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## Conformational disorder and its effect on structural phase transitions in tricosane $C_{23}H_{48}$

S.A. Gureva <sup>1</sup>✉, V.A. Marikhin <sup>1</sup>, E.N. Vlasova <sup>2</sup>

<sup>1</sup>Ioffe Institute, St. Petersburg, Russia;

<sup>2</sup>Institute of Macromolecular Compounds, St. Petersburg, Russia

✉ [swet.gurjewa@gmail.com](mailto:swet.gurjewa@gmail.com)

**Abstract.** The kinetics of the first-order solid-solid structural phase transition in monodisperse n-alkane samples of odd tricosane  $C_{23}H_{48}$  was studied by FTIR spectroscopy. The detailed study of the structure rearrangements of long-chain molecular crystals of n-alkanes during solid-state transitions has been carried out and the existence of many irregular conformers in solid phases of tricosane, the concentration of which reaches a maximum when approaching the melting point, has been demonstrated. The presence of these conformational defects has been found to promote the development of a new phase in the bulk of the initial one and to facilitate the transitions between different intermediate rotator phases in the solid state. Thus, the significant role has been demonstrated for the appearance of various intramolecular conformational defects during heating of n-alkanes, which promote interfacial transitions from the solid to the liquid state, weakening the intermolecular interaction and increasing the freedom degree of molecules.

**Keywords:** n-alkane, phase transition, IR spectroscopy

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Материалы конференции

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## Конформационный беспорядок и его влияние на структурные фазовые переходы в трикозанае $C_{23}H_{48}$

С.А. Гурьева <sup>1</sup>✉, В.А. Марихин <sup>1</sup>, Е.Н. Власова <sup>2</sup>

<sup>1</sup>Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия;

<sup>2</sup>Институт высокомолекулярных соединений РАН, Санкт-Петербург, Россия

✉ [swet.gurjewa@gmail.com](mailto:swet.gurjewa@gmail.com)

**Аннотация.** Методом ИК-Фурье спектроскопии исследована кинетика твердофазного структурного перехода первого рода в монодисперсных n-алканах на примере нечетного трикозана  $C_{23}H_{48}$ . Проведено детальное изучение перестроений структуры длинноцепочечных молекулярных кристаллов n-алканов при твердофазных переходах и показано существование множества нерегулярных конформеров в твердых фазах трикозана, концентрация которых достигает максимума при приближении к температуре плавления. Обнаружено, что возникновение конформационных дефектов способствует развитию новой фазы в объеме старой и облегчает переходы между различными промежуточными ротационными фазами в твердом состоянии. Таким образом, продемонстрирована существенная роль возникновения различных внутримолекулярных конформационных дефектов при нагревании n-алканов, которые способствуют

межфазным переходам из твердого состояния в жидкое, ослабляя межмолекулярное взаимодействие и увеличивая степень свободы молекул.

**Ключевые слова:** n-алкан, фазовый переход, ИК-спектроскопия

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## Introduction

Monodisperse long-chain molecular crystals (LCMCs) of normal alkanes (n-alkanes) with the general formula  $C_nH_{2n+2}$  and variable chain length are convenient model objects for polymers, which makes it possible to study the development of phase transitions (PTs) at a quantitative level.

It was shown by DSC [1–3] that when various LCMCs (i.e., n-alkanes, n-alcohols, mono- and dicarboxylic acids) are heated, these compounds initially undergo a first order solid-solid (structural) phase transition (PT-1) at temperatures  $T_{PT-1} < T_m$ , followed by an order-disorder phase transition (PT-2) accompanied by melting of structures at  $T_m$ .

The object of present research was one of the representatives of n-alkanes, namely, tricosane  $C_{23}H_{48}$  produced by Sigma-Aldrich Company. The samples possess a very high degree of purification (about 99.9%). Moreover, the samples are characterized by monodispersity with an accuracy of one carbon-carbon bond along the chain length. Since odd n-alkanes are characterized by sub-cells with molecules perpendicular to the basal planes of the lamellae (in the particular case, sub-cells of orthorhombic symmetry [4]), the chain length and each lamella thickness of the studied samples are the same and are about 3 nm.

The highlight of our study series on these samples is that we can use FTIR spectroscopy to detect the slightest step-by-step changes of the molecular packing in crystalline sub-cells inside the lamella based on specific shifts in the vibrational spectra of molecules with increasing temperature.

In our previous works [5, 6] we have already studied the kinetics of the PT-1 development in monodisperse n-alkanes with odd chain lengths, using tricosane  $C_{23}H_{48}$  as an example. Soundly based on the results obtained on the temperature changes in the vibrational modes of the methylene  $CH_2$  trans-sequences in the crystalline lamella cores, it was found that the PT-1 develops according to a heterogeneous mechanism with the formation of a new phase nanonuclei in the volume of the old one in the temperature range  $\Delta T = 1-2$  °C in agreement with the theory of diffuse first order phase transitions [7]. The revealed frequency shifts of the bands in the IR spectra indicate a gradual weakening of intermolecular interactions due to the transformation of the initial orthorhombic sub-cells into hexagonal ones. In addition, a new manifestation of the parity effect of n-alkanes was discovered, which consists in the fact that during the structural transition the initial nuclei of the hexagonal phase are formed in the interlamellar space containing the terminal  $CH_3$  and closest to them  $CH_2$  groups, and only then the transition affects the lamella cores (for even alkanes, an inverse relationship is observed [6]).

The present work is devoted to an even more detailed study of the structure rearrangements of long-chain molecular crystals of n-alkanes during solid-solid phase transitions. For this purpose, special attention is paid to the study of the nucleation and development of conformational defects, i.e., various combinations of trans- and gauche-conformers in the chains.

## Experimental section

The sample preparation procedure was as follows: monodisperse tricosane in the original form of synthesized flakes was placed on NaCl plates of FTIR spectrometer, and then flakes were melted and slowly cooled to obtain an equilibrium crystal structure. The sample thickness was 10–20  $\mu m$ . The absorption spectra of tricosane samples were recorded by the Bruker IFS-88 FTIR spectrometer in the temperature range from 21 to 48 °C with a step  $\Delta T = 2$  °C overall and

a finer step  $\Delta T = 0.1\text{ }^\circ\text{C}$  in the PT-1 region. The samples were kept for 10 min at each step of temperature increase to achieve the appropriate equilibrium state.

To reveal changes in the concentrations of conformational defects in chains during heating, the spectral region of  $\nu = 1200\text{--}1400\text{ cm}^{-1}$  was studied (Fig. 1), which contains information about a large number of defects [8]. A complication in the selection of bands associated with conformers is caused by the presence of a weak progression of methylene wagging vibrations in the spectrum. Thus, the separation of overlapping bands into individual components and their subsequent processing were performed using the Fityk 1.3.1 program (Fig. 1) [9].

It is well known that a number of wagging progression bands are expected in the IR spectra of short trans-chains, since their presence indicates a high regularity in the crystalline cores of the lamellae (Fig. 1). It should be noted that the bands are arranged in a progression at approximately equal distances from each other, and for odd molecules there are twice as many allowed absorption bands as was observed for even ones in [10].

For tricosane irregular conformers of the following types were found in the studied region of the spectrum at room temperature: 1) kinks  $gtg^*$  ( $\nu = 1312\text{ cm}^{-1}$ ) and  $gtg$  ( $\nu = 1371\text{ cm}^{-1}$ ), 2) double gauche-conformers  $gg^*$  ( $\nu = 1353\text{ cm}^{-1}$ ), 3) end gauche-conformers  $gt_m$  ( $\nu = 1339\text{ cm}^{-1}$ ) [11–13], where  $t$  and  $g$  denote the regular trans and irregular gauche portions of the chain, respectively. All of the above types of defects are present in the spectrum of Fig. 1. The change in the intensity of the corresponding IR bands upon heating of n-alkane indicates an increase in the concentration of conformers, which leads to a violation of the crystallographic order of the molecular packing in the lamellae.

In addition, a clearly pronounced band of the symmetric scissoring  $B_{\text{CH}_3}^{\text{S}}$  vibrations of terminal  $\text{CH}_3$  groups are observed in the studied frequency range (in an even alkane, the corresponding band overlaps the kink  $gtg$  [10]).

Heating LCMCs of n-alkanes leads, firstly, to a thermal expansion of crystals, and secondly, to an accompanying process — the thermal activation of various conformational defects. Thus, there is an increase in the freedom of a molecule movement, and the probability of the violation of the chain regularity also increases. The strongest increase in the intensity of the corresponding absorption bands is observed at a temperature close to the melting point of the sample  $T_m = 47.4\text{ }^\circ\text{C}$  [14] (Fig. 2).

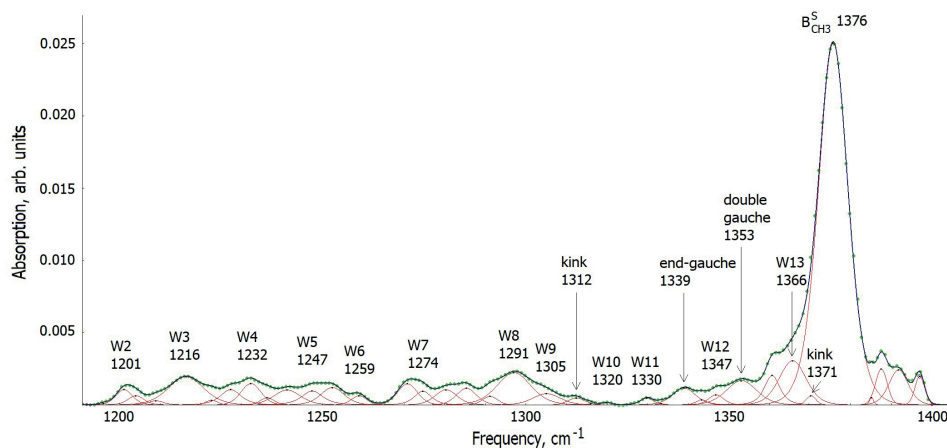


Fig. 1. The IR spectrum of tricosane  $\text{C}_{23}\text{H}_{48}$  in the region of wagging vibrations at  $21.0\text{ }^\circ\text{C}$

In turn, the increase in the concentration of the conformational defects leads to a decrease in the regularity of the molecule structure in the lamella cores, and, consequently, a reduction in the number of bands in the wagging vibration progression. Fig. 2 shows the essential reduction in the band number in the wagging vibration progression of methylene at the sufficiently high temperature, which indicates a violation of the regular arrangement of oscillators (methylene  $\text{CH}_2$  groups) along the chain. However, the fact that the band progression is retained even in the near-melt state indicates the presence of short trans-sequences in the crystalline cores of the lamellae near  $T_m$ .

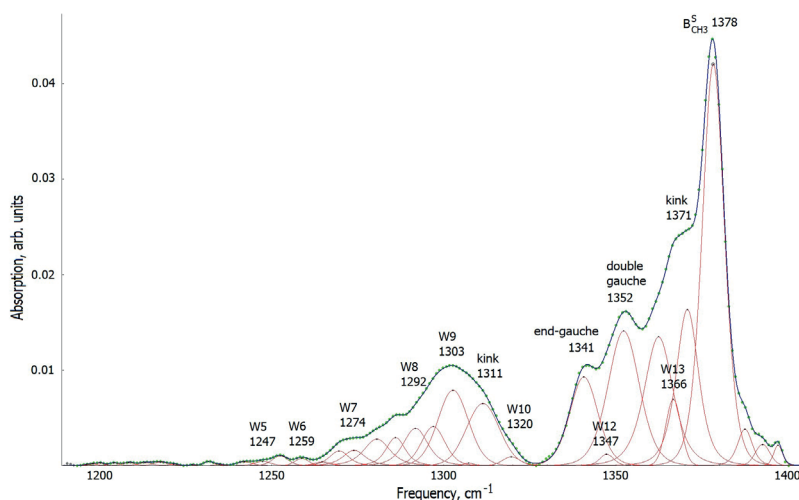


Fig. 2. The IR spectrum of tricosane  $C_{23}H_{48}$  in the region of wagging vibrations at  $47.8\text{ }^{\circ}C$

### Results and Discussions

It is known that n-alkanes are characterized by the formation of a number of intermediate rotator phases during transitions between fully ordered crystalline and isotropic liquid states. According to [14, 15], when tricosane is heated, the following sequence of phases is expected to occur: the orthorhombic crystal, the  $R_V$  phase (tilted  $R_I$ ), the  $R_I$  phase (distorted hexagonal structure), true hexagonal  $R_{II}$  phase, the liquid. Our earlier study [6] confirmed the possibility of the formation of rotator phases upon heating of tricosane based on changes in the spectral range of the C-H bond stretching vibrations. It has been suggested that the detected changes in the contact between the terminal groups of molecules in adjacent lamellae at  $40.6\text{--}40.8\text{ }^{\circ}C$  may be associated with the  $R_I\text{--}R_{II}$  transition, during which the type of molecular stacking in lamellae changes from two-layer ABAB to three-layer ABC. It can be assumed that the thermal activation of conformational defects facilitates the transitions between rotator phases, and, consequently, sharp changes in the concentrations of conformers should occur at appropriate temperatures.

Indeed, the analysis of the temperature dependences of the intensities of the absorption bands corresponding to different types of defects demonstrates sharp changes in the PT-1 region for tricosane  $C_{23}H_{48}$  (Fig. 3 and 4).

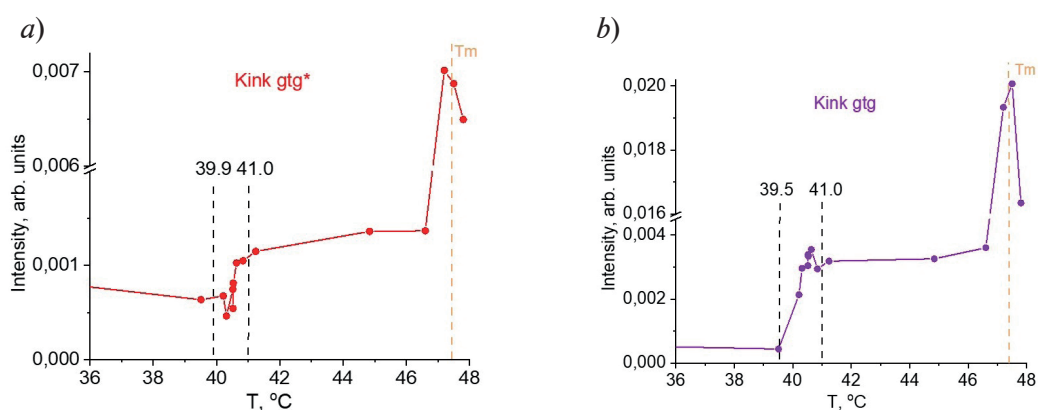


Fig. 3. Temperature dependences of the intensities of the absorption bands associated with nonplanar conformers: (a) kinks  $gtg^*$  ( $\nu = 1312\text{ cm}^{-1}$ ), and (b) kinks  $gtg$  ( $\nu = 1371\text{ cm}^{-1}$ ), in tricosane  $C_{23}H_{48}$

Based on Figures 3 and 4, it can be concluded that the content of a small number of irregular conformers is still in the initial orthorhombic phase, then their concentration gradually increases when the sample is heated. It can be seen that the jumps in the intensity of two types of kinks observed at a temperature of about  $40.6\text{ }^{\circ}C$  (Fig. 3, a, b) indeed confirms the existence of some additional structural transition (the  $R_I\text{--}R_{II}$  transition). It can be argued that the increase in the

number of defects for the odd n-alkane occurs at a later stage of the structural transition than was found for the even n-alkane [10], for which the preliminary  $R_V$ - $R_I$  transition was clearly observed.

Upon further transition to the fully hexagonal phase  $R_{II}$  at  $T \geq 41.0$  °C, the kink concentrations increase by factors of 1.8 and 6.9 for  $gtg^*$  and  $gtg$ , respectively (Fig. 3, *a*, *b*) as compared to the corresponding values in the initial phase. The increase in the number of kinks is consistent with a higher freedom degree of molecules in hexagonal packing. On the contrary, the number of double gauche conformers becomes 2.2 times less (Fig. 4, *b*), which was also obtained for even tetracosane [10]. The concentration of end defects gradually increases upon heating, experiencing almost no significant changes throughout the entire structural transition (Fig. 4, *a*).

As expected, the most considerable growth in the number of conformers is characteristic of the transition of the hexagonal phase  $R_{II}$  to the melt (Fig. 3 and 4).

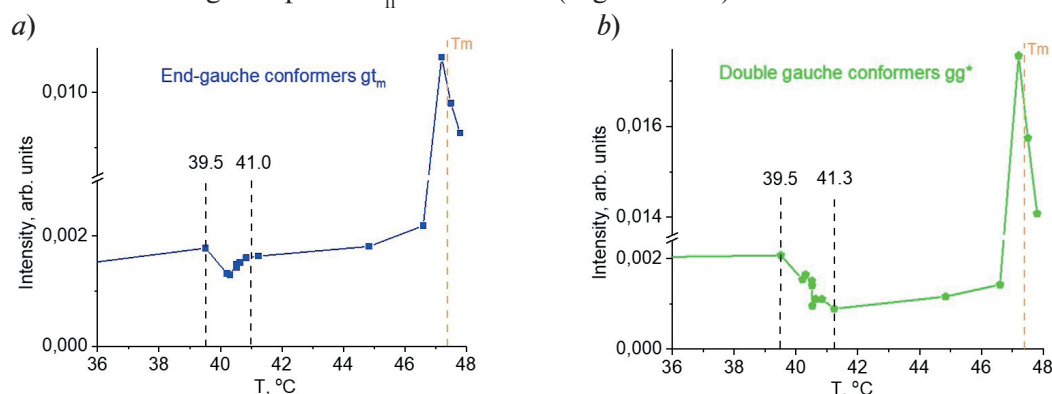


Fig. 4. Temperature dependences of the intensities of the absorption bands associated with nonplanar conformers: (a) end-gauche conformers  $gt_m$  ( $\nu = 1339$   $\text{cm}^{-1}$ ), and (b) double gauche conformers  $gg^*$  ( $\nu = 1353$   $\text{cm}^{-1}$ ), in tricosane  $\text{C}_{23}\text{H}_{48}$

It can be noted that changes in the concentrations of all considered types of defects (both terminal and intrachain) occur in the same temperature range. Therefore, it is most likely that  $gtg^*$  and  $gtg$  kinks are predominantly generated in the near-surface layers of lamellae.

Moreover, it can be concluded that the thermal activation of conformational defects contributes to the structural transformations of tricosane in the temperature range  $\Delta T = 39.5$ – $41.3$  °C, which corresponds to the interval of the PT-1 development in the interlamellar space (containing the terminal  $\text{CH}_3$  and closest to them  $\text{CH}_2$  groups) previously determined in [6]. Thus, it can be argued that in odd n-alkanes the conformers that appear at the chain ends are directly involved in the mechanism of the formation of the nanonuclei of the new hexagonal phase.

### Conclusion

The kinetics of the first-order solid-solid structural phase transition in monodisperse n-alkane samples of odd tricosane  $\text{C}_{23}\text{H}_{48}$  was studied by FTIR spectroscopy. In order to elucidate the mechanism of the formation of the new phase nanonuclei in tricosane, the absorption bands associated with conformational defects were considered in detail. Analysis of the intensity temperature dependence of irregular conformer absorption bands showed the sharp jump in their concentration at the  $R_I$ - $R_{II}$  transition, i.e., at the transition to completely hexagonal packing of molecules.

It has been determined that upon transition to the hexagonal phase the number of low energy defects, such as  $gtg^*$  and  $gtg$  kinks, is the most probably to increase by a factor of 2–7 at the chain ends. This can be explained by the fact that during the thermal expansion of crystals the formation of kinks in some molecules in the near-surface layers of the lamellae is energetically favorable; accordingly, the distance between neighboring chains increases. As a consequence, the ends of 3 to 4 carbon atoms slip out more easily from the lamellae cores. Furthermore, it is advantageous for these chains segments to rotate and become parallel to the lamella base planes in the interlamellar space. In addition, during the transition to the hexagonal phase the interlamellar space increases too, which also contributes to the formation of conformational defects. The results obtained demonstrate the high sensitivity of FTIR spectroscopy to initial changes in the molecular structure and the nature of their stacking in lamellae.





Therefore, the significant role has been demonstrated for the appearance of various intramolecular conformational defects during heating of n-alkanes, which consists in the fact that the defects contribute to the interfacial transitions from the solid to the liquid state, weakening the intermolecular interaction and increasing the freedom degree of molecules.

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## THE AUTHORS

**GUREVA Svetlana A.**  
swet.gurjewa@gmail.com  
ORCID: 0000-0001-7426-7304

**VLASOVA Elena N.**  
spectra@imc.macro.ru  
ORCID: 0000-0002-4644-0445

**MARIKHIN Vyacheslav A.**  
v.marikhin@mail.ioffe.ru  
ORCID: 0000-0001-7088-5914

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