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Influence of conformational disorder on the development of solid-solid phase transitions in tetracosane

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The polymorphic transformations of tetracosane $C_{24}H_{50}$ upon heating were studied using Fourier transform infrared spectroscopy. A violation of the regularity of chains in the cores of the lamellae was revealed based on temperature changes in the progressions of rocking vibrations of CH_2- groups and stretching (skeletal) vibrations of $C-C$- bonds. The occurrence of end gauche defects was discovered, the number of which increases at each transition between intermediate rotator phases (R_I, R_{II}, R_V). A mechanism for structural rearrangements in tetracosane has been proposed.

Keywords: n-alkanes, lamellae, phase transitions, rotator phases, IR spectroscopy.

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1. Introduction

The monodisperse (with an accuracy of one C−C-bond in chain skeleton) normal alkanes (n-alkanes) C_nH_{2n+2}, commercially fabricated with different chain lengths ($16 \leq n \leq 60$) and purity $\geq 95\%$ are the long chain molecular crystals (LCMCs) featuring the most simple chemical structure. Such compounds are unique model objects to tackle at quantitative level many disputable issues on structure formation specifics in crystallization from melts and solutions, determination of relationship between the structure and physical and chemical properties of emerging supermolecular compounds, finding mechanism of structural conversions with the change of the crystal phase state and etc.

The characteristic feature of LCMCs of n-alkanes is the formation during crystallization from melts or solutions of a multilevel supermolecular structure comprising disoriented long stacks formed from specific layered lamellar nanocrystals of CSC (crystals from straightened chains) type. The nanolamellae thicknesses are comparable to the length of molecule (units nm) of considered homologue; transverse dimensions of lamellae (and, respectively, stacks) vary depending on crystallization conditions and can be from units to−tens μm, up to units of mm.

Depending on even/odd number of carbon atoms in the chain (the so called „parity effect") the symmetry of individual molecules of n-alkanes (trans- or cis-form) changes, and, as a result, the nature of regular trans-zigzags position changes in the crystalline cores of nanolamellae relative to the base planes of terminal methyl CH_3-groups — vertical position for odd homologues and inclined position for even homologues [1].

For similar model compounds, in recent years, a number of researchers, including us, obtained more accurate quantitative data on the structure and properties of n-alkanes using a set of modern physical methods, improved methodic developments and new theoretical approaches. In particular, in samples of n-tetracosane $C_{24}H_{50}$ crystallized from the melt by method of high-resolution synchrotron X-ray diffraction [2] the correct data were obtained on parameters of triclinic crystallographic subcells characterizing mutual arrangement of trans-molecules in crystallographic cores of nanolamellae (according to the International X-ray Diffraction Database of ICDD); the thicknesses of nanolamellae („long periods") were determined with high accuracy (to 0.01 nm), confirming the inclined position of molecules relative to the base planes of methyl groups. At that, small radial half-width of small-angle reflexes of all orders (about 0.2°) indicates the formation of long stacks (large number of nanolamellae in stacks), high homogeneity of nanolamellae across thickness, and regular arrangement of nanolamellae relative to each other in them, that was predictable for a monodisperse sample $C_{24}H_{50}$. It was this high-order and perfect structure of tetracosane that was used by us to initiate the studies of nature and kinetics of the crystal phase state changes under the action of temperature.

By DSC method it was identified [3,4] that in tetracosane in heating–cooling cycles the transition from solid to liquid state and vice versa occurred in two stages. It was demonstrated for the first time that if DSC method-specific errors are removed we can determine actual thermodynamic parameters of phase transitions, in particular, presence of a true temperature hysteresis. Based on the presence/absence of the true hysteresis and analysis of thermal capacity peaks it was found that low-temperature solid-solid phase transition PT-1 is the first-order phase transition, determined by change of symmetry type of molecules packing in crystal cores of nanolamellae, and high-temperature phase transition PT-2 corresponds to the second-order transition of order–disorder type (melting/crystallization of n-alkane). It was found that PT-1 in LCMCs, unlike low-molecular compounds, during heating occurs in a quite wide temperature range $\Delta T = 1-3°\mathrm{C}$, which allowed attributing such transitions to Λ-shaped diffuse phase transitions of first order [5–7]. The developed theory of such transitions [4,7] considers the heterogeneous mechanism of fluctuation occurrence of stable nanonuclei (other symmetry relative to initial one) within a crystal, and further propagation of the occurred interface due to appearance of new nuclei.

The suggested model of PT-1 development was confirmed by experiments during study *in situ* of kinetics of phase transition development in tetracosane by method of high-resolution synchrotron X-ray diffraction [2]. Analysis of the obtained *in situ* data array makes it possible to conclude that in initial nanolamellae with inclined arrangement of trans-molecules $C_{24}H_{50}$ relative to base planes of end CH_3-groups (triclinic symmetry) the nuclei with vertical arrangement of trans-zigzags occur (hexagonal packing of molecules with increased value of „long period“). Thus, during PT-1 development in the temperature range $\Delta T \approx 1°\mathrm{C}$ there is gradual disappearance of initial nanolamellae due to their transition into new lamellae with increased thickness.

Change in the packing symmetry of n-alkane molecules in crystalline cores of nanolamellae in the region of solid-solid phase transition PT-1 was also confirmed by us using Fourier-transform infrared spectroscopy (FTIR) [8–10], as frequencies of series of fundamental oscillating modes from long methylene sequences depend on the type of symmetry of subcells (energy of intermolecular interaction). It was shown that changes in the energy of intermolecular interaction result in a noticeable shift of bands of rocking and scissoring vibrations of CH_2-groups: vibration frequencies $\nu_{\mathrm{rock}} = 717.1\,\mathrm{cm}^{-1}$ and $\nu_{\mathrm{sciss}} = 1471\,\mathrm{cm}^{-1}$, inherent to subcells of triclinic symmetry in crystalline cores of nanolamellae, in narrow temperature range $\Delta T < 3°\mathrm{C}$ gradually transform into $\nu_{\mathrm{rock}} = 721\,\mathrm{cm}^{-1}$ and $\nu_{\mathrm{sciss}} = 1468\,\mathrm{cm}^{-1}$, inherent to hexagonal symmetry subcells. It should be noted that modern Fourier-transform IR spectrometers may register the changes of intermolecular interaction energy by shift of vibration frequency with an accuracy of $< 1\,\mathrm{cm}^{-1}$, thus enabling to study the thin effects during phase transitions.

It should be emphasized that besides base phase transitions (PT-1 and PT-2), n-alkane are subjected to a series of preparatory low-energy solid-solid phase transitions during heating. With the temperature increase, all n-alkanes are characterized by polymorphic transformations of its structure; in particular, a few degrees before the melting point, the intermediate states arise between the crystal and the isotropic liquid, associated with the appearance of molecules rotation around their main axis throughout the entire bulk of the crystal. Such phases are called rotator phases, R [11–14]. Note that rotation of individual molecules can occur locally due to the defects formation at any temperatures.

R-phases differ by type of crystallographic main cells and subcells, by vertical or inclined arrangement of molecules relative to the base planes of terminal groups, and by nature of mutual arrangement of nanolamellae in stacks. Occurrence of possible rotator-crystalline phases was considered in detail in previous article [10], where for tetracosane we identified the occurrence of three rotator phases during heating: R_V, R_I and R_{II}, which accompany the transition of initial subcells into hexagonal ones. Phases R_V and R_I have orthorhombic subcells, but they differ by parameters from the actual orthorhombic subcells of odd n-alkanes [15]. At that, molecules are vertical in phase R_I, and therefore the main cells are considered as face-centered orthorhombic cells, while in phase R_V molecules are arranged at a certain angle forming monoclinic main cells. Both phases are characterized by a double-layer sequence of ABAB type lamellae packaging. The high-temperature phase R_{II} is characterized by vertically arranged molecules in lamellae with hexagonal (rhombohedral) main cells and subcells, at that the lamella packing turns into a three-layer ABC with a reduced relative shift of molecules relative each other in adjacent layers.

It should be noted that in rotator-crystalline R-phases the molecular rotation is decelerated and limited by discrete turns around the axis of chain, so the additional difference of R-phases from each other is that the number of possible equally probable orientations of molecules in subcells is continuously growing.

For R-phase it is typical that in the crystalline core of nanolamellae the long-range order is preserved in macromolecules centers arrangement relative to each other (distance ordering), but at the same time the strict arrangement of planes of long methylene trans-sequences (orientation arrangement) is disturbed because of molecules rotation, which determines the type of subcell symmetry of R-phases. In hexagonal phase (R_{II}) a total orientation disorder occurs due to not only molecular rotation, but also significant weakening of the intermolecular interaction upon thermal expansion of the crystal. As a result in hexagonal subcells any orientations of planes of trans-zigzags relative to each other become equally probable.

Thus, a complex mechanism is considered for polymorphic transformations in n-alkanes through multi-stage rearrangement of the initial crystallographic structures into hexagonal packing with the successive occurrence of various types of rotator phases with the growing energy of their formation.

The present article is a continuation of the previous paper [10] on identification of the mechanism of structural transformations in n-alkanes, and kinetics of their development using Fourier-transform infrared spectroscopy.

Nature of rotator phases and mechanisms of transition between them are yet unclear. It is obvious that more high-temperature phases are characterized by the increasing degree of position and orientation disorder, if this may be interpreted as any deviations from regular crystallographic arrangement of trans-chains inherent to the low-temperature crystalline state. In this paper, we consider primarily one of the disordering processes occurring in long-chain substances: the appearance of conformational changes in the structure. We show that Fourier-transform IR-spectroscopy is sensitive to the presence of even few out-of-plane conformers that can occur in long regular sequences, and cause the above „disorder" in solid phases of n-alkanes.

The important issue is identifying the behavioral trends of the entire straightened trans-chain of n-alkane in nanolamellae cores during heating, and especially in the region of solid-solid phase transitions, and not only individual short trans-sequences, which has been already done in our previous papers [8–10]. Besides, it is necessary to identify the role of inevitably occurred during heating simplest conformational defects of kink type and of the end gauche defects, to identify interrelationship of structural transformations and appropriate polymorphous transformations of n-alkanes.

Note that in the rotator phases model described in the literature the occurrence of conformational defects based on their insignificant concentrations is generally neglected. As to our opinion, these two models shall be combined, because, as it will be showed below, it is the conformational disorder that is crucial in the processes of R-phases rearrangement.

Due to performed studies a generalized model of solid-solid phase transitions may be suggested to occur not only in n-alkanes but also in all LCMC representative samples.

2. Coupled Oscillator Model

When discussing spectra of n-alkanes it is important to classify vibrations in two types [16]. The first type — non-localized vibrations that cover large number of atoms in molecule or even the entire chain. These non-localized modes lead to occurrence of specific set of interrelated bands, so-called band sequences (progressions). Because of the non-localized nature of vibrations the number, frequencies and intensities of bands in the progression depend on both length of chain, and its conformation. Such vibrations are very sensitive to structural changes in the structure of trans-consequences. Second type of vibrations comprise movements localized in definite parts of the chain and covering small number of chemical bonds. The rocking vibrations of the methyl group at frequency near $890\,\mathrm{cm}^{-1}$ are an example of localized mode. Frequencies of these vibrations depend only on the local conformation, and, unlike the non-localized modes do not depend on both, the chain length, and conformation of the rest of the molecule.

One of the simplest methods of calculation of non-localized vibrations of long chain molecules is based on model of linear chain of coupled oscillators, where each oscillator is an electrical dipole [17,18]. The coupled oscillator model does not provide frequencies of absorption with high accuracy, unlike calculations based on geometric models and force constants of stretching and deformation vibrations. Nevertheless, the model of oscillators can be applied to many chain molecules and is widely used to determine chain structures, in particular, long-chain n-alkanes.

If there is no coupling between oscillators, in IR-spectrum only one absorption band will be observed near frequency of free uncoupled oscillator ω_0. But the interaction of oscillations leads to occurrence of system of coupled oscillators with N degrees of freedom, where N — number of monomer units in the chain or number of coupled dipoles. Such system has N normal vibrations, so we can expect splitting of the absorption band to N components provided that all these components are active in IR-spectrum. Actually already in case of infinite chain only one normal vibration is active, but for chains with finite length many of the bands of series can be active [17].

During mathematical analysis of vibrations of finite chain of coupled oscillators the models of parallel or anti-parallel dipoles are used depending on type of vibrations being studied. For instance, during wagging and rocking vibrations of CH_2-groups in normal hydrocarbons the changes of all dipole moments are parallel, but during scissoring and symmetrical stretching vibrations of CH_2-groups the adjacent oscillators vibrate in opposite directions. Besides, for finite chains the Born-Karman boundary conditions are not applicable, and cases with free and fixed ends are considered. But, when considering normal hydrocarbons the model with fixed ends is more realistic.

Simple coupled oscillator model for the chain of parallel/antiparallel dipoles with fixed ends allows determining N possible discrete vibration frequencies [17]:

$$\omega_i^2 = \omega_0^2 + 2\omega^{*2}\Big(1 \pm \cos\frac{i\pi}{N+1}\Big),\ i = 1, \ldots, N, \qquad (1)$$

where ω_0 — frequency of unperturbed oscillator, ω^* — interaction parameter, having dimension of frequency, ω_i — frequency of i-th oscillator. Set of frequencies with sign „+" corresponds to vibrations of the parallel dipoles chain, with sign „–" — chain of antiparallel dipoles. For a chain of parallel dipoles we obtain that at $i = N + 1$ vibration occurs at frequency ω_0, and at $i = 0$ — at frequency equal to $\sqrt{\omega_0^2 + 4\omega^{*2}}$. Thus, all values ω_i^2 (at $i = 1, \ldots, N$) are in range of $4\omega^{*2}$ (similar for vibrations of antiparallel dipoles). Thus, the most low-frequency band of the series is shifted towards frequency ω_0 and approaches it asymptotically as the chain length increases to infinity.

Again, note that not all vibrations of interacting oscillators can be active in IR-spectrum. For example, for system of two interacting parallel dipoles, having two normal vibrations (in phase and out of phase), in IR-spectrum only vibration of dipoles in phase is active, since, in this case, the system general dipole moment is changing. During dipoles vibration in antiphase the changes of dipole moments of oscillators suppress each other, so the vibration is inactive in the IR-spectrum. Similarly, the vibrations of dipole chain may be considered. Thus, the number of IR-active vibrations or observed bands in progressions is determined as $N/2$ or $(N+1)/2$ depending on parity of value N.

Besides, it shall be stressed that in both cases (parallel and antiparallel dipoles) the most low-frequency band in the spectrum is significantly more intensive than other bands of the series, as band intensity very quickly decreases upon approaching the high-frequency boundary of the branch [17].

We may suggest that the appearance of absorption band progressions in the spectra is a unique property of relatively short trans-sequences of CH_2-groups. At that, occurrence of progressions is due to difference in value of phase shift of vibrations of the neighboring oscillators. Because of this, the band frequencies in progressions fit into the phonon dispersion curves calculated for polymethylene chains in the trans-conformation [18–20].

Thus, by studying the temperature transformations of band progressions during heating of n-alkanes we may trace the gradual change of the structure of molecules trans-section at different phase transitions.

3. Experimental part

The paper investigates the features of kinetics of polymorphic transformation of crystallographic phases of even n-alkane in tetracosane n-$C_{24}H_{50}$ (trans-symmetry), monodisperse samples (with purity 99%) of which were prepared by Sigma-Aldrich in the form of plate flake synthesis products.

Micrometer-thick samples were prepared by depositing n-alkane flakes on NaCl polished plates. Then they were melted and subsequently slowly cooled until an equilibrium crystalline structure was obtained.

Absorption spectra were recorded in the region $\nu = 400-5000\,\mathrm{cm}^{-1}$ on Bruker IFS-88 FTIR spectrometer with a resolution of $2\,\mathrm{cm}^{-1}$. When recording the number of scans was 50. To eliminate possible distortion of the spectra, the spectra of atmospheric moisture and CO_2 were subtracted using the built-in software from Bruker.

The absorption spectra were recorded in the range of T_{room} to the melting point of sample ($T_{\mathrm{m}} = 50.7^\circ\mathrm{C}$) during stepped increase by $\Delta T = 2-3^\circ\mathrm{C}$, except for temperature range of solid-solid phase transitions, and the measurements were performed in a more detailed way, with step $\Delta T = 0.1-0.3^\circ\mathrm{C}$, to determine kinetics of polymorphous transformations. Besides, samples at each step were held at a certain temperature for 10 min to reach the equilibrium state. Temperature was measured with an accuracy of $\Delta T = \pm 0.05^\circ\mathrm{C}$ using special Chromel-Kopel differential thermocouple (using wires 0.1 mm in diameter), one end of which was placed in close proximity to the sample, and the other one — in liquid nitrogen to stabilize the temperature difference and increase sensitivity of thermocouple.

Values of frequencies in band progressions of rocking (P_k) and skeletal (R_k) vibrations of tetracosane $C_{24}H_{50}$ at $T = 19^\circ\mathrm{C}$

Designation (as per [22])	Observed frequency, cm^{-1}
P_1	717.1
P_7	728.6
P_9	744.9
P_{11}	774.1
P_{13}	816.2
P_{15}	866.6
β (P_{CH3})	891.5
P_{17}	920.7
$P_{19} + R_8$	972.6
R_{10}	980.0
R_{12}	1007.6
$P_{21} + R_6$	1016.0
R_{14}	1036.0
$P_{23} + R_{16}$	1051.9
R_{18}	1060.0
R_4	1075.6
R_2	1125.9

The separation of overlapping absorption bands in the experimentally obtained IR-spectra into individual components and their subsequent analysis were carried out using Fityk 1.3.1 program [21] and Pearson VII function. To compare the integral intensities of the bands in the progressions, and to ensure that background contributions are taken into account correctly when changing the spectra, the baseline was subtracted uniformly in the entire spectral range $\nu = 670-1200\,\mathrm{cm}^{-1}$ of each spectrum during heating. The simultaneous analysis of ~ 70 bands of each spectrum enables us to compare with high reliability the band of progressions both, with each other at the same temperature, and their transformation at each temperature step.

4. IR spectrum of tetracosane $C_{24}H_{50}$ at room temperature

The most strong progression of bands in IR-spectrum of n-alkanes occurs in region $\nu = 700-1100\,\mathrm{cm}^{-1}$, it is associated with rocking vibrations of CH_2-groups (designations as per Snyder nomenclature [22]: P_k). In this case all CH_2-groups oscillate simultaneously in same direction, i.e. like are set of parallel dipoles. High-frequency edge of this region is made by overlapping of second progression of vibrations due to stretching (skeletal) vibrations of C−C-bonds (R_k) and occupying the frequency range $\nu = 950-1150\,\mathrm{cm}^{-1}$. Besides, both progressions are greatly effected by band β (or P_{CH3}) near $890\,\mathrm{cm}^{-1}$, belonging to localized in-plane rocking vibration of the terminal methyl CH_3-group.

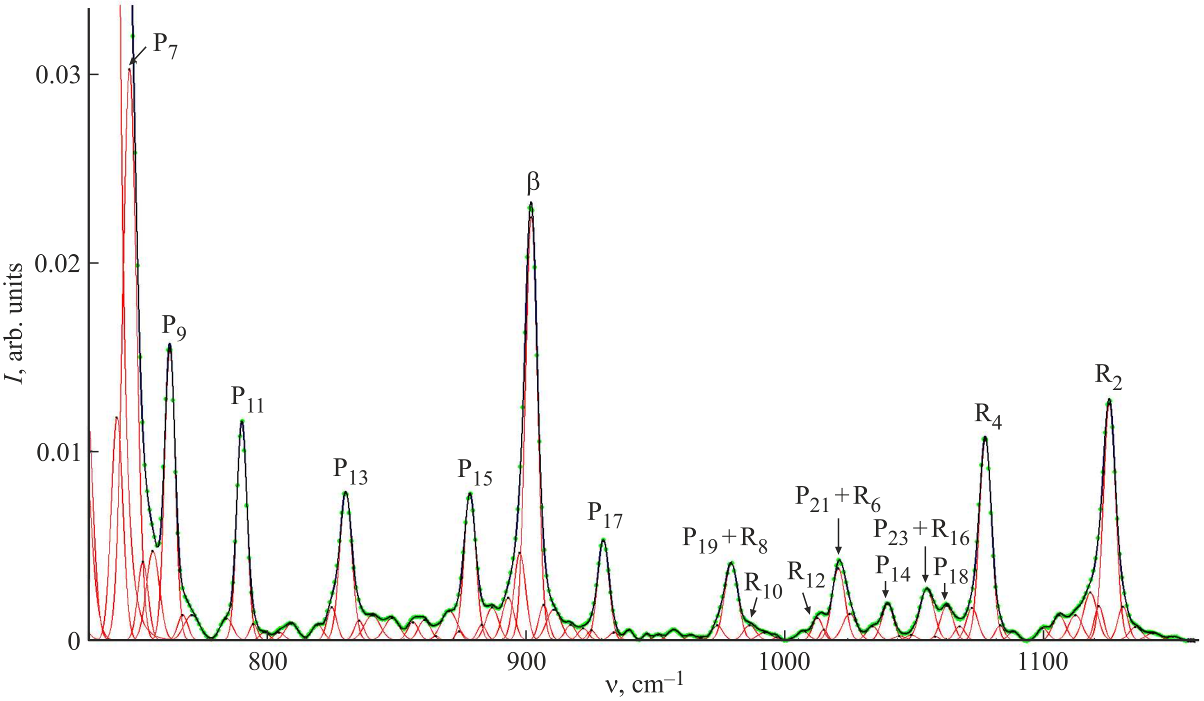

Figure 1. IR spectrum of tetracosane $C_{24}H_{50}$ at $T = 19^\circ C$. Absorption bands attributed to rocking vibration progressions of CH_2-groups (P_k) and stretching vibrations of C—C-bonds (R_k) are specified, and characteristic rocking vibration (β) of methyl CH_3-group is highlighted. The green dots designate the experimental data. Red curves represent decomposition made by program Fityk 1.3.1 using function Pearson VII. Full coincidence of experimental data and decomposition is demonstrated by a cumulative blue curve.

Spectrum of tetracosane $C_{24}H_{50}$ is presented in Figure 1, bands were assigned in accordance with papers [22,23]. Experimental values of frequencies are presented in Table.

Note that members of progression of rocking vibrations in CH_2-groups (P_k) at $k = 3$ and 5 are covered by strong limit band P_1 $(k = 1)$. We highlight the band P_7 as branch at P_1, as it is clearly expressed, and similarly is observed in spectra in paper [23], besides, frequency ideally fits on the dispersion dependence (see below).

It should be emphasized that the coupled oscillator model is ideal for describing those modes of vibration, that weakly interact (mixed) with vibrations of the terminal methyl groups. In cases when actually strong interaction occurs, the additional mode $k = 0$ or $k = N + 1$ is observed [22], it is associated with out-of-plane rocking vibration of CH_3-group. Therefore, occurrence of band P_{23} in our spectrum at $k = N + 1$ is not surprising for tetracosane, in this case the number of monomer units in the chain, i.e. CH_2-groups is $N = 22$. In this relation the rules of selection for IR-active bands can be more correctly written as follows: $N/2 + 1$ or $(N + 1)/2$ for even and odd N, respectively.

In Figure 2 frequencies of observed progression bands of rocking vibrations of CH_2-groups (P_k) are presented in form of dependence on φ/π, where phase shifts between two neighboring oscillators $\varphi = \frac{k\pi}{N+1}$, $k = 1, \ldots, N + 1$ $(k = N - i + 1, k$ — integer and odd) for chains with fixed ends. The experimentally determined frequency-phase dependence indicates correctness of made assignment of bands to progression [18,19,22–24].

For further evaluations we may assume that the most low frequency band $(717.1\,\text{cm}^{-1})$ in the area of rocking vibrations $C_{24}H_{50}$ is ω_0, and most high frequency $(1051.9\,\text{cm}^{-1})$ corresponds to $(\omega_0^2 + 4\omega^{*2})^{1/2}$. Hence, we may find the mean value of oscillator interaction parameter $\omega^* = 384.8\,\text{cm}^{-1}$. The obtained value is well consistent with the same value in [17].

From expression (1) it follows that, in accordance with the coupled oscillator model the frequency of absorption bands in progression is a simple function of number of oscillators N and parameter i, so the square of frequencies of rocking vibrations of CH_2-groups shall linearly depend on parameter $(1 + \cos\frac{i\pi}{N+1})$. The appropriate theoretical calculation with values ω_0 and ω^*, see above, is presented in form of red straight line in Figure 3. But squares of experimental values of frequencies of rocking vibrations (P_k) fit on smooth curve (Figure 3), not corresponding to simple theory of interacting oscillators. The main reason for the experimental curve deviation from the straight line is simplification of the theory; for more accurate analysis it is necessary to allow for interaction of not only the nearest neighbors, but also of the oscillators following them [17]. Probably, the maximum deviation of vibration frequencies from simple theory occurs due to effect on middle of chain of interactions with many far oscillators.

Besides progression of rocking vibrations similarly the progression of stretching (skeletal) vibrations of C–C-bonds in trans-zigzag of chain (R_k) was studied. Figure 4 presents the experimental dispersion curve of skeletal vibrations of tetracosane $C_{24}H_{50}$, it confirms correct assignment of progression bands [18,19,22–24]. In this case the number of monomer units in chain, i.e. C–C-bonds, $N = 23$ for tetracosane. At that for n-alkanes with even number of carbon atoms in chain only even members of progression R_k are observed [22] up to R_{18} for tetracosane.

The frequency-phase dependence of skeletal vibrations (R_k) is distinguished by the presence of minimum (Figure 4). According to [22], interaction between the skeletal vibrations and rocking vibrations β of the terminal methyl group leads to the necessity to use values φ_{k-1} during plotting the dispersion curve in the small phase shift area until the minimum is reached.

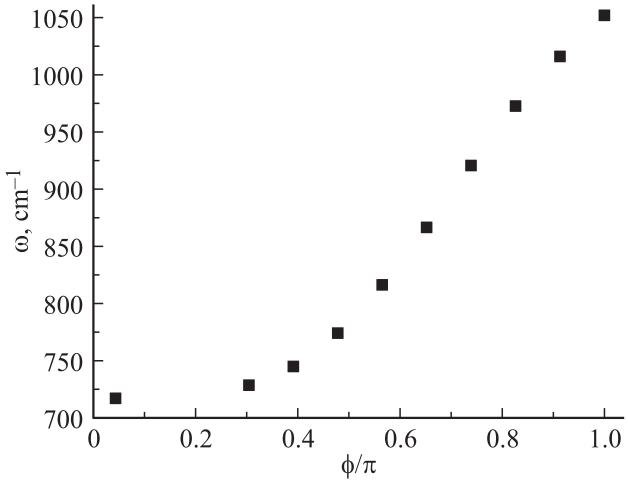

Figure 2. Experimental frequency-phase dependence for rocking vibrations (P_k) of methylene groups of tetracosane $C_{24}H_{50}$ at $T = 19°C$.

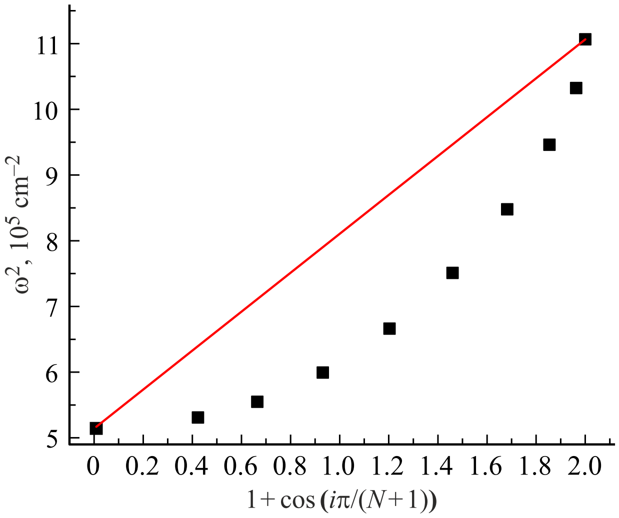

Figure 3. Squares of experimental values of frequencies of rocking vibrations (P_k) of methylene groups of tetracosane $C_{24}H_{50}$ at $T = 19°C$ versus $(1+\cos\frac{i\pi}{N+1})$. The theoretically expected linear dependence is shown in red.

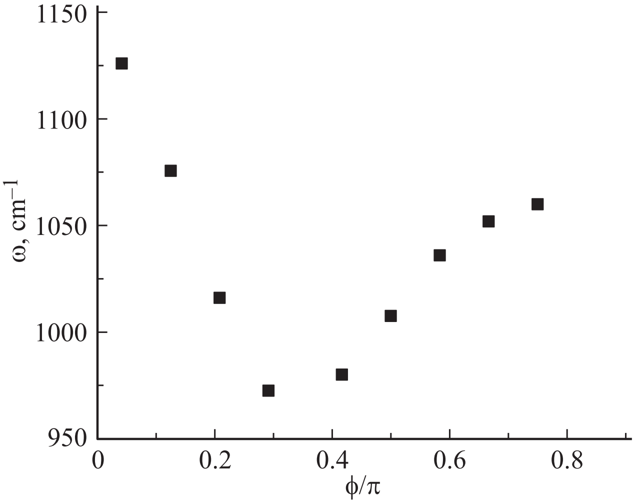

Figure 4. Experimental frequency-phase dependence for skeletal vibrations (R_k) of tetracosane $C_{24}H_{50}$ at $T = 19°C$.

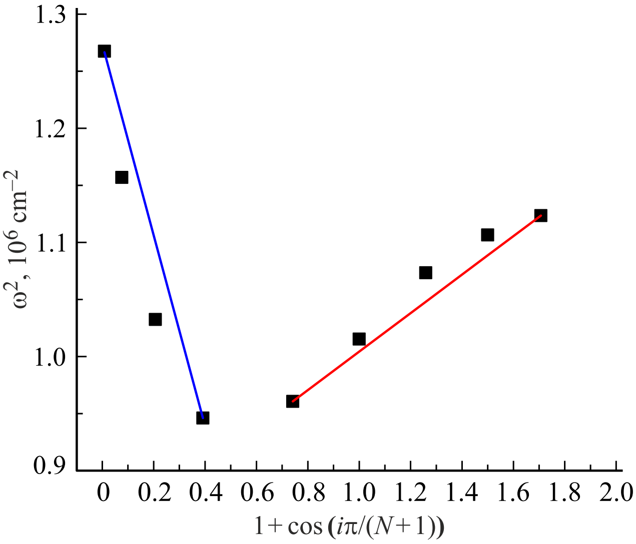

Figure 5. Squares of experimental values of frequencies of stretching vibrations of C–C-bonds (R_k) of tetracosane $C_{24}H_{50}$ at $T = 19°C$ versus parameter $(1+\cos\frac{i\pi}{N+1})$. The theoretically expected linear dependences are represented in red and blue colors.

It was discussed earlier, the square of frequencies of skeletal vibrations (R_k) shall linearly depend on parameter $(1 \pm \cos\frac{i\pi}{N+1})$. The presence of minimum on the dispersion curve may indicate transition from the antiparallel dipoles to the parallel dipoles condition at $\varphi/\pi = 0.3-0.4$, so these regions shall be considered individually. As it is difficult to determine accurate boundary values of frequencies of two regions, then suppose that end points in both regions detected by experiments belong to the

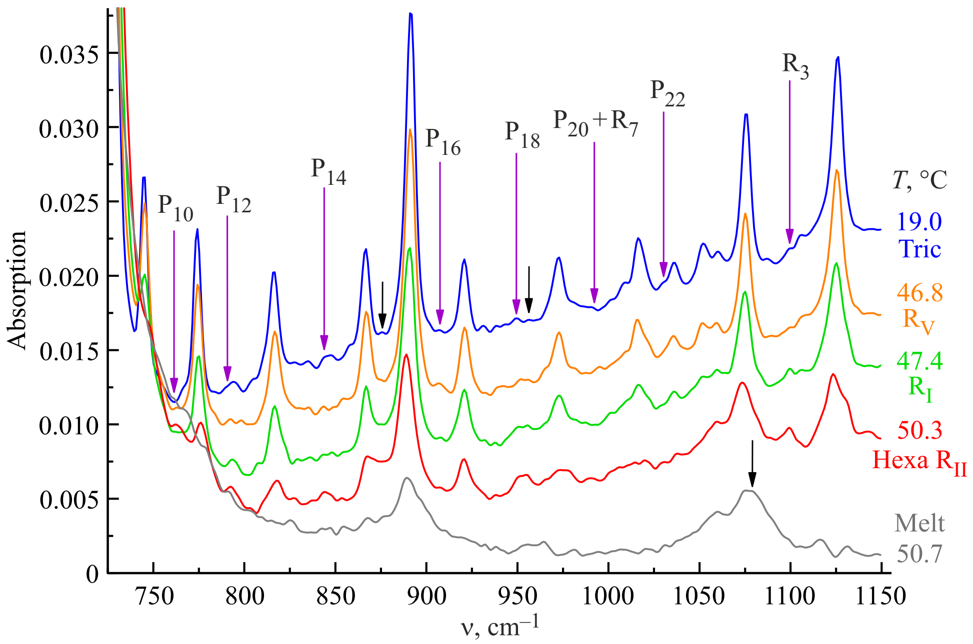

Figure 6. IR-spectra of different phase states of tetracosane $C_{24}H_{50}$ during heating from 19.0 to 50.7°C. The black arrows indicate the occurrence of bands of constant frequency associated with localized vibration modes. Purple arrows indicate the occurrence of bands P_{even} and R_{odd}.

theoretical curve. Then it is possible to evaluate the values of parameters in the region of antiparallel dipoles: $|\omega_0'| = 635.0$ and $\omega^{*\prime} = 647.5\,\text{cm}^{-1}$, and in parallel dipoles region: $\omega_0'' = 914.0$ and $\omega^{*\prime\prime} = 290.5\,\text{cm}^{-1}$. At that, ω_0' for antiparallel dipoles is a purely imaginary value which results in abrupt decrease in frequencies in this region and their transformation to zero at parameter $(1 - \cos\frac{i\pi}{N+1}) \approx 0.48$. But this does not occur: vibrations do not stop, but transit to mode of parallel dipoles at parameter value $(1 + \cos\frac{i\pi}{N+1}) \approx 0.44$.

The theoretical analysis of dependence of squares of frequencies of skeletal vibrations (R_k) can be presented in Figure 5 as a blue straight line for mode of antiparallel dipoles and red straight line for the mode of parallel dipoles (in both cases dependences are reduced to parameter $(1 + \cos\frac{i\pi}{N+1})$). Note that similarly to results for rocking vibrations the squared experimental frequencies of R_k fit on some curve (Figure 5), also not complying with simple theory of interacting oscillators.

It shall be noted that interaction parameter of antiparallel dipoles R_k with small phase shifts ($\omega^{*\prime}$) is significantly higher than for parallel dipoles of skeletal $R_k(\omega^{*\prime\prime})$ and rocking $P_k(\omega^{*})$ vibrations. We suppose that this strong interaction causes decrease in vibration frequencies with phase shift increasing of oscillators, this leads to at some time moment to transition to vibration mode of parallel dipoles R_k.

In addition to the interaction parameters of the oscillators, the force of their coupling can be evaluated by inclination coefficients of the calculated straight lines of squared vibration frequencies in the progressions shown in Figures 3 and 5. Thus, for squared frequencies of rocking vibrations (P_k) the straight line inclination coefficient κ_1 is $3.0 \cdot 10^5$, but for skeletal vibrations (R_k) in case of antiparallel dipoles $\kappa_2 = -8.4 \cdot 10^5$ and in case of parallel dipoles $\kappa_3 = 1.7 \cdot 10^5$. Thus, skeletal vibrations with small phase shifts (antiparallel dipoles) interact with each other by several times stronger than the same with large phase shifts (parallel dipoles) or rocking vibrations.

5. Temperature changes in IR-spectrum of tetracosane $C_{24}H_{50}$

The observed progressions of IR-adsorption bands of rocking (P_k) and skeletal (R_k) vibrations (Figure 1) are inherent to molecules completely present in trans-conformation without any conformation defects in initial triclinic structure of tetracosane. But significant interest relates to possible conformation changes of n-alkanes due to different polymorphous transformations occurred during heating up to their melt points T_{m}. Such transformations we observed in [10].

Figure 6 presents spectra of tetracosane in region $725{-}1150\,\text{cm}^{-1}$ at temperatures corresponding to different phases that we described in previous paper [10]. We may see that progressions of bands P_k and R_k remain clearly pronounced in initial triclinic phase (up to $T < 46.0$°C), and also in rotator phases R_V ($\Delta T = 46.0{-}47.1$°C) and R_I ($\Delta T = 47.1{-}47.5$°C), but with already decreased intensities. In high-temperature hexagonal R_{II}-phase ($\Delta T = 47.5{-}50.3$°C) intensity of all bands in progressions

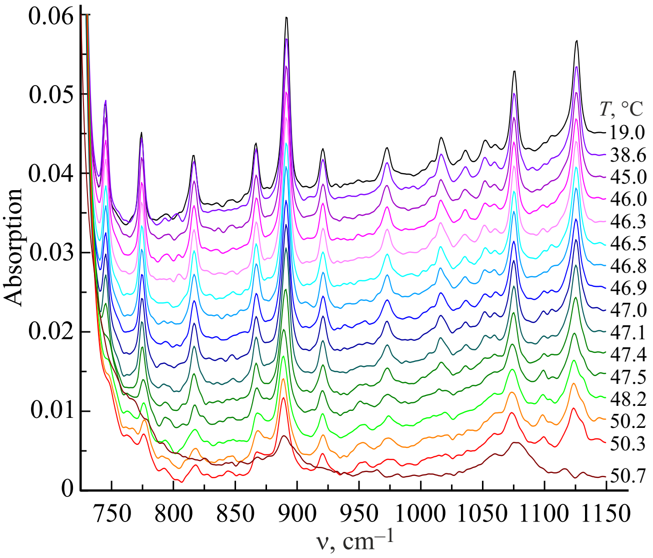

Figure 7. Array of IR-spectra of tetracosane $C_{24}H_{50}$ during heating from 19.0 to 50.7°C.

significantly decreases; yet, all bands are still visible, i. e. most of the molecules keep regular trans-conformation. In spectrum of melt (at $T = 50.7°C$) the number of bands in the progressions significantly decreases, and instead of them there remain several broad maxima, caused by the superposition of bands of large number of different conformers localized in certain parts of the chains. Note that the band of the localized node β (near $890\,cm^{-1}$) still is clearly visible.

Figure 7 presents a full array of tetracosane IR-spectra variations in region $725-1150\,cm^{-1}$ during heating. Based on such data we can note the appearance of very weak bands between members of progression of rocking vibrations. Let's emphasize that significant changes occur in the regions between the bands when heated, namely: some bands appear, others disappear without any visible dependence on temperature. By comparing it with literature data [25] we may suppose that frequencies of some new bands are identical to frequencies of bands in liquid spectrum, they are inherent to localized vibration modes.

In Figure 6 the black arrows indicate the above mentioned bands of constant frequency associated with localized vibration modes. The proximity of these frequencies to the bands corresponding to progressions from the molecule, being completely in the trans-conformation, suggests there's a slight deviation of the conformation from planar chain. In such case the specified bands shall be associated with conformers localized at ends of chains [16]. In this conformation the next-to-last bond of chain is in gauche position (g or g*), while the rest bonds — in trans (t) position. This conformer can be designated as gt_{n-4}, where n relates to common number of carbon C atoms in the chain. Note that actually the localized modes differ by „degree of localization". The localization measure is designated as an integer number m [16]. Then conformation of the end gauche-defect shall be designated as gt_m, where m is assumed as number of neighboring trans-bonds. For end gauche-defect m varies from 1 to 8 depending on vibration, i. e. at $m = 8$ vibration is strongly localized due to presence of long section of 8 trans-bonds. Thus, in our spectra of tetracosane several types of end gauche-defects gt_m were identified at frequencies $\nu = 875.4\,cm^{-1}$ $(m > 5)$, $\nu = 956.1\,cm^{-1}$ $(m > 8)$ and $\nu = 1079.0\,cm^{-1}$ $(m > 1)$, this is in full agreement with literature data [16,26].

Besides the bands associated with conformers, also new weak bands occur located approximately in the middle between k-odd bands of rocking mode (P_k) and even between k-even bands of skeletal mode (R_k); they are marked by purple arrows in Figure 6. We may suppose that these bands are associated with non-localized modes of vibrations and correspond to k-even rocking (P_{even}) and k-odd skeletal (R_{odd}) modes. As these modes in accordance with selection rules shall be IR-inactive for all-trans-chain, their appearance may indicate the occurrence of non-planar conformations. However, the coexistence of even and odd members of the progression indicates a slight deviation of the chain structure from the all-trans conformation, so it can be assumed that many of the end defects arise for the rest in planar chains (< 1 of defect per molecule). Same conclusions were made by authors of papers [16,20,26–28] during study of other homologues of n-alkanes. Moreover, bands P_{even} and R_{odd} have measured intensity also in initial triclinic structure, i. e. small part of molecules is non-planar even in most low-temperature solid phase at room temperature.

As noted earlier, during the transition from the initial triclinic phase to the high-temperature hexagonal R_{II} the intensity of bands P_{odd} inherent to all-trans chain decreases (Figure 8). We can state that all-trans molecules still remain basic and in phase R_{II}, though also non-planar molecules are clearly present. But decreased intensity of bands P_{odd} can not be actual indicator of portion of molecules that remain planar in high-temperature phase. We can suppose that the observed loss of intensity of these bands during transition into R_{II}-phase is facilitated also by other factors, additionally to changes in concentration of conformers.

Figure 8, a and c show temperature dependences of maxima positions of most strong band of progression P_1, P_7, P_9, P_{11}. It turned out that in range $\Delta T = 47.1-47.4°C$ (phase R_I) there is an abrupt change of frequencies of these bands by $\Delta\nu = 1-2\,cm^{-1}$, but for the most intense absorption bands (P_1 and P_7) the frequencies decrease (Figure 8, a), while frequencies of next members of progression (P_9, P_{11} etc.) grow up (Figure 8, c). Shifts in vibration frequencies are associated with small changes in intermolecular interactions during transformation of crystallographic cells parameters.

Figure 8, b and d present temperature dependences of integral intensities for all observed progression bands (P_{odd}). Note that during heating the band P_1 $(\nu = 717.1\,cm^{-1})$, corresponding to initial triclinic subcell, overflows into band

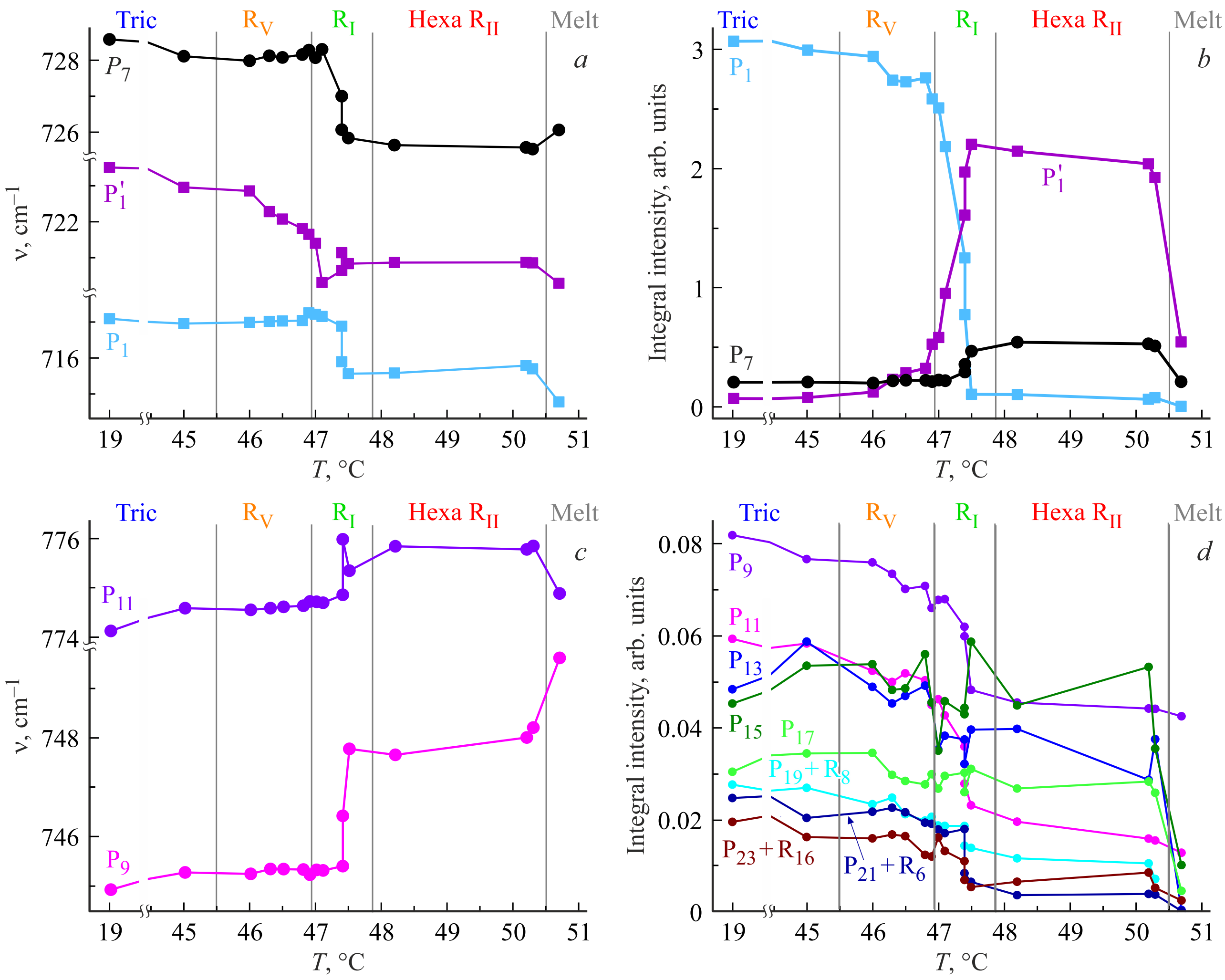

Figure 8. Temperature changes of IR-spectra of tetracosane $C_{24}H_{50}$ in region of progression of rocking vibrations (P_k): temperature dependences of maximum positions of most strong progression bands (*a, c*), temperature dependences of integral intensities for all progression bands (*b, d*). The temperature ranges of the indicated phase states are taken according to [10] (same designations are used in next Figures also).

P'_1 ($\nu = 720.9\,\mathrm{cm}^{-1}$), corresponding now to rhombohedral subcell (phase R_{II}), (Figure 8, *b*). Band P'_1 gradually increases in intensity during heating and becomes a noticeable branch in range $\Delta T = 46.0-47.4\,^{\circ}$C (phases R_V and R_I). We associate the existence of these two bands with presence of specific doublet („Davydov splitting") from several distorted orthorhombic subcells in phases R_V and R_I [10]. The increase in intensity P'_1 apparently causes some rise of neighboring band P_7 at $T = 47.4-47.5\,^{\circ}$C (phase R_I).

On the other hand, Figure 8, *d* demonstrates the decrease in integral intensities of bands of progression P_{odd} from P_9 to P_{23} during heating. At that, the most abrupt decrease in the intensities occurs in very narrow temperature range $\Delta T = 47.4-47.5\,^{\circ}$C, near transition $R_I \rightarrow R_{II}$. Moreover, we may assume that at $T = 47.5\,^{\circ}$C members of the progression P_{21} and P_{23} disappear at all, this indicates a decrease in trans-sequences length, and, hence, an increase in the number of end defects. Note that strong effect of rocking vibrations β of the terminal methyl group results in a complex nature of changes of neighboring bands P_{15} and P_{17} and a slight, on average, decrease of intensity of these bands with the temperature growth. Note that relationship between intensities of bands P_{15} and P_{17} and vibrations of the methyl group is due to the fact that the bands in the series (progression) center correspond to modes with significant dipole moments variations exactly at ends of the chains [17], therefore, these particular modes are most subjected to the effect of CH_3-group. However, in the melt, due to the violation of the regularity of the trans-zigzags, the intensity of all progression members drops significantly, leaving only poorly distinguishable bands on the background caused by the superposition of large number of different conformers.

A similar analysis of temperature dependences in the region of progression of skeletal vibrations (R_k) is given in

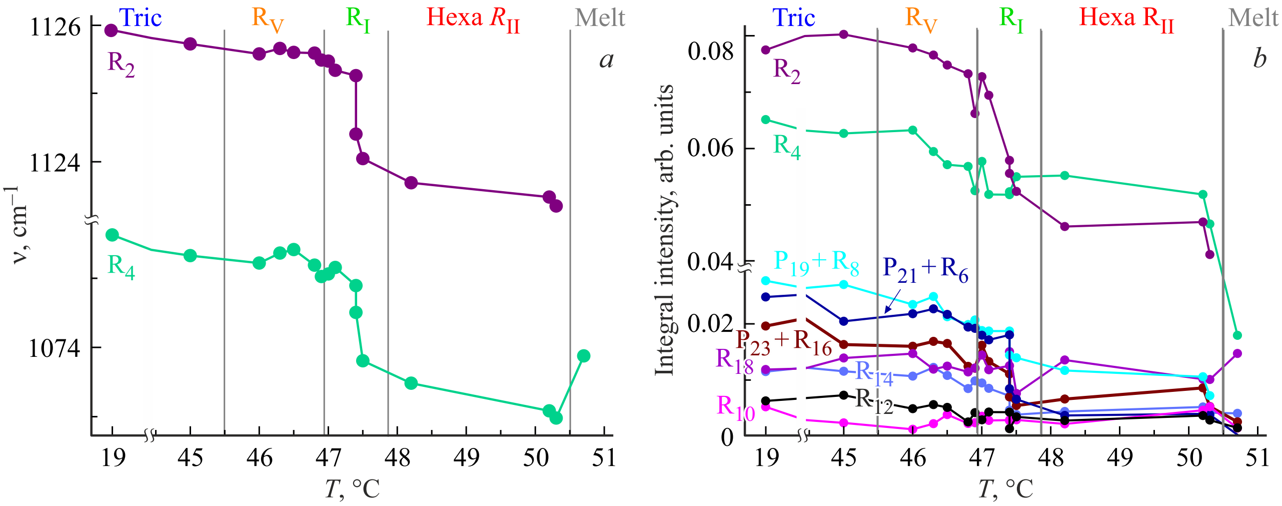

Figure 9. Temperature changes of IR-spectra of tetracosane $C_{24}H_{50}$ in region of progression of skeletal vibrations (R_k): *a* — temperature dependences of maxima position of the most intensive bands of progression, *b* — temperature dependences of integral intensities for all bands of progression.

Figure 9. Figure 9, *a* presents the temperature dependences of maxima positions of the most intense progression bands R_2 and R_4, which also demonstrate an abrupt change in the vibration frequencies decreasing again by $\Delta\nu \approx 2\,\mathrm{cm}^{-1}$ at a temperature of $T = 47.4{-}47.5\,^\circ\mathrm{C}$. Figure 9, *b* present temperature dependences of integral intensities for all observed progression bands (R_{even}). As can be seen, the intensity of band R_2 significantly decreases throughout the phase R_{I}; this band totally disappears in the melt. The intensity of band R_4 varies less clearly during transitions between rotator phases, we associate this with the occurrence of an end gauche defect at $\nu = 1079.0\,\mathrm{cm}^{-1}$ (see below), due to this, the band stays visible also in the melt spectrum. The intensity of other bands of progression R_{even} (from R_6 to R_{18}) also goes down in a very narrow range $\Delta T = 47.4{-}47.5\,^\circ\mathrm{C}$, and in spectrum of phase R_{II} only bands R_8 (more precisely, $P_{19} + R_8$) and R_{18} remain weak but visible. The band R_{18} is also observed in the melt.

Thus, intensity decreasing of bands P_{odd} and R_{even} is observed during each change in phase state of n-alkane, including during intermediate transition, at the same time the intensity of bands referred to modes P_{even} and R_{odd} of non-planar molecules rises, especially during transition into phase R_{II}. With temperature increasing in IR-spectra intermittent changes are observed, they correspond to the concentration spikes of non-planar conformers during transitions $R_{\mathrm{V}} \to R_{\mathrm{I}}$ and $R_{\mathrm{I}} \to R_{\mathrm{II}}$ But concentration of non-planar conformers shall not be considered constant in the given phase: it gradually rises with the temperature increase.

Some of the simplest and low-energy irregular conformers are end gauche defects. Figure 10 illustrates the changes in the integral intensities of bands (concentration) detected in the studied spectrum of end gauche defects gt_m during tetracosane heating. As mentioned above, even in the initial triclinic phase there is a small number of molecules with end defects. In particular, there are some minor concentrations of low-energy gt_m-defects at frequencies $\nu = 875.4\,\mathrm{cm}^{-1}$ ($m > 5$) and $956.1\,\mathrm{cm}^{-1}$ ($m > 8$); however, the number of first defects is higher by an order of magnitude, as per data on integral intensities of appropriate absorption bands. During transition into phase R_{V} the number of end gauche defects with $\nu = 875.4\,\mathrm{cm}^{-1}$ increases 1.7 times, and with $\nu = 956.1\,\mathrm{cm}^{-1}$ — it practically does not change. Then, in transition into phase R_{I}, some concentration spikes occur for defect of both types, then at $T = 47.4\,^\circ\mathrm{C}$ the defect concentrations increase 2.8 and 2.9 times, respectively, as

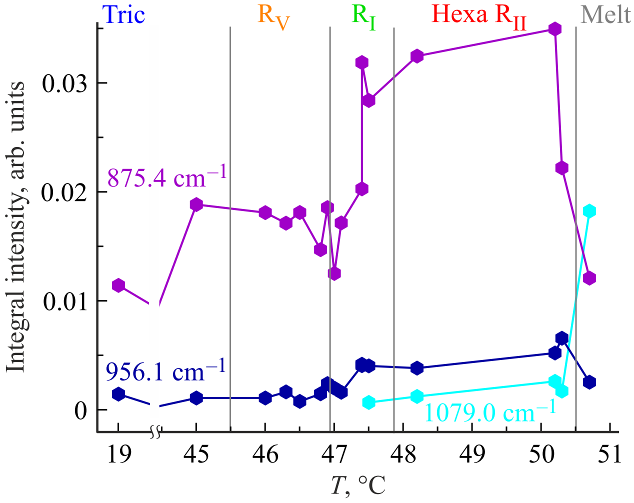

Figure 10. Temperature dependences of integral intensities of IR-bands of tetracosane $C_{24}H_{50}$, associated with end gauche defects gt_m, identified in the region of progressions of rocking vibrations of CH_2-groups (P_k) and stretching oscillations of C–C-bonds (R_k).

compared to initial values. At 47.5°C a new band $\nu = 1079.0\,\text{cm}^{-1}$ $(m > 1)$ occurs, also associated with the presence of end gauche defects gt_m, that, probably, have higher energy. In phase R_{II} the concentrations of all identified defects gradually increase. But in the melt spectrum the first two defects have concentrations going back to initial values, as the number of defects with $\nu = 1079.0\,\text{cm}^{-1}$ increases 10.7 times as compared to its value in phase R_{II}. Therefore, there remains a large number of defects with low localization degree in the melt, while in the initial triclinic and R_{V}-phases only highly localized defects in near-surface layers of lamellae are present. We may conclude that in phase R_{II} molecules with more than one defect per chain occur (probably, kinks appear in the lamellae cores as well), and their number significantly grows in the melt.

As it was mentioned earlier, the spectra of n-alkanes clearly show rather intense absorption bands attributed to the rocking vibrations of the terminal methyl CH_3-groups. The band of almost constant frequency near $890\,\text{cm}^{-1}$ (β) belongs to mixed skeletal vibrations and rocking vibrations in-plane of the methyl group, and these vibrations are localized on the ends of the molecule [22,29]. For sufficiently long molecules the mode with vibrations of both ends in phase practically degenerates into the mode with the out-of-phase ends, since the methyl groups of one molecule are located very far away and are not directly bound to each other. In case of short n-alkanes (up to $\text{C}_{10}\text{H}_{22}$) two ends of molecule, of course, clearly interact resulting in band $890\,\text{cm}^{-1}$ splitting in two symmetrical components, both are active for molecules with odd numbers. Because of this, the existence of two bands in the considered region of spectrum for tetracosane becomes clear. Note that among them the one which is more weak and having lower frequency shall be attributed to vibration β of the two terminal methyl groups in phase, and the one which is more intense and with higher frequency — to β in out-of-phase.

Thus, in tetracosane spectrum at $T = 19°\text{C}$ we may specify a strong absorption band of rocking vibration in-plane of CH_3-groups in out-of-phase (β^-) at frequency $\nu = 891.5\,\text{cm}^{-1}$, and its weak low-frequency branch associated with vibrations of CH_3-groups in phase (β^+), at frequency $\nu = 886.8\,\text{cm}^{-1}$ (Figure 11). According to [20], the vibrations β are remarkably conformation dependable, which makes it possible to study the head (or tail) structure of the hydrocarbon chain. In this regard, the temperature variation in region $890\,\text{cm}^{-1}$ was analyzed for tetracosane during heating (Figures 11 and 12). It turned out that frequencies of these localized modes do not remain constant in the studied temperature range, and also demonstrate frequency shifts at temperatures corresponding to transitions between the rotator phases.

Figure 12, *a* illustrates the temperature dependences of frequencies of β^+ and β^- bands during tetracosane heating. It is obvious that the strongest of bands, β^-, does not demonstrate frequency shifts during transition from the initial triclinic phase into R_{V}, and then into R_{I}. But weaker band β^+ demonstrates particular jumps of frequency during transition $\text{R}_{\text{V}} \rightarrow \text{R}_{\text{I}}$. It is characteristic that in a very narrow temperature range $\Delta T = 47.4{-}47.5°\text{C}$ the vibration frequencies of both bands abruptly shift by $\sim 2\,\text{cm}^{-1}$, to values that are kept in phase R_{II}, $\nu(\beta^-) = 888.7\,\text{cm}^{-1}$ and $\nu(\beta^+) = 883.6\,\text{cm}^{-1}$. Shifts of frequency β at solid-solid phase transition was also observed in [20], but no explanation of its causes was suggested. We may suppose that this band for all n-alkanes is shifted towards lower frequencies as result of conformation disorder increase.

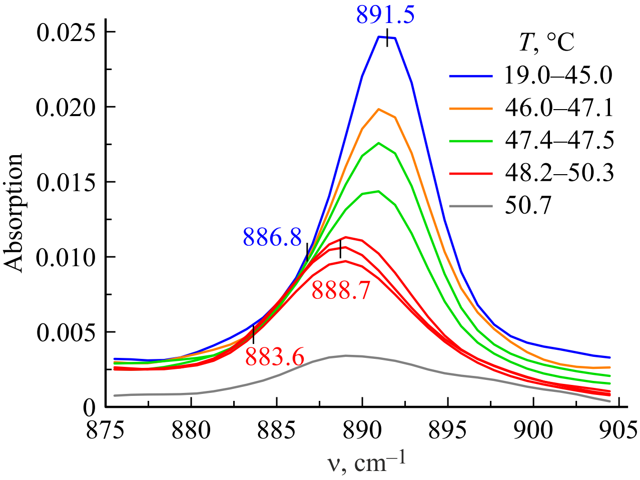

Figure 11. Temperature dependences in region $890\,\text{cm}^{-1}$, corresponding to rocking vibrations in-plane of methyl CH_3-groups of tetracosane $\text{C}_{24}\text{H}_{50}$.

Figure 12, *b* shows temperature dependences of integral intensities of the studied bands in tetracosane heating. The portion of vibrations of CH_3-groups in phase (β^+) turned out to grow during transition $\text{R}_{\text{V}} \rightarrow \text{R}_{\text{I}}$ and reach maximum value at $T = 47.4°\text{C}$, the portion of vibrations in out-of-phase (β^-) decreases, respectively. Thus, some portion of vibrations in out-of-phase transit into vibrations in phase. At $T = 47.5°\text{C}$ a sudden back transition of vibration modes is observed.

Based on Snyder papers [22,23,30] where absorption bands were attributed to homologous n-alkanes, we may suppose that frequencies of rocking vibrations β of methyl group slightly differ for n-alkanes depending on the type of symmetry of their crystal lattice: in triclinic structure a single band is observed near $893\,\text{cm}^{-1}$, but for monoclinic and orthorhombic structures the doublets 888/893 and $891/894\,\text{cm}^{-1}$ are typical, respectively. Probably, these bands can be useful during identification of crystalline structures of n-alkanes, but it should be noted that frequencies β depend exactly on definite type of interaction of the terminal methyl groups in neighboring lamellae. Therefore, these frequencies are defined by surface structure of the lamellae, not by structure of their cores [27].

It may be ascertained that significant transformations of frequencies and intensities of β-vibrations are associated specifically with the interlamellar space during transition

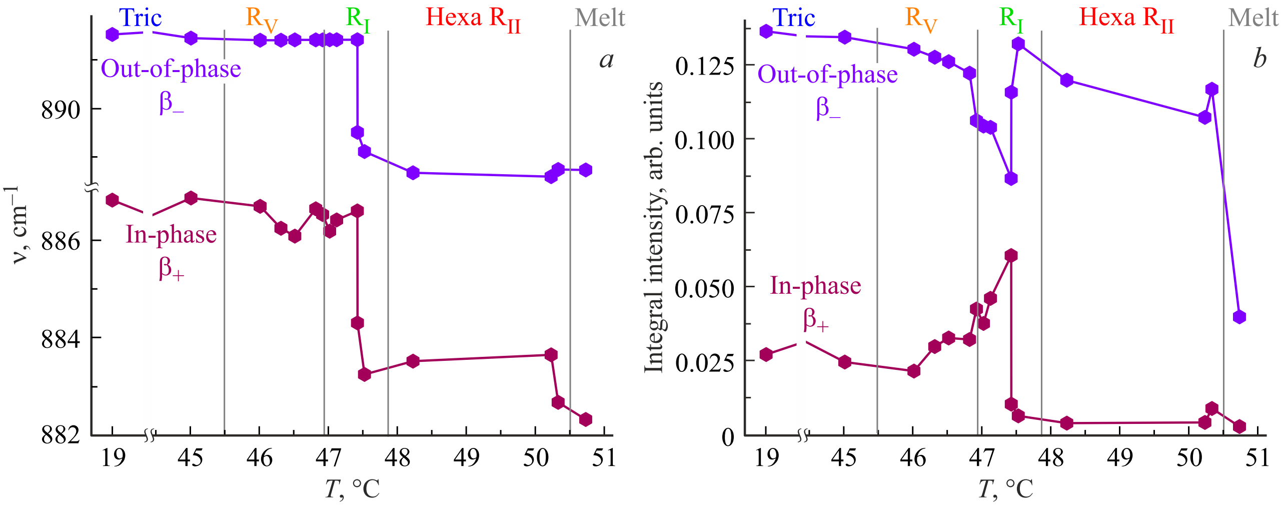

Figure 12. Temperature dependences of IR-spectra of tetracosane $C_{24}H_{50}$ in region $890\,cm^{-1}$, corresponding to rocking vibrations in-plane of methyl CH_3-groups: *a* — temperature dependences of maxima positions for absorption bands of vibrations of terminal groups in phase (β^+) and in out-of-phase (β^-), *b* — temperature dependences of integral intensities for appropriate bands.

into high-temperature phase R_{II}, which results in weakening of Van der Waals interaction between the terminal groups of neighboring lamellae ($CH_3 \cdots CH_3$) and to a possibility of some turn of terminal CH_3-groups relative to the rest of the chain. Thus, the terminal groups need to change their spatial arrangement in a certain way in a more free interlamellar space, which corresponds to transition of the two-layer stacking sequence of lamellae (ABAB) in phases R_V and R_I to the three-layer (ABC) sequence in phase R_{II}.

Also, we pay attention to the decrease in intensity of absorption bands during transition from solid phase into liquid phase. The observed effect is explained by the change in electro-optical intermolecular interactions during the transition from ordered state to „random“ one [20].

6. Conclusion

The conformation changes occurring in polymorphous transformations of tetracosane $C_{24}H_{50}$ during heating were analyzed in details based on the observed FTIR-spectra temperature variations in region $\nu = 700{-}1200\,cm^{-1}$, comprising progressions of rocking vibrations of CH_2-groups (P_k) and stretching (skeletal) vibrations of C−C-bonds (R_k), and rocking vibration in-plane of CH_3-groups (β).

Analysis of progressions of bands (P_k and R_k) was performed based on a model of one-dimensional linear chain of coupled oscillators. Due to this we could found that interaction of dipoles of skeletal R_k vibrations with small phase shifts in chain is significantly stronger than similar ones with large phase shifts or than interaction of dipoles of rocking P_k-vibrations between each other. Such strong interactions, apparently, lead to a decline in vibration frequencies as the phases shift of oscillators increases, thus resulting at a certain moment of time in transition from vibration mode of antiparallel dipoles R_k to the mode of parallel dipoles R_k. However, the simple model of coupled oscillators does not allow us to establish strict patterns in the relationship between vibrations, since for a more accurate analysis it is necessary to take into account the interaction of not only the nearest neighbors, but also the oscillators following them.

Note that absorption bands of variable frequency, i.e. depending on, e.g., chain length, are related to molecules having high degree of conformation order. Band progressions are specifically referred to as such. They are characterized by regular trans-sequences in cores of lamellae of n-alkanes, and, therefore, shall be sensitive to structural re-arrangements. Bands of constant frequency are related to definite local conformation structures, and their occurrence in spectrum ensures detection of even small deviations in regularity of chains (from all-trans conformation).

Note that in IR-spectrum of n-alkane in all regular trans-conformation only k-odd members of rocking mode (P_k) and k-even members of skeletal mode (R_k) are active. It is identified, however, that selection rules are not followed, and in progressions the bands, corresponding to k-even rocking (P_{even}) and k-odd skeletal (R_{odd}) modes occur. Such bands can be active, only if chains of n-alkanes contain at least one gauche conformer. Additionally, simultaneous coexistence of even and odd members of progression indicates insignificant deviation of chain structure from all-trans conformation, this can be associated only with the presence of conformers localized at chain ends. As it turned out, even in the initial triclinic structure a small portion of the molecules has a non-planar nature(< 1 defect per molecule). Thus, the occurred end gauche defects gt_m do not violate the rest part of planar elongated chains, and, hence, do not significantly deform the crystalline structure in the lamellae cores, which is proved by the band progressions preservation.

The increase in degree of conformation disorder during n-alkane heating is of the highest interest. It was found, that intensity of bands P_{odd} and R_{even} decreases with each transition between the rotator-crystalline phases ($R_V \to R_I \to R_{II}$), but the intensity of bands considered as modes P_{even} and R_{odd} of non-planar molecules is rising, especially during transition to phase R_{II}. Note that the concentration of end gauche conformers is not constant in the given phase: it gradually grows with temperature increase, demonstrating sharp spikes during transitions between rotator phases $R_V \to R_I$ and $R_I \to R_{II}$. Moreover, the decrease in the number of members of progressions from regular chains occurs only during transition into phase R_{II}, this indicates shorter lengths of trans-sequences in the lamellae cores (by one-two C−C-bonds), and, accordingly, significant increase of the number of end defects.

It was found that the end defects occurred during polymorphous transformations of tetracosane differ in degree of their localization in chain. Thus, in initial triclinic and R_V-phases there are only strongly localized defects located in the near-surface layers of lamellae, which is consistent with the assumption that a chain may contain no more than one defect in these phases. During transition $R_I \to R_{II}$ defects with low degree of localization occur, that permit occurrence of other defects in the chain. So, in phase R_{II} the defects occurrence at both ends of the chains is not excluded, as well as, for example, occurrence of the kink defects in the lamellae cores in addition to the end gt_m defect. Naturally, in melt spectra the end defects with low degree of localization prevail.

We may state that the local conformation of the end gauche defect is also demonstrated by rocking vibration in-plane of CH_3-groups (β), its frequency shifts towards lower frequencies upon conformation disorder increase. It was found that the most significant changes of β-vibration are inherent to transition $R_I \to R_{II}$. This fact is easy to understand, since the two-layer sequence of lamellae packaging (ABAB) here is transformed into a three-layer sequence (ABC), i.e. the contact of the terminal methyl groups $CH_3 \cdots CH_3$ in the neighboring lamellae changes drastically. Thus, due to the thermal expansion of crystal the interlamellar space increases during transition into phase R_{II}, this leads to weakening of Van der Waals interaction between lamellae, and to a potential turn of the terminal CH_3-groups relative to the rest of the chain.

We may conclude that planar regular molecules in trans-conformation, containing end gauche defects, and, probably, kinks, prevail even in high-temperature R_{II}-phase. Accordingly, if these two defects are present in the planar chain the general form of the all-trans molecule has a tendency for being preserved. This highlights the difference between the conformational disorder present in rotator phases and that in liquid [16]. Such violation of regularity turned out to be compatible with new high-temperature crystal structure where the parallel arrangement of chains is preserved, but there is a decelerated rotation of molecules around their axes, limited to discrete turns at certain angles, which leads to mutual disordering of molecules in azimuthal orientation in the lamellae. It is obvious that the end defects change the contact between lamellae, and the kink defects break the lateral packaging of chains compared to the highly ordered initial (triclinic) phase only if the kinks are not also located near the lamellae surface.

We may suppose the following mechanism of polymorphous re-arrangements of tetracosane during heating. As the temperature increases due to thermal expansion of the crystal (initially in the cores of the lamellae, as it is demonstrated in our paper [9]), at a certain moment of time the librational energy of the molecule around its main axis will become sufficient to allow the hops between several positions (orientations) of the trans-zigzag of molecules relative to their main axes. Moreover, we cannot exclude possible rototranslational (helical) movements of molecules, when molecules leave the core of the lamellae by one C−C-bond and at the same time turn by angle 180° [31]. Probably, due to this mechanism the domains with molecules packaging of „herringbone" type occur in initial triclinic structure, which corresponds to the appearance of subcells of orthorhombic symmetry. Helical motions of molecules can promote the formation of small number of end gauche defects and the transition of the initial triclinic structure to monoclinic one R_V. At that, presence of specific weak doublet of rocking vibrations (P_1/P'_1) also confirms formation of several somewhat distorted orthorhombic subcells of phase R_V [10]. Most probably, the defects are concentrated exactly at boundaries of domains of new phase, so their total concentration is not so large. With further increase in temperature, the magnitude of the doublet splitting (Davydov splitting) of rocking bands decreases during transit to phase R_I, since the degree of freedom of molecular rotation around their main axis increases: instead of two equally probable orientations of the molecules in R_V-phase their number becomes four in R_I. The subsequent increase in the molecules freedom of rotation in phase R_{II} leads to a complete orientation disorder, corresponding to hexagonal packaging of cylinders. In this case, the thermal expansion of both, the interlamellar space and the intermolecular distance in the cores of the lamellae during transition into phase R_{II} again contributes to the formation of different gauche defects. In our opinion, it is the conformational disorder that plays a key role in processes of re-arrangement of rotator-crystalline R-phases.

The results presented in this paper provide the basis for using FTIR-spectroscopy to study conformational disorder, chain end packing, and to identify crystalline structures during phase transitions of various nature.

Conflict of interest

The authors declare that they have no conflict of interest.

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