

Phase Transitions in Molecular Crystals of *n*-Alkanes: Tri-, Tetra-, and Pentacosane

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Abstract—Phase transitions in normal alkanes, such as tricosane ($C_{23}H_{48}$), tetracosane ($C_{24}H_{50}$), and pentacosane ($C_{25}H_{52}$), were studied by differential scanning calorimetry. The elimination of some procedural errors provided the possibility to obtain true values for the thermodynamic parameters of phase transitions and ascertain their nature. The comparative analysis of heat capacity jumps was performed on the basis of the theory of diffuse first-order phase transitions.

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The study of the homological series of different long-chain molecular crystals (of *n*-alkanes and their derivatives) opens new opportunities for the establishment of quantitative regularities between the structure of polymers and their thermodynamic properties, as these compounds do not contain any chemical defects and can be synthesized with a purity unattainable for conventional polymers.

One of the important problems in solid-state physics is the clarification of a number of controversial questions about the nature of first- and second-order phase transitions. The clarification of these questions is important not only from the fundamental viewpoint, but also for the solution of many practically important problems, as the manufacturing of articles from polymers is always accompanied by phase transitions at different stages of their processing.

One of the efficient methods for the study of phase transitions is differential scanning calorimetry (DSC), which is widely used for the investigation of molecular crystals of different type [1–5], including crystals of paraffins [6–8]. As a rule, most published works do not describe and analyze any studies in heating–cooling cycles, which are important to ascertain the nature of phase transitions and obtain the true profiles of endo- and exotherm in thermogravimetric curves as shown in this work. Moreover, procedural errors, which are produced by the effect of thermal resistance in DSC measurements and may lead to appreciable distortions in the thermodynamic characteristics of phase transitions, have not been eliminated in the overwhelming majority of works. The latter circumstance is very essential for the experimental data analysis, which can be performed using the currently

developed theories of diffusion first- and second-order phase transitions ([9, 10] and [11], respectively).

In this work, samples of *n*-alkanes with an even and odd number of carbon atoms in their chain were studied to ascertain (see below) the effect of evenness on the kinetics of the development of phase transitions in *n*-alkanes. Tricosane ($C_{23}H_{48}$), tetracosane ($C_{24}H_{50}$), and pentacosane ($C_{25}H_{52}$) samples were acquired from the Sigma company. Thermal properties were studied on a Seiko DSC 6100 calorimeter at heating and cooling rates varied within a range of 0.6–5 K/min. A small weight of samples for experiments at a level of 3–5 mg provided a minimum thermal resistance in a calorimetric cell and decreased procedural errors.

Figure 1 illustrates the DSC curves obtained during the heating and cooling of samples of tricosane (1), tetracosane (2), and pentacosane (3). As can be seen from Fig. 1, the endothermic phase transition from a crystalline state into a melt under heating occurs for these paraffins in two stages: The DCS curves can be seen to contain a doublet with maximum temperatures $T_{\max 1}$ and $T_{\max 2}$. The backward process of melt–crystal change in the phase state under cooling also occurs in two stages (the minimum temperatures of the exotherms corresponding to them are $T_{\min 1}$ and $T_{\min 2}$). It should be noted that the shapes of endotherms for the transition from a crystalline state into a melt have some specific features for each of the studied materials, their analysis is given below.

Such a picture in the general form corresponds to the results of the published works, so it might be expected that the endotherm with $T_{\max 1}$ under heating is likely to be due to the structural solid-state phase transition T_{s-s} followed by the melting of a sample at a

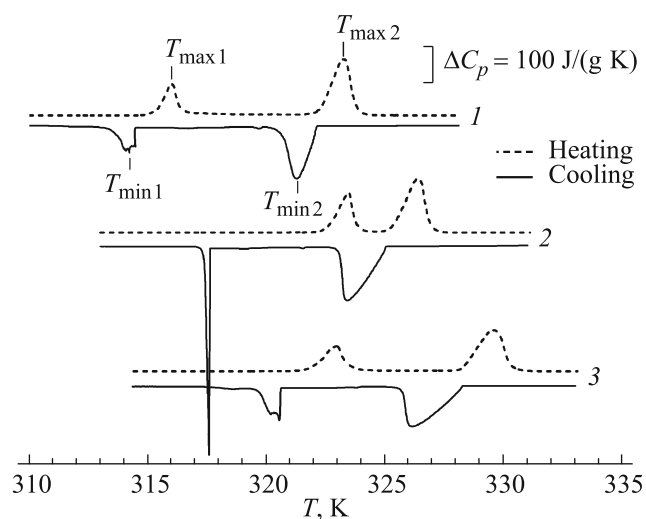


Fig. 1. DSC curves obtained under the heating (dashed) and cooling (solid) of (1) tri-, (2) tetra-, and (3) pentacosane samples. Scanning rate $V = 0.6$ K/min.

temperature $T_{\max 2}$. Correspondingly, the inverse picture is observed in this case under cooling from a melt: they crystallize at $T_{\min 2}$ with a solid-phase transition at $T_{\min 1}$ [6–8].

To understand the physical nature of the transitions detected in the thermogravimetric curves, it is necessary to clarify the picture with the observed temperature discrepancy between the peaks. The DSC curves demonstrate the displacements of the relative positions of endo- and exotherm peaks in heating–cooling cycles ($T_{\max 1} - T_{\min 1}$) and ($T_{\max 2} - T_{\min 2}$) (so-called effect of lag). It is important that the displacements for each peak of the doublet have its particular nature governed by both procedural and physical causes. It is known [12] that some procedural errors (peak displacements) appear during differential scanning calorimetry due to the thermal resistance of a tested sample in a calorimetric cell, and this resistance appreciably depends on the sample mass and the scanning rate. In the work [13], it is shown that these procedural errors can be eliminated as follows: depen-

dences $T_{\max, \min} = f(V^{1/2})$ are plotted by experimental data at a varied scanning (heating or cooling) rate V and must be linear in the absence of structural transformations. The extrapolation of linear dependence to $V \rightarrow 0$ gives true temperatures of transitions without procedural errors.

Figure 2 demonstrates similar dependences for the studied samples of tricosane (a), tetracosane (b), and pentacosane (c) in heating–cooling cycles. The extrapolation (true) phase transition temperatures and lags obtained from these dependences are given in Table 1. From these data it can be concluded that the heating–cooling cycles actually have no thermal lags for the second maxima, and the difference observed in the experimental DSC curves between their positions on the temperature scale is due to procedural causes. At the same time, the elimination of procedural error with the use of extrapolation dependences provided the possibility to reveal the existence of a true lag for the low-temperature transition in these samples.

The enthalpy ΔH and entropy ΔS of transitions in the DSC method do not depend on the rate of scanning by temperature and are determined from the relationships $\Delta H_{\text{exp}} = \int C_p(T) dT$ and $\Delta S_{\text{exp}} = \int C_p(T) d(\ln T)$. The summary enthalpy ΔH_{summ} and ΔS_{summ} and their components for the first- and second-order transitions (ΔH_1 , ΔS_1 and ΔH_2 and ΔS_2 , respectively) are given in Table 2.

As is known [11], the presence or absence of a thermal lag in a physical property, including the peaks in the thermal dependence of the heat capacity, is one of the important features by which phase transitions are classified among first- or second-order transitions, respectively. For this reason, the absence of a lag for the second maxima immediately points to that the high-temperature peaks in the doublets belong to second-order transitions. If the data obtained at one rate of scanning by temperature (Fig. 1) are used alone without the extrapolation dependences $T_{\max, \min} = f(V^{1/2})$ applied in this work, the high-temperature peaks can be mistakenly assigned to first-order transitions and, unfortunately, this takes place in a number

Table 1. Thermal parameters of phase transitions in tricosane, tetracosane, and pentacosane (according to the results of extrapolation to zero scanning rate)

Sample	Scanning type	Peak 1 in the doublet			Peak 2 in the doublet		
		T_{\max} , K	T_{\min} , K	ΔT , K	T_{\max} , K	T_{\min} , K	ΔT , K
Tricosane	Heating	315.4		0.5	322.3		0
	Cooling		314.9			322.3	
Tetracosane	Heating	322.9		5.5	325.5		0
	Cooling		317.4			325.5	
Pentacosane	Heating	322.4		1.3	328.5		0
	Cooling		321.1			328.5	

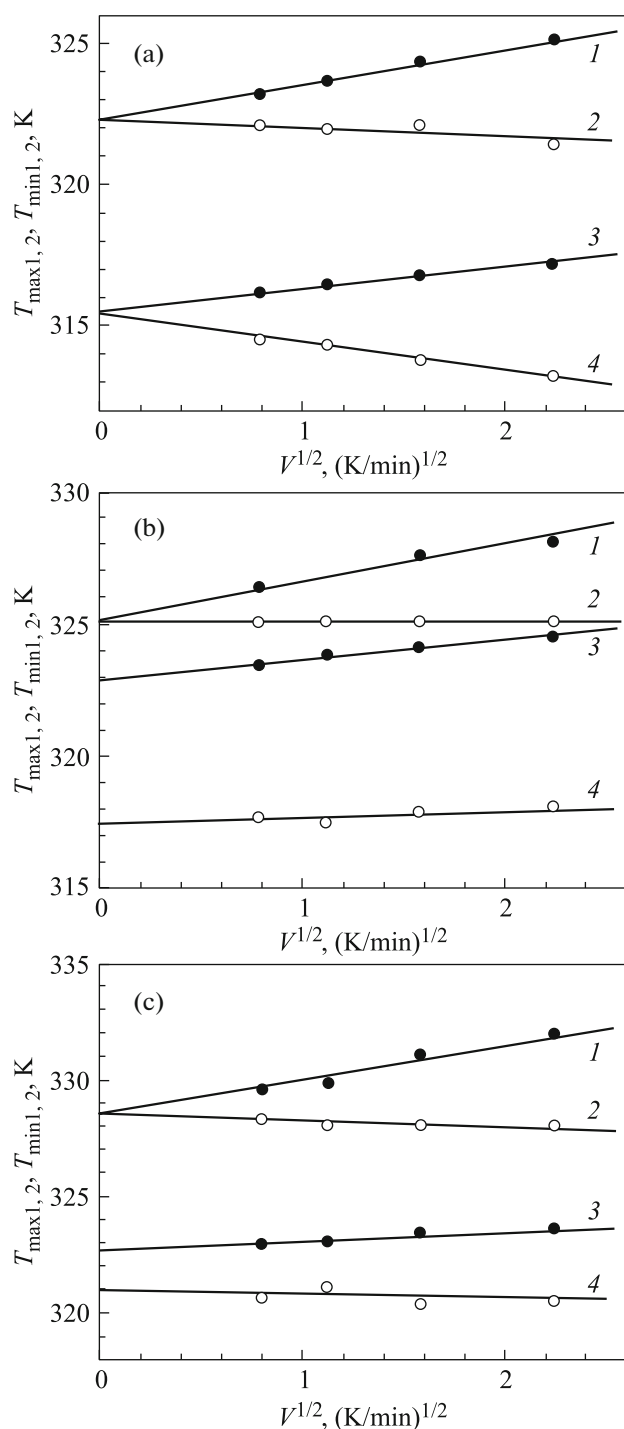


Fig. 2. Phase transition temperature versus scanning rate for (a) tricosane, (b) tetracosane, and (c) pentacosane under heating (dark points) and cooling (light points): (1) $T_{\max 2}$, (2) $T_{\min 2}$, (3) $T_{\max 1}$, (4) $T_{\min 1}$.

of papers. On the other hand, the presence of a true lag for the low-temperature peak provides the possibility to classify this transition as a solid-phase (structural) first-order transition associated with the change of the crystal symmetry type on the basis of DSC data. In the

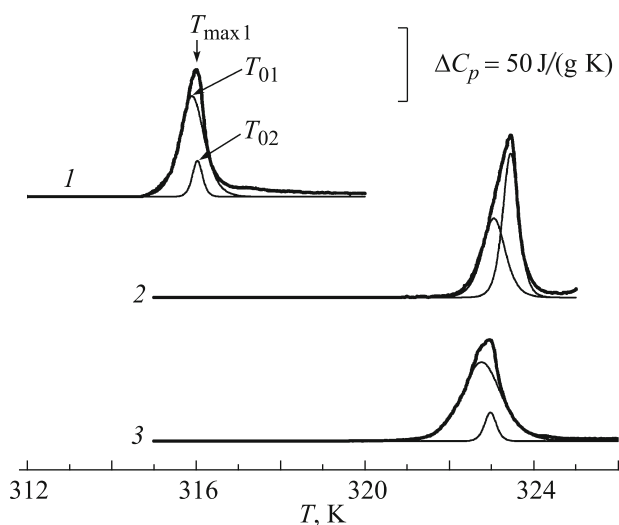


Fig. 3. Endotherms corresponding to the solid-phase transitions in (1) tri-, (2) tetra-, and (3) pentacosane for experimental data (solid line) and the result of calculation by Eq. (1) (fine line).

earlier works [2, 14–16], it has been shown using X-ray diffraction that the symmetry of molecular crystals is really changed within the temperature range corresponding to the heat capacity peak with $T_{\max 1}$: an orthorhombic unit subcell becomes hexagonal in the crystalline cores of lamellae.

If first- and second-order transitions are spaced apart on the temperature scale, the solid-phase transition peak can be analyzed in this case independently from the first-order transition. As can be seen from Fig. 1, the C_p endo- and exotherms corresponding to first- and second-order phase transitions in a heating-cooling cycle (the transition from a crystalline state into a melt and the backward transition from a melt into a crystal) for the studied samples are pronouncedly spaced apart on the temperature scale. This circumstance allows us to distinguish two endotherms corresponding to structural first-order phase transitions (Fig. 3). From Fig. 3 it can be seen that the peaks have proven to be asymmetric, and this may be due to the existence of at least two components. These specific features in the shape of peaks are discussed below.

The peaks obtained by the above described method were analyzed within the thermodynamic self-consistent field theory [9, 10, 17] as applied to diffusion Λ -shaped first-order phase transitions. The fact that the transition becomes diffusion means that the change in the phase state is not sudden, but gradual and occurs within a certain temperature range. The theory provides the possibility to analyze the change in the phase state of a system of interacting particles of different phases, including the formation and further growth of stable nuclei of a new phase in the matrix of the old phase. The nucleation mechanism is heterogeneous, and new phase nuclei are formed on crystal defects of

Table 2. Thermodynamic parameters of phase transitions in tricosane, tetracosane, and pentacosane

Sample	ΔH_1 , J/g	ΔS_1 , J/(g K)	ΔH_2 , J/g	ΔS_2 , J/(g K)	ΔH_{summ} , J/g	ΔS_{summ} , J/(g K)
Tricosane	61	0.193	172	0.534	233	0.727
Tetracosane	89	0.276	153	0.470	242	0.746
Pentacosane	79	0.245	155	0.472	234	0.717

Table 3. Thermodynamic parameters of the first-order phase transition in tricosane, tetracosane, and pentacosane

Sample	Peak in the doublet	Share in the transition energy, %	T_0 , K	B	ΔC_{max} , J/(g K)	q_0 , J/g	ω , nm ³
Tricosane	1	87	315.9	1650	70	54	128
	2	13	316.03	4000	25	8	2700
Tetracosane	1	44	323.05	1800	55	39	250
	2	56	323.45	2600	100	50	290
Pentacosane	1	91	322.76	1250	55	68	100
	2	9	322.97	3500	20	7	2800

different kind, thus leading to the appearance of a phase interface, which is the characteristic sign of a first-order transition. The main idea of the theory consists in the notion that numerous fluctuations are located in a limited volume in the old phase in the form of stable nuclei of a new phase, i.e., so-called elementary transition volumes ω . Further, as the transition develops, the motion of the phase interface occurs via the sequential additions of nuclei with a volume ω to the formed phase interface. The formation of domain nuclei requires the change in the temperature at a small value, which is determined by the energy required for the appearance of such domains. Just this factor leads to diffusion in the transition by temperature. For example, it has been shown for ferroelectric materials that elementary transition volumes are comparable with the so-called Kenzig domain ($\sim 10^{-18}$ – 10^{-17} cm³) and located at a mesoscopic level by their scale [18, 19].

The sizes of stable nuclei ω can be determined from the shape of C_p peaks corresponding to first-order transitions. In the work [20], the temperature dependence of the heat capacity in a diffusion phase transition is derived in the form

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

where T_0 is the temperature of a first-order phase transition, ΔC_m is the maximum heat capacity at $T = T_0$, and B is the athermic parameter.

Nonsymmetric peaks were divided into two symmetric Λ -shaped peaks, assuming the equality of the enthalpy of an experimentally obtained peak to the sum of the enthalpies of two symmetric peaks. Varying the parameters T_0 , ΔC_{max} , and B for each symmetric

peak, it was possible to attain coincidence with either the right (high-temperature) or left (low-temperature) shoulder of the peak. The best coincidence between experimental and calculated dependences was observed for the parameters given in Table 3 (peaks 1 and 2). The results of the calculation of Λ -shaped peaks by Eq. (1) and the experimental dependences of the heat capacity $\Delta C_p(T)$ are plotted in Fig. 3.

The parameter B in Eq. (1) contains the most interesting information about the physical nature of a phase transition, as it is related with the maximum heat capacity ΔC_m as

$$\Delta C_m = q_0 B / 4T_0, \quad (2)$$

where q_0 is the transition heat, and the elementary transition volume ω as

$$B = \omega \rho q_0 / k T_0, \quad (3)$$

where k is the Boltzmann constant, and ρ is the density.

The parameter B proves to be structurally sensitive, as it characterizes the volumes of new phase nuclei in materials with diffusion phase transitions [10]. The specific transition heat (enthalpy) can be determined from Eq. (2), and the elementary transition volume ω can be estimated from Eq. (3) (assuming in the first approximation that the density of paraffin crystals $\rho \sim 0.8$ g/cm³ [1]). The results of calculations by these equations are listed in Table 3.

In the earlier works [3–5], it has been established for a broad range of molecular crystals of n -alkanes and their derivatives that the elementary volumes of new phase nucleation domains associated with a solid-phase transition depend on the evenness of the number of C–C bonds. Thus, the volumes ω for even n are

two times larger than for odd n and attain ~ 200 and ~ 100 nm³, respectively. From the comparison of ω given in Table 3 (peak 1) it can be seen that this ratio is fulfilled as a whole (for 87 and 91% of the mass of a crystal of tricosane and pentacosane, respectively). The estimation of the number of molecules participating in the formation of a new phase in tricosane and pentacosane shows that elementary transition volumes ($\omega \sim 100$ – 130 nm³) contain ~ 200 – 250 molecules at the first phase transition stage, i.e., the transition covers a rather great domain. The phase transition in tetracosane also occurs in two stages (peaks 1 and 2, Table 3), which appreciably differ from each other by their elementary transition volume containing ~ 500 – 600 molecules. A much greater number of molecules (~ 5000) participate in the formation of new phase nuclei at the second phase transition stage in tricosane and pentacosane (peaks 2, Table 3).

When considering the possible local region of the appearance of stable new phase nuclei, it is necessary to take into account the shape and location of new phase domains or nuclei. For the reason of minimizing the internal energy, it is natural to suppose that, first, a new phase nucleus can be located within a stack of two lamellae as shown in [21] and, second, the phase interface cannot pass through a molecule part, i.e., through the strongest chemical bonds in the methylene part of molecules (C–C and C–H), and seems to pass through the relatively weak van der Waals bonds between the methylene groups of neighboring molecules and the terminal CH₃ groups. Hence, a domain can be described as a parallelepiped built of parallelly packed “rods,” whose base contains 200–600 methylene chains. The further growth of a new phase in volume, as mentioned above, will more readily occur due to the addition of new volumes to the side surface. This growth will occur until the appearance or accumulation of hindrances increasing the side surface energy on the side surface. In this case, methylene groups must overcome the surplus barrier preventing the addition of new volumes to the side surface besides intermolecular interaction forces (IIFs).

As mentioned above, the forces of bonds between structural units in the case of molecular crystals of paraffins are IIFs. For the side surfaces of an elementary volume, they represent the force of van der Waals interaction between $-\text{CH}_2-$ groups. For the end surfaces ($-\text{CH}_3$ groups) they also are van der Waals interaction forces. The quantitative measure of IIFs is the cohesion energy E_c determined as the energy required for the destruction of intermolecular contacts and the transition of a solid into a gas phase through a liquid state. A decrease in the intermolecular interaction energy upon phase transition occurs due to a partial decrease in the cohesion energy ΔE_c . The experimental estimation of this decrease for the compounds consisting of polyatomic molecules is difficult. The energy ΔE_c can be compared with the potential barrier for the

motion of a molecule in local liquid-like acts of motion in a solid. This barrier determined by experiment for glassy liquids and solid oligomers, which appreciably differ from each other by the character of IIFs and the structure and shape of molecules, including compounds with a developed system of hydrogen bonds, is equal to $\sim 0.4E_c$ [22].

The energy E_c can experimentally be determined only for low-molecular-weight bodies able to exist in the gas phase. The process of vaporization is preceded by destruction for the majority of oligomers, polymers, and molecular crystals, so the cohesion energy is determined for them in an indirect way or calculated [22, 23]. In this work, the cohesion energies given in the monography [22] for the contributions of $-\text{CH}_2-$ groups $E_{c1} = 3.6$ kJ/mol are used.

As can be seen from Fig. 3, the phase transition initiated by the nucleation of new phase domains with a volume $\omega \sim 100$ – 130 nm³ occurs at the first stage with the overcoming of the IIF barrier equal to $0.4E_{c1}$. The phase transition in the greater part of a crystal (this follows from the ratio between the heat values and the transition at the first and second stages, Table 3) leads to the exhaustion of defect-free crystal regions and an increase in the surface energy due to the accumulation or appearance of hindrances in the remaining crystal part, which has not sustained phase transition. At the second stage of phase transition in tricosane and pentacosane with $\omega \cong 2700$ – 2800 nm³, the phase transitions associated with the overcoming of formed or accumulated hindrances occurs in the remaining part of a crystal.

To estimate the potential barrier created by these hindrances, let us turn to the dependence relating one of the geometric parameters, namely, the lamella thickness L with the elementary transition act volume ω as

$$L = \omega^{1/3}(E_c/E_{c1})^{2/3}, \quad (4)$$

where E_{c1} and E_c are the cohesion energies of the methylene and terminal groups, respectively [21].

The constancy of E_c follows from the assumption that a further increase in the volume of a new phase on overcoming the surplus barrier will occur via the addition of new volumes to the side surface, i.e., without changing the wall thickness. The latter allows us to use Eq. (4) to obtain the relationship

$$E_{c2} = \omega_2^{1/2}\omega_1^{-1/2}E_{c1}$$

and determine the sought potential barrier equal to $\sim 0.4E_{c2}$. For tricosane, tetracosane, and pentacosane, these values have proven to be 6.6 kJ/mol (1.6 kcal/mol), 3.9 kJ/mol (0.4 kcal/mol), and 7.6 kJ/mol (1.8 kcal/mol), respectively.

The comparison of the obtained values with the known literature data on paraffins [24] allows us to interpret these potential barriers as barriers preventing

the motion of molecular defects like kinks $2g1$ along the axis of a molecule by the flip-flop mechanism. These defects, whose motion is associated with the shift at one $-\text{CH}_2-$ group and the simultaneous rotation of *trans*-zig-zag at 180° , have two potential barriers. One of them (~ 1.7 kcal/mol) prevents the displacement of the $-\text{CH}_3$ group exerting into the interlamellar layer and the motion of a paraffin macromolecule inside the lamellar core, and the other barrier (~ 0.6 kcal/mol) prevents the motion in the opposite direction.

In the work [25], it is shown that the number of irregular conformers like kinks $2g1$ and terminal *gauche*-conformers like $g-t_m$, where t_m is a *trans*-sequence of $-\text{CH}_2-$ groups at $m \geq 5$, abruptly grows under the heating of *n*-alkanes (especially in the region of phase transitions). The appearance of these irregular conformers destroys the initial structure of the crystalline core of lamellae of *n*-alkanes and, naturally, this occurs during a first-order phase transition. We believe that these conformation defects are concentrated during the development of a phase transition predominantly of the phase interfaces of appearing nuclei, thus creating hindrances for the further propagation of an interface. The overcoming of appearing potential barriers requires additional energy provided by a further increase in the temperature.

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