic parameters, *e.g.*, ν_c , the viscosity or diffusion coefficient, vary as T_g is approached from higher temperatures is independent of the molecular nature of the substance. It is T_g that has the appearance of a transition temperature and not some temperature many degrees below.

Having used the term amorphous, we should be alert to possible misunderstandings. There will always be local order in condensed phases, and the amount of order or disorder is not qualitatively different in the liquid, supercooled liquid, or glassy state. Thus, it may be fruitless to seek a description of glass transition phenomena based on entropy considerations alone. Of course, the variation of the entropy with temperature suggests a second-order transition, and the interest in entropy calculations is understandable.

There is abundant documentation of the empirical fact that long-range motion does not occur at all below T_g . The cessation of long-range motions is the central fact associated with the glass transition. Nmr relaxation studies reveal that some types of local motion do occur below T_g . Methyl and side-group rotations have been discussed above. A more subtle but significant effect is observed in $T_{1\rho}$ curves. These curves vary smoothly through the glass temperature; they do not cut off sharply on the low-temperature side. This invites the suggestion that motions of progressively smaller amplitude and segment size are frozen out as the temperature is lowered.

The depths of the T_1 and $T_{1\rho}$ minima and the magnitudes attained by T_2 at temperatures well above T_g preclude any specialized motions in the rubbery or liquid range. When T_2 is as large as 10^{-3} sec, no restrictions on molecular activity, in the sense of single axis of specific bond rotations, can be supported. The discussion given earlier on this point should be entirely general.

It is difficult to summarize the state of knowledge concerning glass transition phenomena because of the absence of a good physical model. Recognizing the essentially kinetic nature of the processes associated with T_g , it is perhaps not too surprising that a suitable theory has not been developed.

In partially crystalline polymers nmr is particularly

useful for characterizing the chain mobility of the amorphous regions. The amorphous fraction undergoes a glass transition that is similar in character to glass transitions observed in entirely amorphous substances, but the constraints imposed on the molecules in the amorphous regions by the intimately attached crystallites are apparent in the nmr results. T_2 reaches magnitudes of $\sim 10^{-4}$ sec in many polymers well below the crystalline melting point. For example, in branched poly(ethylene) (Figure 10), $T_2 \sim 10^{-4}$ sec at about 65°C. The amorphous T_2 in semicrystalline polymers often gives evidence of going from the rigid state, $T_2 \sim 10^{-5}$ sec, to the rubbery state, $T_2 \geq 10^{-3}$ sec, in two stages. This has been interpreted as the onset of fairly specialized motions at low temperatures and more generalized motions at higher temperatures. However, T_2 does not always exhibit a plateau between the stages, and it has not been possible to make an unequivocal assignment. Also, we know of no specialized motion that leads to calculated T_2 's as long as 0.8×10^{-4} sec, the plateau for polyethylene (Figure 10).

Fiber studies of highly drawn polymers usually give no indication of amorphous orientation. This is an important result as the nmr data would be fairly sensitive to orientation. The morphological implications of this finding have not been developed. The use of nmr relaxation studies in the determination of orientation functions has been described by McBrierty and Ward.⁴⁶

Conclusions

We have seen how nmr relaxation can be used in the study of molecular motion in polymeric systems. Side-group motions, specialized main-chain motions, and glass transition phenomena are all amenable to the method. The molecular information obtained is often uniquely explicit. At this stage of development nmr relaxation has been established, along with dielectric relaxation, as a leading technique for the characterization of polymers.

I am indebted to Drs. W. P. Slichter, D. C. Douglass, and V. J. McBrierty for assistance and encouragement in the development of this material.

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