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Study of the Kinetics of the Phase Transition of the First Order in Tetracosane $C_{24}H_{50}$ by Fourier-Transform IR Spectroscopy

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Abstract—The kinetics of the development of the structural phase transition of the first order in monodisperse samples of tetracosane $C_{24}H_{50}$ has been studied using Fourier-transform IR spectroscopy. Temperature dependences of frequencies and intensities of rocking (in the region of $\nu \sim 720$ cm^{-1}) and bending (in the region of $\nu \sim 1470$ cm^{-1}) vibration modes of CH_2 groups in trans methylene sequences in crystalline cores of elementary lamellae has been analyzed. It has been shown that the solid-phase transition of the first order develops by the heterogeneous mechanism in a narrow temperature interval $\Delta T \sim 2$ K according to the theory of diffuse phase transitions of the first order and is caused by changes in the symmetry of crystallographic cells.

Keywords: *n*-alkanes, phase transitions, theory of diffuse phase transitions, IR spectroscopy

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1. INTRODUCTION

It is known [1–3] that, during heating–cooling cycles of different long-chain molecular crystals (LCMCs) (*n*-alkanes, *n*-alkane alcohols, mono- and dicarboxylic acids, and others), there can occur two types of temperature phase transitions:

(1) The first-order solid phase (structural) transition (PT-1) at a temperature significantly below the melting temperature T_m, and

(2) The second-order phase transition (PT-2) of the order–disorder type due to the melting of crystals at the temperature T_m.

According to differential scanning calorimetry (DSC) investigations [2, 3], the first-order phase transition in LCMCs occurs within rather narrow but different from zero temperature ranges ΔT, as it should be in the case of perfect single crystals [4]. Such transitions with $\Delta T \geq 1$ K are called the diffuse first-order phase transitions and denoted as the Λ transitions [5, 6]. To describe diffuse first-order phase transitions, the self-consistent-field theory [6] was proposed.

The fact that the transition in LCMCs becomes diffuse means that the change in the phase state of the crystal occurs not suddenly in the whole volume (as, e.g., the homogeneous transition in metals during melting, i.e., at $\Delta T \sim 0$ K), but according to the heterogeneous mechanism via the appearance of fluctuation nanonuclei of the new phase with a volume ω on defects of different nature.

The gradual increase in the volume of the new phase is implemented discretely due to extension of the appeared interphase boundary with addition of new stable nanonuclei with the volume ω to it.

Using DSC, we have demonstrated [2, 3] that volumes of such specific nanonuclei amount to $\omega \sim 100$–200 nm^3 and can contain up to several hundred molecules of considered LCMCs.

X-ray diffraction investigations of the initial and final states during PT-1 demonstrated [7, 8] the change in the crystallographic symmetry of elementary cells in LCMC crystalline lamella cores; however, the kinetics of structural transformations during phase transitions was not studied in those works.

Experimental data about the type of symmetry of elementary crystallographic cells can be also obtained by analyzing IR absorption spectra because frequencies of some fundamental vibrational modes from long trans methylene sequences in crystalline lamella cores depend on the cell symmetry [9–11]. Besides, there is the possibility to obtain intense IR Fourier spectra with a high resolution from LCMCs during short time intervals.

In this work, the kinetics of the development of the first-order phase transition in tetracosane $C_{24}H_{50}$ is studied.

n-Alkanes with the general formula $CH_3(CH_2)_nCH_3$ are the simplest representatives of the LCMC family. At present, there is a vast and reliable base of literature data about the structure and properties of *n*-alkanes with $17 \leq n \leq 40$. Most detailed theoretical and experimental investigations of IR absorption spectra of *n*-alkanes were carried out in all currently available IR ranges, which seems to be important for the correct interpretation of obtained experimental data [11, 12]. Moreover, nowadays it is possible to carry out investigations on commercially available *n*-alkanes with a very high degree of chemical purity and, as a consequence, monodispersity of the molecular mass (99.9%). The absence of structural and conformational defects is also of considerable interest for solving many controversial issues of polymer physics, in particular, for the development of quantitative models for the description of phase transitions.

2. EXPERIMENTAL

Samples of monodisperse (pure 99.9%) tetracosane $C_{24}H_{50}$ (Sigma-Aldrich) were studied. The absorption spectra in the region of 400–5000 cm^{-1} were recorded on an IFS-88 IR Fourier transform spectrometer (Bruker, Germany); the number of scans was 30. The accuracy of measuring the position of absorption band maximums was $\Delta\nu = 0.01$ cm^{-1}. Computer decomposition of complex IR spectra of overlapping absorption bands was carried out using the program written by V.F. Drobot'ko (Donetsk Institute for Physics and Engineering) in the MATLAB package.

The samples of necessary thickness were prepared by depositing the synthesis products—-lamellar flakes of tetracosane—on NaCl plates, their melting, and subsequent slow cooling until an equilibrium crystalline structure was obtained.

Temperature variations of the IR spectra were studied with the use of special temperature attachments in the interval from 0 to 373 K. The temperature was measured with an accuracy $\Delta T = \pm 0.05$ K using a differential chromel–copel thermocouple.

The IR absorption spectra were measured discretely with a step-by-step increase in the temperature by $\Delta T = 2$ K in the region from T_{room} to the temperature separated from the PT-1 temperature by 2 K. Then, in the region of PT-1, measurements were carried out with a step-by-step increase in the temperature by $\Delta T = 0.1$ K as the sample was kept at each measurement temperature during 10 min until reaching the equilibrium state at the given temperature.

To eliminate the possible spectrum distortion, the spectra of atmospheric moisture and CO_2 were subtracted by special programs.

3. RESULTS AND DISCUSSION

Figure 1 presents the Fourier-transform IR spectrum of thin polycrystalline tetracosane films crystallized upon slow cooling to T_{room} in the region from $\nu = 500$ cm^{-1} to $\nu = 3300$ cm^{-1}.

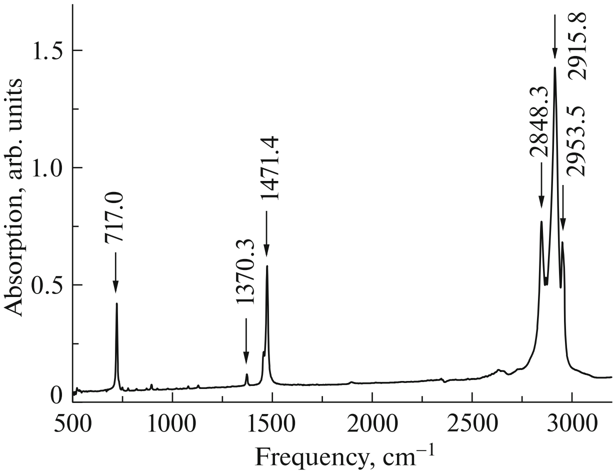

Fig. 1. Fourier-transform IR spectrum of tetracosane $C_{24}H_{50}$ in the region of 500–3500 cm^{-1}.

The spectrum exhibits intense characteristic absorption bands corresponding to different vibrational modes of methylene CH_2 groups in trans sequences, vibrations of terminal methyl CH_3 groups, and valence C–H vibrations in molecules of tetracosane $C_{24}H_{50}$. Frequencies of all observed absorption bands correspond to literature data [11, 12].

As shown in [9, 10, 13–15], there is a good correlation between the position of absorption bands in the region of rocking ($\nu \sim 720$ cm^{-1}) and bending ($\nu \sim 1470$ cm^{-1}) vibrations of CH_2 groups and type of the crystalline subcell formed of trans methylene subsequences. This correlation is determined by the potential energy of molecules in the equilibrium field of the crystal; in *n*-alkanes, this energy is caused mostly by van der Waals interactions.

In [16], it was shown that the densest packing of trans methylene sequences is characteristic of triclinic subcells because, in this case, displacements of the molecules relative to each other can occur along all vectors of the cell, which just provides the strongest van der Waals interactions between tetracosane molecules.

An increase in the interaction potential energy in triclinic cells leads to a noticeable shift of bands of rocking and bending vibrations of CH_2 groups toward lower frequencies as compared to calculated values of frequencies for individual molecules of *n*-alkanes or experimental values of frequencies of these vibrations in melts or solutions [9, 13–15] (ν (CH_2 rocking) ~ 720–722 cm^{-1} and ν (CH_2 bending) ~ 1467 cm^{-1}).

In a triclinic subcell, the planes of trans zigzags of tetracosane molecules are parallel to each other. Therefore, a triclinic subcell contains one effective centrosymmetric molecule including two methylene groups. The symmetry of IR vibrations in this case will

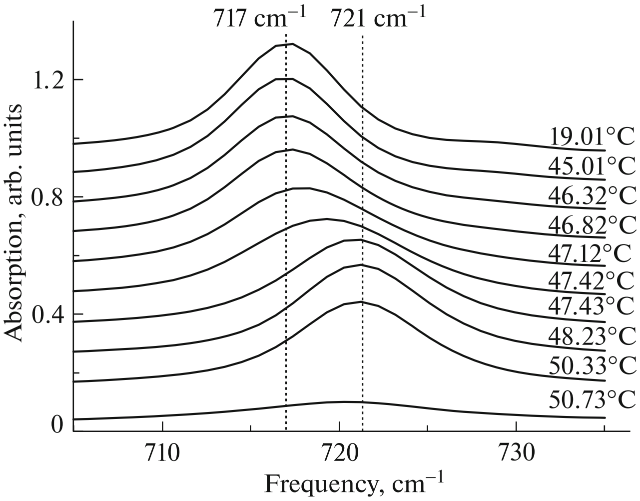

Fig. 2. Temperature variations of the IR spectrum of tetracosane in the region of rocking vibrations of CH_2 groups.

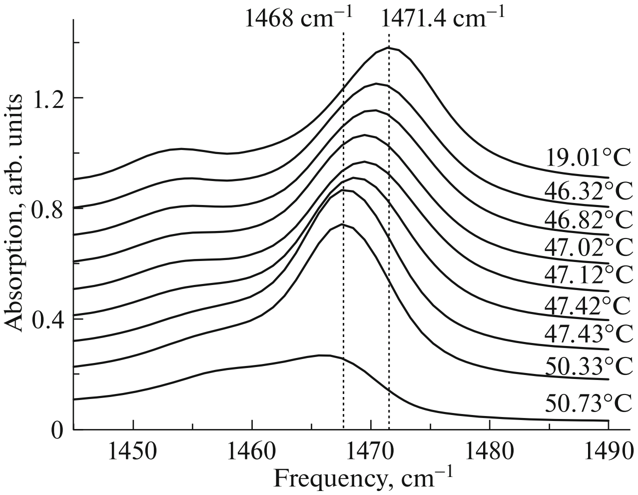

Fig. 3. Temperature variations of the IR spectrum of tetracosane in the region of bending vibrations of CH_2 groups.

be approximately the same as for an individual trans molecule with the C_{2h} symmetry. Therefore, for each of the fundamental vibrations, including the rocking and bending vibrations, only one component will be observed in the IR spectra (the Davydov splitting typical for the orthorhombic subcell is absent) [12].

The presence of intense characteristic bands in the IR spectrum (Fig. 1) at $\nu \sim 717$ cm^{-1} (rocking vibrations) and $\nu \sim 1471$ cm^{-1} (bending vibrations) allows one to say that, in the tetracosane samples obtained in our study by cooling the melt to T_{room}, there appeared lamellar nanocrystals in the cores of which methylene sequences form subcells with the triclinic symmetry [13–15].

The most intense bands in the region of 2800–3000 cm^{-1} correspond to symmetric and asymmetric valence vibrations of C–H-bonds in trans methylene sequences: $\nu^{s}_{C-H} = 2848$ cm^{-1} and $\nu^{as}_{C-H} = 2916$ cm^{-1}, respectively. In the region of $\nu \sim 2950$–2960 cm^{-1}, one can also observe a series of bands corresponding to C–H valence vibrations in the terminal methyl groups (to be discussed in the next paper).

In this work, a large array of IR spectra has been obtained in the studied temperature range from $T = 19$°C to T_{m} under stepwise increase in temperature (see the Experimental).

Figures 2 and 3 present series of sample spectra demonstrating significant temperature transformations of the spectra in the region of rocking (Fig. 2) and bending (Fig. 3) vibrations.

Based on these data, temperature dependences of the positions of absorption band maximums were constructed for rocking (Fig. 4) and bending (Fig. 5) vibrations of CH_2 groups in triclinic subcells of tetracosane.

It follows from Figs. 2 and 4 that the frequency of rocking vibrations in the initial triclinic subcell $\nu \sim 717$ cm^{-1} remains almost constant up to a temperature $T = 46.3$°C (319.3 K) and only later a gradual increase in the frequency to $\nu \sim 721$ cm^{-1} is observed in a narrow temperature range ΔT from $T = 46.3$ to $T = 48.2$°C (the intermediate values are $\nu \sim 717.2$; 717.5; 717.7; 719.0; 720.5; 720.8; and 721.0 cm^{-1}).

As shown in [9, 15, 17, 18], the frequency $\nu = 721$ cm^{-1} is peculiar to subcells of *n*-alkanes with hexagonal symmetry; they were considered for the first time in [19]. In this case, a dense packing of macromolecules approximated by effective cylindrical rods is

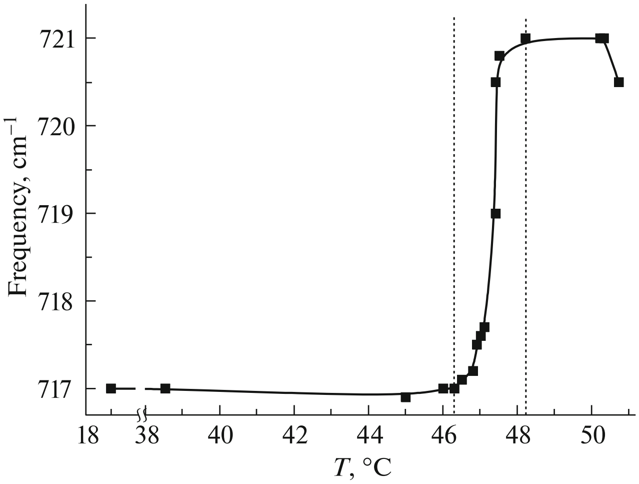

Fig. 4. Temperature variations of the frequency of rocking vibrations of CH_2 groups in tetracosane.

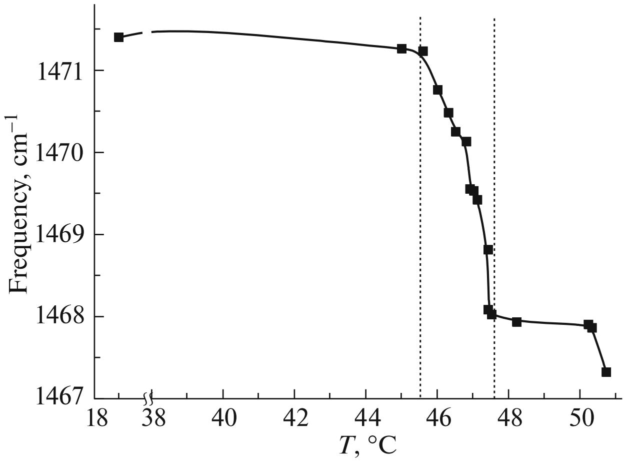

Fig. 5. Temperature variations of the frequency of bending vibrations of CH_2 groups in tetracosane.

considered, because rotation of planar chains with respect to their axis is allowed.

The uncorrelated oscillations with a limited amplitude relative to the middle position with the minimum displacement of the molecular axes result in statistical misorientation of the mutual arrangement of the planes of molecules in the matrix of the crystalline core of the lamellae. At the same time, the van der Waals contacts between neighbors are retained, which provides (primarily due to the attractive forces) the preservation of the sample in the solid phase.

It is known [16, 19] that the solid-phase transition of the first order is accompanied by the transition of trans zigzags in the crystalline core of lamellae from the tilt position relative to the base planes from terminal methyl CH_3 groups in triclinic subcells to the vertical arrangement in hexagonal cells.

As follows from our IR spectroscopic data for n-alkane $C_{24}H_{50}$, this transition is implemented in the temperature region of the solid-phase transition of the first order sufficiently smoothly, because we observe (Fig. 4) a permanent variation in the frequency of rocking vibrations of CH_2 groups from $\nu = 717$ cm^{-1} to $\nu = 721$ cm^{-1}.

We explain the smooth variation in the frequency by gradual attenuation of the van der Waals interaction between individual molecules due to thermal expansion.

In [20], when studying phase transitions by Fourier-transform IR spectroscopy in tridecanoic acid $CH_3(CH_2)_{11}COOH$, we also observed the transition from a triclinic subcell to a hexagonal one in the PT-1 region in a narrow temperature range $\Delta T \leq 1$ K. In this case, however, the transition was accompanied by a sharper change in the frequency of rocking vibrations of CH_2 groups from $\nu = 716$ cm^{-1} to $\nu = 721$ cm^{-1}, in contrast to the smoother frequency change we observe in n-alkane.

It is known [1] that hydrogen bonds forming in monocarboxylic acids on one of the lamella surfaces between carboxylic groups are significantly stronger than van der Waals bonds. They play to a certain extent the part of mechanical “clamps” impeding the increase in the mobility of molecule trans zigzags in crystalline cores when heating molecular crystals. For this reason, melting temperatures of carboxylic acids noticeably exceed T_m for n-alkanes with the same length of methylene sequences [1].

We believe that it is the presence of “clamps,” i.e., hydrogen bonds in tridecanoic acid (in contrast to n-alkanes), that impedes the gradual increase in intermolecular distances in triclinic subcells on heating and, as a consequence, leads to sharper changes in frequencies of rocking and bending vibrations in the region of the phase transition of the first order.

Analysis of the behavior of bending vibration bands of CH_2 groups in the region of 1450–1490 cm^{-1} (Figs. 3 and 5) demonstrates that the character of the variation in the IR spectrum in the region of PT-1 is similar to rocking vibrations. Namely, with an increase in temperature, the band $\nu = 1471.4$ cm^{-1} which is peculiar to the triclinic subcell is transformed into the band $\nu = 1468$ cm^{-1} indicating the appearance of a hexagonal subcell of n-alkanes [9, 15, 17, 18].

At the same time, the gradual character of the variation in this vibration mode is also observed: values $\nu_{CH_2}^{bend} = 1471.4$, 1470.8, 1470.5, 1470.2, 1469.6, 1469.4, 1468.8, and 1468.0 cm^{-1} are distinctively recorded approximately in the same narrow temperature range ΔT from $T = 45.5$ to $T = 47.5$°C.

The kinetics we have revealed in the development of the phase transition of the first order indicates the generation of nanonuclei of a new phase with the hexagonal type of the subcell in the crystalline core of initial lamellae with triclinic subcells and the gradual increase in the number of new nuclei with the development of the phase transition in a narrow temperature interval $\Delta T \sim 1$ K according to the theory of diffuse phase transitions of the first order [6].

With the further increase in temperature from $T \sim 47.5$°C to $T \leq 50$°C (the region between PT-1 and PT-2 (melting of tetracosane)), the value $\nu = 1468$ cm^{-1} is retained, which testifies about the hexagonal phase of tetracosane. The change in the frequency of bending vibrations to $\nu = 1467$ cm^{-1} occurs only at a temperature somewhat above $T_m \sim 52$°C (Fig. 5). This frequency is peculiar to isolated chains of liquid or solved n-alkanes [9, 15]. Individual bands become significantly wider and asymmetric (Fig. 3), which is, certainly, related to an increase in the rotatory power of the molecules and appearance of conformational defects of different types: GTG⁻-kinks, T_mG-end-gauche defects, GG and GTTG defects, and others.

Each of the considered types of conformational defects is associated with certain absorption bands in the region of $\nu = 1200–1450$ cm^{-1} [21] which we also observed in our Fourier-transform IR spectra at higher temperatures (these data will be presented in the next paper).

Values of the observed frequencies $\nu = 720$ cm^{-1} for rocking vibrations and $\nu = 1467$ cm^{-1} for bending vibrations for tetracosane in the melt correspond to literature data for *n*-alkanes with a varying number of CH_2 groups in different phase states, namely, in the liquid state at small $n = 6–15$ and melts or solutions up to $n = 34$ [11, 12, 15, 21]. In all cases, the frequencies of rocking and bending vibrations turn out to be near $\nu = 720$ and 1467 cm^{-1}, respectively. It means that the effective intermolecular potential in these states turns out to be approximately the same and attenuated as compared to the potential for different types of initial crystalline subcells (triclinic, monoclinic, and orthorhombic ones) that are formed during crystallization of *n*-alkanes depending on the *n* number of C–C bonds.

4. CONCLUSIONS

Using Fourier-transform IR spectroscopy, the kinetics of the development of the solid-phase structural transition of the first order in monodisperse samples of tetracosane $C_{24}H_{50}$ has been studied. It has been shown that, in a narrow temperature interval $\Delta T \sim 2$ K, there appear nanonuclei of the new (hexagonal) phase with a volume $\omega \sim 100–200$ nm^3 by the fluctuation mechanism, and the new phase gradually propagates to the whole volume of the initial (triclinic) phase due to the advance of the interphase boundary by adding new stable nanonuclei with the volume ω to it according to the theory of diffuse phase transitions of the first order.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. D. M. Small, *The Physical Chemistry of Lipids* (Plenum, New York, London, 1986).
2. V. M. Egorov, V. A. Marikhin, and L. P. Myasnikova, Polymer Sci., Ser. A **49**, 1270 (2007).
3. V. M. Egorov, V. A. Marikhin, and L. P. Myasnikova, Phys. Solid State **55**, 1057 (2013).
4. L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics*, Vol. 5: *Statistical Physics* (Nauka, Moscow, 1976; Pergamon, Oxford, 1980).
5. B. N. Rolov and V. E. Yurkevich, *Physics of Blurred Phase Transitions* (Rostov. Univ., Rostov-on-Don, 1983) [in Russian].
6. G. A. Malygin, Phys. Usp. **44**, 173 (2001).
7. T. Yamamoto, K. Nozaki, and T. Hara, Phys. Chem. **92**, 631 (1990).
8. R. Popovitz-Biro, Y. L. Wang, Y. Majewski, E. Shavit, L. Leiserowitz, and M. Lahav, Am. Chem. Soc. **116**, 1179 (1994).
9. R. G. Snyder, Mol. Spectrosc. **7**, 116 (1961).
10. G. Zerby, R. Magni, M. Gussoni, K. H. Moritz, A. Bigotto, and S. Dirlikov, Chem. Phys. **7**, 3175 (1981).
11. Y. C. Koenig, *Spectroscopy of Polymers* (Am. Chem. Soc., Washington, 1992).
12. P. C. Painter, M. M. Coleman, and Y. C. Koenig, *The Theory of Vibrational Spectroscopy and Its Application to Polymeric Materials* (Wiley, New York, 1982).
13. R. G. Snyder, Mol. Spectrosc. **4**, 411 (1960).
14. R. F. Holland and I. R. Nielsen, Mol. Spectrosc. **8**, 383 (1962).
15. D. Chapman, Chem. Soc., 4489 (1957).
16. A. I. Kitaigorodskii, *Molecular Crystals* (Nauka, Moscow, 1971) [in Russian].
17. H. L. Casal, Can. J. Chem. **61**, 1736 (1983).
18. H. L. Casal, H. H. Mantsch, and D. G. Cameron, Chem. Phys. **77**, 2825 (1982).
19. A. Muller, Proc. R. Soc. London, Ser. A **138**, 5 (1932).
20. V. A. Marikhin, L. P. Myasnikova, E. I. Radovanova, B. Z. Volchek, and D. A. Medvedeva, Phys. Solid State **59**, 331 (2017).
21. R. G. Snyder, Chem. Phys. **47**, 1316 (1967).

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