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## Polarized Infra-Red Radiation as an Aid to the Structural Analysis of Long-Chain Polymers. I.

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An experimental procedure is described for measuring dichroism in the infra-red spectrum of oriented materials. Oriented films of polythene, polyvinyl alcohol, polyvinyl chloride, polyvinyl acetate, and Nylon have been examined in the region  $3600\text{--}700\text{ cm}^{-1}$ , and the species (parallel or perpendicular) of many bands has been identified. The bearing of these results on current ideas concerning the structure of these polymers is discussed. A general result is that frequencies involving the motion of hydrogen atoms show rather low dichroism. On the other hand, very high dichroism has been found in some frequencies in which the motion is believed to be confined to other atoms.

### INTRODUCTION

WHEN unpolarized radiation, which contains electric vector components vibrating in an infinite number of planes perpendicular to the direction of propagation, is passed through a purely random spatial arrangement of molecules such as we find in a gas, a liquid, or an amorphous solid, there is an equal probability of interaction between the radiation and all the possible modes of vibration of the molecules. Consequently, all the permitted frequencies will be absorbed. If, however, we consider the case of a substance in which the molecules are uniformly oriented, as in a perfect crystal, this is no longer true, and the intensity of absorption should be a function of the angle between the direction of change of the dipole moment and the plane in which the electric vector is vibrating. To take an extreme case, the absorption coefficient should be zero for those vibrations in which the moment changes parallel to the direction of the incident radiation. Intensity changes of this kind, depending on the orientation of a crystal relative to unpolarized radiation, have been recorded by Barnes<sup>1</sup> in the case of quartz, by Plyler<sup>2</sup> for ice, and very recently by Glatt and Ellis in films of oriented paraffins,<sup>3</sup> but such preferential absorption has received surprisingly little attention, although combined with the results of x-ray analysis it might prove a valuable aid to vibrational analysis.

Even more detailed information about the nature of the vibrational frequencies should be forthcoming from absorption spectra obtained with plane-polarized radiation, particularly where the crystal structure has already been determined by x-ray analysis, but here too investigations have until recently been confined almost entirely to studies of relatively simple salts and minerals.<sup>4</sup> The first recorded attempt to apply the technique to the study of polymers was made by Thompson,<sup>5</sup> who, however, obtained only inconclusive results in an attempt to discover the nature of the polythene band at  $720\text{ cm}^{-1}$ . Recently, Glatt and Ellis<sup>3</sup> have made some measurements on oriented films of polythene and some high molecular weight paraffin waxes, but their investigations have been confined to the overtone region between 0.6 and 2.7  $\mu$ . Nevertheless, the results obtained are of considerable interest. Using a new type of transmission polarizer,<sup>6</sup> we have been able to study a number of polymers in the fundamental region up to 14  $\mu$ ; the results, though not yet complete, are now presented for the four compounds, polythene, polyvinyl-alcohol, polyvinyl-chloride, polyvinyl-acetate, together with preliminary results ob-

<sup>4</sup> C. Schaeffer and F. Matossi, *Das Ultrarote Spektrum* (Verlag Julius Springer, Berlin, 1930); J. W. Ellis and J. Bath, *J. Chem. Phys.* **6**, 221, 723 (1938), **5**, 862 (1939), *Phys. Rev.* **77**, 1098 (1939); J. Mann and H. W. Thompson, *Nature* **160**, 17 (1947), D. A. Crookes, *ibid.*; G. B. B. M. Sutherland, and A. Vallance-Jones, *Nature* **160**, 567 (1947).

<sup>5</sup> H. W. Thompson and P. Torkington, *Proc. Roy. Soc.* **184A**, 3 (1945).

<sup>6</sup> A. Elliott and J. Ambrose, *Nature* **179**, 641 (1947); A. Elliott, J. Ambrose, and R. B. Temple, *J. Opt. Soc. Am.* **38**, 212, (1948).

<sup>1</sup> R. B. Barnes, *Phys. Rev.* **39**, 562 (1932).

<sup>2</sup> E. K. Plyler, *J. Opt. Soc. Am.* **9**, 545 (1924).

<sup>3</sup> L. Glatt and J. W. Ellis, *J. Chem. Phys.* **17**, 880 (1947).

tained on two more, namely, polyisobutene and Nylon.

### EXPERIMENTAL

The production of highly oriented and sufficiently thin layers of these polymers presents considerable practical difficulties which have so far been only partly overcome. Under carefully controlled conditions, it is possible to obtain substances which crystallize readily from solution or from the melt, in the form of thin layers which exhibit considerable double refraction when viewed between crossed Polaroids, and which must therefore be highly oriented. Such methods are generally inapplicable to long-chain polymers, many of which remain in a disordered state when cooled below their melting point. The molecules of such substances can be at least partially oriented by stretching or rolling. Stretching tends to produce orientation in the plane of the film parallel to the direction of stretch, whereas rolling may, in certain cases, produce three-dimensional orientation.<sup>7</sup> The chief difficulty is to obtain oriented films which are thin enough to give adequate transmission. For the very strongly absorbing materials it is not possible to stretch films of the requisite thinness, and a method which we have found satisfactory is to roll the material between jeweller's rolls, either in the form of a "sandwich" between two pieces of silver chloride (which is transparent over the whole of the rocksalt region) or cast on a piece of lead foil, from which it is later stripped. The thickness of the films is conveniently measured by an optical lever.

The degree of orientation produced in the crystalline region of the material can be determined from x-ray photographs by the method of Hermans and Platzek,<sup>8</sup> which involves measuring the spread of the polar arcs. We suggest that information on the degree of orientation can be obtained by measuring the quantity

$$\frac{\log I_0/I_\pi}{\log I_0/I_\sigma},$$

where  $I_0$  represents the intensity of the incident

radiation and the subscripts  $\pi, \sigma$  refer to the cases where the  $E$ -vector is, respectively, parallel and perpendicular to the direction of stretching of the polymer. Such a measurement must, of course, be carried out on a band which is known to be associated with a change of dipole moment exclusively parallel or perpendicular to the chain axis of the polymer. This quantity is known as the "dichroic ratio." In the case where the change of dipole is parallel to the chain axis, it can be shown that

$$\frac{\log I_0/I_\pi}{\log I_0/I_\sigma} = 2 \cot^2 \theta,$$

and, similarly, for a change of dipole perpendicular to the axis

$$\frac{\log I/I_\pi}{\log I_0/I_\sigma} = \frac{2 \sin^2 \theta}{2 - \sin^2 \theta},$$

where  $\theta$  is the semi-angle of a cone described about the axis of stretching.  $\theta$  represents the average direction of orientation of the molecular chains in the material, this method of representation being first used by Hermans and Platzek in determining the degree of orientation from refractive index measurements.

The spectrometer used is a Perkin-Elmer model 12A,<sup>9</sup> with a 60° rocksalt prism in a Wadsworth-Littrow mounting. It has been modified by the introduction of a Hilger-Schwarz vacuum-type compensated thermocouple and suitable condensing mirror. This spectrometer is used in conjunction with a General-Motors contact-modulated amplifier,<sup>10</sup> feeding a photographic recorder of our own design, which has a full-scale sensitivity of 70 microamperes. A full description of this recorder has appeared elsewhere.<sup>11</sup> The polarizer slides into a slot just in front of the entrance slit of the spectrometer. Although attempts have been made to dry the air in the body of the spectrometer in order to minimize atmospheric absorption, it has not proved possible to reduce the intensities of the strongest water lines at 6  $\mu$  below about 20 percent and to make it possible to measure the

<sup>7</sup> C. W. Bunn and E. V. Garner, *Proc. Roy. Soc.* **189A**, 39 (1947).

<sup>8</sup> P. H. Hermans and P. Platzek, *Kolloid Zeits.* **88**, 68 (1939).

<sup>9</sup> R. B. Barnes, R. S. McDonald, Van Zandt Williams, and R. F. Kinnaird, *J. App. Phys.* **16**, 77 (1945).

<sup>10</sup> M. D. Liston, C. E. Quinn, W. E. Sargent, and G. G. Scott, *Rev. Sci. Inst.* **15**, 194 (1946).

<sup>11</sup> A. Elliott and J. Ambrose, *J. Sci. Inst.* **24**, 324 (1947).

percentage absorption of bands in the water vapor region, the system is designed to record the atmospheric absorption simultaneously with that of the specimen. For this purpose, the specimen is mounted on a small rocker arm, pivoted just behind the polarizer, which is moved in and out of the beam at regular intervals by an electromagnetic mechanism actuated by the prism drive. The oscillations of the meter are recorded continuously and provide a simultaneous record of the background absorption as well as that of the material being examined. To convert these records to percentage absorption or optical-density curves, it is, of course, necessary to measure up the trace at all points at which we are interested, but the labor involved has been greatly reduced by the use of suitable scales, marked on india rubber, which are stretched to suit the size of the spectrum being measured. Above about 3.5  $\mu$  a Pyrex shutter is used to correct for scattered radiation.

## RESULTS AND DISCUSSION

### A. Polythene

Previous investigations of the spectrum at 3  $\mu$  were carried out with unpolarized radiation by Fox and Martin,<sup>12</sup> using a grating spectrometer, while Thompson and Torkington<sup>5</sup> studied the longer wave-length regions with the aid of fluorite, rocksalt, and sylvine prisms. The overtone region from 0.6 to 2.7  $\mu$  has recently been investigated by Glatt and Ellis,<sup>3</sup> using plane-polarized radiation. Figure 1 shows the spectrum of oriented polythene films which were prepared by melting between Pyrex plates and quenching with cold water; this gave a clear transparent film. The films were oriented by stretching to breaking point at room temperature. From x-ray measurements the crystallites were contained within a cone of semi-angle  $46^\circ$  around the direction of stretching in the specimen examined.

A striking feature of the polythene spectrum is its simplicity. The spectra of very long chain polymers are often considerably less complicated than those of the parent monomers and simpler related substances, and it is obvious that some

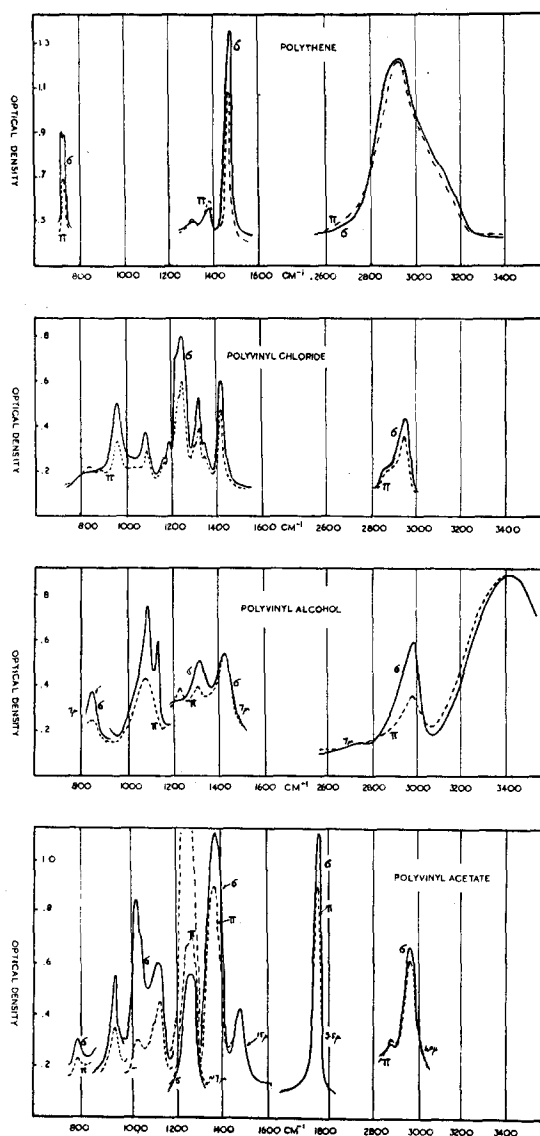


FIG. 1.

factor or factors operate to limit the number of vibrations which can interact with the radiation. One possible explanation is that the effect of the end groups is much reduced, but a more important limiting factor is probably to be found in the phase relationships which must exist between different parts of the molecule if absorption is to take place.<sup>13</sup> It is generally considered that a given vibration can only give rise to absorption if it produces a change of dipole

<sup>12</sup> J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* **157A**, 961 (1940).

<sup>13</sup> S. E. Whitcomb, H. H. Nielsen, and L. H. Thomas, *J. Chem. Phys.* **8**, 143 (1940).

moment for the molecule *as a whole*, and in a long chain this can only be so if the changes in dipole moment arising in neighboring units are nearly in the same direction. For parallel bands the vibrations must therefore be in phase, while for perpendicular modes they must be  $180^\circ$  out of phase, and these requirements greatly reduce the total of active vibrations. For a long hydrocarbon chain, the most general normal mode will be one in which the phase of the vibration changes by a constant angle from one unit to the next, corresponding to the passage of waves along the chain, to be reflected from the ends to form standing waves. In such a chain it is evident that both symmetrical and antisymmetrical C—H stretching frequencies will give rise to perpendicular-type bands, while C—H deformation modes will include both parallel and perpendicular vibrations. For example, a parallel band could be produced if all the hydrogen atoms were to move parallel to the chain in one direction, while all the carbon atoms moved simultaneously in the other. Such a vibration has not been observed in polythene, and it is interesting to inquire how it could occur in a very long chain. If the chain were bent or coiled to a large extent, the total change of dipole would be very small and the absorption coefficient correspondingly low. On the other hand, the greatest intensity would be expected when the chains were fully extended and oriented with the direction of the change of dipole moment parallel to that of the *E*-vector of the incident radiation. Since amorphous and unoriented long-chain polymers do possess strong absorption bands, it is apparent that the chains do not, in fact, vibrate as whole units but in sections, probably as a result of interference with the neighboring chains.

As a result of x-ray investigations,<sup>14</sup> it is known that there are two molecules in the unit cell of polythene in which the chains are parallel but with the fully extended zigzags mutually at right angles. On stretching, the crystallites become oriented with the chains parallel to the direction of stretch. The C—H bonds are thus in planes perpendicular to the chain axis, and the stretching vibrations should therefore show

maximum absorption when the *E*-vector is vibrating perpendicular to the axis. This is seen to be so in Fig. 1, although the dichroism is less marked than with the deformation band in the region of  $1400\text{ cm}^{-1}$ . The C—H stretching vibrations include both methylene and methyl group vibrations, and it will be shown later that this could (at least in part) account for the small degree of dichroism observed. The symmetrical methylene deformation should also be confined to the plane at right angles to the chain axis and has therefore been correlated with the strong band at  $1475\text{ cm}^{-1}$  which shows marked perpendicular dichroism. This is not in agreement with the assignment proposed by Whitcomb, Nielsen, and Thomas in their mathematical treatment of an infinite hydrocarbon chain.<sup>13</sup> These authors attributed the  $1475\text{-cm}^{-1}$  band to a fundamental mode in which the hydrogen atoms vibrate in phase against all the carbon atoms in a direction parallel to the chain axis. This explanation has already been criticized by Glatt and Ellis.<sup>3</sup>

The weak band at  $1375\text{ cm}^{-1}$  has been attributed by Thompson and Torkington to the presence of methyl groups, which were first detected in polythenes by Fox and Martin.<sup>12</sup> Previously it had been thought that polythene consisted of simple chains of  $\text{CH}_2$  groups.  $1375\text{ cm}^{-1}$  is exactly the frequency normally attributed to the symmetrical deformation of a methyl group. If the methyl groups were attached directly to the main polythene chain, the dipole change associated with its symmetrical deformation would be expected to occur in a direction perpendicular to the chain. It is found, however, that this frequency exhibits parallel orientation. The most plausible explanation of this is that the methyl groups are end groups attached to side chains of sufficient length to orient parallel to the main chains. This would show itself in reduced dichroism of the  $\text{CH}_2$  stretching frequency, on which the methyl group stretching frequencies are superimposed. The methyl groups on the side chains presumably arise when the radical participates in a chain transfer with the polymer already produced. This results in the formation of an active center in the polymer molecule from which a side chain grows, and this probably terminates in a methyl group. More information about the symmetrical defor-

<sup>14</sup> C. W. Bunn, Trans. Faraday Soc. **37**, 482 (1939).

mation of the methyl group was obtained from measurements made with poly-isobutene. The particular specimen of this substance available could not be maintained in the stretched state for more than a few minutes, but the absorption at  $1380\text{ cm}^{-1}$  resulting from the methyl groups was found to be more intense in the perpendicular direction. This molecule is thought to have a spiral structure with the *Me* groups projecting at an angle of  $63^\circ$  to the axis,<sup>15</sup> and the dichroism observed is small because of this inclination.

Solid polythene shows a doublet band at about  $728\text{ cm}^{-1}$ , which is replaced by a single shallower band on melting.<sup>5</sup> Sutherland and Sheppard have recently compared the spectra of a long-chain paraffin and that of the fully deuterated analog<sup>16</sup> and have shown that this band, which is found in all paraffins containing the group  $\text{CH}_3$ ,  $(\text{CH}_2)_n$  where  $n \geq 3$ , is a deformation mode of the  $\text{CH}_2$  groups. Examination with polarized radiation gives the following results. The perpendicular position gives the sharp doublet, as found by Thompson and Torkington, but with parallel radiation only a single broad and much less intense band appears, one component of the doublet being entirely absent or at least very much weaker. We can attribute the component which disappears to the rocking of the  $\text{CH}_2$  groups *across* the chain, since the other possible modes are either known to be of too great a magnitude or else would produce a dipole change in the wrong direction. The nature of the other component is obscure. Since it is reminiscent of the single band which occurs in the molten polymer, it may be due to the amorphous regions of the material. The phenomenon requires further experimental investigation.

### B. Polyvinyl Alcohol

This was high solubility material known as "Du Pont de Nemours RH 349." Films of suitable thickness were cast from aqueous solution on glass plates and oriented by stretching in a current of warm air. Thicknesses of the order of 7 microns were found suitable. Most of the results were obtained with films which had

not been exhaustively dried, but later experiments were made with a film that had been dried in a vacuum over phosphorus pentoxide, to discover whether any marked changes in the spectrum accompany the removal of water. The spectrum of this substance has already been recorded by Thompson and Torkington,<sup>17</sup> but the use of polarized radiation reveals some interesting new features. (See Fig. 1.)

The C—H stretching frequency at  $2975\text{ cm}^{-1}$  shows the expected perpendicular orientation to a considerable extent, in contrast to the very strong —OH valency band at about  $3400\text{ cm}^{-1}$  which appears completely unoriented. Furthermore, the breadth of the latter suggests that considerable hydrogen bonding is taking place. That this band is not the result of absorbed water is shown by the examination of the thoroughly dried film in which the breadth and intensity of the band remain unchanged. Hydrogen bonding is in accordance with the structure proposed for the crystalline material by Mooney,<sup>18</sup> although it must be admitted that this structure has been criticized by Bunn.<sup>19</sup> The hydrogen atoms are believed to be bonded to the oxygen atoms of neighboring molecules, the angle between the axis and the O—H—O bond being about  $60^\circ$ . The O—H—O bonds of adjacent groups are not parallel but inclined at  $60^\circ$  to the chain axis in opposite senses. It will readily be seen that the effect of this is to produce a lower dichroic ratio than for a perpendicular bond. Although the low value obtained for the dichroic ratio is in agreement with the structure suggested by Mooney, the *breadth* of the —OH band is not easily reconciled with an exact crystalline structure, which we should expect to give rise to a sharp band at a frequency lower than that associated with an hydroxyl group not subjected to hydrogen bonding.<sup>20</sup> If, however, the oxygen atoms did not always lie on the same side of the chain, as suggested by Bunn,<sup>21</sup> the degree of hydrogen bonding might vary and give rise to a broad band.

<sup>17</sup> H. W. Thompson and P. Torkington, *Trans. Faraday Soc.* **41**, 246 (1945).

<sup>18</sup> R. C. L. Mooney, *J. Am. Chem. Soc.* **63**, 2828 (1941).

<sup>19</sup> C. W. Bunn, *Recent Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1946), Vol. III.

<sup>20</sup> J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* **175A**, 208 (1920).

<sup>21</sup> C. W. Bunn and H. S. Peiser, *Nature* **159**, 161 (1947).

<sup>15</sup> R. Brill and F. Halle, *Naturwiss.* **26**, 12 (1938); C. S. Fuller, C. J. Frosch, and N. R. Pape, *J. Am. Chem. Soc.* **62**, 1905 (1940).

<sup>16</sup> G. B. B. M. Sutherland and N. Sheppard, *Nature* **159**, 739 (1947).

The strong band at  $1450\text{ cm}^{-1}$  has been assigned to a deformation of the methylene group by Thompson and Torkington. This is not borne out by the complete absence of dichroism, and it seems probable that it is, in fact, a deformation mode of the  $-\text{OH}$  group, the motion of which largely concerns the H atom. The Raman spectra of a number of alcohols contain a line at approximately this frequency. In addition, the intensity of this band appears much greater than might be expected for a methylene vibration. It is possible, however, that the two frequencies are coincident. The perpendicular band at  $1340\text{ cm}^{-1}$  may also be due to a hydrogen deformation mode.

The two bands near  $1100$  are of considerable interest. Comparison with the spectrum of polyvinyl chloride (see below) leads to the belief that they are connected with the presence of the oxygen atoms. The most striking feature is the apparent disappearance of the component at  $1146\text{ cm}^{-1}$  when parallel radiation is used. This recalls the polythene band at  $728\text{ cm}^{-1}$  already discussed, also an overtone band at  $4216\text{ cm}^{-1}$  reported by Glatt and Ellis.<sup>3</sup> Because of the uncertainty of the level of the background between absorption bands, and because of imperfect resolution, it is not possible to be certain that the band has completely disappeared; the dichroic ratio is certainly higher, possibly much higher, than 8:1 in polyvinyl alcohol. No other band in the spectrum of this substance shows such a high degree of orientation. The dichroic ratio for the C-H stretching frequency, for example, was 2:1, the same as for the band at

$1100\text{ cm}^{-1}$ . An x-ray photograph showed that the crystalline material was highly oriented, with the crystallites contained in a cone of semi-angle  $11^\circ$ . The dichroic ratio calculated for this degree of orientation is 25:1, so that the effect observed at  $1146\text{ cm}^{-1}$  is not unexpected. The general low value obtained from the other bands needs explanation, however.

### C. Polyvinyl Acetate

It is interesting to compare the spectrum of polyvinyl alcohol with that of the corresponding acetate, from which it is prepared by hydrolysis. The polyvinyl acetate examined was a sample of "Gelva-60," kindly supplied by Shawinigan Electrochemicals, Ltd., and had an approximate molecular weight of 180,000 (measured by viscosity). Films were cast from benzene solution and the material oriented by stretching in a current of warm air. The spectrum obtained is shown in Fig. 1 and agrees generally with that already recorded by Thompson and Torkington,<sup>17</sup> although the results obtained with polarized radiation present some interesting features.

The three most intense bands in the spectrum are, in order of intensity, those at  $1740$ ,  $1240$ , and  $1375\text{ cm}^{-1}$ , respectively. The first and the last show the same degree of perpendicular dichroism (dichroic ratio  $\sigma/\pi=1.26$ ), while the band at  $1240\text{ cm}^{-1}$  shows parallel dichroism ( $\pi/\sigma=1.3$ ). All three of these bands were considered by Thompson and Torkington to arise from the vibrations of the acetate group, that at  $1740\text{ cm}^{-1}$  from the stretching of the carbonyl radical, the band at  $1375$  from the symmetrical deformation of the methyl groups, and that at  $1240\text{ cm}^{-1}$  to be connected with a mode of vibration of the  $\text{C}\cdot\text{O}\cdot\text{CO}\cdot\text{C}$  skeleton.<sup>22</sup> These assignments are supported by our polarization measurements, which point to a structure in which the acetate groups are oriented relative to the chain as shown in the Fig. 2. In this figure, all the acetate groups are shown on one side of the chain for simplicity. A random distribution would, however, be equally compatible with the infra-red spectrum. It will be seen from the figure that both the C:O stretching vibration and the

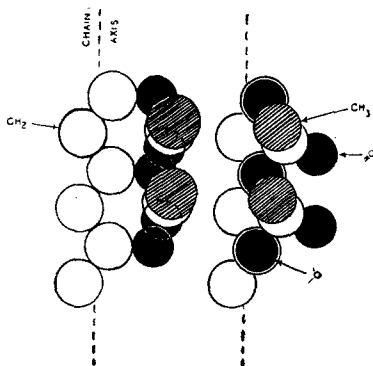


FIG. 2.

<sup>22</sup> H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945).

symmetrical  $\text{CH}_3$  deformational vibration should show predominately perpendicular character. In the skeleton  $\text{R}_1-\text{C}^1-\text{O}^2-\text{R}_2$ , where  $\text{R}_2$  represents the main chain, we may expect to find two frequencies which are mainly controlled by the stretching of the two C—O bonds 1 and 2. It was suggested by Thompson that the  $1240\text{ cm}^{-1}$  band in acetates is to be associated with bond 1, while that arising from bond 2 is to be found in the region from  $1000$ – $1100\text{ cm}^{-1}$ . The results we have obtained with polyvinyl alcohol and acetate appear to confirm this assignment. Reference has already been made to the polyvinyl alcohol band at  $1146\text{ cm}^{-1}$ , which shows a very high degree of perpendicular orientation and it will be seen that a high dichroic ratio is, also exhibited by the acetate band at  $1025\text{ cm}^{-1}$ , which is also highly perpendicular in character. The  $1240$  band, on the other hand, showing parallel orientation, is peculiar to the acetate (the very weak parallel band which occurs in the alcohol, merely suggesting, as Thompson remarks, the presence of a small residue of unhydrolyzed material). The facts, therefore, suggest very strongly that the strong perpendicular bands in the region of  $1000$ – $1150\text{ cm}^{-1}$  in the two materials arise mainly from the stretching of bond number two in the above formula, while the parallel acetate band at  $1240$  is due to bond number one. There are a few further points to be noted about the spectrum. The band at  $2930$  arising from the stretching of the C—H bonds shows only slight perpendicular orientation. That at  $1475\text{ cm}^{-1}$ , which is presumably caused by a hydrogen deformation mode, appears to be completely unoriented. Both facts can be explained by assuming the superposition of two or more frequencies of opposite configuration. In the former we have unresolved methylene and methyl group frequencies, and if the methyl groups are arranged very nearly perpendicular to the chain axis as suggested, the asymmetric  $\text{CH}_3$  stretching mode should have a parallel component which may compensate for the other perpendicular modes. Similarly, we may attribute the absence of dichroism at  $1475\text{ cm}^{-1}$  to superposition of the antisymmetrical methylene and methyl group frequencies.

TABLE I.

$\nu$	$D_\pi/D_\sigma = \log \frac{I_0}{I_\pi} / \log \frac{I_0}{I_\sigma}$
$2950\text{ cm}^{-1}$	0.73
1435	0.72
1260	0.70
Mean	0.72

#### D. Polyvinyl Chloride

This was an unplasticized specimen whose previous history is unknown, but since the spectrum appears to agree with that previously recorded by Thompson and Torkington,<sup>17,23</sup> this is unimportant. As will be seen from Fig. 1, the spectrum obtained with  $\pi$ -radiation is an almost exact replica of that in the  $\sigma$ -direction, with the band intensities slightly reduced. The two exceptions are a band at  $1200\text{ cm}^{-1}$ , which appears to be unoriented, and a very weak band at  $840\text{ cm}^{-1}$ . Only a few bands in the spectrum can be identified with particular modes. The very strong perpendicular vibration at  $1260\text{ cm}^{-1}$  which has no corresponding band in polyvinyl alcohol and which is the strongest band in the spectrum, presumably involves the chlorine atoms. It is probably connected with the rocking of the hydrogen atoms on the  $-\text{CHCl}-$  groups. The band at  $1450$  is obviously due to the normal deformation of the  $\text{CH}_2$  groups.

Although the dichroic ratio of the polyvinyl chloride bands is practically constant (except for the weak bands noted above), it should be remarked that probably hydrogen atoms, not chlorine atoms, are concerned in the corresponding vibrations. It may therefore be that the particular dichroic ratio (average value  $D_\pi/D_\sigma = 0.72$ , see below) shown corresponds to the average orientation of the C—H bonds. The value of the average orientation angle  $\theta$  corresponding to a dichroic ratio of  $0.72$  is  $44^\circ$ . It is quite possible that the band characteristic of the C—Cl stretching frequency, which is outside the region we have investigated, would show a different amount of dichroism. This will be investigated later.

<sup>23</sup> H. W. Thompson and P. Torkington, Proc. Roy. Soc. **184A**, 21 (1945).



### E. Nylon

Some preliminary results have been obtained with three specimens of "Nylon," a commercial specimen of "Nylon-66," a material prepared in this laboratory by the method of Chambert,<sup>24</sup> and an interpolymers of unknown constitution obtained from Du Pont de Nemours.

The Nylon type of polymer is interesting because this class of molecules is built up by the introduction of a simple polypeptide link into a straight hydrocarbon chain. The spectrum of Nylon-66 has already been investigated by Thompson and Torkington, using unpolarized radiation.<sup>17</sup> The absorption arising from the peptide link appears to be much stronger than that caused by the hydrocarbon chain. This is to be expected, of course, because of the highly polar nature of the atoms forming it.

Some interesting results have been obtained with polarized radiation, although the interpretation is at present not completely satisfactory. All three Nylons have bands in the regions of 3290, 3080, 2900, 1650, and 1550  $\text{cm}^{-1}$ ; below 1500  $\text{cm}^{-1}$  there are differences in the spectra. Two perpendicular bands at 2922 and 2875  $\text{cm}^{-1}$  can be assigned to the symmetrical and anti-symmetrical  $\text{CH}_2$  valency vibrations, respectively. The stronger and rather broader perpendicular band at about 3290  $\text{cm}^{-1}$  is certainly due to the N-H valency vibration. Measurements made by Richards and Thompson<sup>25</sup> on solid *N*-mono-substituted amides, and on the same compounds at widely different concentrations in chloroform, indicate that "free" N-H groups, have a valency vibration of about 3430  $\text{cm}^{-1}$ , while when the conditions are most favorable for hydrogen bonding (i.e., in the solid), a single band appears at about 3270  $\text{cm}^{-1}$ . In concentrated solutions both bands appear simultaneously. The presence of a single fairly broad band at 3290  $\text{cm}^{-1}$  in Nylon therefore indicates that the degree of hydrogen bonding taking place is very considerable, and probably nearly complete.

Further evidence for the existence of hydrogen bonding is afforded by the bands in the region

from 1500–1700  $\text{cm}^{-1}$ , which appear to be characteristic of the peptide link. Measurements made with unpolarized radiation on a natural polyglutamic acid and on a similar synthetic polymer prepared by Hanby, Waley, and Watson,<sup>26</sup> show that almost identical frequencies occur in both free acids and their silver salts. Similar results have been observed by Darmon and Sutherland, in the case of a denatured keratin and a keratin-type synthetic polypeptide.<sup>27</sup> There is a strong perpendicular band at 1650  $\text{cm}^{-1}$  which has been assigned to the stretching mode of the C:O link. This value is considerably lower than that found in the esters and ketones<sup>22</sup> and in *N*-mono-substituted amides in very dilute solution in dioxane,<sup>25</sup> but a similar shift towards low frequencies occurs in the latter compounds in the solid state. This indicates that the double-bond character has been reduced through the formation of hydrogen bridges, and the similar low value in Nylon is further evidence for the presence of the same phenomenon. All three Nylons show a strong parallel band at 1550  $\text{cm}^{-1}$ . This has been identified with an N-H deformational vibration by Richards and Thompson, who showed that a corresponding frequency is observed in the spectra of unsubstituted and *N*-mono-substituted amides, but not in those of the *NN*-di-substituted compounds. The vibration appears to take place in a plane parallel to the axis of the molecule. According to Bunn and Garner,<sup>7</sup> the carbon, oxygen, and nitrogen atoms linked by hydrogen bonds between parallel chains lie in an approximate straight line. Assuming a normal disposition of the valency bonds about the nitrogen atom, it is therefore clear that the hydrogen atom must lie to one side of the plane containing the carbon, nitrogen, and oxygen atoms, and this may favor the parallel deformation of the N-H bond. The very weak band found at 3080  $\text{cm}^{-1}$  is possibly the overtone of this N-H deformation, and if this is so, it is interesting to note that it appears to have changed its species to a perpendicular type band.

Quite striking differences were observed in the

<sup>24</sup> F. Chambert, Bull. Soc. Chim. 14, 283 (1947).

<sup>25</sup> R. E. Richards and H. W. Thompson, J. Chem. Soc., 1248 (1947).

<sup>26</sup> W. E. Hanby, S. G. Waley, and J. Watson, Nature 161, 132 (1948).

<sup>27</sup> S. E. Darmon and G. B. B. M. Sutherland, J. Am. Chem. Soc. 69, 2074 (1947).

spectra of two films of the interpolymer, one of which had been rolled and the other stretched. These differences must arise from the different types of orientation produced in the two cases. In the stretched film only unidirectional orientation of the chains is produced parallel to the direction of stretch. In the rolled material, the first effect of the compressional force is to produce a planar orientation of the plate-like Nylon crystals, with the 010 planes parallel to the sheet, directional orientation being produced by further rolling. The C:O bonds are thought to lie only slightly out of the 010 planes,<sup>7</sup> and it was found that whereas the corresponding band showed no apparent dichroism in the case of the stretched specimen, quite high perpendicular dichroism was observed in the spectrum of the rolled material. In the stretched Nylon, many of the C:O bonds will lie out of the plane of the sheet and therefore also out of the plane of vibration of the incident light. In an imperfectly oriented specimen, the component of the change of dipole moment resolved into the plane of vibration of the incident light can have a component parallel to the direction of stretching.

In fact, where the C:O bond lies in a plane perpendicular to the plane of the sheet, the component resolved in the plane of the sheet is parallel to the axis of stretch. This effect tends to reduce the amount of dichroism exhibited by a perpendicular band. On the other hand, when the C:O bonds are lying in the plane of the sheet as in the rolled specimen, a small degree of orientation of the bonds will produce an appreciable amount of dichroism. The infra-red data are therefore in agreement with Bunn and Garners' views concerning the disposition of the C:O bonds.

As already stated, the spectra of the three substances are not identical below  $1500\text{ cm}^{-1}$ , although the interpretation of these differences is not yet apparent. The material prepared by the method of Chambert showed very sharp absorption bands, which indicates that the crystal structure is very uniform. An x-ray powder photograph of the same material showed nine diffraction rings, also indicative of a high degree of crystallinity.

The presence of peptide links in a hydrocarbon chain at fairly long intervals may make it

possible for portions of the chain to vibrate as nearly independent units which are unaffected by the phase relationships which prevent the occurrence of parallel chain vibrations in molecules such as polythene. There are, in fact, two strong parallel vibrations in the spectrum of the Nylon copolymer: a doublet at about  $1130$  and a single band at about  $930\text{ cm}^{-1}$ . It would be interesting to determine whether similar parallel vibrations also occur in a continuous polypeptide chain.

### CONCLUSION

The results obtained so far indicate that the spectra obtained with the aid of polarized radiation can yield interesting information about the orientation of particular bonds in high polymers. Since the method is particularly suitable to the study of carbon-hydrogen bonds, it may yield complementary evidence to that obtained from x-ray analysis. One of the more puzzling results is that in all cases studied so far, the C-H bonds appear to exhibit much less than the expected degree of orientation. This phenomenon, which has already been noted by Glatt and Ellis,<sup>3</sup> may in some cases be due to the imperfect resolution of overlapping bands. In other cases, however, the effect is undoubtedly genuine. An x-ray photograph of one specimen of polyvinyl-alcohol, for example, showed a very high degree of orientation which was accompanied by very high dichroism of the C-O stretching frequency but only moderate dichroism of the C-H frequencies. As the above workers have found in the case of the overtones of polythene, the effect is much greater than imperfect alignment of the polarizer and the use of a converging beam of radiation can account for. It may therefore be that the degree of orientation varies considerably for different parts of the molecule, and that the low dichroism exhibited by the C-H bonds means that in the crystalline state the hydrogen atoms are considerably displaced from their expected positions. Although this explanation may hold for a material such as polyvinyl acetate, in which large side groups render the formation of stretched chains difficult, in other cases an alternative explanation may be that put forward by Glatt and Ellis, who suggest

that the coupling of a large number of  $\text{CH}_2$  groups, which must occur in a hydrogen chain, may produce a change of dipole moment which has a component parallel to the chain axis.

If it were possible to produce planar orientation in addition to that produced by stretching, more information could be obtained about the directions of the various bonds in the crystallites. Since it is known that rolling produces planar orientation in Nylon-66, this seems a suitable material for future study, in order to develop the technique, and it is hoped to extend the treatment to other polymers. The use of completely crystalline substances also offers attractive possibilities, and here again Nylon-66 seems suitable for experiment, since crystals of it can be grown

by the controlled polymerization of hexamethylene diammonium adipate.<sup>24</sup> It is also important to re-investigate several of the polymers already described under the higher resolving power obtainable with a lithium fluoride prism, and work on these lines is now proceeding. Since this increase of resolving power is particularly marked in the 3- $\mu$  region, it is intended to make use of it to obtain more definite information about the orientation of methylene and methyl groups.

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## On the Photo-Chemistry of Some Ions in Solution

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The absorption spectra of chlorate, bromate, iodate, and hypobromite ions and of hypobromous acid were measured.

The decomposition of bromate ion was investigated in the light of a mercury arc in the spectral region: 1900Å to 2600Å. The quantum yield of the decomposition is 0.19. The main decomposition reaction leads to the formation of hypobromite and molecular oxygen. The irradiation of hypobromite ions leads to the formation of bromide and bromate ions in a ratio of about 4 to 1 and to the evolution of oxygen. The decomposition of chlorate ion and iodate

ion is analogous to that of bromate. It is assumed that in all these cases the primary process of light absorption consists of the transfer of an electron to the hydration layer. In the case of halate ions, the photo-chemical reaction can be formulated as a decomposition of the complex  $(\text{XO}_3^- \cdot \text{H}_2\text{O})$  to  $\text{XO}^- + \text{H}_2\text{O} + \text{O}_2$ ; in the case of the hypobromite, as the decomposition of  $(\text{XO}^- \cdot \text{H}_2\text{O})$  to  $\text{X}^- + \text{H}_2\text{O} + \text{O}$ . In the latter case the oxygen atoms formed are responsible for the formation of bromate.

### INTRODUCTION

THE photo-chemical decomposition of ions in aqueous solution was the subject of a number of investigations.<sup>1-4</sup> Farkas and Farkas<sup>2</sup> have suggested that the primary process of light absorption consists of the transfer of an electron from the absorbing ion to one of the water

molecules\*\* in the hydration layer. If we assume that during this process the water molecules in the hydration layer remain oriented and retain their potential energy, the long wave-length limit of the absorption for an anion is given by the equation

$$h\nu_0 = E_- + H_- - E\text{H}_2\text{O}, \quad (1)$$

where  $E_-$  is the electron affinity of the anion in

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<sup>1</sup> E. Rabinowitsch, *Rev. Mod. Phys.* **14**, 112 (1942).

<sup>2</sup> A. Farkas and L. Farkas, *Trans. Faraday Soc.* **34**, 1113 (1938).

<sup>3</sup> J. Weiss, *Trans. Faraday Soc.* **37**, 467 (1941).

<sup>4</sup> L. J. Heidt, *J. Chem. Phys.* **10**, 297 (1942).

\*\* Professor J. Franck recently suggested that the primary light absorption process consists of the transfer of the electron to a "conduction band" of the hydration layer. According to his view, the electron is not attached to an individual molecule, but is spread over all the oriented water molecules (private communication).