NUCLEAR MAGNETIC RELAXATION IN POLYTETRAFLUOROETHYLENE, TETRAFLUOROETHYLENE-HEXAFLUOROPROPYLENE COPOLYMER, AND POLYCHLOROTRIFLUOROETHYLENE

by

Ronald Edward Watras

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STATEMENT BY AUTHOR

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APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

Donald C. Hofer
DONALD C. HOFER
Assistant Professor of Chemistry

May 5, 1972
DATE

TO MY WIFE AND DAUGHTERS

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ABSTRACT

Nuclear magnetic pulse methods have been applied in the study of polytetrafluoroethylene, polychlorotrifluoroethylene, and a copolymer of polytetrafluoroethylene and polyhexafluoropropylene. T_1 and $T_{1\rho}$ data have been obtained as a function of temperature. The results give an interpretation of the molecular motion which in the case of teflon are in accord with previous studies using both nuclear magnetic resonance and other mechanical relaxation methods. A qualitative analysis of the molecular motions involved is hypothesized. Finally, this study suggests that $T_{1\rho}$ measurements may be more significant than those of T_1 in molecular motion studies of polymeric solids.

INTRODUCTION

In analyzing the results of the many investigations which have taken place in the last twenty years, one can readily see that high polymers possess considerable molecular motion at temperatures well below their melting point and their glass transition temperature. The character of this molecular motion to a large extent determines many of the properties of the polymers. These motions contribute to the experimentally observed values of specific heat and coefficient of expansion (Sauer 1971). In many cases they manifest themselves by means of mechanical dispersion experiments or through dielectric loss maxima in dielectric dispersion experiments (Sauer 1971) if the groups involved in the motion are polar. Furthermore, if the nuclei of the moving atoms possess magnetic moment, or spin, then any thermally activated molecular motion will give rise to steplike changes in line width or second moment studies of nuclear magnetic resonance lines, as well as give rise to minima in the spin lattice relaxation time temperature relation (Sauer 1971).

Molecular motions in polymeric solids are generally due to three types of relaxation processes. They are usually referred to as δ, for those occurring below $80^{\circ}K$; and either γ or β processes for those occurring between $80^{o}K$ and $300^{o}K$. Generally, the molecular process giving rise to the γ-relaxation arise from motion of the side chains or from motion of short sequences of the main chain in the $100^{o}K$ to $180^{o}K$ temperature range. The relaxations occurring in the $180^{o}K$ to $270^{o}K$ temperature range are usually termed β relaxations. However, these are arbitrary divisions and overlapping frequently occurs (Sauer 1971).

This thesis will not be concerned with the δ process since our studies were conducted in the $-180^{o}C$ to the $+100^{o}C$ temperature range. Also since in this range the polymer under observation remained in the solid state, this paper will confine its attention to molecular motion in the solid state. Furthermore, it is the purpose of this report to attempt to explain molecular motions present in teflon-like polymers, namely in polychlorotrifluoroethylene and tetrafluoroethylene/hexafluoropropylene copolymer.

Solids have their own shape unlike liquids or gases which assume the shape of their container, and since solids do not generally flow, the molecular motion involved is limited. Furthermore, the motion of molecules in a solid must be confined and is in many cases a vibration, oscillation, or a hindered rotation about a fixed point. However, in this thesis we are interested in motion other than that of a simple vibration.

Depending on the polymer structure and whether or not it is symmetrical, the γ-processes are usually associated with twisting or reorientational motion of several CH_2 or equivalent chain groups between temperatures ranging from $100^{o}K$ to $240^{o}K$. On the other hand, β-relaxations are usually associated with twisting or reorientational motions of polar side chains between temperatures from below $200^{o}K$ to $300^{o}K$ (Sauer 1971). Other molecular motions in the temperature range above $300^{o}K$ are not discussed in this thesis since they occur beyond the temperature range reported here.

Non-NMR Methods

Early non-NMR studies of polymers were conducted to determine molecular stiffness by either thermodynamic methods or relaxation methods. The relaxation methods used, employed the application of either a mechanical force or an electromagnetic field to the polymer under consideration. Most common were dielectric dispersion methods, which applied an electric field to a sample causing the dipoles in the sample to align themselves with the field. The mechanical information derived from this method can give results which when fitted with an appropriate model correlate well with such properties such as tacticity, the arrangement of atoms in polymers; crystallinity, the symmetrical internal structure of polymers; and the dynamics of molecular motion in polymers.

Degree of Crystallinity

The use of these non-NMR methods to study crystallinity were successful, because for most polymers the mechanical properties are directly related to the fraction of the polymer which is crystalline, i.e., the degree of crystallinity. That is to say, the distinct differences in the mechanical properties noted depend on whether the polymer regions studied were crystalline or amorphous. This is especially true if the amorphous regions are above their glass temperatures.

Also, polymer chemists theorized that polymers could never become 100% crystalline because the portions of the molecules in amorphous regions would become strained, and this strain would prevent any further crystallization (Miller 1966). Thus many experiments on the same polymer, which have been reported in the literature by different researchers, could easily give different results depending on the percentage of crystallinity of the polymer.

In addition, a review of the literature shows that the techniques used for the determination of degree of crystallinity, which include x-ray diffraction, calorimetry, and infrared spectroscopy, give results that are not always in agreement. This is due to the fact that some methods are more sensitive to certain types of motions than other methods are. This should be kept in mind when NMR techniques are compared with the non-NMR techniques.

Molecular Motion

In summary of the non-NMR methods, one finds that efforts to physically characterize polymers have proceeded via the establishment or definition of a number of properties, such as tacticity or crystallinity. In the case of tacticity, efforts are made to determine whether or not other methods, can be correlated with the relative degree of tacticity obtained in mechanical measurements. Researchers tried to do every physical measurement that they could and determine if they correlated with anything. Thus, prior to the advent of NMR methods the properties were not related to molecular motion, even though individual motion studies were conducted. However, these studies still had their limitations, i.e., dielectric dispersion methods have been restricted to polymers such as nylon with polar groups. Thus, in studying polymers such as polyethylene and polytetrafluoroethylene, i.e., teflon, which do not have any appreciable polar groups, this method is of little value. This brings us to the NMR methods which especially for molecular motional studies show their importance.

NMR Methods

Nuclear magnetic resonance, NMR, spectroscopy has been quite important in the study of polymers in the last fifteen years. For the sake of this paper we will divide NMR studies into two classes, the continuous wave and the pulse methods. Since the form, width, and second moment of an NMR line depend on the structure of the chain and the movements of portions of the chain in a solid, they must ultimately be related to such empirically physical properties as tacticity and crystallinity. In some cases the degree of crystallinity has been perceived through second moment studies. Also, by noting the change in widths of a line with temperature, it has been possible to characterize molecular motion in a polymer.

Degree of Crystallinity

The literature contains the results of many research studies concerned with determining the degree of crystallinity of polymers. Early studies by Wilson and Pake (1953a, -b) showed that over a definite temperature range the NMR line of ^{1}H in polyethylene and ^{19}F in polytetrafluoroethylene has a structure which is characteristic of a two phase system.

In determining the degree of crystallinity the results of the NMR method compared with x-ray methods were less than 2% of each other and the NMR method had the advantage of better reproducibility and insensitivity to orientation, (Slonim and Lyubimov 1970). Comparison of the other non-NMR methods, i.e., infrared spectroscopy and density methods also were in good agreement. There were NMR cases which did not compare favorably with non-NMR results, but most of these could be explained (McCall, Douglass, and Falcone 1967; Wilson and Pake 1957; and Slichter 1958). One explanation attributed the differences to the degree of crystallinity of the samples. Another was in the methods themselves, in that, x-ray, specific volume, and NMR methods measure different physical values. X-ray methods establish the degree of order. Specific volume depends on density. NMR results depend not only on the position of groups in the polymer, but also the character of the intermolecular motion. Thus, a complex NMR line may be due to atoms of the same element being present in two phases in the system with the tacticity or degree of crystallinity of the two phases being different. The crystallinity of the two phases may be determined from the ratio of the areas of the components under the complex line (Slonim and Lyubimov 1970).

Molecular Motion

As investigation of polymers by NMR methods continued, a correlation between the different properties of polymers and the molecular motion in the polymer became evident. Thus, the degree of crystallinity is ultimately explained by molecular motion. Also, the mechanical and physicochemical properties of polymers are largely determined by the character of the molecular motions of individual groups. Thus, the justification for using NMR techniques is evident, and in fact, most of the papers on NMR in polymers are concerned with the study of molecular motion in polymers through the temperature dependence of the form, width, or second moment of the line.

The following is a general review of some of the molecular motion accomplishments of continuous-wave NMR studies as may relate to the pulse techniques discussed in this paper. For instance, studying the temperature dependence of the form of the NMR line makes it possible to interpret the character of the intermolecular forces which determine molecular mobility in a polymer. Also, second moment studies are valuable because the experimental results obtained can be compared with theoretical results calculated for a rigid structure. The change in the second moment with temperature makes it possible to perceive the motions of the main chain and side groups of the polymer. Even if the NMR line is complex, it is possible to calculate separately the second moment for the narrow and broad components of the line and compare them with theoretical values (Slonim and Lyubimov 1970). Further information on the character of the molecular motion in a polymer can be obtained by either; one, studying a polymer with two forms of magnetic nuclei usually hydrogen and fluorine, and comparing the temperature dependence of the line width and second moment for both nuclei, or secondly, by the use of isotopic replacement, i.e., deuteration. Still more information can be obtained by studing the temperature dependence at different pressures (Slonim and Lyubimov 1970).

Besides using the data obtained to predict the degree of crystallinity and other properties, it is possible to calculate the correlation frequency, and the activation energy associated with the various types of molecular motion in polymeric solids. However, Powles (1960) has shown that the calculation of activation energy from the correlation frequency should be approached with caution. This is because in many cases the molecular motion in a polymer can not be described by means of only one value of the correlation frequency when in fact there may be a spectrum of correlation frequencies.

Pulse Methods

In discussing pulse methods, we will confine ourselves to spin lattice relaxation times and a newer method involving relaxation in the rotating frame. From pulse NMR methods it is possible to accurately determine the relaxation times in polymers. This makes it possible to study molecular motion in more detail than by using only broad line methods. In some cases, molecular weight determinations as well as self-diffusion coefficients can be estimated (Slonim and Lyubimov 1970). The pulse method is further explained in both the theory and the experimental sections.

Literature

Since the literature contains very few experimental studies of $T_{1\rho}$ measurements, it is best to start by reviewing other NMR methods. This is by no means an all inclusive review, but does cover many studies which have led to the development of this report. As early as 1957, Wilson and Pake (1957) reported that teflon had two coexisting phases, one crystalline, the other amorphous and each characterized by their own relaxation times T_1 and T_2. The method used was based on the decomposition of the resonance line to identify the fraction of the crystalline and amorphous regions. These results compared favorably with x-ray techniques. They also used the Bloembergen, Purcell, and Pound (1948) theory to calculate the activation energy.

In 1958 a review by Slichter (1958) suggested that molecular motional studies could explain the degree of crystallinity in polymers and examined the steady-state methods. He also suggested that pulse studies on polymers could be of potential importance in the future.

Nishioka (1959) reported line shapes, line widths, and second moment NMR studies for polychlorotrifluoroethylene which compared favorably with the mechanical, thermal, and electrical properties independently studied by others. However, the report failed to make any conclusions on crystallinity.

Powles (1960) reviewed the broad line NMR methods that had been reported. Even more importantly, was the inclusion of a thorough bibliography on nuclear magnetic resonance studies in polymers.

Another review in the same year by Sauer and Woodward (1960) not only discussed the dependence of molecular motion in a given polymer on composition and temperature using NMR second moment methods, but compared these results favorably with the dynamic mechanical methods.

One of the first reports of pulse methods for polymers was by McCall and Douglass (1963) who reported T_1 measurements for polyethylene. T_1 was measured by means of a $180^\circ - 90^\circ$ pulse sequence, with the 90° pulse coming a time t after the 180° pulse. The time t was varied until the nuclear signal following the 90° pulse is zero, at t_{null}. It can be shown that $T_1 = t_{null}/\ln 2$. The authors concluded that their results were better than the steady-state saturation methods of Wilson and Pake (1957).

Also in 1963, there was a good study of high resolution NMR methods by Bovey and Tiers (1963). However, since high resolution NMR methods deal with the study of solutions and melts, no discussion will be given here other than to state that the results were in good agreement with mechanical as well as other NMR studies.

In an expanded NMR relaxation study, Slichter (1966) discussed multiple relaxations for a series of polymers, (n-α-olefins). His conclusion, that the occurrence of multiple T_1 minima is ascribable to different types of motion that become predominant at NMR frequencies as a function of temperature, is confirmed by the present work.

A low molecular weight NMR study of polychlorotrifluoroethylene was reported in 1968 by Hara et al. (1968). They related many of the properties of polymers to molecular weight. They showed that depending on molecular weight the same polymer had different apparent values for a particular property. In other words, one should refrain from stating that a particular study is or is not in agreement unless the comparision is valid, i.e., the molecular weight distribution is equal in both cases.

Lastly, in 1970, the effect of molecular motion on the second moment of the NMR absorption spectrum was reported for long-chain alkanes. The authors attempted to hypothesize on the molecular mechanisms for the γ process and α process (Olf and Peterlin 1970).

As far as studies of the longitudinal relaxation time in the rotating frame, $T_{1\rho}$, only two papers are discussed. The first studied nuclear magnetic relaxation in polytetrafluoroethylene (McCall, Douglass, and Falcone 1967). In this study using pulse methods, T_1, T_2, and $T_{1\rho}$ data were obtained as a function of temperature. The results were interpreted in terms of molecular motions and correlated with dielectric and mechanical relaxation results.

The second paper by Connor (1970) discussed T_1 and $T_{1\rho}$ measurements in atactic polystyrenes. It is mentioned here since our study is similar in that T_1 and $T_{1\rho}$ data has been obtained even though it is on another polymer.

In conclusion, the nuclear magnetic resonance measurements reported here for polytetrafluoroethylene, teflon, are in good agreement with previous studies (McCall et al. 1967; and Wilson and Pake 1957). This suggests that the data for polychlorotrifluoroethylene and a copolymer of teflon and polyhexafluoropropylene should be of significance. The copolymer has also been cited in the literature as FEP Teflon, perfluorinated-ethylene-propylene copolymer (Schonhorn and Ryan 1969).

THEORY

Detailed information on molecular motions in a polymer are obtained when relaxation times T_1, T_2, and $T_{1\epsilon}$ are measured as a function of temperature. However, since there is still no complete theory of NMR relaxation for such complex systems as polymers, the interpretation of the results is quite tedious. The theory that is used was developed for liquids by Bloembergen, Purcell, and Pound (1948). However, the temperature dependence of T_1 and T_2 from experiments involving polymers differ from the predicted theory. The differences have been explained in some cases by the cooperative character of molecular motions in the samples and in other cases as in second moment studies, by the presence of a broad spectrum of correlation frequencies (Slonim and Lyubimov 1970).

In this study a small radio-frequency magnetic field is applied to a sample whose response is recorded on an oscilloscope, X-Y recorder, or more elaborately by a computor. The rather low sensitivity in the nuclear magnetic resonance experiment is the result of the fact that there is a very small difference in the Boltzmann populations of the $+m_I$ and $-m_I$ spin states. That is if one subtracts the number of spins in one state from the spins in the other state, the difference is on the order of 10^{-5} of the total number of spins. For this reason it is necessary to study bulk samples. Initially, the nuclear spins will be in thermal equilibrium with their surroundings or lattice. Then the populations of the energy levels change as outlined in a simple quantum mechanical description (Slichter 1963).

The applied magnetic field H produces an interaction energy of the nucleus of amount $-u \cdot H$, where u is the total magnetic moment of the nucleus. The total Hamiltonian may be represented as:

$$H = H_{Zeeman} + H_{Pert} + H_{Spin\ Lattice} + H_{Dipole}$$

However, a very simple Hamiltonian can be used as an introduction to understanding resonance phenomena, namely the Zeeman term, since it is always much larger than the other terms anyway, and it is the zero order Hamiltonian for many systems.

$$H_z = -\sum_i \vec{u}_i \cdot \vec{H}_o$$

If we take the field to be H_o along the z-direction, then

$$H = -\sum_i \gamma_i \hbar H_o I_{zi}$$

where the terms are defined as follows:

H_{Zeeman} is the term due to the interaction of the magnetic moments with the dc field.

Pert, i.e., perturbation term, is the term due to the interaction of the oscillating rf field with the magnetic moments,

Spin Lattice incorporates those terms in the Hamiltonian which provide for spin lattice relaxation,

Dipole is the term associated with the dipolar interaction of the nuclei in a fixed solid,

γ = coefficient that is known as the gyromagnetic ratio and is a nuclear characteristic,

$\hbar$ = the reduced Planck constant ($\hbar = h/2\pi$),

H_o = external magnetic field,

I_z = the spin number, spin of nucleus, and may be integer, half integer, or zero, depending on the type of nucleus.

Since only multiples of ($\gamma\hbar H_o$) are allowed,

$$E_m = -\gamma\hbar H_o m \qquad \text{where} \quad m = I,\ I - 1,\ \ldots\ldots,\ -I,$$

or E_m is the quantum mechanical expectation value of the Zeeman Hamiltonian, $\langle I,m_I \mid I_z \mid I,m_I \rangle = m_I$.

The angular frequency w (56.4 MHz for ^{19}F at 14,000 gauss) is related to ΔE by, $\hbar w = \Delta E$, where ΔE is the energy difference between the initial and final Zeeman energies.

Using an alternating magnetic field applied perpendicular to the static field to produce magnetic resonances, and writing the alternating field in terms of amplitude H_x^o, gives a perturbing term in the Hamiltonian of

$$H_{Pert} = -\sum_i \gamma_i \hbar H_x^o I_{xi} \cos wt.$$

The selection rule for transitions is $\Delta m = \pm 1$, also

$$\hbar w = \Delta E = \gamma \hbar H_o$$

or

$$w = \gamma H_o$$

As shown by Slichter and others the above result can be obtained by a classical treatment. In both cases the motion with respect to the laboratory is a fixed vector so that u rotates at an angular velocity with respect to the laboratory giving the angular frequency γH_o which is called the Larmor frequency.

Quantum mechanically the probability of transition up is the same as the probability of the transition down. However, because of the populations of the two levels when a rf field is applied, there are more transitions up than there are down since the lower level is more densely populated. If this were not true, then the resonance would not be observable.

This argument is used to show that nuclear spins are informed of the temperature of the lattice and come into thermal equilibrium with it. After a collection of nuclear spins have been perturbated away from the equilibrium Boltzmann population, they relax back to an equilibrium Boltzmann population. Even though a single time constant does not always describe the trend of nuclear spins toward equilibrium with the lattice, it is used to give a time scale of the process and is given the name spin-lattice relaxation time, T_1.

As shown by Slichter,

$$\frac{dn}{dt} = \frac{n_o - n}{T_1}$$

giving

$$n = n_o + Ae^{-t/T_1}$$

where A is a constant of integration, n_o represents the thermal equilibrium population difference, and T_1 is the characteristic time associated with the approach to thermal equilibrium.

The experimental determination of T_1 can be obtained by realizing that M_z, the total magnetization in the z-direction equals nu. Thus instead of dn/dt we have

$$\frac{dM_z}{dt} = \frac{1 \; (M_o - M_z)}{T_1}$$

It is found that T_1 varies all the way from 10^{-3} seconds in solutions to several hours in low temperature crystals. As shown in the experimental section T_1 can be measured by calculating the time interval from the polarization inversion to the point where the signal amplitude goes through zero.

In an analogous manner $T_{1\rho}$, a longitudinal relaxation time in the rotating reference frame can be measured. In such a system the time dependence of H_1 can be eliminated by using a coordinate system that rotates about the z-direction at frequency w_1. In this system not only H_1, but since the axis of rotation coincides with the direction H_o, H_o will be static as well as H_1. Physically this means that in the rotation frame the moment acts as though it experienced a static magnetic field. Thus the moment precesses in a cone about the effective magnetic field. The magnetic moment that is parallel to the static field initially will then precess in the X-Y plane remaining perpendicular to H_1. For example, if a sample is placed in a coil, initially in thermal equilibrium, there will be an excess of moments parallel to H_o. If a 90^o pulse is applied through the proper adjustment of H_1, and t_w, the wave train of proper duration, the excess moments precess perpendicular to H_o. The moments will produce a flux through the coil which will alternate as the spins precess, resulting in the observation of the induced emf. Since the interaction of the spins with their surroundings causes a decay, the induced emf does not persist indefinitely. This technique for observing free induction decay is a commonly used technique for observing resonances.

However, the method used for our determination of $T_{1\rho}$ differed in that not a single 90° pulse was transmitted after the initial 90°_x pulse, but at time t a 90°_y pulse was transmitted and then after a time 2t another 90°_y pulse was transmitted. The train of pulses at t and 2t after the initial pulse was able to be set so that from a 500 to a 1500 90°_y pulse train could be transmitted.

One of the primary differences between T_1 and $T_{1\rho}$ is the difference in the quanta of energy used to implement the relaxation in the two frames. The essential factor which makes $T_{1\rho}$ sensitive to lower frequencies of motion is simply that lower frequency motions provide small Fourier components or quanta of low energy. Therefore if a measurement requires quanta of low energy to cause the relaxation, it will be more sensitive to the low frequency motions.

Thus, for T_1 measurements the characteristic frequency of motion at the resonant frequency of 56.4 MHz facilitates T_1 relaxation. Whereas in $T_{1\rho}$ relaxation, the characteristic frequency of motion, which is at 56.4 KHz, facilitates $T_{1\rho}$ relaxation. Because the polymers studied are solid and of large molecular weight, it is expected that these low frequency motions will be rather prominent. Therefore, $T_{1\rho}$ measurements are more sensitive due to the more abundant low frequencies of motion being present.

A typical expression for a $T_{1\rho}$ measurement is as follows (Abragam, 1961, p. 520):

$$\frac{1}{T_{1\rho}} \simeq \frac{2}{3} \gamma^2 \left|\vec{H}_1\right|^2 \frac{\tau_c}{1 + w_1^2 \tau_c^2}$$

or

$$T_{1\rho} \simeq \frac{3}{2 \gamma^2 \left|\vec{H}_1\right|^2} \left(\frac{1 + w_1^2 \tau_c^2}{\tau_c}\right)$$

where τ_c is the correlation time, a time characterictic of the random motion. It is a measure of the time taken for the field H(+) to lose memory of a previous value (Pople 1959). H_1 is the magnetic field in the rotating frame, and γ and w are as previously defined.

The $T_{1\rho}$ expression associated with relaxation in the rotating frame is in general analogous to the T_1 expression in the laboratory frame. The differences are that the H_1 field is in one case the dc field and in the other case it is the rf field in the rotating field; the characteristic absorption frequencies in T_1 is w_o or γH_o, while in $T_{1\rho}$ it is w_1 or γH_1, which are much smaller; and the correlation frequencies, τ_c, may not be the same in T_1 as in $T_{1\rho}$. The above expression is true for one mechanism of relaxation.

One other time constant T_2, the transverse or spin-spin relaxation time is the characteristic time in which individual precessing nuclei are out of phase with each other. This corresponds to the decay rate of M_x and M_y the transverse components of magnetization. Since no T_2 relaxation measurements have been made for this report, further studies may give still further insight to the motions involved.

EXPERIMENTAL

Because it seems quite obvious from a survey of the literature found in the introduction and a survey of the theoretical aspects of the literature found in the theory section, the relationship between the physical properties of polymers and the microscopic nature of molecular motion is rather evasive. This is particularly true because molecular motion is not very well understood in polymeric solids. With this in mind instead of simply proceeding as previous investigators to find an empirical relationship between the results of the measurements and the physical properties determined by another method, the purpose of this report is simply to understand as well as possible in a preliminary fashion the motions that take place in polymeric solids.

Although samples that were not particularly well characterized in terms of their physical properties, such as molecular weight distribution, crystallinity, and purity were used in this study, they were not necessary in this preliminary study. The object of this paper was to determine whether or not a series of measurements between T_1 and $T_{1\rho}$ would establish the point that the $T_{1\rho}$ measurement can be more sensitive to the motions that take place in polymeric solids. As can be seen in the discussion section, this is indeed borne out.

The nuclear magnetic resonance spectrometer magnet was a commercial one manufactured by Varian Associates. However, all other components were designed and constructed by Dr. Donald C. Hofer, Professor of Chemistry at The University of Arizona. The only exceptions were my construction of a transmitter and oscillator designed by Dr. Hofer. A multiple pulse generator is the heart of the system (Hofer)

It is completely solid state and was instrumental in the T_1 measurements. Using a storage oscilloscope the pulse time was varied until there was zero magnetization. Instrumentation was so precise that a change of $t = \pm .02$ seconds was definitely noticeable on the oscilloscope. The calculation of T_1 was based on the following (Abragam 1961):

$$M_z = -M_o(1 - 2e^{-t/T_1})$$

At saturation $M_z = M_o$ equals zero magnetization.

$$\frac{M_z}{M_o} = -1 + 2e^{-t/T_1}$$

Taking ln gives:

$$T_1 = t/\ln 2$$

The apparatus was adjusted so that an initial 180^o_x pulse was transmitted followed at time t by a 90^o_x pulse.

The time between pulses was varied until there was zero magnetization. For $T_{1\rho}$ measurements the nuclear magnetization was aligned with the rotating field at the beginning of the pulse as explained in the theoretical section. Then the pulse generator was set up such that after an initial 90°_{x} pulse, at time t a 90°_{y} pulse was transmitted and then after a time 2t another 90°_{y} pulse was transmitted. The pulse generator was adjusted so that from a 500 to 1000 90°_{y} pulse train was transmitted after the initial 90°_{x} pulse.

The signal was detected by the receiver and stored on a Fabri-Tek computor. Then the exponential wave form was plotted on a X-Y recorded. From the plot (see Fig. 1, 2, 3, and 4) $T_{1\rho}$ was calculated. In the experiments reported here t was 8×10^{-6} seconds in all cases. Other t's were tried, but 8×10^{-6} seconds gave results which permitted more accurate calculations. Thus by knowing t and the number of cycles $T_{1\rho}$ was calculated for each temperature. As an example, choosing figure 2, copolymer at 0°C, the number of pulses half through the exponential curve equals 79.0 pulses, which gives $T_{1\rho}$ as follows. Since at that point (McCall et al. 1967)

$$\frac{V(t)}{V_o(t)} = -0.5 = e^{-t/T_{1\rho}}$$

and,

$$T_{1\rho} = \frac{t}{\ln 2}$$

where t equals the number of pulses in the pulse train

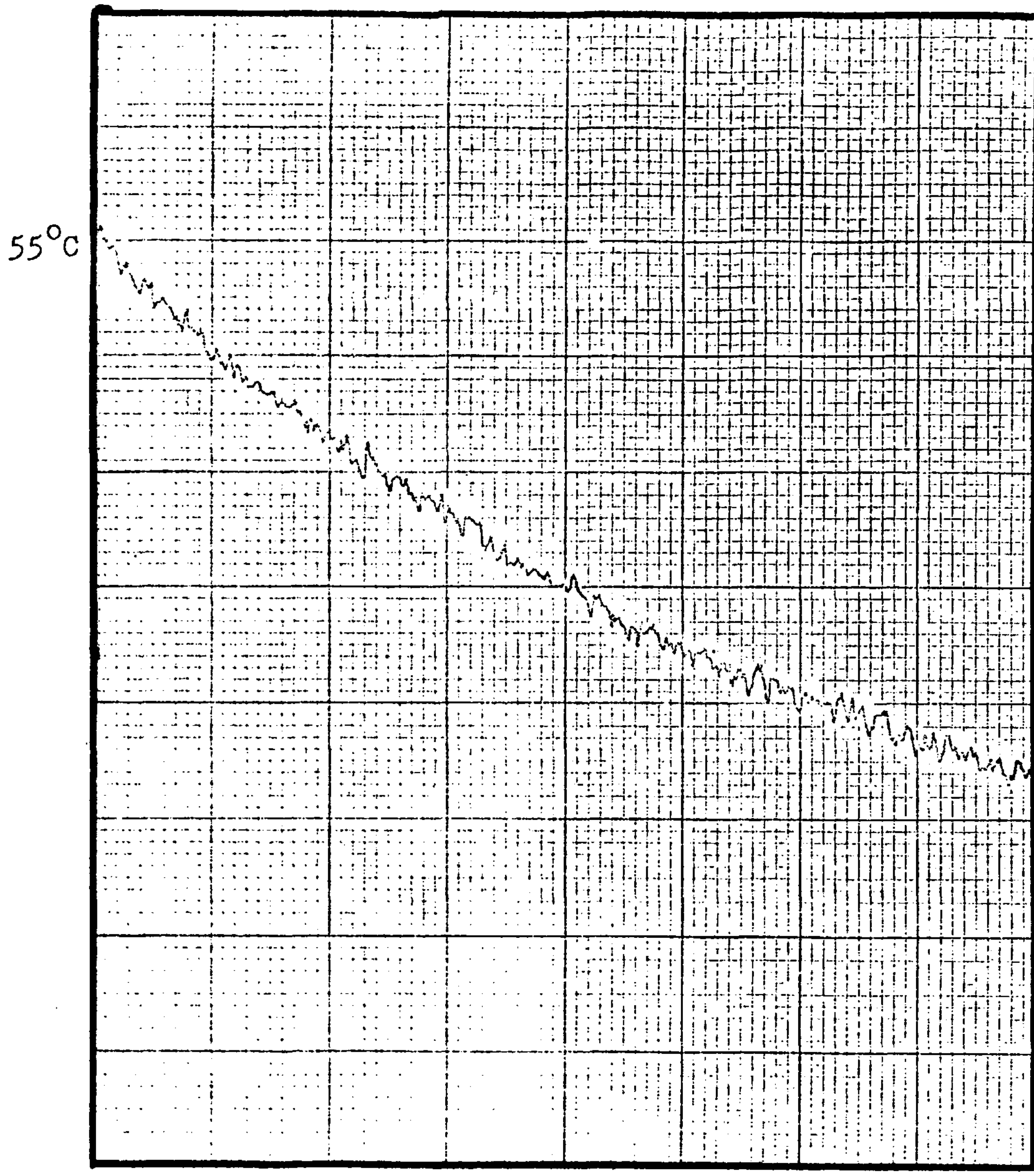
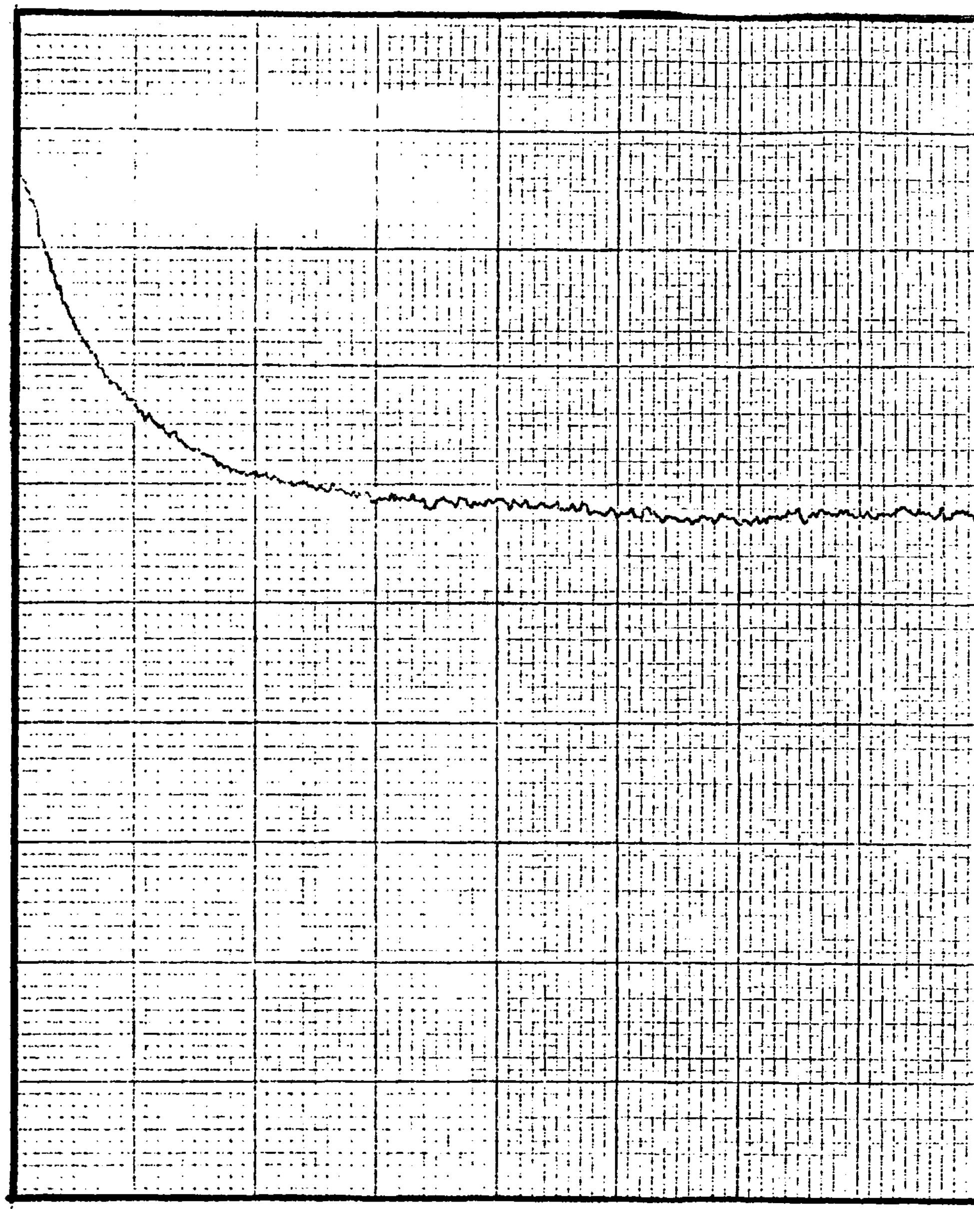


FIG. 1. Copolymer $T_{1\rho}$ Exponential Decay at 55°C

0°C



1400 cycle pulse train at 8×10^{-6}↑

FIG. 2. Copolymer $T_{1\rho}$ Exponential Decay at 0°C

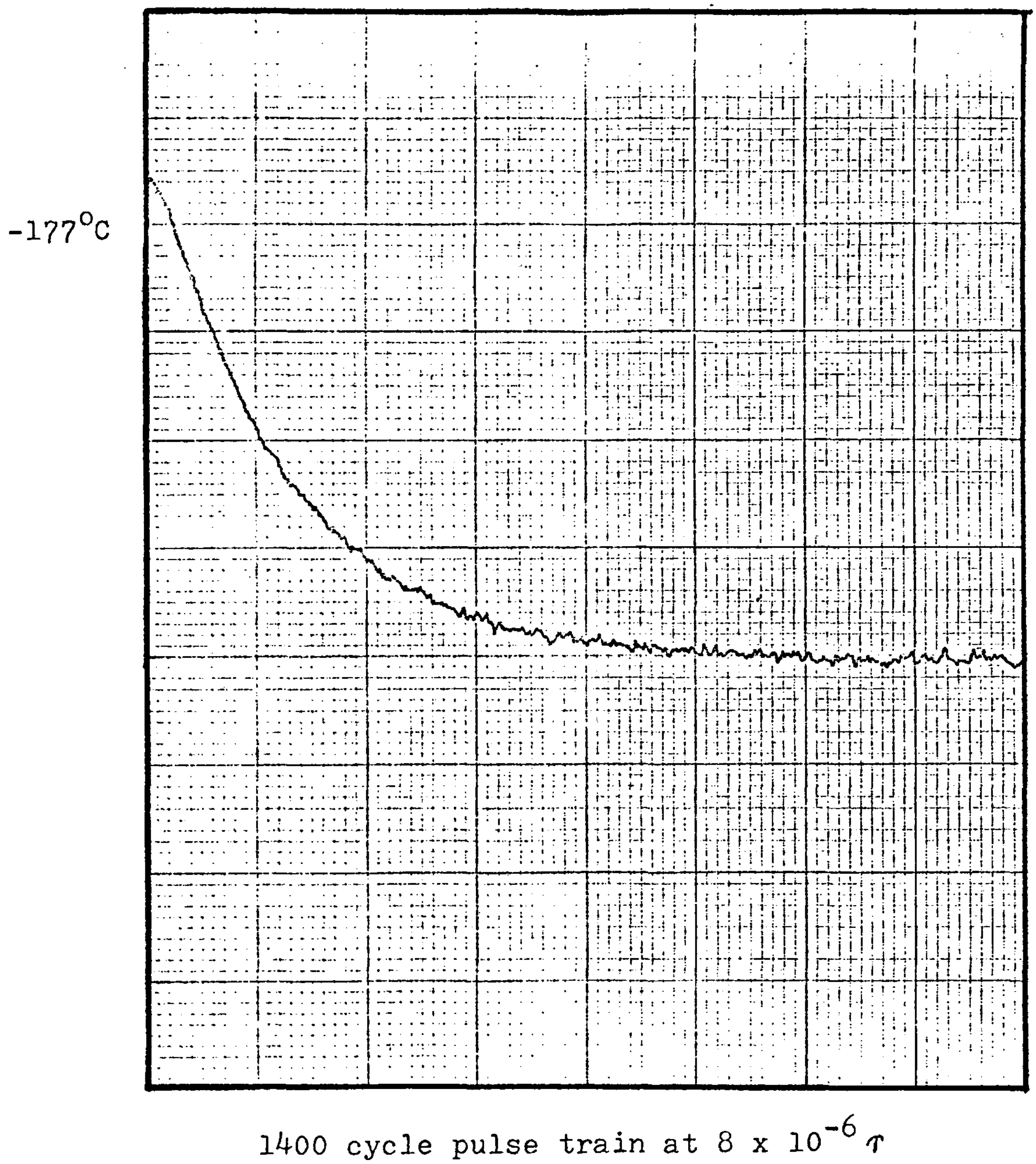


FIG. 3. Copolymer $T_{1\rho}$ Exponential Decay At -177°C

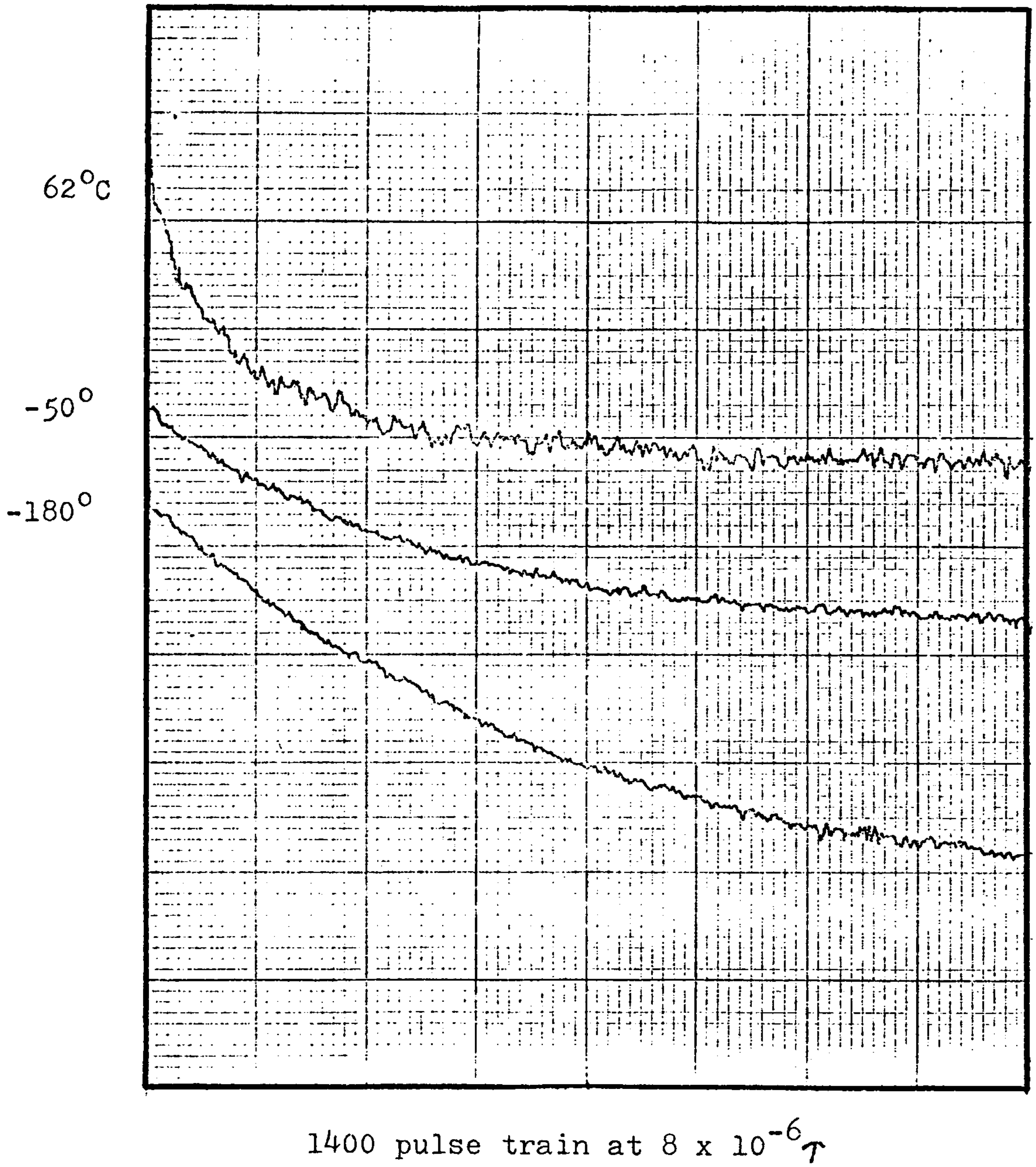


FIG. 4. KEL-F $T_{1\rho}$ Measurements at Three Temperatures

at that point times 8 x 10^{-6} seconds/pulse. Thus,

$$T_{1\rho} = \frac{79.0 \times 8 \times 10^{-6} \text{ sec}}{0.693} = 9.12 \times 10^{-4} \text{ sec},$$

which is shown on figure 9, p. 39.

For both T_1 and $T_{1\rho}$ low temperature measurements, a special probe designed by Dr. Hofer was used. Surrounding the sample holder is a dewar through which nitrogen gas cooled by liquid nitrogen is passed. A copper-constantan thermocouple was used to measure temperatures at the sample. Each temperature was maintained for approximately ten minutes prior to taking a measurement. For higher temperatures the same dewar probe was used, but the nitrogen gas was heated by a heater coil prior to reaching the sample. The accuracy of the temperature measurements was better than $\pm$ 0.10°C. Duplication verified the measurements.

As previously stated the teflon and KEL-F samples were of unknown crystallinity and purity. The copolymer was a finely divided power, DuPont 13268 - 71 - 3. The powder was heated and the air evacuated to form a sample. All samples were machined to fit in a 5 mm glass sample holder. All were approximately 1.5 cm long.

RESULTS AND DISCUSSION

I have measured spin lattice relaxation times in the laboratory frame, T_1, as well as spin lattice relaxation times in the rotating frame, $T_{1\rho}$. A comparison of the T_1 curves as a function of temperature indicates that the motion going on in the three solid polymers discussed here are qualitatively different.

In the case of teflon the curves appear to be qualitatively the same as prior T_1 studies (McCall et al. 1957; and Wilson and Pake 1957) even as to the duplication of the abrupt transition at about 293°K as shown in figure 5.

It is important to mention that it is not the intention of this paper to make detailed comparisons with previous results but rather qualitative comparisons. One reason is that in this study the samples are not well characterized. However, since this is a preliminary study to show that spin lattice relaxation measurements in the rotating frame may provide more information about the motion in a particular sample than spin lattice relaxation measurements in the laboratory frame, the use of these samples is justified.

Figure 6 shows the spin lattice relaxation times for the copolymer, perfluorinated-ethylene-propylene. This

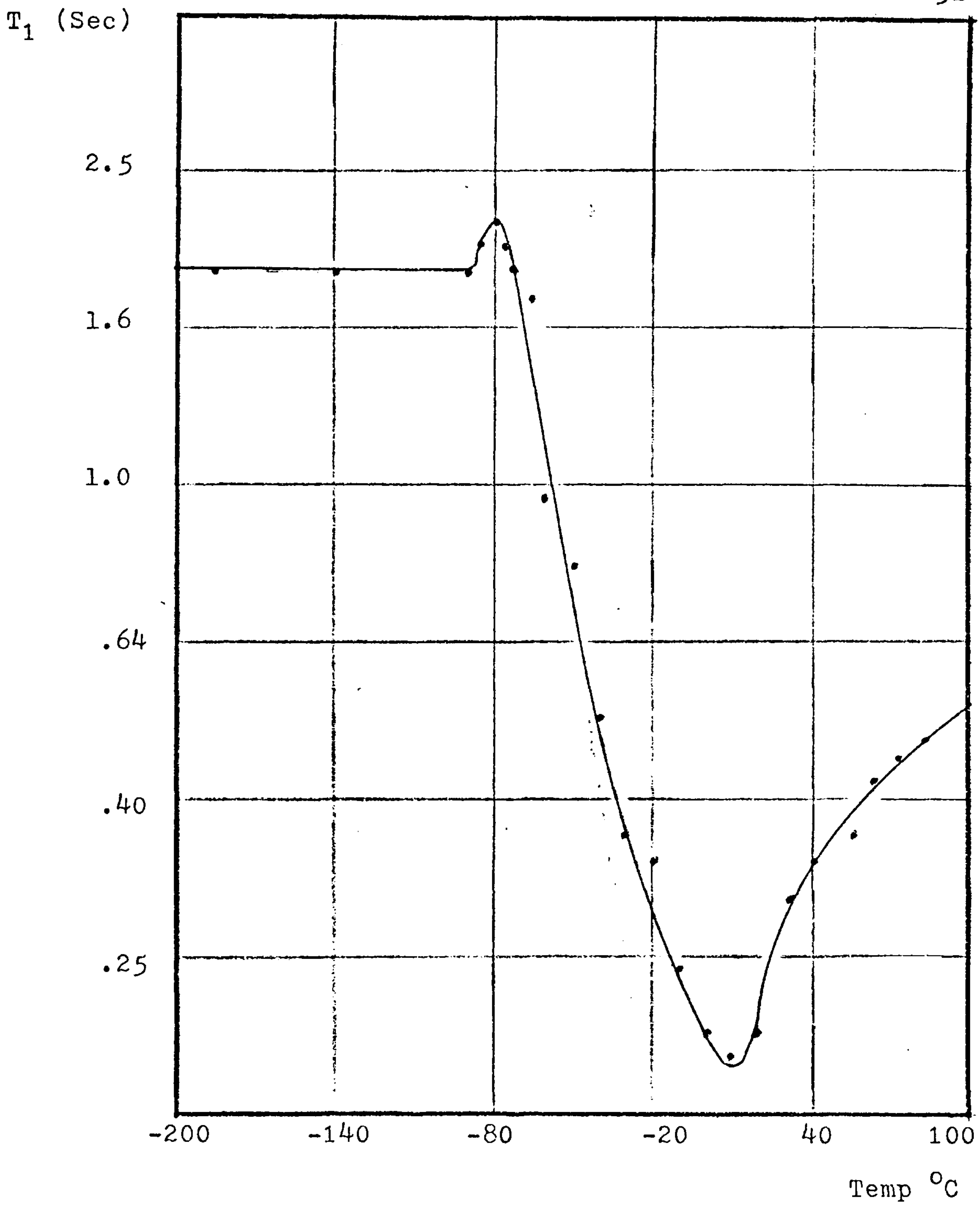


FIG. 5. T_1 vs. Temp of Teflon

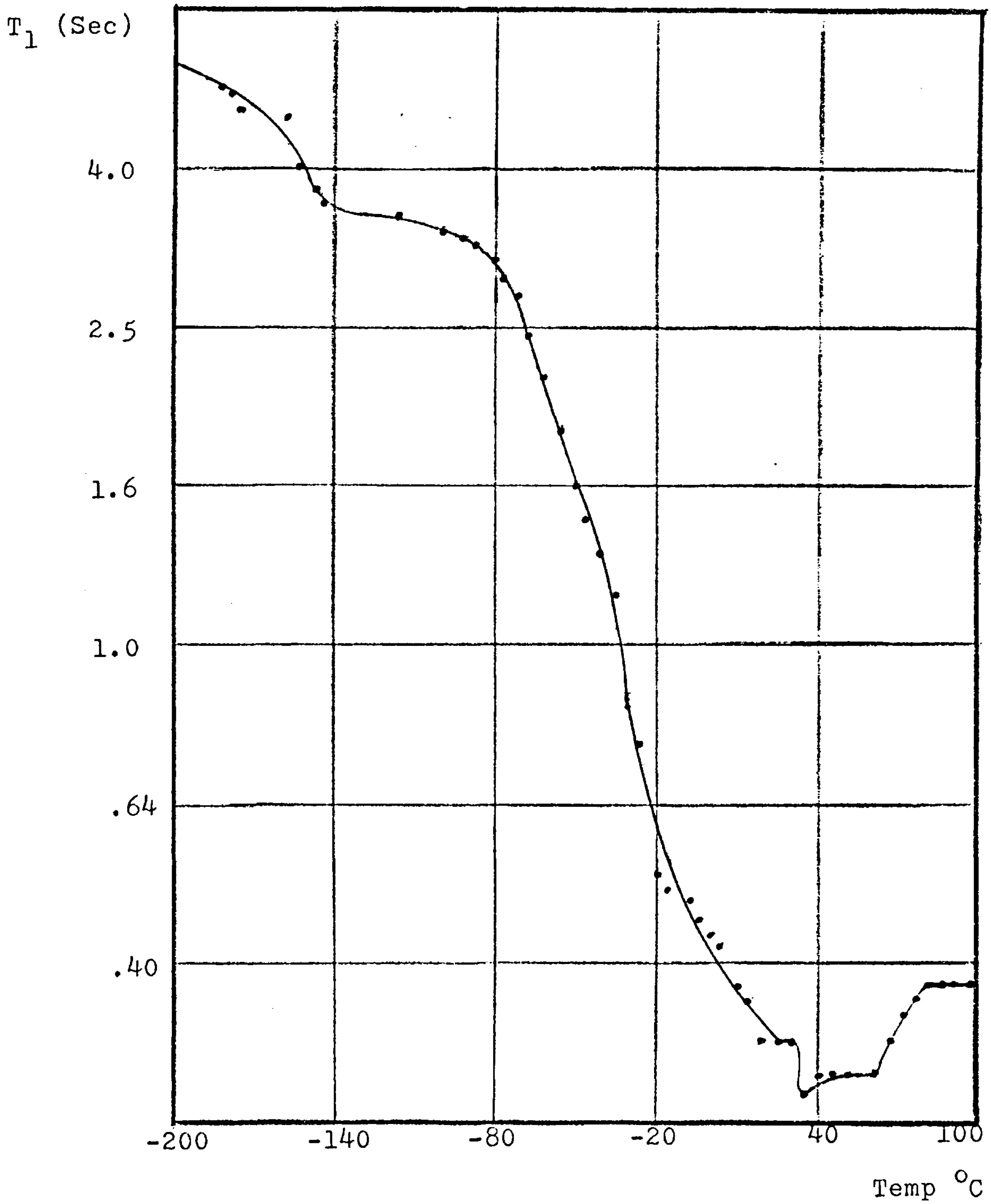
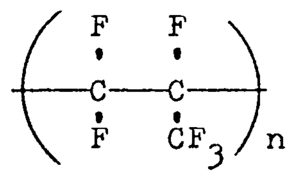


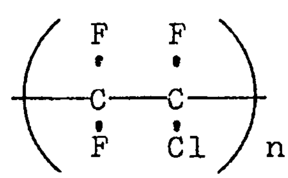
FIG. 6. T_1 vs. Temp of Copolymer

is prepared by thermal degradation of the polymers tetrafluoroethylene and perfluoroalkenes (Dixon 1969).
The hexafluoropropylene polymer is different from teflon mainly in that now the polymer is branched:



As can be seen the motions are quite different then teflon and even at -180°C studies have shown that for teflon the polymer is not yet rigid (Filipovich, Knutson, and Spitzer 1965). No comparisons can be made since there do not appear to be any other studies of this copolymer in the literature.

Figure 7 gives the T_1 times as a function of temperature for polychlorotrifluoroethylene, PCTFE, known commercially as KEL-F. The shape and structure of the curves are characteristic of the type of motion that is going on in the polymeric solids. As can be seen there is again a difference in motions as compared with teflon, especially at



higher temperatures where there do not appear to be any major transitions. All relaxation times are larger than for teflon. There have been other studies done on KEL-F. However, these

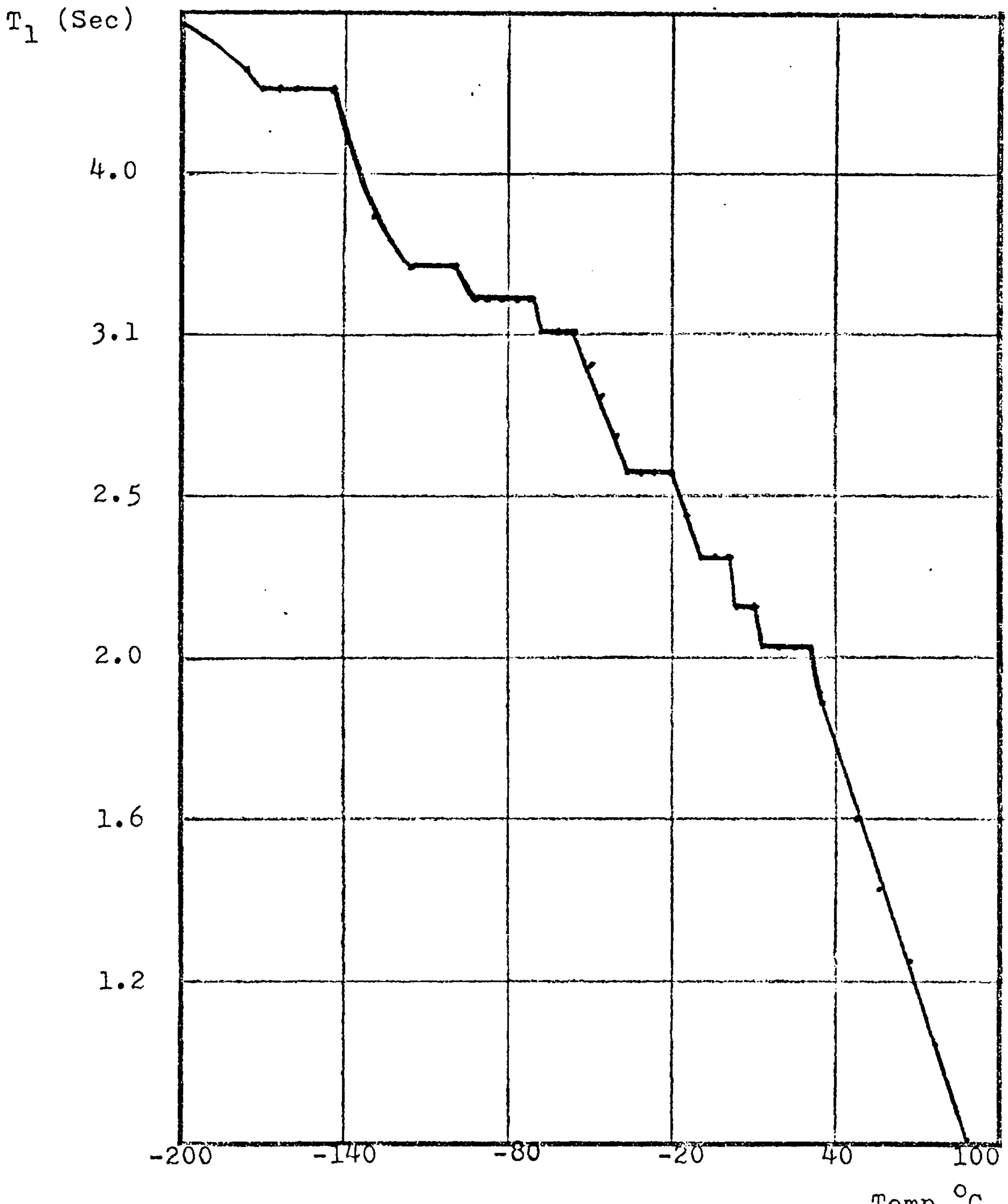


FIG. 7. T_1 vs. Temp of KEL-F

have studied the polymer by mechanical methods (Baccaredda and Butta 1960; and Crissman and Passaglia 1966) or the second moment approach to nuclear magnetic resonance (Hara et al. 1968; and Nishioka 1959).

However, since these prior studies did not involve any measurement of T_1 or $T_{1\rho}$, it is not really valid to compare them with ours. In these prior studies an attempt was made to produce a model to show a correlation not a direct measurement of different types of motion taking place in the polymer. This correlation was made through the study of line shape, line width transition, and mechanical relaxation in crystalline polymers. However, in our study one can make comparisons of spin lattice relaxation times for different polymers in order to qualitatively describe the motion. In making this comparison of KEL-F and teflon, one notices that KEL-F have no minima but does have many observable steps while teflon has one minimum in the T_1 as a function of temperature curves.

Figures 1, 2, 3, and 4 are sample plots taken off the X-Y recorder after being stored in the Fabri-Tek for $T_{1\rho}$ measurements. As mentioned in the experimental section the calculations of $T_{1\rho}$'s as a function of temperature were made from these plots. No curve fitting program was used and it can be seen that some of the curves have less of an exponential shape than others, giving support to the hypothesis that more than one type of motion is taking place.

Figures 8, 9, and 10 show the $T_{1\rho}$'s, the longitudinal relaxation time in the rotating frame, for teflon, copolymer, and KEL-F respectively. Again for teflon there is very good agreement with the literature except that the relaxation curves were not fit into multiple relaxations. This is not an experimental limitation since it is hoped that a computor fitting program can be constructed to resolve the data at a later date. McCall et al. (1967) gives minimum values of 0.3 and 1.0 milliseconds which compare with the values reported here of about 0.35 and 0.85 msec at the same respective temperatures of -50° and $+50^{\circ}C$. The rotating frame decays give further support to the presence of other time constants involved in the molecular motions, as well as supporting our premise that $T_{1\rho}$ measurements can be more pronounced than T_1 measurements, since the minima are more pronounced. As stated in the theory section this is because the motion going on is of the more abundant lower frequency type which facilitate $T_{1\rho}$ relaxation.

There have not been reported in the literature any $T_{1\rho}$ studies on the copolymer. Our $T_{1\rho}$ measurements, figure 9, show a well defined minimum at about $-35^{\circ}C$ and perhaps the onset of another at a temperature higher than that measured in this study. Again as in teflon the minimum is much more pronounced for the spin lattice relaxation measurements in the rotating frame.

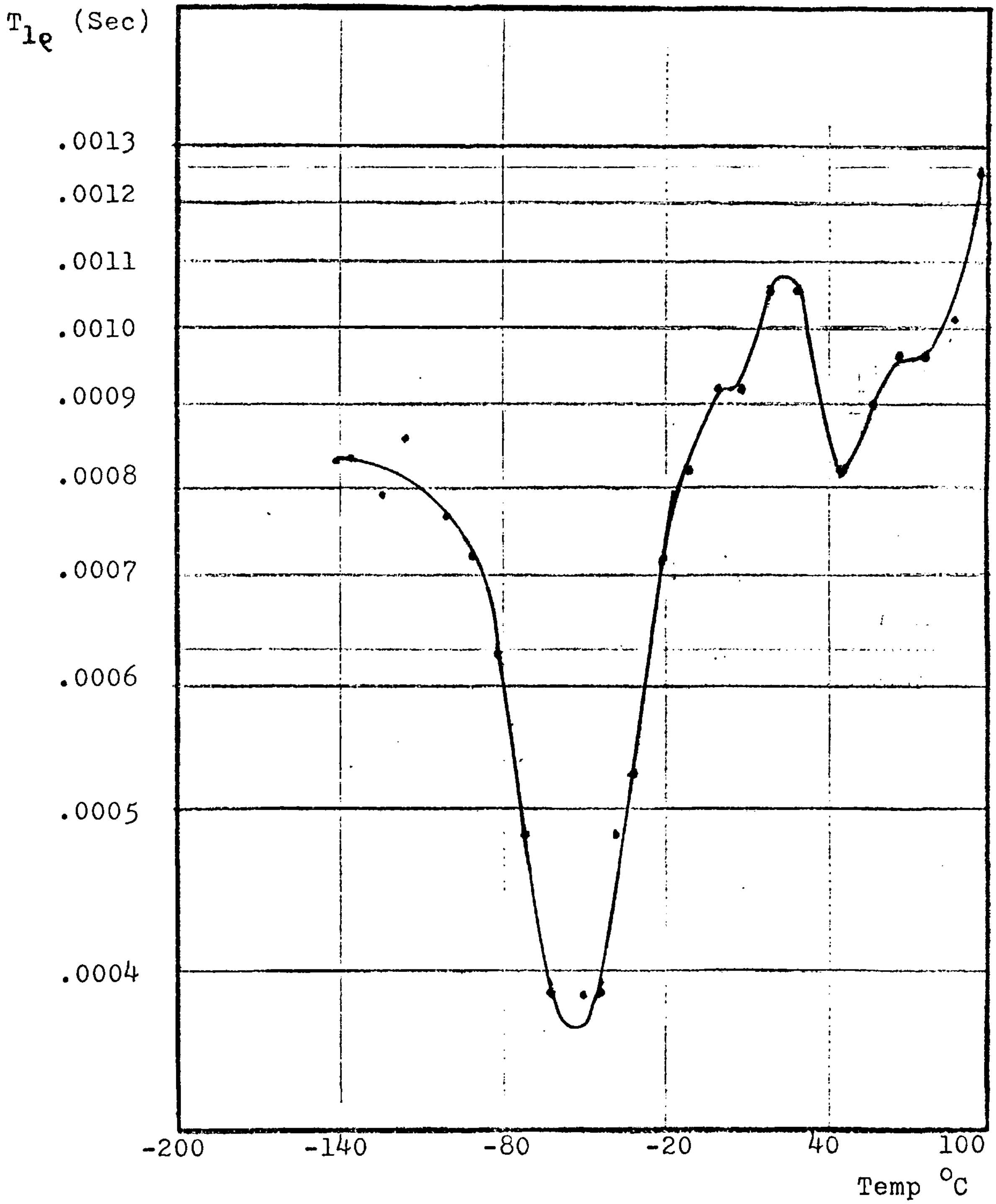


FIG. 8. $T_{1\varrho}$ vs. Temp of Teflon

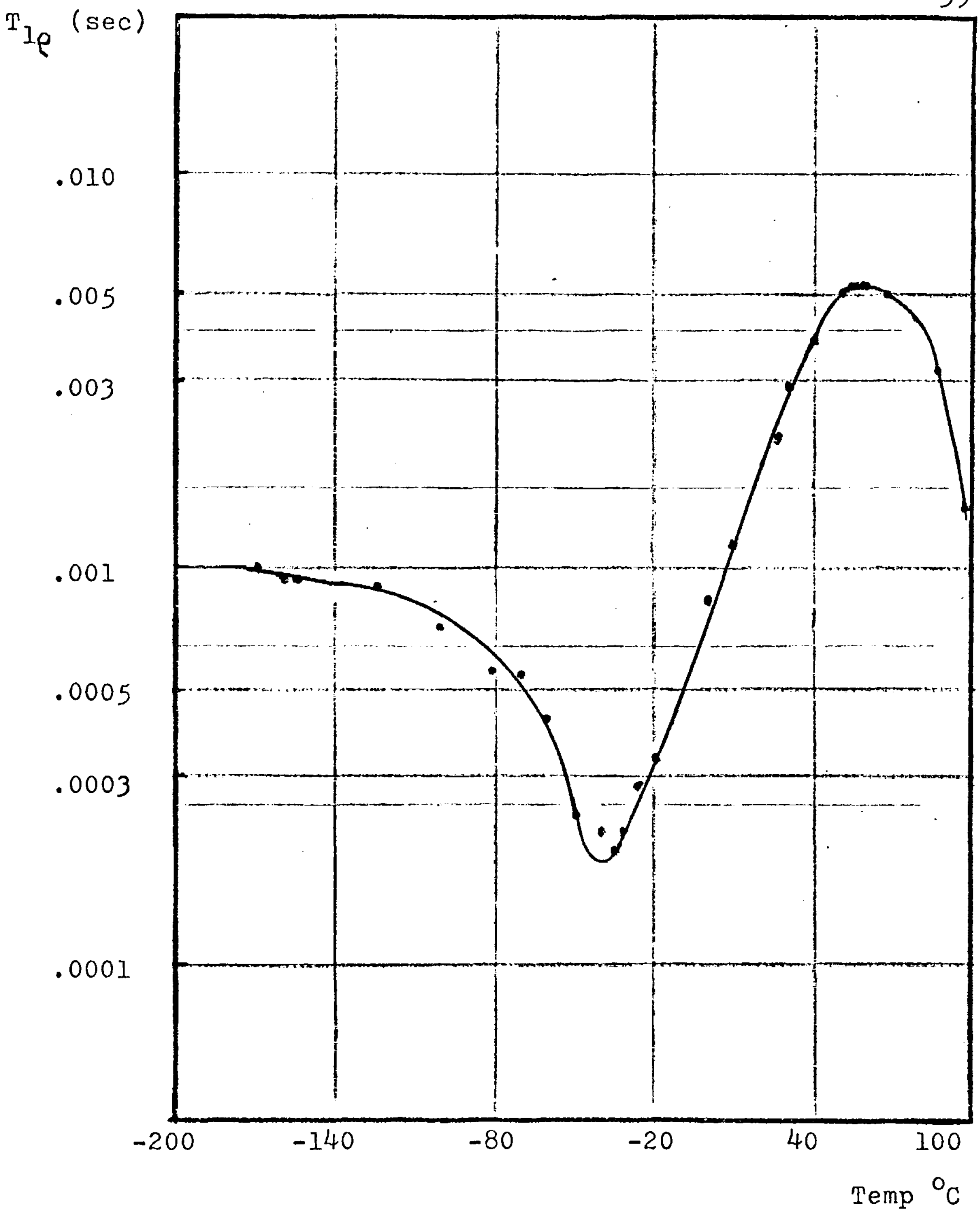


FIG. 9. $T_{1\rho}$ vs. Temp of Copolymer

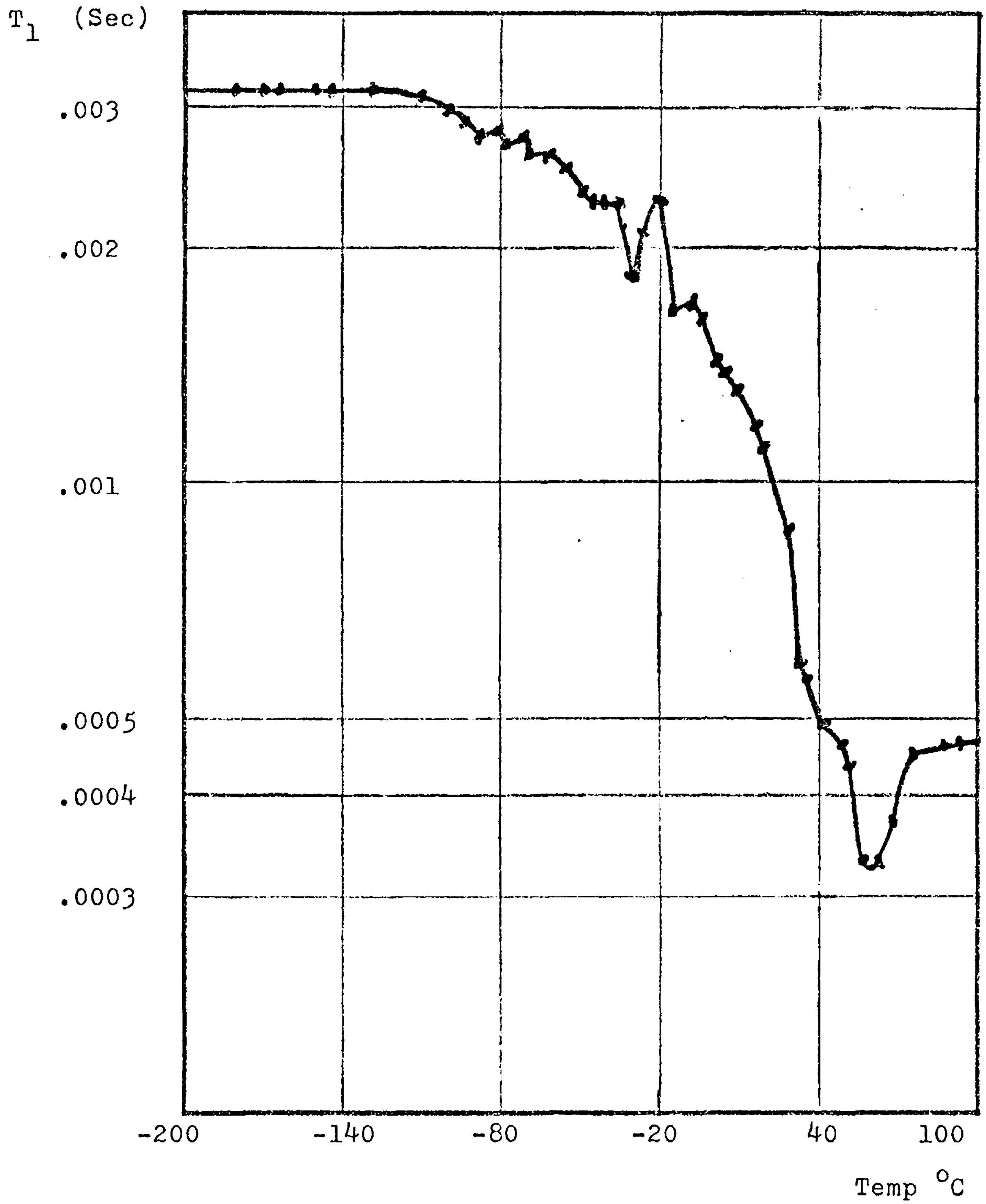


FIG. 10. $T_{1\rho}$ vs. Temp of KEL-F

As with the copolymer, there have not been any $T_{1\rho}$ studies of KEL-F reported in the literature. Figure 10 when compared with figure 7 shows the most significant difference between the T_1 and the $T_{1\rho}$ measurements. As previously mentioned, figure 10 shows one well defined minimum as well as definite changes at lower temperatures which could very well be minima associated with the steps shown in figure 7. This again readily supports a contention for the future use of $T_{1\rho}$ measurements.

Correlation Times

Using the equation from the theoretical section (Abragam 1961):

$$T_{1\rho} = \frac{3}{2\,\gamma^2 \left|\vec{H}_1\right|^2} \left(\frac{1 + w_1^2\,\tau_c^2}{\tau_c}\right)$$

consider the following three cases.

(1) $\tau_c < 1/w_1$, or $\tau_c^2 w_1^2 \ll 1$

then $T_{1\rho} \simeq \dfrac{3}{2\,\gamma^2 \left|\vec{H}_1\right|^2 \tau_c}$

(2) $\tau_c \simeq 1/w_1$

then $T_{1\rho} = \dfrac{3}{2\,\gamma^2 \left|\vec{H}_1\right|^2} \left(\dfrac{1 + w_1^2\,\tau_c^2}{\tau_c}\right)$

(3) $\tau_c > 1/w_1$, or $w_1^2 \tau_c^2 \gg 1$

then $T_{1\rho} \simeq \frac{3}{2}\tau_c$, since $w_1 = -\gamma H_1$, or $w_1^2 = \gamma^2 H_1^2$.

If we make a plot of $T_{1\rho}$ for some correlation time we find:

Region 1: $\tau_c < 1/w_1$

$$\frac{\partial T_{1\rho}}{\partial \tau_c} = -\frac{3}{2\,\gamma^2 |\vec{H}_1|^2\,\tau_c^2}$$ where

the slope is negative and gets smaller as τ_c gets larger.

Region 2: $\tau_c \simeq 1/w_1$,

$$\frac{\partial T_{1\rho}}{\partial \tau_c} = \frac{3}{2\,\gamma^2 |\vec{H}_1|^2}\left(\frac{-1 + w_1^2\,\tau_c^2}{\tau_c^2} + 2w_1^2\right)$$

Here, as τ_c increases and as $\tau_c w_1 \rightarrow 1$, the slope gets less until at slope = 0,

$$2w_1^2\tau_c^2 = +1 + w_1^2\tau_c^2$$

or $$1 - w_1^2\tau_c^2 = 0$$

which gives, $$(1 + w_1\tau_c)(1 - w_1\tau_c) = 0$$

Upon taking the more realistic $(1 - w_1\tau_c) = 0$, which gives a physical meaningful result because the correlation time and frequency are both positive quantities, $w_1\tau_c = 1$, or $\tau_c = 1/w_1$, which says that when the slope is zero the correlation frequency, τ_c, is equal to one over the characteristic frequency in the rotating frame, w_1, which is about on the order of 10^3 less than the characteristic frequency in the laboratory frame, w_o. The factor of 10^3 less can be shown approximately as follows:

$$H_1 = 1/\text{total time} \times (\text{sum of the fields during times})$$

$$H_1 = 1/9 \times (60 + 0) \cong 7,$$

$$w_1 = \gamma H_1 = \gamma \cdot 7 \text{ gauss, but since}$$

$$w_o = \gamma \cdot 10^4 \text{ gauss, there is a factor of } 10^3.$$

Region 3: $\tau_c > 1/w_1$,

$$\frac{\partial T_{1\rho}}{\partial \tau_c} = \frac{3}{2}, \text{ which is positive.}$$

These three regions give a minimum at a particular temperature. The correlation time may be related to temperature for a thermally activative process as follows:

$$\tau_c = \tau_o e^{-\Delta E/kT} \qquad \text{(Powles 1960).}$$

Therefore if a minimum appears on a curve we know that at that minimum which is associated with a particular temperature, the correlation time is equal to one over the characteristic frequency, i.e., $\tau_c = 1/w_1$.

Thus for the three polymers studied here the minimum at a particular temperature gives a corresponding correlation time. Figure 8 shows two minima which according to our interpretation suggests there should be two correlation times. This supported for teflon in the literature by Slichter

(1966) and McCall et al. (1967) who report that teflon has two correlation times.

Figure 9 shows one well defined minimum and suggests another at a temperature above 100°C, again suggesting two correlation times for the copolymer.

Figure 10 shows one well defined minimum and suggests other not so well defined minima at lower temperatures. Thus KEL-F is much more complicated then our simple minded theory brings out.

The theory which was just discussed for correlation times in the rotating frame may apply equally well for correlation times in the laboratory frame. The initial equation from Abragam has different values corresponding to the characteristic frequency and field used in the laboratory frame as previously mentioned in the theoretical section.

Conclusion

Thus the preliminary objectives have been borne out. It has been shown that spin lattice relaxation measurements in the rotating frame may be superior to spin lattice relaxation measurements in the laboratory frame, because the characteristic frequency associated with the experiment is closer to the characteristic frequencies of motion. It has also been shown that for a minimum at a given temperature there exists a corresponding correlation time.

In order to make more rigid comparisons of work that has been reported in the literature or to report on new polymers we must first perform the measurements on well characterized polymers. Secondly, although it has been suggested (Filipovich et al. 1965) that many polymers especially those similar to teflon, reach a state of rigidity prior to 77°K and have the same state of motion at 4.2°K as at 77°K, no such statement can be made at higher temperatures. Thus, studies must be made at higher temperatures. Thirdly, as already suggested in the literature (McCall et al. 1967) the exponential decays are likely to be the sum of two or more separate exponential decays. Therefore the studies should be done again using a computor curve fitting program designed to give better resolution. Finally, future studies should involve measurements of $T_{1\rho}$ at different average fields so that one can find the minima within reasonable temperature ranges. This will enable one to find conditions where the characteristic frequency in the rotating frame is on the order of one over the correlation time, and to determine the constants in $\tau_c = \tau_o e^{-\Delta E/kT}$.

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