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The Regularity Bands in the Infrared Spectra of Polymers with Distortions in Structural Periodicity

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Studies of the microstructures of polymers by methods based on the measurement of infrared band intensities are examined. The cluster model, within the framework of which a band classification has been proposed and the possibilities of infrared spectroscopy for the determination of different structural parameters of macromolecules have been analysed, is justified. The bibliography includes 142 references.

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I. INTRODUCTION

The latest advances in both practical and theoretical infrared spectroscopy of polymers are associated primarily with the study of the structures and vibrational properties of macromolecules with more or less pronounced distortions in structural periodicity. The interest in these studies is understandable because the vast majority of polymeric materials consist precisely of such macromolecules and the microstructures of polymer chains are known to influence directly or indirectly the physicochemical properties of polymers and to reflect the mechanisms of their formation.

Much attention is devoted in these studies to the analysis of the maximum intensities of the so-called regularity bands; this is mainly because, among all the spectural parameters, this one is perhaps the most sensitive to the degree of order in the macromolecular structure. In the course of its development the modern vibrational spectroscopy of polymers has encountered many problems and it appears useful to begin the review with their brief examination.

II. FUNDAMENTAL PROBLEMS OF THE INFRARED SPECTROSCOPY OF IRREGULAR POLYMERS

For many years infrared spectroscopy remained and still remains one of the most accessible and universal instruments for the investigation of the microstructures of polymers, and empirical methods of interpreting the experimental results still occupy a notable position in it. By varying any structural parameters, for example the length of the entire macromolecule or of its regular component, the degree of tacticity, or the sequence length of the polymer, the investigator is able to discover the spectral changes arising under these conditions, which are then used in the form of calibration relations in the study of the structures of a wider range of compounds.

In the last two decades there has been a growth of interest in the vibratonal spectroscopy of irregular polymers also among theoreticians. A series of new approaches have been created on the basis of the perturbation theory[1,2] and numerical methods[3-5] and attempts have been made to apply the methods of the dynamic theory of defective crystals, which have been well known for a long time in solid state physics, such as the method of Green functions[6-9], the method of negative eigenvalues[10,11], the method of transport matrices[12,13], and the method of moments[14] for the analysis of the vibrational spectra of real macromolecules. There are in general no fundamental obstacles to their application, but there are certain difficulties associated with the large number of vibrational degrees of freedom in the repeating monomeric unit, and, what is more significant from the standpoint of practical applications, with the wide variety of types of distortions in the regularity of the structure within the limits of a single chain.

Procedures widely known in theoretical spectroscopy are used to overcome the first difficulty. For example, in the so-called skeletal approximation[6,7,15,16] some of the atomic groups are replaced by point masses. In the method of bound oscillators[1,17] the repeating monomeric unit is modelled by oscillating dipoles, whose frequencies correspond approximately to the "normal" frequencies of the isolated units. There exist also other approaches[1,2] but we shall not consider them.

In the analysis — both theoretical and experimental — of the spectroscopic manifestations of structural distortions it is possible to proceed via two pathways. The first pathway involves a scrupulous allowance for all the versions of the structure by observing and analysing the spectral lines reflecting the vibrations of the corresponding molecular fragments. The experimental studies based on this approach began to appear literally from the instant of the introduction of infrared spectroscopy into practical laboratory research and nowadays they still make a very considerable contribution. Serious theoretical studies have recently begun to appear in this field. Among these, we may mention as an example studies[10,18] in which determinations were made by the method of negative eigenvalues of the frequency distribution in the spectra of hydrocarbons with different combinations of conformers, both specified artificially and generated at random, or studies[1,19-22] in which calculations were made by the authors' novel method[23-26] of the frequencies and intensities of the infrared bands in the spectra of a series of polymers with different configurational and conformational variants of the chain structure.

The second pathway is associated with the study of the behaviour of the infrared bands reflecting the vibrations of structurally regular frequencies of monomeric units in polymer chains; the nature of the defects terminating these sequencies is then usually not specified and it is implied that

their concentration is fairly small. This pathway is extremely promising, as can be seen from the rapid increase of the number of publications, in which, however, the validity of the application of this approach is usually not analysed.

The differentiation of research trends mentioned above is based on the existence of two types of spectral bands, namely bands due to local vibratons, i.e. vibrations localised in the vicinity of defective units or fragments whose intensity and frequency depend mainly on the nature and concentration of these defects, and bands due to chain vibrations in which the large regular sections of the chain distributed between the defects vibrate as a single whole and whose spectroscopic parameters depend only slightly, in contrast to the previous bands, on the nature of the defects, being determined mainly by the structure and length of the periodic part of the chain.

The sub-division of vibrations into local and chain vibrations is arbitrary: in a vibrating system there is always a greater or smaller mixing of such vibrations but in many instances such mixing is nevertheless insignificant and may be treated as a perturbation and taken into account appropriately. In a more rigorous approach it is also necessary to take into account the possibility of the appearance of quasi-local or resonance vibrations[27,28], the use of which for the analysis of the structure in the sense indicated is incorrect.

The polymer chain can naturally be so disordered that there can be no question of the existence of any chain vibrations embracing large sections of macromolecules. However, many problems of practical importance are associated precisely with the analysis of the microstructures of polymers with molecules containing fairly long regular segments interrupted by individual defective units or small irregular fragments.

The approximation, in which account is taken only of the vibrations of the regular chain sections and the mutual independence of the vibrations of different regular sections within the limits of the same chain is postulated, is referred to as the cluster approximation and plays a very important role in spectroscopic studies. In the majority of investigations by vibrational spectroscopic methods of the stereoregularity of polymers[29-31], the conformations of macromolecules in solution[32-34], the sequence length of copolymers[35-48], and the degree of branching of polymers[49], the cluster approximation is in essence employed, although this is frequently not stipulated. In view of the particular importance of this approximation for the subsequent description, Section III of this review is devoted to a brief analysis of its principles.

The chain vibration bands satisfying the criteria of the cluster approximation are of special interest in our case, since they include the regularity bands according to Zerbi's classification[50]. In a series of studies[29-31,35-48] bands of this type have been referred to as spirality, iso- or syndiotacticity, etc., bands. It is noteworthy that such terms are not entirely unambiguous. For example, the isotacticity band at 998 cm^{-1} in the spectrum of polypropylene can be referred to simultaneously also as the helix band, since the changes it undergoes with decrease of the length of the macromolecular helix observed on fusion of the polymer are broadly the same as those occurring following a decrease of the degree of its isotacticity[30].

In many instances the frequency of the maximum of such a band is independent of or depends only slightly on the regularity of the macromolecule and the band intensity is the structure-sensitive parameter. Henceforth, in speaking of regularity bands, we shall have in mind precisely such bands.

A number of characteristics of the behaviour of regularity bands can be discovered by following the changes in them when the structure of the macrochains is varied. As a rule, these bands appear in the spectra when the regular, in both structural and chemical respects, sequence of monomeric units reaches a critical length, characteristic of precisely this band. For example, the 973 and 998 cm^{-1} bands in the spectra of ethylene–propylene copolymers arise when the isotactic polypropylene sequences reach lengths of 5 and 10 units respectively[35,36], while the 565 and 750 cm^{-1} bands in the spectra of epoxypropane–tetrahydrofuran copolymers refer to the vibrations of polytetrahydrofuran fragments containing at least 4 and 2 units respectively[47].

Another important feature of the regularity bands is the monotonic increase of their intensity with increase of the average length $\bar{N}$ of the regular sequences of units in the polymer and the more or less rapid attainment of a limiting intensity for fairly high values of $\bar{N}$. The increase of the maximum intensity can take place both owing to the increase of the integral band intensity and owing to the decrease of the half-width of the band.

The very fact that the band intensity depends on the length of the regular segments in polymer chains usually leads to the possibility of using this relation to analyse polymer microstructures, in particular, the possibility of measuring the average sequence length of the copolymers and of the degree of tacticity of stereoregular homopolymers. However, the problem of whether such measurements are sufficiently correct and of the nature of the averaging in the experimental determination of these quantities have still not been adequately investigated.

This review is devoted to a detailed analysis of the factors influencing the dependence of the chain vibration band intensities and widths in the infared spectra of polymers on the lengths of structurally regular sequences of units. The criteria governing the choice of regularity bands, both with the aid of a set of empirical features and on the basis of an *a priori* investigation of the structural-force characteristics of macrochains are analysed. Some attention has been devoted to bands containing information about the structure of the helix and to crystallinity bands.

III. THE STRUCTURAL MODEL AND THE CLUSTER APPROXIMATION

A configurationally regular polymer chain is known[51] to be capable of passing under certain conditions to a conformationally regular state. This transition is accompanied by the occurrence of the so-called long-range conformational order in which the chain consists of an ideal helix with the corresponding spatial symmetry. The formation of fairly long helical fragments can be observed in the crystallisation of a polymer or (sometimes) with decrease of the temperature of its solutions.

We shall now assume that under the experimental conditions all the configurationally regular fragments of the macromolecules have passed to the conformationally regular helical state. In this case the fraction of conformationally regular segments attain saturation due solely to the configurational or chemical defects and the distribution of the helices in the specimen with respect to length reflects and to the length distribution of the regular sequences of the monomeric units in the polymer. The necessity for monitoring the conformational defectiveness in the course of spectroscopic measurements becomes clear from the foregoing, since its presence can lead to an apparent decrease of the degree of configurational irregularity of the polymer determined from spectroscopic data.

The main idea of the cluster approximation consists in the fact that, in the analysis of vibrations, the polymer molecule, consisting of alternating regular helical sections and defective regions, is imagined to be ruptured at the sites of the defects and the vibrational spectrum of such a molecule in the frequency range of the chain vibration analysed is represented as a superposition of the vibrational spectra of mutually independent helices.

We emphasise that not all spectral regions satisfy the cluster approximation. The existence of local vibrations of the defects, the occurrence of quasi-local or resonance vibrations—all these can hinder or preclude the application of a given frequency range to structural analysis in terms of the given approximation. A test of the applicability of the cluster approximation in each specific instance can be carried out either experimentally by analysing the spectra of model compounds or theoretically.

The experimental test can consist, for example, in comparing the spectra of polymer specimens differing in the nature of the defects. The application of the cluster approximation is correct for bands whose frequency and intensity vary little in a series of polymers having identical distributions of regular segments with respect to length but containing defects of different types.

In the majority of experimental studies where the cluster approximation has in fact been used for the analysis of polymer microstructures (albeit without the term itself being actually employed), such a test has been carried out in one way or another. Fig.1 illustrates the results of one of the versions of such an investigation for the low-frequency 720 cm^{-1} band for a system of wagging-torsional vibrations of polymethylene fragments in polymer chains of different structure. Evidently the dependence of the relative intensities on the lengths of the regular polymethylene segments in a series of specimens with different types of distortions in structural regularity fits on a single curve, which constitutes an experimental confirmation of the possibility of employing the cluster approximation in the given instance[142].

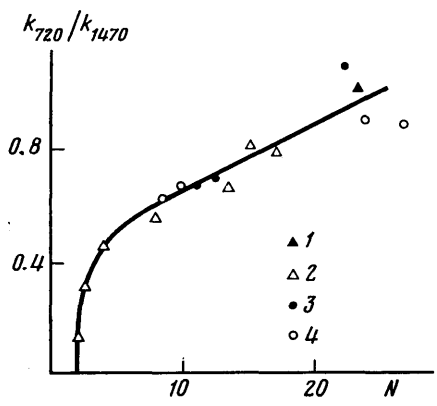


Figure 1. Dependence of the absorption coefficient of the wagging vibration band (720 cm^{-1}), referred to the absorption coefficient of the scissors vibration band (1470 cm^{-1}), on the average length of the polymethylene segments for n-paraffins(1) and copolymers of ethylene with ethylene-d_4(2), but-1-ene(3), and allene(4) at room temperature[142].

Another experimental test is based on the analysis of the form of the dependence of the band intensities on the lengths of regular segments; this will be discussed in detail in Section VI.

The question of the theoretical criteria of the applicability of the cluster approximation has been studied in detail[52] and we shall consider briefly the final results of these studies. The introduction of a defective unit into an initially ideal polymer chain leads in general to complex changes in the vibrational spectrum of the macrochain as a whole. With some approximation, these changes reduce to the appearance of local and resonance vibrations and the mixing of various chain vibrations. At the same time it can be shown that, when certain relations between structural-force parameters of the regular part of the chain and of the defective units are fulfilled, one or several of the chain vibrations of the fragment, located between two defects, can be regarded as independent of all other chain vibrations; it is then immaterial whether the latter refer to the given fragment, to defective units, or to adjacent sections of the chain.

Anticipating, we emphasise that the structure and parameters of the force fields of the majority of real polymeric molecules are such that a fairly large number of bands, referring to this type of independent chain vibrations of regular fragments or, in other words, bands satisfying the criteria of the cluster approximation, can always be found in their vibrational spectra.

These criteria assume the simplest form in terms of the so-called normal coordinates of the repeating unit (NCRU). In terms of these coordinates, the vibrating polymer chain with r degrees of freedom in a repeating unit can be represented by a set of r systems of linked oscillators and each of its r frequency branches forms its own system, which in the case of a defect-free chain is independent of the remaining systems. These coordinates can be referred to as the natural coordinates of the model of linked oscillators. A transformation whereby one can achieve a conversion to such coordinates from any initial coordinates, for example, from cartesian or natural coordinates, has been proposed[53].

The application of this transformation makes it possible to calculate the parameters of systems of linked oscillators modelling any polymer molecule including, among others, an irregular molecule, from its force constants specified in terms of any representation, for example, in the generalised valence force field representation.

The possibility of determining the parameters of the model of linked oscillators in the vicinity of "defective units" of the polymer chain appears to be the most important in this instance. These parameters can then be readily tested for their correspondence to the criteria of the cluster approximation.

Readers interested in further details of this problem are referred to Chukanov and coworkers[52,53]. Here we shall attempt to illustrate the theoretical criteria of the applicability of the cluster approximation in relation to the example of a hypothetical regular polymer molecule with a single defect and two degrees of freedom in the repeating unit. Such a molecule can be brought into correspondence with the model of linked oscillators illustrated schematically in Fig.2. In this model oscillators with intrinsic frequencies ω and ω' are combined into two chains via elastic forces with bond constants α and α'. The interaction between the chains with a force constant δ takes place only via "defective" oscillators, whose frequencies are ω_e and ω_e' and whose linkage to the periodic component of the chains is described by the interaction constants β and β' respectively. The fulfillment of the

conditions

$$\begin{aligned} |\beta| &\ll |\omega^2 - \omega_e^2| \\ |\delta| &\ll |\omega_e^2 - (\omega_e')^2| \\ |\beta'| &\ll |(\omega')^2 - (\omega_e')^2| \end{aligned} \qquad (1)$$

leads to the "breakdown" of such an integral vibrational system into four oscillator chains, each of which vibrates independently of the others[52].

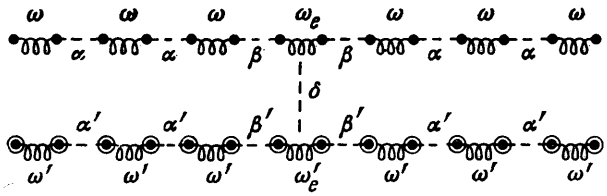


Figure 2. The system of linked oscillators modelling a polymer molecule with two degrees of freedom in the repeating cell and a single defective unit.

We may note that the fulfillment of only the first or only the last relation (1) makes it possible to apply the cluster approximation to oscillator chains with frequencies ω and ω' respectively.

Eqns.(1) thus express the quantitative criteria of the applicability of the cluster approximation to the system considered. In a more general approach one must naturally compare the vibrational frequency of a defective oscillator with the frequency of the chain vibration under consideration and not with the frequency of the intrinsic vibration of an individual non-defective oscillator.

The treatment in all subsequent sections of this review is based on the cluster approximation. Here it is understood that all the spectral bands analysed satisfy the theoretical or experimental criteria of this approximation.

IV. AN EMPIRICAL APPROACH TO THE STUDY OF THE MICROSTRUCTURES OF POLYMERS

Numerous experimental data which have accumulated hitherto indicate the possibility of deriving specific relations for the entire wide variety of spectroscopic manifestations accompanying the structural changes in polymers. Analysis of relations of this kind is very greatly simplified by employing the cluster approximation. Above, it was already noted that the cluster approximation has in fact been used for a long time in experimental studies of polymer spectra. In this section we shall consider studies of this kind, which will be grouped in terms of the types of bands whose intensity is sensitive to particular characteristics of the polymer structure.

Among all the infrared bands, it is reasonable to isolate three large groups from the standpoint of the study of the microstructure: the bands due to the local vibrations of the defects, the characteristic bands of the repeating units, and the regularity bands.

1. The Bands of the Local Vibrations of Defects

The criteria of the cluster approximation (1) at the same time constitute the criteria of the local nature of the vibrations of the defective unit to which correspond oscillators with frequencies ω_e and ω_e' in the NCRU system. However, in practice the demonstration of the local nature of the vibrations does not necessitate the use of Eqns.(1) in each case; it is sufficient to show merely that in a series of polymers with different degrees of regularity the frequency of the given vibration is constant and the intensity of the corresponding band is proportional to the concentration of defects of the given type.

This simplest type of vibration can in fact be used to investigate a whole series of structural characteristics. These include, firstly, the analysis of *the nature and concentration of the terminal functional groups*. The relevant methods have been developed for poly(ethylene terephthalate)[54], poly(ethylene glycol)[34,55], polystyrene (carbonyl groups)[56], and other polymers[34]. In a number of studies the local vibration bands have been used to determine the degree of branching of polyethylene[57,58], poly(vinyl chloride)[59], polycaproamide[60], ethylene-vinyl acetate copolymers[61], and others[34].

The knowledge of the concentration of the functional groups and also of the degree of branching makes it possible to estimate the *functionality* of the oligomer, which is important from the standpoint of its subsequent polymerisation. For a polymer with a known functionality, the concentration of the end groups is unambiguously related to *the molecular weight*. The intensities of the local vibrations of the "contacts" between units of different kinds in the copolymer have been used to determine *the average length of the block* in vinyl chloride–vinylidene chloride[41], epoxyethane–epoxypropane[62], and tetrafluorethylene–chlorotrifluoroethylene[63] copolymers.

It has been shown[27] that single distortions of the *stereoregularity* of isotactic polypropylene lead to the development of local vibrations. The concentration of single polyethylene units in ethylene–propene copolymers has been determined[64] from the intensity of the 733 cm^{-1} band.

2. Characteristic Vibrations of the Repeating Chain Units.

The vibrations of the macrochains for which the frequencies and absorption coefficients of the corresponding bands depend only slightly on the regularity of the polymer structure can be assigned to this class. The intensities of these bands are determined mainly by the content in the polymer of units of the given type and can be used, for example, for the analysis of the composition of the copolymer[65].

The bands can apparently be made more characteristic by measuring the spectra of conformationally irregular copolymers; for example, it is possible to investigate copolymers in the form of solutions at high temperatures or melts.

Calibration curves for the determination of the compositions of ethylene–propene[66], ethylene–but-1-ene[67], propene–but-1-ene and propene–oct-1-ene[68], vinyl acetate–vinyl chloride[69], propene–vinyl chloride[70], ethylene–propene and ethylene–hexene[71], ethylene–vinyl acetate[61], epoxyethane–epoxypropane[55], and many other copolymers have been published. The corresponding references can be found in a monograph[34]. Unfortunately the absence of a dependence of the extinction coefficient on the regularity of the polymer has not been tested in all the investigations.

A number of studies in the same series have been devoted to the *isomeric composition* of the polymers, particularly polybutadiene[72], polypentenamer, and polyoctenamer[73].

3. Regularity Bands

As already mentioned, a characteristic feature of bands of this type is a sharp decrease of their intensity (frequently to zero) in those cases where the average length $\bar{N}$ of the regular sequence of monomeric units falls below a certain threshold value N_0.

The factors determining the average length $\bar{N}$ of a regular sequence of units of a given type may be stereoregularity, conformational order, the extent of the block structure (in the copolymer), the molecular weight, and the degree of crystallinity. Depending on the objects of study, the regularity bands can be divided into several types. According to the classification adopted by Zerbi et al.[50], the conformational bands are those whose frequency and intensity depend on the conformational state of the unit. No account is then taken of the fact that the band parameters depend on the conformational state of the neighbouring units, as suggested, for example, by the complete disappearance of certain conformational bands on fusion of the polymers or when the temperature of their solutions is raised[34,37,75]. The latter implies that a threshold length of the regular sequence exists for such conformational bands, as for regularity bands.

Assuming that the absorption coefficient is independent of the length of the conformationally regular sequence, *the conformational structures* of polyethylene[76], poly(ethylene terephthalate)[77], *trans*-1,4-polybutadiene[78], and a number of other polymers have been analysed. In particular, measurements of the spectra of atactic polystyrene in polarised light[79] made it possible to isolate the spectral contribution of fragments having the *trans*-conformation. However, the hypothesis used in the above study[79] that the vibrations are characteristic requires a rigorous proof and by no means always holds. Thus the spectrum of polystyrene contains a band at 540 cm^{-1}, which is sensitive to sequences containing at least four *trans*-C–C bonds in the main chain[40].

The crystallinity bands have been used to determine *the crystal structures* and *degrees of crystallinity* of polyethylene[80-83], polyesters of the type $[-CO-O-(CH_2)_m-]_n$,[84] polybutadiene[85], isotactic poly(vinyl alcohol)[86], poly(vinyl chloride)[87], poly(vinyl-β,β-d_2 chloride)[88], polytetrafluoroethylene[89], and dextran[90], using simultaneously diffuse bands, assigned to the vibrations of the amorphous regions, in some of the studies[80,82,88,90].

The amorphous structure bands occupy a special place among the structure-sensitive bands. Factors such as the presence of "amorphous" conformations, the infringement of selection rules associated with the helical symmetry of the chain, the scatter of the regular helices with respect to length, and fluctuations of the molecular environment play a role in their formation. Since the amorphous structure bands are not regularity bands in the sense defined above, we shall not consider their analysis.

A method has been proposed[91], for the resolution of the spectrum into components referring to the amorphous and crystalline regions on the assumption that their contributions to the spectrum are additive. Having applied this method to the poly(ethylene terephthalate) spectrum, the authors[91] concluded that, although the *trans*--isomers are present in both phases, their characteristic bands, referring to the amorphous phase, are not manifested in the spectrum, since they are smeared out as a consequence of the marked scatter of the intermolecular interaction energies. However, another explanation of this effect is possible, namely one based on the assumption that the lengths of the sequence of *trans*-isomers in the amorphous phase do not reach the threshold lengths for the regularity bands.

Empirical methods for the analysis of the microtacticity of polypropylene have been developed[30,35]. It has been shown that the 998 and 973 cm^{-1} bands appear in the spectrum for lengths of the isotactic chains greater than those corresponding to 10 and 5 units respectively.

A detailed analysis of bands sensitive to isotactic, syndiotactic, and heterotactic sequences in the polyproylene molecule has been carried out[92]. The 690 cm^{-1} band in the poly(vinyl chloride) spectrum is sensitive to the concentration of the isotactic diads[93]. A method for the determination of the concentration of the diads of polybutadiene units in the 1,4-*cis*- and 1,4-*trans*-configurations has been described[94].

The determination of the sequence length of copolymers constitutes an important problem. In most studies devoted to the determination of this parameter with the aid of regularity bands, the power function method was used, according to which the dependence of the absorption coefficient on the length of the regular segment is described by a function of the type

$$k(N) = \begin{cases} 0 \text{ when } N < N_p \\ k \text{ when } N \geqslant N_p \end{cases}$$

The power function method has been used in the analysis of the sequence length of styrene–methyl methacrylate[38], styrene–butadiene and styrene–acrylonitrile[39,95], methyl methacrylate–acrylonitrile[46], ethylene–propene[30,35,96], propene–propene-1,1,2-d_3, styrene–α-monodeuterostyrene[37], tetrahydrofuran–epoxypropane[47], and epoxyethane–epoxypropane[48] copolymers. It is of interest to note that in almost all cases the threshold length of the sequence of monomeric units analysed is almost independent of the nature of the neighbouring blocks. For example, for all the styrene copolymers enumerated above, $N_p = 3-4$ corresponds to the 543 cm^{-1} band, $N_p = 9-11$ corresponds to the 998 cm^{-1} band of isotactic polypropylene fragments, etc. Furthermore, the intensities of the regularity bands in the spectra of the oligomeric fractions and tetrahydrofuran (THF) copolymers depend on N in the same manner[47]. All this demonstrates the applicability of the cluster approximation to the systems enumerated above.

Table 1 presents the results of studies of the regularity bands–their frequencies and the characteristic lengths of the monomeric unit sequences measured with their aid. The quantity N_0 represents the extrapolated average length of the regular segment for which the given band appears in the spectrum and N_p is the length for which the band intensity reaches half its maximum value. Tables 2 and 3 present the analogous lists for crystallinity and amorphous structure bands.

Despite the fact that the intensities of the regularity bands are extremely sensitive to the polymer microstructure, their use for the analysis of sequence length, stereoregularity, etc. is coupled with certain difficulties.

One of the main difficulties is the absence of model compounds necessary for the derivation of calibration relations between the extraction coefficients and the length of the regular chain. The description of these relations with the aid of a power function[37,47] constitutes a fairly rough approximation.

The need to derive a theoretical expression for the function $k(N)$, which must be fairly general and must contain as few as possible empirically determined parameters, follows from the foregoing. The knowledge of this function would

make it possible to solve yet another problem, namely to establish the type of averaging of the lengths of the regular segments in polymers measured with its aid as well as the place of the average quantities in the series of those generally accepted, namely number-average, weight-average, etc. A detailed examination of these problems is presented below.

Table 1. Regularity bands.

Type of regular sequence	ν, cm^{-1}	N_n	N_p	Polymer system	Refs.
Polymethylene	730	11	17	Crystalline orthorhombic n-paraffins	[43]
ditto	720	11	17	ditto	[43]
Isotactic polypropylene	998	—	12	Propene–ethylene copolymers	[30,35,36]
ditto	973	—	4	ditto	[30,35,36]
"	998	—	10	Propene–propene-1,1,2-d_3 copolymers	[37]
"	842	—	10	ditto	[37]
"	899	—	—	Crystalline and amorphous polypropylene	[97]
"	809	—	—	ditto	[97]
cis-1,4-Polybutadiene	778	2	—	Solution of polybutadiene in carbon disulphide	[94]
Isotactic polystyrene	1194	1.5	6	Highly crystalline isotactic styrene–styrene-α-d_1 copolymers	[37]
ditto	1053	2.1	10	ditto	[37]
"	920	—	10	"	[37]
"	1084	—	5	Solutions of isotactic styrene–styrene-α-d_1 copolymers in carbon disulphide at −104 °C	[37]
"	920	—	10	ditto	[37]
"	898	—	16	"	[37]
"	1194	1.8	4	"	[37]
"	543	—	3	Styrene–methyl methacrylate copolymers	[38]
"	540—545	—	4—5	Styrene–butadiene and styrene–acrylonitrile copolymers. Homopolymers	[39,40]
Isotactic poly(vinyl chloride)	1434	—	2	Vinyl chloride–vinylidene chloride copolymers	[41]
ditto	1247	—	3	ditto	[42,44]
Poly(ethylene oxide)	1350	2	5	Solutions of glymes and poly(ethylene glycol) at −90 °C	[43,55]
ditto	1283	2.1	5	ditto	[43,55]
"	1283	0.5	6	Solid glymes, poly(ethylene glycols) and epoxyethane–epoxypropane copolymers	[43]
Polytetrahydrofuran	750	1.1	4	Solutions of oligomers and tetrahydrofuran–epoxypropane copolymers in carbon disulphide at low temperatures	[47]
ditto	565	3.2	6	ditto	[47]
Poly(methyl methacrylate)	1060	—	3	Methyl methacrylate–acrylonitrile copolymers	[46]
Polymethacrylonitrile	1215	—	—	Methacrylonitrile–acrylonitrile copolymers	[45]
Polyacrylonitrile	775	—	—	Homopolymers	[98]

V. DEPENDENCE OF THE INTENSITIES AND WIDTHS OF THE REGULARITY BANDS ON THE LENGTH OF THE MACROMOLECULAR HELIX

In interpreting spectroscopic data, experimenters usually prefer to deal with the absorption coefficients of bands at their maxima (k_{max}), because this spectroscopic parameter is in fact most readily susceptible to direct measurement. At the same time the integral absorption coefficient k and the band width $\Delta\nu$ are known to have a direct physical significance; k_{max} is related to them unambiguously; $k_{max} = Ak/\Delta\nu$, where A is a constant which depends on the units of the quantities in the expression. The factors determining the form of the $k(N)$ and $\Delta\nu(N)$ relations [and hence also of $k_{max}(N)$] are complex and numerous. In particular, one can specify tens of factors influencing the form of the function $\Delta\nu(N)$. They include, for example, the changes in density and refractive index when the microstructure is damaged[34,128], the interaction of vibrations of different types as a consequence of their anharmonicity[129,130], intermolecular interactions[128,129], the resonance of vibrations[131], a non-rigorous validity of the selection rules with respect to the phase parameter[1], polydispersity of the polymer[132], the presence of an amorphous phase and a folded structure in the polymer[34], internal stresses[133], the distribution of the paths traversed by the optical phonon with respect to length[52], band splitting under the influence of the field in the polymer crystal[34], and many others.

Table 2. Crystalinity bands.

Polymer	ν, cm^{-1}	Refs.
Orthorombic polyethylene	1894	[76]
ditto	1178	[76]
"	1050	[76]
"	731	[99,100]
Triclinic polyethylene	721	[101]
Monoclinic polyethylene	717	[83]
ditto	715	[102]
Polyisoprene	1130	[34]
Tetragonal polybut-1-ene	905	[103]
Orthorhombic polybut-1-ene	510	[103]
Hexagonal polybut-1-ene	925	[103]
ditto	1096—1098	[104,105]
"	1059—1062	[104,105]
"	1028	[104,105]
"	922—924	[104,105]
"	848	[104,105]
"	816	[104,105]
Poly(vinyl chloride)	1426	[87]
ditto	1333	[87]
"	1254	[87]
"	1229	[87]
"	957	[87]
Poly(vinylidene chloride)	884	[106]
ditto	753	[106]
Polychlorotrifluoroethylene	1285	[107,108]
ditto	580	[107,108]
Poly(ethylene terephthalate)	1685	[91]
ditto	1386	[91]
"	1130	[91]
"	1110	[91]
Poly(vinyl alcohol)	1146	[111]
Poly(n-butyl acrylate)	1255	[112]
ditto	1215	[112]
Amylose	855	[113]
Polytetrafluoroethylene	625	[89]
ditto	516	[89]
Polyoxyethylene	1283	[114]
ditto	1244	[114]
"	1236	[114]
"	1062	[114]
"	947	[114]
"	963	[114]
Orthorhombic polyoxymethylene	1488	[115]
ditto	1466	[115]
"	1237	[115]
"	1220	[115]
"	434	[115]
"	428	[115]
Trigonal polyoxymethylene	1434	[116]
ditto	1381	[116]
Orthorhombic polyesters $[-(CH_2)_m-O-]_n$ (m = 6,8,10,12)	730	[117]
Pentone	1325	[118]
Polychlorotrifluoroethylene	506	[107,108]
ditto	490	[107,108]
"	438	[107,108]
Poly(vinylidene fluoride)	1075	[109]
ditto	980	[109]
"	855	[109]
"	798	[109]
"	762	[109]
Polychloroprene	952	[110]
ditto	782	[110]
Orthorhombic polyesters $\left[-(CH_2)_m-\overset{\overset{O}{\|}}{C}-O-\right]_n$	1724	[84]
Monoclinic polyesters $\left[-(CH_2)_m-\overset{\overset{O}{\|}}{C}-O-\right]_n$	1732	[84]

Some of these factors are unimportant and in most real cases their influence can be neglected compared with the marked changes in the intensities and widths of the regularity bands (frequently by a factor of several tens) when N is altered. The influence of other factors can be reduced to a minimum by selecting the appropriate experimental conditions. Henceforth we shall deliberately restrict the range of bands considered to those for which the dependence of the intensity on the structure is not complicated by factors difficult to take into account, such as resonance. As a result, there remain a small number of factors whose influence on the $k(N)$ and $\Delta\nu(N)$ relations must be considered[43].

Table 3. Amorphous structure bands.

Polymer	ν, cm^{-1}	Refs.	Polymer	ν, cm^{-1}	Refs.
Polyethylene	1350	[121]	Pentone	1027	[119]
ditto	1340	[122]	Poly(n-butyl acrylate)	1240	[112]
»	1304	[121,123]	ditto	1035	[112]
»	722—723	[80,3]	Poly(ethylene terephthalate)	1580	[91]
»	1367—850	[120]	ditto	1453	[91]
Polytetrafluoroethylene	850	[125]	»	1248	[91]
ditto	778	[125]	»	1180	[91]
»	718	[125]	»	1120	[91]
»	640	[89]	»	1100	[91]
Polychlorotrifluoroethylene	755	[107,108]	»	1042	[91]
Poly(vinylidene fluoride)	740	[109]	»	897	[91]
Polyoxymethylene	1420	[116]	»	502	[126]
ditto	1390	[116]	Polyamide-66	1329	[127]
Polyoxyethylene	1296	[114]	ditto	1224	[127]
ditto	1249	[114]	Amylose	1295	[113]
«	1038	[114]			
«	945	[114]			

1. Integral Intensity

In order to determine the dependences of the integral intensities of the longitudinal vibration bands on N, it is necessary to take into account first the dilution effect, which arises because the fraction of chain units in the vicinity of the defect have force constants and configurations somewhat different from those for units remote from the defect due to the influence of the latter. The fraction of the energy of the normal vibration corresponding to the units near the defect can then decrease sharply even for an insignificant degree of perturbation[52]. In other words, a chain with a length shorter than the actual length N is effectively involved in the longitudinal chain vibration, which leads to the following dependence of the integral absorption coefficient k on N [43]:

$$k(N) \propto 1 - N_0/N \,. \qquad (2)$$

The $k(N)$ relation for transverse vibration bands is characterised by the presence of maxima and minima. It can be shown[1,52] that in this case the following expression holds for sufficiently high values of N:

$$k(N) \propto \frac{1}{N} \cos^2 \frac{mN\pi}{n} \,, \qquad (3)$$

where n is the number of units of the macromolecule with helical symmetry, corresponding to m turns of the helix. Evidently Eqn.(3) has deep minima which repeat with a period corresponding to n units.

2. Broadening of the Bands

We shall consider initially the case of a dilute polymer solution. There are several theories explaining the broadening of the spectral bands in the liquid phase[5,128,130,134–137]. Among these, the most promising theory, yielding the best agreement with experimental data, is the fluctuation theory developed by Bakhshiev[128]. According to it, the main cause of the broadening of the bands in the spectrum of the liquid phase is the fluctuation of the microdensity of the immediate environment of the molecule.

Allowance for the influence of these fluctuations in the first-order perturbation theory in the NRCU system leads to the following dependence of the chain vibration band width on the chain length and temperature[43]:

$$\Delta\nu \propto (T/N)^{1/4} \,. \qquad (4)$$

This result is not unexpected bearing in mind that the fractional fluctuation of a physical quantity (in this case frequency) for a system consisting of N equivalent objects (in the given case units), whose fluctuations are independent, is inversely proportional to $N^{1/2}$.

The assumption of the independence of the perturbations[138] of the individual units, which is valid in the case of a solution, becomes incorrect in the general case for a polymer in bulk, for example, for a polymer crystal. In the latter case the microdensity fluctuations are caused mainly by the acoustic vibrations of the lattice and hence are to some extent correlated along the chain. The $\Delta\nu(N)$ relation must then be weaker. We shall explain this by a simple example. We shall assume that the perturbing influence of the medium is such that it leads to a synchronous change in the force constants of all the units (the case of maximum correlation). Here the fluctuations in the frequency of the macromolecule, leading to a broadening of the band, are evidently the same as for a single unit, i. e. are independent of N.

In the case of a partial breakdown of the correlation of the acoustic lattice vibrations, as a consequence of anharmonicity, it can be shown[43] that, in the terms of the first-order perturbation theory, the dependence of $\Delta\nu$ on N is

$$\Delta\nu(N) \propto \frac{T^{1/4}}{(N+1)^{3/4}} \left[\sum_{i,j,k=1}^{N} \sum_{k_t=1}^{N_t} \sin^2 \frac{i\pi}{N+1} \cdot \sin^2 \frac{j\pi}{N+1} \times \right.$$
$$\left. \times \sin \frac{ik\pi}{N+1} \cdot \sin \frac{jk\pi}{N+1} \cdot \frac{e^{-|i-j|/N_p^a}}{\omega_{kk_t}^2} \right]^{1/4} , \qquad (5)$$

where N_t is the number of chains constituting the crystal, N_p^a the characteristic length of the section of the chain participating in the correlated acoustic vibrations and having the same physical significance as the average length of the free path of the acoustic phonon, and ω_{kk_t} are the frequencies of the acoustic branch, which are defined by the following relation when account is taken of only the short-range interactions in the NCRU system:

$$\omega_{kk_t}^2 \propto \sin^2 \frac{k\pi}{2(N+1)} + \sigma \sin^2 \frac{k_t\pi}{2(N_t+1)} \,.$$

Here the parameter σ characterises the "interaction" of the oscillators of the neighbouring chains in the NCRU.

Analysis of Eqn.(5) shows that, for low values of N_p^a ($N_p^a < 10$) and high values of σ ($\sigma > 0.5$), the nature of the relation $\Delta\nu(N) \propto N^{-1/2}$ is the same as for a polymer solution [see Eqn.(4)]. Comparison of Eqn.(5) with the experimental $\Delta\nu(N)$ relations shows that this limiting case in fact usually obtains for regularity bands.

Table 4. The form of the $k_{max}(N)$ relations for regularity bands of different types.

Type of vibration	Local vibrations of terminal defects, "contacts", etc.	Characteristic vibrations of repeating units;	Chain vibrations; $N_p^0 \lesssim 1$		
			$\omega(N)$=const		$\omega(N) \neq$ const
			longitudinal	transverse	
$N_p^a \gg 1$ (macromolecule in crystallite)	$k_{max} \sim N^{-1}$ $N \gg 1$	$k_{max}(N)$=const $N > N_p^0$	$k_{max} \sim 1 - N_0/N$ $N < N_0$	$k_{max} \sim \cos^2(\pi mN/n) \cdot N^{-1}$ $N \gg N_0$	Spectral curve has a complex contour
$N_p^a \lesssim 1$ (macromolecule in solution)	$k_{max} \sim N^{-1}$ $N \gg 1$	$k_{max}(N)$=const $N > N_p^0$	$k_{max} \sim N^{1/2}(1 - N_0/N)$ $N_0 < N < N_p^0$	$k_{max} \sim \cos^2(\pi mN/n) \cdot N^{-1/2}$ $N > N_0$	

We may note that a marked breakdown of the correlation of perturbations can then be favoured not only by the anharmonicity of the acoustic vibrations but also by the stationary breakdown of the regularity of the immediate environment of the macromolecule (non-ideality of the crystal structure, defects of the neighbouring molecules, etc.).

3. The Intensities at the Regularity Band Maxima

It follows from Eqns.(2) and (4) that, for longitudinal vibration bands, we have:

$$k_{max}(N) \propto N^{1/2}(1 - N_0/N) \quad . \qquad (6)$$

We may note that Eqns.(4)–(6) do not take into account the finite length of the free path of the optical phonon N_p^0 which amounts for certain regularity bands, as will be shown below, to several tens of units and can be estimated from the value of N for which the experimental $\Delta\nu(N)$ and $k_{max}(N)$ relations deviate from those defined by Eqns.(4)–(6).

VI. CLASSIFICATION OF THE INFRARED BANDS OF POLYMERS

After the principal mechanisms of the influence of the length of the regular segments in macromolecules on the intensities and widths of the infrared bands have been elucidated, it is possible to isolate, within the framework of the cluster approach, groups of bands differing in the nature of the dependence of their absorption coefficients on the length of the segment.

Several attempts have been made at a classification of the structure-sensitive bands in the infrared spectra of polymers, which, however, are only qualitative[50,74]. Our proposed classification is based on the type of dependence of the frequency ω and the absorption coefficient at the band maximum k_{max} on the length of the regular segment N. According to this classification, it is possible to isolate in the infrared spectrum bands which can be more or less definitely assigned to one of the types of vibration of the macromolecular chain: local, characteristic, or chain. In order to make this classification more informative and clearer, we also introduced into consideration parameters characterising the lengths of the paths of the phonons of the optical vibration considered (N_p^0) and the low-frequency acoustic vibrations (N_p^a) with which the given optical vibration interacts. The types of the $k_{max}(N)$ relations and the corresponding values of N_0, N_p^0 and N_p^a as well as the ranges in which N varies and the band polarisations are given in Table 4.

We shall consider the problem of the kind of information about the structure of the polymer contained in each band type. The bands due to the local vibrations of the defects ($k_{max} \propto N^{-1}$) can be used to determine the nature and concentration of the defects, particularly the "contacts" between blocks of different kinds and hence the number-average sequence length or the number-average molecular weight in the case of oligomers.

The characteristic bands of the chain vibrations ($N_p^0 \lesssim 1$, $k_{max} \cong$ const.) can be used to determine the chemical, isomeric, and conformational compositions of the polymers.

The $k_{max}(N)$ relation for the transverse vibration bands at $N_p^0 \gg 1$ contains information about the nature of the helical symmetry of the regular section of the chain (parameters m and n). However, such bands are unsuitable for the determination of the average length $\bar{N}$ of the regular segments as a consequence of the non-monotonic $k_{max}(N)$ relation.

The longitudinal vibration bands for $N_p^0 \gg 1$ and $N_p^a \lesssim 1$, for which there is a strong monotonic dependence of k_{max} on N defined by Eqns.(6), are the most suitable for the determination of the average length of the regular segments in macromolecules. As mentioned above, when these bands are used, the question of the nature of the averaging of the length arises.

VII. THE REGULARITY BANDS AND THE DISTRIBUTION OF THE REGULAR SEGMENTS IN MACROMOLECULES WITH RESPECT TO LENGTH

In conformity with the cluster approximation, each segment makes an independent contribution to the integral absorption coefficient at the specified frequency. Taking this fact into account as well as Eqn.(2), it is easy to obtain an expression for the absorption coefficient of the specimen in terms of the distribution function with respect to the lengths of the segments $w(N)$:

$$k(\bar{N}) \propto \sum_{N=N_0}^{\infty} w(N) \cdot \left(1 - \frac{N_0}{N}\right) \quad .$$

On the other hand, by measuring the optical density of a specimen with an unknown distribution function and using Eqn.(2) as the calibration relation, we obtain

$$1 - \frac{N_0}{\bar{N}} = \sum_{N=N_0}^{\infty} w(N) \cdot \left(1 - \frac{N_0}{N}\right) \quad ,$$

whence

$$\bar{N} = \left(\sum_{N=N_0}^{\infty} \frac{w(N)}{N} \right)^{-1} \equiv \bar{N}_n \quad .$$

Consequently *the integral absorption coefficient of the regularity band contains information about the number-average length of the regular segments.*

The dependence of the absorption coefficient at the regularity band maximum on the function $w(N)$ can be analysed analogously[43]. It follows from Eqn.(6) that

$$k_{max}(\bar{N}) \propto \sum_{N=N_0}^{\infty} w(N) \cdot N^{1/2}\left(1 - \frac{N_0}{N}\right) \quad . \qquad (7)$$

Analysis of Eqn.(7) shows that, for relatively high values of N (for $N \gg N_0$), the square of the experimental optical density is proportional to $\bar{N}_1$ defined by the relation

$$\bar{N}_1 = \left[\sum_{N=N_0}^{\infty} w(N) \cdot N^{1/2}\right]^2 \quad .$$

On the other hand, if values of N in the range $N_0 \leqslant N < 2N_0$ are characteristic of the main bulk of the polymer molecules, the optical density is proportional to $\bar{N}_2$:

$$\bar{N}_2 = \sum_{N=N_0}^{\infty} [w(N)N] - N_0 \equiv \bar{N}_w - N_0 \quad .$$

In the general case the following relation holds for the "spectroscopic average" length $\bar{N}_S$:

$$\bar{N}_n < \bar{N}_1 \leqslant \bar{N}_s \leqslant \bar{N}_2 < \bar{N}_w \quad .$$

where $\bar{N}_n$ and $\bar{N}_w$ are the number-average and the weight-average lengths of the regular segments respectively.

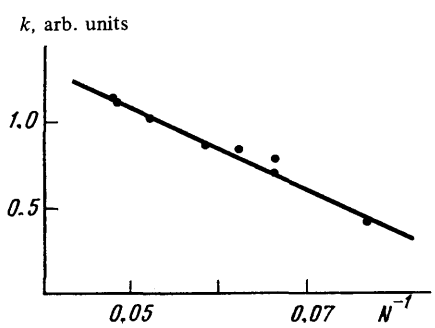


Figure 3. Dependence k on N^{-1} for the wagging vibration band (720 cm^{-1}) of orthorhombic n-paraffins at 173 K.[43]

Thus *the average length of the regular segments in macromolecules determined from the absorption coefficient at the regularity band maximum lies in the range between the number-average and weight-average lengths and usually approaches the latter.*

Finally we may note that the ratio of the average lengths of segments measured on the basis of the peak and integral regularity band intensities $\bar{N}_S/\bar{N}_n$ characterises the width of the distribution $w(N)$.[52,139]

VIII. SOME EXAMPLES OF STUDIES ON THE MICROSTRUCTURES OF POLYMERS WITH THE AID OF REGULARITY BANDS

Since regularity bands can belong to one type or another indicated in Table 4, the dependence of their parameters (k_{max} and $\Delta\nu$) on N (or on T) should have different linearising coordinates defined by Eqns.(2), (4), and (6). We shall quote several typical examples of experimental relations of this kind.

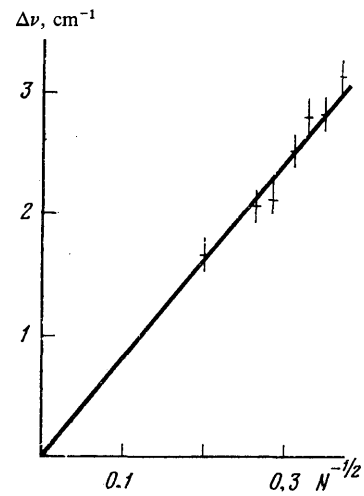


Figure 4. Dependence of $\Delta\nu$ on $N^{-1/2}$ for the forbidden band of the wagging-torsional vibrations of triclinic n-paraffins (735–770 cm^{-1}) at 100 K.[43]

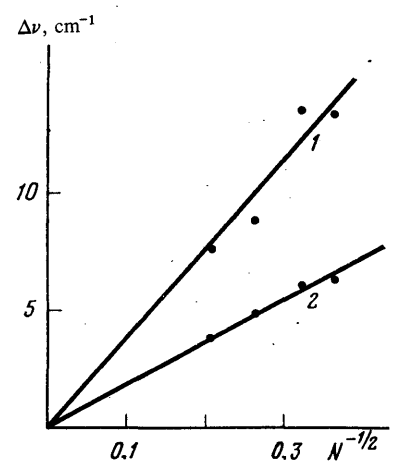


Figure 5. Dependence of $\Delta\nu$ on $N^{-1/2}$ for the C–O stretching vibration and CH_2 wagging vibration bands (845 cm^{-1}, line *1*) and the fanwise CH_2 vibrations (1346 cm^{-1}, line *2*) of the urethanes C_4H_9–NH–CO–O–$(CH_2$–CH_2–O$)_N$–CO–NH–C_4H_9 at 100 K.[52]

Fig. 3 shows that the coordinates (k, N^{-1}) [see Eqn. (2)] are linearising for the band due to the wagging vibrations of n-paraffins.

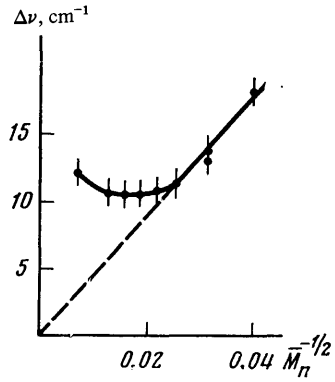


Figure 6. Dependence of $\Delta\nu$ on $\bar{M}_n^{-1/2}$ for the 845 cm^{-1} band in the spectra of crystalline poly(ethylene glycols) at 10 °C.[43]

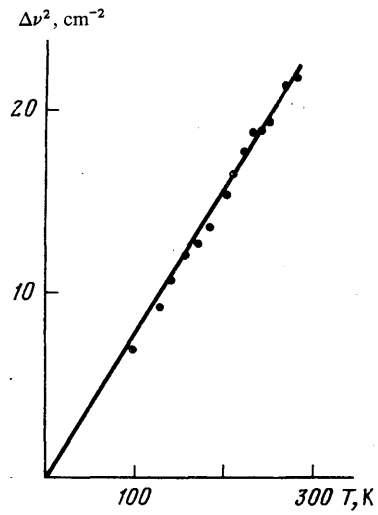


Figure 7. Dependence of $\Delta\nu^2$ on T for the wagging vibration band (720 cm^{-1}) of triclinic n-tetradecane.

When the correlation of the acoustic vibrations undergoes a pronounced distortion in conformity with Eqn. (4), the coordinates $(\Delta\nu, N^{-1/2})$ are also linearising, provided that the chain length does not exceed the length of the free path of the optical phonon N_p^0. Figs. 4 and 5 show that, for not unduly high values of N, the plots of $\Delta\nu$ against $N^{-1/2}$ for certain regularity bands in the spectra of polymers containing polymethylene and polyoxyethylene segments are straight lines passing through the origin of coordinates. The deviation from Eqn. (4) in the case of the 845 cm^{-1} band of poly(ethylene glycols) with molecular weights $\bar{M}_n > 2000$ (Fig. 6) can be accounted for by the finite length of the free path of the optical phonon as a consequence of the anharmonicity of the vibrations or the appearance of a folded structure.

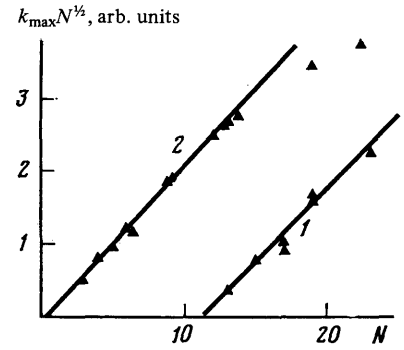


Figure 8. Dependence of $k_{max}N^{1/2}$ on N for different bands: *1*) wagging vibrations (720 cm^{-1}) of orthorhombic n-paraffins at 170 K;[52] *2*) torsional vibrations (1283 cm^{-1}) of glymes, poly(ethylene glycols), and epoxyethane-expoxypropane copolymers at 170 K.[48]

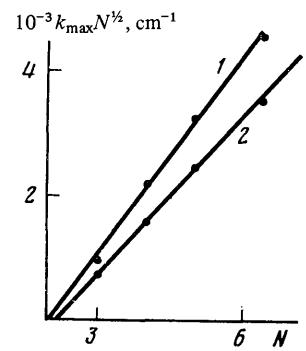


Figure 9. Dependence of $k_{max}N^{1/2}$ on N for the fanwise vibration (1350 cm^{-1}) (line *1*) and torsional vibration (1285 cm^{-1}) (line *2*) bands of glymes and poly(ethylene glycol) with $\bar{M}_n = 300$ at 180 K;[48] solvent-carbon disulphide.

The temperature variation of the regularity bands considered is also described by Eqn. (4). An example of such a relation is presented in Fig. 7.

According to Eqn. (6), the dependence of $k_{max}N^{1/2}$ on N should be linear under the condition $N_p^0 \leq 1$ and $N < N_p^0$. The linearity of this relation has been observed for a series of regularity bands of polymers containing polymethylene, polyoxyethylene, and polystyrene sequences of units in the crystalline state and in the form of solutions at low temperatures (see, for example, Figs. 8–10).

However, in some cases the hypothesis of a pronounced distortion of the correlation of perturbations along the chain and Eqns. (4) and (6) derived on this basis do not allow a

satisfactory description of the $k_{max}(N)$ relation. For example, such relations for certain structure-sensitive bands in the spectra of compounds containing polyoxybutylene and polystyrene sequences of units can be described only with the aid of the exact Eqn.(5) for the band width with the optimised parameters N_p^a, σ, and N_0 (Figs.11–13).

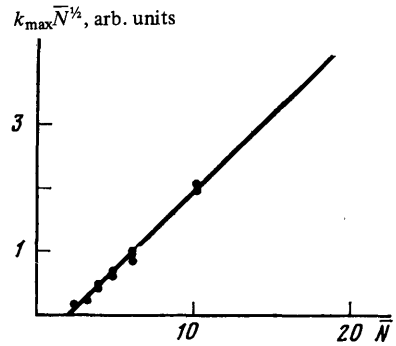


Figure 10. Dependence of $k_{max}\bar{N}^{1/2}$ on $\bar{N}$ for the 1053 cm^{-1} band of the isotactic crystalline styrene–styrene-α-d_1 copolymer[37] ($\bar{N}$ is the average length of the polystyrene segment).

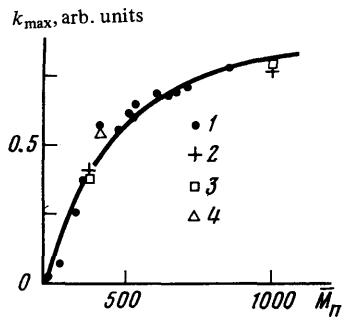


Figure 11. Dependence of k_{max} for the 565 cm^{-1} band on the number-average molecular weight of the polyoxybutylene block for low-temperature solutions in carbon disulphide; *1*) of oligomeric fractions of polytetrahydrofuran; *2*) of initial oligomers; *3*) of acetylated oligomers; *4*) of the tetrahydrofuran–epoxypropane block copolymer[47]. The continuous curve has been calculated by Eqn.(5) with the optimised values of the parameters N_p^a and σ.

1. Analysis of the Helical Structure of Polymer Chains

The bands of transverse vibrations with fairly high values of N_p^o ($N_p^o > 2n$, see Table 4) are sensitive to the type of helical symmetry. In order to determine the parameter n of the helix, it is desirable to use bands which correspond to low values of N_p^a; for such bands, the amplitude of the oscillations in the $k_{max}(N)$ relation does not decay unduly rapidly.

In the case of polymethylene chains whose skeleton has a planar zigzag conformation and hence the helical symmetry 2_1 (i.e. two units per turn of the helix), an alternation (with a period of two units) of maxima and minima in the $k_{max}(N)$ curve is to be expected for the transverse vibration bands. Such alternation has indeed been observed for a series of n-paraffins in the region of torsional vibrations (950–1060 cm^{-1}), since the bands corresponding to these vibrations are absent from the spectra of molecules containing an odd number of carbon atoms[124]. For polymers containing regular polyoxyethylene segments with narrow distribution functions with respect to their lengths, the period of the oscillations of the corresponding experimental $k(N)$ relation is equal to seven units (Fig.14). This finding is in good agreement with X-ray diffraction data[140], according to which the polyoxyethylene chain consists of a 7_2 helix.

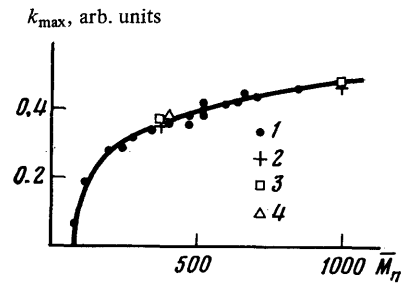


Figure 12. Dependence of k_{max} for the 750 cm^{-1} band in the spectra of low-temperature solutions of model compounds (for legend, see Fig.11) in carbon disulphide on the number-average length of the polyoxybutylene block[47].

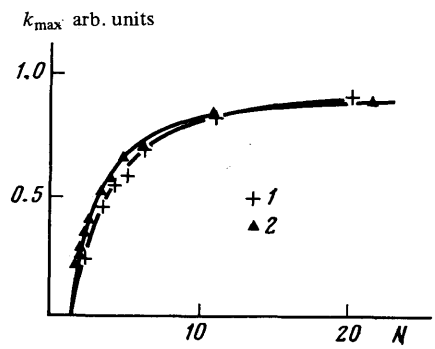


Figure 13. Dependence of k_{max} on the average length of the polystyrene segment for the 1194 cm^{-1} band of the isotactic styrene–styrene-α-d_1 copolymer; *1*) solution in carbon disulphide at −104 °C; *2*) crystalline specimens[37]. The continuous curves have been calculated by Eqn.(5) with optimised values of the parameters N_p^a and σ.

2. The Sequence Length of Tetrahydrofuran-Epoxypropane Copolymers

The structures of such copolymers have been analysed only for polyoxybutylene blocks[47]. Table 5 presents the average lengths $\bar{N}$ of these blocks in copolymers of different composition determined with the aid of the curves illustrated in Figs.11 and 12. Table 5 also presents the number-average ($\bar{N}_n$) and weight-average ($\bar{N}_w$) lengths calculated from kinetic data[141]. As was to be expected, the lengths determined by the spectroscopic method have intermediate values.

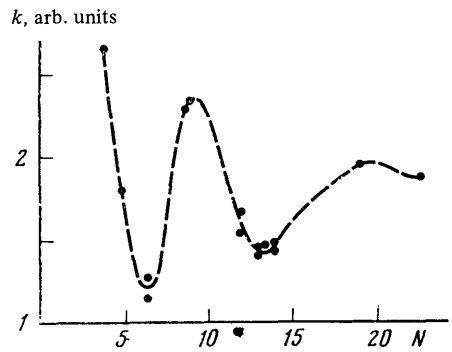


Figure 14. Dependence of k on the length of the polyoxyethylene segment for the 1366 cm^{-1} band in the spectra of glymes, poly(ethylene glycols), and epoxyethane–epoxypropane copolymers at −100 °C.[43]

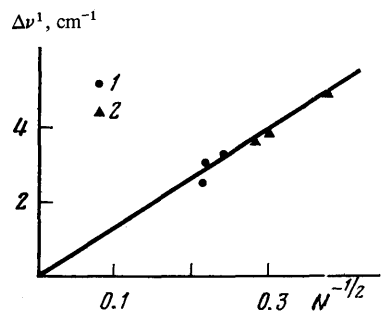


Figure 15. Dependence of the width of the high-frequency wing of the wagging vibration band (730 cm^{-1}) in the spectra of the crystalline component of n-paraffins (1) and ethylene–but-1-ene copolymers (2) on the length of the polymethylene segment[43].

3. The Sequence Length of Epoxyethane–Epoxypropane Copolymers

The Pluronic block copolymers of epoxyethane and epoxypropane (Wyandotte Chemical Co), whose compositions, degrees of block structures, and molecular weights are rigorously correlated with one another, are convenient for testing the spectroscopic method for the analysis of the sequence length. In order to measure the average lengths of the polyoxyethylene POE segments, the dependence of the 1283 cm^{-1} bend intensity on the length of the POE block was used (Fig.8). Table 6 presents the average lengths of the POE segments measured spectroscopically and determined from the data provided by the Company. Evidently an entirely satisfactory agreement was obtained between these quantities.

Table 5. The lengths of the PTHF sequences in tetrahydrofuran–epoxypropane (EP) copolymers[47].

THF:EP*	$\bar{N}_w$**	$\bar{N}_n$**	$\bar{N}$
1:2	2.2	1.8	2.05
1:1	2.6	2.2	2.5
2:1	3.1	2.4	2.85

* The ratio of the mole fractions of the THF and EP units in the copolymer.

** Kinetic data[141].

Table 6. The lengths of polyoxyethylene (POE) segments in epoxyethane-epoxypropane block-copolymers (Pluronic)[48].

Brand	Average length of POE block	
	Company's data	spectroscopic data
PL-44	9.1	8.8
PL-61	2.2	1.7
PL-62	5.0	4.8
PL-64	12.8	13.7
PL-72	5.9	6.1

4. The Degree of the Block Structure of Ethylene-But-1-ene Copolymers

The development of a method for the measurement of the lengths N of polymethylene blocks is of practical importance in connection with the necessity to investigate the structures of branched polyethylenes. The copolymers of ethylene with other α-olefins can be regarded as models of such polyethylenes.

Fig.15 shows that the dependence of the half-width of the 730 cm^{-1} band on $N^{-1/2}$ for crystalline copolymers and n-paraffins is described by a single straight line passing through the origin of coordinates, in conformity with Eqn.(4) and the cluster model[43]. The spectra of the crystalline component of the copolymer were obtained by the method of compensations spectroscopy; the spectrum of the polymethylene blocks of the amorphous part of the copolymer was modelled by the spectrum of liquid pentadecane.

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In conclusion we may note that we did not mention in this review all the possibilities for structural studies which can be formulated in a wider analysis of regularity bands. For example, one can point to the method based on the analysis

of the temperature variation of the regularity band intensities—the so-called low-temperature spiralisation method[52], which makes it possible to obtain information about the distribution of regular sequences of monomeric units with respect to lengths. Unfortunately, the limited size of the review did not allow us to consider the advantages of the method of analysis using the contour of a complex spectral band whose components are the bands of chain vibrations with frequencies sensitive to the lengths of the regular segments[1,32].

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