Solid-state phase transition in n-alkanes of different parity

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Abstract. The kinetics of the first-order solid-state structural transition in monodisperse n-alkanes samples of tricosane C_{23}H_{48} and tetracosane C_{24}H_{50} was studied by DSC and 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 lamella 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 a fundamental study of temperature phase transitions (PTs) in long-chain molecular crystals (LCMCs), using the example of normal alkanes with the general formula CH_{n}(CH_{2})_{m}CH_{3}, by differential scanning calorimetry (DSC) and IR Fourier spectroscopy.

N-alkanes are model systems for studying the regularities of PTs in LCMCs and polymers, and also have important practical applications as PCM (phase change materials). The objects of research are monodisperse samples of n-alkanes tricosane C_{23}H_{48} and tetracosane C_{24}H_{50} with a very high purity ~ 99.9% produced by Sigma – Aldrich Company. During crystallization of n-alkanes, thin lamellar crystals are formed, in which depending on the number parity of methylene CH_{2} groups molecules stacked in triclinic or orthorhombic subcell for even and odd n-alkanes, respectively.

Under studying of various LCMCs (i.e. n-alkanes, n-alcohols, mono- and dicarboxylic acids) by the DSC technique [1 – 4], it was found that the transition from the solid to the liquid state (and vice versa) is carried out in two stages. The initial stage is a first order solid-phase (structural) transition (PT-1) occurring at temperatures T_{PT1} < T_{m}. The final stage is a second order phase transition of the order-disorder type or melting at T_{m}.

The main attention was paid to the study of PT-1, which is associated with a change in the type of the subcell symmetry in the crystalline cores of elementary lamella. It was shown [2] that PT-1 develops according to a heterogeneous mechanism (i.e. with the formation of a new phase nuclei) in a narrow temperature range ΔT ~ 2K in accordance with a theory of the diffuse first order phase transitions [5]. It was found that the transition is due to the change in the initial subcell symmetry to the hexagonal one. According to the theory, nanonuclei of new phases appear in the initial phase volume, and then the interfaces gradually propagate to the entire sample volume by adding similar nuclei to the resulting phase boundary.

In our previous works [6, 7], the development kinetics of structural PT-1 in monodisperse sample of odd tricosane C_{23}H_{48} and even tetracosane C_{24}H_{50} was studied by FTIR spectroscopy. Considering the lamellar structure of LCMCs, it is possible to consider the development of PT-1 in two quasi-independent structural components: in the lamella cores containing methylene sequences and in interlamellar layers formed by the van der Waals interactions between the terminal methyl groups of adjacent lamellae. The study of the transformations in the crystalline lamella cores was carried out on
the basis of the frequency temperature dependences analysis of various vibration CH$_2$ modes in methylene trans-sequence. It was shown that in the cores PT-1 develops 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. It was found that in the PT-1 temperature range a hexagonal phase nucleus appear in the volume of the initial triclinic or orthorhombic phase, and the amount of the new phase gradual increase occurs due to the disappearance of the former one.

From a fundamental point of view, it was necessary to find out the location of a first hexagonal nucleus in the volume of the initial phase. The nucleation can occur both in the lamella cores and in the interlamellar space. Thus, considerable interest was a study of changes in the interlamellar layers formed by the van der Waals contacts between the terminal methyl CH$_3$ groups of the neighboring lamella.

2. Experiments and results

FTIR spectroscopic analysis reveals the kinetics of a first-order solid-state phase transition (PT-1) by the smallest displacements in the molecular vibration spectra, which are due to changes of the subcell symmetry in the crystalline cores of elementary lamella.

The samples with a 10 – 20 μm thickness 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 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 $\Delta T = 0.1^\circ$C in the temperature range $\Delta T = 40.3^\circ$C and $\Delta T = 0.1^\circ$C in the PT-1 region and the samples were 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 $\nu = 2800 – 3000$ cm$^{-1}$ was studied that shown in figure 1. According to [8], eight absorption bands are observed in the spectral range under study, the frequencies of which differ slightly for n-alkanes with various chain lengths. Adopted the following notations bands:

$r^\prime$, $r^\prime\prime$, $r^\prime\prime\prime$, $r^\prime\prime\prime\prime$, $r^\prime\prime\prime\prime\prime$, and $r^\prime\prime\prime\prime\prime\prime$ are the antisymmetric stretching vibrations in CH$_3$ groups, in-plane and out-of-plane components, respectively ($\nu$(C$_{24}$H$_{50}$) = 2961.5 and 2953.5 cm$^{-1}$).

$d^\prime$, $d^\prime\prime$, and $d^\prime\prime\prime$ 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$^{-1}$).

In addition, there are 2 bands ($r^\prime_{FR}$ and $d^\prime_{FR}$) due to the Fermi resonance of symmetric stretching vibrations $r^\prime$ and $d^\prime$ with an overtone of the CH$_2$ groups bending vibrations inside the crystalline lamella cores.

**Figure 1.** The IR spectrum of tetracosane C$_{24}$H$_{50}$ in the stretching vibrations region at 19°C. Spectrum decomposition was performed in the Fityk 0.9.8 program.
Samples of tricosane and tetracosane weighing 0.4 – 1.2 mg were studied on a DSC 500 calorimeter with varying scanning speeds in the range 0.2 – 5 K/min. Low sample weights and scan speeds ensures the minimum thermal resistance of the calorimeter cell and minimizes the effect of thermal delay. The dependences of heat capacity on temperature were received for tricosane and tetracosane samples with variable scanning speeds. Figure 2 shows PT-1 on DSC curves obtained at a scan rate of 0.2 K/min. Methodological errors were eliminated by a special method of extrapolating the peak temperatures to zero scanning speed [3].

![DSC curve](image)

**Figure 2.** DSC PT-1 curve for tricosane (a) and tetracosane (b).

### 3. Results and discussions

In the work, we investigated the features of the rearrangement in the interlamellar space on the basis of the temperature dependences of the various C – H bond stretching vibrations modes in the terminal methyl CH₃ groups, where radical changes in the PT-1 range were found (figure 3 and 4).

![Temperature dependences](image)

**Figure 3.** Temperature dependences of the absorption band positions of \( r' \) (a), \( r''_w \) \( r''_b \) (b), \( d' \), \( d'' \) (c) and \( d''_w \) (d) stretching vibrations of C – H bonds in the tricosane \( C_{31}H_{68} \).

![Temperature dependences](image)

**Figure 4.** Temperature dependences of the absorption band positions of \( r' \) (a), \( r''_w \) \( r''_b \) (b), \( d' \), \( d'' \) (c) and \( d''_w \) (d) stretching vibrations of C – H bonds in the tetracosane \( C_{32}H_{50} \).

The temperature study of the CH₂ stretching vibrations \( d'' \) in the lamella cores confirms the results obtained in our previous works [6, 7]. The change of \( d'' \) frequencies in the lamella 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)).

It was established that for tricosane PT-1 begins with a change of the stretching vibrations \( r' \) in the terminal CH₃ groups and \( d''_w \) in the CH₂ groups closest to them at \( \Delta T = 39.5 - 41.0^\circ C \) (figure 3(a, b, d)). The rearrangement of the tetracosane crystal structure manifests in changes of vibrations in the terminal groups at more higher temperatures \( \Delta T = 46.2 - 47.8^\circ C \) (figure 4(a, b, d)) as compared to the
vibrations inside the lamella. It can be concluded that for even n-alkane C_{2n}H_{50}, the initial nuclei of a new phase arise precisely in the lamella cores and only then gradually extend over the entire volume. It is assumed that in this case before a complete transition to the hexagonal symmetry it is energetically more favorable for molecules inclined relative to the base plane of the lamellae to occupy a vertical position, and only after that to change the molecules packing and the contact of the terminal groups.

DSC researches were carried out to confirm and refine the results obtained by FTIR spectroscopy. The temperature dependences of the heat capacity in the PT-1 range at a scanning rate of 0.2 K/min for the samples under study are shown on figure 5. It can be seen that the transition covers the interval ΔT = 40.6 – 41.3°C for C_{23}H_{48} and ΔT = 47.2 – 48.4°C for C_{24}H_{50}, that is consistent with IR data on the complete transition to the hexagonal phase.

The peak shapes were analyzed according to the thermodynamic theory of a self-consistent field [5, 9, 10] as applied to symmetric Λ – shaped diffuse PT-1. The theory analyzes the change in the system of interacting particles of different phases, in particular, the formation and subsequent growth of stable nuclei of a new phase in the matrix of the old one. The main idea of the theory is that in the old phase volume, localization of numerous fluctuations occurs in the form of stable nuclei of a new phase, the so-called elementary transition volumes $\omega$. Further new phase propagation is carried out by successive additions of nuclei with a volume of $\omega$ to the arising interphase boundary.

The relation for the temperature dependence of the heat capacity at a diffuse phase transition has the form [11]:

$$\Delta C_p(T) = 4\Delta C_{\text{max}} \cdot \exp \left[ \frac{B(T-T_0)}{T_0} \right] \left[ 1 + \exp \left[ \frac{B(T-T_0)}{T_0} \right] \right]^{-2},$$

where $T_0$ is a temperature of the PT-1 peak, K; $\Delta C_{\text{max}}$ is a maximum value of heat capacity at $T = T_0$, J/(g·K); B is an athermal parameter.

As can be seen from figure 5, the shape of the DSC curve is asymmetric in both cases, however, for the self-consistent field theory, the symmetric Λ – shaped peaks are required. Therefore, according to the ratio (1), the separation into symmetric peaks was performed using the previously developed method [12]. As shown in figure 5, the main peak is divided into two Λ – shape peaks (peaks 3 and 4 for tricosane and peaks 1 and 2 for tetracosane). Also, on the tricosane curve it was possible to distinguish additional peaks preceding the main one (peaks 1 and 2), and for tetracosane – peak after the main one (peak 3). The enthalpies for the main and secondary peaks are compared with the calculated values of the transition energies in the lamella cores $\Delta H_{\text{CH}_2} = (n - 4) \cdot 3.84$ J/g (where $(n - 4)$ – number of CH$_2$ groups in the lamella cores) and in the interlamellar space $\Delta H_{\text{CH}_3+2\text{CH}_2} = 16$ J/g (two terminal and nearest to them CH$_3$ groups) [13, 14]. The experimental values of enthalpies for C_{23}H_{48}: $\Delta H_{\text{peak1}} + \Delta H_{\text{peak2}} = 14$ J/g, $\Delta H_{\text{peak3}} + \Delta H_{\text{peak4}} = 72.4$ J/g; and for C_{24}H_{50}: $\Delta H_{\text{peak1}} + \Delta H_{\text{peak2}} = 71.9$ J/g, $\Delta H_{\text{peak3}} = 12.6$ J/g (figure 5). Comparison of experimental and calculation data is presented in table 1.
Table 1. Enthalpies of interlamellar space and lamella cores of the samples under study.

| Samples | $\Delta H_{\text{interlam.space}}$ (J/g) | $\Delta H_{\text{lam.cores}}$ (J/g) | $\Delta H_{\text{interlam.space}}$ (J/g) | $\Delta H_{\text{lam.cores}}$ (J/g) | $\Delta H_{\text{interlam.space}}$ (J/g) | $\Delta H_{\text{lam.cores}}$ (J/g) |
|---------|----------------------------------------|------------------------------------|----------------------------------------|------------------------------------|----------------------------------------|------------------------------------|
| C$_{23}$H$_{48}$ | 16 | 73.0 | 4.56 | 14 | 72.4 | 5.17 |
| C$_{24}$H$_{50}$ | 16 | 76.8 | 4.8 | 12.6 | 71.9 | 5.71 |

As can be seen from the table 1, the experimental data correspond to the calculated ones with good accuracy. However, it should be noted that an underestimation of the total enthalpy is observed for the tetracosane sample. This may be due to some measurement error, since the ratio between the enthalpies of the lamella cores and the interlamellar space corresponds to the calculated one, and there is also a tendency towards an increase in the chain length.

4. Conclusion

The kinetics of the first-order solid-state structural transition in monodisperse n-alkane samples of odd tricosane C$_{23}$H$_{48}$ and even tetracosane C$_{24}$H$_{50}$ was studied by FTIR spectroscopy and DSC. It is shown that the hexagonal nucleus in the initial phase matrix appears by the fluctuation mechanism in a narrow temperature range $\Delta T \approx 2 - 3^\circ$C for the samples under study. The present investigation made it possible to study in more detail the sequential structure rearrangement of different parity n-alkanes during the phase transition. In addition, the initial nuclei location of the new phase was revealed. The process of crystal structure rearrangement of even n-alkanes is initiated in the crystalline lamella cores, when the molecules tend to line up vertically. Further, the transition includes the terminal groups, and the molecular packing in the layers changes. But in odd n-alkanes, it was shown that PT-1 begins in the interlamellar space with changes in the terminal group contacts, and only then the transition spreads to the lamella cores. FTIR spectroscopy and DSC have demonstrated the influence of the parity effect of n-alkanes depending on the chain length on the development of the structural phase transition.

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