The effect of the n-alkane evenness on structural phase transitions

S A Gureva\(^1\), V A Marikhin\(^1\), I P Myasnikova\(^1\), B Z Volchek\(^2\) and D A Medvedeva\(^2\)

\(^1\)Ioffe Institute, 26 Polytechnicheskaya, St. Petersburg 194021, Russia
\(^2\)Institute of Macromolecular Compounds, 31 Bolshoy pr., St. Petersburg 199004, Russia

e-mail: swet.gurjewa@gmail.com

Abstract. The kinetics of the first-order solid-state structural transition in monodisperse \(n\)-alkanes samples of odd tricosane \(C_{23}H_{48}\) and even tetracosane \(C_{24}H_{50}\) was studied by FTIR spectroscopy. The initial nuclei location of the new phase was revealed. The process of crystal structure rearrangement is initiated in the interlayers between neighboring lamellar for odd tricosane, while the nanonuclei in even tetracosane arise in the crystalline lamellas cores. Thus, the influence of the number evenness of carbon atoms in the \(n\)-alkanes chains on the first-order structural phase transition has been proved.

1. Introduction
The purpose of this work was the investigation of structural transformations in long-chain molecular crystals (LCMCs) of normal alkanes at the temperature phase transitions (PTs) by Fourier-transform IR spectroscopy.

DSC showed [1-3] that in various LCMCs (i.e. \(n\)-alkanes, \(n\)-alcohols, mono- and dicarboxylic acids) during the transition from the solid state to the melt there are observed two types of phase transitions: a first order solid-phase (structural) transition (PT-1) occurring at temperatures \(T_{PT-1} < T_m\), and a second order phase transition of the order-disorder type or melting at \(T_m\).

In early works [4] of the structural PT-1 in LCMCs and polymers, the concept of rotator phases associated with the rotation of molecules around the main axis was introduced. More detailed studies were carried out by Sirota et al. [5, 6]. In particular, the existence of five possible rotator phases was established when \(n\)-alkanes LCMCs are heated to a completely isotropic liquid. These are more subtle stages of restructuring that arise during the PTs. The general phases for chain lengths less than 27 carbon atoms are crystal, \(R_V\), \(R_h\), \(R_{II}\), liquid. The tilted \(R_V\) and distorted-hexagonal \(R_h\) rotator phases have a bilayer stacking sequence. The \(R_{II}\) phase as well as \(R_I\) is untitled. The \(R_{II}\) is characterized by hexagonal packing of molecules within lamellas with a trilayer stacking sequence.

IR spectroscopic analysis allows one revealing the subtle shifts in molecular vibration spectra associated with a change in the type of the subcell symmetry in the crystalline cores of elementary lamellas during the PT-1.

The development kinetics of structural PT-1 in the LCMCs of \(n\)-alkanes: tricosane \(C_{23}H_{48}\) and tetracosane \(C_{24}H_{50}\) was studied in our previous works [7, 8] using FTIR spectroscopy. Temperature dependences of frequencies and intensities of rocking (in region of \(\nu \sim 720\) cm\(^{-1}\)) and bending (in region of \(\nu \sim 1470\) cm\(^{-1}\)) vibration modes of extended methylene CH\(_2\) trans sequences in the lamellas
cores were investigated. There is a correlation between the absorption band positions in these vibrational regions of CH₂ groups and type of the crystalline subcell formed of trans methylene sequences [9]. This correlation in n-alkanes is determined by the potential energy of molecules in the equilibrium crystal field, i.e. this energy is caused mostly by van der Waals interactions. The observed in [7, 8] frequency changes are evidence of the crystal structure rearrangement. We explained the smooth variation in the frequency by gradual attenuation of the van der Waals interaction between individual molecules due to thermal expansion. It was shown that in the lamellas cores PT-1 develops to a heterogeneous mechanism in a temperature range \( \Delta T = 40.3 - 41.7^\circ C \) for tricosane and \( \Delta T = 45.5 - 47.6^\circ C \) for tetracosane in accordance with the diffuse phase transitions theory [10]. According to the theory, nanonuclei of new phases appear in the initial phase volume, and then there is the interface gradual propagation to the entire volume of the sample. It was found that the transition is due to a change in the crystallographic subcells symmetry with the transformation of the initial into the hexagonal one.

From a fundamental point of view, it was necessary to find out the location of an initial hexagonal phase nuclei in the volume of the former one. The nucleation can occur both in the lamellas cores and in the interlamellar space. Thus, the study of changes in the interlamellar layers formed by the van der Waals contacts between the terminal methyl CH₃ groups of the neighboring lamellas was of considerable interest.

2. Samples
The objects of this research were normal alkanes of different chain evenness: tricosane C₂₃H₄₈ and tetracosane C₂₄H₅₀ produced by Sigma–Aldrich Company. The samples used have a purity of about 99.9% and are monodisperse with an accuracy of one carbon-carbon bond. The chains length or the thickness of each lamella of the test samples is approximately 3 nm.

Depending on the number of methylene groups, crystallization conditions and sample temperature, regular trans sequences in the lamella cores can form crystalline unit subcells of different symmetries. In particular, tricosane which is a representative of n-alkanes with an odd number of carbon atoms in a chain, it has crystallographic subcells of orthorhombic symmetry at room temperature. In this case, the n-alkane molecules are located perpendicular to the lamellas base planes from the terminal methyl groups. At the same time, the even n-alkane tetracosane has triclinic symmetry, the packing of which is the densest when considering molecules as cylindrical rods [11]. The chains tilting relatively to the base planes from the terminal CH₃ groups is determined by the so-called even / odd effect of the CH₂ methylene groups number.

Van der Waals contact of nearby lamellas for odd n-alkanes is shown schematically in figure 1. The lamellae interaction is carried out by terminal hydrogen atoms, which are located along the axes of their molecules.

![Figure 1](image-url)

**Figure 1.** 3D modeling of molecular interaction using the ArgusLab 4.0.1 program.
In the literature, there is a very limited number of publications on the study of changes in C–H bonds stretching vibrations during the PT-1. It was believed that such vibrations are less sensitive to changes in phase state than the other types of vibrations (rocking, bending, etc.). Our task was to investigate in more detail the kinetics study of the solid-phase transition PT-1 to the hexagonal phase in the samples under study. For this reason, changes in the vibrational frequencies of C–H bonds in methylene sequences and terminal methyl groups were researched during phase transitions, what characterizes the differences in vibrational behavior in the lamella cores and interlamellar layers. Thus, we drew attention to the possibility of studying structural changes in the interlamellar space.

3. Experiment

The samples with a thickness of 10 – 20 μm were prepared by depositing the synthesis products – lamellar flakes of tricosane C_{23}H_{48} and tetracosane C_{24}H_{50} – on NaCl plates, their melting, and subsequent slow cooling until an equilibrium crystalline structure was obtained.

The absorption spectra of monodisperse samples of tricosane and tetracosane were recorded on IFS-88 FTIR spectrometer (Bruker, Germany). Temperature variations of IR spectra were studied in the interval from 19 to 51°C with steps ΔT = 2°C and ΔT = 0.1°C in the region of PT-1 and the sample was kept during 10 min until reaching the equilibrium state at the given temperature.

To detect changes in the interlamellar layers, stretching vibrations of C–H bonds in the spectral region \( \nu = 2800 – 3000 \text{ cm}^{-1} \) was studied that shown in figure 2. According to [12], eight absorption bands are observed in the frequency range under study, the frequencies of which differ slightly for \( n \)-alkanes with various chain lengths. Adopted the following notations bands:

- \( r^+ \) are the symmetric stretching vibrations in terminal CH_{3} groups (\( \nu(C_{23}H_{48}) = 2871.0 \text{ cm}^{-1} \) and \( \nu(C_{24}H_{50}) = 2870.6 \text{ cm}^{-1} \));
- \( r^- \) are the antisymmetric stretching vibrations in CH_{3} groups, in-plane and out-of-plane components, respectively (\( \nu(C_{23}H_{48}) = 2960.6 \) and 2955.0 cm\(^{-1}\), \( \nu(C_{24}H_{50}) = 2961.5 \) and 2953.5 cm\(^{-1}\));
- \( d^+ \), \( d^- \) are the symmetric and antisymmetric stretching vibrations in CH_{2} groups in chain (\( \nu(C_{23}H_{48}) = 2849.0 \) and 2918.4 cm\(^{-1}\), \( \nu(C_{24}H_{50}) = 2848.7 \) and 2916.1 cm\(^{-1}\));
- \( d^-w \) are the symmetric stretching vibrations in w-CH_{2} groups adjacent to CH_{3} (\( \nu(C_{23}H_{48}) = 2858.3 \text{ cm}^{-1} \), \( \nu(C_{24}H_{50}) = 2859.3 \text{ cm}^{-1} \))

Figure 2. The IR spectrum of tetracosane C_{24}H_{50} in the region of stretching vibrations at 19°C. Spectrum decomposition was performed in the Fityk 0.9.8 program.
In addition, there are 2 bands ($r_{FR}$ and $d_{FR}$) due to the Fermi resonance of symmetric stretching vibrations $r^+$ and $d^+$ with an overtone of the CH$_2$ groups bending vibrations inside the crystalline lamellas core.

4. Results and discussions
It was found that the C–H stretching vibrations undergo a frequency shift about 1 – 2 cm$^{-1}$ in the PT-1 region. The observed frequencies changes for different types of C–H stretching vibrations in the studied $n$-alkanes are shown in figures 3 and 4.

![Figure 3](image)

**Figure 3.** Temperature dependences of the absorption band positions of $r^+$ (a), $r_a^-$, $r_b^-$ (b), $d^+$, $d^-$ (c) and $d_{w}^-$ (d) stretching vibrations of C–H bonds in the tricosane C$_{24}$H$_{50}$.

The temperature study of the methylene CH$_2$ stretching vibrations in the lamellas cores confirms the results obtained in our previous works [7, 8]. The change in the stretching vibrations frequencies in the lamellas cores occurs in the temperature range $\Delta T = 40.3 – 41.0^\circ$C for tricosane (figure 3(c)) and $\Delta T = 45.0 – 47.4^\circ$C for tetracosane (figure 4(c)). Nevertheless, for tricosane, the complete change in the frequencies of stretching vibrations finishes already at 41.0$^\circ$C, while changes in rocking and bending vibrations continues up to 41.7$^\circ$C. This underlines the fact that the structural PT-1 proceed differently in $n$-alkanes of different evenness.

Figure 3(a, b) demonstrates that for tricosane the PT-1 begins with a change of the stretching vibrations in the terminal CH$_3$ groups in $\Delta T = 39.5 – 41.0^\circ$C. Consequently, it can be established that the first nuclei of a new phase appear in the interlamellar space in odd $n$-alkanes. At 40.6$^\circ$C a sharp change in the stretching vibrations occurs, which we associate with the transition of molecules to a hexagonal stack, at which contact with other molecules is formed in the adjacent lamella. We believe that this process corresponds to the rotator transition from the R$_0$ to the R$_{III}$, in which the layer stacking changes from ABAB to ABC (figure 5) as was shown by Sirota using x-ray and DSC method [5, 6].

The rearrangement of the tetracosane crystal structure manifests in changes of vibrations in the terminal groups at more higher temperatures 46.2 – 47.8$^\circ$C (figure 4(a, b)) as compared to the vibrations inside the lamellas. It can be concluded that for even $n$-alkane C$_{24}$H$_{50}$ the initial nuclei of a new phase arise in the lamellas cores and then gradually extend over the entire volume. We explain...
this effect by the fact that it is energetically beneficial to verticalize of initially tilted molecules in triclinic subcells before a complete transition to the hexagonal phase. The terminal groups maintain the structure integrity up to 47.0°C, when all the molecules become vertical. The abrupt changes observed in each components of stretching vibrations correspond to this (figure 4). In our opinion, this is the $R_V - R_I$ tilting transition [5, 6]. It is interesting to note that in the temperature range $\Delta T = 47.0 - 47.8^\circ C$, a linear change in frequency occurs, appropriating to the thermal expansion of the crystals. The transition to the $R_{II}$ phase with a change in the layer stacking occurs at a temperature of 47.5°C, which is consistent with [5, 6].

![Figure 4](image1.png)  
**Figure 4.** Temperature dependences of the absorption band positions of $r^+$ (a), $r^-_a$, $r^-_b$ (b), $d^+$, $d^-$ (c) and $d^{+}_{w}$ (d) stretching vibrations of C–H bonds in the tetracosane $C_{24}H_{50}$.

![Figure 5](image2.png)  
**Figure 5.** Layer stackings a) ABAB and b) ABC. Cylindrical rods approximate extended trans molecules of $n$-alkanes.

Upon transition to the hexagonal phase, the component of antisymmetric C–H stretching vibrations in terminal CH$_3$ groups corresponding to the perpendicular vibrations relative to the molecules axis disappears in both samples (figures 3(b) and 4(b)). This fact confirms the molecular packing modification, in which the terminal groups interactions of neighboring lamellas have changed.
It is characteristic for both samples that the symmetric C–H stretching vibrations in w-CH$_2$ groups adjacent to CH$_3$ behave similarly to the vibrations in the terminal groups (figures 3(d) and 4(d)). The rather complex nature of the behavior of C–H methylene vibrations attracts attention in tetracosane (figures 4(d)), which is due to a strong change in the environment of the molecules during the transformation of triclinic subcells, in which the molecules move from a tilted to a vertical position relative to the lamellas base planes.

5. Conclusion
The kinetics of the first-order solid-state structural transition in monodisperse n-alkanes samples of odd tricosane C$_{23}$H$_{48}$ and even tetracosane C$_{24}$H$_{50}$ was studied by FTIR spectroscopy. It is shown that the hexagonal nucleus in the initial (orthorhombic or triclinic) phase matrix appears by the fluctuation mechanism in a narrow temperature range $\Delta T \approx 2^\circ$C in accordance with the diffuse phase transitions theory. The present investigation made it possible to study in more detail the sequential structure rearrangement of different evenness n-alkanes during the phase transition. In addition, the initial nuclei location of the new phase was revealed. Studying the behavior of the C–H bonds stretching vibrations in methylene sequences in the lamellas cores and in terminal methyl groups in the interlamellar layers allowed to find that the process of crystal structure rearrangement is initiated in the interlayers between neighboring lamellar for odd tricosane C$_{23}$H$_{48}$, while the nanonuclei in even tetracosane C$_{24}$H$_{50}$ arise in the crystalline lamellas cores. Thus, the influence of the number evenness of carbon atoms in the n-alkanes chains on the first-order structural phase transition has been proved. It was also shown that upon heating n-alkanes, the transition to the hexagonal structure is accompanied by mutual transitions between the different rotator phases R$_I$, R$_{II}$ and R$_V$.

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References
[1] Egorov V M, Marikhin V A and Myasnikova L P 2013 Physics of the solid state 55 975
[2] Egorov V M and Marikhin V A 2016 Physics of the solid state 58 2482
[3] Borisov A K, Egorov V M and Marikhin V A 2019 J. Phys.: Conf. Ser. 1400 055020
[4] Muller A 1932 Proc. R. Soc. London, Ser. A 138 514
[5] Sirota E B, King H E, Singer D M and Shao H H 1993 Chem. Phys. 98 5809
[6] Sirota E B and Singer D M 1994 Chem. Phys. 101 10873
[7] Marikhin V A, Gur’eva S A, Myasnikova L P, Volchek B Z and Medvedeva D A 2019 Physics of the solid state 61 1785
[8] Gureva S A, Marikhin V A, Myasnikova L P, Volchek B Z and Medvedeva D A 2019 J. Phys.: Conf. Ser. 1400 055040
[9] Zerby G, Magni R, Gussoni M, Moritz K H, Bigotto A and Dirlikov S 1981 Chem. Phys. 75 3175
[10] Malygin G A 2001 Physics-Uspethki 171 187
[11] Kitaygorodskiy A I 1971 Molecular crystals (Moscow: Science) p 424
[12] MacPhail R A, Straws H L and Snyder R G 1984 J. Phys. Chem. 88 334