Crystal structure transformations during phase transitions in homologues of n-alkanes: C_{23}H_{48}, C_{24}H_{50}, C_{25}H_{52} as revealed by FT-IR spectroscopy

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Abstract. The dependence of the IR absorption spectrum on the type of symmetry of crystallographic cells allowed us to investigate the kinetics of phase transitions. It is confirmed that the first order solid-phase transition develops by a heterogeneous mechanism in a narrow temperature range \( \Delta T \geq 1 \) K.

1. Introduction
One of the most important fields of solid-state physics is the investigation of the phase transitions (PT), especially their nature and evolution in solids, including polymers and long-chain molecular crystals (LMC). The study of PT in LMC allows to reveal the common quantitative structure/property relationships since LMC are a model of chemically defectless objects for the investigations.

It is known [1] that two types of phase transitions occur during heating of n-alkanes to the melting point \( T_m \). The first type is a first order solid-phase structural transition (PT-1) with \( T_{PT-1} \leq T_m \). It is associated with a change in the type of symmetry of the elementary crystallographic subcells. The second type is an order-disorder transition at \( T_m \) (melting n-alkanes).

DSC (differential scanning calorimetry) showed [2] that the PT-1 in LMC occurs in the rather narrow temperature ranges \( \Delta T \neq 0 \), as it should be in the case of ideal single crystals [3]. Such transitions with \( \Delta T \geq 1 \) K are called diffuse first order phase transitions.

The purpose of this work is to study the kinetics of structural transformations at the phase transition temperatures in LMC of n-alkanes by IR - Fourier spectroscopy.

2. Samples
The most commonly used n-alkanes are \( C_nH_{2n+2} \) with the number of CH\(_2\) methylene groups in the chain \( n = 20 \div 40 \). The crystallization of n-alkanes from melts or solutions results in formation of the stacks of numerous nano-lamellae several nanometers thick (figure 1). The transverse dimensions of the lamellae can reach tens of micrometers [4]. The lamellae are formed by a set of linear chains connected by van der Waals forces. Depending on the number of methylene groups, crystallization conditions and sample temperature, regular trans-sequences in the lamella cores can form crystalline unit cells of different symmetries, such as monoclinic, triclinic, orthorhombic and hexagonal.
The objects of this research were tricosane (C_{23}H_{48}), tetracosane (C_{24}H_{50}) and pentacosane (C_{25}H_{52}) produced by Sigma–Aldrich Company. The crystallization of tricosane and pentacosane is accompanied by the formation of an orthorhombic subcell (figure 2). The crystallization of tetracosane produces a triclinic subcell (figure 3), molecular chains being stacked at an angle to the crystal axis. The slope of the chains in the lamellae is determined by the even/odd effect of the number of CH_{2} methylene groups.

Figure 1. Crystal structure of LMC n-alkanes C_{n}H_{2n+2}.

Figure 2. Projection of the tricosane C_{23}H_{48} or pentacosan C_{25}H_{52} orthorhombic subcell onto the plane.

Figure 3. Projection of the tetracosane C_{24}H_{50} triclinic subcell onto the plane.

Our task was to investigate the kinetics of the solid-phase transition PT-1 in the samples under study. That is, the transformation of the initial elementary crystallographic subcells into hexagonal ones in which the molecular chains are arranged vertically relative to the crystal axis in all the investigated samples.

3. Experiment
One of the effective techniques for studying the PTs of n-alkanes is IR-Fourier spectroscopy, since the IR absorption spectrum significantly depends on the type of symmetry of the crystallographic cells. This is due to the fact that the force constants of the excited oscillations transform when one type of unit subcell turns into another one, because of the change in the characteristic distance between molecular chains. The force constant determines the oscillation frequency, and accordingly, such transitions are felt in the IR spectrum.
When IR radiation spectrum is applied to \( n \)-alkanes, certain functional groups in molecules (in our case, CH\( _2 \) methylene groups in trans-zigzags and CH\( _3 \) end groups) are excited, which leads to the appearance of characteristic absorption bands corresponding to various types of vibrational motions of these groups.

Figures 4, 5, 6 show the infrared absorption spectrum of the samples investigated in the range of 500–3200 cm\(^{-1} \) at room temperature and temperature above the solid transition temperature, determined with the help of a Bruker IFS-88 FTIR spectrometer (Germany).

Comparison of the frequencies of the characteristic vibrations of the spectrum (figure 4) with the data available in the literature for the frequencies of the rocking \( (\nu \sim 720 \text{ cm}^{-1}) \) and deformation (bending) \( (\nu \sim 1470 \text{ cm}^{-1}) \) vibrations of the CH\(_2\)-groups and the stretching vibrations of the CH-bonds \( (\nu \sim 2800 – 3000 \text{ cm}^{-1}) \) really indicates that in the C\(_{23}H_{48}\) crystals have orthorhombic unit subcells at the room temperature. For the orthorhombic subcell, the Davydov splitting of the absorption bands takes place, which we observe in the form of doublet bands in the studied spectral regions [5].

With \( T > T_{PT-1} \), the IR spectrum (figure 4) indicates the transition of the initial orthorhombic cells to hexagonal ones, since the changes in the frequencies of the rocking and deformation (bending) vibrations of the CH\(_2\)-groups are observed in accordance with the available literature data [6].

Similar discourse was carried out for pentacosane C\(_{25}H_{52}\) (figure 5).

Figure 4. IR-spectrum of C\(_{23}H_{48}\) and vibration types of functional groups.

Figure 5. IR-spectrum of C\(_{25}H_{52}\) and vibration types of functional groups.

Figure 6. IR-spectrum of C\(_{24}H_{50}\) and vibration types of functional groups.
The same way figure 6 demonstrates that the triclinic subcell of tetracosane \( \text{C}_{24}\text{H}_{50} \) becomes hexagonal one too.

To identify the kinetics of PT-1 in our samples, we recorded a large number of spectra with a stepwise increase in temperature from 292 K to 325 K with a step of 2 K before and after the PT and with a step of 0.1 K in the region of PT.

4. Results and discussions

The changes in the frequency of the most intensive bands of the rocking and deformation (bending) vibrations of the \( \text{CH}_2 \)-groups in the regions of 720–730 cm\(^{-1}\) and 1460–1470 cm\(^{-1}\), respectively, evidences the specificity of structural changes in the PT-1 region.

Figure 7 demonstrates that instead of doublets of the 719.6 / 729.0 cm\(^{-1}\) and 1463.8 / 1472.6 cm\(^{-1}\) bands characteristic of the tricosane \( \text{C}_{23}\text{H}_{48} \) sample with orthorhombic subcells, in the region of the PT-1 at \( T \approx 40.3 – 41.7 \) °C appear the single bands \( \nu = 721.3 \) cm\(^{-1}\) and \( \nu = 1468.2 \) cm\(^{-1}\), characteristic of hexagonal unit subcells. The new phase is observed in the temperature range of 5.8 °C.

![Figure 7. Temperature changes of doublets of bands in the \( \text{C}_{23}\text{H}_{48} \).](image)

Figure 8 demonstrates that instead of the 717.0 cm\(^{-1}\) and 1471.4 cm\(^{-1}\) bands characteristic of the tetracosane \( \text{C}_{24}\text{H}_{50} \) sample with triclinic subcells, in the region of the PT-1 at \( T \approx 45.5 – 47.6 \) °C appear the bands \( \nu = 721.0 \) cm\(^{-1}\) and \( \nu = 1468.0 \) cm\(^{-1}\), characteristic of hexagonal unit subcells. The new phase is observed in the temperature range of 2.7 °C.

Figure 9 demonstrates that instead of doublets of the 719.7 / 729.8 cm\(^{-1}\) and 1463.2 / 1472.7 cm\(^{-1}\) bands characteristic of the pentacosane \( \text{C}_{25}\text{H}_{52} \) sample with orthorhombic subcells, in the region of the PT-1 at \( T \approx 47.0 – 48.6 \) °C appear the bands \( \nu = 721.2 \) cm\(^{-1}\) and \( \nu = 1468.3 \) cm\(^{-1}\), characteristic of hexagonal unit subcells. Besides the bands \( \nu = 726.0 \) cm\(^{-1}\) and \( \nu = 1466.0 \) cm\(^{-1}\) are very weak compared to those considered earlier. The new phase is observed in the temperature range of 5.5 °C.

The bands of 720 – 721 cm\(^{-1}\) and 1467 cm\(^{-1}\) observed in all the samples at \( T \approx T_m \) are attributed to rocking and bending oscillations, accordingly, characteristic of isolated \( \text{n} \)-alkane chains.

These data are the IR-spectroscopic confirmations of the structural phase first order transition in a narrow temperature range.

Based on the data we can conclude that the transition from the triclinic phase with inclined chains requires larger and more prolonged supply of heat to transfer chain in a vertical state of the hexagonal phase. This is confirmed by the fact that the enthalpies of these transitions are sufficiently high: for tricosane \( \text{C}_{23}\text{H}_{48} \) – 61 J / g, for tetracosane \( \text{C}_{24}\text{H}_{50} \) – 89 J / g, for pentacosane \( \text{C}_{25}\text{H}_{52} \) – 79 J / g.
Figure 8. Temperature changes of bands in the C_{22}H_{50}.

Figure 9. Temperature changes of doublets of bands in the C_{25}H_{52}.

The even/odd effect of the number of methylene groups in the chains is presented in figure 10. This effect manifests both in the initial structure of the samples and in the development of the PT-1. As a consequence, the transition from the triclinic subcell requires a larger temperature range.

Figure 10. Temperatures of PTs.

5. Conclusion
IR-Fourier spectroscopy was used to study the kinetics of the first order solid-phase structural transition in monodisperse samples. It is shown that, in a narrow temperature range ΔT ≥ 1 K, the new nucleus (hexagonal) phase appears by the fluctuation mechanism. Moreover, the new phase is gradually spreading over the entire volume of the initial phase, promoting new interfacial nuclei in accordance with the theory of diffuse first order phase transitions.
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