Investigation of structural transformations of long-chain molecular crystals during phase transitions by IR-spectroscopy

S A Gureva¹ ² and V A Marikhin²

¹ Peter the Great St. Petersburg Polytechnic University, 29 Polytechnicheskaya, St. Petersburg, 195251, Russia
² Ioffe Institute, 26 Polytechnicheskaya, St. Petersburg 194021, Russia

e-mail: swet.gurjewa@gmail.com

Abstract. The dependence of IR absorption spectrum on the type of symmetry of crystallographic cells allows us to investigate the kinetics of the development of phase transitions. Using the proposed technique, confirmations of the structural first order phase transition are obtained and the existence of conformational defects is proved.

1. Introduction

The purpose of this work is the study of structural transformations at phase transition temperatures (PT) in long-chain molecular crystals (LMC) of \(n\)-alkanes by IR - Fourier spectroscopy.

Revealing the nature and evolution of the PT in solids, including polymers and LMC, is one of the most important fields of solid-state physics. However, a significant dispersion of the characteristics of polymers both at the molecular and at different hierarchical levels of supramolecular organization leads to a noticeable blurring of the PT parameters. This greatly complicates the determination of phase transformations patterns depending on the polymer structure and the analysis of the experimental data based on the currently developed phase transitions theories.

In view of this, the study of PT in molecular crystals of chain structure opens up new possibilities for the establishing of the summarized quantitative patterns of the structure/property relationships since the current studies may be performed on a model chemically defectless homologous series of \(n\)-alkanes with a previously unattainable degree of purity (up to 99.9 %).

2. Sample

The most commonly used \(n\)-alkanes are \(\text{CH}_3(\text{CH}_2)_n\text{CH}_3\) with the number of methylene groups in the chain \(n = 20 \div 40\), during crystallization of which from melts or solutions stacks are formed of numerous nano-lamellas of units nanometer thick (figure 1). The transverse dimensions of the lamellae can reach tens of micrometers [1].

Depending on the number of methylene groups, crystallization conditions and sample temperature, regular trans-sequences in lamella cores can form crystalline unit cells of various types of symmetry (monoclinic, triclinic, orthorhombic and hexagonal).

The object of research in the work is the tricosane \(\text{C}_{23}\text{H}_{48}\) produced by Sigma Company, the crystallization of which produces an orthorhombic cell (figure 2). In this sample, the crystals are
formed from stretched chains, respectively, in the initial state, it has the minimum number of conformational defects.

**Figure 1.** Crystal structure of LMC $n$-alkanes $C_nH_{2n+2}$.

**Figure 2.** Projection of the tricosane $C_{23}H_{48}$ orthorhombic cell onto the plane.

It is known [2] that during the transition of $n$-alkanes from the solid state to the melt, two types of phase transitions are observed:

1) a solid-phase structural transition of the first order (PT-1) with $T_{PT-1} < T_{melt}$

2) an order-disorder transition at $T_{melt}$ (melting $n$-alkane).

Our task was to study the kinetics of the development of the solid-phase transition PT-1, associated with a change in the type of symmetry of the elementary crystallographic cells — for $C_{23}H_{48}$ this is the transformation of orthorhombic into hexagonal cells.

3. Experiment

One of the effective methods for studying of the PT of $n$-alkanes is IR-Fourier-spectroscopy, since the IR absorption spectrum significantly depends on the type of symmetry of the crystallographic cells.

When a wide spectrum of IR radiation is applied to $n$-alkanes, certain functional groups in molecules (in our case, methylene CH$_2$ groups in trans-zigzags and the end CH$_3$ groups) are excited, which leads to the appearance of characteristic absorption bands corresponding to various types of vibrational motions of these groups.

Figure 3 shows the infrared absorption spectrum of $C_{23}H_{48}$ in the region of 500–3000 cm$^{-1}$ at room temperature and at the temperature above the solid transition temperature, obtained using a Bruker IFS-88 FTIR spectrometer.

Comparison of the frequencies of the characteristic vibrations of the spectrum with the data available in the literature for the frequencies of the rocking and deformation vibrations of the CH$_2$-groups and the stretching vibrations of the CH-bonds really indicates that in the $C_{23}H_{48}$ crystals have orthorhombic unit cells at room temperature.

At the same time, with $T > T_{PT-1}$, the IR spectrum (figure 3) indicates the transition of the initial orthorhombic cells to hexagonal ones, since the changes in the frequencies of the rocking and deformation (scissoring) vibrations of the CH$_2$-groups in accordance with the available literature data are observed [3].

To identify the kinetics of the development of PT-1, we obtained a large number of spectra with a stepwise increase in temperature with a step of 0.1 K from 294 K to 320.8 K. In addition, the task was to clarify various types of irregular conformational defects that can occur when $n$-alkanes are heated, namely: 1) $gtg$ kinks with $\nu = 1308$ cm$^{-1}$ and 1368 cm$^{-1}$, 2) double gauche-conformers $gg$ with $\nu = 1352$ cm$^{-1}$, 3) ending gauche-conformers $gtm$ $\nu = 1344$ cm$^{-1}$. 
4. Results and discussions

When solving these issues at a quantitative level, we are faced with the problem of a correct computer separation of complex experimental spectra into the separate absorption bands, as it is seen in figure 4.
For this purpose, the approximating profile functions of Gauss, Lorentz and various combinations of them in the form of Pearson VII and Voight were used. The decomposition was carried out using PeakFit, OPUS, MATLAB, Fityk programs [4]. A comparative analysis of various types of decomposition showed that Pearson VII function is the most convenient profile for the peak separation. For example, the decomposition of the spectrum in Figure 4 allows one to isolate the absorption bands corresponding to the above listed conformational defects (gtg, gg and gm) with a high confidence.

The determined changes in the frequency bands of doublets of the rocking and deformation vibrations of the CH₂ groups in the regions of 720–730 cm⁻¹ and 1460–1470 cm⁻¹, respectively, evidences the specificity of structural changes in the PT-1 region. In addition, decomposition of the spectra of complex superimposed bands in these regions was also performed.

Figure 5 demonstrates that instead of doublets of the 719.6 / 729 cm⁻¹ and 1463.78 / 1472.64 cm⁻¹ bands characteristic of the initial samples with orthorhombic cells, in the region of the PT-1 at T ≈ 40.5 – 41.0°C appear the single bands ν = 721.3 cm⁻¹ and ν = 1468.5 cm⁻¹, characteristic of hexagonal unit cells. These data are the IR-spectroscopic confirmations of the structural phase first order transition in a narrow temperature range, which was the purpose of our research.

![Figure 5. Temperature changes of doublets of bands.](image)

At T ≈ T_melt bands of 720 – 721 cm⁻¹ appear, which are attributed to rocking oscillations characteristic of isolated n-alkane chains in the available literature.

5. Conclusion
Using the proposed technique, we confirmed the existence of the structural phase first order transition as well as the existence of conformational defects: gtg’ kinks, gg’ double gauche conformers, gm ending gauche conformers in the substances investigated.

References
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