Solid-state phase transition of tetracosane C\textsubscript{24}H\textsubscript{50}

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Abstract. The heterogeneous structural phase transition in the even \textit{n}-alkane tetracosane C\textsubscript{24}H\textsubscript{50} was studied by IR spectroscopy and DSC. It was found that the initial nanonuclei of the hexagonal phase are formed in the lamellas cores and their volume was calculated.

1. Introduction

The purpose of this work was the fundamental study of the temperature phase transitions (PTs) in normal alkanes with even chain lengths using tetracosane C\textsubscript{24}H\textsubscript{50} as an example.

The objects of research are long-chain molecular crystals (LCMCs) of \textit{n}-alkanes, consisting of numerous nanolamellas layered on each other (thick~3 nm for tetracosane). Lamellar cores are extended trans sequences of methylene CH\textsubscript{2} groups, the stacking of which corresponds to the triclinic symmetry of the unit sub-cells for tetracosane. The van der Waals interaction of neighboring lamellas is carried out by the contact of terminal methyl CH\textsubscript{3} groups.

DSC (differential scanning calorimetry) showed \cite{1–4} that in various LCMCs (i.e. \textit{n}-alkanes, \textit{n}-alcohols, mono- and dicarboxylic acids) during the transition from the solid state to the melt two types of PTs are observed. The first type is a studied structural first order solid-state phase transition (PT-1) occurring at temperatures \(T_{PT-1} < T_m\). The second type is an order-disorder transition or melting at \(T_m\).

In our previous works \cite{5,6}, the development kinetics of structural PT-1 in monodisperse tetracosane samples was studied by FTIR spectroscopy. Temperature dependences of frequencies and intensities of rocking (\(v \sim 720\) cm\(^{-1}\)) and bending (\(v \sim 1470\) cm\(^{-1}\)) vibrational modes of extended methylene CH\textsubscript{2} trans sequences in the lamellas cores were investigated. It was shown that in the cores PT-1 develops to a heterogeneous mechanism in a temperature range \(\Delta T = 45.5 - 47.6^{-1}\) in accordance with the diffuse phase transitions theory \cite{7}. It was found that the transition is due to a change in the crystallographic sub-cells 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 tetracosane crystals. The nucleation can occur both in the lamellas cores and in the interlamellar space. Thus, we set the task to study of changes in the surface lamellae layers formed by the van der Waals contacts between the terminal methyl CH\textsubscript{3} groups of the neighboring lamellas. To solve this problem, we studied the temperature behavior of the IR spectra and confirmed the results using DSC.

2. Experiments

IR Fourier-transform spectroscopic analysis reveals the subtle shifts in the molecular vibration spectra that occur when the symmetry of sub-cells in the crystalline cores of elementary lamellas changes during a first-order solid-state phase transition (PT-1).
The absorption spectra of monodisperse tetracosane \( C_{24}H_{50} \) 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 \( \Delta T = 2 \) °C and \( \Delta T = 0.1 \) °C in the PT-1 region and the sample was kept during 10 min until reaching the equilibrium state at the given temperature.

Our task was to continue the kinetics study of the PT-1 to the hexagonal phase in the samples under study. To detect changes in the surface lamellar layers, vibrations in terminal methyl groups was studied. For this reason, changes in the stretching vibrational frequencies of C–H bonds in the spectral region \( v = 2800 – 3000 \) cm\(^{-1}\) (figure 1) were investigated in detail during phase transitions. According to [8], 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 (\( v = 2870.6 \) cm\(^{-1}\));
- \( r_a^-, r_b^- \) are the antisymmetric stretching vibrations in \( CH_3 \) groups, in-plane and out-of-plane components, respectively (\( v = 2961.5 \) and 2953.5 cm\(^{-1}\));
- \( d^+, d^- \) are the symmetric and antisymmetric stretching vibrations in \( CH_2 \) groups in chain (\( v = 2848.7 \) and 2916.1 cm\(^{-1}\));
- \( d_w^+ \) are the symmetric stretching vibrations in \( \omega \)-\( CH_2 \) groups adjacent to \( CH_3 \) (\( v = 2859.3 \) cm\(^{-1}\)).

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.

![Figure 1. IR spectrum of \( C_{24}H_{50} \) in the region of C–H stretching vibrations at 19°C.](image)

Using DSC, the temperature dependence of the heat capacity was obtained for tetracosane samples of different masses. The studies were performed on a DSC 500 calorimeter with varying heating rates in the range 0.1–5 K/min. The mass of the samples was \( m = 0.25 \) mg and \( m = 2.7 \) mg, this ensures the minimum thermal resistance of the calorimeter cell and minimizes the effect of thermal delay.

Figure 2(a) shows the DSC curve obtained by heating a tetracosane sample at 0.1, 1, and 5 K/min. As can be seen from the figure, the phase transition from the crystalline state to the melt is carried out in two stages: a doublet with maximum temperatures \( T_{max1} \) and \( T_{max2} \) is visible on the DSC curve. The endothermic peak with \( T_{max1} \) is associated with a first-order phase transition in the solid state. At a higher temperature \( T_{max2} \), a second order phase transition of the order-disorder type occurs. It can be seen that, depending on the scanning speed, the peaks shift along the temperature scale. As can be seen from the figure, the endo peaks corresponding to the phase transitions of the first and second order are clearly spaced on the temperature scale. This circumstance made it possible to isolate the peak corresponding to the structural phase transition of the first order (figure 2(b)) and determine its enthalpy equal to 89 Jg\(^{-1}\). The 1 K/min tetracosane curve was taken for analysis to minimize thermal delay and instrument error. Methodological errors were eliminated by extrapolation to zero scanning speed [2].
3. Results and discussions

It was found that the C–H stretching vibrations undergo a frequency shift about $\Delta v = 1 - 2$ cm$^{-1}$ in the PT-1 region. Temperature dependences of the positions of absorption band maximums were constructed for symmetric and antisymmetric C–H bonds stretching vibrations of tetracosane on figure 3.

The temperature study of the methylene CH$_2$ stretching vibrations in the lamellas cores confirms the results obtained in previous works [5, 6]. The change in the stretching vibrations frequencies in the lamellas cores occurs in the temperature range $\Delta T = 45.5 - 47.4^\circ$C for tetracosane (figure 3(c)).

The rearrangement of the tetracosane crystal structure manifests in changes of vibrations in the terminal groups at higher temperatures $\Delta T = 46.2 - 47.8^\circ$C (figure 3(a, b)) as compared to the vibrations inside the lamellas. The vibrations in the $\omega$-CH$_2$ groups behave similarly to the vibrations in the terminal groups (figures 3(d)). Consequently, the interlamellar space consists of layers where the lamellas are in contact, as well as the adjacent layers of $\omega$-CH$_2$ groups, i.e., two terminal carbon atoms from each end of the molecule.

It can be concluded that for even $n$-alkane $\text{C}_{24}\text{H}_{50}$ 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 sub-cells before a complete transition to the hexagonal phase. The terminal groups maintain the structure integrity up to $47^\circ$C, when all the molecules become vertical. The abrupt changes observed in each components of stretching vibrations correspond to this explanation (figure 3). In the temperature range $\Delta T = 47.0 - 47.8^\circ$C, a smooth change in frequency occurs, appropriating to the thermal expansion of the crystals.

Figure 2(b) shows that the transition covers the interval $\Delta T = 47.0 - 48.1^\circ$C according to DSC, which is consistent with the IR data on the complete transition to the hexagonal phase.

Upon transition to the hexagonal phase, the component of antisymmetric vibrations $r_a^-$ corresponding to the perpendicular vibrations relative to the molecules axis disappears (figures 3(b)). This fact confirms the molecular packing modification, in which the terminal group interactions of neighboring lamellas have changed.
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 C$_{24}$H$_{50}$.

Let us consider the analysis of the solid-solid phase transition in terms of thermodynamics. It can be seen from figure 2(b) that the peak shape turned out to be asymmetric, which may be due to the presence of at least two components. The analysis of the peaks obtained by the above method was carried out according to the theory of a self-consistent field [7, 9, 10] as applied to $\Lambda$-shaped diffuse first-order transitions. The relation for the temperature dependence of the heat capacity at the diffuse PT has the form

$$\Delta C_p(T) = 4\Delta C_m \cdot \exp[B \cdot (T-T_0)/T_0] \cdot [1+\exp[B \cdot (T-T_0)/T_0]]^2,$$  \hspace{1cm} (1)

where $T_0$ is the temperature of the PT-1, $\Delta C_m$ is the maximum heat capacity at $T = T_0$, and $B$ is the athermal parameter. In asymmetric peaks, when parameter $B$ was varied, it was possible to match either the right (high temperature) or left (low temperature) shoulder of the peak. It turned out that the best agreement between the calculated dependence and the selected peak for tetracosane was obtained with the left (low temperature) shoulder of the peak. Subtracting the calculated peak from the initial peak obtained experimentally, the second peak of the $\Lambda$-shaped form is obtained. The dependence $\Delta C_p(T)$ was also calculated from the second peak using equation (1). Both dependencies are shown in figure 4. In the calculation, temperatures $T_0$ equal to 47.57°C and 47.64°C were used, as well as parameters $B$ equal to 3650 and 13000, respectively, for the “calculated” and “additional” peaks.

The quantity of heat of transitions $q_0$ for the peaks obtained by dividing the initial peaks into two components were found by the following relation [7]:

$$q_0 = 4 \cdot T_0 \cdot \Delta C_m / B$$ \hspace{1cm} (2)

For tetracosane, the $q_0$ values were $q_{01} = 79.1 \text{ Jg}^{-1}$ and $q_{02} = 8.4 \text{ Jg}^{-1}$, respectively, for the “calculated” and “additional” peaks. Next, we can determine the volumes of nanonuclei according to the equation:

$$\omega = B \cdot k \cdot T_0 / (\rho \cdot q_0),$$ \hspace{1cm} (3)

where $k$ is the Boltzmann constant and $\rho$ is the density of tetracosane.
Thus, the volumes of nanonuclei are $v_1 = 255 \text{ nm}^3$ and $v_2 = 8564 \text{ nm}^3$, which corresponds to 500 and 17000 molecules for the “calculated” and “additional” peaks, respectively.

![Figure 4](image_url)

**Figure 4.** Decomposition of the asymmetric peak of heat capacity PT-1 into two symmetric ones.

The presence of two components in the PT-1 noted above may be due to the coexistence of two quasi-independent structural components involved in the phase transition – the lamellae or cores formed by methylene sequences and interlayers containing CH$_3$ groups. In this regard, it is interesting to find the ratio of the energy contributions of these components to the total change in the energy of intermolecular interaction (IMI) during the PT.

Consider the energy component of the system consisting of two structural units – methylene sequences (-CH$_2$-) and terminal groups (-CH$_3$). The total transition enthalpy $\Delta H$ is an integral characteristic and reflects a general decrease in the intermolecular interaction energy $\Delta E_{\text{IMI}}$. In $n$-alkanes, the energy of the intermolecular interaction $E_{\text{IMI}}$ consists of the so-called universal (van der Waals) interaction, which includes the interaction of methylene groups with each other, as well as terminal groups (-CH$_3$). A quantitative measure of the IMI is the cohesion energy $E_\text{c}$, defined as the energy needed to break the intermolecular contacts and transfer the solid through the liquid state to the gaseous phase. The decrease in the energy of the intermolecular $\Delta E_{\text{IMI}}$ interaction occurs due to a partial decrease in the cohesion energy $E_\text{c}$ during the PT. It is difficult to determine experimentally this decrease ($\Delta E_\text{c}$) for substances consisting of polyatomic molecules. $\Delta E_\text{c}$ can be compared with the value of the potential barrier to the movement of a molecule in local liquid-like motion acts in a solid. The value of this barrier, experimentally determined for vitrified liquids and solid oligomers, which differ sharply in the nature of intermolecular interaction, the structure and shape of molecules, including substances with a developed system of hydrogen bonds, is $mE_\text{c}$, where $m \leq 0.5$ [11].

Then the change in the energy of such a two-component system during the phase transition can be represented as

$$\Delta E_{\text{IMI}} = \Delta E_1 + \Delta E_2 = N_1 m E_{\text{c1}} + N_2 m E_{\text{c2}} = m(n M_1 E_{\text{c1}} + 2 M_2 E_{\text{c2}}) / M_c = m E_{\text{IMI}},$$

where $E_{\text{IMI}}$ is the total energy of intermolecular interaction; $N_1$ and $N_2$ are the relative shares of each of the components; $n$ is the number of moles of CH$_2$ groups in one mole of $n$-alkane, equal to the number of methylene groups in one molecule; $M_1 = 14 \text{ g/mol}$ – molecular weight of the CH$_2$ group; $M_2 = 15 \text{ g/mol}$ – molecular weight of the CH$_3$ group; $M_c = n M_1 + 2 M_2$ is the molecular weight of one molecule; $E_{\text{c1}}$ and $E_{\text{c2}}$ are the cohesion energies of the CH$_2$ and CH$_3$ groups, respectively.

Experimentally, $E_\text{c}$ is determined only for low molecular weight bodies that can exist in the gas phase. For most oligomers, polymers, and molecular crystals, the evaporation process is preceded by destruction, therefore, the cohesion energy for them is determined indirectly or calculated [11, 12]. In this work, we use the values of cohesion energy given in the monograph [11] for contributions from the CH$_2$ groups: $E_{\text{c1}} = 860 \text{ cal/mol}$ and from the CH$_3$ groups: $E_{\text{c2}} = 990 \text{ cal/mol}.$
The calculation results from equation (3) of the change in the energy of the intermolecular interaction of the $E_{IMI}$ and individual contributions from the intralamellar ($\Delta E_1$) and interlamellar ($\Delta E_2$) IMI for the PT-1 are shown in Table 1. In the calculation, the coefficient $m$ was found from a comparison of the experimental value $\Delta H_1$ and the total energy of the $E_{IMI}$ in the ratio $m = \Delta H_1 / E_{IMI}$.

**Table 1.** Thermodynamic parameters of phase transitions in tetracosane.

| $\Delta H_1$ (J/g) | $E_{IMI}$ (J/g) | $m$ | $\Delta E_1$ (J/g) | $q_{01}$ (J/g) | $\Delta E_2$ (J/g) | $q_{02}$ (J/g) |
|-------------------|----------------|-----|-------------------|----------------|-------------------|----------------|
| 89                | 258            | 0.345 | 80.7             | 79.1           | 8.3               | 8.4            |

The table shows that the heats of transformation $q_{01}$ and $q_{02}$ within the accuracy of estimating the cohesion energy are close to $\Delta E_1$ and $\Delta E_2$, and their sums ($q_{01} + q_{02}$ and $\Delta E_1 + \Delta E_2$) are close to $\Delta H_1$. Thus, the adopted model is in good agreement with experimental data and allows one to estimate the relative contributions of the intralamellar and interlamellar interaction to the total change in the transition energy.

From the data obtained from DSC, we can conclude that PT-1 begins with the formation of nanonuclei in the cores of the lamellas at a temperature of 47°C. Further, at temperatures of 47.5 – 47.7°C, a rapid formation of nuclei, including terminal groups, occurs.

### 4. Conclusion

The kinetics of the first-order solid-state structural transition in monodisperse $n$-alkanes samples of 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 $\Delta T \approx 2 – 3°C$. The present investigation made it possible to study in more detail the sequential structure rearrangement of even $n$-alkanes during the phase transition. In addition, the initial nuclei location of the new phase was revealed. The process of crystal structure rearrangement is initiated in the crystalline lamellas cores. Next, the transition covers the terminal groups. The FTIR spectroscopy turned out to be more sensitive to structural changes during the phase transition.

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