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NUCLEAR MAGNETIC RESONANCE IN HIGH POLYMERS

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I. INTRODUCTION

The method of nuclear magnetic resonance (NMR) was applied to polymers shortly after its discovery[1,2]. Since reliable and comparatively simple NMR spectrometers have become available in many countries, the number of experiments in this field is increasing rapidly.

The NMR method is especially valuable in its application to the investigation of stereospecific polymers and in the study of microstructure and molecular motion in polymers[3-6].

The purpose of the present review is to discuss the main trends in the investigation of high polymers by means of NMR. We assume that the reader is familiar with the principles of the method which is described in books[7-13] and in review articles published here[14-20] and abroad[21-24]. Reviews discussing the application of the NMR method to polymers have also been published[25-36].

In discussing NMR phenomena in polymers we must keep in mind certain special features of structure and properties of polymeric substances. There are two structural units in polymers, namely chain molecules and repeat (monomeric) units; "superstructures" can also be formed[37,38].

In the crystalline polymers there are non-ordered non-crystalline regions, non-crystallised packets, so that it is possible to have a "gaslike" structure with the chain centres forming crystalline domains with random orientation[39]. In glasslike polymers individual structural units may retain freedom of reorientation down to very low temperatures. A polymer in a viscoelastic state may be considered glasslike as far as whole chain molecules are concerned but liquid-like if only individual units are considered. Obviously the spectrum of a solid polymer will then be like that of a crystal or a liquid, depending on experimental conditions.

A very important property of polymers, which has to be taken into account when discussing the NMR data, is the complex nature of their relaxation processes. Dielectric and dynamic-mechanical measurements show that polymers do not have a single correlation frequency of molecular motion but rather a distribution of frequencies which in certain cases may be very broad. Therefore, the simple theory of nuclear magnetic relaxation, whose applicability to small molecule substances has been confirmed in many cases, may be applied to polymers only with reservations; sometimes this simple theory is not even in qualitative agreement with experiment.

The results obtained for the longitudinal, T_1, and the transverse, T_2, relaxation times in polydimethylsiloxane[40]

can be used as an example of a very pronounced divergence between theory and experiment. At the minimum of T_1 it was found that $T_1/T_2 \simeq 1300$, while the theory predicts $T_1/T_2 \simeq 2$. It is not surprising then that the interpretation of NMR data in high polymers is difficult. Often from the same experimental results different conclusions may be deduced (*e.g.* in the investigation of vulcanisation of rubber[30,41]).

These difficulties will probably be resolved with further developments of theory (see for example Ref. 42), and also because of the rapid progress in experimental techniques such as the use of high-resolution spectrometers for polymer solutions and melts, investigations of a large number of polymer homologues over a wide range of temperatures, application of spinning of a solid sample[43], isotopic substitution, study of oriented polymers, strained polymers, etc. Naturally, the NMR method should not be used alone but in conjunction with other physical and chemical methods.

II. THE STUDY OF THE STRUCTURE OF POLYMERS BY NMR

The NMR method has the advantage that it can give information about the location of protons, which cannot be obtained by the X-ray method commonly used in structural studies. At the same time we must remember that the amount of information contained in an NMR spectrum of a solid is rather small. It is not possible to determine even slightly complicated crystal structures merely on the basis of NMR data (*e.g.* second moment of the NMR line and its dependence on the crystal orientation in the magnetic field). Nevertheless the NMR spectrum can provide decisive evidence when, for example, we have to decide between two or more possible structures. In certain cases when the substance contains small groups of nuclei, *e.g.* protons in the water of crystallisation in gypsum[44] or in Rochelle salt[45], it is possible to determine the directions and magnitudes of interatomic vectors. The work of Aleksandrov[46-48] can serve as a good example of a successful analysis of crystal structure with the aid of NMR.

1. Crystalline Polymers

Even from the very early NMR experiments on polymers it was apparent that crystallisation of polymers strongly influences the magnitude and the shape of the signal. Holroyd *et al.*[49] showed that on rapid cooling of natural rubber to -35°C the signal remains large, since crystallisation does not take place, but when the sample is held at -25°C, close to the optimum crystallisation temperature, the line broadens and the signal becomes weaker.

The effect of crystallinity on line width was demonstrated for polytetrafluoroethylene[50]. Attention was drawn to the connection between the NMR spectrum and crystallinity by the work of Wilson and Pake[51,52], which showed that in a certain temperature interval the ^1H line in polyethylene and the ^{19}F line in polytetrafluoroethylene has a two-phase structure (Fig. 1). For temperatures above 0°C the line has two components, narrow and broad, as indicated by the dotted line in Fig. 1. Wilson and Pake showed that the narrow line corresponds to the amorphous part and the broad line to the crystalline part of the sample. In the absence of saturation effects the area under the line is proportional to the number of nuclei. Therefore, we can say that the ratio of the areas under the lines corresponding to

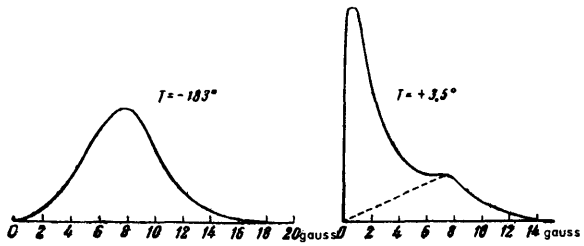


Fig. 1. Derivative of NMR absorption curve for polyethylene[51] (only right-hand half of the curve is shown).

the broad and the narrow line components is equal to the ratio of the numbers of nuclei in the crystalline and the amorphous regions of the sample. The area under the first derivative of the line, shown in Fig. 1, corresponds to the first moment of the line. Hence, it is possible to determine the "degree of crystallinity". Application of this principle to polyethylene at room temperature proved to be highly successful. For a number of polyethylenes[53] with a degree of crystallinity ϵ between 59–93%, the disagreement between ϵ as determined by X-ray and NMR methods was less than 1.8%; the NMR method had the advantage that the results were insensitive to orientation and had a better reproducibility. Smith[54] used the NMR method for a number of polyethylenes and ethylene copolymers with propene and but-1-ene. In the plot of crystallinity *vs.* specific volume the NMR points and the X-ray points fall on the same straight line; the infra-red measurements also give very similar values of ϵ. The composite line method for determining the degree of crystallinity was also used by Collins[55] in his studies of crystalline recovery of quenched polyethylene, by Fujiwara[56] for polyethylene and poly(vinyl chloride), by Fuschillo[57] for a number of polyethylenes, and by Nishioka[58] for polypropylene.

Attempts to apply this method to determine the crystallinity of other polymers and to use it over a wide range of temperatures did not give satisfactory results. Fuschillo and Sauer[59] note that for polyethylene and nylon over a wide range of temperatures the percentage of crystallinity as determined by the NMR method does not agree with the X-ray results. This is further confirmed by measurements made on irradiated polymers, *i.e.* though crystallinity is reduced to zero by irradiation the line remains broad due to the formation of cross-links. Subsequent experiments by Sauer *et al.*[60] on polybutene and polypropylene, and by Slichter and Mandell[61] on irradiated polyethylene, with the method of Wilson and Pake also gave values of crystallinity which were in disagreement with those obtained from X-ray and density measurements.

Slichter and McCall[62] and Fuschillo *et al.*[63] explained this discrepancy. In each of the three methods employed to measure crystallinity, the X-ray specific volume, and the NMR method, different physical quantities are being measured. The X-ray analysis obviously enables us to determine the degree of ordering in the sample, the specific volume depends on the closeness of packing; whereas the NMR signal does not depend on configuration of the chains and groups but on the nature of their motion. If a solid contains certain groups in motion, then the NMR line narrows as a result of averaging of local magnetic fields;

the narrowing occurs when the correlation time is smaller than 10^{-4} sec. If the sample contains regions (crystalline) with $\tau_{cc} \gg 10^{-4}$ sec and regions (amorphous) with $\tau_{ca} \ll \ll 10^{-4}$ sec, then it is possible to consider the sample as a two-phase system. The resulting line is compound and from the ratio of its components it is possible to derive the degree of crystallinity. Schematically we can represent other possible cases as shown in Fig. 2.

Curves *a*, *b*, *c*, and *d* represent the change in the shape of the absorption line as the temperature is increased: (*a*) $\tau_{ca} > 10^{-4}$ sec and $\tau_{cc} > 10^{-4}$ sec (low temperature), both phases give a broad line; (*b*) $\tau_{ca} \simeq 10^{-4}$ sec and $\tau_{cc} > 10^{-4}$ sec, certain segments or groups in the amorphous phase begin to move, and the curve shows an inflection; (*c*) $\tau_{cc} \gg 10^{-4}$ sec $\gg \tau_{ca}$, the amorphous phase has a narrow line, while the crystalline phase has a broad line; (*d*) $\tau_{cc} < 10^{-4}$ sec and $\tau_{ca} \ll 10^{-4}$ sec (high temperature), there is appreciable motion in both cases, even below the melting point, resulting in a single narrow line.

Obviously, the determination of crystallinity by the NMR method is possible only in case *c*. The condition that $\tau_{cc} \gg 10^{-4}$ sec $\gg \tau_{ca}$ can be satisfied only at a certain temperature; in some polymers, such as natural rubber[41], this condition is not satisfied at any temperature, because the line does not have any structure. Slichter and McCall[62] found that for linear polyethylene the NMR method gives a constant value of ϵ, in agreement with other methods, between 240° and 300°K, but for branched polyethylene the apparent value of ϵ decreases rapidly with temperature. Fuschillo *et al.*[63] compared the percentage of crystallinity of polyethylene (with $CH_3/CH_2 = 0.2$, and $M_n = 25\,000$) determined by NMR and density measurements. The two methods give the same value of ϵ only over a limited range of temperatures.

The difficulties associated with the determination of crystallinity by NMR arise also from the nature of crystalline polymers, which consist in fact of a number of crystalline regions. Hyndman and Origlio[64] recorded NMR spectra of parallel bundles of polyethylene fibres, oriented at various angles to the field (Fig. 3). In addition to the narrow and broad components, there is a third component giving rise to the middle peak in Fig. 3*a*. After annealing the third peak disappears. The authors conclude that the third component corresponds to amorphous regions which are oriented in drawing of the fibres. Miller[65], using a number of methods, including NMR, showed that when

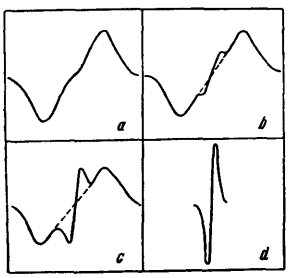


Fig.2. Dependence of NMR line shape on correlation times in a two-phase system[62].

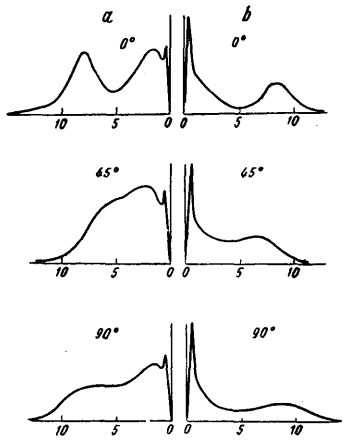


Fig.3. NMR spectrum of a bundle of polyethylene fibres oriented at various angles w.r.t. the field: *a*) cold-drawn; *b*) annealed[64].

molten polypropylene is poured into cold water one obtains a substance which is intermediate between crystalline and amorphous polymers. This he calls a "non-crystalline polypropylene" and concludes that it has a helical chain structure, but with little transverse order. Slichter[66] also observed this intermediate stage in the case of cold-drawn polyethylene fibres. The analysis of X-ray data and of the dependence of the second moment of the NMR line on temperature indicate that in these samples there are regions where chains are packed in a pseudohexagonal lattice, but configurational disorder remains due to the random orientations of zig-zag chains around the axes. Such structures may be considered as crystalline, but with major lattice imperfections. NMR can also reveal lattice defects in irradiated polyethylene[61] and in heat-treated polyethylene[67]. Comparative studies of polypropylene and polybutene by NMR and dilatometric methods over a wide range of temperatures[68] show that in polybutene the crystals are less perfect than in polypropylene. Therefore in a number of cases it is incorrect to describe the degree of ordering with a single parameter such as the "percentage of crystallinity". According to Kitaigorodski[5], this concept does not have any precise physical meaning. Apparently, the ratio of areas under the broad component and under the whole line, N_c/N, should be called an "index of high-frequency rigidity" of a polymer rather than the "percentage of crystallinity"[59,69]. If this index is high, the polymer is rigid and glasslike. This will be true whether the large value of N_c/N is due to high crystallinity, cross-linking, low temperature, hydrogen bonding, or dipolar effects. The value of N_c/N indicates to what degree the thermal motion of chains overcomes inter- and intra-molecular constraints.

In this way measurements of the relative intensity of the two components of a compound line can provide us with valuable information about the structure of the polymer. This method was used extensively in studies of the mechanism of the effects of radiation[70,71] and on polymers and of their degradation[72].

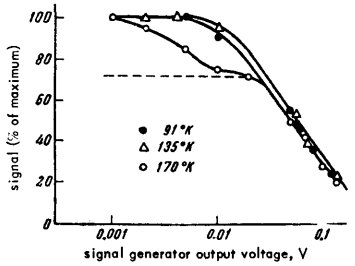


Fig.4. ^{19}F absorption curves at several temperatures in polytetrafluoroethylene[77].

If the line has a structure similar to that shown in Fig. 2*c*, then the "amorphous" and the "crystalline" components can be fairly accurately resolved simply by inspection. If, however, the derivative curve does not have distinct narrow and broad components, then special methods must be used. Urman[72], working under the direction of M.B.Heiman, G.I.Likhtenshtein , and Iu.S.Konstantinov, used the method of linear anamorphs to resolve the NMR line of polypropylene[73].

Other authors[74,75] in determining the two components, assume that the broad component does not vary with temperature and that it is given by the resonance line obtained at very low temperatures (below -150°C) when all motions are hindered. In polyethylene[76] this line shape resembles the line calculated for a proton pair.

The "two-phase" nature of a partially crystalline polymer is revealed not only by the line but also by the presence of two spin–lattice relaxation times, T_1, which can be determined either by the spin echo or the saturation method. For example, in polytetrafluoroethylene at 170°K,[76,77] the relationship between signal amplitude and r.f. field strength (Fig.4) has a step. Initially only 28% of all ^{19}F in the sample is saturated, and the remaining 72% becomes saturated later. For the narrow line (amorphous part) with $T_2 = 5 \times 10^{-5}$ sec, saturation occurs at a lower strength of the r.f. field than for the broad line with $T_2 = 0.9 \times 10^{-5}$ sec. The area under the narrow component is also close to 30% of the total area, *i.e.* the degree of crystallinity is 70%. As the temperature is lowered the relaxation times in the two phases become equal and at 135°K the usual saturation curve is obtained.

2. Stereoregularity

The study of the effect of stereochemical structure, *i.e.* stereoregularity, on properties of polymers presents one of the most pressing problems, as pointed out by Vol'kenshtein[78]. The NMR method can be used in this study. Here we shall consider only experiments on stereospecific solid polymers; some of the very interesting investigations of the stereochemical structure of macromolecules in solution will be discussed in Section V.

Bazhanov *et al.*[78] studied the stereoregularity of poly(methyl methacrylates). NMR spectra were recorded, between room temperature and 200°C, for five poly(methyl methacrylate) samples, two of which were atactic, in the form of technical Plexiglas obtained by radical polymerisation, and the remaining three samples (isotactic) were prepared by catalytic polymerisation.

In isotactic samples the line narrowing occurs much more abruptly and at lower temperatures than in atactic polymers (Fig.5). The higher mobility of chains in isotactic samples is in agreement with their lower glass points. Bazhanov *et al.* note that this rather unexpected result (increase in mobility with higher stereoregularity) implies a complicated relationship between dynamic and structural properties of this polymer.

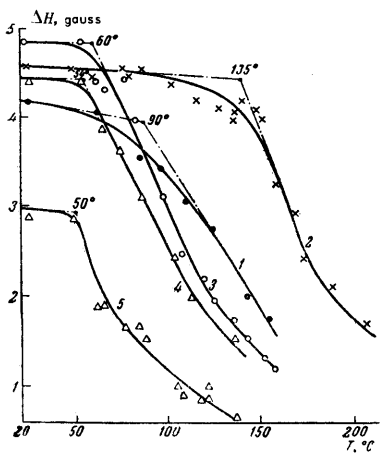


Fig.5. Temperature dependence of line width for poly(methyl methacrylate): 1) and 2) atactic; 3), 4), and 5) isotactic[78].

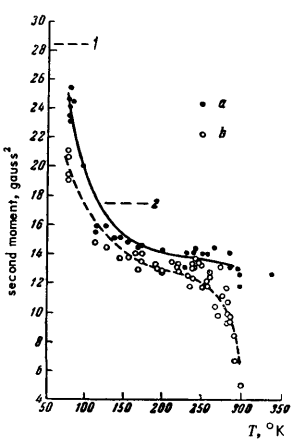


Fig.6. Temperature dependence of the second moment for polypropylene: *a*) isotactic; *b*) atactic. The theoretical values of ΔH_2^2 for rigid (1) and rotating (2) CH_3 groups are also shown[79].

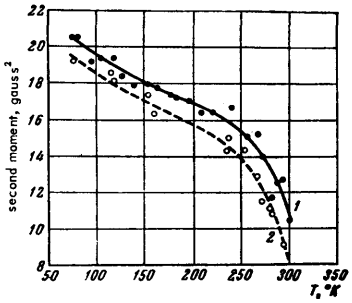


Fig.7. Temperature dependence of the second moment for polybutene: 1) isotactic; 2) atactic[34].

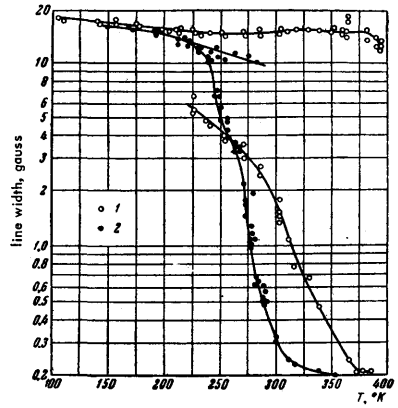


Fig.8. Temperature dependence of line width for polyethylene: 1) linear; 2) branched[86].

The effect of stereospecificity on NMR is more readily explained in other polymers. In their detailed study of polypropylene Slichter and Mandell[79,80] showed that the narrowing of the narrow component on heating occurs at a lower temperature in atactic polypropylene than in the isotactic variety, because crystallites impede motion in the amorphous region. The broad component remains constant; consequently there is little motion in the crystalline region. At low temperature the transition in the second moment in these polymers occurs within the same temperature range (Fig.6). Obviously, the rotation of CH_3 groups is independent of configurational ordering.

Sauer *et al.*[81] found that the decrease in ΔH_2^2, corresponding to the β-transition (glass transition in the amorphous region), for isotactic polypropylene takes place about 30° higher than in the atactic polymer. Nuclear magnetic resonance in isotactic polypropylene and polybutene was also reported by Sauer *et al.*[68]

Slichter[34] found that the second moment is smaller for atactic than for isotactic polybutene (Fig.7). In polystyrene at low temperatures the second moment does not depend on stereoregularity. With increasing temperature ΔH_2^2 (atactic) decreases faster than ΔH_2^2 (isotactic), since motion in the amorphous region, on account of its lower density of packing, is more intense than in the crystalline region. Tyuzyo[82] examined a theory of NMR in stereospecific polymers and obtained theoretical expressions and experimental data for relaxation times in polyethylene and polypropylene.

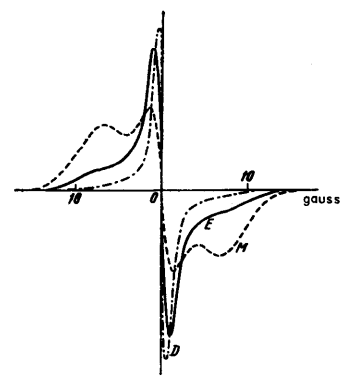


Fig.9. NMR line shape for three polyethylene samples at 20°C: *M*) linear; *E*) and *D*) branched[88].

3. Chain Structure

Chain structure [combination of the configurational order of repeat units (the way they are linked up) and of the degree of branching], which affects the density of packing and the mobility of molecular groups in polymers, should be reflected in NMR spectra of solid polymers. For asymmetric repeat units, the second moment of the "head-to--head" chain should be different from that of the "head-to--tail" chain. Thus, the chain structure can be determined by a comparison of experimental and theoretical values of ΔH_2^2.

High-resolution NMR spectra of polymers in solution also may be used to determine uniquely the configurational order of repeat units[83,84]. We shall consider this question in more detail later.

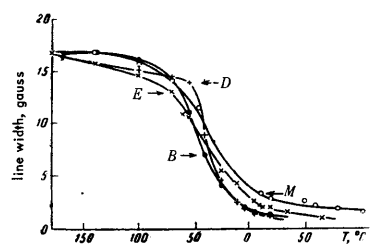


Fig.10. Temperature dependence of line width for four polyethylene samples: *M*) linear; *B*), *D*), and *E*) branched[88].

A number of experiments on polyethylene[57,66,85,86] indicate that in the branched polyethylene the mobility of spins is higher and the line narrower than in the linear polymer (Fig.8).

Peterlin *et al.*[87,88] undertook a special study of the degree of branching and crystallinity of polyethylene using dilatometric and NMR methods. The large difference in line shapes at room temperature is shown in Fig.9; similar differences are observed also at -170°C. The residual intensity of the narrow component at -170°C is proportional to the CH_3/CH_2 ratio in the polymer. The correlation frequency ν_C can be deduced from the narrowing of the line with temperature (Fig.10). In linear polyethylene the slope of $\log \nu_C$ *vs.* $(1/T)$ corresponds to an activation energy of 2.8 kcal mole^{-1}. For the branched polyethylene, there are two straight lines, intersecting at -63°C, corresponding to activation energies of 2.0 and 5.8 kcal mole^{-1}.

4. Orientation

The NMR signal is strongly affected by any change in the orientation of polymer molecules, such as occurs in drawing of fibres. Ward[89] observed that in poly(ethylene terephthalate) and in a number of other polyesters the second moment increases with an increase in the degree of orientation; apparently, in stretched oriented polymer films molecular motion is considerably reduced. An analogous effect, *i.e.* increase in the line width on cold drawing, is observed in linear polyethylene[66], while in branched high-pressure polyethylene, there is no significant difference between NMR signals of unoriented and stretched samples.

Further opportunities for studying the structure of polymer fibres and films are furnished by the dependence of the NMR signal on the angle between the axis of orientation and the direction of the magnetic field. In this connection we have to distinguish between two cases, one of a rigid oriented lattice and the other of rotation of an interatomic vector around an axis. If the sample consists of weakly interacting pairs of atoms, and the interatomic vector is perpendicular to the molecular axis, then the dependence of the second moment on the angle θ between the molecular axis and the magnetic field is given by

$$\Delta H_2^2 = \tfrac{5}{4}(\Delta H_2^2)_{\text{isotr.rigid}}\left(\tfrac{27}{8}\sin^4\theta - 3\sin^2\theta + 1\right), \qquad (1)$$

where $(\Delta H_2^2)_{\text{isotr.rigid}}$ is the second moment of the rigid lattice in the absence of molecular orientation.

McCall and Slichter[86] measured the second moment for polyethylene fibres at room temperature. For the linear polyethylene, the experimentally determined dependence of ΔH_2^2 on θ is close to that given by theory if a certain degree of mobility of the chains, namely harmonic oscillations with an angular amplitude of 15° are allowed. For the branched polyethylene, the discrepancy between the experimentally and theoretically determined dependence of ΔH_2^2 on θ is much larger than in the linear polymer.

When molecules of the sample are oriented and interatomic vectors, perpendicular to the molecular axis, rotate about the axis with a frequency $\gg 10^4$ c/s, the variation of the second moment with θ is given by

$$\Delta H_2^2 = \tfrac{5}{4}(\Delta H_2^2)_{\text{isotr.rigid}}\,\tfrac{1}{4}(3\cos^2\theta - 1)^2. \qquad (2)$$

Fig.11 shows the change in ΔH_2^2 for polytetrafluoroethylene at room temperature[90]. The continuous curve is derived from Eqn. (2), with the origin and the scale on the ordinate axis chosen such that the experimental and the theoretical values at $\theta = 0°$ and 90° coincide. The remaining experimental points also fall close to the theoretical curve. In contrast with theory, the second moment at $\theta = 54°$ is not equal to zero, which implies incomplete orientation of molecules in the sample. Sometimes the NMR line of oriented polymers may have a compound structure as in the case of cold-drawn polyethylene fibres discussed earlier (see Fig.3).

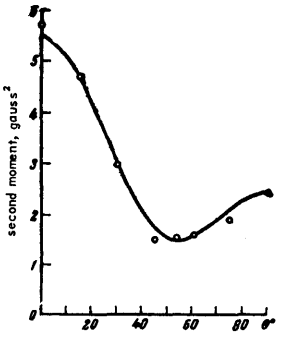


Fig.11. ΔH_2^2 as a function of θ, the angle between polytetrafluoroethylene fibres and the direction of the magnetic field[90].

5. NMR in Strained Polymers

NMR measurements in strained polymers have been done so far only in natural rubber. Experiments with vulcanised natural rubber subjected to moderate elongation (70%) did not reveal any appreciable change in the NMR spectrum[41]. However, Cohen-Hardia *et al.*[91] showed that the temperature variation of T_2 depends on elongation (Fig. 12). At low temperatures (between -20° and -30°C) T_2 is longer for stretched samples, and at high temperatures (between 10° and 20°C) stretching decreases T_2. For elongations between 70 and 300% and temperatures between -10° and 10°C, the slope $\Delta T_2/\Delta T$ decreases linearly with elongation. The authors

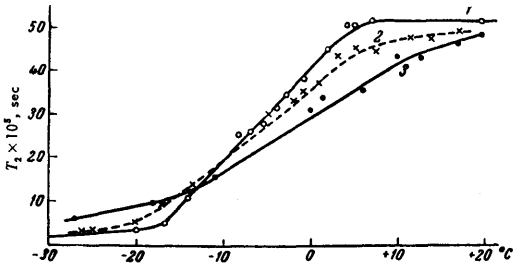


Fig.12. Temperature dependence of the transverse relaxation time T_2 for natural rubber at various degrees of elongation[91]: 1) 10%; 2) 170%; 3) 300%.

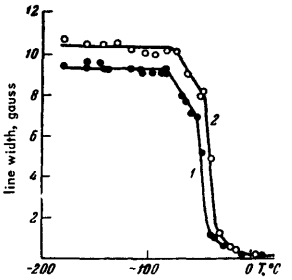


Fig. 13. Temperature dependence of line width for natural rubber: 1) unstretched; 2) with 500% elongation[92].

do not give any theoretical explanation of the observed effect. Lösche[27] assumes that this effect is associated with a decrease in the molecular spacing in stretched rubber; Oshima and Kusumoto[92] observed nuclear magnetic resonance in natural rubber subjected to a large elongation (500%) over a wide range of temperatures (Fig. 13). Between room temperature and -15 °C elongation does not affect the line width δH. As the temperature is lowered further, δH increases between -38° and -52 °C for unstretched samples and between -30° and -45 °C for stretched samples; it appears that the orientation of molecules hinders segmental motions. At low temperatures the second moment of the line is 20.3 gauss^2 and 18.5 gauss^2 in stretched and unstretched samples respectively. Slichter[30] and Powles[28] think that the increase of the second moment with elongation arises from closer packing of molecules resulting in a reduction of interproton distances. Vol'kenshtein[6] notes that this explanation can hardly be correct, since there is practically no change in density of rubber with elongation.

Probably more detailed information could be obtained by examining NMR in strained samples with different orientations between the axis of elongation and the magnetic field.

The effect of stretching on nuclear magnetic resonance in rubber is discussed by Tyuzyo[93].

6. The Effect of Fillers

Introduction of fillers into high polymers, for example, carbon black into rubber, is a commonly used method for achieving certain desirable properties of materials. In view of this even in the very early (1947) NMR experiments on polymers[94], such as natural rubber and its vulcanisates, the effect of loading with carbon black of natural and synthetic rubber was also investigated. Loading was found to produce a slight broadening of the line. Broadening of the line in synthetic rubber GR-S (70 : 30 butadiene–styrene copolymer) on loading with carbon black was also observed by Holroyd *et al.*[49,95]. At room temperature $\delta H \leq 0.19$ gauss for unvulcanised GR-S rubber (inhomogeneity of the magnetic field was 0.19 gauss). For vulcanised polymer δH = = 0.27 gauss; introduction of 30 and 50% of carbon black increased the line width to 0.57 and 0.67 gauss respectively. Mrowca and Guth[96] also reported a slight broadening of the line due to carbon black loading of natural rubber and of a number of synthetic rubbers. Holroyd *et al.*[97] made a detailed study of the effect of loading on nuclear magnetic resonance. In experiments on natural rubber, GR-S, and Hycar OS-10 (50 : 50 butadiene–styrene copolymer) it was found that there is no appreciable broadening on introduction of carbon up to 50%, but the signal decreases slightly. In butyl rubber, loaded with different types of carbon black, the broadening is only a little greater than the experimental error. These authors conclude that very weak physical bonding forces exist between rubber molecules and carbon. Slichter[30] points out that this conclusion is not sufficiently substantiated and suggests that the observed decrease in the signal strength arises from the reduction of the number of protons per unit volume of the sample. Lösche[27] suggests that NMR at very low temperatures, corresponding to the onset of CH_3 group rotation, would give more precise data on the effect of fillers.

III. THE STUDY OF MOLECULAR MOTION IN POLYMERS BY NMR

The properties of solid polymers in the glassy and especially in the viscoelastic state are intimately connected with motions of individual groups and chain segments. The NMR method is particularly well suited to the study of molecular motions; the method was used in one of the first demonstrations of rotation about the bonds in polymer chains[95].

NMR can be used to study molecular motions because they average out local magnetic fields and consequently narrow the line. By recording the NMR spectrum of the sample over a wide temperature range, we can observe "melting" of various molecular motions. Powles[98] notes that NMR measurements can determine in principle the nature of reorienting groups as well as the character and rapidity of their motion.

1. Variation of Line Width with Temperature

As the temperature is increased (or decreased) the line narrows (or broadens) in steps for a number of polymers; each change of δH corresponds to a certain change in the molecular motion. For example, Thurn[36,99] measured the line width of polyisobutene (molecular weight 1.75×10^6) and poly(methyl methacrylate). In polyisobutene (Fig. 14) there are three line-width transitions: at about -100 °C, between -30° and 10 °C, and between 30° and 40 °C. Correlating NMR data and results obtained by other methods, Thurn concludes that the first transition is connected with rotation of CH_3 groups about the axis of symmetry C_3, and the second with the onset of motion of the main chain. The third transition between 30° and 40 °C, observed only for samples of high molecular weight, is apparently associated with motions of large segments of the chain.

In poly(methyl methacrylate) there are four transitions, indicated in Fig. 15 by vertical broken lines. The same transitions were also observed by the dynamic-mechanical method. The transition at 75 °C is due to 0.2% of moisture present in the sample and the remaining transitions are associated with the onset of motion of CH_3 groups, monomeric units, and large segments of the chain.

Line-width transitions are in most cases interpreted in terms of rotational motions of individual groups or segments of the polymer chain. However, if δH continues to

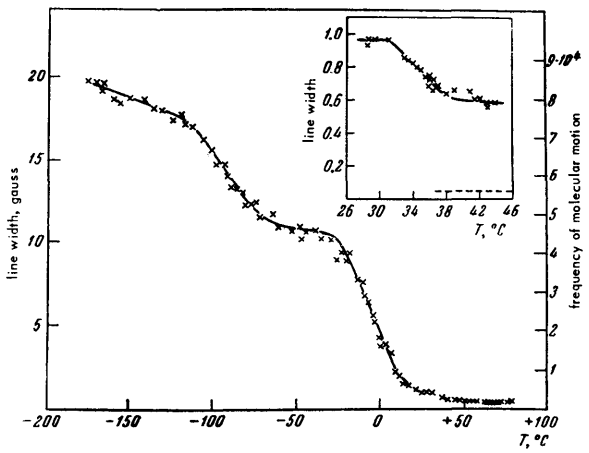


Fig.14. Temperature dependence of line width for polyisobutene[99].

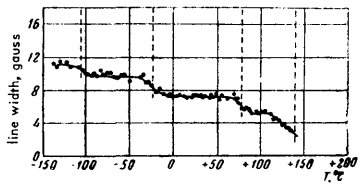


Fig.15. Temperature dependence of line width for poly(methyl methacrylate) containing 0.2% of water[99].

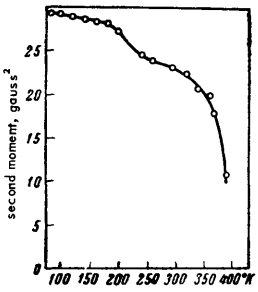


Fig.16. Temperature dependence of the second moment for high-density polyethylene[101].

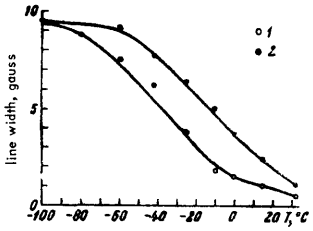


Fig.17. Temperature dependence of line width for polyisobutene: 1) at atmospheric pressure; 2) at 1060 atm.[104]

decrease to very small values (*e.g.* to 0.019 gauss in polydimethylsiloxane at 200°K and above[100]), then translational motion in crystallites must be possible. This unexpected conclusion was confirmed by other methods.

We should remember, however, that for certain polymers, changes in molecular motion, reflected by changes in a number of properties, do not affect the NMR line. For example, in high-density polyethylene[101] appreciable reduction in $\delta H_{max.slope}$ line width occurs only in the region of 200°K. The second moment of the line (Fig.16) exhibits two transitions: at 200°–250°K, due to the onset of cooperative motions of a small number of segments of the chain in the amorphous region of the polymer, and at ~350°K, due to disordering and melting of crystalline regions. In this case the second transition does not affect the line width $\delta H_{max.slope}$ because the maximum of the derivative curve is determined mainly by the magnitude of the narrow component of the compound NMR line, whereas melting of crystalline regions is associated with changes in the broad component.

If the line is compound, the temperature dependence of the line width may depend on the method of measurement. Thus, in polytrifluoroethylene[102] the half-height line width $\delta H_{\frac{1}{2}}$ and the maximum slope line width $\delta H_{max.slope}$ have different temperature dependence resulting in different activation energies and transition temperatures.

At temperatures considerably above the glass transition temperature of the polymer, the line width, as in liquids, is proportional to viscosity and inversely proportional to absolute temperature. A plot of $\log(\delta HT)$ *vs.* $(1/T)$ gives a straight line with a slope which is determined by the activation energy E of the liquid. Collins[103] found that for linear polyethylene at 134°C, E = 8.2 kcal mole^{-1}. For high-pressure polyethylene, the plot of $\log(\delta HT)$ *vs.* $(1/T)$ is curved; this is believed to be due to branching and changes in composition of the amorphous phase upon cooling. The apparent activation energy at high temperatures is 11.8 kcal mole^{-1}, which agrees reasonably well with the value of 12.8 kcal mole^{-1} derived from viscosity measurements above the melting point of the polymer.

Measurements of the temperature dependence of the line width in polymers subjected to different pressures can provide some information about their molecular motions. Nolle and Billings[104] showed (Fig.17) that an increase in pressure from 1 to 1000 atm broadens the line, which implies a reduction in molecular motion. The present author accounts for this effect by the reduction of the free volume in the polymer†.

† Igonin *et al.*[105] gave a direct demonstration of a reduction in molecular motion in polymers with an increase in pressure.

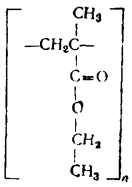
2. Variation of the Second Moment of the Line with Temperature

In polymers the second moment (ΔH_2^2) is the most important characteristic of the NMR line because ΔH_2^2 can be calculated for the rigid lattice as well as for the case of motion of individual molecular groups, so that experiment and theory may be readily compared.

It is convenient to consider the second moment of a polymer to be composed of two parts: the intramolecular contribution, arising from the dipole–dipole interaction of nuclei within a molecule, and the intermolecular contribution, associated with the interaction of nuclei located in different molecules. Since in the Van Vleck expression for ΔH_2^2 the internuclear distance enters to the power of -6, the magnitude of the second moment is determined mainly by the interaction between neighbouring atoms. In view of this, the intermolecular contribution is considerably smaller than the intramolecular one.

An estimate of the intramolecular contribution to the second moment of a polymer chain may be obtained by summing ΔH_2^2 for individual groups. Values of ΔH_2^2 calculated from the Van Vleck expression with the appropriate values of moments and interatomic distances are summarised in Table 1.

For example, a monomeric unit of poly(ethyl methacrylate) has 10 hydrogen atoms, 4 of which are in methylene groups and 6 in methyl groups.



$$\Delta H_2^2 = \frac{4}{10}\Delta H_{2(CH_2)}^2 + \frac{6}{10}\Delta H_{2(CH_3)}^2 =$$
$$= \frac{4}{10} \times 11.2 + \frac{6}{10} \times 22.5 =$$
$$= 4.5 + 13.5 = 18.0 \text{ gauss}^2.$$

The experimentally determined value of ΔH_2^2 for poly(ethyl methacrylate) is 21.5–22.0 gauss² (see Table 3). The difference is due to the intermolecular contribution. In certain cases, *e.g.* for polyethylene, this type of calculation cannot be used even as a rough estimate.

The quantity ΔH_2^2 can be calculated more accurately if the configuration of polymer chains is known. This calculation is most readily performed for a flat chain. Usually, however, the chains in crystalline polymers are coiled (as indicated by X-ray data), so that it is necessary to know the coordinates of each atom before any calculation of ΔH_2^2 may be attempted. Theoretical values of the second moment of spiral structures were derived for polyisobutene[106], polypropylene[59,79], and polytetrafluoroethylene[107]. In the amorphous region the polymer chains have many possible spatial arrangements depending on the angle between neighbouring segments (pairs of monomers). The chain conformation may be characterised by a local regularity parameter ξ — the fraction of bonds having the *gauche*-conformation. Miyake[108,109] calculated second moments for a number of amorphous vinyl polymers for the case where the fractions of *gauche*- and *trans*-bonds are ξ and $(1-\xi)$ respectively. In this calculation the following values of interatomic distances were used: C–H 1.09 Å; C–C 1.54 Å; C–F 1.33 Å; C–C 1.74 Å; and the following values of magnetic moments: $\mu_H = 2.793\ \mu_0$; $\mu_F = 2.627\ \mu_0$; $\mu_{Cl} = 0.7893\ \mu_0$, where $\mu_0 = 5.05 \times 10^{-24}$ erg gauss^{-1}. The second moment is given by

$$\Delta H_2^2 = a + b\xi + c\xi^2 + (d + e\xi + f\xi^2) \text{ gauss}^2, \qquad (3)$$

where the values of coefficients a, b, c, d, e, f are given in Table 2. For extended polyamide chains $[NH(CH_2)_mNHCO.(CH_2)_nCO]_p$, the intramolecular contribution to the second moment may be calculated from the following equation[110]:

$$\Delta H_2^2 = [18.5 - 22.7/(m + n + 1)] \text{ gauss}^2. \qquad (4)$$

For $m, n \geq 5$, the error in ΔH_2^2 derived from Eqn. (4) is less than 1%; if the paraffin segments separating amide groups contain less than five C atoms, then Eqn. (4) does not apply.

The intermolecular contribution to the second moment for a rigid lattice may be calculated directly from the Van Vleck equation only if the relative distribution of chains is known. For example, Bateman *et. al.*[111] using X-rays determined the parameters of an orthorhombic lattice in polyethylene terephthalate and other glycol terephthalate polymers and calculated both contributions to the second moment. Slichter[110] made a similar calculation for even-even polyamides (*m* and *n* even), based on X-ray data, and

TABLE 1. NMR second moment of molecular groups.

Group	$-CH_2$	$-CH_3$	$-CF_2$	$-CF_3$
ΔH_2^2, gauss	11.2	22.5	2.1	4.2

TABLE 2. Second moment of amorphous vinyl polymers[108,109].

Polymer	Stereoregularity	Resonance	Coefficients in the equation $\Delta H_2^2 = a + b\xi + c\xi^2 + (d + e\xi + f\xi^2)$, gauss²					
			a	*b*	*c*	*d*	*e*	*f*
Polyethylene $-CH_2-CH_2-$		^1H	18.82	—2.08	0.72	—	—	—
Polytetrafluoroethylene $-CF_2-CF_2-$		^{19}F	7.86	—1.46	0.63	—	—	—
Poly(vinyl chloride) $-CH_2-CHCl-$	isotactic	^1H	13.47	—2.89	1.34	0.06	0.01	—0.02
	syndiotactic	^1H	12.81	—0.90	—0.16	0.08	—0.05	0.03
Polytrifluorochloroethylene $-CF_2-CFCl-$	isotactic	^{19}F	6.08	—2.88	1.29	0.04	0.03	—0.03
	syndiotactic	^{19}F	5.40	—0.84	—0.23	0.07	—0.05	0.03
Poly(vinyl fluoride) $-CH_2-CHF-$	isotactic	^1H	13.47	—2.89	1.34	1.24	0.32	—0.26
	syndiotactic	^1H	12.81	—0.90	—0.16	1.51	—0.50	0.36
	isotactic	^{19}F	4.18	1.08	—0.88	2.50	—4.39	2.60
	syndiotactic	^{19}F	5.10	—1.68	1.19	0.47	1.70	—1.97
Polytrifluoroethylene $-CF_2-CHF-$	isotactic	^1H	3.70	0.96	—0.79	2.83	—4.97	2.94
	syndiotactic	^1H	4.52	—1.50	1.06	0.53	1.93	—2.25
	isotactic	^{19}F	6.08	—2.88	1.29	1.40	0.35	—0.29
	syndiotactic	^{19}F	5.40	—0.84	—0.23	1.71	—0.57	0.40
Poly(vinylidene fluoride) $-CH_2-CF_2-$		^1H	14.93	—3.41	0.98	1.11	0.32	—
		^{19}F	5.99	—2.69	0.56	1.25	0.37	—

TABLE 3. Second moment of the NMR line in polymers.

Polymer	Calculated ΔH_2^2, gauss^2: structure	intramolecular contribution	intermolecular contribution	total second moment	Measured ΔH_2^2, gauss^2: temperature, °K	ΔH_2^2	References
1	2	3	4	5	6	7	8
Natural rubber (vulcanised)	rigid structure rotn. of CH_3 group			18.5 11.8	77 225	18.4 13.0	41
Natural rubber (vulcanised) Ditto (elongated 500%)					77—190 77—190	18.3 20.3	92
Natural rubber					90	18	118
Natural rubber					82	18,4	119
Polyisobutene (Vistanex)					91	37	119
Polyisobutene	rigid flat structure spiral structure	20	4	24 33—40	77	41	106
Polychloroprene-(neoprene W)					82	22.0	119
Polystyrene (degree of polymerisation 4200)	rigid structure	7.7			room	11.9	120
Polystyrene	**rigid structure**	6.8			room	12.5	121
Poly(vinyl alcohol) ($M = 3.4 \times 10^4$)	rigid structure CH protons: syndiotactic structure isotactic structure *OH protons*	 9.6 8.2 2.0	7—8	19—20	293	20.4	122
Poly(vinyl acetate) (degree of polymerisation 2000)	rigid structure	7.85			room	11.0	120
Poly(vinyl chloride)	**rigid structure**	11.5			room	14.5	121
Poly(vinyl chloride)	**rigid flat structure**	12.7			room	14.4	120
Poly(vinyl chloride)	**rigid flat structure** **isotactic** **syndiotactic**	 12.7 12.1			243	14.6	123
Poly(methyl methacrylate) atactic	**rigid structure** **rotn. of CH_3 group** **rotn. of monomeric unit**	18.8 9.8 2.5	4 3 2	22.8 12.8 4.5	77	11.5	113
Poly(methyl methacrylate)	rigid structure rotn. of one CH_3 group rotn. of both CH_3 groups	19.7 13.5 7	5 3.5 2	24.7 16.9 9	77 198 403	24.1 15.7 8.0	112
Poly(methyl methacrylate)	**rotn. of CH_3 group**	7.8			room	8.5	121
Poly(methyl methacrylate)	**rotn. of two CH_3 groups**	6.9			room	9.0	120
Poly(methyl methacrylate)	**rigid structure**			26	77	21	124
Poly(methyl methacrylate) (isotactic, $M = 3 \times 10^5$)					323 393	7.8 1.9	78
Poly(methyl methacrylate) (atactic)	**rigid structure** rotn. of one CH_3 group rotn. of both CH_3 groups rotn. of monomeric unit	22.9 16.1 9.4 2.4	5 4 3 2	27.9 20.1 12.4 4.4	77	18.6	113
Poly(ethyl methacrylate)	**rigid structure**	18.0	4.0	22.0	93	22	28
Poly(ethyl methacrylate) (atactic)	**rigid structure** rotn. of ethyl group rotn. of ethyl and methyl groups rotn. of monomeric unit	21.5 13.6 8.2 2.0	5 4 3 2	26.5 17.6 11.2 4.0	77	21.5	113

TABLE 3.(cont'd.)

Polymer	Calculated ΔH_2^2, gauss^2: structure	intramolecular contribution	intermolecular contribution	total second moment	Measured ΔH_2^2, gauss^2: temperature, °K	ΔH_2^2	References
1	2	3	4	5	6	7	8
Poly(butyl methacrylate)	rigid structure			2.3	77	23	124
Poly(isobutyl methacrylate)	rigid structure			24	77	20	124
Poly(cyclohexyl methacrylate)	rigid structure			25	80	23.5	124
Poly(methyl α-chloroacrylate)	**rigid structure**	18	2	20	80	17	112
Poly(methyl α-chloroacrylate)	rigid structure rotn. of CH_3 group			24 10.5	77	11	124
Nylon 66	rigid extended chain rotn. of H about chain axis	16.8 5.5	9.7 3	26.5 8.5	77 298	26 18	110
Nylon 57	rigid chain rotn. of H	16.8 5.5	3	8.5	77 298	26 16	110
Nylon 79	**rigid chain** rotn. of H	17.2 5.6	3	8.6	77 298	26 13	110
Nylon 88	rigid chain rotn. of H	17.2 5.6	9.7 3	26.9 8.6	77 298	27 14	110
Nylon 610	rigid chain rotn. of H	17.2 5.6	9.7 3	26.9 8.6	77 298	28 15	110
Nylon 1010	rigid chain rotn. of H	17.4 5.7	9.7 3	27.1 8.7	77 298	28 15	110
Nylon 1018	rigid chain rotn. of H	17.7 5.7	9.7 3	27.4 8.7	77 298	28 15	110
Poly(ethylene terephthalate) (amorphous sample)	**rigid structure**	8.1	2.0	10.1	90	15.1	125
Poly(ethylene terephthalate)	rigid flat structure, orthorhombic lattice	8.2	1.9	10.1	90	13.0	111
Poly(ethylene deuterophthalate)	rigid structure			15.3	90	18.2	125
Poly(tetramethylene terephthalate)					90	19.3	111
Poly(pentamethylene terephthalate)					90	22.3	111
Poly(hexamethylene terephthalate)	rigid flat structure, orthorhombic lattice	14.4	1.8	16.2	90	23.1	111
Poly(hexamethylene terephthalate)					90	21.5	111
Poly(decamethylene terephthalate)	rigid flat structure, orthorhombic lattice	16.5	1.4	17.9	90	22.5	111
Polyethylene	**rigid structure**	19	8	27	87	28	126
Polyethylene	**rigid structure**	17.8	7.7	25.5	84	26.3	123
Polyethylene (high-pressure branched, $M_n = 25\,000$)	rigid structure	18.7	8.3	27	77	27.2	69
Polyethylene, (high-pressure, 70% cryst.)	rigid structure synchronous rotn. of CH_2 groups random rotn. of CH_2 groups	18.7	5.3	24.0 8.5 2.7	150	28	86
Polyethylene (cationic catalysis, 90% cryst.)	**rigid structure** **synchronous rotn. of CH_2 groups** **random rotn. of CH_2 groups**	18.7	7.6	26.3 8.5 2.7	100	34	86
Polypropylene (isotactic)	rigid spiral structure	23.5	5	28.5	77	23—25	79

TABLE 3. (cont'd.)

Polymer	Calculated ΔH_2^2, gauss²				Measured ΔH_2^2, gauss²		References
	structure	intramolecular contribution	intermolecular contribution	total second moment	temperature, °K	ΔH_2^2	
1	2	3	4	5	6	7	8
Polypropylene	rigid spiral structure	26.6					58
Polybut-1-ene					77	20	60
Poly(vinyl fluoride)							90
NMR-^{1}H	rigid structure	14.3	3.3	17.6	77	18.8	
	chain rotn.	4.8	1.1	5.9	310	10	
NMR-^{19}F	rigid structure	5.8	3.8	9.6	77	11.0	
	chain rotn.	1.9	0.9	2.8	340	3	
Poly(vinylidene fluoride)							90
NMR-^{1}H	rigid structure	15.7	2.6	18.3	77	18.9	
NMR-^{19}F		7.1	3.1	10.2	77	10.5	
Polytrifluoroethylene							90
NMR-^{1}H	rigid structure	5.9	4.2	10.1	77	12.2	
NMR-^{19}F		6.8	4.1	10.9	77	9.8	
Polytrifluoroethylene NMR-^{19}F	rigid flat structure				101	7.7	123, 126
	isotactic	7.4	0.6	8.0			
	syndiotactic	6.4	0.5	6.9			
Polytetrafluoroethylene	**rigid spiral structure**	8.4	2.5	10.9	77	11.5	107
Polytetrafluoroethylene NMR-^{19}F	rigid flat structure	9.2	2.4	11.6	100	11.7	123
Polytetrafluoroethylene NMR-^{19}F	rigid structure	7.5	2.5	10.0	77	10.9	90
	chain rotn.	2.2	0.6	2.8	400	2	
Polytetrafluoroethylene, 90% cryst.	rigid structure			11.4	200	13	50
Silicone rubber					77	10.0	127
Silicone fluid (Fluid 200 Dow Corp.)	rotn. of CH_3 group	5.4	2–3		77	7.8	128
Silicone resin (Gum 400 Dow Corp.)	rotn. of CH_3 group	5.4	2–3		77	8.4	128
Silicone rubber (Silastic 80 Dow Corp.)	rotn. of CH_3 group	5.4	2–3		77	8.4	128
Polydimethylsiloxane $M = 7.5 \times 10^4$	rotn. of CH_3 group	5.4	1.6	7.0	80	7.0	100

found that the intermolecular contribution is 9.7 gauss². In amorphous polymers the average interchain distance can be determined from the amorphous halo in the *X*-ray pattern; the method was used by Slichter[90], for example, for fluorine derivatives of polyethylene.

The theory of NMR in solids (see Refs. 7 and 9) enables us to calculate ΔH_2^2 for several types of molecular motion in polymers. For polyamides, in the case of rotation of protons around the chain, the intermolecular contribution to the second moment is 3 gauss², and the intramolecular contribution is

$$\Delta H_2^2 = [5.9 - 4.7/(m + n + 1)]\ \text{gauss}^2. \quad (5)$$

For torsional harmonic oscillations with a 15° amplitude,

$$\Delta H_2^2 = [17.0 - 21.2/(m + n + 1)]\ \text{gauss}^2, \quad (6)$$

and with a 30° amplitude,

$$\Delta H_2^2 = [12.3 - 15.4/(m + n + 1)]\ \text{gauss}^2. \quad (7)$$

Fig. 18 shows the intramolecular contribution to the second moment of polyamides for rigid chains, oscillations,

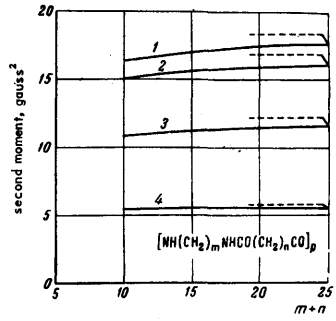


Fig. 18. Dependence of intramolecular contribution to the second moment on the number of methylene groups for several polyamides: 1) rigid structure; 2) 15° amplitude oscillation; 3) 30° amplitude oscillation; 4) free rotation[110]; the broken line corresponds to $(m + n \rightarrow \infty)$.

and free rotations as a function of the number of CH_2 groups in the monomeric unit. Fig. 19 shows the experimental and the calculated values of ΔH_2^2 for Nylon 610(polyhexamethylenesebacamide). It appears that chain motions start at ~360°K, *i.e.* some 100° below the melting point.

Further examples of changes in ΔH_2^2 with temperature are illustrated in Figs. 7 (polybutene) and 16 (polyethylene).

Fig. 6 shows the temperature dependence of ΔH_2^2 in isotactic and atactic polypropylene together with the theoretical values for rigid and rotating methyl groups.

In the case of a compound resonance line it is possible to determine the second moments of the narrow and the broad component and compare these results with theoretical values. The results of such an analysis are shown in Fig. 20 for linear and branched polyethylenes[86].

If the monomeric unit contains several molecular groups, then again ΔH_2^2 can be calculated for a rigid molecule and for rotation of any number or all the groups. Thus, Powles[112]

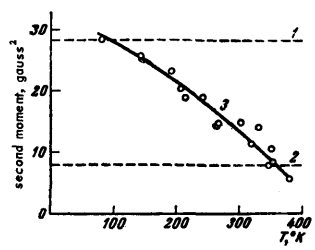


Fig. 19. Temperature dependence of the second moment for Nylon 610: 1) theoretical, rigid lattice; 2) theoretical, rotating chains; 3) experimental[110].

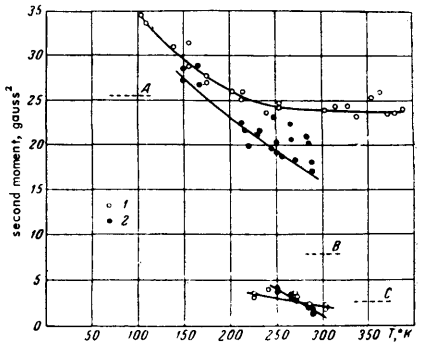


Fig.20. Temperature dependence of the second moment for polyethylene: 1) linear; 2) branched. A, B, C are the calculated values of the second moment: A) rigid lattice; B) synchronous rotation of neighbouring CH_2 groups; C) random rotation[86].

showed that for poly(methyl methacrylate) between 200°K and 340°K the experimental value of ΔH_2^2 agrees with the value calculated for rotation of main-chain CH_3 groups; at much higher temperatures the methyl groups attached to the oxygen atom also begin to rotate. Sinnot[113] performed analogous calculations for poly(ethyl methacrylate).

The temperature dependence of the second moment in polymers has been treated theoretically by Miyake *et al.*[114-117]

Table 3 lists some theoretical and experimental values of the second moment for a number of polymers.

Correlation of data obtained by different authors is made difficult by the fact that the samples used had different molecular weights and structure. There is some divergence in the calculated values of ΔH_2^2 since various models with different interatomic distances and angles were used. Also we have to remember that the accuracy of calculations and experimental determinations of ΔH_2^2 is not very high. Nevertheless, analysis of Table 3 leads to certain conclusions about molecular motion in polymers. In many cases (*e.g.* polyacrylates and polyesters) the experimental value of ΔH_2^2 is considerably smaller than the calculated one even at liquid nitrogen temperatures; apparently there is still some motion of molecular groups in polymers at these low temperatures.

Experimental data on transitions obtained from measurements of line width and second moment as a function of temperature for a number of polymers are listed in Table 4. In several polymers it was possible to identify the type of motion associated with each transition by comparing NMR data with results obtained by other methods. In particular, the glass transition is often accompanied by a change in δH or ΔH_2^2.

Kosfeld and Jenckel[134] working with pure and plasticised polymers obtained good agreement for the glass transition temperature as determined from narrowing of the NMR line and by other methods. The temperature at which the line width (in units of frequency) was equal to the correlation frequency was taken as the glass transition temperature.

TABLE 4. Polymer transitions, revealed by changes in NMR line width and in the second moment with temperature.

Polymer	Transition temperature, °K	Molecular motion associated with the transition	References
1	2	3	4
Natural rubber, vulcanised	155 225	rotn. of CH_3 group segmental rotn., glass transition	41
Natural rubber	195	rotn. of CH_3 group	129
Natural rubber, vulcanised Ditto, (elongated 500%)	221—235 228—243	rotn. of CH_3 group, glass transition ditto	92
Natural rubber	198 230	reorientation of CH_3 groups reorientation of segments	118
Divinyl – acrylonitrile copolymer (65 : 35)	140		129
Polyisobutene	140 240	reorientation of some CH_3 groups chain motion, glass transition	106
Butyl rubber	125—150		129
Polyurethane (Vulcalane)	253	glass transition	96
Polystyrene (degree of polymerisation 4200)	353 393	glass transition	120
Poly(methyl methacrylate)	270—290	monomeric reorientation, glass transition	113
Poly(methyl methacrylate)	313	glass transition at 276 °K	120
Poly(methyl methacrylate)	163 343	reorientation of CH_3 groups, glass transition	112
Poly(methyl methacrylate)	348 403	glass transition at 343 °K	120
Poly(methyl methacrylate) (atactic, $M \cong 10^6$)	363	glass transition	78
Poly(methyl methacrylate) (atactic)	130 360—370	rotn. of CH_3 groups segmental rotn., glass transition	113
Poly(methyl methacrylate) (isotactic, $M = 1.2 \times 10^6$) Ditto, ($M = 3 \times 10^5$) Ditto, ($M = 1.3 \times 10^5$)	333 327 323	glass transition glass transition glass transition	78
Poly(ethyl methacrylate) (atactic)	110 290 350	rotn. of CH_3 group rotn. of ester group glass transition	113
Poly(vinyl alcohol)	293—323 343—373	dilatometric measurements show transitions at 288° and 343 °K	130
Poly(vinyl acetate) (degree of polymerisation 2000)	323	glass transition at 303 °K	120
Poly(vinyl chloride) (degree of polymerisation 1300)	358	glass transition at 348 °K	120
Poly(ethylene terephthalate)	370	rotn. of phenyl groups	131
Polyethylene	245	segmental motion, glass transition at 243° K	132
Polyethylene	173	segmental motion	123
Polyethylene (high-pressure)	173 243 290	segmental motion segmental motion in amorphous regions motion in crystalline regions	75
Polyethylene (low-pressure)	173 273 348	segmental rotn. segmental motion in amorphous regions motion in crystallites	75
Polypropylene (atactic)	233	glass transition	58
Polypropylene (isotactic, 60% cryst.)	300	chain motion in amorphous regions	81
Polypropylene (isotactic)	263	glass transition	58
Polytetrafluoroethylene, NMR-^{19}F	210 270—310	2/3 of CF_2 groups rotating all CF_2 groups rotating	107
Polytetrafluoroethylene, NMR-^{19}F	173	segmental motion	123

TABLE 4.(cont'd.)

Polymer	Transition temperature, °K	Molecular motion associated with the transition	References
1	2	3	4
Polytetrafluoroethylene, NMR-^{19}F	285	rotn. in cryst. regions	133
Polytrifluorochloroethylene, NMR-^{19}F	243	segmental motion	123
Silicone rubber	164	crystallisation	127
Silicone rubber	150—180	rotn. about Si—O bond	128
Silicone resin	90	spiral motion of $(CH_3)_2$ Si groups	128
	150—180	rotn. about Si—O bond	
Silicone fluid	90	spiral motion of (CH_3) Si groups	128
	140—170	rotn. about Si—O bond	
Polydimethylsiloxane ($M = 7.5 \times 10^4$)	180	rotn. about Si—O bond and translational motion in crystallites	100

Nohara[135] notes that the agreement between transition temperatures determined by NMR and mechanical methods is closer in symmetric polymers (polyethylene, polytetrafluoroethylene) than in asymmetric polymers (buna-N, polystyrene).

The nature of a transition accompanied by a change in line width or in the second moment is more readily interpreted if the sample is oriented. Hyndman and Origlio[133] showed that rotation in crystalline regions of Teflon fibres at 285°K affects the NMR line width only when they are not parallel to the magnetic field.

3. Relaxation Times, Correlation Frequency, and Activation Energy of Molecular Motions in Polymers

Measurements of relaxation times T_1 and T_2 over a wide range of temperatures also provide information about polymer structure and internal motions.

Since high polymers may be considered as liquids (at least in the viscoelastic state), as far as motion of individual groups is concerned, the theory of relaxation for liquids may be employed in the interpretation of results. For example, spin-echo measurements of the spin–lattice relaxation time in natural rubber[118] show a typical liquid-like dependence of log T_1 on $1/T$, with a minimum (Fig.21). However, the shape of this curve is slightly different from the one predicted by theory. The disagreement cannot be accounted for by a distribution of correlation frequencies; an explanation in terms of cooperative molecular motions has been suggested[118]. In poly(methyl methacrylate) T_1, determined by the spin-echo method, exhibits complex behaviour with two minima[136].

The spin–spin relaxation in polymers also cannot always be described by a single relaxation time T_2. For instance, Powles *et al.*, using the spin-echo method, measured T_1 and T_2 in polyisobutene[137] and in dimethylsiloxane polymers[40]. T_2 is determined by using 90° and 180° pulses separated by time τ; the echo amplitude h at time 2τ is proportional to $\exp(-\tau/T_2)$ if the effect of self-diffusion is small. A plot of $\ln(h/h_{max})$ *vs.* 2τ should give a straight

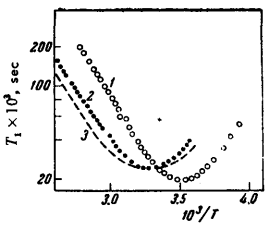


Fig.21. Temperature dependence of the longitudinal relaxation time T_1 in: 1) natural rubber; 2) vulcanised natural rubber; 3) a theoretical curve for vulcanised natural rubber[118].

line. In polyisobutene above 170°C the plot of $\ln(h/h_{max})$ *vs.* 2τ (Fig.22) shows two transverse relaxation times T_{21} = = 2.8 msec and T_{22} = 10.6 msec. Two values of T_2 were also found, above -42°C, in a number of dimethylsiloxane polymers whose chains contained more than 1000 atoms. It appears that the second relaxation mechanism involves an interaction between chains. Two T_2 values were also observed in polyethylene[138]. Measurements of T_1, line width, or the second moment as a function of temperature enables us to calculate the correlation frequency ν_c and the activation energy E of molecular motions. Such calculations were made for a number of polymers: branched and linear polyethylene[86,101], rubber[41], polyisobutene[106], and fluorine derivatives of polyethylene[90].

The activation energies deduced from the temperature dependence of ν_c, derived from ^{1}H and ^{19}F resonance in polytrifluoroethylene, were found to be 2.6 and 3.2 kcal × × mole^{-1} respectively[90]. For polyethylene[86] the plot of log ν_c *vs.* $1/T$ consists of two straight lines (Fig.23). The activation energies of molecular motions responsible for

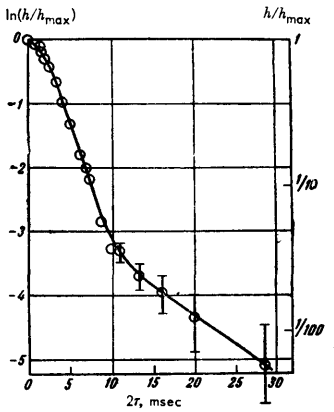


Fig.22. Determination of T_2 by the spin-echo method for polyisobutene at 194°C.[137]

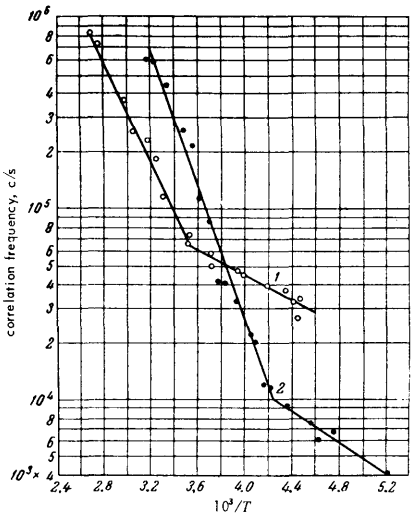


Fig.23. Correlation frequency as a function of temperature in polyethylene: 1) linear; 2) branched[86].

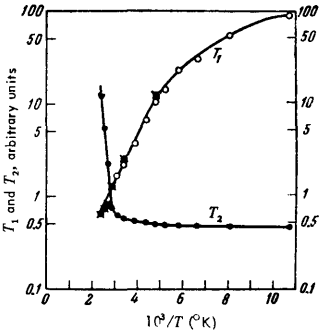


Fig.24. Temperature dependence of relaxation times for two polyethylene deuteroterephthalate samples[141].

the low-temperature and the high-temperature line-narrowing are respectively 1.5 and 6.1 kcal mole^{-1} in linear polyethylene, and 2.0 and 8.8 kcal mole^{-1} in branched polyethylene. However, a comparison of activation energies derived from NMR and other methods indicates that caution should be exercised in the calculation of E from the correlation frequency. Powles[28,139] gives a number of examples where low values of E were obtained on account of a distribution of correlation frequencies in polymers. Nolle and Billings[104] also found a large discrepancy in the value of E determined by NMR and that derived from viscosity measurements on a polyisobutene melt; they point out that the line width is affected by motion of individual methyl groups, while viscous flow involves cooperative motion of a large number of segments.

In addition to relaxation times, the coefficient of self-diffusion D can also be measured by the spin-echo method[17]. The lower limit of the method ($D \geq 10^{-7}$cm^2 sec^{-1}) allows measurements of D only in polymer melts. McCall *et al.*[140] measured D in polyethylene melts between 130° and 200°C and calculated the self-diffusion activation energy E. For chains longer than C_{20}–C_{30}, E becomes independent of chain length. The dependence of D on molecular weight is given by D = const $n^{-5/3}$, where n is the number of C atoms in the molecule.

4. Use of Isotopic Substitution in the Study of Motions in Polymers by NMR

The interpretation of NMR results in polymers, as in other branches of spectroscopy, is made easier by the use of isotopic substitution. Deuteration, *i.e.* replacement of ^{1}H by D, is most commonly used. The gyromagnetic ratios of ^{1}H [$\gamma/2\pi$ = 4257 (c/s) gauss^{-1}] and ^{2}H [$\gamma/2\pi$ = 654 (c/s) gauss^{-1}] are very different, so that deuterium resonance does not interfere with the hydrogen resonance.

Ward *et al.*[89,125,141] found that substitution of three H atoms in the benzene ring of polyethylene terephthalate by D gives rise to a compound line, because the remaining single proton in the ring interacts weakly with other protons and therefore has a narrow line, while methylene protons have a broad line. The line remains compound even down to -180°C. The mobility of CH_2 groups in polyethylene terephthalate can be measured if all the ring protons are replaced by deuterons. The temperature dependence of relaxation times in polyethylene deuteroterephthalate (Fig.24) indicates that between 200° and 400°K there is a hindered rotation of CH_2 groups about the C–C bond, with an activation energy of ~ 2 kcal mole^{-1}. Glick *et al.*[142] showed that the substitution of D for H in amide groups in amorphous regions of polyhexamethyleneadipamide has little effect on the temperature dependence of the second moment. Yoshida *et al.*[143] examined nuclear magnetic resonance in films of normal and deuterated polyvinyl alcohol. The method of isotopic substitution is also used for high-resolution NMR measurements of polymers in solution. Bovey *et al.*[144] employed the substitution of D for H in assigning peaks in the spectrum of polystyrene in solution.

5. Comparison of NMR Data with Results Obtained by Other Methods

A comparison of NMR data with dynamic-mechanical results was made even in Alpert's original nuclear resonance experiments on rubber[94]. A discussion of the relation between mechanical, dielectric, and nuclear resonance absorption in polyisobutene, poly(methyl methacrylate) and poly(methyl α-chloroacrylate) was given by Powles[98]. Sauer and Woodward[29] compared NMR and dynamic mechanical measurements for a number of polymers, both amorphous [polyisobutene, poly(methyl methacrylate)] and highly crystalline [poly(vinyl chloride), polyethylene, irradiated polyethylene, polypropylene, polybutene, polystyrene, polyamides, polytetrafluoroethylene]. In many cases a transition causing narrowing of the NMR line also appears in mechanical measurements as a sharp maximum in the logarithmic decrement of damping Δ and a decrease in the dynamic shear modulus G. A transition of this type is

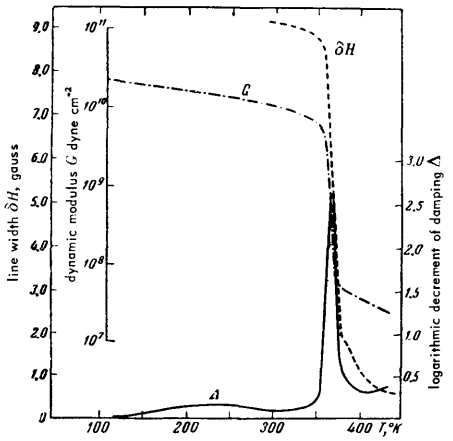


Fig.25. NMR line width, dynamic modulus, and logarithmic decrement of damping as a function of temperature for poly(vinyl chloride)[29].

observed for example in poly(vinyl chloride) at 350°–360°K, which corresponds to the glass transition temperature (Fig.25). The second slight maximum in Δ at ~240°K apparently corresponds to weak vibrations of methylene groups which have no appreciable effect on the NMR line width. Sauer and Woodward[29] conclude that the melting of crystallites is more readily apparent in dynamic-mechanical properties of the polymer, since local rotation and reorientation in the solid state generally narrow the NMR line prior to melting of crystallites so that any further narrowing is imperceptible.

The dynamical-mechanical method is superior also in detecting secondary amorphous transitions involving main chain segmental motion, such as the low-temperature transitions in polyamides. The glass transition (primary amorphous transition) is readily detectable by both methods, though with some discrepancy in the transition temperatures, possibly on account of different frequency ranges employed. The NMR method is much more sensitive to the rotation of side chains, *e.g.* CH_3 groups in polyisobutene, poly(methyl methacrylate), and polypropylene, than the mechanical method. Thus, the two methods are complementary.

Molecular motion in polymers containing polar groups can be investigated also with the aid of dielectric measurements. Thurn[36] gave an extensive review of mechanical, dielectric, and nuclear resonance measurements for many polymers.

IV. THE STUDY OF CHEMICAL PROCESSES IN POLYMERS

Chemical reactions between high polymers play an important role in engineering and biology and consequently their investigation belongs to one of the most important, though so far little explored, fields of polymer chemistry and technology. The known chemical reactions of macromolecules fall into four main groups: (1) intramolecular reactions, (2) polymer analogue transformations, (3) reactions involving a decrease in the degree of polymerisation, *e.g.* degradation due to the influence of various physical, chemical and mechanical factors, including high-energy radiation, and (4) reactions involving an increase in the degree of polymerisation, in particular, cross-linking, resulting in formation of three-dimensional structures (see for example, review articles by Berlin[145,146] and the Proceedings of the International Symposium on Macromolecular Chemistry, Moscow[147]).

The NMR method may be helpful in solving many problems connected with reactivity of macromolecules, and the structure and properties of end-products, but so far very few papers have been published in this field. We shall deal here only with cross-linking and degradation of polymers, with the effect of radiation on polymers, and with experiments on polymerisation related to this problem.

1. Polymerisation

The possibility of using NMR in the study of polymerisation was pointed out by Lösche[148]. Polymerisation measurements for ethyl acrylate, acrylonitrile, and methyl methacrylate were made by Shibata[149]. The increase in the second moment on polymerisation of ethyl acrylate under the influence of ^{60}Co γ-rays is shown in Fig.26. Theoretical interpretation of these results requires calculation of the effect of viscosity on relaxation times.

2. Cross-Linking of Polymer Chains

The effect of vulcanisation on NMR in rubber was described by several investigators. As long ago as 1950, Holroyd *et al.*[95] discovered that vulcanisation of GR-S (butadiene–styrene rubber 70:30), Hycar OS-10(butadiene–styrene rubber 50:50), and butyl rubber broadens the NMR line at room temperature. Measurements of the temperature dependence of the line width for Hycar, made by Holroyd *et al.*[49,96,150] (Fig.27) also show an appreciable difference in the nature of molecular motions of vulcanised and unvulcanised rubber, especially between -15° and -5°C. These authors conclude that vulcanisation impedes the formation of regions of unhindered rotation. Honnold *et al.*[97] studied the effect of vulcanisation of natural rubber on its NMR line width and showed that with 8% of sulphur the increase in δH for natural rubber is smaller than for butadiene–styrene copolymer; they argue that the cross-linking

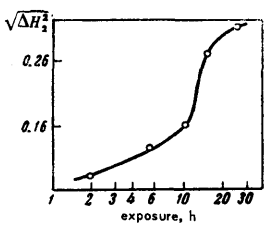


Fig.26. Variation of the second moment on polymerisation of ethyl acrylate under the influence of γ-rays.[149]

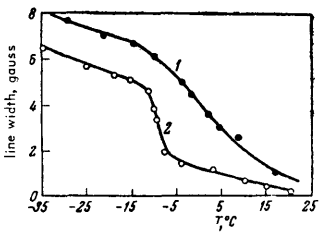
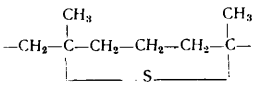


Fig.27. Temperature dependence of line width for Hycar OS-10 (butadiene–styrene 50 : 50 copolymer): 1) vulcanised; 2) unvulcanised[49].

taking place during vulcanisation is more "physical" in natural rubber and more chemical in synthetic rubber. Gutowsky *et al.*[41,118] showed that vulcanisation has a large effect on the NMR spectrum. It was found that in the region between 140° and 170°K an increase in the curing time of natural rubber appreciably shifts the narrowing of the line (due to CH_3 motion) to higher temperatures. The line-narrowing in the region of 225°K (due to segmental motion) is not affected by curing (vulcanisation) time. The activation energy, corresponding to the low-temperature narrowing, is 2.7 kcal mole^{-1} for a sample cured for 30 min, and it increases to 4.5 kcal mole^{-1} for a curing time of 90 min. The line width depends not only on the quantity of combined sulphur in the vulcanisate but also on the amount of raw sulphur in the initial mixtures. Also, the temperature of minimum T_1 (spin–lattice relaxation time) increases with the quantity of combined sulphur. The authors suggest that the formation of ring structures



and not cross-linking is the primary process in vulcanisation of rubber.

Slichter[30] notes that this hypothesis is not adequately substantiated and that more complete observations are required. Oshima and Kusumoto[151], who studied the NMR spectrum of rubber with 2–30% *S* over a wide range of temperatures, propose to apply NMR to the control of the degree of vulcanisation.

The effect of cross-lining on NMR of polymers was also investigated in connection with hardening (curing, heat-aging) of epoxy-resins[27,45,148,152]. The hardening process was found to have two stages. Jain[153] observed changes of the NMR line during hardening of epoxy-resin-modified esteramide. In a partially hardened resin the line is compound on account of protons in hardened and non-hardened regions. The percentage of the non-hardened material may be deduced from the ratio of the two components of the line.

3. The Effect of Radiation on Polymers

The effect of radiation on high polymers was studied by means of NMR mostly in polyethylene and to some extent in polytetrafluoroethylene and other polymers.

Fuschillo and Sauer[69,70,154] investigated the effect of irradiation of polyethylene with atomic pile neutrons and ^{60}Co γ-rays. The dynamic-mechanical method was used in addition to NMR. Irradiation with 8×10^{18} neutron cm^{-2} changes the absorption line at room temperature. The NMR line for polyethylene is compound and irradiation affects mainly the narrow component, associated with amorphous regions of the polymer. In strongly irradiated samples the line is similar to the one obtained in unirradiated samples at much lower temperatures.

Irradiation has little effect on the line shape at 77°K. The number of cross-links in the polymer was deduced from the value of the dynamic modulus. Changes in the properties of polyethylene induced by irradiation are summarised in Table 5.

The effect of irradiation on polyethylene can be explained in terms of two superimposed processes: (1) destruction of crystallites and (2) cross-linking. With a dosage of 0.3×10^{18} neutron cm^{-2} the first process predominates and the second moment decreases somewhat. With dosages of 1.2×10^{18} neutron cm^{-2} and above the second process is dominant and ΔH_2^2 increases. The index of high-frequency rigidity N_c/N has a similar radiation dosage dependence.

Slichter and Mandell[61] obtained analogous results on irradiation of polyethylene in an atomic pile and with electrons. The line narrows for all temperatures above 100°K even for small (5×10^8 rep) electron dosages (Fig. 28). In polyethylene exposed to high neutron dosages the line width at 250°K is larger than in unirradiated samples. In order to explain irradiation effects, these authors evaluated the

TABLE 5. Effect of irradiation on properties of polyethylene.

Dosage, 10^{18} neutron cm^{-2}	0	0.3	0.6	1.2	2.8	5.5	8.0
Number of cross-links per 100 C atoms	0	4	10	20	30		
% crystallinity (from X-ray data)	55	50	25		10	0	0
ΔH_2^2 at 77 °K, gauss^2	27.2	23.2	25.0	27.4		27.5	28.0
ΔH_2^2 at 295 °K, gauss^2	14.5	11.3	13.4	13.3	14.3	15.2	17.0
"% crystallinity" N_c/N (from NMR)	59	54		55	64	67	76

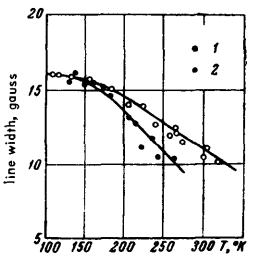


Fig.28. Effect of irradiation with an electron beam on the NMR line of polyethylene[61]: 1) unirradiated sample; 2) irradiated with 5×10^8 rep.

correlation frequency ν_c. The plot of log ν_c *vs.* $(1/T)$, for polyethylene irradiated with 1.8×10^{18} neutron cm^{-2}, consists of two linear sections. At low temperatures a process (apparently small amplitude libration) with an activation energy E = 1.4 kcal $mole^{-1}$ is observed. At much higher temperatures, where large amplitude rotation, vibration, or even translational motion, are possible, the activation energy is 7.4 kcal $mole^{-1}$. For very large radiation does (1.49×10^{19} neutron cm^{-2}), $\log \nu_c = f(1/T)$ is represented by a single straight line ($E = 1.8$ kcal $mole^{-1}$); this implies that molecular chain movements are strongly hindered by the large number of cross-links. Glick *et al.* [101], who made a detailed study of neutron irradiation effects on high- and low-density polyethylene, confirmed these findings. The second moment falls on irradiation with small dosages (0.25×10^{18} neutron cm^{-2}) owing to the destruction of crystallites, but it rises when the dosage is increased beyond a critical value because of the effect of the large number of cross-links (Fig. 29). The critical dosage is higher for high-density polyethylene than for the low-density polymer.

Fujiwara *et al.* [71] observed changes in the NMR spectrum on irradiation of polyethylene with an intense beam of cyclotron-accelerated deuterons.

Irradiation of polytetrafluoroethylene film with accelerated deuterons in a vacuum results in broadening of the NMR line [155]. It is argued that molecular motion in polymers is hindered by the formation of double bonds cyclic units, and cross-links. Burget and Saha [156] also observed that the line width in Teflon increased by a factor of $1\frac{1}{2}$ after a 5 h exposure to 10^{12} neutron cm^{-2} sec^{-1} (total dosage 1.8×10^{16} neutron cm^{-2}).

Irradiation of poly(vinyl alcohol) films with less than critical dose range of γ-rays decreases the second moment and the "NMR degree of crystallinity"; [122] with doses larger than the critical the proportion of the broad component in the NMR line and ΔH_2^2 increases. The critical dose range is about 10^6 rad; its value depends on experimental conditions and intensity of radiation (dose rate).

Lösche also noted a large effect of dose rate [27,157,158]. Prolonged irradiation, for up to 5 months, of polyamides with a weak source (30 mc radium), resulting in absorption of 10^{16} γ-photons, produces a sharp decrease of the second moment from 14–16 $gauss^2$ to 0.07 $gauss^2$, at room temperature. It appears that with small radiation intensities very few cross-links are formed, since the probability of two photons striking simultaneously two neighbouring sites in the sample is quite small. This large change in the NMR line width following a prolonged exposure to low-intensity radiation is of interest in connection with dosimetry.

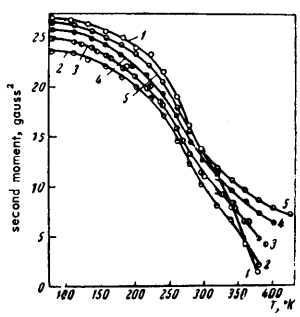


Fig. 29. Temperature dependence of the second moment for low-density polyethylene irradiated in a nuclear reactor. Neutron dosage (10^{18} neutron cm^{-2}): 1) 0; 2) 0.25; 3) 0.6; 4) 1.3; 5) 2.8. [101]

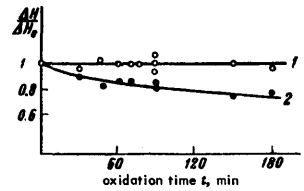


Fig. 30. Variation of NMR line width in polypropylene with oxidation: 1) broad component; 2) narrow component [72].

4. Degradation of Polymers

Aging of polymers by heat, light, atmospheric oxygen, and other factors, as well as irradiation, results in chain rupture, cross-linking, and reactions between functional groups, leading to changes in structure and in internal motions of polymers.

Urman [72] recorded a number of NMR spectra of polypropylene, oxidised at elevated temperatures. The lines were resolved into two components by the method of linear anamorphs. It was found that on oxidation the broad component remains unchanged and that the narrow component becomes narrower (Fig. 30). This implies [72] that oxidation takes place much faster in the amorphous phase than in the crystalline phase.

V. NMR IN "POLYMER–SMALL MOLECULE" SYSTEMS

1. Homogeneous (Single-Phase) Systems

(*a*) Changes in the NMR polymer spectrum on swelling. Nuclear magnetic resonance in swollen polymers enables us to follow any changes in the mobility of a chain as neighbouring macromolecules are replaced by small molecules of the solvent. So far very few experiments have been reported in this field, though it appears that, by using polymers and solvents with different nuclei (*e.g.* fluorine-containing solvents for organic polymers), one can obtain valuable results by examining NMR spectra over a wide range of temperatures and component ratios.

Holroyd *et al.* [49] showed that swelling of Hycar with benzene narrows the line and lowers the transition temperature (Fig. 31). They argue that the narrowing is caused by increased intermolecular distances due to swelling. As noted by Slichter [30], this explanation is incorrect, since the intermolecular contribution to the line is considerably smaller than the intramolecular one, and therefore a slight

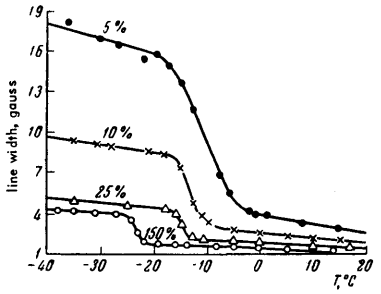


Fig.31. Temperature dependence of line width for Hycar OS-10 at various degrees of swelling with benzene[49].

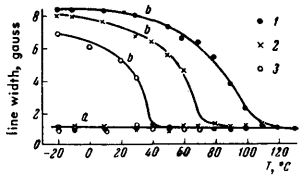


Fig.32. NMR line width for polystyrene as a function of the degree of swelling with methylene dichloride: *a*) narrow component; *b*) broad component[160]; 1) 55% CH_2Cl_2; 2) 11% CH_2Cl_2; 3) 15.7% CH_2Cl_2.

change in the interchain separation cannot cause any appreciable narrowing of the line. The effect of the solvent arises from enhancement of segmental motion in the polymer chain.

Cohen-Hardia and Gabillar[91] showed that, on swelling of natural rubber with CCl_4, T_2 increases (with 25% swelling T_2 rises from 6×10^{-4} to 8×10^{-4} sec). Narrowing of the line on swelling was also noted by Odajima and Nagai[159], who studied swelling of polystyrene in carbon disulphide and of other polymers in solvents not containing hydrogen. Kosfeld[134,160] examined in detail nuclear magnetic resonance in plasticised polystyrene. Plasticisers containing hydrogen (methylene dichloride and cyclohexane) and without hydrogen (CCl_4) were used. For the polystyrene–CH_2Cl_2 system, the line is compound, with a narrow and a broad component; as the temperature is increased, the line width of the narrow component remains unchanged but that of the broad component decreases (Fig. 32). Obviously, even when the system is in a glassy state the plasticiser retains most of its mobility. On lowering the temperature below the glass transition temperature, the intensity of the narrow component decreases, more of the molecules in the plasticiser become fixed. The diffusion coefficient D was also measured in these systems[134,160]; it was found that below the glass transition temperature D falls by several powers of ten. Probably, the molecular motion in the plasticiser is mainly rotational and not translational. In the polystyrene–CCl_4 system the narrow line is absent and swelling produces only narrowing of the whole line.

Powles[108,161] studied NMR in polyisobutene–benzene and polyisobutene–CCl_4 systems. He found that there is a critical solvent concentration at which the chains of the polymer become "free". This concentration corresponds to a ratio of one molecule of benzene, or CCl_4, to six monomeric units of polyisobutene. For molecular ratios of benzene to polymer larger than 1:6, the drop in the second moment occurs at temperatures 30° lower than in pure polymer. The activation energy of molecular motions can be calculated from the temperature dependence of the second moment; it appears that the activation energy is almost the same in both pure and swollen polymers, while the entropy of activation increases sharply with swelling, from 6.1 to 22.3 units. This large increase in the chain mobility of the polyisobutene–CCl_4 system, in the critical concentration region, is also indicated by a sharp increase in the transverse relaxation time T_2 and a decrease of the correlation time τ_C in this region (Fig. 33).

Deuterated solvents, among others not containing protons, may be used in NMR experiments on swelling. For example, Yoshida *et al.*[143] observed proton resonance in poly(vinyl alcohol) films swollen with heavy water.

(*b*) NMR in polymer solutions. NMR measurements in polymer solutions may be divided into two groups, one involving molecular motions in solutions and the other concerned with chain structure and polymer composition. The first group is based on measurements of relaxation processes in solution and is directly connected with problems discussed in the preceding section on polymer swelling.

Nolle[162,163], using the spin-echo method, measured relaxation times in solutions of polyisobutene and polystyrene in CCl_4. Odajima[164], combining Nolle's results and his own measurements on polyisobutene and polystyrene dissolved in CCl_4 and CS_2, developed a theory of relaxation

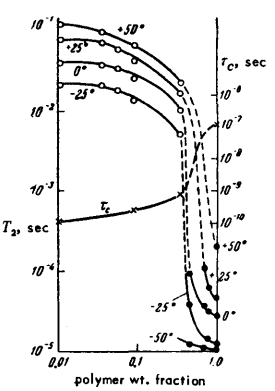


Fig.33. The transverse relaxation time T_2 and the correlation time τ_C as a function of the weight fraction of the polymer in the polyisobutene–CCl_4 solution[161].

for polymers in solution. He derives a formula for the critical concentration of solution at which the relaxation times change abruptly, *i.e.*

$$W_C = 7.1\, M_S^{3/2}/\alpha A l^3 M^{1/2}, \qquad (8)$$

where W_C is the critical concentration g cm^{-3}, M_S the molecular weight of the monomeric unit, α the "excluded volume", A Avogadro's number, l the segment length, and M the molecular weight; the formula is valid for $M > 10^5$. It was shown that for polyisobutene in solution the kinetic unit consists of a segment composed of 10 monomeric units. The activation energy of segmental motion approaches that of the solvent for small concentrations, but for high concentrations it is appreciably larger.

High-resolution NMR spectra of polymer solutions enable us to measure the relaxation of individual molecular groups, because we can determine the relaxation times T_1 and T_2 for each peak in the spectrum. T_1 may be obtained for example by direct measurement of signal amplitude recovery and T_2 from the line width. Bovey *et al.* [144] obtained NMR spectra for several polystyrene solutions with various number-average degrees of polymerisation.

The spectra of solutions of polystyrene, with number-average degree of polymerisation P_n = 500, and its small-molecule hydrocarbon analogue cumene $CH_3-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_3$, are shown in Fig. 34. The chemical shift in parts per million (p.p.m.) is plotted as the abscissa. Tetramethylsilane was used as a standard with τ = 10. The polystyrene spectrum has four peaks: (1) *ortho*-protons in the aromatic ring, (2) *meta*- and *para*-protons in the ring; (3) protons in CH_2 and CH_3 chain groups, (4) reference standard peak from tetramethylsilane. These authors also compared the spectrum of high-molecular-weight polystyrene with those of polystyrene with P_n = 5–20 (Fig. 35). The line widths in the polystyrene spectrum are considerably larger than in the cumene spectrum and they do not depend on molecular weight or concentration of solution (for concentrations less than 50–60%). This shows that segmental motion and not motion of the whole molecule takes place. It should be noted that the viscosity of these solutions varied between that of the pure solvent to several thousand cP (slow-flowing liquid). In normal small-molecule liquids the value of $1/T_2$, and consequently the line width, is proportional to viscosity. Obviously, for polymers in solution the line

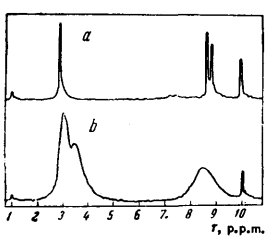


Fig.34. High-resolution spectra of CCl_4 solutions of (*a*) cumene (10% solution) and (*b*) polystyrene with $P_n \simeq$ ≃ 500 (15% solution) [144].

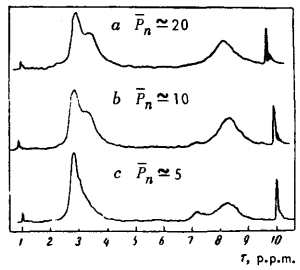


Fig.35. NMR spectra of CCl_4 solutions of polystyrene of low molecular weight [144].

width is determined by the local viscosity in the immediate vicinity of chain segments. The local viscosity is independent of molecular weight and the concentration affects it only when neighbouring segments begin to hinder motions. The magnitude of T_1 for the polystyrene benzene ring is 0.4 sec while T_1 in pure benzene at 25°C is 18.9 sec. It follows then that benzene rings in polystyrene chains rotate some 40–50 times slower than benzene molecules.

The spin-echo method may also be used in studies of relaxation phenomena of polymers in solution. McCall and Bovey [165] used this method for polystyrene dissolved in tetrachloroethylene and carbon disulphide and determined T_1 for aliphatic protons and for *ortho*-, *meta*-, and *para*-protons of the phenyl group.

The second group of high-resolution NMR measurements of polymers in solution is concerned with the determination of macromolecule structure and polymer composition.

Gutowsky [118] gives a spectrum of natural rubber dissolved in CS_2. The spectrum has four peaks corresponding to protons located in CH_3, CH, and two non-equivalent CH_2 groups.

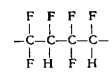
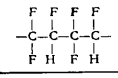
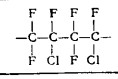
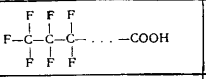
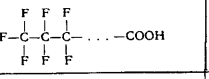
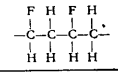
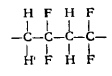
Spectra of several biological substances have also been recorded, *e.g.* deoxyribonucleic acid [166], and solutions of ribonuclease [167] and proteins [168] in heavy water. Jardetzky [169] gives an interpretation of the NMR spectrum of ribonuclease, assigning peaks to protons in aromatic groups and amino-acid α-CH and CH_2 groups. The development of NMR spectrometers with a field homogeneity of 1 in 10^8 has provided many new possibilities in the study of chemical structure of polymers. Several papers were published pointing out the great possibilities of the method. In two of these [83,84] fluorine-containing polymers are considered. Naylor and Lasoski [84] determined the chemical shift $\Delta\nu$, in frequency units, relative to trifluoroacetic acid, for a number of polymers in solution (Table 6).

Analysis of Table 6 leads to general rules for the effect of substitution on ^{19}F resonance.

(a) Substitution of F or Cl for H bound to the same carbon atom as F shifts the F resonance to higher frequencies. This agrees with the data obtained for small-molecule substances, *i.e.* raising the electronegativity of the substituent shifts the resonance to higher frequencies.

(b) Substitution of F for H bound to a carbon atom adjacent to the one with F shifts the resonance to lower frequencies. Apparently this shift is determined by the direct interaction between the F atom and the substituent at the

TABLE 6. Chemical shift of fluorine resonance[84].

Polymer	Structure (the atom in question is denoted by heavy type)	$\Delta\nu$ relative to CF_3COOH, c/s
Polytrifluoroethylene		—3950
Polytrifluoroethylene		—1150
Polytrifluorochloroethylene		—1500
Perfluorodecanoic acid		—1250
Perfluorodecanoic acid		— 100
Poly(vinyl fluoride)		—3100
Poly(vinylidene fluoride)		— 400

neighbouring C atom. The spectrum of poly(vinylidene fluoride) dissolved in dimethylformamide (Fig. 36) has two peaks, $\Delta\nu$ = 400 c/s (larger) and $\Delta\nu$ = 1100 c/s; the peaks correspond to two possible structures: "head-to-tail" and "head-to-head" configurations. The relative intensities of the two peaks show that poly(vinylidene fluoride), obtained by polymerisation with a diazo-type initiator, contains 8–10% of "head-to-head" structure.

Similarly, Fergusson[83], using semiempirical structure–chemical shift rules, analysed NMR spectra for a number of vinylidene fluoride–hexafluoropropylene copolymers (Fig. 37). Using the chemical shift and line intensity of the nine lines of ^{19}F resonance, he showed that the copolymers have a "random" linear structure, without a regular sequence of hexafluoropropylene residues — block polymer segments and branches. The structure of the copolymer may be represented by

$$\left[\left(\begin{array}{c}CF_3\\|\\CH_2CF_2CF_2CF\end{array}\right)_{0.93}-\left(\begin{array}{c}CF_3\\|\\-CH_2CF_2CF-CF_2\end{array}\right)_{0.07}-\right]_{1-n}-$$

$$-[(-CH_2CF_2CH_2CF_2)_{0.95}-(CH_2CF_2CF_2CH_2)_{0.05}]_{n/2},$$

where $n = (x-50)x$ and x is the mole % of vinylidene fluoride in the copolymer. The composition of the polymer may be determined to within 1% from the intensity of CF_2 and CF_3 lines.

The work of Kubota and Takamura[170] may serve as a further example of the use of high-resolution NMR in determining polymer composition; they developed a quantitative analysis for copolymers based on the relative intensity of lines associated with individual groups. The method was successfully applied to the determination of

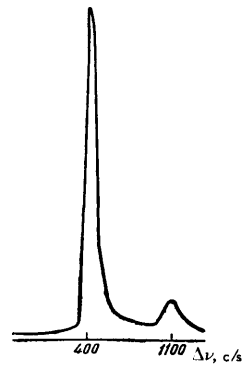


Fig.36. NMR spectrum of poly-(vinylidene fluoride) dissolved in dimethylformamide[84].

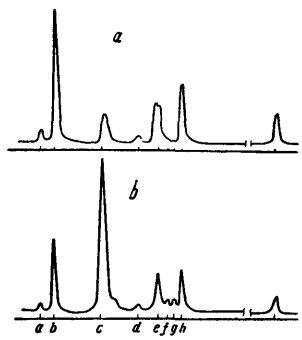


Fig.37. Fluorine NMR spectra of 50% acetone solutions of vinylidene fluoride–hexafluoropropylene copolymers; *a*) 61 mole % vinylidene fluoride; *b*) 85 mole % vinylidene fluoride[83].

phenyl and methyl groups in methylphenylsiloxane polymers dissolved in dioxane; the solvent serves also as an internal standard of signal intensity.

Stereoregularity of polymers can be determined from their high-resolution NMR spectra. Bovey and Tiers[171] studied spectra of chloroform solutions of a number of poly(methyl methacrylate) samples polymerised under the influence of γ-rays and with different initiators. Fig. 38 shows the spectra of poly(methyl methacrylate) prepared with (*a*) benzoyl peroxide in toluene at 100°C, resulting in a mainly syndiotactic configuration, and (*b*) prepared with butyllithium in toluene at -62°C, having predominantly isotactic structure. The peak at the extreme left in these spectra corresponds to chloroform protons and the one on the right is due to the reference substance (tetramethylsilane). The methoxy-group peak is at 6.40 τ. The α-methyl group gives a triplet at 8.78, 8.95, and 9.09 τ; the relative intensities of this triplet are proportional respectively to the amount of isotactic (*ddd*, *lll*), heterotactic

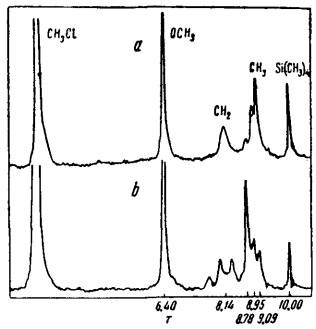


Fig.38. NMR spectra of chloroform solutions of poly(methyl methacrylate); *a*) syndiotactic; *b*) isotactic [171].

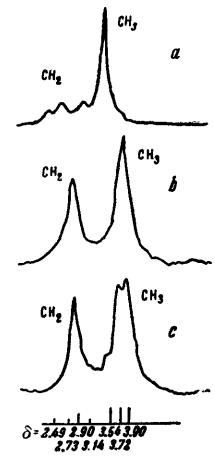


Fig.39. Sections of NMR spectra of chloroform solutions of poly-(methyl methacrylate): *a*) isotactic; *b*) syndiotactic; *c*) atactic [172].

(*ldd*, *dll*, *ddl*, *lld*), and syndiotactic (*ldl*, *dld*) sequences in the polymer chain. CH_2 protons give a signal at 8.14 τ. In the syndiotactic polymer (*a*) both protons are equivalent and give a single line. In the isotactic poly(methyl methacrylate) (*b*) the CH_2 protons experience different screening fields and consequently are non-equivalent. Each proton, due to spin–spin interaction, gives a doublet resulting in four peaks (one of the peaks is obscured). Thus it is possible to determine the polymer structure from the analysis of the NMR spectrum of poly(methyl methacrylate).

Johnson and Tessmar [172] come to similar conclusions by comparing NMR spectra of three samples of poly(methyl methacrylate). Sections of NMR spectra of poly(methyl methacrylate) dissolved in chloroform with CH_2 and α-CH_3 lines are shown in Fig.39 (the chemical shift δ is expressed in p.p.m. relative to H_2O). In the atactic polymer the methyl protons have a triplet with δ = 3.54, 3.72, 3.90. In the isotactic polymer there is only one line with δ = 3.54, and in the syndiotactic polymer δ = 3.90. It appears that the structure of ordinary atactic poly(methyl methacrylate) is similar to that of the syndiotactic polymer.

Nishioka *et al.* [173] obtained high-resolution spectra for 3% chloroform solutions of several stereoregular poly-(methyl methacrylate) of samples prepared with various Grignard reagents. It was found, in agreement with the results discussed above, that in the spectrum of the isotactic polymer, having a helical conformation, the CH_2 signal shows a hyperfine splitting arising from different screening effects for the two protons by the carboxyl group. In the syndiotactic poly(methyl methacrylate) the shielding of the two protons is identical, so that a single broad line is obtained.

Kern and Pustinger [174] found that the NMR spectrum of isotactic polystyrene dissolved in deuterochloroform and in thionyl chloride contains two lines due to protons in CH and CH_2 chain groups in addition to those for *ortho*-, *meta*-, and *para*-protons. The spectra of technical atactic polystyrene and of polystyrene prepared with an n-alkyllithium or alkylsodium catalyst contain only one line due to chain protons.

Analysis of high-resolution NMR spectra enables us to distinguish between *trans*- and *cis*-isomers. Chien and Walker [175] showed that the spectra of solutions of *trans*- and *cis*-isomers of dimethyl 1,4-cyclohexanedicarboxylate are different and that the spectra of samples prepared with ethylene glycol polyesters are identical. Comparison of line intensities in the polyester and dimethyl ester spectra shows that on polyesterification parts of the resulting polymer have *trans*- and *cis*-configuration in the ratio of 3 : 2, independently of whether the initial ester has *cis*- or *trans*--configuration.

2. Heterogeneous (Two-Phase) Systems

The shape of the NMR signal obtained from a two-phase sample, containing a polymer (solid) and a small-molecule substance (liquid or gas), depends on the nature of interaction between the molecules of the two phases.

The degree of mobility of molecules of the low-molecular-weight substance plays a decisive role. We can distinguish three possible cases: (1) the gas or liquid is loosely bound to the solid phase and retains most of its mobility, (2) the structure of the small-molecule substance is somewhat changed under the influence of the solid phase and the mobility is partially reduced, and (3) the gas or liquid molecules are strongly bound to the solid. All the three cases are encountered in real systems and the NMR technique enables us to obtain data on the composition and interaction of the two phases.

If the sample consists of a solid and a loosely bound liquid, the NMR line has two components. A strong narrow liquid line is superimposed on a weak broad line of the solid material; the intensity of the narrow line depends on the amount of the small-molecule substance. A line shape of this type has been observed in nylon containing 5% of water [176]. This characteristic line structure of a two-phase system, solid–water, enables us to determine the moisture content of hygroscopic materials. Shaw and Elsken [177] show that the height of the derivative of the water absorption line

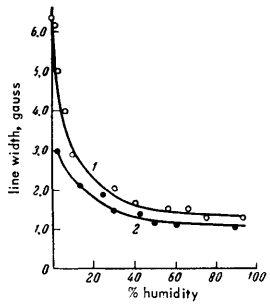


Fig.40. NMR line width for water adsorbed on (1) cellulose and (2) charcoal as a function of relative humidity of the air [197].

in various materials, *viz.* wood, apple pulp, etc., is proportional to the water content. The NMR method of determining moisture content is used for many plant materials [178], and is particularly useful for granulated materials [179]. It has many advantages [180]: the determination takes only a few minutes, the sample is not damaged, and the method is quite general. Equipment required for the determination of moisture content by NMR has been described [241] — commercial NMR spectrometers have become available [181].

NMR spectra of many large molecule–water systems reveal that there is an interaction between water molecules and polymer macromolecules, so that the structure of water changes, resulting in an appreciable broadening of the water signal. This phenomenon was investigated in detail for a starch–water system [182,183]. It was shown that broadening of the water line in starch gels is accounted for by formation of a four-coordinate water lattice. Icelike orientations of water molecules were also revealed by NMR spectra of biological substances; suspension of tobacco mosaic virus [184], eye humour [185], etc.; the water proton signal is also broadened in the presence of deoxyribonucleic acid [186].

An appreciable broadening of the line is observed when molecules of the low-molecular-weight substance are strongly bound to the polymer, *e.g.* adsorbed on its surface. The theory of nuclear magnetic resonance of a system in adsorption equilibrium [187,188] shows that the relaxation time depends on the rate of exchange between free and adsorbed phases. The NMR method was used in measurements of adsorption of vapours and gases on activated charcoal [189], water and methane on titanium dioxide [190,191], water on silica gel [187,192] and clays [193], organic materials on various sorbents [194–196], and other systems, but a discussion of these results falls outside the scope of the present review. The dependence of line shape [197] and correlation time τ_c [198,199] on ambient humidity was studied in a cellulose–water system. Fig. 40 shows the dependence of absorbed water line width on the ambient humidity of air [197]. It appears that even for high humidities (40%) (considerable adsorption) the line remains broad. Correlation of the dependence of δH on humdity with adsorption isotherms [197] indicates that multimolecular layers are formed on cellulose. Comparison of correlation frequencies obtained from NMR and from dielectric measurements shows that the water adsorbed on cellulose has low mobility [199]. Sasaki *et al.* [200], using the spin-echo method, determined the mean lifetime of adsorbed water molecules in the water–cellulose system.

The theory of relaxation in water adsorbed by polymers was developed by Miyake [201].

VI. BIBLIOGRAPHY OF NMR EXPERIMENTS ON POLYMERS‡

Natural rubber [41,49,91–97,118,129,131,150,151,202–205].
Butadiene copolymers [49,94–97,129,135,150,202,204,205].
Isobutene polymers and copolymers [49,95–99,104,106,115,119,129,137,161–164,167,216].
Polyisoprene, polychloroprene [119].
Polyurethane [119].
Polystyrene [49,120,121,132,135,144,159,160,163–165,168,174,206–210].
Polyacrylates [49,78,98,99,112,113,120,121,124,134,136,149,171–173,210–215,217–222].
Poly(vinyl chloride) [56,108,109,120,121,123,131,132,159,223,224].
Poly(vinyl alcohol) [122,130,134,143,225–228].
Poly(vinyl acetate) [120,136,212,213].
Polyamides [59,110,131,142,157,158,176,229–237].
Polyesters [89,111,125,131,141,175,226,238,239,242–247].
Polyethylene [41,52,54–57,59–64,66,67,69–71,74,75,77,85–88,94,97,101,103,108,109,123,132,135,138,140,201,228,248–254].
Polypropylene [58,64,65,68,72,79,80,81,97,103,255–258].
Polybutene [34,68,258].
Polypentene [68,258].
Epoxy-resins [45,148,152,153].
Proteins [144,166–169,233,234,240,259–261].
Fluorine-containing polymers [50,52,76,77,83,84,90,102,107,108,109,123,126,131,133,135,155,156,223,228,262–270].
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