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# "Hydrophobic Bonds"? A Study of Long-Range Interactions in Polymers

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# "Hydrophobic Bonds"? A Study of Long-Range Interactions in Polymers

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## SUMMARY

Inelastic neutron scattering spectroscopy offers a unique method of studying the intermolecular forces binding molecular crystals and polymers. The results from incoherent and coherent neutron spectroscopy are here related. For polyethylene they lead to the conclusion that the interchain forces are nearly two orders of magnitude weaker than the valence forces in a chain.

## 1.0 INTRODUCTION

The hydrogen bonding forces in natural and synthetic polymers, although not very well understood, can at least be studied by reference to model compounds. By contrast, the so-called "perpendicular forces" [1] or "hydrophobic bonds" often invoked in discussions of biological macromolecular structure are at least quantitatively obscure. They are thought to occur between the aromatic rings of the DNA bases for example. A considerable part of this type of structuring can be accounted for, as in micelle formation, not by specific "hydrophobic bonds" but rather as the geometrical rearrangement of the system of macromolecule plus solvent to minimum free energy. In cases where the polymer is formed or in contact with water, this means that the chain structure arranges to minimize destruction of the high energy water structure.

Nevertheless, when all of this has been accounted for, and in synthetic polymers most usually, there still remain forces within and between the chains which could be properly called "hydrophobic." Although often small compared to the chain binding forces, these play a vital role in the mechanical and thermal properties of the polymer. Only with the arrival of inelastic neutron scattering spectroscopy (INSS) has it been possible to quantify these forces at the microscopic level. The method used is to measure the frequencies of vibrational waves excited by the ambient temperature in the whole polymer structure. These waves are quite analogous to the phonons or lattice vibrations which have been the key to modern knowledge of forces in simple single crystals. The unique feature of INSS is that both the frequency and the wavelength of the waves can be measured simultaneously. Hence the velocity of sound ($v = \nu\lambda$) and the force constant (elastic modulus) in the propagation direction come directly from the measurement. A most important feature is that the range of these forces is measured at the same time. In suitably oriented materials, all of the forces may be determined, in principle, by experiments where the neutron beam impinges on the sample along chosen symmetry directions. Where this is impossible, the interchain forces, for example, can be found by studying the interaction of waves in one chain with those in the next. The virtue of this whole method for studying polymer structure is that vibrations of the whole structure of interest are studied rather than those of side groups attached to the main framework, as has hitherto only been possible by IR and other types of techniques.

This paper sketches the neutron technique and illustrates its application to polymers by the results already obtained.

## 2.0 SIMPLE THEORY OF CHAIN VIBRATION

There are two reasons why the chain vibrations in polymers have been neglected by spectroscopists in favor of higher frequency modes. First, it is instrumentally easier to study IR and Raman spectra in the energy range above ca. 500 $\text{cm}^{-1}$. Second, when one looks into the far IR or low frequency Raman there is often little or no structure (e.g., polyethylene has only one strong band below 200 $\text{cm}^{-1}$ at ca. 70 $\text{cm}^{-1}$). This is a puzzle since we know from specific heat data that many low frequency vibrations must exist. The difficulty is that they are for the most part optically inactive. This is the first important entré of INSS for these modes can be plainly seen by that method. Before following up this method it is instructive to look at what kind of modes could be observed by IR, optical Raman, and Brillouin scattering spectroscopy and see at how far these observations would take us to understanding the so called "acoustic" vibrations of the chains. These vibrations are called "acoustic" for they are responsible for the transmission of sound in polymers.

## 2,1 Chain Modes

The normal vibrations of a rod of constant density have been considered in several texts on solid-state physics [2] and with particular reference to the dynamics of simple normal hydrocarbons [3]. If such a rod of length, L, Young's modulus, E, and density, $\rho$, is struck at one end, standing waves are set up whose frequency, $\nu$, is given by the formula

$$\nu = \left(\frac{\eta}{2L}\right)\left(\frac{E}{\rho}\right)^{\frac{1}{2}} \tag{1}$$

$$= \left(\frac{E}{\rho}\right)^{\frac{1}{2}}\left(\frac{1}{\lambda}\right) \tag{2}$$

where $\lambda$ is the wavelength in the material and $\eta$ indicates the harmonic number.

Thus we see there is a constant linear relationship between $\nu$ and $1/\lambda$, whose slope is the velocity of sound.

Solid-state textbooks also consider the case of vibrations of a linear chain of mass points whose mass is M, distance apart a, and connected by springs of force constant C [2]. For this system the angular frequency, $\omega$, is related to the inverse wavelength (or wave vector $\mathbf{K} = 2\pi/\lambda$) by a different formula (Eq. 4).

$$\omega^2 = \frac{2C}{M}(1 - \cos \mathbf{K}a) \tag{3}$$

or

$$\omega^2 = \left(\frac{4C}{M}\right)^{\frac{1}{2}} \sin \tfrac{1}{2}\mathbf{K}a \tag{4}$$

A plot of angular frequency as a function of **K** is shown in Fig. 1 which shows the repeating sinusoidal function called the acoustic dispersion relation. It could be expected that when the wavelength of the waves was very great compared to the separation of the atoms (i.e., for very low frequency sound) the mass point model would give a similar result to that

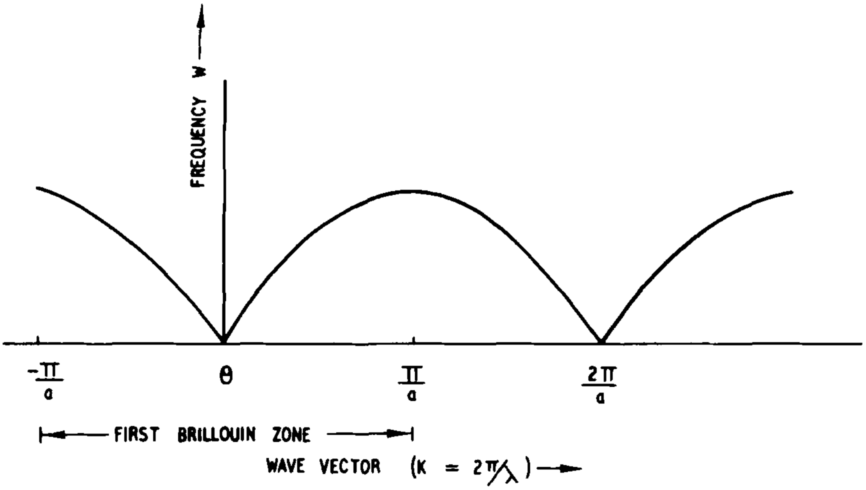

**Fig. 1.** Plot of angular frequency, ω, of a chain vibrational mode as a function of wave vector (K = 2π/λ) for the case of a single force constant per atom per mode.

for the continuous elastic rod. This can be seen if we consider the form of Eq. (4) for small values of **K**. We have

$$\nu = \frac{\omega}{2\pi} = \left(\frac{a^2 C}{2M}\right)^{1/2} \frac{1}{\lambda} \qquad (5)$$

Again it can be seen that the wave frequency is directly proportional to the inverse wavelength. The work of Schaufele and Shimanouchi [3] shows how well this equation applies to simple paraffin hydrocarbons.

If the chain of atoms has not only direct force constants between nearest neighbor atoms, but also long range force constants, the form of the dispersion curve is modified. If $C_p$ is the force constant for atoms removed from one another by p units of a (the interatom distance), then the general dispersion relation is

$$\omega^2 = \frac{2}{M} \sum_{p>o} C_p (1 - \cos [pKa]) \qquad (6)$$

If this is plotted, it can be seen that the dispersion curve is a combination of sinusoidal waves. Should this be observed in an experimental determination of the dispersion curve, it would be a qualitative indication that the forces are of longer range than nearest neighbor. The number of force constants involved can be found by taking a space Fourier transform of the experimental dispersion curve using the method of Foreman and Lomer [4]. In metals, long-range force constants between atoms separated by about ten atomic spacings have been detected in this way. By contrast, in pyrollytic graphite the same method proves that only forces between neighboring planes need be considered for longitudinal vibrations perpendicular to the graphite sheets [5]. For polyethylene chain modes, as we shall see, a nearest neighbor forcefield is a good fit to some of the INSS data [9a].

## 3.0 LONG-CHAIN HYDROCARBONS

The optical observation of acoustic vibrations in polymers is considerably limited by the three main spectroscopic selection roles. First, the electromagnetic interaction requires a change in permanent molecular dipole moment following vibrational excitation by IR absorption. Also, for Raman scattering there must be an appreciable change in the molecular polarizability. Given that energy conservation must occur, the next binding principle is the requirement that momentum conservation for the photon and the molecular or acoustic excitation must occur jointly. Since the momentum available from the photon of ordinary visible light is very small (remember $\lambda \approx 5000$ Å, hence by de Broglie's principle ($mv = \hbar/\lambda$), the momentum is very small), i.e., only waves in the polymer of very great wavelength can be excited. By reference to the dispersion curves, above, it is clear that these long waves have very low frequencies and that the major part of the high frequency spectrum of the chain may not be observed because of the momentum restriction. By contrast the massive neutron carries a great deal of momentum and so can excite chain vibrations of very short length in the polymer.

Despite these restrictions some beautiful experiments with laser Raman scattering have been performed [3] on long-chain hydrocarbons. Because of the polarizability selection rule, only every second overtone of the "accordion" mode for $C_{94}H_{190}$ at 300°K was observed. Despite the weakness of the lines it was possible to construct a plot of the frequency of the mode as a function of the inverse wavelength and this is shown in Fig. 2.

It can be seen that deviations from straight-line behavior of a continuous elastic medium occur when the wavelength of the wave is below about ten times the atomic spacing. It is also very clear that only a very small fraction of the Brillouin zone (see Fig. 1) is covered by the optical data because of the momentum restriction (v.s.).

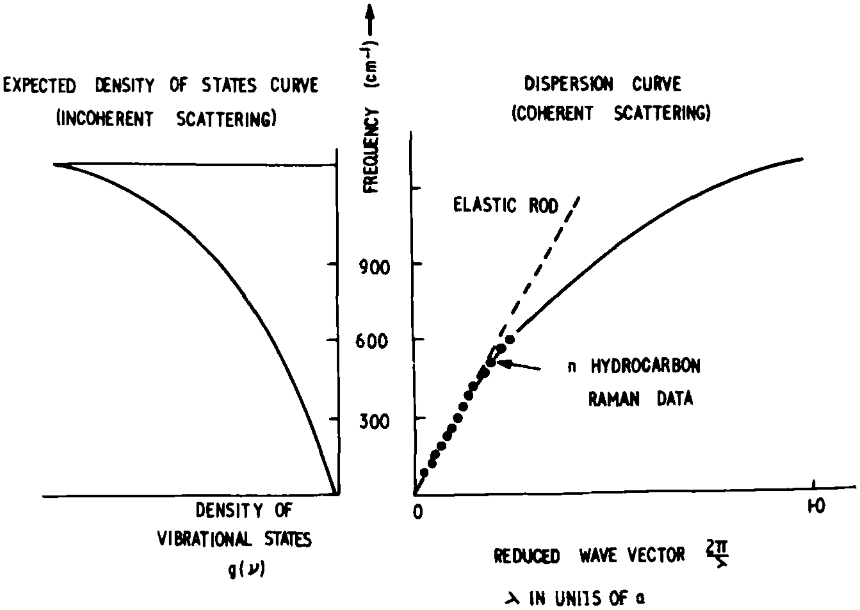

Fig. 2. Relation of the acoustic dispersion curve for chain modes to the vibrational "density of states curve."

Each point on the right-hand curve of Fig. 2 represents a particular line observed by Raman scattering spectroscopy. If we were to plot not the actual spectrum itself but the number of lines observed per unit frequency increase, through the spectrum, it is clear that this number increases steeply to a maximum and then drops to zero at the Brillouin zone edge (where $2a/\lambda = 1$). Such a plot is shown in Fig. 2a using the same frequency scale as the dispersion curve. The plot is called the density of states spectrum and along with the dispersion curve has great theoretical importance. If $\nu(\mathbf{K})$ is the equation of the dispersion curve, then the density of states curve $g(\nu)$ relates to $\nu(\mathbf{K})$ by

$$g(\nu) = \left(\frac{\partial \mathrm{K}}{\partial \nu}\right) \nu(\mathrm{K}) \tag{7}$$

## 4.0 INELASTIC NEUTRON SCATTERING SPECTROSCOPY

Two main methods of inelastic neutron scattering spectroscopy are being developed for studying polymer dynamics and structure. Incoherent inelastic scattering spectroscopy, which uses choppers and time-of-flight spectrometers, is most suitable for studying hydrogenous materials, and the technique yields the density of states spectrum immediately (see Fig. 2). Coherent inelastic neutron scattering spectroscopy is an extremely powerful technique but at present may only be applied to substances without hydrogen present or with deuterium replacing it. This is because the strong incoherent scattering from hydrogen can completely mask the small coherent scattering effects. This technique leads to a direct determination of the dispersion curve (see Fig. 2). To some extent these two methods are complimentary and much present work has been devoted to relating them experimentally for ease of application. In 1969 a technique was developed which promises to unite the two and to make possible coherent measurements even on fully hydrogenated material. This is the method of neutron polarization analysis [6]. A general review of types of instruments suitable for carrying out bcth coherent scattering and incoherent scattering experiments with references to experimental details is available [7]. Here we describe only the principles of the coherent scattering technique.

The power of this method can be illustrated when it is seen that the experimenter has it within his power to observe the frequency for a chosen wavelength and mode of the vibration. A long, stretched-out chain in a polymer can be considered as a one-dimensional diffraction grating. At absolute zero all of the atoms in this chain are at rest, and if a plane wave of neutrons, whose wavelength is $\lambda$, were shone onto the chain, elastic diffraction would result with the angle of diffraction being given by the Bragg equation

$$n\lambda = 2a \sin \theta/2 \tag{8}$$

which relates the half angle of diffraction, $\theta/2$ to the neutron wavelength, $\lambda$, and the interatomic spacing, a, in the polymer. (Incidentally, neutron diffraction should become more important for studying long-range (~ 2000 Å) polymer structures since $\lambda$ can be made large.)

A monochromatic incident neutron wave may be obtained by selection from a beam of all wavelengths using Bragg diffraction from a suitably oriented single crystal (e.g., of a metal). One could be sure that the diffracted wave from the polymer was unchanged in wavelength, and hence momentum and energy (remembering the de Broglie relation), by placing a second monochromator crystal in the outgoing beam and verifying that the Bragg angle for it was the same as the angle used for an identical crystal in the selecting monochromator.

As the sample temperature is raised from absolute zero, thermal energy causes the chain to vibrate. Since the longest wavelength waves are of the lowest frequency, these are exited before those waves of higher frequency. When such a wave is excited, a standing wave is set up in the polymer chain and an extra periodicity is imposed by some atoms being at antinodes and some at nodes, etc. The essence of the coherent scattering method is that this wave-imposed periodicity can be again detected by diffraction. Accordingly, if a monochromatic beam is shone onto the polymer with its standing wave, diffraction can be expected at angles satisfying not only the distance between the atoms but also the distance between antinodes, for example. This is because the distance between antinodes is now a characteristic repeat distance in our one dimensional crystal. By selecting the diffracted neutron beam at this new angle we would know we were looking at neutrons scattered by atoms separated by one vibrational wavelength. A very interesting difference between this scattering and that at absolute zero arises if the wavelength of the outgoing diffracted wave is determined by a second crystal as mentioned above. No longer is the outgoing wavelength equal to the incident wavelength; in fact, it is found that the outgoing wave contains three components. Usually there is a component at the incoming wavelength (and hence at the incoming energy) due to elastic incoherent scattering. In addition we may find components displaced to high and low energy (and hence correspondingly in wavelength) from the incident neutron energy by increments equal to the energy of the chain mode in the polymer (compare Raman scattering). These components arise because the neutron has been inelastically scattered and has respectively gained or lost a quantum of lattice vibrational energy from or to the polymer vibration. In this measurement, which is usually performed with a three-axis spectrometer [7], we have been able to measure the frequency of a lattice wave of simultaneously determined wavelength. If more than one wave is present in the polymer because the temperature is much greater than absolute zero, then other inelastic diffraction angles can be chosen and other frequencies corresponding to those wavelengths measured. In this way one builds up the whole of the dispersion curve. Because of the high available incident momentum of the neutron, the curve may be measured up to the Brillouin zone edge and even into higher zones than the first.

Such a measurement is practical for stretch oriented polymers where the incident neutrons can be impinged along the orientation direction. Both the acoustic and "optic" modes of vibration may be studied without limitation by electromagnetic selection rules. The matrix elements for vibrational excitation by neutrons are almost independent of the molecular electrons whose agency is essential to optical excitation. The consequence of this is that the neutron impact may be thought to be equivalent in many ways to mechanical excitation of vibrations in the bulk material. A full description of the theory of neutron excitation is available [8]. Experiments of this kind have been carried out successfully for the longitudinal vibrations in polyethylene [9] and Teflon [10a]. In these experiments the polyethylene was fully deuterated, and Teflon has the advantage that it is a strongly coherent scatterer with no hydrogen present. Measurements are also in progress on various forms of polyoxymethylene [11].

General reviews of the relationship between coherent and incoherent scattering from polymers had been given by Safford and Naumann [12], Trevino and Boutin [13], and Trevino [14]. These papers pioneer the field but mostly report work using the beryllium filter technique of neutron spectroscopy which has a resolution limited to about 40 $cm^{-1}$. Recent developments of chopper spectrometers which provide incident line spectra [15] as well as new schemes for optimizing three axis spectrometers in coherent scattering experiments, have added great excitement to this field.

## 5.0 COHERENT SCATTERING IN POLYETHYLENE AND TEFLON

Figure 3 shows a comparison of the observed [9a] and theoretical [16, 9a] dispersion curves for the longitudinal chain vibrations in polyethylene with the observed density of states spectrum [13]. The theoretical curve was calculated using a single chain, single force constant per atom model. It can be seen that although the experimental points are uniformly lower than the theoretical curve in Fig. 3 (right), the agreement is nevertheless very good. As indicated by the theoretical curve [16] mixing of the $\nu_5$ and the $\nu_9$ modes should occur at a reduced wave vector coordinate of about 0.08. Although the authors take care to point out that in this experiment the resolution and intensity were limiting factors, no real evidence of this mixing can be seen. Indeed, nothing is seen of the expected interaction of the $\nu_5$ and the $\nu_9$ modes again at a reduced wave vector coordinate of about $0.8 \times q_{max}$.

Both the general shape of the curves and the above detailed features point to the small value of the interchain forces which cause the mixing.

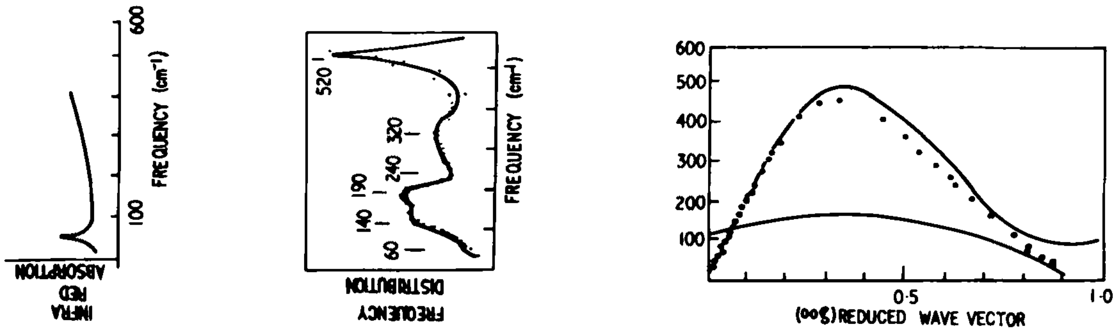

Fig. 3. (left) Observed IR absorption spectrum [20] and vibrational density of states curves from incoherent neutron scattering [13], compared for polyethylene. (center) Calculated dispersion curves – for deutero-polyethylene assuming noninteracting chains [16, 9a]. (right) Observed dispersion curve (o-o) and calculated curve (–) for the longitudinal acoustic mode in deutero polyethylene [9a]; (••) experimental.

The general shape indicates that the force constant is almost purely nearest neighbor in the chain, in complete contrast to the situation in metals and some molecular crystals. These data indicate that the interchain, "hydrophobic" forces are only about a few per cent of the main force constants.

Extra information is given by the observed density of states spectrum obtained by incoherent neutron scattering spectroscopy. It can be seen that the incoherent spectrum reproduces features expected from the dispersion curves given. In particular, the large peaks at about 550 and 180 $cm^{-1}$ correspond to the points at which the dispersion curves flatten off towards the edge of the Brillouin zone. An interesting feature may also be seen in the region of the expected curve crossings [cf. Fig. 3 (center)], when $\nu_5$ and $\nu_9$ mix and some intensity from the now longitudinally polarized $\nu_9$ mode comes into the incoherent scattering. The broad peak at about 230 $cm^{-1}$ is unexplained by the dispersion curves shown and indicates that the present measurements along the chain axis by no means complete the picture of the forces binding the system. It is possible that this and similar unexplained modes indicate Van Hove singularities associated with the interchain vibrations which will be found when coherent scattering techniques can be applied to crystals or highly ordered material oriented in more than one direction with respect to the neutron beam. This is now an experiment of the greatest importance for measuring the interchain forces.*

With stretch oriented Teflon there is again a good agreement between the observed dispersion curve and that calculated for a chain valence force field [10b], particularly when generalized to twenty parameters [21]. Again conclusions about the smallness of the interchain force constants and about the weakness of long-range force constants for this mode can be drawn but the same reservations as for polyethylene must be maintained. We are seeing only the forces in one direction of the material. The indication is that carbon-carbon binding forces predominate again and that the modulus of elasticity is likely to be an isotropic in oriented material.

## 6.0 USE OF INCOHERENT NEUTRON SCATTERING SPECTROSCOPY

From above, the supplementary action of coherent neutron scattering spectroscopy and incoherent data can be seen, for example, where extra

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*Note added in proof. The elastic modulus of deutero polyethylene crystals has now been reported from neutron measurements in the a direction as 8 X $10^{10}$ dyne $cm^{-2}$ (Twistleton and White, Moretonhampstead 1970, and to be published).

peaks in the density of states of polyethylene prompt a closer look at the dispersion curves. Because of the difficulty of getting suitably oriented polymer samples, many polymers cannot be immediately studied by the coherent method and so there is at present some urgency about developing methods of refining and interpreting data from incoherent neutron scattering spectroscopy.

The approaches which have proved successful for model systems have been isotopic or atomic substitution techniques [17, 18] and changes in polymer "tacticity" [18]. The atomic substitution method can be used to identify modes of vibration due to side groups on the main chain. For example, in a polymer such as polyaceteldehyde or polypropylene, the $CH_3$ torsional vibration, which has a large amplitude of hydrogen motion (and hence a great neutron intensity) [15], appears as a strong feature in the neutron spectrum overlying the frequencies associated with the chain modes. This feature can be removed by substituting the hydrogen of the methyl group either by fluorines as in polytrifluoroacetaldehyde, or deuterium as in trideutero polypropylene [19].

When the orientation of methyl groups or other side chains is changed with respect to the polymer axis, considerable changes in the chain modes due to chain distortion may be expected. This method is also successful for assigning the chain modes as can be seen with reference to the spectra of isotactic and atactic polyacetaldehyde [18] (Fig. 4). In the highly ordered (isotactic) material two maxima at about 30 and 80 $cm^{-1}$ appear in the chain mode spectra. These can be identified with corresponding maxima associated with the $\nu_5$ and $\nu_9$ modes of vibration in the polyethylene and polyoxymethylene spectra. In changing from a regularly ordered polymer to one where the methyl groups sometimes poke in and sometimes out of the chain direction, this regular vibrational pattern is completely disturbed and the center of gravity of the spectrum is shifted towards very low frequencies. This would be expected for an amorphous material. In addition to identifying the modes as chain modes, this "substitution" method may prove to be of even greater practical use for assessing tacticity and structural disorder in polymers. It is clear that the low frequency chain modes are very sensitive indicators of perturbing forces and probably much more so than the traditionally used high frequency motions.

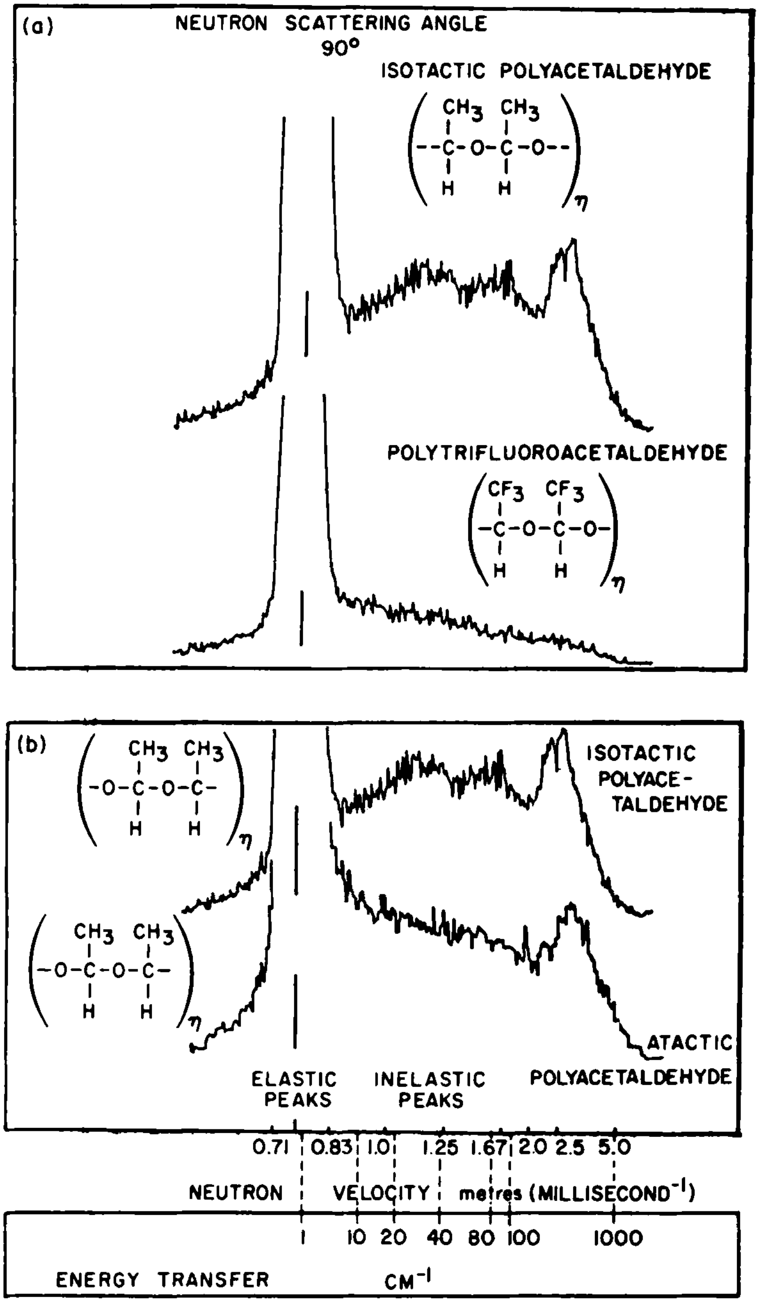

Fig. 4. Incoherent neutron scattering spectra taken at room temperature and 90° angle of scattering for (a) isotactic polyacetaldehyde and polytrifluoroacetaldehyde and for (b) isotactic and atactic polyacetaldehyde.

## 7.0 CONCLUSIONS

Inelastic neutron scattering spectroscopy offers unique possibilities for assessing the intrachain and interchain forces in polymers. Several methods are available and all are in very early stages of development. Improved methods of orienting polymers would make a direct measurement of the interchain forces possible and new neutron methods such a polarization analysis offer a diversification of the technique to general polymer systems.

Interchain forces, detected in IR spectrometry because of mixing of transverse and longtitudinal modes to give IR activity, e.g., in polyethylene, do not show up strongly when neutron spectra are measured along the chain axis. Even allowing for experimental limitation, at present this limits the size of the interchain force constant in the fiber direction to about 10% of the chain constant. The chain vibrations are thus decoupled. In the perpendicular direction, where no dispersion curves have been obtained, the density of states curves indicate stronger forces and hence a microscopic elastic modulus with pronounced anisotropy.

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