The influence of conformational defects on the development of structural phase transition in tetracosane $C_{24}H_{50}$

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Abstract. 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. The existence of many irregular conformers in solid phases of tetracosane, the concentration of which reaches a maximum when approaching the melting temperature, has been demonstrated. The existence of these defective molecules promotes transitions between different rotator phases in the solid state.

1. Introduction

Structural transformations of long-chain molecular crystals (LCMCs) of normal alkanes at temperatures of the phase transitions (PTs) were investigated by FTIR spectroscopy, which makes it possible to reveal specific shifts in molecular vibration spectra upon symmetry changes of crystallographic subcells. N-alkanes are model objects for studying the fundamental regularities of PTs in LCMCs and polymers, and also have the important practical applications as PCM (phase change materials) [1].

Under studying of various LCMCs (i.e. n-alkanes, n-alcohols, mono- and dicarboxylic acids) by the DSC technique [2 – 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 $T_{PT-1} < T_m$. The final stage is a second order phase transition of the order-disorder type or melting at $T_m$.

The object of this research was n-alkane tetracosane $C_{24}H_{50}$ produced by Sigma – Aldrich Company. The samples have a very high degree of purification (about 99.9%), i.e. the samples are monodisperse with an accuracy of one carbon-carbon bond. The chain length and each lamella thickness of the investigated samples is about 3 nm.

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. In our previous works [5 – 7], the development kinetics of structural PT-1 in monodisperse sample of even n-alkane tetracosane $C_{24}H_{50}$ was studied by FTIR spectroscopy. Taking into account the lamellar structure of LCMC, the PT-1 development was investigated for two quasi-independent structural components – the lamella cores containing methylene sequences and interlamellar layers formed by the van der Waals interactions between the terminal methyl groups of adjacent lamellae. Based on the temperature changes in the vibrational modes of methylene CH$_2$ trans-sequences in the crystalline lamella cores, it was shown that
PT-1 develops according to a heterogeneous mechanism (i.e. with the formation of a new phase nuclei) in a narrow temperature range $\Delta T \sim 2$K in accordance with a theory of the diffuse first order phase transitions [8]. It was found that the transition is due to the change in the initial subcell triclinic 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 addition, it was detected that the effect of n-alkane evenness influences the development of PT-1; in particular, even n-alkanes are characterized by the appearance of the initial nanonuclei of the new phase in the lamella cores. It has been suggested that in the transition from triclinic to hexagonal symmetry it is energetically more favorable for molecules initially inclined relative to the basal plane of the lamellae to take a vertical position, and only after that to change the type of molecular packing. In this case, the modification of the terminal group contacts of neighboring molecules takes place.

In the work, special attention is paid to the study of a nucleation and development of conformational defects, including various combinations of trans and gauche conformers, and their effect on the PT-1 kinetics.

2. Experiment of tetracosane $C_{24}H_{50}$

The samples of a 10 – 20 $\mu$m thickness were prepared as follows: the synthesized tetracosane flakes were placed on NaCl plates of IR spectrometer, then were melted and slowly cooled to obtain an equilibrium crystal structure. The absorption spectra of monodisperse tetracosane samples were recorded by IFS-88 FTIR spectrometer (Bruker, Germany) in the temperature range from 19 to 51°C with the steps $\Delta T = 2$°C and $\Delta T = 0.1$°C in the PT-1 region. The samples were kept during 10 min until reaching the equilibrium state at each temperature step.

To detect changes in the trans-zigzag structure of molecules and the appearance of conformational defects, the spectral region $\nu = 1200$ – 1400 cm$^{-1}$ was studied (figure 1), in which actually the weak absorption bands of methylene wagging progression are observes. Every local conformational structure corresponds to a certain absorption band in the IR spectrum, and most of them are located in the studied spectral region [9]. In this spectral region, absorption bands strongly overlap each other, thus separation into individual components was performed using the Fityk 0.9.8 program (figure 1).

![Figure 1. The IR spectrum of tetracosane $C_{24}H_{50}$ in the region of wagging vibrations at 19.0°C.](image-url)
It is well known that in IR spectra of short trans-zigzag chains displays a number of wagging progression bands, which clearly indicate a high regularity in the crystalline lamella cores (figure 1). Besides, it was found the following types of irregular conformational defects: 1) kinks gtg* (\(\nu = 1307\) and 1369 \(\text{cm}^{-1}\)), 2) double gauche conformers gg* (\(\nu = 1352\) \(\text{cm}^{-1}\)), 3) end-gauche conformers gt\(_{m}\) (\(\nu = 1339\) \(\text{cm}^{-1}\)) \([10 – 12]\) for n-alkanes at room temperatures. The band at 1369 \(\text{cm}^{-1}\) mainly originates from the gtg* structures, but this spectral region is complicated by the existence of a \(\text{CH}_2\) wagging mode sequence, which coincides with the symmetric scissoring \(\text{B}^{\text{CH}_3}\) motions of terminal \(\text{CH}_3\) groups near 1370 \(\text{cm}^{-1}\). All types of these defects are seen on the spectra of figure 1.

On heating n-alkane crystals, the number of different rotational isomers increases, which leads to an ever-greater disorder of the system. A strong increase in the intensity of the corresponding absorption bands is shown in figure 2 at a temperature close to the sample melting \(T_m\). An increase in the concentration of conformational defects led to the fact that the structure regularity of molecules in the cores reduces, and, consequently, the number of bands in the wagging progression decreases. It can be seen that the progression of methylene wagging modes becomes less pronounced for the even n-alkane at high temperatures (figure 2). This indicates the preservation of short trans-sequences in the crystalline cores of lamellae even near \(T_m\).

![Figure 2. The IR spectrum of tetracosane \(\text{C}_{24}\text{H}_{50}\) in the region of wagging vibrations at 50.7°C.](image)

3. Results and discussions
It is known \([13, 14]\) that the transition from a triclinic to a hexagonal structure is accompanied by the formation of a several intermediate rotator phases. It should be noted that the following phase sequence is realized in tetracosane: triclinic crystals, rotator phases \(R_V, R_l, R_{II}\) \(\equiv\) hexagonal phase, a liquid. We supposed \([7]\) that the molecules initially tilted in the triclinic subcell are verticalized in the temperature range from 45.5 to 47.0°C. In our opinion, this is the \(R_V - R_l\) tilting transition. And the transition to the \(R_{II}\) phase with a change in the layers stacking occurs at a temperature of 47.5°C. It can
be assumed that, as the n-alkane heats up, sharp changes in the concentration of nonplanar conformers should occur at temperatures corresponding to the transitions between the rotator phases.

Indeed, it was found that the intensities of the studied absorption bands corresponding to various defects undergo sharp changes in the PT-1 region, which is shown in figures 3 and 4 for tetracosane C\textsubscript{24}H\textsubscript{50}.

**Figure 3.** Temperature dependences of the intensities of the absorption bands associated with nonplanar conformers: (a) kink gtg\(^*\) \((\nu = 1307 \text{ cm}^{-1})\) and (b) end-gauche conformers gt\(_m\) \((\nu = 1339 \text{ cm}^{-1})\) in the tetracosane C\textsubscript{24}H\textsubscript{50}.

**Figure 4.** Temperature dependences of the intensities of the absorption bands associated with nonplanar conformers: (a) double gauche conformers gg\(^*\) \((\nu = 1352 \text{ cm}^{-1})\) and (b) kink gtg\(^*\) \((\nu = 1369 \text{ cm}^{-1})\) in the tetracosane C\textsubscript{24}H\textsubscript{50}.

It can be seen from the figures 3(a, b) and 4(a) that nonplanar conformers are also observed in the initial triclinic phase. As the sample is heated, their concentration gradually increases, and intermittent jumps in intensity occur upon transition near temperature 47.0°C. It was found that the kinks concentration increases by 2.0 times upon the transition to the R\(_1\) phase (figure 3(a)). Similarly, the number of end defects rises by 1.7 times (figure 3(b)). The behavior of the double gauche conformer
concentration is more complex, but nevertheless, abrupt changes are also observed near 47.0°C (figure 4(a)). It can be concluded that an insignificant increase in the concentration of conformational defects of various types creates sufficient friability of the crystal lattice for the transition to the vertical R_I rotator phase.

In the transition to hexagonal R_H rotator phase (T ≥ 47.8°C), the increase in the conformers concentrations is observed again. Thus, the concentration increases by 4.0 times for kinks (figure 3(a)) and 2.4 times for end-gauche conformers (figure 3(b)) as compared to the corresponding values in the initial triclinic phase, which is consistent with a higher molecular freedom in the hexagonal packing.

Figure 4(b) demonstrates that the absorption frequency in the region of methyl symmetric deformation (ν = 1370 cm⁻¹) tends to a new value of about ν = 1378 cm⁻¹, while the intensity flows into a new component of the band in the PT-1 region. The 1378 cm⁻¹ band is characteristic of highly disordered crystals and is observed in the liquid state for many materials [11].

The concentrations of conformational defects of various types increase strongly near the sample melting point T_m = 50.6°C. It is indeed seen from figure 4(b) that the band at 1369 cm⁻¹ also originates from kinks, since their concentration increases strongly at temperatures close to T_m.

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. Analysis of the intensity temperature dependence of irregular conformer absorption bands showed a sharp jump in their concentration at the R_V–R_I transition temperature between two rotator phases differing in the chains slope as regard to basal planes of lamellae. In this case, the molecules from the initially tilted position in the triclinic subcells pass into the vertical one with the formation of various conformational defects. It was found that significant changes in the irregular conformer concentration occur at temperatures corresponding to the R_I–R_H transition, i.e. transition to completely hexagonal packing of molecules. It was established that during the transition to the hexagonal phase is most likely to increase the number of low-energy defects, such as end-gauche conformers and kinks, by 2 – 4 times. When the intermolecular interaction is weakened, the formation of kinks in some molecules in the near-surface layers of the lamellae is energetically favorable, which increases the distance between adjacent chains. As a consequence, the ends of 3 to 4 carbon atoms slip out more easily from the lamellae cores. Further, it is advantageous for these chains segments to rotate around the gauche connection in order to be parallel to the lamella base planes in the interlamellar space. In addition, in the transition to the hexagonal phase, the interlamellar space increases too, which also contributes to the formation of conformational defects.

We have demonstrated that a clear increase in the concentration of conformational defects in the structural phase transition temperature range of the even n-alkane tetracosane C_{24}H_{50} leads to the nucleation and subsequent development of a new crystallographic phase.

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