Investigation of the influence of the nano-nuclei habit on the specifics of phase transitions in long-chain molecular crystals and polymers

A K Borisov, V M Egorov and V A Marikhin

Ioffe Institute, 26 Polytechnicheskaya, St. Petersburg, 194021, Russia
E-mail: Borisov.ak@bk.ru

Abstract. The thermodynamic parameters of a long chain molecular crystals (LCMCs) set are analyzed. We revealed the dependence of LCMC’s melting points with a different chain length on the habitus of the first-order phase transition’s elementary volume. It was shown that LCMCs with the same chemical structure of the “core” (normal alkanes \( \{ \text{CH}_n(\text{CH}_2)_n \text{CH}_3 \} \), normal alkanols \( \{ \text{CH}_2(\text{CH}_2)_n \text{COH} \} \), diols \( \{ \text{COH}(\text{CH}_2)_n \text{COH} \} \), carboxylic \( \{ \text{CH}_3(\text{CH}_2)_n \text{COOH} \} \) and dicarboxylic \( \{ \text{COOH}(\text{CH}_2)_n \text{COOH} \} \) acids) lose their individual thermodynamic properties and approach the properties of polymethylene with an increase in the number of \(-\text{CH}_2-\) groups.

1. Introduction

Long chain molecular crystals (LCMCs) are the convenient model objects for studying the features of structural transformations during phase transitions, depending on the chain length and the type of end groups [1]. Due to monodispersity and the absence of chemical defects, LCMCs have a number of advantages over conventional polydisperse and chemically defective polymers in establishing quantitative generalizing regularities of the structure-property relationship.

2. Samples and experiment

In this work, we study the influence of the elementary volume shape (habit) of the phase transformation (\( \omega \)) on the thermodynamic parameters of long chain molecular crystals (LCMC) and polymethylenes. Aliphatic compounds were chosen as LCMC: \( n \)-alkanes \( \{ \text{CH}_3(\text{CH}_2)_n \text{CH}_3 \} \), \( n \)-alkanols \( \{ \text{CH}_2(\text{CH}_2)_n \text{COH} \} \), diols \( \{ \text{COH}(\text{CH}_2)_n \text{COH} \} \), carboxylic \( \{ \text{CH}_3(\text{CH}_2)_n \text{COOH} \} \) and dicarboxylic \( \{ \text{COOH}(\text{CH}_2)_n \text{COOH} \} \) acids, where \( n \) - the number of \(-\text{CH}_2-\) groups. Their supermolecular structure consists of nanocrystalline plates (lamellas) of a few nanometers thickness, having an ordered “core” of straightened \( \text{CH}_2 \) segments and surface layers from various end groups (–\( \text{CH}_3 \), –\( \text{OH} \), –\( \text{COOH} \)) [2]. Since methylene sequences from the same \(-\text{CH}_2-\) groups form the “core” of molecular crystals, a certain sequence is realized in these compounds according to the degree of interaction between the end groups. The interaction varies from the van der Waals forces for \(-\text{CH}_3 \) groups (paraffins and alcohols) to the so-called “Specific” interaction with the formation of hydrogen bonds for \(-\text{COH} \) (alcohols and diols) and \(-\text{COOH} \) (carboxylic acids) groups. By changing the chain length in these model homologous series of LCMCs (by changing \( n \)), one can precisely vary the ratio of volumetric and surface energies in lamellas. These variations lead to a change in the thermodynamic characteristics of the LCMC, for example, the melting temperature \( T_m \), depending on \( n \) (shown in figure 1). These data were obtained by differential scanning calorimetry for all LCMCs considered in this work with varying the number of \(-\text{CH}_2-\) groups.
from \(n = 6\) (dicarboxylic acids) to \(n = 44\) (\(n\)-alkanes). The results obtained are consistent with the literature data [3, 4].

\[T_m = T_0(1 - \frac{A}{L}),\]  

(1)

where \(T_0 = 414.5\) K is the melting temperature of polymethylene (bulk material); \(L\) is the lamella thickness equal to \(L = a \cdot n\), \(n\) is the number of carbon atoms in the molecular chain, \(a = 0.1273\) nm is the projection of the C-C bond onto the axis of the molecule; \(A\) is a parameter that takes into account surface energy, the density of the crystalline core of the lamella and the transition enthalpy. In the first approximation, the last two parameters can be considered common and independent of \(n\) for the entire LCMCs set investigated in this work, since methylene sequences from the same –CH\(_2\)– groups form the “core” of molecular crystals.

As can be seen from figure 1, the melting temperatures of various molecular crystals satisfactorily fit into the dependences constructed by relation (1). These dependences suggest that individual molecular lamellas form a crystalline structure in molecular crystals. However, lamellas can overlap each other, preserving the crystallographic order at large distances and forming thicker “effective” crystals. In this case the observed effect can be explained by the mismatch between the thickness of one lamella \(L\) used in the calculation in accordance with equation (1) and the graph in figure 1, where the actual (“effective”) thickness \(L^*\) exceeds the value of \(L\) by several times. To find the relationship
between the parameters $L$ and $L^*$, it is necessary to find a balance between the volume and surface energies, which determines the habit of the new phase nuclei.

A peak shape quantitative analysis based on the diffuse phase transitions theory made it possible to determine the volumes of new phase nanonucleus ($\Omega$), which ensure the gradual propagation of the interphase boundary upon transition [6, 7]. It was shown that, depending on the ratio of the end and lateral surface energies of the LCMCs the new phase nuclei habit changes from a nanoprismatic form ($n$-alkanes) to a nanofibrillar one, covering a stack of 6–7 layered lamellas (dicarboxylic acids). This effect is due to the type of packaging symmetry of both the molecules in the lamellas and the lamellas in the stacks, as well as the formation of dimeric hydrogen bonds between adjacent lamellas [8]. It turned out that the actual thickness of the lamella is determined by the equation

$$L^* = \frac{1}{2} \left( \frac{e_{en}}{E_{el}} \right)^{\frac{2}{3}}$$

where $E_{el}$ and $E_{en}$ are the cohesion energies of the methylene group and end groups, respectively. In this work, we use the cohesion energy values [9] for contributions from: $-\text{CH}_2-$ groups $E_{el} = 3.6 \text{ kJ/mol}$; $-\text{CH}_3$ groups $E_{en} = 4.14 \text{ kJ/mol}$; the hydrogen bond of $-\text{COH}$ groups $E_{el} = 13.4 \text{ kJ/mol}$ and the dimeric hydrogen bond of $-\text{COOH}$ groups $E_{el} = 26.8 \text{ kJ/mol}$. Taking the minimum surface energy for paraffin from a given series as a unit, the following sequence of $L^*$ values was obtained by equation (2): paraffins ($L^*_1 = 1$), alcohols ($L^*_2 > 1.5$), carboxylic acids ($L^*_3 > 1.7$), diols ($L^*_4 > 3.0$), dicarboxylic acids ($L^*_5 > 6.9$).

Figure 2 shows the dependences of the melting temperature $T_m$ for all the studied LCMCs on the number ($n$) of $-\text{CH}_2-$ groups contained in lamellas with actual thickness $L^*_{1-5}$. It can be seen from the figure that the experimental points fit into a dependence $T_m(n)$, constructed according to equation (1) for paraffins. Those, the dependence $T_m = f(n)$, constructed on the balance principle of the internal and surface energies of crystalline lamellas, is common for LCMCs with different chemical structures.

![Figure 2. Dependence of the melting temperature ($T_m$) of LCMCs on the number of methylene groups $-\text{CH}_2-$ ($n$) contained in lamellas with actual thickness $L^*_{1-5}$.](image)

Analyzing this dependence, it is clear that molecular crystals with an increase in the number of $-\text{CH}_2-$ groups must lose their individual properties and evolve to the properties of polymethylene. In the study of melting and crystallization of lamellar polymer crystals (in particular, polymethylene) the Thomson-Gibbs equation [10] is widely used, similar to equation (1)

$$T_m = T_0 \left( 1 - \frac{2\gamma}{\Delta H_0 \rho L_0} \right).$$

(3)
In this case, the lamella thickness \((L_0)\), end surface energy \((\gamma)\), enthalpy \(\Delta H_0\) and the melting temperature \(T_0\) of an equilibrium infinite crystal are used as the dimensional parameter. For polymethylene, \(\Delta H_0 = 290 \text{ J/g}, T_0 = 414.5 \text{ K} [10]\). The lateral surface energy is neglected, since at sufficiently large transverse dimensions of the lamella, the area of the end surface is much larger than the side surface. The use of the Thomson-Gibbs equation for molecular crystals requires, in addition to taking into account surface energy, an estimate of the real thicknesses \(L^*\) of effective macrocrystals - stacks of lamellas.

In [10], the data on the melting temperature of lamellar crystals of polyethylene were analyzed for a wide range of objects: non-oriented samples crystallized from melt and grown from solution. These data in the form of the dependence of \(T_m\) on the inverse lamella thickness are presented in figure 3. As can be seen from the figure, the experimental points fit on a straight line, the equation of which is

\[
T_m = 414.2 \left[1 - 6.27/L_0\right] \pm 0.8 \text{ K}.
\]

Extrapolation of this straight line leads to \(T_m = 414.2 \text{ K}\), which corresponds to the equilibrium melting temperature of crystals from extended chains of high molecular weight polymethylene.

![Figure 3. Melting point as a function of lamella thickness \(L^*\) for LCMCs and polymethylene [10].](image)

The same figure presents data on \(T_m\) for LCMCs in the coordinates of the inverse thickness \(L^*\). These data significantly expand the range of sizes of lamellar formations under consideration. It can be seen that the points fit satisfactorily on a straight line describing the behavior of the lamellar structure of polymethylene.

4. Conclusion

The analysis of the melting points of molecular crystals with different chain lengths is carried out. It was found that the habit of elementary volumes of the phase transformation determines the temperature of the phase transition in molecular crystals. With a quantitative increase in the \(-\text{CH}_2-\) groups, molecular crystals lose their individual thermodynamic properties and approach the properties of polymethylene due to a change in the ratio of volume and surface energies.

Acknowledgments

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