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Influence of Intermolecular and Intramolecular Order on the Infrared Absorption Spectra of Polymers

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In the investigation of the vibrational spectra of macromolecular compounds it has been noticed that, when a polymer passes from the amorphous to the crystalline state, new absorption bands appear in the spectrum, or else splitting occurs in bands present in the spectrum of the amorphous substance. With certain polymers it has been established that several bands increase in intensity on passage from the crystalline to the amorphous state. The former group have been termed "crystalline" bands, and the second group "amorphous" bands. The origin of these absorption bands will become clear from a general theoretical examination of the vibrations described by an individual polymer chain and the crystalline unit cell formed by the chains. The method of theoretical examination of the normal vibrations of the crystalline polymer[1-5] is based on the application of group theory and is analogous to the method employed to investigate the vibrations of molecular crystals[6-8]. In a crystalline polymer the potential field of the crystal acts on the molecule in the same way as in molecular crystals. This should lead to a change in the spectrum of the crystalline polymer as compared with the amorphous material. Certain types of vibrations, which are inactive in an individual polymer molecule, may be active in the unit cell of a three-dimensional or one-dimensional crystal, since the symmetry of a molecule in a crystal field is usually lower than the symmetry of a free molecule. This results in a weakening of the selection rules found for an isolated molecule. It must be noted that, if degenerate vibrations occurred in an isolated molecule, the change in selection rules might result in elimination of the degeneracy. The appearance of "crystalline" bands also may be due to a change in the configuration of the molecular chain in the crystal cell of the polymer compared with its configuration in the amorphous state. Consideration of the vibration of an individual molecule in the crystal field is not complete, since it takes no account of the interactions of vibrations between chains in the crystal cell. This can be done in a theoretical investigation of vibrations in the unit cell of a crystal as a whole.

In the spectra of many polymers, transition from the amorphous to the crystalline state is accompanied not only by weakening of the selection rules but also by splitting of the main vibration frequencies. Physically such splitting occurs as a result of the resonance interaction of analogous vibrations undergone by individual chains in the unit cell. If n molecules are contained in the unit cell, as a result of resonance interaction, there will be n vibrations corresponding to each undegenerate vibration of an isolated molecule. The magnitude of the resonance splitting of frequencies will depend on the intermolecular interaction; it may be so small as to be unobservable experimentally. Furthermore, not all components of the resolved band are active in the infrared absorption spectrum.

Considerable interest attaches to study of the vibrational spectra of polymers having a regular chain structure (isotactic and syndiotactic polymers). In several cases these polymers show resonance splitting of the bands associated with interaction between analogous groups located along the polymer chain. Thus polymers having a helical chain structure, for example, show splitting of certain vibrations into two components polarised respectively parallel to the axis of the helix and perpendicular to the plane of the helix[9], and in this case the magnitude of the splitting depends on the type of interaction between the groups involved in the vibrations. In several cases new bands are found—"amorphous" absorption bands—on passing from the crystalline to the amorphous polymer. The appearance of these absorption bands may be caused either by breakdown in the selection rules operating in the crystal or by the existence in the amorphous phase of rotational isomers which are absent in the crystalline phase. The intensity of the "amorphous" bands is usually low. This is probably

linked with a minute fraction of new isomers appearing when the substance passes between the amorphous and the crystalline states. It must be noted that the theoretical calculation of "crystalline" and "amorphous" frequencies is difficult for several reasons, and in most cases such absorption bands have been discovered experimentally in the polymers. The detection of "crystalline" and "amorphous" absorption bands and their variation with the state of aggregation of the substance are not only of theoretical interest but also of great practical value. Examination of these two types of absorption bands enables the degree of crystallinity of the polymer to be determined, as well as the melting point of the crystals, their degree of orientation, and transitions of one crystalline modification into another. In several cases their study enables conclusions to be drawn on the configuration of the molecular chains in the various states of aggregation of the polymer. The present review presents data on the development, in the infrared spectrum of several polymers, of absorption bands due to intermolecular and intramolecular interaction between the polymer chains, and on the possibility of using these absorption bands to determine physical characteristics of the polymers.

POLY(VINYL ALCOHOL) $[-CH_2-CH(OH)-]_n$

A large number of papers have recently been published, especially by Japanese workers, on investigations of the structure of poly(vinyl alcohol) (p.v.a.). It has been shown[10-13] that the conditions of polymerisation influence the stereospecificity of the resulting polymer. X-Ray results indicate that poly(vinyl alcohol) is a crystalline substance having a repeat distance of 2.52 ± 0.02 Å in the direction of stretching, independently of the conditions of polymerisation[11,14]. Fig. 1 reproduces the infrared absorption spectra of isotactic and syndiotactic poly(vinyl alcohol). The spectrum of the polymer contains bands at

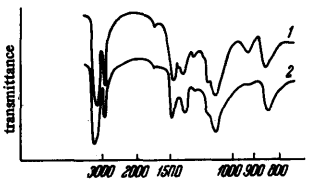


Figure 1. Infrared absorption spectrum of poly(vinyl alcohol):
1) syndiotactic (ordinary) specimen; *2*) isotactic specimen.

1141 and 916 cm^{-1} which are sensitive to intermolecular and intramolecular order. The intensity of the former band increases on heating[5] in parallel with increase in the degree of crystallinity of the polymer, determined by means of X-rays, the sorption of water, and the degree of coloration with iodine. This indicates that the absorption band at 1141 cm^{-1} is "crystalline". The intensity of the band at 916 cm^{-1} decreases[12] on such treatment (Fig. 2). As is evident from Fig. 1, this band is absent from the spectrum of isotactic specimens of the polymer. Transition from the syndiotactic to the isotactic structure is accompanied by a diminution in intensity of the absorption band at 1141 cm^{-1}.

The assignment of the absorption bands at 1141 and 916 cm^{-1} to corresponding modes of vibration is at present uncertain[15-19]. A theoretical calculation has been made[20] of the spectrum of syndiotactic and isotactic poly(vinyl alcohol), and it has been shown that the vibration $\nu(CO)A_1$ should appear in the region of 900 cm^{-1} in the spectrum of

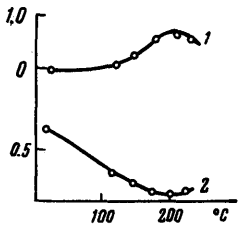


Figure 2. Effect of the temperature of heat-treatment of poly(vinyl alcohol), on relative optical densities in the bands: *1*) 1141 cm^{-1}; *2*) 916 cm^{-1}.

the syndiotactic polymer, and should be absent in that of isotactic specimens. This absorption can be identified with that at 916 cm^{-1} observed in the spectrum of syndiotactic poly(vinyl alcohol). The ratio of the optical densities in the absorption bands at 916 and 850 cm^{-1} (the latter band being taken as internal standard) has been used to determine the degree of stereoregularity of poly(vinyl alcohol) (Fig. 3) as a function of the temperature of polymerisation of the original material, which was poly(vinyl trifluoroacetate). However, it was pointed out that the ratio

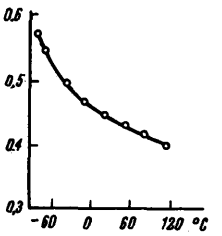
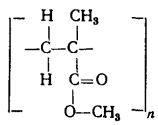


Figure 3. Dependence of ratio of optical densities of the 916/850 cm^{-1} bands on the temperature of polymerisation of poly(vinyl alcohol).

D_{916}/D_{850} itself depends on the optical density of the specimen in the region of 850 cm^{-1}. Measurements independent of the thickness of the specimen can be made when the optical density of the latter for the 850 cm^{-1} band exceeds 0.3. This fact is most probably due to the diffuseness of the reference band at 850 cm^{-1}. Estimation of the degree of syndiotacticity of a specimen from the band at 916 cm^{-1} is uncertain also because the intensity of this band (Fig. 2) depends on the degree of crystallinity of the specimen. However, the crystallinity of a specimen obtained under definite conditions of polymerisation depends on how the specimen had been prepared (humidity, temperature, etc.).

The assignment of the 1141 cm^{-1} band is uncertain. Krimm[18] originally attributed it to a ν(C–O–C) vibration, relating this absorption to the cross-linking of poly(vinyl alcohol) on heat-treatment of the polymer. Subsequently[21] this band was assigned to the vibration ν(CO) of some of the chains having intramolecular hydrogen bonds on one side of the plane of the zigzag of the main chain. It has been shown[11], however, that the isotactic poly(vinyl alcohol) model—rather than the atactic or the syndiotactic polymer—is associated with the formation of intramolecular hydrogen bonds. The 1141 cm^{-1} absorption band has been attributed[11,22] to skeletal vibrations of the atactic or syndiotactic part of the polymer. Irrespective of its assignment, this absorption band can be used to determine the degree of crystallinity of an atactic or a syndiotactic specimen of poly(vinyl alcohol).

POLY(METHYL METHACRYLATE)



Under certain conditions the polymerisation of methyl methacrylate may yield isotactic or syndiotactic poly(methyl methacrylate) or else a mixture of these forms[23–28]. Specimens of the stereoregular polymer can be crystallised, and differ from one another in glass point, melting point of the crystals, and density. X-Ray investigation of isotactic poly(methyl methacrylate) has shown[29,30] that the crystalline conformation of its chains corresponds to a 5_2 or 5_1 helix. The same conformations have been calculated theoretically[31] for the isotactic polymer. Such definite results do not exist for the syndiotactic structure: X-ray photographs of the syndiotactic polymer[29] are identical with those of an isotactic specimen. It has therefore been concluded[29] that the chains of syndiotactic poly(methyl methacrylate) also give a helical conformation. Calculations show[31] that the minimum potential energy for the syndiotactic polymer corresponds to a conformation which is closely similar to a proposed structure[32] or to a *trans*-chain. The infrared absorption spectra of these polymers differ. It has been found[33] that in the amorphous state the syndiotactic polymer is characterised by absorption bands at 1482, 1060, 910, and 822 cm^{-1}, which are very weak in an isotactic sample (Fig. 4). A method has therefore been proposed for the quantitative determination of the percentage syndiotacticity of specimens[33] from the 1060 cm^{-1} absorption band. An empirical method has been suggested[34] for calculating the stereoregularity of poly(methyl methacrylate) from the factor A, where A is a number indicating the character and degree of regularity:

$$A = 179\,(D_{1060})/D_{990} + 27;$$

$$A = 81.4\,(D_{1482})/D_{1390} - 43.$$

The parameter A has the approximate values 100–115 and 25–35 for the completely isotactic and the completely syndiotactic polymer respectively.

Hagai[35] noted an absorption band in the region of 750 cm^{-1} in the infrared spectrum, which had a rather higher frequency for isotactic than for syndiotactic poly(methyl methacrylate), and could be used in principle for quantitative calculations of the degree of stereoregularity of the polymer. Bands in the range 1050–1300 cm^{-1} are also sensitive to the intramolecular order[36]. The infrared spectra of both forms have been studied[37,38] after treatment of the specimens with heptan-4-one, which should result in their crystallisation[24]. On such treatment the infrared absorption spectrum showed the appearance of new bands in the range 1500–1600 cm^{-1}, which varied with the temperature in parallel with the X-ray pattern. It has been shown[39], however, that the appearance of these absorption bands may be due to the presence of an impurity in the specimen. The X-ray pattern observed when poly(methyl methacrylate) is treated with heptan-4-one also may be linked with the presence of this impurity. It is interesting that crystallisation of an isotactic specimen of the polymer has also been observed[34] when it was suspended in water, but no qualitative change in the spectrum was observed.

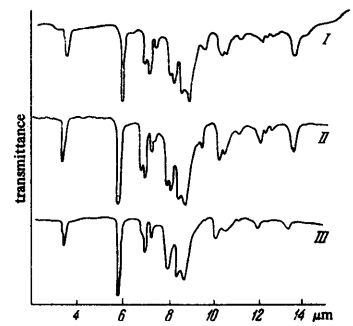
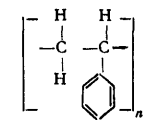


Figure 4. Infrared absorption spectrum of poly(methyl methacrylate):
I) syndiotactic; *II*) atactic; *III*) isotactic.

It is evident from the above discussion that, although differences in the stereospecificity of poly(methyl methacrylate) specimens are revealed in the infrared absorption spectrum, the quantitative determination of syndiotactic and isotactic sequences in samples is relative in character. Such determination is less accurate than the nuclear magnetic resonance (n.m.r.) method[40].

POLYSTYRENE



It has been shown[41–46] that the infrared absorption spectrum of atactic polystyrene differs from that of the isotactic polymer in both crystalline and amorphous states. Fig. 5 reproduces the infrared spectra of atactic polystyrene and the spectra of isotactic polystyrene in the melt, in carbon disulphide solution, and in the quenched and crystalline states. Three classes of changes in the infrared spectrum can be distinguished[46] on passing from an atactic to an isotactic specimen of polystyrene.

1. The intensity of several absorption bands increases, or new bands appear, in the spectrum of an isotactic specimen of polystyrene. The bands at 1365, 1297, 1260, and

1187 cm^{-1} can be regarded as of this type. Study of deuteriated derivatives of isotactic polystyrene has shown that these bands are not associated with vibration of the benzene ring.

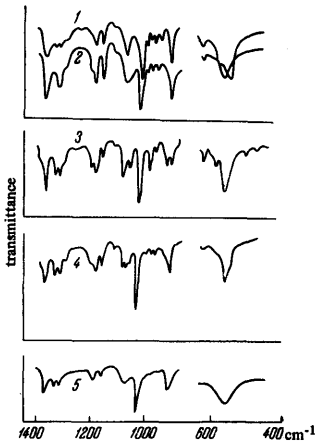


Figure 5. Infrared spectrum of polystyrene in various states of aggregation:
1) atactic; *2*) amorphous isotactic at 20°C; *3*) crystalline isotactic; *4*) isotactic dissolved in CS_2; *5*) molten isotactic.

The bands at 1365 and 1297 cm^{-1} represent deformation vibrations of CH_2 and CH groups, and the bands at 1187 and 1260 cm^{-1} stretching vibrations of the carbon chain. The appearance of absorption bands at 1187 and 1260 cm^{-1} in the spectrum of isotactic polystyrene can be explained by the formation of a helical conformation, which is characteristic of an isotactic sample[47,48]. The change in intensity of the bands at 1365 and 1297 cm^{-1}, however, is linked with some change in mode of the normal vibrations (in the present case deformation vibrations of CH and CH_2 groups) on helication of the carbon chain or on change in the spatial environment, in particular change in the interaction with other modes of vibration.

2. The band at 1070 cm^{-1} and probably that at 1312 cm^{-1} can be included in the second group of absorption bands.

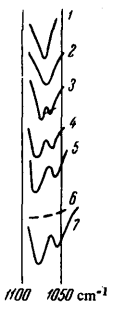


Figure 6. Absorption of polystyrene in the region of 1000 cm^{-1}: *1*) atactic; *2*) molten isotactic; *3*) quenched isotactic; *4*) isotactic dissolved in CS_2; *5*) crystalline isotactic; *6*) isotactic oriented along electric vector $E_\perp$; *7*) isotactic oriented along electric vector $E_\parallel$.

On passing from an atactic to an isotactic specimen these bands are split into two components. This splitting remains in a quenched specimen and in solution, although it is smaller (Fig. 6).

In an oriented specimen in polarised radiation the two components of the resolved bands have the same σ-dichroism. Study of deuteriated specimens has shown that these absorption bands may be due to vibrations of the benzene ring. Since both components of the resolved absorption bands exhibit σ-dichroism, it is difficult to link the splitting with intermolecular or intramolecular ordering of the chains in an isotactic specimen. The reason for splitting of this type is obscure.

3. The bands at 982, 906, 757, and 700 cm^{-1} can be placed in this group. On passing from an atactic to an isotactic specimen they are split into two components close together, which differ in polarisation. Since splitting of the bands is observed only in the crystalline state, it may be regarded as associated with the development of intermolecular order in a crystalline isotactic specimen of polystyrene. Study of deuteriated specimens shows that these absorption bands are due to vibration of the benzene ring.

The absorption range 600–500 cm^{-1} is also of interest in the spectrum of polystyrene. In the crystalline isotactic polymer absorption bands are observed at 567 and 570 cm^{-1} in this range. In solution bands are found at 560 and 544 cm^{-1}, and in the quenched state a broad band occurs at 546 cm^{-1}. The spectrum of atactic polystyrene also contains an absorption band at 546 cm^{-1} and a shoulder at 560 cm^{-1}. Takeda et al.[45] proposed using the ratio of optical densities in the bands at 546 and 560 cm^{-1} to determine the relative degree of "isotacticity" of polystyrene specimens. Pokrovskii and Fedorova[49] have recently suggested a quantitative method for calculating the degree of isotacticity from the ratio of the optical densities in these bands based on the fact that the integral intensity in the range 500–600 cm^{-1} is always constant in a solution of any specimen of polystyrene (isotactic or atactic). Most authors assign these absorption bands to $\nu_4(B_2)$ deformation vibrations of the benzene ring. Variation in the band envelope with the type of stereoregularity of a polystyrene specimen is due to the sensitivity of this vibration to various types of intramolecular order over short sections of the carbon chain. Hence we cannot agree that the integral ratio of the optical densities of the bands[49] 543/560 cm^{-1} does actually determine the absolute degree of stereoregularity in a sample. This is also indicated by the dependence of the envelope of these bands on the state of aggregation of the specimen. Unfortunately, the n.m.r. method, use of which might have given a reference point for subsequent quantitative measurement, by means of the infrared absorption spectra, of the degree of stereoregularity in polystyrene, has not at present been developed for measuring this parameter[50]. The bands at 1260, 1187, or 567 cm^{-1} can be used to determine the relative degree of crystallinity of polystyrene. Takeda[45] proposed the absorption band at 1030 cm^{-1} as internal standard for such measurements.

POLY(VINYL CHLORIDE) $[-CH_2-CHCl-]_n$

The relation between the structure of poly(vinyl chloride) [p.v.c.] and its infrared absorption spectrum over the range 400–1600 cm^{-1} has been investigated by several workers[51-58]. Attention has been directed mainly at the range 400–700 cm^{-1}, in which stretching vibrations of the

C–Cl bonds appear. Fig. 7 reproduces the infrared absorption spectrum of a feebly crystalline specimen of poly (vinyl chloride). The spectrum consists of strongly overlapping absorption bands at 693, 685, 638, and 615 cm^{-1}.

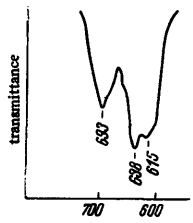


Figure 7. Infrared spectrum of poly(vinyl chloride) in the region of 600 cm^{-1}.

When such a specimen is heat-treated, and also on the polymerisation of poly(vinyl chloride) at −78°C or on channel complexes with urea, the bands at 638 and 683 cm^{-1} diminish in intensity, while fairly sharp bands appear at 603 and 640 cm^{-1} (Fig. 8). These bands disappear when

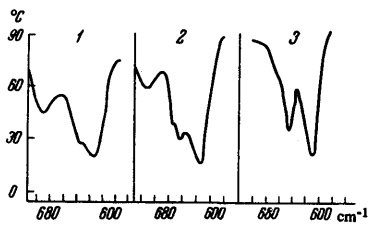


Figure 8. Infrared spectrum of poly(vinyl chloride) obtained under various conditions of polymerisation: *1*) at 50°C; *2*) at -70°C; *3*) on complexes with urea.

the polymer melts or dissolves[58]. Hence most authors[53,54] attribute the bands at 603 and 640 cm^{-1} to intermolecular interaction in the crystalline portion of the polymer. On the assumption that the low-temperature polymerisation of poly(vinyl chloride), like polymerisation on channel complexes with urea, promotes formation of a syndiotactic structure[53,55,59], the 603 and 640 cm^{-1} vibrations are assigned respectively to the B_1 and A_1 types of C–Cl-stretching vibrations. It has been shown[60,61] that the absorption band at 640 cm^{-1} has perpendicular dichroism, while the 603 cm^{-1} band has parallel dichroism, on stretching 2–2½ times; when, however, the specimen is stretched ~ 7 times, the dichroism of the 603 cm^{-1} band becomes perpendicular (Fig. 9). These effects are interpreted as reflecting a change in the intramolecular packing in the crystalline portion of the polymer at different degrees of extension.

Assignment of the absorption bands at 615, 638, 685, and 693 cm^{-1} is difficult; these bands overlap strongly, the degree of overlap depending on their relative intensities. These intensities have been shown to vary appreciably with the conditions of polymerisation of the poly(vinyl chloride) specimens, the heat-treatment of the specimens, their orientation, and finally the way in which the specimen is prepared for exposure (as tablets with potassium bromide, films, etc.). Interpretation of these absorption bands is made difficult also by the fact that no reliable data are yet available on the stereoregularity of specimens obtained under different conditions of polymerisation. X-Ray results[62] indicate that no perfect syndiotactic structure is present even in specimens of the polymer prepared by low-temperature polymerisation. Data on the structure of poly(vinyl chloride) obtained by the n.m.r. method are also as yet fairly indefinite[63,64].

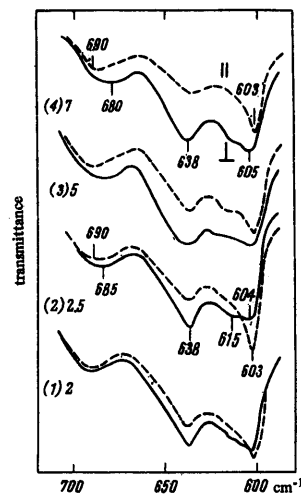


Figure 9. Dependence of dichroism in bands at 603 and 640 cm^{-1} on the stretching of isotactic poly(vinyl chloride).

Owing to the closeness of the absorption frequencies and also the uncertainty in the type of stereoregularity in the specimens, theoretical calculations on the assignment of these frequencies are also in considerable measure approximate[65]. A detailed study of secondary alkyl chlorides[57] has shown that the position of the ν(C–Cl) stretching frequencies is strongly dependent on the nature of the substituent attached to both adjacent C–C bonds located in the *trans*-position relative to the chlorine atom. In view of this, and also the dependence of the ν(C–Cl) vibration frequency on the conformation of the molecular chain, the bands at 615 and 693 cm^{-1} have been assigned to stable and unstable rotational isomers of the syndiotactic part of the polymer, while the absorption bands at 638 and 683 cm^{-1} are correspondingly assigned to unstable and stable isomers in the isotactic part of the poly(vinyl chloride) specimen. On the basis of this assignment of the absorption bands it is possible in principle to calculate several molecular parameters of the polymer: the intensity ratio of the absorption bands 615/638 cm^{-1} provides a measure of the isotactic and syndiotactic configurations present in the stable conformation; the band intensity ratios 615/693 cm^{-1} and 683/638 cm^{-1} define respectively the ratios of stable to unstable conformations in the syndiotactic and isotactic parts of the polymer. However, great caution must be exercised with respect to such measurements. Firstly, owing to the difficulties mentioned above, the assignment

of the absorption bands required for such measurements is not entirely unambiguous. Thus, for example, it is not clear why the absorption bands corresponding to the unstable rotational isomer diminish in intensity when a specimen of the polymer is heated to 180°C, whereas the quantity of unstable rotational isomers usually increases under these conditions. On the other hand, quantitative measurements are inaccurate because of the strong overlapping of the absorption bands. Somewhat better results can be obtained by examining the intensities of these bands in solutions of poly(vinyl chloride).

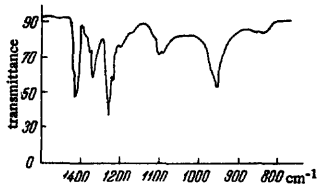


Figure 10. Infrared spectrum of poly(vinyl chloride).

The infrared spectrum of poly(vinyl chloride) in the range 1600–800 cm^{-1} is illustrated[58] in Fig. 10. The variation in absorption coefficients of a series of bands was investigated as a function of the density of the specimen, i.e. its crystallinity. The density of the specimens examined varied from 1.3887 to 1.4022. The ratio of the intensities of the bands at 1428, 1254, 1226, and 963 cm^{-1} to that of the 2920 cm^{-1} band increased linearly with the degree of crystallinity of the sample. A less marked increase occurred in this ratio for the bands at 1434, 1355, and 831 cm^{-1}. At the present time the assignment of these bands by different authors[58,66] is ambiguous. Irrespective of the assignment, these bands are sensitive to the three-dimensional order in the polymer. It is noteworthy that the sign of the dichroism of the 963 and 1254 cm^{-1} bands depends on the degree of stretch of the specimen (just as with the 603 cm^{-1} band).

POLY(VINYLIDENE FLUORIDE) $[-CH_2-CF_2-]_n$

A study has been made[67] of the infrared spectra of poly(vinylidene fluoride) in crystalline and amorphous states. The spectrum of films of this polymer prepared from solution in dimethyl sulphoxide is found to contain absorption bands at 1075, 980, 855, 798, and 762 cm^{-1}. These bands diminish in intensity or disappear when the specimens are heated above 165°C, which corresponds to the melting point of the polymer. Cooling the specimen to room temperature results in the reappearance of these absorption bands. Analogous behaviour is shown by the weak bands in the region of 3700, 3620, and 3380 cm^{-1}. All the above bands can be regarded as "crystalline", since they characterise the intermolecular ordering of the polymer chains. The 740 cm^{-1} band can be regarded as "amorphous", since its intensity increases when the specimen melts.

The infrared spectrum of poly(vinylidene fluoride) has been investigated[68] in greater detail in the range 3000–400 cm^{-1}. In this case films of the polymer were prepared from a solution in boiling acetone. The spectrum of such specimens contains bands at 484, 510, 840, 1073, 1180, and 1235 cm^{-1}, which disappear when the polymer is heated to 220°C. Nor are these bands observed in a spectrum of a solution of the polymer in acetone. For all these reasons the bands can be regarded as "crystalline". The crystalline modification of poly(vinylidene fluoride), whose spectrum is characterised by the above six bands and by a definite X-ray pattern, has been called the α-form. The bands at 600, 740, and 905 cm^{-1}, the intensity of which increases when the polymer melts, are regarded as "amorphous". The content of the amorphous phase in the polymer, determined by means of these bands, is ~ 50%. When a film of the polymer which has been heated to 220°C is cooled to room temperature, new sharp bands appear in the spectrum at 488, 531, 612, 765, 796, 857, 977, 1071, 1152, 1185, 1215, and 1385 cm^{-1}, which are characteristic of the crystalline state of the polymer. The variation in these bands with temperature, together with X-ray investigations, suggest that in this case another crystalline modification of the polymer—the β-form—can exist. Study of the spectra of oriented specimens of poly(vinylidene fluoride) in polarised infrared radiation confirms the existence of α- and β-forms[69]. The different crystalline forms correspond to different conformations of the polymer chain.

Analysis of data obtained from the infrared absorption spectra, together with X-ray structural analysis, shows[70–72] that in the α-conformation the molecular chains have a planar zigzag structure, and in the β-modification they have the TG–TG′ conformation. The existence of a third conformation has been suggested[72], the infrared spectra of which differ from that of the α-conformation in the intensities of certain absorption bands. The most marked differences are observed in the range 250–400 cm^{-1}.

POLYAMIDES

Many authors have been concerned in correlating[73–78] the infrared spectra of polyamides with the intermolecular and intramolecular order in the polymer. It has now been firmly established[79–83] that, depending on the number of methylene groups between the amide groups or on the treatment of the specimens, polyamides can exist in three crystalline modifications—α, β, and γ—or contain these forms together in various proportions. Whereas the α- and β-forms have a monoclinic crystal cell, in which the methylene chain is in the form of a flat zigzag lying in the same plane as the amide group, the γ-configuration has hexagonal packing (the plane containing the amide group is inclined at ~ 30° to the plane of the methylene chain).

Fig. 11 gives the infrared spectra of polycaprolactam in α- and γ-forms and of molten and quenched specimens of the polyamide. It is seen that the monoclinic α-form is characterised by absorption bands at 575, 692, 930, 960, 1201, 1420, 1470, and 1477 cm^{-1} (I). The crystalline γ-form is represented by bands at 625 and 711 cm^{-1} (II). Bands at 976, 1170, 1440, and 1460 cm^{-1} (III) are present in the γ-modification and in the molten polyamide, but are weaker or completely absent in polymers containing only or predominantly the α-modification. The bands at 590, 700, 1240, and 1280 cm^{-1} (IV) increase in intensity on fusion of the specimens. Bands of group I are associated[75,76] with the conformation of the molecular chain in the crystal cell characteristic of the α-form; the bands forming group II are probably linked with the intermolecular order in the γ-form of the crystals; those of group III are associated with the conformation in which the methy-

lene chain is not in the same plane as the amide group; and group IV are associated with the appearance of a coiled conformation of the molecular chains on fusion of the polyamides. A good criterion of the presence of α- and γ-crystalline forms is the position of the amide band[84] V, which in the α-form is located in the range 680–690 cm^{-1}, whereas in the γ-form it lies in the range 711–730 cm^{-1} (Fig. 12).

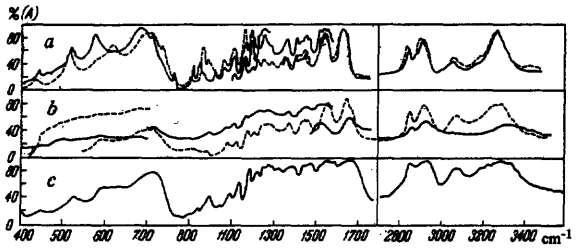


Figure 11. Infrared spectrum (A = absorption, %) of a polyamide: *a*) highly crystalline polymer ($\alpha + \beta$-form), the broken line representing the γ-form; *b*) molten polymer (245°C), the broken line representing the quenched polymer at 110°C; *c*) quenched polyamide at 20°C.

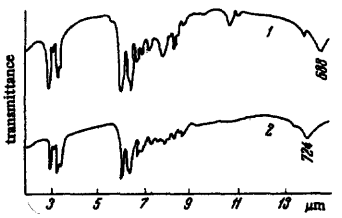


Figure 12. Position of amide V in a polyamide in the modifications:
1) α; *2*) γ.

Since a partly crystalline polyamide at ordinary temperatures exhibits bands characteristic of both α- and γ-forms of the crystal cell, the problem of determining the degree of crystallinity in polyamides is complicated. The 930 cm^{-1} band is most widely used[73,74,86] for this purpose. Such determination is valid provided that the specimen contains only or predominantly the α-form. The intensity of the band is then proportional to the degree of crystallinity of the polymer (Table 1). In all other cases measurement of the crystallinity on the basis of the 930 cm^{-1} band may result in large errors. As already mentioned above, the most convenient method is to determine the degree of crystallinity from "amorphous" absorption bands. However, such bands at 590, 700, 1240, and 1270 cm^{-1} in polyamides overlap other bands, and are unsuitable for quantitative determinations.

Novak et al.[86] have proposed a method for estimating the degree of crystallinity of poly-ϵ-caprolactam from the absorption bands at 930, 1076, and 1118 cm^{-1} (the latter two of which were regarded as "amorphous"). A complicated dependence of crystallinity on orientation was discovered: the orientation of quenched fibres increases the crystallinity, and the orientation of fibres of high crystallinity produces a decrease; finally, with degrees of crystallinity of 18–20% the content of the crystalline phase is unaffected by deformation.

Table 1. Determination of crystallinity in a polyamide as a function of the heat-treatment of the specimen.

Crystallisation temp., °C	Crystallinity, %, from 930 cm^{-1} band	Crystallinity, %, from density	Crystallisation temp., °C	Crystallinity, %, from 930 cm^{-1} band	Crystallinity, %, from density
—	23	24	132	29	25
—	24	24	132	32	22
—	25	27	160	27	20
—	24	22	160	30	41
100	29	29	160	41	41
100	30	29	180	27	25
100	30	29	180	42	43
100	30	29	180	44	44
100	29	21	185	45	43
100	25	17	185	45	53
100	22	17	185	46	51
132	35	36	210	48	50
132	35	36	210	46	57
132	36	36	210	47	57
132	36	36	210	48	56
132	28	23	210	51	55

POLYPROPYLENE

$$\left[-CH_2-\underset{\displaystyle CH_3}{\overset{|}{C}}H-\right]_n$$

The spectrum of isotactic polypropylene contains several strong and moderately strong absorption bands in the range 1200–800 cm^{-1} (Fig. 13). These bands are interesting because their intensity depends greatly on the degree

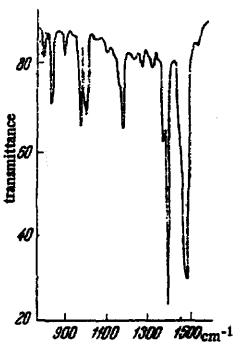


Figure 13. Infrared spectrum of crystalline isotactic polypropylene.

of microtacticity and crystallinity of the specimen, as well as on its state of aggregation. Thus the bands at 841, 997, and 1167 cm^{-1} disappear at 180°C, the melting point of polypropylene[87–90]. The bands at 841, 973, 997, 1153, and 1167 cm^{-1} are absent in specimens of polypropylene which has been prepared on non-stereospecific catalysts[91,92].

In a quenched specimen[93,94] the differential intensity of the bands at 841, 997, and 1167 cm^{-1} is diminished, while those at 973 and 1153 cm^{-1} remain practically unchanged. The 973 cm^{-1} absorption band remains, though diminished in intensity, when polypropylene is dissolved in benzene. X-Ray examination of quenched propylene shows[91] a peak at $2\theta = 22.2°$ besides an amorphous halo: i.e. the intermolecular ordering of molecular chains is partly preserved in a quenched specimen.

Differences in the infrared absorption spectra of different polypropylene fractions, specimens of different degrees of crystallinity, and specimens examined at 20° and 180°C may be associated with variation in both intramolecular and intermolecular order. The behaviour of the bands at 997, 841, and 1167 cm^{-1} on fusion and quenching of the polymer may indicate that these bands are due to the intermolecular order in polypropylene specimens. This order disappears in molten polypropylene, but is partly preserved in a quenched specimen, although X-ray examination indicates such a specimen to be amorphous. This explanation[96,97] is consistent with the fact that the intensity of the 997 cm^{-1} band increases in proportion to the degree of crystallinity of the specimen. The 1153 and 973 cm^{-1} bands may be due to intramolecular order in isotactic polypropylene[93,94]. Natta has shown that the molecular chains in isotactic polypropylene have the configuration of a 3_1 helix.

The Raman spectrum at 20° and 180°C has recently been obtained[98] for specimens of isotactic polypropylene (Fig.14). The changes produced in the Raman spectrum by fusion of the specimen are the same as observed in the infrared absorption spectrum. Since the unit cell of isotactic polypropylene belongs to the symmetry group C_{2h} and has a centre of inversion, this may be expected to lead to mutual exclusion of the frequencies in the Raman and infrared absorption spectra. As these spectra are identical at 20°C, it may be assumed that the spectrum of polypropylene is determined mainly by the chain structure alone.

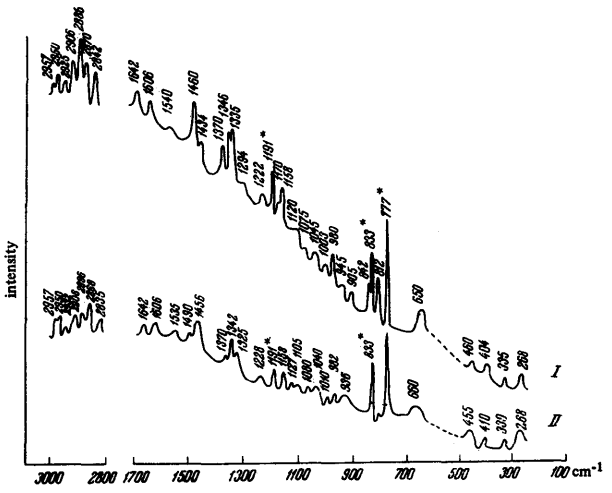


Figure 14. Raman spectrum of isotactic polypropylene: *I*) crystalline; *II*) molten.

Thus the absorption bands at 997, 841, and 1167 cm^{-1} may be associated either with intermolecular ordering of the polypropylene chains or with intramolecular order over large sections of the chains. The 974 and 1153 cm^{-1} bands, however, are probably linked with short-range intramolecular order. It thus becomes possible to measure[93,94,99] the relative "microtacticity" of polypropylene specimens from the intensity of the 974 cm^{-1} band, and the intermolecular ordering of the molecular chains from the 997 cm^{-1} band. A method has been proposed[100] for estimating the degree of isotacticity of polypropylene from the lack of symmetry of the former band. Appropriate fractions of the polymer and mechanical mixtures thereof were used to calibrate the method. The percentage isotacticity determined by this method was shown to agree well with the degree of crystallinity of the same specimen measured by means of the 997 cm^{-1} band at medium values of the isotacticity, and to differ markedly for its extreme values.

Fig. 15 shows the spectrum[101] of isotactic and atactic polypropylene in the range 410–100 cm^{-1}. It is seen from Figs. 15 and 16 that, whereas the spectrum of the isotactic polymer contains well separated absorption bands at 321, 251, 210, 200, 169, and 155 cm^{-1}, the atactic polymer has a diffuse absorption spectrum. There is no exact assignment of these bands to a definite type of vibration. In view of the sign of the dichroism, it is assumed that the bands at 398, 251, 200, and 155 cm^{-1} are due to vibrations of symmetry A, and those at 321, 210, and 169 cm^{-1} to symmetry E ($2\pi/3$) (Fig. 16). It may be supposed that these bands are due to skeletal deformation vibrations or correspond to frequencies of internal rotation in the polymer.

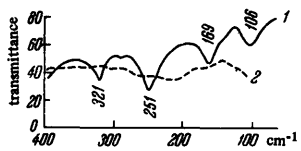


Figure 15. Infrared spectrum of polypropylene: *1*) crystalline isotactic; *2*) atactic.

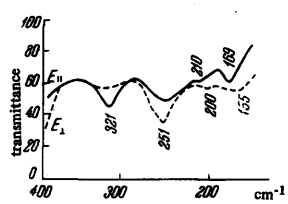


Figure 16. Infrared spectrum of isotactic polypropylene in polarised radiation.

Natta and his coworkers[102,103] synthesised syndiotactic polypropylene at low polymerisation temperatures (−70°C) on homogeneous catalytic systems obtained from a vanadium compound. The resulting polymer had fairly low crystallinity, which probably indicated that it was very inhomogeneous. The infrared spectrum of syndiotactic polypropylene differs somewhat from that of an isotactic specimen[104,105]: several absorption bands, e.g. at 997 and 458 cm^{-1}, are absent from the spectrum of syndiotactic polypropylene, and many bands are either displaced in frequency compared with the spectrum of an isotactic specimen or are characteristic only of this spectrum, e.g. 1005 and 970 cm^{-1}.

Zambelli et al.[104] suggested a method for determining the degree of syndiotacticity of polypropylene specimens using the ratio of the optical densities in the bands at 11.53, 2.32, and 2.35 μm:

$$A = D_{11.53}/^1/_2 (D_{2.32} + D_{2.35})$$

where A is the relative syndiotacticity index. It must be noted that the index is strongly dependent on temperature over the presumed melting range of the specimen[106].

A helical conformation has been suggested for syndiotactic polypropylene. However, a new crystalline modification of syndiotactic polypropylene has been obtained[107]. This modification is formed by the orientation of a quenched specimen of the syndiotactic polymer. The molecular chains then form a planar zigzag. The new modification is characterised by absorption bands at 1005, 1130, 960, and 830 cm^{-1} having parallel polarisation, and bands of lower intensity in the region of 1320 and 820 cm^{-1} having perpendicular polarisation.

The study of deuteriated specimens of polypropylene has enabled several of the above absorption bands to be related to vibrations of certain groups[87,105] (Table 2).

Table 2. Assignment of absorption bands of polypropylene.

Absorption bands, cm^{-1}		Type of vibration
syndiotactic	isotactic	
866	841	CH_2 rocking (A), CH_3 rocking (A), C-C stretching (A)
962	973	CH_3 rocking (A), CH_2 rocking (A), C-C stretching
977	997	C-C stretching (A), CH_3 rocking (A), CH_2 rocking (A)
1083	1102	C-C stretching
1005	1042	
1152	1153	CH_3 wagging
1157	1167	CH_3 wagging, C-C stretching (A)
485	458	C-C deformation

POLYETHYLENE $[-CH_2-CH_2-]_n$

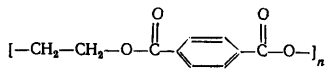
Polyethylene has a simple absorption spectrum, which has been well deciphered[108-110]. The greatest interest is presented by the absorption bands at 720, 730, 1308, 1464, and 1473 cm^{-1}, which are present in the partly crystallised polymer. In the amorphous state the band at 730 cm^{-1} has disappeared from the infrared spectrum, while that at 1303 cm^{-1} has increased in intensity; the doublet 1464–1473 cm^{-1} has been replaced by a single band at 1460 cm^{-1}.

It has been shown theoretically[109,110] that the appearance of the doublets 720–730 and 1464–1473 cm^{-1} is due to resonance interaction of deformation vibrations (rocking and wagging respectively) of methylene groups in the crystal cell, but the polarisation of the resolved components obtained in these papers did not agree with that determined experimentally.

It has since been shown that the type of splitting and the polarisation of the bands can be explained[111] by choosing an appropriate potential taking into account the interaction not only of hydrogen atoms adjacent to the chains but also of more remote hydrogen atoms. The 1303 cm^{-1} band is of especial interest, since it becomes stronger when polyethylene melts, which makes it possible to determine quantitatively the crystalline content[112-114] of the polymer by a method independent of X-ray examination. This band is assumed[112] to be characteristic of the presence of a skew rotational isomer in the amorphous part of the polymer. The presence of rotational isomers in polyethylene[115] has been confirmed also by an investigation of the stretching of the polymer. The 1460/1303 band absorption coefficient ratio increases when polyethylene is stretched by 1000% of its original length, owing to transition of the skew isomer into a *trans*-isomer. The conversion of skew isomers into *trans*-isomers on stretching has since been confirmed by measuring the energy changes accompanying stretching of cross-linked polyethylene[116].

The absorption bands at 1308, 1350, and 1365 cm^{-1} have been used[117,118] to investigate polyethylene single crystals. A method has been suggested[117] which will in principle enable us, by means of the variation in the intensities of these absorption bands, to distinguish the amount of disordered material in the polymer from the amorphous part formed when the polymer is packed into folded crystals.

POLY(ETHYLENE TEREPHTHALATE)



Spectroscopic study of this polymer[119-121] indicates that the changes observed in the spectrum (Fig. 17) on passing from the crystalline to the amorphous state are associated with rotational isomerism. Table 3 lists the absorption band frequencies which are sentitive to a change in crystalline state[119]. It has been shown that these bands do not completely disappear in the above transition.

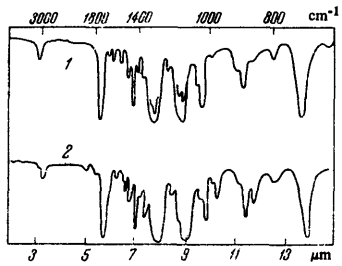


Figure 17. Infrared spectrum of poly(ethylene terephthalate):
1) amorphous; *2*) crystalline.

The absorption spectrum of a model compound (ethylene dibenzoate) in solution contained the same absorption bands as did the molten polymer. It might be supposed that the changes in intensity of the polymer bands indicated in Table 3 were due to intermolecular or intramolecular interaction. Examination of the model compound (ethylene dibenzoate) showed that the intensity remained unchanged on dissolution of the compound in carbon tetrachloride over a wide range of concentrations. In crystalline ethylene dibenzoate, on the other hand, the 1375 and 1100 cm^{-1} bands disappear: they are "frozen out". All this indicates that the bands in Table 3 are not due to intermolecular interaction, but represent different conformations[119] of the polymer.

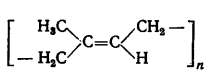
It may thus be supposed that the observed changes in the spectrum of poly(ethylene terephthalate) are associated with the phenomenon of rotational isomerism. When the polymer is stretched, a change is observed[121] in the intensities of the absorption bands in Table 3. It is interesting that the absorption bands which are most sensitive to a change in conformation of the chain are due to normal vibrations including ester and ethylene groups.

Table 3. Absorption bands sensitive to crystalline state.

ν, cm^{-1}	Change in intensity with increasing crystallinity
1475	increases
1375	decreases
1340	increases
1130	increases
1100	decreases
975	increases

An investigation has been made[122] of the dependence on the applied load of the positions of the absorption band maxima associated with vibrations of the main chain and side-chains for poly(ethylene terephthalate), polyethylene, and poly-ϵ-caprolactam. This showed that under load the absorption maxima associated with the main chain move to lower frequencies, while those associated with side-chains are shifted to higher frequencies. These results enable infrared spectroscopy to be used to study the stress in bonds in a polymer subjected to tension, and to compare the mechanical stress produced in the specimen with the true stress acting on a deformed bond.

GUTTA-PERCHA



At 20°C gutta-percha can exist in two crystalline modifications—α and β—melting at 65° and 56°C respectively. α-Gutta-percha is the stable modification, which can be obtained from a solution of the polymer; β-gutta-percha is obtained by rapidly cooling the amorphous polymer which has been heated to 70°C. X-Ray data indicate[123] that the unit cell of β-gutta-percha has the parameters—a = 7.78 Å, b = 11.78 Å, and c = 4.72 Å—and contains four isoprene groups. Data on the parameters of the unit cell of the α-form are more uncertain. α-Gutta-percha has a molecular period of c = 8.9 Å, which is produced by two isoprene groups, not one as with β-gutta-percha, where c = 4.72 Å. The two modifications are obviously rotational isomers.

The infrared spectra of the α- and β-forms of gutta-percha differ markedly in frequency and intensity in the range 1700–400 cm^{-1} (Fig. 18).[124–126] Characteristic absorption bands of α-gutta-percha are located at 1150, 1100, 1055–1035 (doublet), 865, 490, and 470 cm^{-1}. β-Gutta-percha is characterised by absorption bands at 1290–1270 (doublet), 1160, 1108, 760, 603, and 475 cm^{-1}. Table 4 gives the probable assignment of these bands. Comparison of the spectrum of crystalline gutta-percha with the infrared absorption spectrum of a melt of α- and β-forms shows that the bands at 1215, 890, 865, 805, 615, 490, and 470 cm^{-1} are "crystalline" in the spectrum of the α-modification. The absorption bands at 1220, 882, 800, 760, 603, and 475 and the 1290–1270 cm^{-1} doublet are "crystalline" in the spectrum of β-gutta-percha. The difference in the frequencies of the "crystalline" bands due to α- and β-gutta-percha is associated with the difference in structure between their unit cells, which are made up of chains having different configurations. These vibrations most probably arise as a result of intermolecular resonance interaction of corresponding vibrations. This certainly applies to the doublets 1055–1035 and 1290–1270 cm^{-1} in the absorption spectra of α- and β-gutta-percha respectively. With polarised radiation the absorption bands of these doublets show opposite polarisation, and in a melt the doublets are replaced by absorption bands at 1040 and 1260 cm^{-1} respectively.

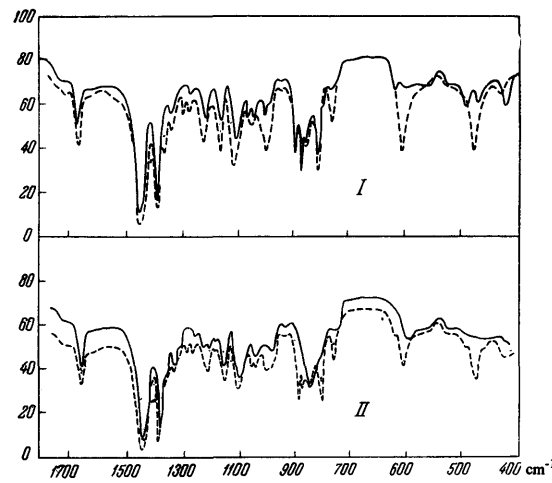


Figure 18. Infrared spectrum of gutta-percha: *I*) α-gutta-percha (full curve) and β-gutta-percha (broken curve); *II*) molten gutta-percha (full curve) and $\alpha + \beta$-gutta-percha (broken curve).

Table 4. Assignment of "crystalline" absorption bands (ν, cm^{-1}) in gutta-percha.

Modification		Assignment
α	β	
	1290	$\gamma_w(CH_2)$, $\gamma_t(CH_2)$
	1270	
1215	1220	
1150	1160	ν (C—C), $\gamma_r(CH_2)$
1100	1108	
1055		
1035		
890	882	
865	760	$\gamma_r(CH_2)$
805	800	
490	603	C—CH_2, C—C—C
475	475	C—C=C deformation
420	425	

In the range 400–700 cm^{-1} the absorption in molten α- and β-gutta-percha and its solution in carbon disulphide is diffuse in character[126]. The appearance of distinct, sharp

absorption bands in this range on crystallisation of the polymer either in α- or β-form, is linked with a change in the selection rules accompanying the transition from amorphous to crystalline gutta-percha. Independently of the reason for the appearance of "crystalline" bands in the α- and β-forms, it is fundamental that these bands characterise, directly or indirectly, the conformation of the chains in the differing crystal cells of α- and β-gutta-percha. This provides a method for studying the crystallinity of the two forms, their melting points, etc. It is also very important that the presence of bands characteristic of α- and β-forms has enabled the rotational-isomerism mechanism of the stretching of polymers to be proved unambiguously[115,126,127]. It has been shown that, when the α-crystalline form of gutta-percha is stretched, it passes into the β-form. This corresponds to conversion of an isomer of shorter chain length (the α-form) into an isomer of longer chain length (the β-form).

The infrared spectra of the α- and β-modifications of gutta-percha differ not only in their "crystalline" bands. The 1108 cm^{-1} band in α-gutta-percha and the 1100 cm^{-1} band in β-gutta-percha are of interest. They are probably due to ν(C–C) vibrations. The 1100 cm^{-1} band characterises the α-conformation of the chain, while the closely situated 1108 cm^{-1} characterises the β-conformation. Fig. 19 shows the infrared spectra in the range 1000–1100 cm^{-1} for the two modifications dissolved in carbon disulphide and for molten gutta-percha. In the spectrum of crystalline α-gutta-percha the main band at 1100 cm^{-1} is accompanied by a weak band at 1108 cm^{-1}, which indicates that the polymer contains, besides chains in the α-conformation, sections of molecular chains in the β-conformation.

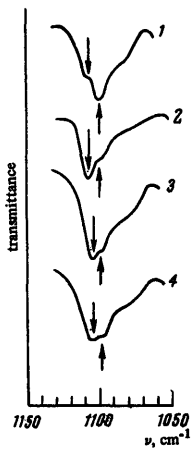
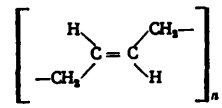


Figure 19. Infrared spectrum of:
1) α-gutta-percha at 20°C; *2*) β-gutta-percha at 20°C; *3*) gutta-percha dissolved in CS_2; *4*) molten gutta-percha at 70°C.

The spectrum of crystalline β-gutta-percha contains a weak band due to the α-conformation. Two absorption bands, corresponding to the α- and β-conformations of the chain, can also be distinguished in the spectrum of a solution in carbon disulphide and of the melt. The presence in the spectrum of gutta-percha of bands characteristic of both conformations provides a method for determining their contents[126] in crystalline specimens at 20°C. It has been found that crystalline α-gutta-percha contains 60% of chains in the α-conformation and 40% in the β-conformation. Crystalline β-gutta-percha contains 60% of chains in the β-conformation and 40% in the α-conformation.

POLY-*trans*-1,4-BUTADIENE



This polymer can exist in two crystalline modifications[128–130]. Modification I exists up to ~ 50°C. Over the temperature range 50–70°C two modifications are present together. Above 70°C the polymer exists as modification II, which gradually melts with rise in temperature, and at 130°C the polymer is in the amorphous state. The infrared spectrum of this polymer (Fig. 20) is characterised by

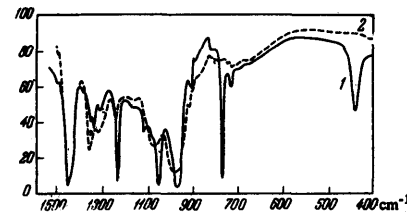


Figure 20. Infrared spectrum of poly-*trans*-1,4-butadiene:
1) crystalline; *2*) amorphous.

"crystalline" absorption bands at 445, 772, 1121, 1235, and 1051 cm^{-1}, the intensity of which decreases with rise in temperature, and "amorphous" bands at 1350 and 1308 cm^{-1}, whose intensity increases with rise in temperature[128]. Fig. 21 shows that the temperature dependence of optical density in "crystalline" and "amorphous" bands[130] is in opposite senses, being associated with transition of modification I into modification II and their fusion. This result is consistent with X-ray investigations[130].

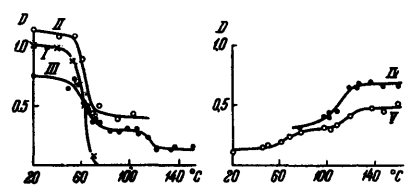


Figure 21. Temperature variation of optical density of poly-*trans*-1,4-butadiene in "crystalline" bands (cm^{-1}):
I) 770; *II*) 1051; *III*) 1235; and in "amorphous" bands at:
IV) 1308; *V*) 1353.

The "crystalline" absorption bands of poly-*trans*-1,4-butadiene can be divided into two groups. The bands at 445, 770, and 1121 cm^{-1} disappear completely on fusion of

the polymer, and their appearance on crystallisation is probably associated with a change in the selection rules. The bands at 1235 and 1051 cm^{-1} become much stronger on crystallisation, but do not disappear completely in the melt. They may be associated with the retention in the melt of a rotational isomer characteristic of the crystalline state of the polymer. The absorption bands at 1308 and 1353 cm^{-1} are especially interesting. Bands at 1353 and 1303 cm^{-1} in polyethylene were assigned to the vibration $\gamma_\omega(CH_2)$ in the amorphous portion of the polymer[18,113]. In poly-*trans*-1,4-butadiene they can probably be assigned to this type of vibration. These absorption bands have been used for the quantitative determination of the crystalline portion in an unoriented specimen.

The process of orientation of poly-*trans*-1,4-butadiene has been investigated in work[131] on the variation in the intensity and dichroism of the bands at 1308, 1235, 1051, 772, and 445 cm^{-1}. This has shown that the quantity of crystalline material in the polymer increases in the course of orientation, and at degrees of orientation of ~ 45% the crystalline portion is completely oriented along the axis of stretch. Calculation of the angle of orientation between the direction of the dipole moment and the axis of the molecule for the vibration $\delta(CH_2)$ showed that the molecular chains in the crystalline portion of modification I of poly-*trans*-1,4-butadiene do not have a planar *trans*-conformation but are somewhat twisted.

In conclusion we give a published[131] assignment of the "crystalline" and "amorphous" bands in this polymer (Table 5).

Table 5. Assignment of "crystalline" and "amorphous" bands in the spectrum of poly-*trans*-1,4-butadiene.

At 20°C, "crystalline"					At 150°C, "amorphous"	
ν, cm^{-1}	intensity	$R = D_\parallel/D_\perp$	α, deg	assignment	ν, cm^{-1}	intensity
1350	m.	?	—	(CH_2) amorphous	1354	m.
1340	m.	?	—	(CH_2) crystalline	—	–
1308	w.	?	—	(CH_2) amorphous	1313	m
1235*	s.	10.72	0—23	(CH_2) crystalline	1243	w.
1121	w.	?	—	crystalline	—	–
1051*	s.	3.53	31—37	crystalline	1063	m.
772*	s.	?	—	(CH_2) crystalline	—	–
445*	s.	0.65	62—61	crystalline	—	–

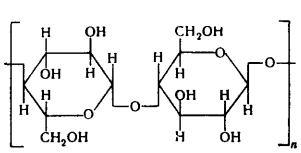
* Band frequencies differ by 2 cm^{-1} with $E_\parallel$ *and* $E_\perp$.

Intensity: m. = medium; w. = weak; s. = strong.

A question mark (?) indicates that the sign of the polarisation is difficult to determine.

The symbol α denotes the angle between the direction of the dipole moment and the direction of orientation.

CELLULOSE



The view is widely held, based on the results of physical methods of investigation, that the supermolecular structure of cellulose contains highly ordered (crystalline) and less ordered (amorphous) chain segments. Several workers do not accept the presence of strict three-dimensional ordering of chains in this polymer[132]. A more detailed discussion of this matter will be found in a monograph[133].

X-Ray examination shows that cellulose can exist in various crystalline modifications (I–IV). The arrangement of the atoms in the unit cells has not been established definitely, and significant information can therefore be obtained from a study of the disposal of atomic groupings by means of polarised infrared radiation.

The early spectroscopic investigations of cellulose showed that hydroxy-groups in it were hydrogen-bonded[134,135]. This conclusion was based on an examination of the first overtone of the hydroxyl vibration. The nitration of cellulose was shown[135] to be accompanied by the release of hydroxyls from hydrogen-bonding. The shift in the band 2ν(OH) to higher frequencies in the spectrum of cellulose II than in that of cellulose I was explained by the weakening of hydrogen bonds in the former modification. A recent spectroscopic investigation of specimens of methylcellulose of low degrees of substitution indicates that increase in the degree of methylation is accompanied by a diminution in the number of hydroxyls involved in the stronger hydrogen bonds[136].

X-Ray data indicate the existence of various types of hydrogen bonds in the crystallographic unit cell of cellulose. This can be established by examining the hydroxyl bands in the infrared spectra.

The OH band, characteristic of a hydrogen bond, has five peaks[137] in the spectrum of highly crystalline cellulose I (*Valonia ventricosa*). Interesting results have been obtained by investigating deuteriated samples of celluloses. The method of deuterium exchange enables the absorption of associated OH groups, present only in the crystalline portion of a polymer, to be observed, since in the early stages deuteriation does not affect the crystals. It has been established[138] by this method that the crystalline portion of cellulose II exhibits four OH peaks, at 3484, 3444, 3322, and 3163 cm^{-1}, characteristic of a hydrogen bond (Fig. 22). The OH absorption bands in crystalline model compounds—cellotetraose and cellopentose—have been observed at the same frequencies. On deuteriation the frequency of the OH peaks in cellulose II is found[136] to decrease by the same amount. All this suggests that various types of hydrogen bonds are present in the crystalline portion of cellulose II. It must be stressed, however, that great caution must be exercised in establishing a relation between the number of peaks of OH- and NH-stretching vibrations and the number of types of hydrogen bonds, since individual peaks may be caused by other factors[138–140].

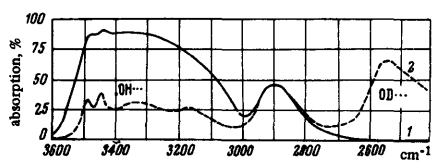


Figure 22. Viscose rayon film:
1) before deuteriation; *2*) after deuteriation for 4 h.

It has been definitely established[140,141] that all hydroxy-groups in the crystalline segments of celluloses I–IV are hydrogen-bonded, since no OH band characteristic of unbonded hydroxyl has been observed in the spectrum.

Replacement of OH by OD in the amorphous portion of cellulose specimens has permitted a detailed investigation of the form of the OH absorption band in the crystalline portion of celluloses I–IV. All four modifications of cellulose were shown[142] to have different spectra (in the range 3100–3600 cm^{-1}). Other workers have concluded[143], however, that all the crystalline forms can be represented by only two types of spectra (in the range 400–3700 cm^{-1}). The difference in the spectra is explained by rotational isomerism of the hydroxymethyl group[143], it being assumed (contrary to Ref. 144) that only two rotational isomers are present in cellulose.

Interesting results have been obtained from a study of oriented deuteriated cellulose specimens in polarised infrared radiation[145,146]. Figs. 23 and 24 show the OH and OD bands observed under these conditions. It is seen that the parallel component is more intense than the perpendicular component. This suggests that in cellulose crystals a large number of OH bonds are arranged parallel—not along the normal—to the chain direction. The hypothesis has been put forward that some of the hydroxyls form part of an intramolecular hydrogen bond between $O_{(3)}$ of one unit and $O_{(6)}$ of another, and between $O_{(5)}$ and $O_{(6)}$, which also belong to different units[146]. The presence in cellulose of intramolecular together with intermolecular hydrogen bonds has been pointed out also by other workers[147].

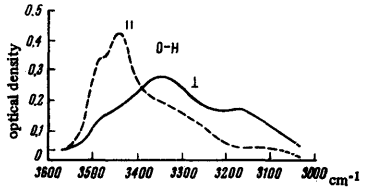


Figure 23. Dichroism of crystalline segments of cellulose II in the region of OH vibrations.

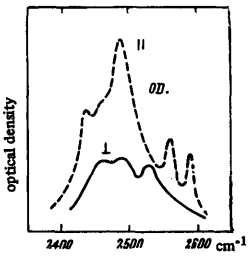


Figure 24. Dichroism of crystalline segments in region of OD vibrations.

The intensities of the bands at 900 and 1430 cm^{-1} are sensitive to structural changes in cellulose[149–151]. Thus they depend on the degree of crystallinity of the specimens[149]. When a sample was ground into powder, the intensity of the latter band diminished, and at the same time that of the 900 cm^{-1} band increased. Hence the 1430 cm^{-1} band was regarded as "crystalline", and the 900 cm^{-1} band as "amorphous". The degree of crystallinity of cellulosic materials is determined from the intensity ratio of the bands at 1430 and 900 cm^{-1}. Other workers have found that these bands change in intensity on passing from cellulose I to cellulose II (on mercerisation), and on this basis have proposed a spectroscopic method for determining this transition[150]. It has been noted also[151] that the intensities of these bands change both with the degree of crystallinity of the specimen and with the extent of conversion of cellulose I into cellulose II. These results show that further study is required of the use of these bands to determine the degree of crystallinity of cellulose and to assess the process of mercerisation. Mention must be made here of work[152] showing that the 900 cm^{-1} band in various specimens of cellulose is composite, consisting of at least two components (Fig. 25). Differences in the position and the intensity of the components in the region of 900 cm^{-1} in different samples of cellulose may be associated with rotational isomerism. A band at 560 cm^{-1} is also sensitive[143] to the transition I → II.

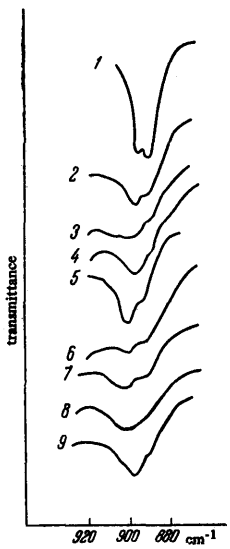


Figure 25. Spectra of:
1) crystalline cellobiose; *2*) amorphous cellobiose; *3*) natural cotton; *4*) mercerised cotton; *5*) cotton which has been activated with ethylenediamine; and of sulphite wood celluloses intended for chemical processing:
6) American; *7*) Japanese; *8*) Priozerskii Kombinat; *9*) as (*8*) mercerised.

The method of infrared spectroscopy is used to estimate the crystallinity of cellulose and assess the conversion of cellulose I into cellulose II. As already mentioned, deuterium exchange takes place in the amorphous portion of cellulose, leaving the crystalline portion practically unaffected. This enables the contents of crystalline and amorphous materials in cellulose to be estimated from the relative intensities of the OH and OD bands[148].

The intensity ratio of bands at 1372 and 2900 cm^{-1} has recently been proposed[153] for estimating the crystallinity of celluloses I and II. The former is regarded as the crystallinity band, while that at 2900 cm^{-1} is used as internal standard. This intensity ratio correlates with the crystallinity of the polymer determined from X-ray data, density, and the sorption of moisture. This correlation is

stated to be of the same form for celluloses I and II as for cellulose which has been treated with alkali, which is not the case with the intensity ratio of the bands at 1430 and 900 cm^{-1}.

It must be pointed out that a_{1372}/a_{2900} does not correlate sufficiently well with the crystallinity of cellulose determined by other physical methods[153]. The overlapping of the absorption band at 1372 cm^{-1} with adjacent bands, and also the difficulty of allowing for the background, are the reasons why structural changes in cellulose cannot be assessed with sufficient accuracy from this ratio.

A method has been proposed[154] for measuring the extent of mercerisation of cellulose from the ratio of the optical densities in infrared bands at 1375 and 1325 cm^{-1}. The sensitivity of this ratio to mercerisation has been established by comparing spectroscopic with X-ray data.

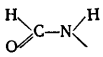
The present review has reported work on the structure of cellulose. Information on the spectroscopic investigation of cellulosic materials (the oxidation of cellulose, its ethers, and its esters, the study of substituted celluloses, etc.) can be found in several publications[155-157].

POLYPEPTIDES

The primary reason for interest in this class of polymers is that polypeptides represent one of the closest analogues of proteins. As a consequence, the application of infrared spectroscopy to the study of these compounds is also associated with the modelling of processes occurring in protein molecules under corresponding conditions. In the present review we shall confine ourselves to a brief account of the possibilities of the infrared method for investigating the secondary structure of polypeptides.

The molecular chains in polypeptides exist mainly in one of three conformations—the α-helix, the β-conformation, or a coil[158-160]. X-Ray data indicate that one turn of the α-helix contains 3.6 amino-acid residues. The identity period along the axis of the helix is 27 Å. The height of one turn of the helix is 1.5 Å. An intramolecular hydrogen bond links amino-acid residues 1 and 3. The β-conformation is characterised by an almost completely extended polypeptide chain. Maximum saturation by intermolecular hydrogen bonds occurs when two polypeptide chains are mutually antiparallel. Owing to steric interaction of the β-carbon atoms, the peptide groups emerge from the plane of the carbon chain, and the polypeptide chains form so called folded layers having parallel and antiparallel arrangement of the chains. In the case of a folded layer having the chains parallel the identity period along the chain is 6.5 Å. The interchain period is 4.7 Å. The corresponding periods for a folded layer having antiparallel chains are 7.0 and 10 Å respectively.

The existence of a coiled conformation in polypeptide chains in appropriate solvents has been established from measurements of viscosity and optical rotation. Several polypeptides have been obtained in a coiled conformation in films, e.g. sodium polyglutamate and poly-*S*-carboxymethyl-L-cysteine[161,162]. The methods most widely used for investigating the secondary structure of polypeptide chains are optical rotation, X-ray diffraction, and infrared spectroscopy. Examination of the optical rotation of polypeptides will provide evidence of the presence of a helical conformation of the polypeptide chain in any solvent, but this method gives no information on other ordered conformations of polypeptides without special hypotheses. The X-ray method enables differences in the conformation of a polypeptide chain to be assessed fairly unambiguously, but it is too cumbersome and difficult for everyday use. Infrared spectroscopy began to be used to investigate the structure of polypeptides in the late 1940s and early 1950s. An empirical relationship was used between the conformation of a polypeptide chain and the position and dichroism of bands due to the peptide group



In practically all polypeptides except polyproline[158] the peptide group is in the planar *trans*-conformation[160,163]. This group has the characteristic absorption bands[164-167]—1650 (amide I), 1550 (amide II), 1300–1250 (amide III), 627 (amide IV), 720 (amide V), 600 (amide VI), and 200 (amide VII)—among which amide I and amide II are most often used for structural investigations. Some 80% of the potential energy associated with the amide I band is due to stretching vibrations of C=O groups, 10% is due to CN, and 10% to deformation vibrations of NH groups. Variation in the dipole moment of this oscillation occurs approximately in the direction of the C=O bond. The amide II vibration is 60% associated with deformation vibrations of NH and 40% with vibrations of CN. Variation in the dipole moment of this oscillation is perpendicular to the NH bond. To a first approximation the amide I and amide II vibrations are localised in the amide group, and are thus independent of the chemical structure of the polypeptide[167,168].

The position and polarisation of the amide I and amide II bands, as well as of the NH-stretching band, are given in Table 6 for various conformations of polypeptides[169].

Table 6.

Vibration	α-Helix	Dichroism	β-Form	Dichroism	Coiled
N-H stretching	3290—3330	∥	3280—3300	⊥	3400
Amide I	1650—1660	∥	1630	⊥	1660—1700
Amide II	1540—1550	⊥	1520—1530	∥	<1520?

An explanation has recently been put forward[170,171] for the observed difference in position and polarisation of the amide I and amide II absorption bands depending on the conformation of the polypeptide chain. Calculation of the dichroism and frequency positions of these bands in various conformations took into account the effect of interaction between amide I and amide II vibrations in neighbouring groups along the chain and between chains. Table 7 gives the results of such calculation, the symbols δ and δ' denoting the phase of the vibration in the adjacent amide group along the chain and between chains respectively.

The calculation[170,171] provides a good qualitative explanation of the dependence of the positions of amide I and amide II on the conformation of the polypeptide chain, but the numerical values thus obtained for the frequencies are not always correct. This is due mainly to the choice of unperturbed amide I and amide II vibrations.

Thus Krimm[172,173], unlike other workers[170], considers that the frequency 1520 cm^{-1}—not 1535 cm^{-1}—corresponds to the unperturbed amide II vibration. The value of ν_0 has been shown[174,175] to vary from 1659 to 1653 cm^{-1} for amide I, and from 1540 to 1566 cm^{-1} for amide II, which indicates that factors other than those connected with the conformation of the polypeptide chain influence the position of these frequencies. In this connection it should be noted that the

so-called coiled conformation of polypeptides may contain segments of chains in various states of order. Therefore values of ν_0 calculated from the infrared spectra of polypeptides in a coil are also not altogether correct. In order to determine the conformations of polypeptide chains it is most correct to use the frequency characteristic of the amide I and amide II bands together with measurements of their dichroism. Recently the amide V frequency, relating to out-of-plane vibration of NH, has begun to be used[176-178] to determine the conformation of polypeptide chains. This vibration is situated at 610–620, 700, and 650 cm^{-1} for the α-conformation, the β-conformation, and a coil. However, the degree to which this vibration is localised in the amide group is not altogether clear at the present time, since the positions of amide V for various conformations of the polypeptide chain have been studied on a relatively small class of polypeptides.

Table 7.

Conformation of polypeptide chain	Frequency assignment (δ, δ')	Amide I frequency		Amide II frequency	
		calc.	obs.	calc.	obs.
Coiled	ν_0	1658	1655 1650 s.	1535	1535
Helix	$\nu_{0\parallel}$	1650		1516	1516 w.
	$\nu_\perp$ $(2\pi/n)$	1647	1652 m.	1546	1546 s.
Folded-chain layer with parallel packing of chains	$\nu_\parallel$ (0, 0)	1648	1645 w.	1530	1530 s.
	$\nu_\parallel$ (π, 0)	1632	1630 s.	1550	1550 w.
Folded-chain layer with antiparallel packing of chains	$\nu_\parallel$ (0, 0)	1685	1685 w.	1530	1530 s.
	$\nu_\perp$ (π, 0)	1632	1632 s.	1540	—
	$\nu_\perp$ (π, π)	1668		1550	—

One of the chief perculiarities of polypeptides is the dependence of the conformation of their polypeptide chain on the nature of the solvent. Thus poly(γ-benzyl L-glutamate) has the α-helical conformation in chloroform solution, but passes into the coiled conformation in dichloroacetic or trifluoroacetic acid[179]. Use of the infrared absorption spectra to investigate the conformation of polypeptides in solution is difficult for two reasons: firstly, most solvents themselves absorb in the range investigated, and it is difficult to choose compensating conditions for such solvents as dichloroacetic and trifluoroacetic acids; on the other hand, as has already been noted, the amide I and amide II frequency characteristics do not always fully reflect the conformation of the polypeptide chain, and measurement of their dichroism in solution requires special apparatus[180,181].

At the present time it has not been accurately established what are the factors affecting formation of one or other conformation of polypeptides. Most authors link the conformation either with the molecular weight of the specimens[182-185] or with the type of amino-acid residue[186,187]. It has been shown experimentally and theoretically[188-190] that the α- and β-conformations are energetically close together. In working with polypeptides in the form of films, therefore, it must be borne in mind that the conformation of the polypeptide chain will depend in some cases on the nature of the solvent and also on other conditions of preparation of the specimen[183,184,189].

Measurement of the intensities of the amide I, amide II, and amide V absorption bands provides in principle a method for estimating quantitatively the presence of the α- and β-conformations and the coiled conformation in polypeptides. However, no accurate values are yet available for the absorption coefficients of these three amides in the various conformations. Preliminary results obtained by Blout and his coworkers[191,192] indicate that the absorption coefficients of corresponding amides are the same for the different conformations. The same conclusion has been reached from a study of the orientation of polypeptides[189].

Several polypeptides can exist under certain conditions in an ω-helical[193] conformation, as a 3_{10} helix[194], or as the so-called β-cross conformation[184,195-198]. Only the last of these three conformations has been well defined by means of infrared spectroscopy. A spectroscopic criterion of this conformation is provided by amide I and amide II frequencies characteristic of the β-structure and the dichroism observed in polypeptides present as α-helices. The positions of amide I and amide II in the spectrum of polypeptides in this conformation and their polarisation are explained by peculiarities in the packing of the polypeptide chain. The chains have a β-extended conformation coiled into the shape of bellows, individual units in which are joined by intramolecular hydrogen bonds. This structure recalls that of the polymer chain in a single crystal. The maximum information on the structure and conformation of the polypeptide chain can probably be obtained by investigating amide VII (200 cm^{-1}), but data on its position in the various conformations are not available at the present time, since the manufacture of standard apparatus for this spectral range started only recently.

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