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Transitions in Polymers by Nuclear Magnetic Resonance and Dynamic Mechanical Methods*

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I. INTRODUCTION

THE physical properties of high polymers at any given temperature are determined to a great extent by the internal mobility of the chains of which they are composed. It is therefore of considerable practical, as well as theoretical, interest to know the types of molecular motions present in a given polymer and how these motions depend on the composition and structure of the polymer as well as on the temperature.

Two of the most useful physical methods for studying internal motions in polymer chains are nuclear magnetic resonance (NMR) and dynamic-mechanical measurements. The latter consist of measuring the in-phase and out-of-phase deformational responses of a polymer specimen subjected to an applied alternating stress. These responses are greatly affected by the structure and nature of the polymer and by the temperature induced mobility of the polymer chains or their segments. During the last ten years many such investigations have been carried out and much of our present-day information concerning the nature of transitions or relaxation processes in polymers has been obtained from such mechanical tests. Some of these results for specific amorphous and partially crystalline polymers are discussed here as well as in review articles.[1–3]

Application of nuclear magnetic resonance methods to study of internal motion in solid polymers is a more recent innovation. Although the nuclear magnetic resonance phenomenon in solids was first reported for paraffin in 1946 by Purcell, Torrey, and Pound[4] and then for natural rubber a year later,[5] only recently has this method been applied to a wide variety of solid polymers. Results of a number of these investigations have been reviewed recently.[6]

The nuclear magnetic resonance method consists essentially of placing a polymer specimen in a strong static magnetic field and measuring its response to a weak radio-frequency field. If conditions are appropriate, as described herein, the polymer absorbs energy from the applied alternating electromagnetic field. This energy absorption, i.e., its dependence on the applied frequency, is a function both of the local environment of the nuclei responsible for the existence of the phenomena and of their motion. The latter fact makes the NMR technique another useful and interesting tool for studying molecular motions and relaxation properties in polymers.

This paper discusses some of the interesting results already obtained by the NMR method in both amorphous and crystalline polymers, and compares this information with that obtained by using dynamic-mechanical methods.

II. NUCLEAR MAGNETIC RESONANCE METHOD†

This method consists essentially of placing a sample having nuclei which possess angular momentum (spin), and hence a magnetic moment, between the poles of a powerful magnet, and then applying at right angles to the static magnetic field a weak oscillating field. If the frequency of the weak electromagnetic field is equal to the frequency of precession of the nuclear magnets in the applied static field, then energy is interchanged between the electromagnetic field and the nuclear spin system, and some of the nuclei change their orientation. This energy loss can be detected by electronic means; the NMR "line" is then a plot of this energy absorption as a function of frequency at constant field or, more usually, as a function of field, which is experimentally varied about some average value H_0 at constant radio-frequency.

Thus, the condition required for observation of nuclear magnetic resonance is that the circular frequency of the weak oscillating electromagnetic field be equal to the precession frequency of the nuclear magnets in the applied field. Another convenient way in which this condition can be stated is that the frequency ν of the oscillating field be such that the energy quantum $h\nu$, where h is Planck's constant, must be equal to the difference of energy between the possible stationary states or orientations of the nuclear moment in the applied field,

$$h\nu = E_{M'} - E_M, \qquad (1)$$

where M' and M are the magnetic quantum numbers specifying the given orientations. According to quantum mechanics, the angular momentum or spin of the nuclei,

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* Supported in part by the U. S. Atomic Energy Commission and the National Science Foundation.

[1] J. D. Ferry, *Die Physik der Hochpolymergen*, H. A. Stuart, Editor (Springer-Verlag, Berlin, 1956), Vol. 4, pp. 373–419.

[2] A. E. Woodward and J. A. Sauer, Fortschr. Hochpolym. Forsch. 1, 114 (1958).

[3] H. Leaderman, Ann. Rev. Phys. Chem. 9, 179 (1958).

[4] Purcell, Torrey, and Pound, Phys. Rev. 69, 37 (1946).

[5] N. L. Alpert, Phys. Rev. 72, 637 (1947).

[6] W. P. Slichter, Fortschr. Hochpolym. Forsch. 1, 35 (1958).

† For a more detailed account of the basic principles of nuclear magnetic resonance, the reader is referred to the reviews of Pake [G. E. Pake, Am. J. Phys. 18, 438, 473 (1950)] and Andrew.[7]

[7] E. R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University Press, New York, 1955).

given by $Ih/2\pi$, where the nuclear spin I is an integer or half-integer, can take only discrete orientations in the presence of an applied field (assumed to be in the z direction). These orientations are specified by the quantum numbers M and M', which can take on values from $I, I-1, \ldots$ to $-I$.

For hydrogen and fluorine, two of the elements frequently found in polymers, $I=\frac{1}{2}$ and only two orientations are possible. The common isotope of carbon, C^{12}, has zero nuclear spin. In general, there are $2I+1$ possible orientations of the nuclear magnets and to each of these is associated a magnetic moment whose z component is $\mu_z = g\beta M_I$, and an energy

$$E_{M_I} = -\mu_z H_0 = -g\beta M_I H_0. \qquad (2)$$

In these expressions g is a constant which has to be determined experimentally, and β is a unit of nuclear magnetism called the nuclear magneton. Since the selection rules governing magnetic dipole transitions allow only transitions in which the magnetic quantum number changes by ± 1, the appropriate energy difference is just the spacing between the levels, and from Eqs. (1) and (2) the resonant condition is

$$h\nu = g\beta H_0. \qquad (3)$$

For protons, using an applied field of 5000 gauss, the resonant frequency is 21.3 megacycles per second.

Equation (3) is the appropriate resonance equation when each nuclear magnet is in the same static applied field H_0. This is usually not the case, as each given nuclear magnet is acted upon not only by H_0 but also by the field of the other nuclear magnets; hence, the total field depends on the configuration of all the other nuclear magnets. For most polymers it is not easy to calculate the local field H_L, because the positions of the other nuclear magnets generally are not known, and because the calculation is difficult. This local field is about 10 gauss in order of magnitude.

The local field effect modifies the resonance condition to

$$h(\nu + \Delta\nu) = g\beta(H_0 + H_L). \qquad (4)$$

The resonance line now is no longer sharp, even for a homogeneous applied field, but has a width of order $\Delta\nu = g\beta H_L/h$.

Van Vleck[8] has shown that even though it is not possible to make an exact calculation of the local field and hence of the NMR line shape, it is possible to make a rigorous calculation, for a rigid lattice, of the second (or fourth) moment of the NMR line. Thus, if the internuclear distances are known or assumed, one can calculate a theoretical second moment. This then can be compared with the measured second moment of the experimental line, either to check an assumed structure or to determine whether the lattice is effectively rigid at the temperature in question.

Bloembergen, Purcell, and Pound,[9] Gutowsky and Pake,[10] and others have shown that the magnitude of the local field acting on any given nuclear magnet is greatly affected not only by its local environment but also by its motion and that of its neighbors. The phenomenon in question is known as "motional narrowing," since the effect of the motion is to average out the local field variations and thereby to narrow considerably the resonance line. The criterion for line narrowing turns out to be that the motional or reorientation frequency must be at least equal to the frequency line width itself. For a line width of about 5 gauss, the critical frequency for line narrowing is about 20 kc/sec. Thus, the width of an observed NMR line is very sensitive to low-frequency internal motion, which is why NMR is an effective tool for studying molecular rearrangements and transitions.

The measured second moments of many NMR spectra, as is demonstrated in the latter sections of this paper, also show a narrowing with increased thermal motion. However, it is known that, apart from second-order effects, the second moment of an NMR spectrum should be rigorously independent of the thermal motions of the nuclei. This apparent conflict between observation and theory is caused by the fact that thermal motion causes the spectrum to develop satellites or side frequencies of weak intensity usually too weak to be observed. If these side frequencies are included in the theoretical treatment, then the second moment is invariant, but if neglected, then the second moment of the central line is found to be affected by motion as in the manner shown by Gutowsky and Pake.[10] Hence, it is still appropriate to speak, as is done at various places throughout this paper, of the narrowing of the second moment with temperature. It should be understood that, in all such cases, the second moment of the observable central part of the spectrum is being referred to. For a full discussion of this topic see the article by Andrew and Newing.[11]

III. DYNAMIC-MECHANICAL METHOD‡

This method consists essentially of measuring the in-phase and out-of-phase deformational response of a polymer specimen subject to a sinusoidal applied stress. Since high polymers are viscoelastic materials, they can be represented to a first approximation by a mechanical model having one relaxation or retardation time τ. This model contains a linear spring G_0 representing the stretching of valence bonds and angles in series with a retarded spring $\tau = \eta/G$ representing the time-dependent configurational response of the polymer chains. In order

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[8] J. H. Van Vleck. Phys, Rev. **74**, 1168 (1948).

[9] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

[10] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. **18**, 163 (1950).

[11] E. R. Andrew and R. A. Newing, Proc. Phys. Soc. (London) **72**, 959 (1958).

‡ For an extended treatment of the linear deformation behavior of high polymers see the article by Staverman and Schwarzl [A. J. Staverman and F. Schwarzl, *Die Physik der Hochpolymeren*, H. A. Stuart, editor (Springer-Verlag, Berlin, 1956), Vol. 4, pp. 1–125].

to include high-temperature behavior in the model, one must add another dashpot in series with the ideal elastic spring and the retarded spring to represent the slip or flow of one polymer chain past another.

When a stress is applied to such a system, both the compliance and the strain consist of an immediate elastic component plus an anelastic or delayed component. If the applied stress is sinusoidal, the compliance may be considered to be complex, and there is an energy loss per cycle which is proportional to the out-of-phase or imaginary component of the strain. A direct measurement of this component gives a measure of the energy dissipated, and a direct measurement of the in-phase component gives a measure of the energy stored.

When the period of the applied stress is very much less than the retardation time τ, conditions are essentially adiabatic and the energy loss is negligible. On the other hand, when the period is very large compared to τ, conditions are essentially isothermal and again little energy is dissipated. When the period of oscillation of the stress is comparable to τ, there is a maximum anelastic strain and maximum energy dissipation.

When an alternating stress is applied to an actual polymer, the response of the specimen is, in reality, very complex. Various types of internal motion may be invoked or slightly altered by the applied stress, and the time response of these internal motions, varying from bond stretching to slipping of whole molecules, covers a wide time scale. When the applied stress frequency comes into resonance with the natural frequency of vibration or oscillation of a particular molecular unit, one detects an increased compliance in that frequency range and an associated maximum in the mechanical absorption curve. Thus, each given material exhibits its own characteristic internal friction spectrum, and the absorption peaks probably are fairly broad. Each such peak, however, or the associated rise in compliance or drop in modulus is a manifestation of resonant responses of some new internal degrees of freedom. Generally, it is not possible to determine the internal motions that are occurring in any great detail from the mechanical data on one specimen alone. However, by comparison of results for different polymers and for polymer specimens in which specific chemical and structural changes have been introduced, tentative assignments for the molecular processes responsible for the observed transitions can be made.

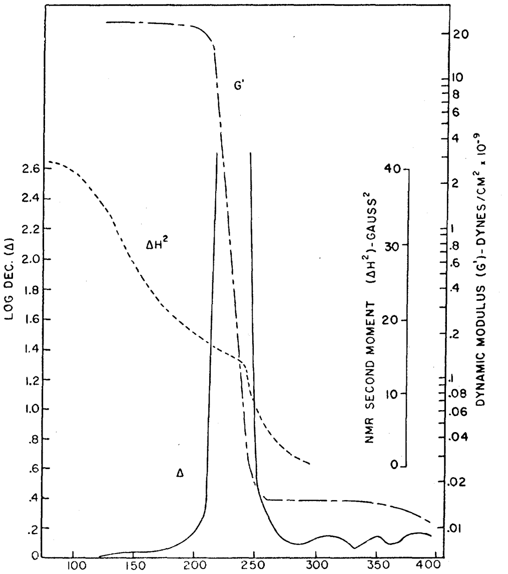

FIG. 1. NMR second moment [Powles[12]; courtesy of the Physical Society (London)], dynamic shear modulus, and damping (Schmieder and Wolf[13]; courtesy of Dr. Dietrich Steinkopff, Editor) as functions of temperature for polyisobutylene.

To obtain an experimental measure of the dynamic-mechanical properties of a given substance, one can perform either a resonance-type experiment or a free-decay experiment. The experimental data frequently are given in terms of the real and imaginary parts of the elastic modulus (E' and E'' if tension, G' and G'' if shear) or in terms of the dynamic modulus (E' or G') and the loss tangent ($\tan\delta = E''/E' = G''/G'$). It is also customary to record the log decrement Δ or the inverse Q of the system,

$$Q^{-1} = \frac{\Delta f}{f_0} = \frac{\text{half-width}}{\text{resonant frequency}},$$

instead of the loss tangent. Each of these gives a measure of the energy dissipated/cycle, and are simply related provided the damping is not large.

IV. AMORPHOUS POLYMERS

Noncrystalline or amorphous polymers can exist in the glassy, rubbery, or liquid state depending on factors such as temperature and polymer molecular weight. Generally, the transition from the glassy to the rubbery or liquid state is quite pronounced with respect to the change in physical properties of the material and therefore is readily seen by dynamic-mechanical or nuclear magnetic resonance measurements. Other motional processes taking place in the glassy polymer cause less pronounced changes in macroscopic physical properties but frequently are revealed both in changes in NMR line characteristics and in dynamic mechanical response at low-stress levels.

In this section the results for two amorphous materials, polyisobutylene and poly(methyl methacrylate) are given.§ Other amorphous materials are considered along with their partially crystalline counterparts in the next section.

1. Polyisobutylene

Nuclear magnetic resonance studies of polyisobutylene for the temperature range from about −200°C to

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§ The source of all original data is given in full although no attempt is made to be all-inclusive.

+50°C have been made by Powles.[12] Figure 1, which gives Powles' data for the second moment as a function of temperature, shows that there are two narrowing processes; one of these, in which the second moment decreases by a factor of about two, occurs over a broad temperature region from about 100°K to 170°K, the other, where the second moment falls from about 14 to 0 gauss^2, takes place in the 240°K to 300°K region. The lower temperature transition is attributed by Powles[12] to the onset of only limited motion of the methyl groups around the C_3 axis and possibly some CH_2 group motion. There is an indication that some of the CH_3 groups are rotating even at liquid nitrogen temperature since the second moment is still increasing at that temperature. The principal transition in the NMR data is the higher temperature process; for this transition an activation energy of 10.2 kcals/mole has been calculated.[12]

Dynamic-mechanical measurements on polyisobutylene have been made by many investigators. The data of Schmieder and Wolf[13] (in terms of shear modulus G' and log decrement) reproduced in Fig. 1 show a large damping maximum at 225°K at a frequency of 1 cps. Assuming that the high temperature transition in the NMR data could be represented by an equation of the form, $\nu_c = \nu_0 e^{-\Delta H/RT}$, one would predict the transition at 225°K to correspond to 9 cps. Hence, there is agreement between the NMR and mechanical data, indicating that both phenomena involve the same molecular process. However, it appears from the mechanical data that the main chain methylene groups do not participate in the motion until the usual glass-rubbery transition range near 225°K is approached. The process causing the second moment drop in the 100°K to 170°K range does not show up in the mechanical properties and therefore would be expected to involve side chain motion without main chain cooperation.

2. Poly(Methyl Methacrylate)

The nuclear magnetic resonance behavior of poly(methyl methacrylate) has been studied by Powles[14] over the temperature range from −200°C to +200°C. At liquid nitrogen temperature and over much of the temperature range studied, the absorption line shape was found to be complex. The actual line could be regarded as the sum of two components, one arising from the protons associated with methyl groups and the other from protons associated with methylene groups.

The variation of the second moment with temperature, as given by Powles,[14] is shown in Fig. 2. The value of 24 gauss^2 at the lowest temperature is in good agreement with the value calculated from Van Vleck's formula[8] on the basis of a rigid lattice. The decrease in the vicinity of 150°K is about 8 gauss^2 which is about what is expected, assuming that one of the CH_3 groups is rotating or reorienting at the critical frequency while the other CH_3 is fixed; however, from these data, one cannot decide whether the methyl group on the main chain or on the side branch is moving. In any event, CH_3 rotation would not be expected to contribute significantly to mechanical compliance. However, a small mechanical loss peak at 253°K at 10^5 cps has been reported by Yamamoto and Wada[15]; Mikhailov[16] found a dielectric loss peak around 170°K at 10^3 cps; and Sinnott[17] recently has reported an increase in the mechanical loss from 26°K to 4.2°K at about 8 cps.

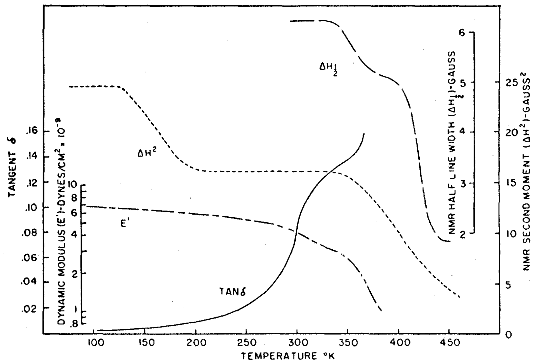

FIG. 2. NMR second moment (Powles[14]; courtesy of Interscience Publishers, Inc., New York), NMR line half-width (Odajima, Sohma, and Koike[18]), dynamic elastic modulus, and mechanical loss (Hoff, Robinson, and Willbourn[19]; courtesy of Interscience Publishers, Inc., New York) as functions of temperature for poly(methyl methacrylate).

Figure 2 shows that the second moment remains practically constant with temperature from −80°C to +80°C but then shows a marked decrease as the temperature rises above 80°C. From observation of the linewidth transition in both Powles' investigation and that of Odajima, Sohma, and Koike,[18] whose results are also given in Fig. 2, it appears that the transition takes place in two stages. This is in accord with the mechanical properties; two damping maxima and, much less apparent, two steps in the modulus have been observed in the 100–500 cps region by Hoff, Robinson, and Willbourn[19] (data given in Fig. 2). Similar maxima have been observed in dielectric data.[20]

There also appears to be a good correlation between values of activation energy determined by the different methods. For example, the NMR narrowing leads to an activation energy of 18 kcal/mole,[14] the dielectric data[20] gives 20 kcal/mole, and dynamic-mechanical loss data[19] gives 18 kcal/mole for the secondary or β process. This process is attributed by Hoff, Robinson, and Willbourn[19]

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[12] J. G. Powles, Proc. Phys. Soc. (London) **69**, 281 (1956).

[13] K. Schmieder and K. Wolf, Kolloid-Z., **134**, 149 (1953).

[14] J. G. Powles, J. Polymer Sci. **22**, 79 (1956).

[15] K. Yamamoto and Y. Wada, J. Phys. Soc. Japan **12**, 374 (1957).

[16] G. P. Mikhailov, Zhur. Tekh. Fiz. **21**, 1395 (1951).

[17] K. M. Sinnott, J. Polymer Sci. **35**, 273 (1959).

[18] Odajima, Sohma, and Koike, J. Phys. Soc. Japan **12**, 272 (1957).

[19] Hoff, Robinson, and Willbourn, J. Polymer Sci. **18**, 161 (1955).

[20] Deutsch, Hoff, and Reddish, J. Polymer Sci. **13**, 565 (1954).

to rotation of the methoxycarbonyl side group, which is consistent with the NMR second-moment data, provided it is also assumed that loosening of the side branch leads to increased freedom of motion and to C_3 reorientation of the main chain methyl group.

V. PARTIALLY CRYSTALLINE POLYMERS

Both nuclear magnetic resonance and dynamic-mechanical behavior of partially crystalline polymers are more complex than for the case of amorphous polymers. The additional complexity arises largely from the fact that partially crystalline polymers are, in effect, multiphase materials. Both amorphous and crystalline phases, as well as partially ordered amorphous crystalline interfaces, coexist at any given temperature. Also, above a given temperature, the proportion of the two major phases may be a fairly rapidly varying function of temperature. For some polymers the nuclear magnetic resonance line can be considered as the sum of two components over a fairly wide temperature range (see Fig. 3[21]) one broad and one narrow, representing respectively, the rigid nuclei and those nuclei which are rotating or reorienting above the critical frequency for line narrowing. If one could assume that all the nuclei in amorphous regions were rotating and all those in crystalline regions were fixed, then from the intensity of the two components, it would be possible to determine directly the percent crystallinity of the sample as suggested by Wilson and Pake.[22] Unfortunately, as shown by a number of workers,[23–25] this is not a good general approximation and hence, using NMR to determine crystallinity, is not always justified. From the comparison of NMR crystallinity with values found by using density and x-ray data for a low-density polyethylene, Fuschillo, Rhian, and Sauer[23] have shown that, over a wide temperature range below the usual glass transition temperature, the NMR value is much too high. However, the ratio of the intensity of the broad component to the intensity of the total line, denoted by N_c/N, does give a measure of the percentage of nuclear spins that are "fixed" and hence also of those that are in motion. Therefore the intensity ratio or NMR "rigidity" ratio is a useful parameter for studying the onset of internal mobility in high polymers although it is not a reliable crystallinity index, except possibly in restricted temperature regions.

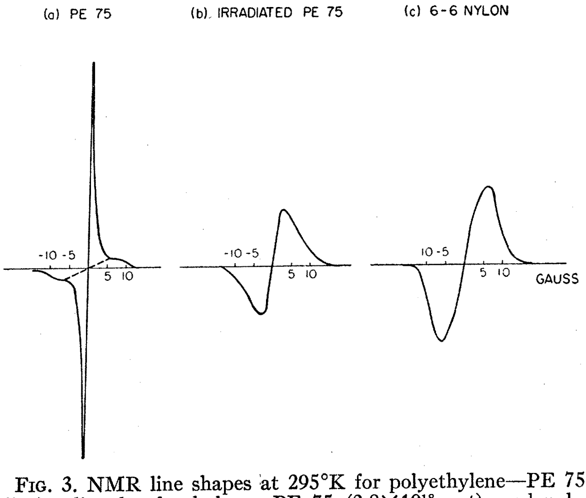

FIG. 3. NMR line shapes at 295°K for polyethylene—PE 75, pile irradiated polyethylene—PE 75 (2.8×10^{18} nvt), and poly-(hexamethylene adipamide) (Gupta and Glick[21]).

1. Poly(Vinyl Chloride)

Poly(vinyl chloride) as ordinarily prepared is only slightly crystalline, and therefore its behavior is more like an amorphous polymer than that of the more highly crystalline polymers. Nuclear magnetic resonance studies of poly(vinyl chloride) from room temperature to 160°C have been reported by Odajima, Sohma, and Koike[18] as shown in Fig. 4. The line width at room temperature ($\sim$9 gauss) decreases only very slightly with increasing temperature up to about 350°K; rapid narrowing to very low values then occurs indicating onset of considerable translation as well as rotation. The calculated second moment, assuming a rigid lattice and zigzag chain, gives 12.7 gauss^2 in fair agreement with the experimental value of 11.0 gauss^2. However, the line width even at room temperature is not constant with temperature, and hence, further increases probably would be found if lower temperature measurements were made.

Dynamic-mechanical data have been taken by various investigators including Schmieder and Wolf,[13] Sauer and Kline,[26] and Becker,[27] these investigators showing that there are two transition regions where dispersion occurs. The low-frequency (0.5–10 cps) results of Schmieder and Wolf[13] are shown in Fig. 4. A primary transition occurs at about 360°K in approximate agreement with the NMR line narrowing. However, the dynamic-mechanical data clearly show a rather broad secondary loss peak having its maximum around 240°K. A similar secondary loss peak also appears in the dielectric data.[28] The broad peak in the dynamic-mechanical data probably is related to the slowly decreasing line width in the NMR data. Evidently some rotational oscillation or tunneling of the methylene group in the main chain is occurring even at room temperature or a little below and gives rise to an increased mechanical compliance and an associated loss peak. However, until

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[21] R. P. Gupta and R. E. Glick (unpublished results).

[22] C. W. Wilson, II, and G. E. Pake, J. Polymer Sci. **10**, 503 (1953).

[23] Fuschillo, Rhian, and Sauer, J. Polymer Sci. **25**, 381 (1957).

[24] Rempel, Weaver, Sands, and Miller, J. Appl. Phys. **28**, 1082 (1957).

[25] W. P. Slichter and D. W. McCall, J. Polymer Sci. **25**, 230 (1957).

[26] J. A. Sauer and D. E. Kline, IXth Intern Congr. Appl. Mech., University of Brussels **5**, 368 (1957).

[27] G. W. Becker, Kolloid-Z. **140**, 1 (1955).

[28] R. M. Fuoss, J. Am. Chem. Soc. **63**, 369 (1941).

the dipolar cohesive forces of the C—Cl link are overcome, no great amount of chain mobility is possible.

2. Polyethylene

The nuclear magnetic resonance behavior of polyethylene has been extensively studied,[22–25,29–32] both branched or low-density polyethylene and linear or high-density polyethylene being investigated. The room-temperature derivative line shape[21] for a low-density polyethylene (PE 75) is shown in Fig. 3(a). As indicated by the dashed line, the complex line shape can be considered to be the result of two lines, one very narrow and intense, arising essentially from the protons in the amorphous regions, and another very broad and diffuse, arising essentially from the protons in the crystalline regions.

Line width *vs* temperature plots for four polyethylenes with different crystallinities[32] are given in Fig. 5. The room-temperature densities of these materials are as follows: PE 75, 0.915; PE 76, 0.922; PE 84, 0.957; and Marlex 50, 0.964 g/cm^3. The PE polyethylenes differ widely in the number of CH_3 groups per 100 CH_2 groups as follows: PE 75, 3.2; PE 76, 1.6; and PE 84, <0.1. Marlex 50, like PE 84, is also essentially a linear polyethylene.

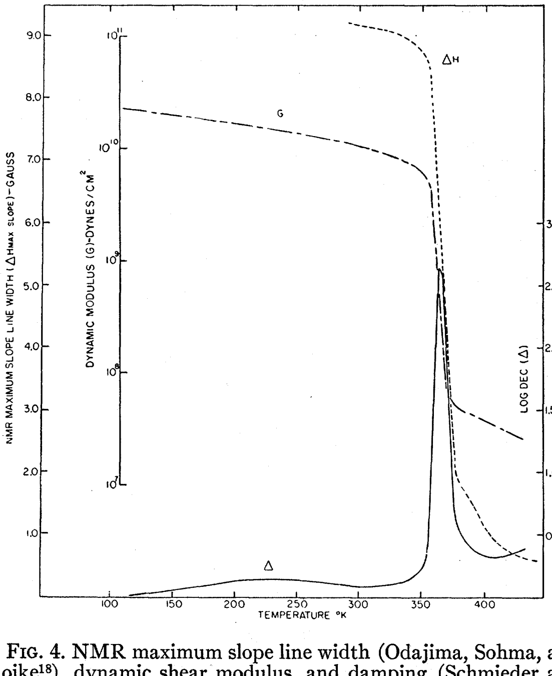

FIG. 4. NMR maximum slope line width (Odajima, Sohma, and Koike[18]), dynamic shear modulus, and damping (Schmieder and Wolf[13]; courtesy of Dr. Dietrich Steinkopff, Editor) as functions of temperature for poly(vinyl chloride).

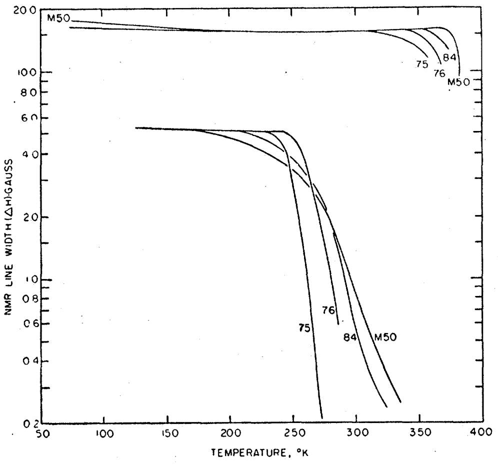

FIG. 5. NMR line width *vs* temperature for four polyethylenes (Fuschillo and Sauer[32]).

At liquid nitrogen temperatures, 77°K, none of these polymers exhibit a narrow component; the observed second moment of 26 gauss^2 for PE 75 and PE 76 and 29 gauss^2 for PE 84 and Marlex 50 are in agreement with the rigid-lattice value of 26.3 gauss^2 calculated from the equation of Andrew[33] for normal paraffins. The narrow line becomes evident between 150°K and 200°K; for all four polymers it is about one-third the width of the broad line at these temperatures. Since the width of the broad line is mainly a function of proton-pair interactions, and since the onset of rotation or rotational oscillation (of sufficient frequency) of the proton pair about an axis to the line joining the pair reduces the line width by a factor of two,[7] the first appearance of the narrow line is associated with rotational motion of some of the CH_2 units in the polymer. As the temperature rises, the narrow line grows in intensity and then undergoes a further marked narrowing, falling to the value of the field inhomogeneity; the temperature at which narrowing occurs depends on the polyethylene tested and increases in the order PE 75, PE 76, PE 84, Marlex 50 as is apparent in Fig. 5. To account for this large change in line width, much more extensive averaging-out motions than mere proton-pair rotations must be involved. It appears that translations of the center of mass or other rapid liquidlike movements must be taking place in the amorphous regions. The broad line, arising principally from interactions of the protons associated with the "stationary" segments in the crystalline phase, shows only a gradual change over the 80°K to 300°K range; above 300°K this line begins to narrow with increasing temperature in the order PE 75, PE 76, PE 84, and Marlex 50, which is the order of increasing density. This narrowing process is indicative of the onset of melting and consequently rotational motion which occurs prior to final melting.

From the behavior of the narrow-line component with

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[29] D. W. McCall and W. P. Slichter, J. Polymer Sci. **26**, 171 (1957).

[30] N. Fuschillo and J. A. Sauer, J. Appl. Phys. **28**, 1073 (1957).

[31] R. L. Collins, J. Polymer Sci. **27**, 67 (1958).

[32] N. Fuschillo and J. A. Sauer, Bull. Am. Phys. Soc. Ser. II 4, 187 (1959).

[33] E. R. Andrew, J. Chem. Phys. **18**, 607 (1950).

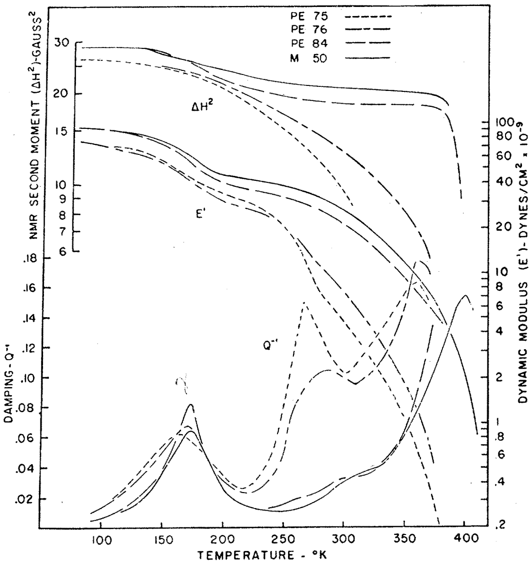

FIG. 6. NMR second moment (Fuschillo and Sauer[32]), dynamic elastic modulus, and damping (Deeley, Kline, Sauer, and Woodward[34–36]) *vs* temperature for four polyethylenes.

polyethylene type, it is apparent that the more crystalline the material the more restricted the amorphous regions and the higher the temperature necessary to bring about the onset of considerable motion in these regions.

The NMR second moment *vs* temperature curves, taken from the same data for PE 75, 76, 84, and Marlex 50, are given in Fig. 6. All four materials exhibit a decrease in the 150–225°K range. The essentially linear materials (PE 84 and Marlex 50) show only a slight further decrease in second moment up to a temperature of about 380°K, whereas the second moment for the branched materials (PE 75 and PE 76) decreases continuously from 150°K to higher temperatures.

The values of the internal friction (damping) and of the dynamic elastic modulus *vs* temperature, obtained by a resonance method in the 100–2100 cps range for the same four polyethylene types,[34–36] are also given in Fig. 6. The mechanical data clearly show the presence of three transitions. A fourth transition, visible as an increase in the damping in the vicinity of the crystalline melting point, has also been reported[13,37] for low-density polyethylene. This transition, probably associated with chain mobility brought about by final crystalline melting, has been described in terms of a change from a rubbery to a liquid state.[2,13]

The highest temperature transition observable in the data given in Fig. 6 is associated with large movements of molecules that can arise as the crystalline portions undergo melting or any other first-order transition. It thus corresponds in the NMR case to the narrowing of the broad line and the final decrease in the second moment; it is apparent that the onset of this process in the dynamic-mechanical case also increases with temperature as the polymer studied becomes more linear.

The other two transitions in the mechanical loss are associated with the onset of mobility in the amorphous regions, the low-temperature or γ process (~165°K) arising from diffusional motion of short chain segments and the next transition (~260°K), the β process, arising from movements involving branch points as well.[13,34] Comparing the NMR and mechanical data, the low-temperature decrease in second moment and the γ process are associated with, respectively, reorientations of the CH_2 group and consequent configurational mobility given thereby to the short chain segments in the amorphous regions. The further NMR line narrowing and therefore the second-moment decrease in the 250°–330°K range are connected with the mechanical β process and with motions of longer parts of the molecular chains. As further corroboration for this assignment, it is noted that the β process is shifted to higher temperatures with decrease of branching just as has been observed for the NMR line narrowing process. In Fig. 6 the magnitude of the peak shift from the damping data is of the order of 30°K, or similar to that reported from the NMR line width data. Finally, the greater decrease in second moment in this region for the branched materials as compared with the linear ones is consistent with modulus and damping data.

A further indication of the relationship between the observed NMR and mechanical transitions can be gathered by comparison of activation energies calculated for the γ and β process. Activation energies have been calculated for polyethylene from the observed shift of the damping peaks on the temperature scale with frequency assuming $\nu = \nu_0 e^{-\Delta H/RT}$, where ΔH is the energy; also, they have been derived by choosing the ΔH which gives the best fit of damping values calculated from a three-parameter spring-dashpot model with the experimental values,[38] assuming a single relaxation time. The former method generally has been found to give values higher than the second method. To calculate an activation energy from NMR data, the method of Gutowsky and Pake[10] is used. This involves the assumption that the averaging process taking place has a single or an average correlation frequency.

For polyethylene the NMR values of ΔH appear to correlate much better with the values from the damping obtained by using the spring-dashpot models. For example, for the γ process the frequency-shift method gives a value of 12–15 kcals/mole from damping measurements[2] and 13 kcals/mole from limited dielectric-loss data,[39] while the model method gives 2 kcals/mole from

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[34] Kline, Sauer, and Woodward, J. Polymer Sci. **22**, 455 (1956).

[35] Deeley, Kline, Sauer, and Woodward, J. Polymer Sci. **28**, 109 (1958).

[36] Deeley, Sauer, and Woodward, J. Appl. Phys. **29**, 1415 (1958).

[37] L. E. Nielsen, J. Appl. Phys. **25**, 1209 (1954).

[38] A. E. Woodward and J. A. Sauer, "The Physical Properties of Polymers," Soc. Chem. Industry Monograph No. 5, Symposium of Plastics and Polymers Group, University of London, April 15–17, 1958, London, England, pp. 245–261.

[39] W. G. Oakes and D. W. Robinson, J. Polymer Sci. **14**, 505 (1954).

damping[38] compared with 3 kcals/mole reported by McCall and Slichter[29] and 2–4 kcal/mole given by Rempel, Weaver, Sands, and Miller[24] from NMR data. For the β process, Kabin[40] reports 16 kcals/mole and Oakes and Robinson[39] find 30 kcals/mole from damping data by using the frequency-shift method, whereas the model method gives 7 kcals/mole[38]; from dielectric data[39] a value of 55 kcals/mole is obtained; the NMR data of McCall and Slichter[29] yields 6–8 kcals/mole and that of Rempel *et al.*,[24] 7–13 kcals/mole.

3. Irradiated Polyethylene

The effect of high-energy irradiation on the dynamic-mechanical properties of polyethylene has been extensively studied.[2,35,36,41–45] Some nuclear magnetic resonance investigations of irradiated polyethylene have also been reported.[30,46,47]

The chief effect of a large amount of neutron and gamma irradiation in a nuclear reactor on the NMR line shape at room temperature is to reduce greatly the intensity of the narrow component as shown in Fig. 3. This reduction of the narrow line intensity is indicative of increasing restraints to the reorientations of many of the proton pairs situated in the amorphous phase of the polymer.

In Fig. 7 the dynamic-mechanical[35,36] and NMR[46] results on some PE 75 specimens irradiated in a Co^{60} source (the 300 mr sample) and in a reactor (doses of 1.3×10^{18} nvt and 2.8×10^{18} nvt) are compared with the data for the unirradiated material.

The densities of the four specimens in the order 0, 300 mr, 1.3×10^{18} nvt, and 2.8×10^{18} nvt are 0.915, 0.918, 0.919, and 0.941 g/cc. The x-ray crystallinities of the 0, 300 mr, and 2.8×10^{18} nvt specimens are 55%, 57%, and 10%.

The following changes in damping are apparent for the four samples in the order 0, 300 mr, 1.3×10^{18} nvt, and 2.8×10^{18} nvt: (1) The peak at 160°K increases in height and total area under the curve and then starts decreasing again. Results[35] on specimens given intermediate- and higher-pile irradiation dosages substantiate these changes. Also, irradiation of high-density polyethylene leads to similar behavior.[36] (2) The peak at 270°K shifts to higher temperatures and decreases in height and area at high dosages. (3) The peak at 360°K decreases in height while shifting to lower temperatures.

The dynamic modulus *vs* temperature curves for these specimens also show marked changes. In the 100°–275°K range, a decrease of the modulus at all temperatures in the order 0, 300 mr, and 1.3×10^{18} nvt occurs, a further increase of the dose to 2.8×10^{18} nvt bringing about a modulus increase. In the 275°–380°K region, the moduli for the 0 and 300 mr samples are essentially the same while an increase occurs as the dose is increased to 1.3×10^{18} nvt and then 2.8×10^{18} nvt. Above about 380°K the 300 mr and 1.3×10^{18} nvt specimens exhibit an increase of modulus with temperature; by using rubberlike elasticity theory, approximate crosslinkings of 2.9% and 20%, respectively, can be calculated for these two samples. The 2.8×10^{18} nvt specimen shows no rubberlike behavior, although the modulus at all temperatures above 380°K remains at a level higher than that for the other sample shown.

The plots of the NMR line width *vs* temperature show that the irradiation acts principally to alter the width of the narrow component, an increase in the temperature of the high-temperature narrowing process of this component occurring in the order 0, 300 mr, 1.3×10^{18} nvt, and 2.8×10^{18} nvt. The line intensities at room temperature are altered somewhat differently with first an increase, then a decrease being observed.[30]

The effect of irradiation on the dynamic-mechanical and NMR properties of polyethylene can be explained in terms of two structural changes which are taking place, the introduction of crosslinks and the loss of

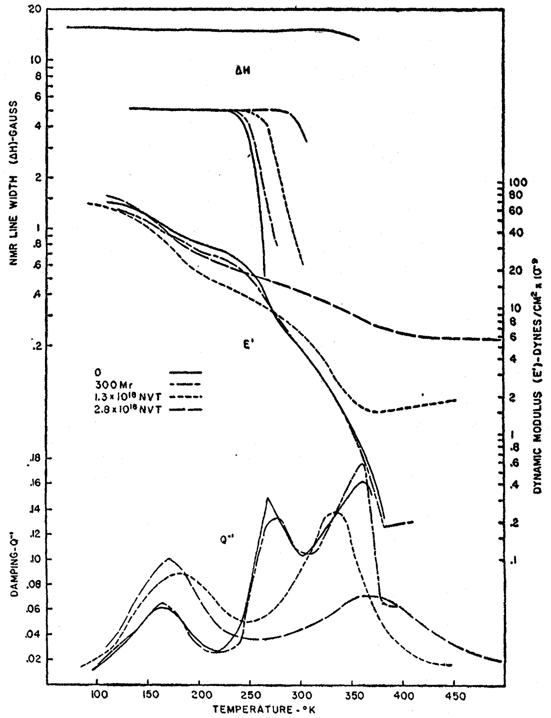

FIG. 7. NMR line width (Fuschillo, Krautkopf, and Sauer[46]), dynamic elastic modulus, and damping (Deeley, Kline, Sauer, and Woodward[35,36]) *vs* temperature for irradiated polyethylene (PE 75).

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[40] S. P. Kabin, Zhur. Tekh. Fiz. **26**, 2628 (1956).

[41] Woodward, Deeley, Kline, and Sauer, J. Polymer Sci. **26**, 383 (1957).

[42] M. Baccaredda and E. Butta, Chim. e ind. (Milan) **40**, 6 (1958).

[43] A. H. Willbourn, Trans. Faraday Soc. **54**, 717 (1958).

[44] See reference 42, p. 983.

[45] E. Butta and A. Charlesby, J. Polymer Sci. **33**, 119 (1958).

[46] Fuschillo, Krautkopf, and Sauer, Bull. Am. Phys. Soc. Ser. II **3**, 131 (1957).

[47] W. P. Slichter and E. R. Mandell, J. Phys. Chem. **62**, 334 (1958).

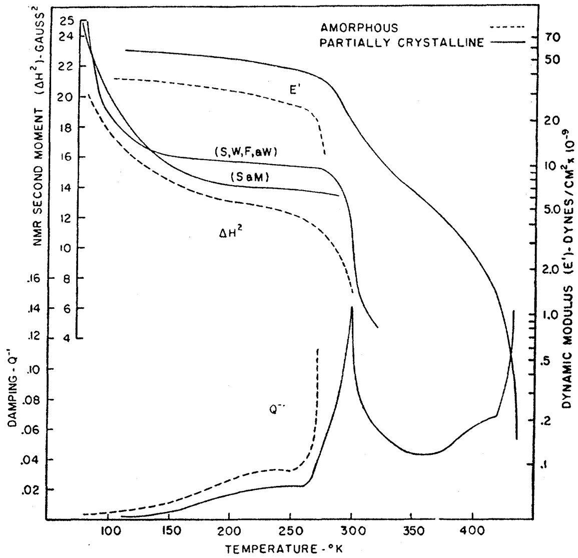

FIG. 8. NMR second moment (Slichter and Mandell[48]), modulus, and damping (Sauer, Fuschillo, Wall, and Woodward[49]) *vs* temperature for amorphous and partially crystalline polypropylene.

crystallinity. There is a competition between the two effects, the first tending to tighten the chain structure and the second tending to loosen it. The changes in the 160°K peak and variation in the modulus in the 100°–275°K range is due to the predominance of the effect of the crystallinity loss over the crosslinking process at the lower dosages, 300 mr and 1.3×10^{18} nvt, and then the reverse at the higher dosage, 2.8×10^{18} nvt. The shift of the damping peak at 270°K to higher temperatures, the increase of the modulus from 275°K up, the shift of the line narrowing at 260°K to higher temperatures, and the reduction of the intensity of the NMR narrow-line component with increasing dose are due to the restraints imposed by the crosslinks on the motion in the amorphous regions giving this transition. Finally, the disappearance of the 360°K damping peak occurs due to the loss of crystallinity.

4. Polypropylene

Nuclear magnetic resonance results from 77°K to about 400°K recently have been reported on crystalline polypropylene samples by Slichter and Mandell[48] and by Sauer, Wall, Fuschillo, and Woodward[49]; the former also have studied an amorphous specimen. The dynamic-mechanical properties of amorphous and crystalline polypropylene over the 77°K–435°K range at 100–2200 cps have been investigated by the latter authors; other dynamic-mechanical studies of this polymer have been reported by Baccaredda and Butta,[42] Willbourn,[43] and Muus, McCrum, and McGrew.[50]

Data given by Sauer, Wall, Fuschillo, and Woodward[49] and Slichter and Mandell[48] for partially crystalline and completely amorphous polypropylene are shown in Fig. 8. The room-temperature crystallinity of the specimen used to study dynamic-mechanical properties was 75–80% while that of the NMR specimen used by Sauer *et al.* was 55%. The mechanical-loss data indicate the presence of at least three transitions located around 240°K, 300°K, and 435°K; a fourth occurring around 400°K also may be present. Only the transitions in the 300°K and 435°K regions are readily apparent in the dynamic elastic-storage modulus. Since the damping peaks which appear around 240°K and 300°K for partially crystalline specimens are observed for amorphous polypropylene, although the latter peak is shifted to lower temperatures, they have been attributed[49] to segmental motion in the amorphous regions involving short and long sections of the chain, respectively; the latter process corresponds to a change from glasslike to rubberlike properties. The rise in the damping and the precipitious fall in the modulus near 435°K for the crystalline material occur near the crystalline melting point and are attributed[49] to the increase in chain mobility accompanying this process. Two small internal friction peaks occurring at 19° and 53°K (6–7 cps), as found by Sinnott,[50] are believed to be due to hindered rotation of the pendant groups in the amorphous and crystalline parts, respectively.

The NMR second-moment data obtained on three other specimens also indicate a marked transition in the 250–330°K range for polypropylene, the data for the amorphous sample exhibiting a decrease at a temperature approximately 50° lower than that for the crystalline samples. This is in agreement with the shift of the primary amorphous transition given by the mechancial data and has been attributed to the restraints imposed by the crystallites on the amorphous parts.[48,49] The decided decrease in the second moment as the temperature is raised from 80°K to 150°K is though to arise as a consequence of pendant methyl group rotation.[48,49] At 80°K the second moment of 24–25 gauss² is below that of the rigid-lattice value[48] of 28.5 gauss², and consequently some type of averaging-out motion is believed to be occurring even at these temperatures.

Above the temperature at which line narrowing starts, the derivative line shape for the partially crystalline material is complex, having a broad and narrow component. As the melting point is approached in the heating process, some narrowing of the broad component occurs.[48]

If the assignments for the NMR and dynamic-mechanical transitions are correct, then it is apparent that, for polypropylene at least, the two methods supplement each other, the principal amorphous transition showing up about equally in either type of measurement but the other secondary transitions being much more predominant in one type of data than the other.

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[48] W. P. Slichter and E. R. Mandell, J. Appl. Phys. **29**, 1438 (1958).

[49] Sauer, Wall, Fuschillo, and Woodward, J. Appl. Phys. **29**, 1385 (1958).

[50] Muus, McCrum, and McGrew, SPE Journal **15**, 368 (1959).

5. Poly(butene-1)

The dynamic elastic modulus and the internal friction from 80°K to 400°K (at frequencies from 3700 cps to 100 cps) have been given for a partially crystalline poly(butene-1) sample (∼30% crystallinity) by Woodward, Sauer, and Wall[51]; data for an amorphous sample over a limited temperature range has also been published by Baccaredda and Butta.[42] Nuclear magnetic resonance second-moment data have been reported for crystalline poly(butene-1) by Slichter[52] and Sauer, Woodward, and Fuschillo[53] (∼30% crystalline) and for an amorphous sample by Slichter.[52] The dynamic-mechanical and NMR data of Woodward, Sauer, and co-workers[51,53] are reproduced in Fig. 9.

The elastic-storage modulus and damping show dispersions and peaks, respectively, at 150°K and 290°K, believed to be caused by segmental motion in the amorphous regions.[51] The 290°K transition is clearly the principal amorphous transition, occurring in the temperature range expected for branched polyolefins.[2,43] The transition at 150°K takes place in the region where numerous partially crystalline high polymers, both linear and branched, as well as branched amorphous high polymers exhibit damping peaks and modulus changes.[2] It appears that this transition is associated with the attainment of alternate configurations of the side chains in the amorphous regions,[19] but for this to be so in the case of poly(butene-1), limited main chain motion involving the CH group must take place as well.[51] At 400°K the modulus decreases further and the damping increases, indicative of the crystalline melting process for this polymer.

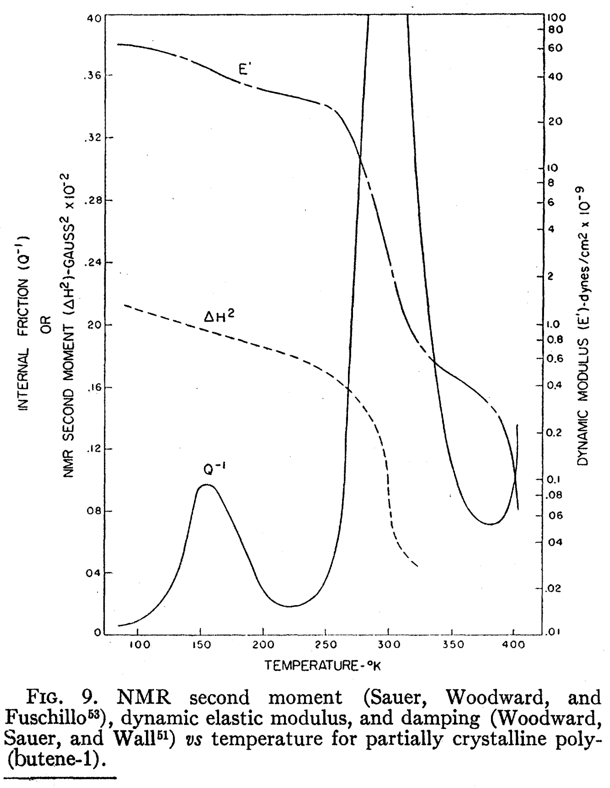

Fig. 9. NMR second moment (Sauer, Woodward, and Fuschillo[53]), dynamic elastic modulus, and damping (Woodward, Sauer, and Wall[51]) *vs* temperature for partially crystalline poly(butene-1).

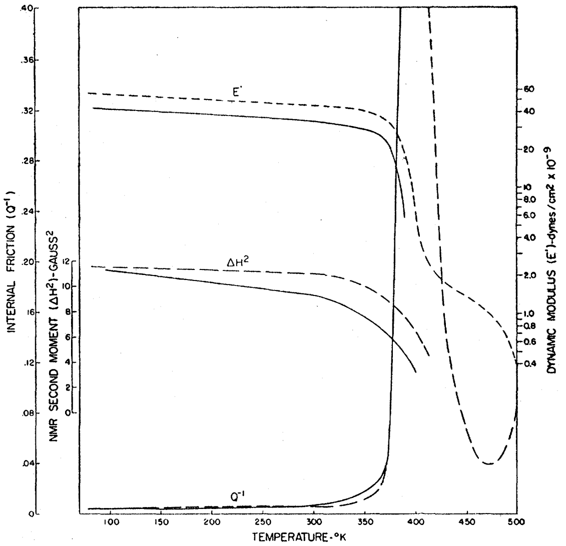

Fig. 10. NMR second moment (Slichter[52]), dynamic elastic modulus, and damping (Wall, Sauer, and Woodward[54]) *vs* temperature for amorphous and partially crystalline polystyrene.

The NMR second moment *vs* temperature for a second crystalline poly(butene-1) specimen shows a slow decrease of about 4 gauss^2 over the 80°K to 270°K range and then a more rapid change from 270°K to 320°K, decreasing to about 5 gauss^2 which is one-third of the 270°K value. This decrease clearly marks the primary amorphous transition in agreement with the large damping peak and associated modulus change found for this material at 290°K.

6. Polystyrene

Numerous dynamic-mechanical investigations have been reported for amorphous polystyrene samples.[2] Only recently have data been given for a partially crystalline specimen (∼40%) by Wall, Sauer, and Woodward.[54] Slichter[52] has made NMR studies on both partially crystalline and amorphous polystyrene from 80°K to about 400°K; Odajima, Sohma, and Koike[18] have reported NMR line-width data from 273°K to 423°K for an amorphous sample.

The mechanical loss,[54] the dynamic elastic modulus[54] (100–2400 cps range), and the NMR second moment[52] as functions of temperature are compared in Fig. 10 for completely amorphous and partially crystalline polystyrene specimens.

The mechanical properties clearly show two transition regions for the crystalline material, the one at 400°K

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[51] Woodward, Sauer, and Wall, J. Chem. Phys. **30**, 854 (1959).

[52] W. P. Slichter, SPE Journal **15**, 303 (1959).

[53] Sauer, Woodward, and Fuschillo, J. Appl. Phys. **30**, 1488 (1959).

[54] Wall, Sauer, and Woodward, J. Polymer Sci. **35**, 281 (1959).

being associated with the glass-to-rubber transition of the amorphous parts and the other at 500°K being due to the crystalline melting process.

The NMR second moment for both the partially crystalline and amorphous polymers decreases slowly from 80°K to 350°K and then decreases more abruptly in the 350°K to 420°K region, the latter decrease corresponding to the amorphous transition given by the dynamic-mechanical properties. The data of Odajima, Sohma, and Koike[18] indicate that the line decrease occurs in two stages, the first supposedly corresponding to side chain rotation and the second to rotation of segments in the main chain.[18]

7. Polyamides

The NMR absorption line of polyhexamethylene adipamide taken at room temperature[21] is shown in Fig. 3. The line shape differs considerably from that of polyethylene also shown in Fig. 3, the chief difference being in the very low intensity of the narrow-line component,‖ presumably characteristic of rotations and reorientations in the amorphous regions. The reason for this low intensity is that in nylon the polymer chains, even in amorphous regions, are held tightly together by both dipolar and hydrogen bond forces and, hence, except for some tunneling or hindered rotation and consequent configurational changes of the short CH_2 portion of the monomer units, there is little internal chain mobility until temperatures comparable to 80°C are reached. The failure of the N_c/N intensity ratio to give a reliable estimate of percent crystallinity at room temperature is very evident for this polymer.

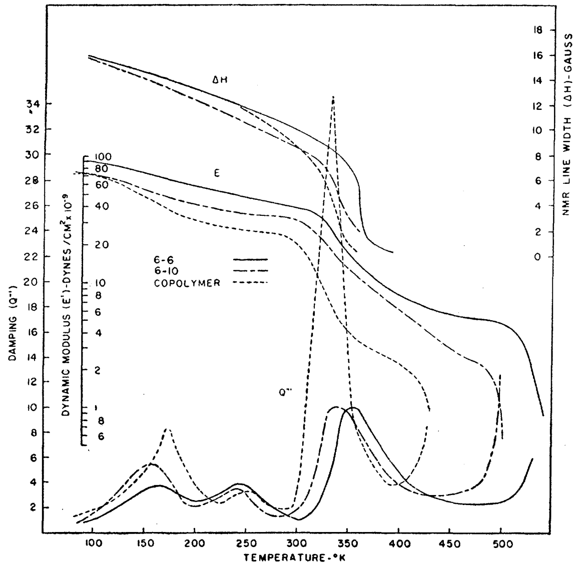

FIG. 11. NMR line width (Slichter[55]), dynamic elastic modulus, and damping (Woodward, Sauer, Deeley, and Kline[56,57]) *vs* temperature for three polyamides.

The line width *vs* temperature for three different polyamides, poly(hexamethylene adipamide), polyhexamethylene sebacamide), and an amorphous copolymer containing units of these two, has been determined by Slichter[55] whose results are shown in Fig. 11. The dynamic-mechanical results on a similar set of specimens determined by Woodward, Sauer, Deeley, and Kline[56,57] in the 200–2000 cps frequency range are also shown in Fig. 11. In both sets of data the most striking feature is the recurrence of a major transition, clearly involving considerable chain motion, in the neighborhood of 340°K and believed to be the principal amorphous transition. Perhaps even more indicative of the correlation that frequently is found between NMR data and dynamic-mechanical data is the relative positioning of this transition for the three different types of polyamides, the specimens having been conditioned similarly.[56] In both investigations the transition centered at the highest temperature (~360°K) comes from the 6-6 nylon, that at the next lower temperature (~340°K) from the less crystalline 6-10 nylon, and that at the lowest temperature (~330°K) from the essentially amorphous copolymer.

The damping spectra also reveal two secondary low-temperature transitions. The γ transition, centered at 165°K, and the β transition, centered at 245°K, have been assigned, respectively, to diffusional motion of the CH_2 segments[13] and to configurational changes involving nonhydrogen bonded amide links in the amorphous regions of the polymer.[56]

It has been found that, if poly(hexamethylene adipamide) is thoroughly dried, profound changes occur in the damping spectra.[57] The γ peak increases in height, the β peak decreases to zero, and the principal amorphous transition shifts to higher temperatures. More recent studies in these Laboratories[58] show that addition of known amounts of water, up to saturation, to the dried polymer brings about a reversal of the changes given with the principal amorphous transition shifting to 280°K at saturation and the γ peak becoming very broad and flat. Although for the polyamides discrete secondary processes are not as clearly revealed by the NMR data as by the mechanical data, the continued decrease of the NMR line width with temperature between 80°K and 340°K shown in Fig. 11 clearly is indicative of an increased molecular mobility with increasing temperature.

8. Polytetrafluorethylene

The NMR absorption of polytetrafluoroethylene (PTFE) arises from the nuclear spin levels of the F^{19} nuclei rather than from the proton spin resonance of the polymers previously discussed. NMR studies on

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‖ This assumes that one is justified in separating the line into two components.

[55] W. P. Slichter, J. Appl. Phys. **26**, 1099 (1955).

[56] Woodward, Sauer, Deeley, and Kline, J. Colloid Sci. **12**, 363 (1957).

[57] Deeley, Woodard, and Sauer, J. Appl. Phys. **28**, 1124 (1957).

[58] J. M. Crissman (unpublished results).

PTFE have been reported by several authors.[6,59,60] The second moment *vs* temperature plot given by Smith[59] is shown in Fig. 12. The experimental value at 100°K for the second moment of 11.7 gauss^2 is in excellent agreement with the calculated rigid-lattice value of 11.6 gauss^2. The molecular chains in PTFE are effectively frozen at liquid nitrogen temperatures and remain so, as is seen from Fig. 12, until the temperature rises to about 200°K. Slightly above this temperature the line width narrows, decreasing rather sharply to a value of about one-half the low-temperature value of 10 gauss and then gradually reducing to about 2 gauss. The motional narrowing of the line is indicative of rotation of the CF_2 group in the amorphous regions and hence we would expect to find, in the mechanical data, a clear indication of a glasslike transition near 200°K. Such a transition has, in fact, been reported by a large number of investigators[2,26,40,61–63] and is readily apparent in the data of Sauer and Kline[26] for a sample 64% crystalline reproduced in Fig. 12. Three independent groups of investigators[40,62,63] have shown, by running tests on samples having different percentages of crystalline material, that this low-temperature transition clearly is related to the onset of segmental mobility in the amorphous regions. It also has been shown recently by Powles and Kail[60] that the NMR line drop in the 200–300°K region is strongly dependent on crystallinity, the low-temperature process disappearing at high crystallinities.

Two other transitions not clearly indicated in the NMR data are discernible in the mechanical data of Fig. 12. The damping peak at room temperature has been associated with a crystalline phase change[2] and that at 440°K with another glasslike transition in the amorphous regions involving a larger group of polymer chain segments.[63] A further transition made evident by an increase in the damping and a decrease in modulus occurs at temperatures near the melting point of this polymer[62,63] (580°K).

VI. SUMMARY AND CONCLUSIONS

The preceding sections have discussed in some detail the application to various types and kinds of polymers of nuclear magnetic resonance studies and dynamic-mechanical studies. The information obtained with regard to the occurrence of transitions is summarized in Table I. In some cases, as where there is a clearly defined loss peak, the transition region is identified by a single temperature; however, it is essential to record also the frequency of the mechanical measurements as transition temperatures of the relaxation type shift with frequency. In other cases, where the transition is noted by a narrowing of the NMR line width or of the second moment, it is difficult to do more than indicate the range of temperature in which the transition is taking place. The frequency of reorientations necessary to narrow a nuclear resonance line is the line-width frequency itself. This frequency thus varies with the particular polymer and the particular transition being discussed, but in most cases it falls in the range from 10^4 cycles/sec to 10^5 cycles/sec. The mechanical measurements discussed here vary in frequency from about 10^1 to 10^3 cps.

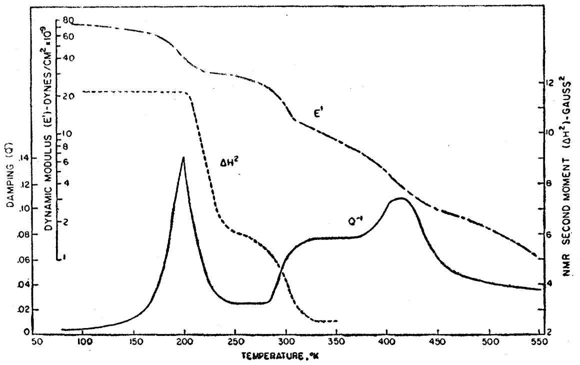

FIG. 12. NMR second moment (Smith[59]; courtesy of the Faraday Society), dynamic elastic modulus, and damping (Sauer and Kline[26]) *vs* temperature for polytetrafluoroethylene.

Reference to Table I and the preceding discussions allows us to draw the following conclusions:

(1) Both amorphous and crystalline phase transitions are detectable by NMR and mechanical methods.

(2) The crystalline melting transition is more readily apparent in the mechanical data than in the NMR data as the onset of local rotations and reorientations in the solid state frequently narrow the NMR line down to such low values that further changes are difficult to detect. Only in the most highly crystalline polymers such as Marlex 50 is there strong NMR evidence for the melting transition.

(3) The primary amorphous transition, associated with loss of cohesion in the amorphous portions, is readily detectable by either NMR or mechanical measurements. In general, it appears that the position of this transition as detected by NMR agrees with that observed by the mechanical measurements when the frequency factor is taken into account. Only in a few cases, such as poly(vinyl chloride), does the NMR-detected transition, despite a higher frequency, appear to fall at, rather than above, the corresponding mechanically detected transition. This may well have been caused by changes in specimen preparation.

(4) In some respects, the NMR and the mechanical methods give equivalent information. For example, the shift to higher temperatures of the β transition in polyethylene with increasing crystallinity of the sample was first seen by mechanical measurements but then attested by NMR measurements. As another example, the low-temperature transition in polytetrafluorethylene near 200°K was shown, by mechanical tests on specimens of

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[59] J. A. S. Smith, Disc. Faraday Soc. **19**, 207 (1955).

[60] J. G. Powles and J. A. E. Kail, J. Polymer Sci. **31**, 183 (1958).

[61] M. Baccaredda and E. Butta, J. Polymer Sci. **31**, 189 (1958).

[62] K. H. Illers and E. Jenckel, Kolloid-Z. **160**, 97 (1958).

[63] N. G. McCrum, J. Polymer Sci. **27**, 555 (1958); *ibid.* **34**, 355 (1959).

TABLE I. Transition temperatures of various high polymers.[a]

Polymer	Crystalline transition temperature °K			Amorphous transition temperatures °K						References	
				Primary transition			Secondary transitions				
		Dyn. mech.			Dyn. mech.			Dyn. mech.			
	NMR	Temp.	Freq.-cps	NMR	Temp.	Freq.-cps	NMR	Temp.	Freq.-cps	NMR	Dyn. Mech.
Polyisobutylene	···	···	···	235–300	225	1	100–225	···	···	12	13
Poly (methyl methacrylate)	···	···	···	350–460	≥365	∼100	125–190	∼325	∼100	14	19
Poly (vinyl chloride)	···	···	···	355–375	365	0.67	···	∼240	8.5	18	13
Polyethylene,											
PE 75	315–355[b]	360	170	235–265[b]	265	790	?	165	1520	32	35
PE 76	340–370[b]	360	200	240–285[b]	285	560	?	170	1200	32	34
PE 84	355–375[b]	≥375	≤500	240–325[b]	∼300	1000	140–200[c]	175[d]	970, 1620	32	34
Marlex 50	375–385[b]	400	310	240–335[b]	∼310	1030	140–200[c]	175[d]	1630	32	36
Irradiated PE 75											
300 mrep	?	360	200	245–275	280	700	?	160	1500	46	36
1.3×10^{18} nvt	?	335	360	270–300	335	360	?	180	1140	46	35
2.8×10^{18} nvt	?	···	···	285–305	365	300	?	175	640	46	35
Polypropylene,											
Amorphous	···	···	···	275–300	≥270	≤1200	80–150	∼235	1480	48	49
Part. cryst.	···	≥435	≤110	285–305	300	1200	75–130	∼250	1840	48, 49	49
Poly (butene-1)	···	≥400	≤120	275–305	295	850	···	155	3160	53	51
Polystyrene,											
Amorphous	···	···	···	325–400	≥390	≤900	···	···	···	52	54
Part. cryst.	···	≥500	≤100	350–415	400	600	···	···	···	52	54
Poly (hexamethylene adipamide)	···	≥535	≤160	350–360	365	570	···	245	910	55	56
							···	165	1100		56
Poly (hexamethylene sebacamide)	···	≥500	≤130	330–360	345	615	···	240	1230	55	56
							···	160	1500		56
Polyamide copolymer	···	≥425	≤160	320–340	330	420	···	250	830	55	56
							···	170	1020		56
Polytetrafluoroethylene	285–320[e]	∼330[e]	∼650[e]	···	415	390	205–230	200	730	59	26

[a] Temperatures for dynamic-mechanical transitions are estimated to the nearest 5°K.
[b] Taken from NMR line-width data.
[c] Taken from NMR second-moment data.
[d] This transition, being the largest of the two amorphous ones, would be the primary transition.
[e] Crystal-crystal transition.

varying crystallinity, to be an amorphous transition. Later, the same fact was confirmed by NMR studies.

(5) Discrete secondary amorphous transitions involving some main chain segmental motion show up much more clearly in the mechanical data than in NMR. In the polyamides, for example, one can readily resolve from the damping measurements two low-temperature transitions, but the NMR data show only a uniform and steady decrease of line width with temperature over this same region. A similar situation prevails in the case of the low-temperature transition in polybutene.

(6) The NMR method is much more sensitive to side chain rotation than the mechanical method. For example, the low-temperature transition, associated with CH_3 rotation, in polyisobutylene, poly(methyl methacrylate), and polypropylene shows up effectively only in the proton resonance data. Another feature of the NMR method is that, where agreement is obtained between the calculated and observed second moments as in polytetrafluorethylene at 150°K or so, one can be certain that no significant transitions can be found at still lower temperatures.

(7) In view of the last two conclusions, it seems that the NMR method and the mechanical method are supplementary. Although they sometimes give equivalent information, as in the location of the β amorphous transition in polyethylene or its change in position with degree of branching or with radiation dose, they frequently give supplementary information which, taken together, enables a more probable interpretation of the transition to be made. For example, the large second-moment change in the vicinity of 150°K in polyisobutylene, and the corresponding lack of any transition in this temperature region in the mechanical data, provides strong evidence that no main chain motion is involved.

(8) There is a great need for experimental data, both of the NMR and mechanical type, on carefully selected and well-characterized specimens. Furthermore, it would be very helpful to have NMR measurements and dynamic-mechanical measurements on specimens having a common origin. Without such a procedure, one does not know how much credence to give to a shift or to a difference in activation energy shown by the two processes. In some cases, as for the β process in poly(methyl methacrylate), it appears that activation energies determined by the two methods are in close agreement, but in other cases, as for the β process in polyethylene, the values given vary from 7 to 30 kcal/mole. These large differences may well be due to some extent to small changes in composition, molding history, or prior treatment. Unfortunately, such information is seldom available.

(9) The combination of NMR studies and dynamic-

mechanical studies is more powerful than either one alone in providing detailed information about the nature of transitions in polymers. However, there are still many unresolved questions. These include the proper assignment of the low-temperature loss peak in poly(vinyl chloride), polypropylene, and polybutene as well as the detailed mechanism of the high-temperature loss peak in polytetrafluorethylene. The very low temperature transitions (below 80°K) also need much more study both by the techniques discussed in this article and other physical methods. The fact that the experimental second moment at 80°K of many of the polymers still has not reached the theoretical rigid-lattice value indicates that low-temperature research should prove quite fruitful in uncovering new transitions and in obtaining definite assignments for those already reported.

(10) It would be helpful to our understanding of the low-temperature transitions in polymers to use the combined power of NMR and mechanical techniques to explore other types of polymers than the ones discussed here. Of particular interest are polymers in which side chain motion is known to influence the low-temperature loss spectra. It would also be helpful to have studies made by the two techniques of controlled copolymers, graft copolymers, and polymers, such as polypropylene, in which the compositions are kept constant but the crystalline-amorphous ratio varied over the widest possible limits.

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Nuclear Reaction Cross-Section Theory

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I. INTRODUCTION

THE problem of estimating nuclear cross sections has been discussed by many authors.[1] In spite of much excellent work on the theory of nuclear reactions,[2] there still exists no completely satisfactory method for accurately predicting nuclear cross sections. A rigorous approach to the description of nuclear reactions has been given by Wigner[3] and his collaborators,[3] and has recently been reviewed by Lane and Thomas.[4] The generality of this R-matrix theory by its very nature requires a formalism, the practical application of which is somewhat formidable. There are, however, more simplified (and thus more restricted) methods which can be adopted to estimate the magnitude and energy dependence of nuclear cross sections. The development presented in the present review is based upon the compound nucleus model, a concept first proposed by Bohr.[5] A survey of the compound nucleus picture and the points at which the picture should be revised have been given by Brown.[6] Except for qualitative mention, scattering cross sections are not discussed herein. These are discussed in the review article by Brown.[6] The purpose of the present review is to provide a systematic and concise summary of compound nucleus processes from which one can estimate nuclear reaction cross sections.

II. FORMATION OF THE COMPOUND NUCLEUS

In discussing the formation of the compound nucleus, one must concern himself not only with the direct-interaction[7] process, but with the possibility of preferential spin-state formation, i.e., the unequal statistical formation of the compound nucleus in the $I+\frac{1}{2}$ and $I-\frac{1}{2}$ states. Sailor[8] has analyzed the statistical weight factor g for $l=0$ neutron resonances. According to these data, it appears that the compound nucleus is formed preferentially in the $I+\frac{1}{2}$ spin state. He emphasizes that his study includes no measurements for weak resonances. His results certainly indicate that predominant resonances within a particular nucleus are preferentially g_+. It is believed that this effect would not affect the results of total (as opposed to differential)

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