



Raman study of local ordering processes of solid *n*-alkanes



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ABSTRACT

The microphase separation of *n*-alkanes with different chain length was investigated by Raman spectroscopy for binary mixture rapidly quenched from the melt. The process was observed as a function of time. The first several minutes after solidification were crucial for the demixing process. For a few weeks old sample the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were calculated based on the analysis of polarized spectra recorded in the area of the formed domains. The measured $\langle P_2 \rangle$ values are significantly greater than zero (from 0.17 to 0.32), which indicates the mutual parallel arrangement of the molecules in the domains composed of *n*-alkanes of the same chain length.

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1. Introduction

Since the nineties of the last century, the issue of local orientational order in polymer mixtures was of interest for scientists who were involved in practical applications of polymers [1–4]. Special attention was paid to research arrangement of molecules in systems with quasi-crystal structure. Long chain *n*-alkanes, with general formula C_nH_{2n+2} , belong to this kind of substances. Experimental studies of crystallization and micro separation in solid paraffin were undertaken many times with the use of various methods including a combination of differential scanning calorimetry (DSC) and temperature-dependent X-ray diffraction (XRD) [5,6] and also by FTIR [7,8], STM [9] and NMR [10]. The issue of ordering of molecules in mixtures of *n*-alkanes has also been the subject of theoretical calculations and computer simulations [11,12]. So far relatively few papers were devoted to Raman studies of solid *n*-alkanes. Among the most interesting publications on this subject is the work of L. Brambilla and G. Zerbi [13], which contains the results of the analysis of temperature Raman spectra and their interpretation based on one dimension crystal model. The use of confocal Raman microscopy creates new possibilities for studying the dynamics of crystallization and structure of mixtures of *n*-alkanes differing in chain lengths. The two-component *n*-alkane solutions can play a role of model system useful for interpreting the results of research and modelling of more complex molecular

systems such as polymer composite materials (plastic, rubber, paint).

In this paper micro-Raman investigation of the process of microphase separation and spontaneous ordering of *n*-alkane molecules in solid binary mixtures has been presented. The orientational order was characterized by the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ determined for four samples of selected binary compounds. The calculations were made based on the model previously used for nematic liquid crystals [14–17]. The integral intensities of CH stretching bands as a function of time were used to analyse the rate of components separation.

2. Experimental

Polarized Raman spectra have been measured with the use of LabRam spectrometer equipped with a confocal Olympus BX-40 microscope and 100× magnification lens. The spectra were recorded in the range of 500–3000 cm^{-1} with the resolution of 1 cm^{-1} . The samples were illuminated by a <10 mW laser operating at 514 nm. The investigated mixtures were composed of long-chain, linear, high purity *n*-alkanes made by Aldrich–Sigma company, and their compositions are presented in Table 1. However, the hydrogen in one of the components was almost entirely replaced by the deuterium atoms (in 99%). This allowed us to better resolve the Raman spectra and determine changes and the influence of each of components.

Samples were prepared by mixing two components at the temperature of a few degrees above their melting point;

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Table 1
Samples of *n*-alkanes mixtures measured by Raman technique in room temperature.

No.	General formula	Molar ratio
1.	C ₂₀ D ₄₂ :C ₃₆ H ₇₄	2:1
2.	C ₂₀ D ₄₂ :C ₂₄ H ₅₀	2:1
3.	C ₂₀ D ₄₂ :C ₂₄ H ₅₀	1:1.2
4.	C ₂₄ D ₅₀ :C ₂₀ H ₄₂	2:1

composition of the mixtures is given in Table 1. The mixture was placed in a circular metal recess, with a radius and depth of 6 mm and 0.2 mm respectively, and heated. The process was followed by the removal of the excess material and subsequent quick cooling to room temperature. For this purpose, the plate was placed and pressed onto a large copper plate kept at 20 °C. The sample was further transferred directly to the microscope table. All Raman spectra (time resolved and for rotated sample) were measured at room temperature and averaged over several samples. The lateral (XY – sample plain) and depth (Z – beam direction) spatial resolution of the Raman microscope were 0.5 μm and 2 μm, respectively. The laser was directed into the single domain, selected under the polarizing microscope. The lateral size of the domain was bigger than the laser beam spot.

2.1. Order parameter calculation

To characterize the orientation of molecules we assumed that the *n*-alkane chains possess a cylindrical symmetry and are tilted at the angle θ to the reference direction. The distribution of their long molecular axis can be characterized by the functions $f(\theta)$, having the form of a series of Legendre polynomials, $P_i(\cos\theta)$:

$$f(\theta) = \sum_{i=0}^{\infty} \left(i + \frac{1}{2}\right) \langle P_i \rangle P_i(\cos\theta),$$

where the coefficients $\langle P_i \rangle$ are the order parameters that are determined experimentally over $i+1/2$ terms ensuring the convergence of the series. Because of the symmetry of molecules, with respect to the mirror plane perpendicular to the long molecular axis, all the odd-order terms vanish. The first even polynomials are given by:

$$P_0(\cos\theta) = 1$$

$$P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$$

$$P_4(\cos\theta) = \frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3)$$

For isotropic sample all coefficients are equal to zero, except $\langle P_0 \rangle$, which is always equal to unity. On the other hand, for perfectly ordered system, in which all molecules are parallel to the reference direction, $\langle P_2 \rangle = 1$ all the higher order parameters are equal to zero. The Raman spectroscopy measurements allow for the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ coefficients calculations [17].

3. Results and discussion

Typically, the spectra of *n*-alkanes are very similar, which makes it difficult to determine the contribution of the bands derived from molecules of different chain lengths in the spectrum of the mixture. However, the replacement of ^1_1H atom by ^1_2H (deuterium) shifts the CH stretching bands to lower frequencies (from about 2900 cm⁻¹ to ~2100 cm⁻¹) preserving intermolecular interactions. This allows for the examination of the binary mixture of deuterated

and “ordinary” *n*-alkane compounds, where the C–H and C–D stretching bands are (almost) separated. Thus, the observation of the molecules with different chain lengths becomes possible (see Fig. 1).

The Raman I_{VV} and I_{VH} polarized spectra of investigated sample number 3 is shown in Fig. 2. Very strong spectral bands in the frequency range 2800–3000 cm⁻¹, relating to the stretching vibrations of functional groups CH₂ and CH₃ have been observed.

The intensity of these bands in some regions of spectrum increased with time from the moment of sample quenching, indicating that the amount of molecules containing hydrogen increased at the expense of molecules containing deuterium. For a thorough comparative analysis some well separated I_{VH} bands with a maximum at around 2880 cm⁻¹ related to asymmetric vibrations of CH₂ group, have been selected.

Fig. 3 presents visible changes in the I_{VH} intensity of the CH₂ band for C₂₀D₄₂:C₂₄H₅₀ (1:1.2) mixture, measured after certain periods of time. The biggest changes in the intensity of spectral lines for the selected regions have been observed between 9 and 35 min after quenching. After this period the changes, although still visible, were considerably smaller and after a few hours gradually diminished below experimental error. This indicates the presence of the ordering processes of molecules. Comparable changes of the intensity of the investigated bands for different mixture – C₂₄D₅₀:C₂₀H₄₂ (2:1), appeared in much shorter time range of several minutes. A similar phenomenon of changes in the spectra of *n*-alkane mixtures has been investigated in our previous work [18], where the intensity ratio of the stronger band at around 1118 cm⁻¹ (C–CH bending) and weaker at around 1031 cm⁻¹ have been analysed. In the course of the first 2 h the intensity of stronger band diminished, whereas the weaker one grew in intensity. These changes occurred in relation to accumulation of one type of molecules and domains growing in size, which is caused by the influence of interaction with semi crystal field of ordering molecules. The ordering of the molecules in the samples examined in this paper was further investigated using the turntable. The results are presented in Fig. 4, where the polar graphs of integral intensity of spectral lines of 2852 and 2855 cm⁻¹ for C₂₀D₄₂:C₃₆H₇₄ (2:1) mixture are shown. The samples were measured after a few weeks since mixing, melting and quenching, for an exactly selected section from the surface of a spontaneously ordering sample.

The sample was rotated by 360° with the 10° step, after which

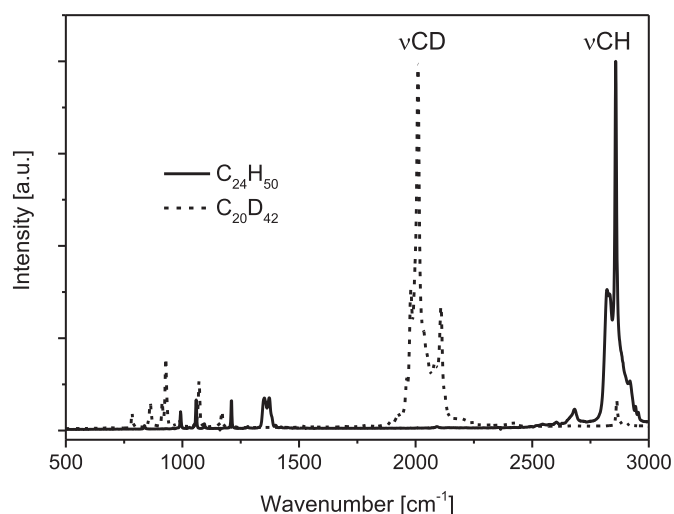


Fig. 1. Raman spectra of deuterated and non-deuterated *n*-alkane showing the frequency separation of the CH and CD stretching vibration bands.

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