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Specificity of the Transformation of End Methyl Groups in the Interlamellar Regions of Tetracosane during the Solid-Solid Phase Transition as revealed by FTIR Spectroscopy

© V.A. Marikhin[1], S.A. Gureva[1], E.N. Vlasova[2]

[1]Ioffe Institute,
St. Petersburg, Russia
[2]Institute of Macromolecular Compounds, Russian Academy of Sciences,
St. Petersburg, Russia
E-mail: v.marikhin@mail.ioffe.ru

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The kinetics of the development of the first-order diffuse structural phase transition in monodisperse samples of tetracosane $C_{24}H_{50}$ was studied by FTIR spectroscopy. The temperature dependences of the frequencies and intensities of the C−H-stretching vibrations in the spectral region $\nu = 2800-3000\,\mathrm{cm}^{-1}$ were studied for 4 different modes in the methylene CH_2 trans sequences of the main chain and for 4 different modes corresponding to the end methyl CH_3-groups. Specific changes in the vibrational frequencies of all investigated modes are found, which are caused by changes in the symmetry of the molecular packing during the first-order phase transition.

Keywords: n-alkanes, phase transitions, theory of diffuse phase transitions, IR spectroscopy.

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1. Introduction

Monodisperse (with accuracy up to one C−C-bond) long-chain molecular crystals (LCMCs) of n-alkanes $H_3C(CH_2)_nCH_3$ with different chain length ($17 \leq n \leq 40$), which have the simplest chemical structure and are stable to external impacts, are unique model compounds for the solving of many debatable issues in solid state physics, in particular, for the development of quantitative models for description of structural transformations during phase transitions.

The DSC method [1,2] has shown that the transition from the solid state to the melt upon heating and the transition from the melt to the solid state upon cooling in n-alkanes occur in two stages, which correspond to two endo- or exothermic peaks of heat capacity C_p, which are several degrees apart on the temperature scale. It was found that the low-temperature peak at $T_{\text{s-s}} < T_\text{m}$ corresponds to a first-order solid-solid phase transition (PT-1), associated with a change in the type of symmetry of the molecular packing in the crystal structure. The next higher-temperature peak C_p is classified as a second-order phase transition (PT-2) of the order−disorder type, which is accompanied by sample melting or crystallization.

It turned out that the PT-1 in LCMCs of n-alkanes, as distinct from low-molecular-weight compounds, takes place in rather a wide temperature range $\Delta T = 1-2^\circ$C, due to which they were categorized as „first-order diffuse phase transitions" [3,4]. Such transitions are characterized by the following fact: the crystal's phase state changes according to a heterogeneous mechanism upon occurrence of fluctuation nuclei of a new phase on various defects. Volume of the new phase increases discretely due to motion of the formed phase interface by addition of the same new stable elementary nuclei to it. The performed size estimations [1,2] make it possible to speak of nano-nuclei of the new phase, with the volume of $\omega \sim 100-200\,\mathrm{nm}^3$, which contain up to several hundreds of molecules of the considered LCMCs.

It was established [5,6] that LCMCs of macroscopic sizes consist of extended stacks of layered (on each other) lamellar formations (nano-lamellae), whose thickness (units of nm) is comparable to length of the n-alkane molecule. During crystallization from a melt or a solution, the chain segments of methylene trans-sequences form three-dimensionally ordered crystalline cores of separate nano-lamellae due to weak van der Waals bonds between CH_2-groups of neighboring molecules. Alternating inter-layers between adjoining nano-lamellae in stacks contain closely contacting planes of end methyl CH_3-groups, which interact by means of van der Waals forces. Sizes of inter-lamellar regions depend on the type of packing symmetry of n-alkane molecules in the crystalline cores of nano-lamellae and vary from 2.74 Å (in a triclinic structure) to 3.15 Å (in an orthorhombic one) [7,8].

We used methods of high-resolution synchrotron X-ray diffraction [8] and Fourier-transform IR spectroscopy [9] to study the kinetics of development of a solid-solid phase transition in crystalline cores of nano-lamellae in poly-crystalline tetracosane n-$C_{24}H_{50}$ during heating of samples crystallized from the melt. In accordance with the literature data [10,11], triclinic symmetry of molecular packing in subcells of crystalline cores of tetracosane nano-lamellae was observed in the initial state at $T = T_{\text{room}}$, i.e. an inclined arrangement of methylene trans-sequences in relation to the base planes of lamellae formed by end methyl CH_3 groups. The formation of nano-nuclei with a different (hexagonal) symmetry and gradual propagation of the formed hexagonal phase across the entire volume of the initial triclinic phase was observed in crystalline cores of nano-lamellae with triclinic subcells upon stepwise heating of samples with increment $\Delta T = 0.2^\circ C$ [8] or $\Delta T = 0.1^\circ C$ [9] in a narrow temperature range of the PT-1 ($\Delta T_{\text{s-s}} = 45-48^\circ C$), in full agreement with the theory of first-order diffuse phase transitions revealed previously by the DSC method. The expected transition from the inclined arrangement of n-$C_{24}H_{50}$ molecules to the vertical one in lamellae' crystalline cores was clearly noted by the a change in the values of the small-angle X-ray period [8].

It must be noted that the initial triclinic and final hexagonal subcells contain one „effective" tetracosane molecule each. Nevertheless, the pattern of their mutual arrangement in crystalline cores of nano-lamellae differs significantly. Molecules in the initial samples with triclinic symmetry are located most tightly to each other and are inclined to the base surfaces of nano-lamellae, consisting of end methyl groups, at an angle of about 72°. It must be emphasized that intermolecular distances increase during heating due to thermal expansion, molecules can rotate around their axis, and hexagonal subcells form in lamellae after a solid-solid phase transition. In the hexagonal phase, a dense packing of molecules is considered when approximating them by effective cylindrical rods, since the planes of trans-zigzags can sixfold rotate in relation to their axes. Uncorrelated oscillations with a limited amplitude in relation to the middle position with the minimum shift of molecule axes cause a statistical disorientation of the mutual position of molecule planes in the matrix of the lamellae' crystalline core. Thereat, the van der Waals contacts between neighbors are maintained.

Along with that, taking into account the structure of nano-lamellae which is non-uniform along the thickness (a crystalline core of three-dimensionally packed methylene CH_2-trans-sequences a few nm thick and two surfaces of end methyl CH_3-groups, each about 0.15 nm thick), it is important to reveal the peculiarities of structural changes in these surface layers in contact with each other during heating (cooling) of n-alkanes and, in particular, during temperature phase transitions. We think that a Fourier-transform IR spectroscopy study of the region of stretching and deformation vibrations of C−H-bonds, inherent in end methyl groups, will provide new and important data, the more so because we did not come across any global publications on this issue.

It was considered in IR spectroscopy for a long time that the region of stretching C−H-vibrations $\nu = 2800-3000\,\text{cm}^{-1}$ is less sensitive and informative to peculiarities of mutual packing of n-alkane molecules with different types of morphologies as compared to other vibration modes of methylene trans-sequences, since stretching C−H-vibrations are to the fullest extent localized and the most energy-consuming ones (the greatest values of force constants) and include almost exclusively the hydrogen atom mobility.

Moreover, given the very small percentage of end methyl groups in PE, their manifestation in the IR spectrum was virtually not analyzed and was used mainly to reveal chemical defects in the shape of side branches. A different situation is typical for long-chain n-alkanes where, naturally, the relative contribution of absorption bands of CH_3-groups increases considerably.

Unexpectedly, the IR spectrum in the region of stretching C−H-vibrations $\nu = 2800-3000\,\text{cm}^{-1}$ turns out to be very complex and informative, because many potential peculiarities of IR spectra of long-chain saturated hydrocarbons manifest themselves to the fullest extent in rather a narrow frequency range. They can include the following aspects:

1. Due to the noticeable differences in values of force constants for stretching vibrations of C−H-bonds in methylene and methyl groups, the corresponding bands stand out distinctly in the total IR spectrum and can be unambiguously identified [12,13].

2. There is an appreciable difference in frequencies of symmetrical and asymmetrical stretching C−H-vibrations both in methylene sequences (d^+ and d^-) and in methyl groups (r^+ and r^-). Thereat, values of asymmetrical vibration frequencies are higher than the corresponding values for symmetrical vibrations, apparently, due to differences in force constants which are conditioned by opposing or unidirectional motion of hydrogen atoms in vibrating bonds.

3. Two-phonon states arise in the studied frequency range of $\nu = 2800-3000\,\text{cm}^{-1}$; they are caused by anharmonic Fermi-resonance interactions of vibrations of identical symmetry and close frequencies [14]. These conditions are met only for symmetrical vibrationsd^+ and r^+ and the overtone of bending (scissoring) vibrations of CH_2-groups, and, as a result, the general spectrum features two bands d^+_{FR} and r^+_{FR} (see below).

4. The influence of end methyl CH_3-groups on the vibrational spectrum of methylene sequences manifests itself distinctly in n-alkanes, in particular, the occurrence of band d^+_w conditioned by a symmetrical stretching vibration in the methylene oscillator which directly adjoins the end group. Force constants of interaction of different vibration modes are introduced during interpretation of such bands (as shown in [12]). Since such effects are not numerous, the corresponding bands may have a small intensity and will not be recorded if the IR spectrometer has an insufficient resolution.

2. Experimental procedure

The subject of research was monodisperse tetracosane n-$C_{24}H_{50}$ (with 99.9% purity) manufactured by

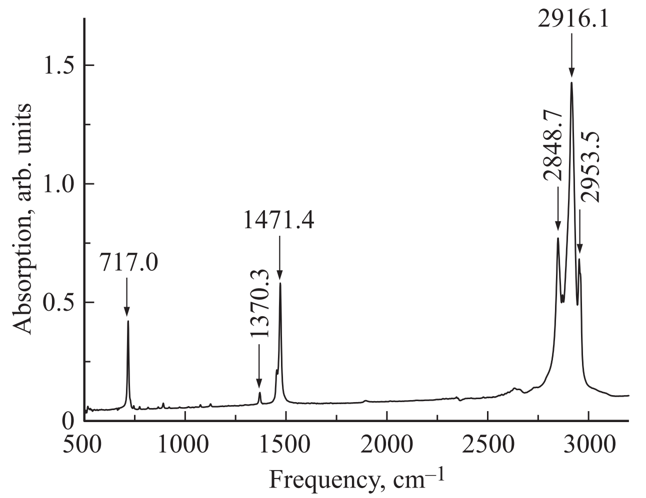

Figure 1. FTIR spectrum of tetracosane $C_{24}H_{50}$ in the region of 500−3500 cm^{-1}.

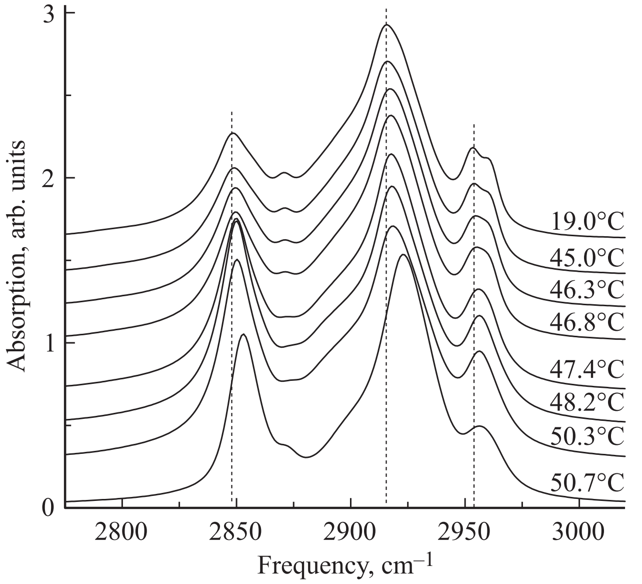

Figure 2. Series of IR spectra of tetracosane in the region of stretching vibrations of C−H-bonds upon heating.

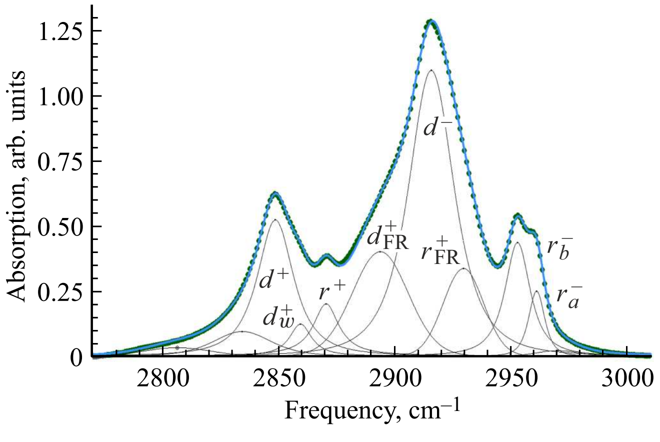

Figure 3. FTIR spectrum of tetracosane in the region of $\nu = 2800{-}3000\,\mathrm{cm}^{-1}$ at $T = 19.0^\circ\mathrm{C}$ after isolation of individual absorption bands.

Sigma−Aldrich. The samples of the necessary thickness were prepared as follows for spectroscopic studies: the synthesized tetracosane flakes were applied on NaCl plates, heated up to melting ($T_\mathrm{m} = 50.6^\circ\mathrm{C}$ [15]) and then were slowly cooled to room temperature in order to obtain an equilibrium crystal structure.

Absorption spectra were recorded using a Bruker IFS−88 Fourier-transform IR spectrometer in the frequency range of 400−5000 cm^{-1} with the resolution of 2 cm^{-1} and signal accumulation number — 30 (Fig. 1).

The IR absorption spectra were measured at a stepwise temperature rise by $\Delta T = 2^\circ\mathrm{C}$ in the range from T_room to T_m, except the PT-1 region, where the spectra were recorded with the increment of $\Delta T = 0.1^\circ\mathrm{C}$ and with sample holding for 10 min at each temperature increment for reliable temperature control. Temperature was monitoring using a chromel−copel differential thermocouple with the accuracy of $\pm 0.05^\circ\mathrm{C}$. The spectra of atmospheric moisture and CO_2 were deduced using the embedded program in order to eliminate possible distortion of the absorption spectra.

Fig. 2 shows a series of IR spectra in the region of stretching vibrations at different temperatures. It is seen that the spectra change radically upon heating.

Subsequent processing and analysis of IR spectra were performed in the Fityk 1.3.1 software [16]. Separation of superimposed absorption bands and isolation of individual components in the spectra when using the Pearson VII function was performed according to the literature data [17–19] (Fig. 3).

3. Results and discussion

As already noted above, the spectral region of $\nu = 2800{-}3000\,\mathrm{cm}^{-1}$ contains absorption bands of stretching vibrations of C−H-bonds both in methylene CH_2-groups (vibrations are designated by symbol d) and in methyl CH_3 groups (r). Accordingly, an analysis of temperature changes of these bands will make it possible to study the development of the PT-1 in two structural units of the lamella: in the crystalline core and in interlamellar regions.

The IR Fourier absorption spectrum of tetracosane (shown in Fig. 3), decomposed into components, makes it possible to distinguish the following bands given in the table, in accordance with [18]:

r^+ — symmetrical stretching vibrations in CH_3-groups;

r^-_a, r^-_b — asymmetrical stretching vibrations in CH_3-groups, in-plane and out-of-plane components in relation to the chain trans-zigzag plane respectively (the frequency difference is due to different force constants for these vibrations);

r_{FR^+} — bands conditioned by Fermi resonance of symmetrical stretching vibrations r^+ with overtone of bendind (scissoring) vibrations of CH_3-groups in interlamellar regions;

Absorption bands of stretching vibrations of C–H-bonds in the region of $\nu = 2800{-}3000\,\mathrm{cm}^{-1}$

Frequencies of stretching C–H-vibrations, cm^{-1}					
1	2	3	4	5	6
Designation	Experimental data for n-$C_{24}H_{50}$ at 19°C	Extended polymethylene chain and n-$C_{20}H_{42}$ at −180°C [17]	n-$C_{20}H_{42}$ at 9 K [18]	n-$D_3C(CH_2)_{20}CD_3$ at 7 K [18]	n-$C_{16}H_{34}$-urea at 9 K [18]
Methylene CH_2-groups of main chain					
d^-	2916.1 s	2920 s	2914 s	2915 s	2902 w 2912 sh, w 2922 s
d^+	2848.7 m	2850 s	2845 s	2846 s	2849
d^+_{FR}	2894.1 br, m	–	2890 br, m	2890 br, m	2883 w 2890 br, m
d^+_w	2859.3 sh, m	–	2853 sh, m	2854 m	2854 sh, m
Methyl end CH_3-groups					
r_a^-	2961.5 m	2962 m	2962 m	–	2954 sh, m 2958 m
r_b^-	2953.5 m	2953 m	2951 m	–	2946 m
r^+	2870.6 m	2873 m	2869 m	–	2867 m
r^+_{FR}	2930.3 sh, m	–	2930 sh, m	–	–

Note. Symbols for describing band intensity and shape: s — strong, m — medium, w — weak, sh — shoulder, br — broad.

d^+, d^- — symmetrical and asymmetrical stretching vibrations in CH_2-groups in methylene sequences in lamella cores;

d^+_w — symmetrical stretching vibrations in CH_2-groups which directly adjoin CH_3-groups;

d^+_{FR} — bands conditioned by Fermi resonance of symmetrical stretching vibrations d^+ with overtone of bending (scissoring) vibrations of CH_2-groups in lamellae' crystalline cores.

The table gives a list of the observed absorption bands in the region of $\nu = 2800{-}3000\,\mathrm{cm}^{-1}$, which are classified as vibrational modes in accordance with [17,18]. The table gives, along with our experimental data (column 2), the results of the theoretical calculations (column 3), as well as one of the most interesting and correct experimental data for isolated chains at very low temperatures, up to $T = 7\,\mathrm{K}$ (columns 4–6).

It follows from the table that the first 4 fundamental bands pertain to stretching C–H-vibrations in methylene trans-sequences of molecules in crystalline cores of nanolamellae of n-alkanes (d^-, d^+, d^+_{FR}, d^+_w). The other bands (r_a^-, r_b^-, r^+, r^+_{FR}) characterize the peculiarities of different modes of fundamentals stretching vibrations of C–H-bonds in end methyl groups of tetracosane.

It should be noted that all the above-mentioned bands in the region of $\nu = 2800{-}3000\,\mathrm{cm}^{-1}$ follow a certain sequence in accordance with the values of the valence force constants of the considered vibration modes. The values of the corresponding force constants are given in [12,13] where one of the highest-precision theoretical calculations of IR absorption spectra of individual molecules in homologues of saturated normal alkanes are described.

IR absorption spectra at very low temperatures, up to 7 K (see the Table data), were obtained for a model series of n-alkanes, including partially-deuterated samples and individual molecules of n-alkanes, placed in natural narrow nanochannels of urea crystals; these spectra were the basis for theoretical calculations of IR spectra of n-alkanes using the valence force field method (VFF) which included up to 35 independently varied parameters. These parameters for the considered vibrations include valence and bending force constants, as well as constants of interaction between different vibration modes possible both between neighboring oscillators and between the next nearest oscillators. The latter allow for revealing the origination of two- and more phonon states and the corresponding frequency change, e.g., symmetrical stretching vibrations of C$-$H-bonds in methylene trans-sequences upon connection of end methyl groups (d_w^+). Several publications (for instance, [12,20]) also give data about the distribution of potential energy of vibrations between particular constituent modes. The force constants from [12,13,20] are used by many authors and given in several monograph on IR spectroscopy.

According to [13], force constant values are the highest for stretching C$-$H-vibrations in end methyl groups ($K_r = 4.699$ mdyn/Å) as compared to similar vibrations in methylene groups of trans-sequences of the molecule skeleton of n-alkanes ($K_d = 4.554$ mdyn/Å). Thereat, it was found experimentally that the wave numbers of asymmetrical stretching vibrations both in methylene and in methyl groups exceed the corresponding values for symmetrical vibration modes ($\nu(d^-) > \nu(d^+)$, $\Delta\nu = 68\,\mathrm{cm}^{-1}$; $\nu(r^-) > \nu(r^+)$, $\Delta\nu = 90\,\mathrm{cm}^{-1}$). We did not find any comments in literature about the reasons of differences in force constants (and, accordingly, frequencies) of asymmetrical and symmetrical vibrations. It can be assumed that the nature of opposing motion of hydrogen atoms as compared to synchronous one in neighboring C$-$H-bonds with a common carbon atom can be one of the reasons of the observed effect.

Naturally, the force constants of bending vibrations (for asymmetrical scissoring vibrations of CH$_3$-groups: $H_\alpha = 0.540\,\mathrm{mdyn}\cdot\text{Å}/(\mathrm{rad})^2$, for scissoring vibrations of CH$_2$-groups: $H_\delta = 0.550\,\mathrm{mdyn}\cdot\text{Å}/(\mathrm{rad})^2$) and force constants of interactions are significantly (by an order and more) less than the valence ones [13], therefore, more significant changes of frequencies of such vibrations can be expected under external impacts, e.g., temperature.

The authors of the initial experimental papers and theoretical *ab initio* calculations did not pay attention (especially in IR spectra of linear polyethylene) to the additional band in the region of stretching C$-$H-vibrations for methylene trans-sequences, namely, to a broad and rather intensive band near $\nu \approx 2890\,\mathrm{cm}^{-1}$. The formation of this band was later explained by the origination of a specific two-phonon state as a result of an intramolecular Fermi-resonance interaction between vibrations of equal symmetry and sufficiently close frequencies [14,17,21]. It turned out that these conditions in n-alkanes are met in the region of $\nu = 2800-3000\,\mathrm{cm}^{-1}$ during interaction between the fundamental symmetrical stretching C$-$H-vibrations in methylene trans-sequences d^+ and the appropriate binary combinations of fundamental bending (scissoring δ) $\angle$HCH vibrations of CH$_2$-groups.

As a result of resonance interaction, there are two new bands, slightly shifted in relation to the initial ones, instead of the initial bands of the basic tone (d^+) and, for instance, the overtone of bending vibration (2δ). Thereat, there is considerable pumping of a significant part of the basic tone intensity into the overtone intensity. For example, when frequencies are equal $\nu(d^+) = \nu(2\delta)$, the band intensities after the Fermi resonance completely equalize, while intensities of overtones and combined bands are usually incomparably smaller than intensities of the fundamental bands.

In particular, the described effect can be also observed in our case for tetracosane (Fig. 3). The following must be assumed in this respect: fundamental symmetrical stretching vibrations of C$-$H-bonds in methylene sequences must in fact include two bands: d^+ and d_{FR}^+.

A band analysis has shown [17,21] that an adequate description of the shape and intensity of this band in n-alkanes requires the consideration of all possible binary combinations of bending vibrations in the entire Brillouin zone, and not only at its center at $\varphi = \pi$, where φ is the phase shift of vibrations between two neighboring oscillators — methylene CH$_2$-groups. In this case, the resultant continuum of binary states leads to a broad secondary band d_{FR}^+. It must be noted that the shape of this band will depend on the form of the dispersion curve for fundamental scissoring vibrations. Since a considerable contribution to intensity of band d_{FR}^+ is made by bending (scissoring) vibrations of CH$_2$-groups, a greater influence of external factors (for example, temperature) on frequency and intensity of bands of such vibrations can be anticipated, as compared to stretching C$-$H-vibrations due to a considerable difference in the corresponding force constants (see above).

Since the specific band d_w^+ includes a considerable contribution by end CH$_3$-groups, a greater influence of external factors (temperature) on frequencies of these vibrations can be also anticipated.

Fig. 4 below gives the summary data on the temperature dependences of the frequencies of the above-mentioned types of C$-$H-bond stretching vibrations in methylene sequences in cores of tetracosane nano-lamellae in the region of the structural phase transition, recorded on the basis of the observed changes in the corresponding IR spectrum frequencies.

The rather complex pattern of frequency changes for stretching vibrations can be noted, as compared to the temperature transformation of the spectrum which we have found earlier [9] for the same CH$_2$-oscillators in methylene sequences, but which are involved in other vibration modes, namely, rocking vibrations (in the region of $\nu \sim 720\,\mathrm{cm}^{-1}$) and scissoring vibrations (in the region of $\nu \sim 1470\,\mathrm{cm}^{-1}$) (Fig. 5).

It turned out that for all the 6 vibration modes of CH$_2$-oscillators (P, δ, d^-, d^+, d_{FR}^+, d_w^+) a similar pattern of temperature dependences of frequencies is observed, namely, the frequencies of the corresponding vibration modes, determined by the triclinic type of packing of trans-methylene sequences in tetracosane subcells, remain virtually unchanged during heating from T_{room} to the temperature of the start of a first-order solid-solid phase transition (PT-1) $T_1 \approx 45-46$°C (Fig. 4 and 5). Upon further heating (in the narrow temperature range varying from $\Delta T = 1.5$°C to $\Delta T = 2.6$°C), all the initial frequency values, determined by the corresponding vibration mode of

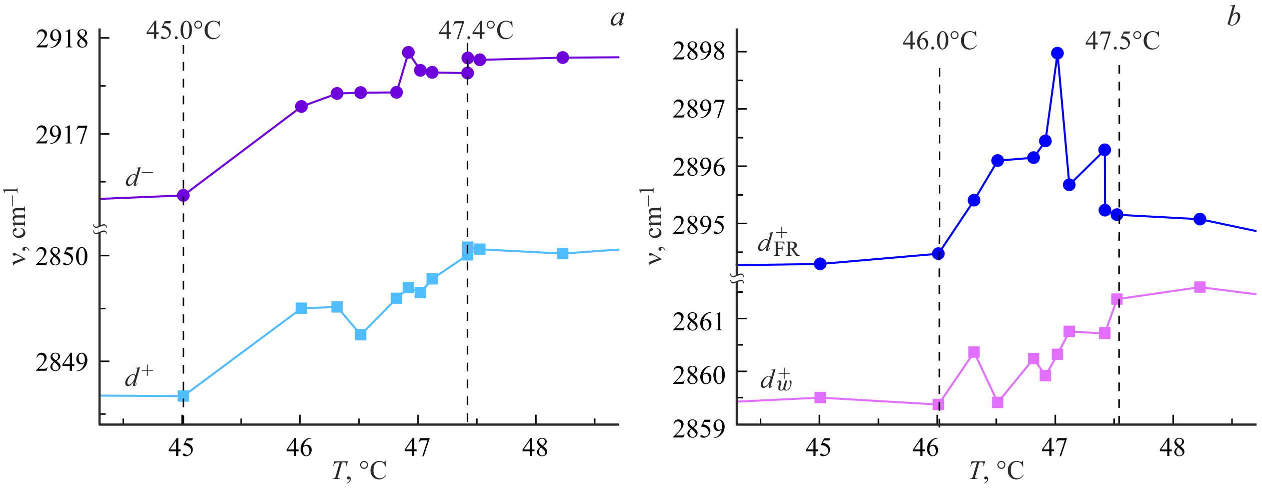

Figure 4. Temperature changes of the tetracosane IR spectrum in the region of stretching vibrations of C−H-bonds in CH$_2$-groups in nano-lamella cores: *a*) d^-, d^+ and *b*) d^+_{FR}, d^+_w.

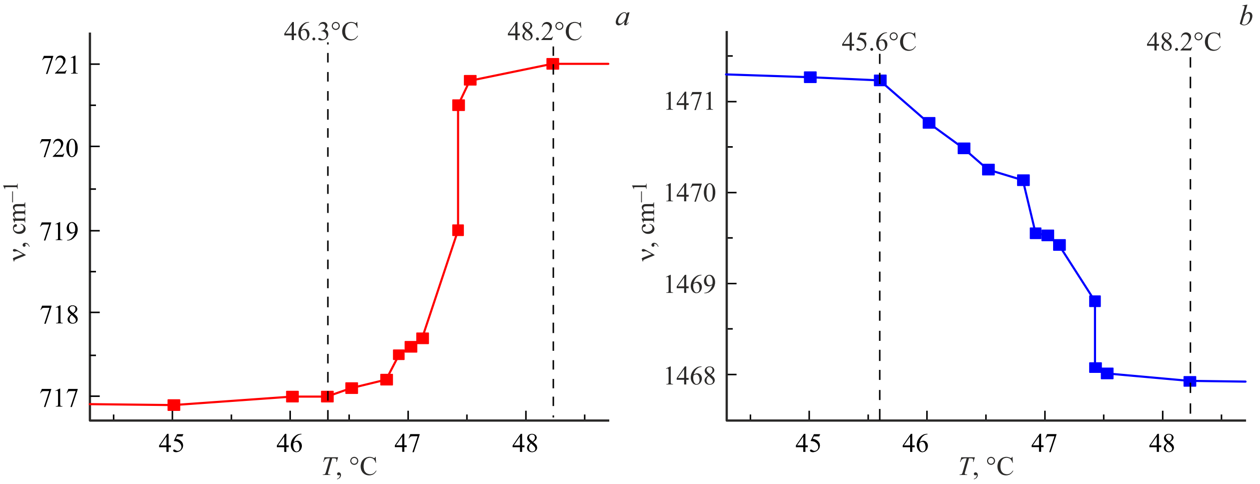

Figure 5. Temperature changes of tetracosane IR spectrum in the region of *a*) rocking (P) and *b*) scissoring (δ) vibrations of CH$_2$ oscillators in nano-lamella cores.

oscillators of CH$_2$-groups in methylene sequences in triclinic subcells, transform into the vibration frequencies typical for hexagonal subcells. However, the development kinetics of the diffuse PT-1 differs radically for all the 6 considered vibration modes of CH$_2$-groups in lamella cores.

The smoothest transition was revealed when analyzing the deformation (rocking and scissoring) vibrations of methylene CH$_2$-groups in the skeleton of the n-alkane molecule, at which hydrogen atoms move symbatically in planes located perpendicularly to the molecule axis. We believe that the smooth transition is conditioned by a gradual change of intermolecular interaction during the thermal expansion of n-alkane. The observed small sudden changes in the values of frequencies d^- and d^+ near the PT-1 completion temperatures are related to the origination of conformational defects and the corresponding absorption bands recorded in our IR spectra at these temperatures.

Attention should be also paid to the fact that a transition from the inclined molecular arrangement to the vertical one in relation to the base planes consisting of end methyl CH$_3$-groups takes place in tetracosane during the PT-1. Thereat, the relative packing of CH$_3$-groups inevitably changes.

The method of small-angle synchrotron X-ray diffraction showed [8] that nanodomains both of the initial triclinic symmetry and the new hexagonal symmetry exist simultaneously in the region of the tetracosane PT-1. As the PT-1 develops, the correlation between these phases gradually changes due to the propagation of the formed phase interface. In our opinion, the IR spectroscopic studies shown in Fig. 5 also confirm the proposed scheme of the development kinetics of diffuse phase transitions, since they characterize deformation vibrations which affect all the CH$_2$-groups in trans-sequences of molecules in crystalline cores.

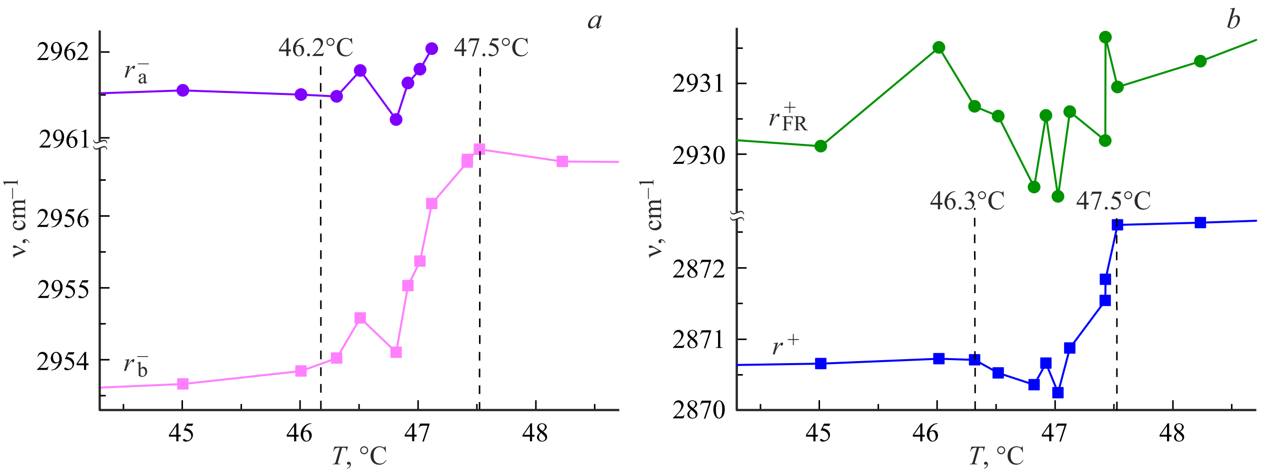

Figure 6. Temperature changes of the tetracosane IR spectrum in the region of stretching vibrations of C—H-bonds in end CH_3-groups: *a*) r_a^-, r_b^- and *b*) r_{FR}^+, r^+.

The analysis of frequency changes of stretching C—H-vibrations revealed a number of interesting additional effects during the restructuring in the temperature range of the PT-1. The temperature changes in the PT-1 region of symmetrical d^+ and asymmetrical d^- stretching vibrations of C—H-bonds, which also apply to all the CH_2-groups of trans-sequences, mainly demonstrate rather a smooth pattern of frequency increase by about $\Delta\nu = 1.4\,\mathrm{cm}^{-1}$ (Fig. 4). Since experimentally and theoretically established dependences between the C—H-bond length and the corresponding stretching vibration frequency is available [22], we can estimate that the revealed frequency change indicates a decrease of the C—H-bond by less than $\Delta l \sim 1 \cdot 10^{-4}$ Å (this effect is discussed below).

As we have supposed, the influence of temperature on stretching vibration frequency to a greater extent affects the modes where a noticeable contribution is made by bending (scissoring) vibrations of many methylene CH_2-groups in the whole chain (band d_{FR}^+ which forms as a result of Fermi resonance) (Fig. 4, *b*).

A similar effect of influence of combined vibrations is also observed for band d_w^+ (Fig. 4, *b*), which is conditioned by the impact of a CH_3-group on the nearest CH_2 oscillator. The frequencies of this vibration modes, especially d_{FR}^+, are characterized by sudden changes of frequencies ($\Delta\nu_{\max}(d_{FR}^+) \approx 2\,\mathrm{cm}^{-1}$ and $\Delta\nu_{\max}(d_w^+) \approx 1\,\mathrm{cm}^{-1}$), and respectively, C—H-bond lengths. We associate these sudden frequency changes with incremental turns of end CH_3-groups. Since nano-domains with a new hexagonal symmetry of packing of vertical molecules originate during the PT-1 development, with an inevitable turn of CH_3-groups, this complex pattern of behavior of the IR spectrum can be easily explained.

Let us consider the peculiarities of temperature dependences for frequencies of stretching vibrations of C—H-bonds in the end methyl groups shown in Fig. 6.

The presence of four different vibration modes of C—H-bonds (r_a^-, r_b^-, r^+, r_{FR}^+) in the IR spectrum of n-alkanes is conditioned by the peculiarities of the molecules' geometrical structure which contains end methyl groups. It turned out that explanation of the experimentally observed equivalence of all four valence shells of a carbon atom (one 2*s*- and three 2*p*-shells) requires (according to Pauling) the introduction of concepts of hybridization (mixing) of these several shells which have different energies. As a result of promotion and hybridization, four atomic hybrid orbitals of type sp^3 (with equivalent energies and shapes) can be obtained by means of mathematical combinations. Taking into account the theory of repulsion of valent electron pairs (RVEP), we come to the conclusion (according to Chillespi) that each carbon atom in n-alkanes is located in a tetrahedral environment of other atoms which form covalent chemical bonds with it. All valence angles in this case make up the so-called normal tetrahedral angles $\theta = 109.5°$. Accordingly, a molecule of n-alkane $H_3C(CH_2)_nCH_3$ in the equilibrium state is a trans-sequence of n methylene CH_2-groups, which form a flat zigzag ($\theta = 109.5°$) molecule skeleton. End methyl CH_3-groups, where tetrahedral angles must also be present between three C—H-bonds, are located on two ends of the trans-zigzag.

It turned out that two C—H-bonds in a methyl group are located in the same way as in methylene groups in the trans-site, i.e. perpendicularly to the molecule chain plane (out-of-plane). At the same time, the third C—H-bond of the end group lies in the trans-zigzag plane (in-plane). It should be noted than stretching vibrations of C—H-bonds in a CH_3-group, which has symmetry C_3, must be degenerate, i.e. have the same frequency. However, the connection of this group to a methylene trans-sequence removes the degeneration effect, and the C—H-bonds located in-plane and out-of-plane in relation to the trans-zigzag plane are no longer equivalent. Thus, in-plane and out-of-plane bonds have different vibration frequencies (force constants) and, accordingly, slightly differ in length. For instance, *ab initio* calculations [23] of the geometry of hydrocarbon molecules indicate a similar difference of C$-$H bond lengths. It should be also noted that the values of vibration frequencies of C$-$H-bonds in methyl groups are higher than the identical frequencies of the corresponding modes for methylene oscillators of the main chain, i.e. CH_3-groups have smaller values of bond lengths.

Paper [24] analyzed the reasons for splitting of asymmetrical stretching vibrations of C$-$H-bonds in methyl group r^- into two components r_a^- and r_b^-. It was shown that this effect is mainly conditioned by intramolecular interactions if a methylene trans-chain with a mobile (rotating) methyl group (the estimated contribution to splitting at low temperatures is $\Delta\nu \approx 8-12\,\mathrm{cm}^{-1}$). Smaller influence is exerted by intermolecular interactions (the corresponding contribution is $\Delta\nu \approx 1-3\,\mathrm{cm}^{-1}$). Moreover, it was found that values of stretching vibration frequencies for a CH_3-group are proportional to an averaged trigonometrical function of methyl group location, which depends on temperature.

Methyl group rotation during rearrangement in the PT-1 region is also indicated by the fact that the IR spectrum does not contain a band corresponding to vibration r_a^- in the trans-zigzag plane (Fig. 6, *a*). This phenomenon can be easily explained, since the initial in-plane vibration leaves the main chain plane and thus, according to symmetry rules, cannot be recorded in the given spectrum region. This effect will be analyzed in the next paper.

The temperature dependences of stretching vibrations of C$-$H-bonds in methyl end groups in Fig. 6 reveal dependences which are similar to the above-mentioned ones for vibrations of methylene oscillators in trans-sequences of the tetracosane molecule skeleton. The initial values of frequencies r_a^-, r_b^-, r^+ and r_{FR}^+, recorded at room temperature, remain virtually unchanged up to the PT-1 origination temperature.

As compared to the dependences in Fig. 4, there is a slight (about $\Delta T \approx 1.2^\circ\mathrm{C}$) delay of the start of frequency change of frequencies r_a^-, r_b^- and r^+ for d^- and d^+, which can be due to the need for activation of mobility of more massive and bulky methyl CH_3-groups in interlamellar regions.

A less uniform pattern of temperature changes of asymmetrical r_a^-, r_b^- and symmetrical r^+ vibrations as compared to d^-, d^+ makes itself conspicuous, namely, the pronounced, recurrent sudden changes in the corresponding frequencies at a temperature change in the narrow range $\Delta T \approx 45-48^\circ\mathrm{C}$ of the PT-1 development.

As we have already noted, such effects might be anticipated, to a greater extent, in the temperature dependences of changes in the frequencies which correspond to the Fermi resonance bands for d_{FR}^+ and r_{FR}^+. Indeed, Fig. 6, *b* clearly demonstrates the expected experimental results, which is not surprising, generally speaking, because a considerable contribution to these composite vibrations is made by bending (scissoring) vibrations in methylene and methyl groups, characterized by considerably lower (by almost an order) force constants as compared to valence ones. It should be also noted that frequency changes begin noticeably earlier (by $\Delta T \approx 1.3^\circ\mathrm{C}$) than for r_a^-, r_b^- and r^+.

4. Conclusion

The development kinetics of the first-order diffuse structural phase transition in monodisperse samples of tetracosane $C_{24}H_{50}$ was studied by the Fourier-transform IR spectroscopy method. Temperature changes of stretching C$-$H-vibrations in the spectral region of $\nu = 2800-3000\,\mathrm{cm}^{-1}$ were studied for 4 different modes in methylene CH_2 trans-sequences of the main chain and for 4 different modes corresponds to end methyl CH_3-groups. Specific changes of vibration frequencies of all the studied modes, conditioned by changes in the molecule packing symmetry during the first-order phase transition, were found. Moreover, it was shown that structural transformations of molecules under temperature impact initially originate in methylene trans-sequence in crystalline cores of lamellae, which is conditioned by the need for a change of the inclined arrangement of chains to a vertical one in relation to the base planes from end methyl group upon a transition from triclinic to hexagonal subcells during the solid-solid phase PT-I.

Changes in the interlamellar space, conditioned by a transformation of mutual arrangement of end methyl groups at their mutual turns in relation to each other, occur at a later stage of phase transition development.

Conflict of interest

The authors declare that they have no conflict of interest.

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