Physics of the Solid State, 2025, Vol. 67, No. 11

07,11,13,15

Effect of Heating Rate on Phase Transition Evolution in Phase Change Materials

© A.K. Borisov, S.A. Gureva, V.A. Marikhin

Ioffe Institute,
St. Petersburg, Russia

E-mail: Borisov.ak@mail.ioffe.ru

Received October 17, 2025
Revised November 7, 2025
Accepted November 10, 2025

The influence of heating modes on the kinetics of phase transformations in phase change materials was studied using differential scanning calorimetry. Using tetracosane as an example, it was shown that changing the heating rate significantly affects the thermodynamic parameters of phase transitions. For each of the studied scanning rates, temperatures, enthalpies, and heat capacities were determined for both the solid-solid phase transition and the melting process. The onset temperatures of phase transformations were found to be sensitive to the heating rate, but to a lesser extent than the temperatures of the transition peaks and end points. A quantitative analysis of solid-solid transformations based on the theory of diffuse phase transitions revealed the influence of the heating rate on the kinetics of their heterogeneous development. Furthermore, the effectiveness of the extrapolation method for determining the true phase transition temperatures was demonstrated; these were found to be equivalent to the experimental data values at a heating rate of 0.1 °C/min.

Keywords: phase transitions, thermal analysis, phase change materials, n-alkanes, calorimetry.

DOI: 10.61011/PSS.2025.11.62963.280-25

1. Introduction

In modern science searching for ways to transition to „green“ power based on environmentally clean and resource-saving technology holds a prominent place. Phase change materials (PCM) [1] play a special role in this process, being able to repeatedly accumulate, store and release thermal energy from various external sources, e. g. sun, due to their own phase transitions. Currently PCMs are becoming more and more popular since they can be used in different spheres, for example, construction [2,3], textile [4], medical [5].

Long-chain molecular crystals (LCMC), in particular, n-alkanes, are one of the most promising and widely used PCMs, since they possess high energy capacity and a unique property of targeted change of phase transition temperature by variation of the molecular chain length, i. e. selection of a certain LCMC homologue [4,6]. This feature opens opportunities for precise adjustment of PCM for specific practical tasks. However, despite the growing interest in practical application of PCM, many fundamental aspects of phase changes in such materials remain understudied, which slows down the search for the ways to improve practically important properties. This study is aimed at analysis of impact of heating temperature modes on the development of phase transitions, which is important not only for the fundamental problems of phase transition physics, but for the practical application of PCM, since the real conditions of their functioning usually include a change in the heating/cooling speed.

The problem of precise measurement of phase transition temperature is becoming more and more relevant in the recent years against the background of substantial increase in the number of studies and publications on PCM. In general practice it is common to conduct calorimetric analysis at rather high scanning speeds, often being limited to just one speed value usually equal to 5−10 °C/min [7–11]. However, such experiment imposes significant limitations on the spectrum of the obtained results, since selection of a certain heating/cooling speed may substantially change the thermodynamic parameters, especially the phase transition temperature. At high scanning speeds some phase transitions may even „absorb“ the others, i.e; they will not be permitted at temperature dependences, especially transitions with small differences in the activation energies.

Besides, there is still no single opinion in thermal analysis about how to define the melting temperature or temperature of any other phase transition appearing as a peak in a thermogram. Some authors take the start of the phase transition peak deviation from the basic line as the sought for temperature, others — note the peak maximum temperature, in some papers the transition point is the crossing of the extrapolated basic line and the tangent to the front of the peak passing through the maximum, for example, [10,12,13]. Note that the authors of paper [14] based on combined experimental and theoretical analysis of PCM heat transfer concluded that peak temperature — is just sample temperature at maximum heat exchange, and it does not indicate the end of the transition.

However, the main problem is that all these methods are not free from the impact of scanning speed at the phase transition temperatures. At high heating speeds the differences in the phase transition temperatures defined by various methods may achieve even dozens of degrees.

Some papers recommend to scan the sample with low heating/cooling speed for precise transition temperature measurement [15–17]. However, selection of the heating/cooling speed was always a compromise between the enthalpy and temperature measurement.

Besides, a question arises, how to define most precisely the entire temperature interval of the phase transition. It is especially difficult to define the end of the transition, since it is the one that mostly depends on the scanning speed. The authors of paper [18] proposed a new method to determine the melting interval for PCM by measurement of the partially melted sample by the method of differential scanning calorimetry. They cyclically heated the sample from the room temperature to the temperature in the PCM melting range with a pitch of 0.5 °C. Therefore, the final melting temperature was found, which in this method does not depend on the heating speed. However, this method seems to be rather labor intensive, since it requires multiple cyclic heating–cooling measurements. Besides, the authors note that the end temperature determined using this method is nearly the same as the temperature measured at low heating speed.

It should be noted that low scanning speeds require a long and continuous experiment, which may be difficult for consistent research. Besides, DSC experiments (DSC — differential scanning calorimetry method) at low speeds are very sensitive to the environmental conditions, especially to temperature oscillations and air currents, which may arise from air conditioners in operation, open windows or doors and even from minor personnel movement. Faster speeds are less sensitive to these factors, since signal-to-noise ratio increases proportionately to speed. Therefore, high-precision performance of DSC experiments at low speeds under real conditions is rather complicated, which requires development of special methods making it possible to avoid such experiments without a substantial loss in measurement accuracy.

The main objective of this paper is to establish the impact of heating speed on thermodynamic parameters of phase transitions and on the features of transformation of crystalline structure of molecular crystals in phase transitions. Besides, the method will be proposed to determine precise temperatures of phase transitions, which is quite simple to use and does not require labor intensive experiments.

2. Experiment

This study was carried out using the differential scanning calorimetry (DSC) method, which makes it possible to study the nature of phase transitions and also to monitor the change of thermodynamic parameters in process of scanning speed variation. Using the theory of diffuse phase transitions (DPT), which we used first for quantitative analysis of DSC thermograms, it is possible to obtain information on phase transition development at nanolevel [19–23]. The DPT theory assumes a heterogeneous mechanism of phase transition development via fluctuation generation of new phase nuclei in the volume of the initial one. Further propagation of the new phase happens by serial layering of nuclei onto each other, whereas at each stage a minor temperature change is necessary, which in the end smears phase transitions by temperature.

The most indicative for calorimetric studies with variation of scanning speeds are normal alkanes (n-alkanes), since most of them has two phase transitions, located in close proximity (up to 10°C) and are characterized with intense peaks in DSC thermograms. A change in the heating speed may cause both the merger of these peaks at high speeds and their complete separation at low speeds.

A sample chosen for the studies was a typical representative of n-alkanes — monodisperse normal tetracosane n-$C_{24}H_{50}$, made by Sigma-Aldrich with purity of 99.0 %. Tetracosane has reversible phase transitions, which makes it possible to conduct cyclic calorimetric studies of heating speed impact in the same sample, thus avoiding distortions of thermograms related to the individual features of every sample.

Thermal properties were determined using a Henven HSC-4 (China) calorimeter in nitrogen atmosphere with speed variation from slow (0.1 °C/min) to fast (50 °C/min). The instrument was calibrated by official representatives of Beijing HENVEN Experimental Equipment Co., LTD. Temperature was adjusted in ice (0°C), indium (156.6°C), tin (231.9°C), lead (327.5°C) and zinc (419.5°C) melting temperatures. Enthalpy was calibrated by tabular values for indium (28.5 J/g), tin (60.7 J/g), lead (22.6 J/g) and zinc (112.2 J/g). The sample weight was 9.7 mg, which provides for intensity of phase transitions that is sufficient for registration at all scanning speeds that we consider, and also minimizes the impact of heat resistance.

DSC thermograms were obtained by heating the tetracosane sample in the temperature range from T_{room} to T_{melt} at speeds of 0.1, 0.5, 1, 2, 5, 10, 20 and 50 °C/min.

3. Results and discussion

Figure 1 shows experimental DSC thermograms of the tetracosane sample in the area of phase transformations with scanning speed variation. From the figure you can see that increase of the heating speed causes increased temperature values in the peak maxima, their half-widths and especially to the specific shift of the rear front of the peak to the high-temperature area.

It should be noted that in tetracosane the phase transformation of solid — melt occurs at least in two stages [24,25]. DSC thermograms demonstrate two intense peaks, the first corresponding to the solid-solid phase transition (PT-1), and the second one — to melting (PT-2). In process of the solid-phase transition the type of the lattice cell changes

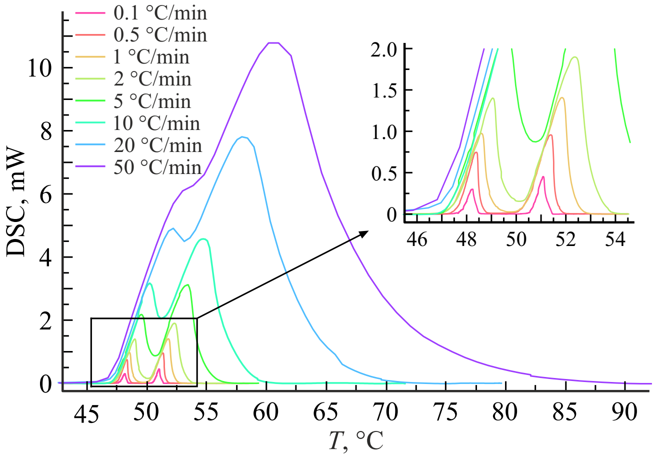

Figure 1. DSC of tetracosane sample thermogram in variation of scanning speeds.

in the molecule packing in nanolamella cores, namely, the initial phase characterized by triclinic symmetry undergoes a transition to the rotation phase R_{II} with rhombohedral (hexagonal) symmetry. Rotation (R) phases represent an intermediate state between a crystal and a liquid, and are characterized by origination of discrete molecular rotation around their main axes [26]. PT-1 and PT-2 in tetracosane are reversible phase transitions, i. e. when cooled from the melt condition, first solidification into the rotation phase is observed, and then a three-phase transition to the stable crystal phase.

Papers [12,27] noted that the peak shift observed in Figure 1 towards higher temperatures with increased heating speed is due to the thermal resistance of the sample causing uneven distribution of temperatures in the sample. I. e. a temperature gradient arises in the sample, as a result of which the inner temperature of the sample turns out to be lower than the temperature of its surface, where the meter of the DSC instrument is installed. For example, in case of the solid-liquid phase transition, the inner part of the sample will absorb heat necessary for the process of phase transformation, even at the time when the surface will already be in the melt state. As a result of which the DSC instrument records the temperature of the molten part of the sample, and the quantity of heat that was also absorbed by the inner part of the sample, which is still undergoing the phase transformation. As a result a prolonged trailing edge of the melting peak will be observed in the thermogram, which stretches to higher temperatures than the available melting temperature of this sample. But in fact this effect is caused by melting of only a part of the sample that at the moment of recording had lower temperature. The prolonged nature of the trailing edge of phase transition peaks substantially deepens with the growth of the scanning speed.

Similar phenomena manifest themselves in cooling, but to a lesser extent due to faster processes of phase transformations. In process of melting the phase transition process starts at the expense of sample thermal conductivity and continues as a result of natural convection, whereas in process of crystallization it is the opposite. Since thermal conductivity in the solid phase is higher compared to the liquid one, the crystallization process develops faster than melting, which is also fair for the crystal phase–rotation phase solid-phase transitions. Therefore, phase transitions in process of cooling happen in a narrower temperature range.

It should be noted that the increase of sample weight also causes the growth of the temperature gradient and accordingly to the shift of temperatures of phase transitions in the high-temperature area [28].

Similar patterns are demonstrated by numerical simulation results. Thus, authors of paper [29] conducted numerical simulation of pure indium heat flux curve depending on temperature. It was shown that with increased heating speed the melting peak expands with the preservation of the transition start point. Besides, in paper [30] it was also found by simulation using finite element method that only the start of the melting peak does not depend on the heating speed. Experimentally this effect was noted by authors of paper [12] in the studies of adipinic acid by DSC method in variation of heating speed from 0.25 to 10 °C/min.

As a result of our experiments in a wider range of heating speeds (Figure 1) the following temperatures were established for each of the phase transitions: temperatures of the start of deviations form the base line T_{start}; temperatures of crossings of the extrapolated base line and tangent to the leading edge of the peak, passing through the maximum, T_{tang}; temperatures of maxima $T_{\max}$ and temperatures of phase transition peak end T_{end}.

From Figure 1 you can see that at high speeds the peaks PT-1 and PT-2, merge. As a result of this the temperatures of PT-1 peak end (T_{end1}) and PT-2 peak start (T_{start2}) could be identified only for speeds up to 1 °C/min. Temperatures of crossings of the extrapolated base line and tangent to the leading edge of the peak passing through the maximum, for PT-2 (T_{tang2}) could be identified only for heating speeds of up to 5 °C/min. Temperatures of PT-1 maxima ($T_{\max 1}$) — only for heating speeds of up to 20 °C/min. All established temperatures of phase transitions depending on the heating speed are presented in Figure 2.

From Figure 2 it follows that the highest impact is provided by the heating speed at the phase transition end temperature, as it was expected according to the literature data. Values of $T_{\max}$ also noticeably decline with the decrease of the heating speed. However, as you can see from the figure, values T_{start}, and also values T_{tang} do not remain stable, but increase with the decrease of the heating speed, which is especially noticeable for the speeds of 1 °C/min and below. Therefore, all temperatures that characterize the phase transition have dependences on the heating speed, but to a different degree.

To study the impact of the heating speed at other thermodynamic parameters and at the kinetics of the development of the solid-solid phase transition, the quantitative analysis of the phase transition peak shape was conducted. However,

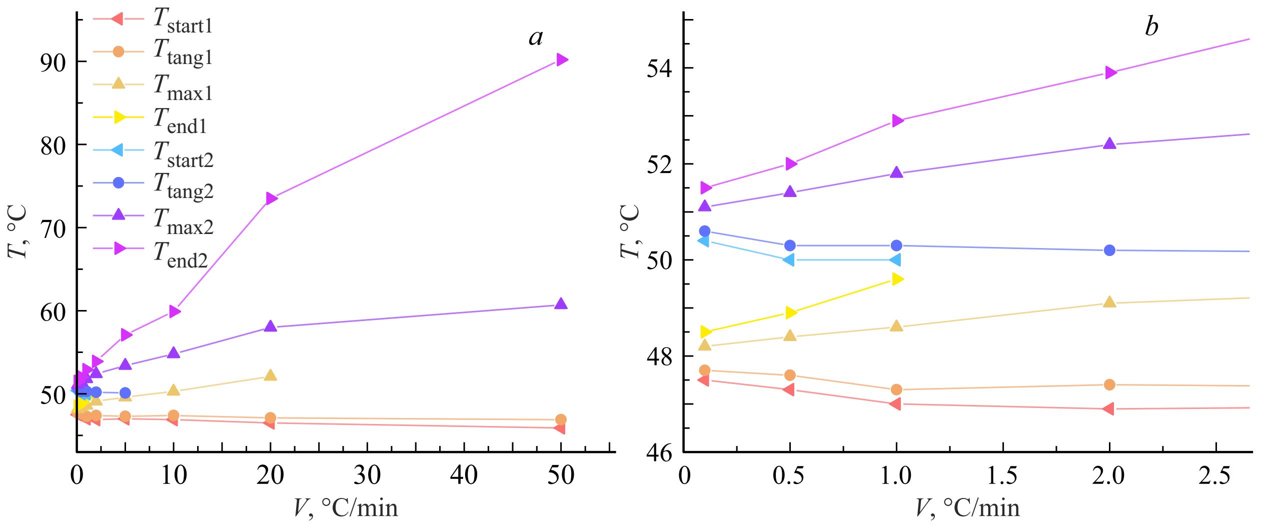

Figure 2. Temperatures characterizing phase transitions in tetracosane sample depending on heating speed (*a*), the increased fragment at slow speeds (*b*).

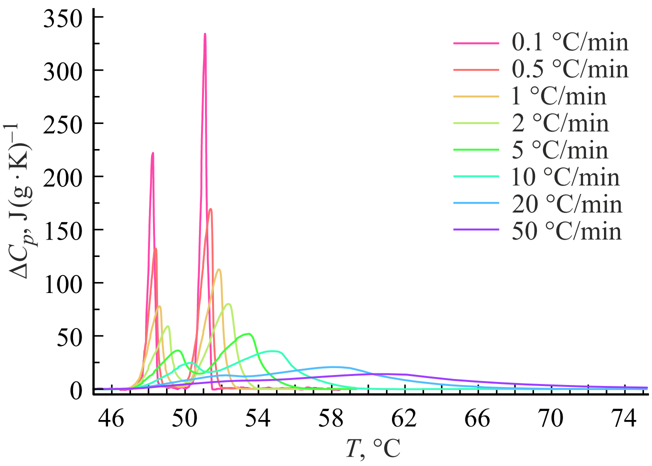

Figure 3. Dependences $\Delta C_p(T)$ of tetracosane sample in the field of phase transitions at different heating speeds.

since the quantitative analysis may only be conducted in dependences of heat capacity on temperature, the source DSCs of the heat flux dependence on temperature (Figure 1) were recalculated in the dependence of heat capacity on temperature (Figure 3), using the values of the heating speed, sample weight and instrument constant.

The dependences of heat capacity on temperature shown in Figure 3 demonstrate the opposite dependence of the phase transition peak intensity on the heating speed compared to Figure 1. Due to preservation of enthalpy in phase transition, the peaks that are most „extended“ in temperature at high speeds have the minimum intensity in the heat capacity scale, and „narrow“ peaks at low speeds that have weak intensity in the source DSCs of the curves, manifested themselves in the dependence of heat capacity in the form of intense maxima.

As it was noted above, the DPT theory makes it possible to obtain information on the development of the phase transition at the nanolevel based on the analysis of the phase transition peak shape. Solid-phase transitions in n-alkanes are exactly the smeared phase transitions, since their half-width is 1–2 °C, i. e. they are „smeared“ along the temperature scale [19]. Therefore, the analysis of the shape of their corresponding heat capacity peaks was conducted according to the DPT theory.

Since at high heating speeds it is not possible to identify a solid-phase transition in pure form, for further analysis the heat capacity peaks were chosen at speeds of 0.1, 0.5, 1, 2 and 5 °C/min.

According to the DPT theory, the peaks of heat capacity shall have a symmetrical Λ-like form. The experimental data shows that our PT-1 peaks are asymmetrical, which makes it possible to consider them as consisting of two peaks in the first approximation. Expansion into symmetrical components was done in accordance with the previously developed method [23]. One of the criteria for this separation is a condition that the enthalpy of the experimentally-obtained peak is equal to a sum of enthalpies of its components. All the studied samples exhibited presence of two symmetrical components and, consequently, we consider development of a solid-solid phase transition as a two-stage one. The thermograms of the solid-solid phase transition at different heating speeds and its expansions into the symmetrical components are shown in Figure 4.

According to the DPT theory, using parameters of symmetrical Λ-shaped heat capacity peaks, you may calculate the volumes of new phase nuclei ω [23,31]. The results of calculations ω_i, where i — peak number by temperature, are given in the table. Besides, the table presents the thermodynamic parameters of the solid-solid phase transition (PT-1) and fusion (PT-2).

Thermodynamic parameters of phase transitions in tetracosane at different heating speeds

V, °C/min	PT	T_{start}, °C	T_{tang}, °C	$T_{\max}$, °C	T_{end}, °C	$C_{\max}$, J(gK)$^{-1}$	ΔH, Jg^{-1}	ω, nm^3
0.1	PT-1	47.5	47.7	48.2	48.5	222	92	470 499
	PT-2	50.4	50.6	51.1	51.5	334	140	–
0.5	PT-1	47.3	47.6	48.4	48.9	132	77	259 628
	PT-2	50	50.3	51.4	52	170	135	–
1	PT-1	47	47.3	48.6	49.6	78	75	187 366
	PT-2	50	50.3	51.8	52.9	113	130	–
2	PT-1	46.9	47.4	49.1	–	59	207	168 300
	PT-2	–	50.2	52.4	53.9	80		–
5	PT-1	47	47.3	49.6	–	36	210	125 161
	PT-2	–	50.1	53.4	57.1	52		–
10	PT-1	46.9	47.4	50.3	–	25	209	–
	PT-2	–	–	54.8	59.9	36		
20	PT-1	46.5	47.1	52.1	–	21	211	–
	PT-2	–	–	58	73.5			
50	PT-1	45.9	46.9	n/a	–	14	207	–
	PT-2	–	–	60.7	90.2			

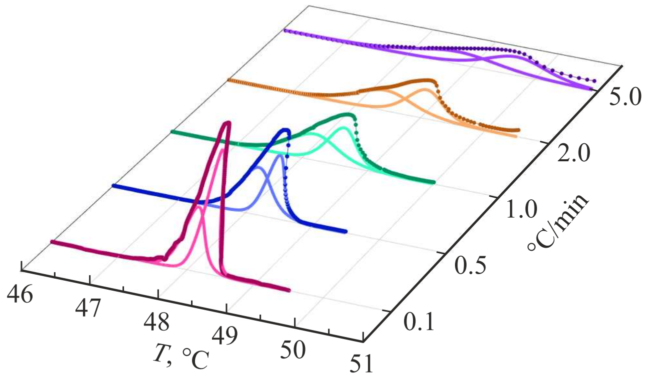

Figure 4. Expansion of experimental peaks of a solid-solid phase transition in tetracosane into symmetrical components depending on a heating speed.

The volumes of new phase nuclei made from 125 to 628 nm^3 depending on the stage of the solid-solid phase transition and heating speed. From the analysis of ω values it follows that as the heating speed increases, the volumes of nuclei of the new phase PT-1 decrease both for the first and the second stages. It can be explained by the fact that fast heating stimulates faster formation of nuclei that turn out to be smaller. Slow heating, on the contrary, promotes formation of larger equilibrium nuclei of the new phase. At heating speed of 0.1 °C/min the nuclei of the first and second stages turn out to be approximately the same, which may indicate a certain equilibrium value $\omega \approx 500\,\text{nm}^3$. As the heating speed increases, the volume values start looking more familiar with formation of small nuclei at the first stage and larger ones at the next one, which corresponds to our previous papers [24,32]. At heating speed of 5 °C/min, when merger of PT-1 and PT-2 starts, the reduction in the volumes of nuclei is observed, as well as approximation of ω_2 to ω_1, which may be related to the formation of temperature gradient in the sample and, accordingly, to the mixing of two transition stages. At higher speeds, due to inability to identify the solid-solid phase transition, it was not possible to identify the volumes of the nuclei, however, you may presume subsequent increase in the values of the volumes and complete mixing of two stages due to high temperature gradient. Based on the values of nuclei volumes, it is possible to assess the number of tetracosane molecules therein. Such assessments show that nanometer nuclei cover from 200 to 1000 molecules depending on the stage of transition and heating speed.

Other thermodynamic parameters also depend on the heating speed. As it follows from the table, the maximum heat capacity $C_{\max}$ reduces significantly with the speed increase, which is also visualized in Figure 3. As the speed changes from 0.1° to 50 °C/min, the value $C_{\max}$ decreased by more than 20 times, which turns out to be quite natural in comparison of temperature intervals of transitions. Temperature variations that characterize the phase transitions were already considered previously when analyzing Figure 2. Note additionally that despite the fact that at 2 °C/min the peaks of PT-1 and PT-2 start merging, T_{start} and T_{tang} values remain practically constant in the speed range of 1–10 °C/min. Further increase of the heating speed results in decrease of these values, and decrease — on the contrary, to increase of T_{start} and T_{tang}. As it should have been expected, the values of general enthalpy of transitions remain practically constant, and for the speeds of 0.5–50 °C/min remain within the limits of 205–212 Jg^{-1}, which makes this speed range suitable for the determination of enthalpy values. However, for tetracosane the peak of the solid-solid phase transition can be separated from the fusion peak only at speeds of 1 °C/min and below, therefore, for the independent assessment of enthalpies of two phase transitions it is necessary to use the speeds of 0.5–1 °C/min. Values ΔH at the speed of 0.1 °C/min are somewhat overestimated, both the general one and the individual ones for PT-1 and PT-2, which may be related to high distortion of such slow heating speed during phase transitions.

Therefore, at most reliable values of phase transition temperatures, the enthalpy values are observed with the highest error, which for the correct and full-scale DSC analysis makes it necessary to conduct at least two experiments. Besides, the change of temperatures at low heating speeds makes it possible to presume that temperature values of transitions obtained at the speed of 0.1 °C/min will differ from the ones obtained at even slower speeds. As a result of this it is desirable to develop a method that makes it possible to obtain the temperature values of phase transitions with a simpler method, which are as close to the values established by labor intensive experiments as possible.

In our previous papers it was shown [32,33] that based on the survey of a series of thermograms with a variation of scanning speeds using a special method you can establish a so called true temperature of phase transition, which is practically free from methodological errors. We will show that this method may be used to obtain the values that provide the best compliance with the experiment at very slow speeds, and the method as such is quite simple to use.

The method is based on extrapolation of the dependence of peak maxima temperatures on the scanning speed to the power of 1/2 to zero value, which in the absence of the irreversible structural changes in the sample must be linear [34]. Figure 5 shows the peak maxima temperatures of phase transitions $T_{\max}$ depending on the heating speed V to the power of 1/2. Linear extrapolation to zero value makes it possible to establish the true temperatures of phase transitions. For the preliminary estimates, you can use several temperature values at different scanning speeds, however, the increased precision requires more points for extrapolation. This paper produced quite a big array of values $T_{\max}$, which we use for this method. The extrapolation results show that the true temperatures of the solid-phase transition and fusion of tetracosane were 47.74 ± 0.15 °C and 50.37 ± 0.25 °C accordingly.

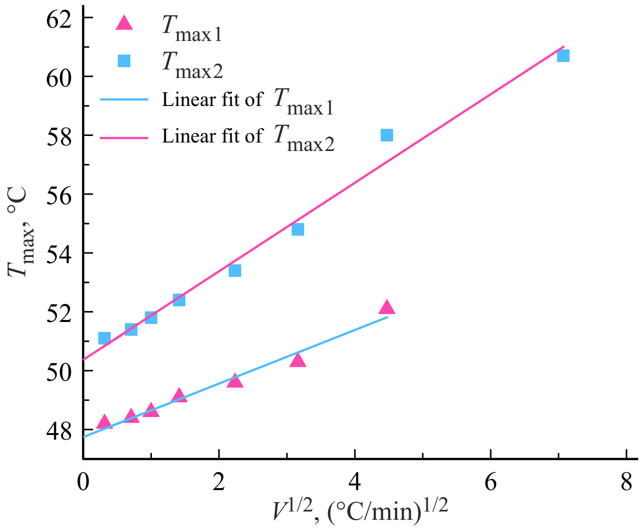

Figure 5. Determination of true temperatures of phase transitions in tetracosane heating.

It turned out that the true temperatures of PT-1 and PT-2 of tetracosane found by this method are in the range of T_{start}–T_{tang} for the least heating speed 0.1 °C/min, which differs from the range of T_{start}–T_{tang} for speeds of 0.5 °C/min and above that provide more distorted values. Since the values T_{start} and T_{tang} are most generally accepted for determination of phase transition temperatures, our method may be deemed similar to the completion of the DSC experiment at scanning speed of 0.1 °C/min.

Therefore, the extrapolation method may replace the labor intensive completion of the experiment at slow scanning speed, such as 0.1 °C/min or less, since to obtain similar values of phase transition temperatures, it is enough to conduct several experiments at fast speeds, for example, 2, 5, 10 °C/min, which will take much less time. It should be noted that these are exactly the scanning speeds make it possible to obtain the accurate enthalpy values, contrary to the slow speeds. However, for qualitative tests, it is still necessary to conduct DSC experiments at very slow speeds, which create at each moment of time the thermal equilibrium in the entire sample volume, since only such study makes it possible to follow the kinetics of development of phase transitions, in particular, the transitions between the metastable phases, which differ in small values in activation energy.

4. Conclusion

The differential scanning calorimetry method was used to study the impact of the heating speed at the development of phase transitions in the materials with the variable phase condition using the example of monodisperse tetracosane n-$C_{24}H_{50}$. The use of a wide range of scanning speeds from 0.1 to 50 °C/min made it possible to follow the change in the values of temperatures, heat capacity, enthalpy, which specify the phase transitions depending on the heating conditions. From the practical point of view, the different heating speeds correspond to temperature variation in real conditions at different applications of PCM. Low speeds are close to the change in the daily temperature of the environment, which is related to use of PCM in the construction industry, and high speeds correspond to drastic variations of temperature, for example, when a person wearing PCM-clothes goes outside in a cold season.

The assessment of thermodynamic parameters of phase transitions showed their substantial dependence on the heating speed. Thus, the values of temperature intervals and maximum heat capacity with speed variation from 0.1 to 50 °C/min differ by more than 20 times. At the same time, the fusion end temperature changed its value from 51.5 to 90.2 °C. These features were noted in the literature previously as well, but so far it was deemed that the start of the phase transitions was not subject to the impact of the heating speed.

In this paper it was shown for the first time that for tetracosane the temperatures related to the start of the phase transitions, namely, the temperatures of the start of deviation from the base line and temperature of crossings of the extrapolated base line and tangent to the leading edge of the peak passing through the maximum remain permanent only for the average values of the scanning speeds 1−10 °C/min. Lower speeds cause a shift in temperatures to higher values, i. e. the phase transition starts later. High speeds, on the contrary, cause a shift in temperatures to lower values, i. e. the phase transition starts earlier.

The results obtained in the paper will promote more effective application of PCM. For the specific use, it is necessary to not only select a certain material using thermal-physical characteristics, but also to take into account their possible deviations from the literature values obtained in other experimental conditions. To obtain the valid data, it is necessary to conduct the experiments at heating/cooling speeds that are as close as possible to the speed expected in real conditions. If it is not possible to do the calorimetric studies, you have to rely on the literature data obtained at corresponding speeds, or take into account the differences in the temperatures with the decrease/increase of the heating/cooling speed.

It turned out that the change in the heating speed had substantial impact both on thermodynamic parameters and kinetics of phase transition development. Based on the theory of diffuse phase transitions, the solid-solid phase transition was analyzed in the monodisperse sample of tetracosane, which made it possible to assess the volumes of nuclei of the new phase with the heterogeneous development of the phase transition. The assessments show that the nuclei have nanometer dimensions and cover several hundreds of the long-chain molecules of tetracosane.

It was found that high heating speeds caused development of the solid-solid phase transition by formation of small nuclei of new phase, which could have been caused by the lack of time for stabilization of the system at each stage of heterogeneous transition development and occurrence of an avalanche-like effect. Besides, at these speeds a high temperature gradient arises in the sample, therefore, two stages of the solid-solid phase transition development are mixed, and the average volumes of the nuclei turn out to be practically equal. Low heating speeds 0.5−2 °C/min demonstrate a natural process for the solid-solid phase transition development with formation of small nuclei at the first stage and larger ones at the next one. At superslow heating of 0.1 °C/min the large nuclei of new phase are formed, which turn out to be equal at the first and second stages. Thermal equilibrium at such heating speed makes it possible to suggest the value of nuclei volumes $\sim 500\,\mathrm{nm}^3$ as true for the heterogeneous transition in tetracosane, which may be confirmed in the future by experiments at even slower speeds.

To solve the problem of the precise definition of the phase transition temperature, the paper compared the values of our proposed method to determine true temperatures to the temperatures obtained at the slowest heating speed of 0.1 °C/min. The compliance of the values of true temperatures obtained by the extrapolation method with the temperatures of the phase transition start shows that this method may be used instead of a labor intensive experiment at the speed of 0.1 °C/min. Therefore, the method we presented to determine the true temperatures makes it possible, using high scanning speeds, to obtain the phase transition temperature values with rather high precision, at the same time with the most accurate values of phase transition enthalpies.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] K. Pielichowska, K. Pielichowski. Prog. Mater. Sci. **65**, 67 (2014).
[2] Y. Cui, J. Xie, J. Liu, J. Wang, S. Chen. Adv. Mech. Eng. **9**, *6*, 1 (2017).

[3] N. Kaushik, P. Saravanakumar, S. Dhanasekhar, R. Saminathan, M.L. Rinawa, R. Subbiah, R. Sharma, P.M. Kumar. Mater. Today: Proc. **62**, 1702 (2022).

[4] S. Mondal. Appl. Therm. Eng. **28**, 1536 (2008).

[5] M. Zare, K.S. Mikkonen. Adv. Funct. Mater. **33**, 2213455 (2023).

[6] V. Daniel. Adv. Phys. **2**, *8*, 450 (1953).

[7] S.A. El-Sayed, T.M. Khass, M.E. Mostafa. Biomass Conv. Bioref. **14**, 17779 (2024).

[8] A. Derkowski, A. Kuligiewicz. Clays Clay Miner. **70**, *6*, 946 (2022).

[9] A. Raghdi, M. Heraiz, M. Rasheed, A. Keziz. J. Indian Chem. Soc. **101**, *11*, 101413 (2024).

[10] I.A. Saranov, O.B. Rudakov, K.K. Polyanskiy, N.L. Kleymenova, A.V. Vetrov. Khimiya rastitelnogo syrya **4**, 291 (2020). (in Russian).

[11] A.E. Chalykh, V.K. Gerasimov, V.A. Tverskoy, R.R. Khasbiullin V sb.: Struktura i dinamika molekulyarnykh sistem / Pod red. A.A. Scherbina. IFKhE RAN, Volzhskiy rayon (2017). S. 40. (in Russian).

[12] H. Fatahi, J. Claverie, S. Poncet. Appl. Sci. **12**, *23*, 12019 (2022).

[13] C.M. Earnest, J. Jones, A. Dunn. Thermo. **2**, *3*, 302 (2022).

[14] T. Kousksou, T. El Rhafiki, A. Jamil, P. Bruel, Y. Zeraouli. Energy **56**, 175 (2013).

[15] B. He, V. Martin, F. Setterwall. Energy **29**, *11*, 1785 (2004).

[16] S. Kahwaji, M.B. Johnson, M.A. White. J. Chem. Thermodyn. **160**, 106439 (2021).

[17] A. Lazaro, C. Peñalosa, A. Solé, G. Diarce, T. Haussmann, M. Fois, B. Zalba, S. Gshwander, L.F. Cabeza. Appl. Energy **109**, 415 (2013).

[18] X. Jin, X. Xu, X. Zhang, Y. Yin. Thermochim. Acta **595**, 17 (2014).

[19] B.N. Rolov, V.E. Yurkevitch. Fizika razmytykh fazovykh perekhodov. Izd-vo Rostov. un-ta, Rostov (1983). 350 s. (in Russian).

[20] M. Fisher. Priroda kriticheskogo sostoyaniya. University of Colorado Press, Boulder, Colorado, U.S.A. (1965). 159 p. 221 s. (in Russian).

[21] G.A. Malygin. UFN (in Russian) **171**, 187 (2001).

[22] G.A. Malygin. FTT (in Russian) **43**, 1911 (2001).

[23] V.M. Egorov, A.K. Borisov, V.A. Marikhin. FTT (in Russian) **63**, *3*, 406 (2021).

[24] V.M. Egorov, V.A. Marikhin, L.P. Myasnikova, P.N. Yakushev. FTT **59**, *10*, 2044 (2017). (in Russian).

[25] S.A. Gureva, A.K. Borisov, V.A. Marikhin, V.M. Egorov. J. Phys.: Conf. Ser. **1695**, 012180 (2020).

[26] E.B. Sirota, H.E. King, D.M. Singer, H.H. Shao. J. Chem. Phys. **98**, *7*, 5809 (1993).

[27] E. Günther, S. Hiebler, H. Mehling, R. Redlich. Int. J. Thermophys. **30**, *4*, 1257 (2009).

[28] X. Sun, K.O. Lee, M.A. Medina, Y. Chu, C. Li. Phase Transit. **91**, *7*, 667 (2018).

[29] G. Wang, I.R. Harrison. Thermochim. Acta **231**, 203 (1994).

[30] G.W.H. Höhne, W.F. Hemminger, H.-J. Flammersheim. Differential Scanning Calorimetry. Springer, Berlin (2003). 298 p.

[31] G.A. Malygin. FTT (in Russian) **36**, *5*, 1489 (1994).

[32] A.K. Borisov, V.A. Marikhin, V.M. Egorov. FTT (in Russian) **66**, *5*, 752 (2024).

[33] V.M. Egorov, V.A. Marikhin, L.P. Myasnikova. Vysokomolek. soed. **47B**, *12*, 2191 (2005). (in Russian).

[34] K. Illers. Eur. Polym. J. **10**, 911 (1974).

Translated by M.Verenikina