An investigation of the thermodynamic properties of molecular crystals by the differential scanning calorimetry

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Abstract. The thermodynamic properties of long-chain molecular crystals (LMC) have been investigated by using differential scanning calorimetry. The impact of the chain length and of the chain end group type on the thermodynamic characteristics of the first and second order phase transitions in LMC has been studied. A method of the analysis of the peak shape of the first order transitions based on the theory of diffused phase transitions has been developed. The method allows one to estimate the size of the new phase nuclei within the bulk of the former phase. To estimate a true peak shape of the first order phase transition, a method to separate the overlapped heat capacity peaks has been proposed for the first time. This new method takes into consideration the hysteresis effects.

1. Introduction
The objects of the study are the nanoscale (3-5 nm) long-chain molecular crystals (LMC). LMCs are promising phase change materials (PCM) for solving the problems of absorption, storage and conversion of a thermal energy flux due to their own thermal effects during phase transitions in the heating / cooling cycles. The LMCs can provide the solutions to these issues in the temperature range from – 40 °C to 80 °C, which is extremely important for creating comfortable living conditions for people in extreme conditions.

Figure 1. Structure of various types of molecular crystals.
The LMC chains comprise of the methylene –CH₂– trans-sequences groups, as well as of the chain-terminated so-called end groups — methyl (paraffins, alkanols), hydroxyl (alkanols, diols, carboxylic acids) and carboxyl (carboxylic and dicarboxylic acids) (figure 1). The chains interact with each other by van der Waals forces and the additional forces arise from the end group interactions. The latter ones are realized both due to the van der Waals forces and due to hydrogen bonds [1]. The number of methylene groups varies from 10 to 50.

By changing the chain length and the type of the LMC end groups allows one to vary the volume and surface energies, respectively. Thus, a model series with variable thermodynamic properties are obtained.

2. Experiment

The dependence of heat capacity on the temperature of the investigated LMC is determined by differential scanning calorimetry (DSC). In figure 2, for example, the DSC curves of paraffins with different chain lengths are shown, on which endothermic (when heated) and exothermic (when cooled) peaks are observed, corresponding, as was shown in [2], to phase transitions of the first and second order. The similar curves are observed for all the above molecular crystals. In the cases when the peaks of the first and second order transitions on the DSC curves fully or partially merge, the shape of the peaks of the first order can be determined using an original method developed by us, that allows one to isolate the solid-phase transition experimentally in a “pure” form.

![Diagram](image)

**Figure 2.** Heat capacity as a function of temperature for paraffins C₂₁H₄₄, C₂₂H₄₆, C₄₄H₉₀.

For this, the property of the first order transition is used - the presence of temperature hysteresis, i.e. differences between transition temperatures during heating and cooling (figure 3 curves 1 and 4). For the experimental separation of the transitions for all the studied LMC samples, the procedures identical to that shown in figure 3 for alkanol with n = 14 were performed — the sample was heated to the melt state at \( T = 330 \) K (curve 1), and then cooled, by passing the exothermic peak, \( T_0 \approx 317 \) K (curve 3). In this way, an intermediate phase state was formed, during which a solid phase first order transition did not occur in the cooling cycle, and the ordering associated with the second order transition was already realized. Reheating to the melting temperature (curve 2) should show in this case a “pure” second-order transition, and thus the peak of the heat capacity will be associated only with an order-disorder phase transition. According to the difference between the peaks in the first and repeated heating curves, endothermic effects can be distinguished, which should only correspond to the first order phase transitions. Thus, according to the difference between the peaks in the primary and repeated heating curves, endothermic effects were identified, resembling \( \Lambda \)-shaped peaks.
Figure 3. DSC curve for alkanol C_{14}H_{29}OH.

The thermodynamic data of the studied LMC obtained in this work are presented in table 1 and 2.

Table 1. A phase transition temperatures in α,ω-diols, n-alkanols and n-alkanes.

| Samples               | \( n \) | \( T_{\text{max 1}} \) (K) | \( T_{\text{min 1}} \) (K) | \( \Delta T_1 \) (K) | \( T_{\text{max 2}} \) (K) | \( T_{\text{min 2}} \) (K) | \( \Delta T_2 \) (K) |
|-----------------------|--------|-----------------------------|-----------------------------|----------------------|-----------------------------|-----------------------------|----------------------|
| 1,4-butanediol        | 4      | 294,0                        | 264,0                        | 30,0                 | -                           | -                           | -                    |
| 1,6-hexanediol        | 6      | 316,1                        | 303,4                        | 12,7                 | -                           | -                           | -                    |
| 1,10-decanediol       | 10     | 346,4                        | 345,0                        | 1,4                  | -                           | -                           | -                    |
| 1,15-pentadecanadiol  | 15     | 350,0                        | 333,4                        | 16,6                 | 361,9                       | 361,9                       | 0                    |
| 1,16-hexadecanediol   | 16     | 365,1                        | 355,6                        | 9,5                  | 366,0                       | 366,0                       | 0                    |
| 1,22-docosanediol     | 22     | 371,7                        | 362,5                        | 9,2                  | 380,1                       | 380,1                       | 0                    |
| 1,44-tetradecanediol  | 44     | 394,5                        | 388,5                        | 6,0                  | 394,5                       | 394,5                       | 0                    |
| tridecanol            | 13     | 305,7                        | 304,2                        | 1,5                  | 305,7                       | 304,9                       | 0.8                  |
| tetradecanol          | 14     | 311,9                        | 308,9                        | 3,0                  | 311,9                       | 311,7                       | 0.2                  |
| pentadecanol          | 15     | 317,4                        | 313,8                        | 3,6                  | 318,3                       | 318,3                       | 0                    |
| hexadecanol           | 16     | 324,9                        | 319,9                        | 5,0                  | 324,9                       | 324,9                       | 0                    |
| heptadecanol          | 17     | 323,8                        | 318,7                        | 5,1                  | 323,8                       | 323,8                       | 0                    |
| nonadecanol           | 19     | 328,7                        | 323,9                        | 4,8                  | 335,4                       | 335,4                       | 0                    |
| eicosanol             | 20     | 338,2                        | 333,9                        | 4,3                  | 338,2                       | 338,2                       | 0                    |
| heneicosane           | 21     | 305,1                        | 304,6                        | 0,5                  | 313,2                       | 313,2                       | 0                    |
| docosane              | 22     | 315,0                        | 312,9                        | 2,1                  | 315,9                       | 315,9                       | 0                    |
| tetratetracontane     | 44     | 359,0                        | 358,5                        | 0,5                  | -                           | -                           | -                    |

\( T_{\text{max 1}} \) and \( T_{\text{max 2}} \) are the temperatures of the first and second order phase transitions, respectively, under heating.

\( T_{\text{min 1}} \) and \( T_{\text{min 2}} \) are the temperatures of the first and second order phase transitions, respectively, under cooling.

\( \Delta T_1 \) and \( \Delta T_2 \) are the temperature hysteresis of the first and second order phase transitions, respectively.
Table 2. Thermodynamic parameters of phase transitions in \( \alpha, \omega \)-diols, \( n \)-alkanols and \( n \)-alkanes.

| Samples          | \( n \) | \( \Delta H_1 \) (J/g) | \( \Delta S_1 \) (J/gK) | \( \Delta H_2 \) (J/g) | \( \Delta S_2 \) (J/gK) | \( \Delta H_{\text{sum}} \) (J/g) | \( \Delta S_{\text{sum}} \) (J/gK) |
|------------------|--------|------------------------|-------------------------|------------------------|-------------------------|----------------------------------|----------------------------------|
| 1,4-butanediol   | 4      | 178                    | 0,605                   | -                      | -                       | 178                              | 0,605                            |
| 1,6-hexanediol   | 6      | 194                    | 0,612                   | -                      | -                       | 194                              | 0,612                            |
| 1,10-decanediol  | 10     | 217                    | 0,624                   | -                      | -                       | 217                              | 0,624                            |
| 1,15-pentadecanediol | 15    | 136                    | 0,390                   | 99                     | 0,272                   | 235                              | 0,662                            |
| 1,16-hexadecanediol | 16   | 140                    | 0,382                   | 105                    | 0,286                   | 245                              | 0,668                            |
| 1,22-docosanediol| 22     | 117                    | 0,313                   | 136                    | 0,361                   | 253                              | 0,674                            |
| 1,44-tetratetracontanediol | 44 | 106                    | 0,269                   | 154                    | 0,390                   | 260                              | 0,660                            |
| tridecanol       | 13     | 105                    | 0,344                   | 113                    | 0,368                   | 218                              | 0,712                            |
| tetradecanol     | 14     | 102                    | 0,325                   | 127                    | 0,407                   | 229                              | 0,732                            |
| pentadecanol     | 15     | 104                    | 0,327                   | 124                    | 0,387                   | 228                              | 0,714                            |
| hexadecanol      | 16     | 106                    | 0,324                   | 131                    | 0,402                   | 237                              | 0,726                            |
| heptadecanol     | 17     | 104                    | 0,323                   | 131                    | 0,402                   | 235                              | 0,725                            |
| nonadecanol      | 19     | 73                     | 0,222                   | 159                    | 0,474                   | 233                              | 0,696                            |
| eicosanol        | 20     | 98                     | 0,288                   | 141                    | 0,416                   | 240                              | 0,704                            |
| heneicosane      | 21     | 54                     | 0,177                   | 189                    | 0,601                   | 243                              | 0,778                            |
| docosane         | 22     | 96                     | 0,302                   | 138                    | 0,437                   | 234                              | 0,739                            |
| tetratetracontane| 44     | 265                    | 0,736                   | -                      | -                       | 265                              | 0,736                            |

\( \Delta H_1, \Delta H_2, \Delta H_{\text{sum}} \) are the enthalpies of phase transitions of the first order, the second order, and their sum, respectively.

\( \Delta S_1, \Delta S_2, \Delta S_{\text{sum}} \) are the entropies of phase transitions of the first order, the second order, and their sum, respectively.

3. Theoretical calculations

The analysis of \( \Lambda \)-peaks was carried out according to the theory of a self-consistent field [3] proposed to diffused first order transitions. The temperature dependence of the heat capacity in this temperature region is given by the equation

\[
\Delta C_p(T) = 4\Delta C_m \cdot \exp[B(T-T_o)/T_o] \cdot [1+\exp[B(T-T_o)/T_o]]^{-2} \tag{1}
\]

where \( T_o \) is the temperature of the first-order phase transition, \( \Delta C_m \) is the maximum value of the heat capacity at \( T=T_o \), \( B \) is the athermal parameter.

The parameter \( B \) in the above equation (1) contains the most interesting information about the physical nature of the phase transition, since it is associated with the heat capacity peak of the specific heat \( \Delta C_m \)

\[
\Delta C_m = q_o B/(4T_o) \tag{2}
\]

where \( q_o \) is the heat of transformation [4], and the elementary volume of transformation \( \omega \):

\[
B = \omega \rho q_o / (kT_o) \tag{3}
\]

where \( k \) is the Boltzmann constant, \( \rho \) is the density.

Parameter \( B \) is a structurally sensitive parameter, since it determines the volumes of the nuclei of a
new phase in materials with diffuse phase transitions [3]. From equation (2), it is possible to estimate the values of enthalpy, from equation (3) - the elementary volume of transformation. The calculation results are given in table 3.

Table 3. A thermodynamic parameters of a first-order phase transition in α,ω-diols, n-alkanols and n-alkanes.

| Sample                  | n  | $T_o$ (K) | B    | $\Delta C_m$ (J/gK) | $q_o$ (J/g) | $\omega$ (nm$^3$) |
|-------------------------|----|-----------|------|---------------------|-------------|------------------|
| 1,15-pentadecanadiol    | 15 | 350,35    | 1900 | 110                 | 81          | 110              |
| 1,16-hexadecanediol     | 16 | 366,1     | 3200 | 185                 | 85          | 175              |
| 1,22-docosanediol       | 22 | 371,87    | 3200 | 175                 | 81          | 206              |
| 1,44-tetratetracontanediol | 44 | 395,35    | 3400 | 200                 | 92          | 202              |
| tridecanol              | 13 | 306,15    | 2200 | 140                 | 78          | 114              |
| tetradecanol            | 14 | 313,12    | 3600 | 208                 | 73          | 204              |
| pentadecanol            | 15 | 317,75    | 3600 | 208                 | 73          | 108              |
| hexadecanol             | 16 | 325,34    | 3300 | 200                 | 79          | 180              |
| heptadecanol            | 17 | 324,1     | 1800 | 115                 | 82          | 94               |
| nonadecanol             | 19 | 329,35    | 1300 | 55                  | 56          | 98               |
| eicosanol               | 20 | 338,92    | 3500 | 190                 | 74          | 212              |
| docosane                | 22 | 319,62    | 3600 | 240                 | 83          | 200              |

Figure 4 shows the experimental temperature dependence of the heat capacity for paraffin C_{22}H_{46}. The curve in the form of points shows the values calculated from the equation (1) with values corresponding to the temperature and amplitude of the peak maximum $T_0 = 319.5$ K and $C_{max} = 240$ J/g·K (figure 2). The best agreement between the calculated and the experimental curves was observed at a value of the parameter $B = 3600$. The parameter $B$ allows one to estimate the size of the microscopic structure of a new phase, i.e. the number of molecules involved in the formation of the nucleus of the new phase.

![Graph](image)

Figure 4. DSC curve for paraffin C_{22}H_{46}.

4. Conclusion
The controlled process of the microscopic structure formation during phase transitions in heating/cooling cycles is necessary for solving the problems of absorption, storage and conversion of
the thermal energy fluxes in the LMC mixtures, i.e. in the phase change materials. It turned out that the structure of the latter ones (and, as a consequence, efficiency) strongly depends on thermal history [5]. The DSC method allows us to simulate the thermal behaviour of the LMC mixtures and analyze their microscopic structure.

References
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