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## PHASE TRANSITIONS IN CHAIN MOLECULAR POLYCRYSTALS OF 1-OCTADECENE

O.M. ALEKSEEV, S.O. ALEKSEEV, L.A. BULAVIN,  
M.M. LAZARENKO, O.M. MAIKO

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Taras Shevchenko Kyiv National University, Faculty of Physics  
(2, Build. 1, Academician Glushkov Ave., Kyiv 03680, Ukraine)

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Phase transitions in 1-octadecene polycrystals are studied by means of thermophysical, dielectric, and spectroscopic methods. An expansion of the intercrystalline space is detected in 1-octadecene at  $-55\text{ }^{\circ}\text{C}$ . At  $-30\text{ }^{\circ}\text{C}$ , there appeared topological solitons of the "one-unit constriction" and "180° reorientation" types. A soliton arises at the terminal  $-\text{CH}_3$  groups, passes along the molecule, is reflected from the double bond of a vinyl group, and returns back. In this case, crystallites of 1-octadecene are transformed to the orthorhombic rotation-crystalline phase. Under heating to  $0\text{ }^{\circ}\text{C}$ , the energy of topological solitons is sufficient for the reorientation of vinyl groups with the simultaneous translation of the molecule along the  $c$ -axis. The concentration of topological solitons increases with the temperature rise. The azimuth correlation between the molecular planes disappears at  $18\text{ }^{\circ}\text{C}$ , and octadecene is transformed into the hexagonal rotation-crystalline phase. Melting of octadecene occurs at  $21\text{ }^{\circ}\text{C}$ .

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### 1. Introduction

In crystals of molecules of linear oligomers, which possess aliphatic carbon chains, the phase transitions into the solid state which are accompanied by a change of the symmetry of the crystal lattice are observed. For paraffins, it is established [1, 2] that the crystals can exist in different (rhombic ( $Or_{\text{crys}}$ ), monoclinic, and triclinic) modifications which pass into the orthorhombic rotation-crystalline modification  $Or_{\text{rot1}}$  at the temperature  $T_{\text{rot1}} < T_m$  ( $T_{\text{rot1}}$  is the temperature of the phase transition in the solid state, and  $T_m$  is the melting temperature). The given transition is characterized by a sharp change of the volume and is a phase transition of kind I. At the further heating,  $Or_{\text{rot1}}$  passes to the hexagonal rotation-crystalline modification  $Hr_{\text{rot2}}$  (a phase transition of kind II) or to a melt. The processes  $Or_{\text{rot1}}$  and  $Hr_{\text{rot2}}$  are called the rotation melting in the literature [1–7], but it is essential that the substance remains in the solid state. By using the methods of X-ray diffraction analysis, incoherent scattering of neutrons, and the other ones, it was established that the  $Or_{\text{rot1}}$  modification is stable, corresponds to the orthorhombic subcell, but has an

uncorrelated azimuth arrangement of some neighboring molecules, and the  $Hr_{\text{rot2}}$  modification is stable and corresponds to a dense packing of cylinders. On this basis, the authors of works [2, 4, 8–10] made conclusion that, in the phase  $Or_{\text{rot1}}$ , the rotation of molecules is hindered and has activation character. That is, under the action of thermal excitation, a molecule overcomes, in the course of rotation, a number of potential barriers. Such a rotation is accompanied by a translation of the molecule along its axis by one link of the carbon chain [10]. Respectively, for the phase  $Hr_{\text{rot2}}$ , the possibility of the free rotation of oligomeric molecules, specifically paraffins, as a whole around the  $c$ -axis of molecules was assumed [2, 4].

There are known other hypotheses concerning the mechanism of rotation of paraffin molecules in crystals formed from elongated chains [11, 12]. For such crystals, the existence of topological solitons which can be excited by a local external action is expected [13]. The probability of the excitation of a soliton is maximal if such an action is realized at the end of a molecular chain. Therefore, it is possible to assume that, for oligomeric systems composed from carbon chains, solitons are excited on a terminal methyl group  $-\text{CH}_3$  which can be reoriented, as it is known [14] from the studies of NMR-spectra in crystals of alkanes. Recently, it was shown [15–17] with the use of the numerical simulation of the dynamics of an infinite thermalized chain in crystalline polyethylene that thermal vibrations can cause the creation of topological solitons corresponding to the tension (constriction) of a zigzag-like chain by a half-period, which is accompanied by a rotation by  $180\text{ }^{\circ}$ . These topological solitons are stable relative to the thermal vibrations of the chain and can propagate along it like Brown particles. The density of topological defects begins to sharply increase in the neighborhood of the melting point, which allows one to consider their accumulation as the initial mechanism of melting in crystals of polyethylene.

The study of the phenomenon of rotation melting in crystals composed of aliphatic chain molecules of other types (fatty acids, olefins, *etc.*) has a rather episodic than a systematic character and does not allow one to unambiguously infer about its molecular nature. Therefore, the study of phase transitions in crystals of oligomers of various types remains urgent.

The purpose of the present work is the study of mechanisms of molecular motion in 1-octadecene in a wide temperature interval including the region of phase transitions.

The object under study is 1-octadecene, whose molecule ( $\text{CH}_2 = \text{CH}(\text{CH}_2)_{15}\text{CH}_3$ ) has methyl and vinyl terminal groups.

## 2. Experiment

We used a number of experimental methods to study the phase transitions in polycrystalline 1-octadecene. In particular, to determine the specific heat capacity in a wide temperature interval, we used a dynamical calorimeter registering a change in the heat flow which enters into a specimen during the heating. We obtained the dependence of the specific heat capacity of 1-octadecene on the temperature  $C_p(T)$  in the interval of temperatures  $-155 \div 80$  °C (Fig. 1) at a heating rate of 2 K/min. The error was at most  $\Delta C/C = 3\%$ .

On the curve  $C_p(T)$ , we see two maxima at  $T_\lambda = -48$  °C and  $T_1 = -11$  °C and a double maximum at  $T_2 = 18$  °C and  $T_m = 21$  °C, respectively. Two peaks ( $T_1$  and  $T_m$ ) were observed earlier in [3, 18] for  $\alpha$ -olefins with the number of carbon atoms  $n$  from 10 to 22. The value of the temperature interval between these peaks for  $\alpha$ -olefins with carbon chains with  $n < 12$  is  $\Delta T_{1m} < 10$  °C, and  $\Delta T_{1m} > 22$  °C for  $n > 12$ . In the authors' opinion, this can be explained by the fact that molecules, starting from those with  $n > 12$ , are crystallized in the state of orientational disorder. Moreover, for  $n = 16$ , the disorder of the arrangement of terminal groups is observed as well. The authors referred the interval of temperatures  $\Delta T_{1m}$  to the existence of polycrystals of  $\alpha$ -olefins in the hexagonal state. But work [4] demonstrated the existence of two phases  $Or_{\text{rot1}}$  and  $Hr_{\text{rot2}}$  in the interval  $\Delta T_{1m}$  for 1-eicosane, where  $T_2$  is the temperature of the transition between the phases. The presence of the first peak at  $T_\lambda$  was not confirmed, because the study was carried out down to  $T > -10$  °C. Work [19] revealed the existence of a peak at lower temperatures  $T_\lambda$  for  $n = 16$ . It was named the  $\lambda$ -type peak, but its nature was not clarified.

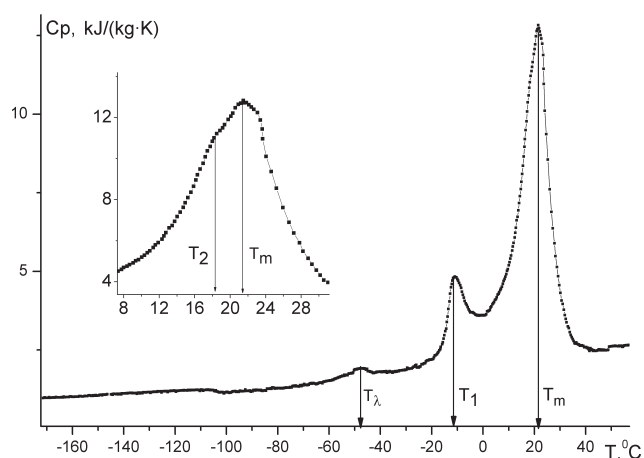


Fig. 1. Dependence of the specific heat capacity on the temperature for 1-octadecene

We assume that the chaotic arrangement of terminal vinyl groups in crystallites of 1-octadecene is possible only if one or two gauche-isomers in near-end links of a plane molecular transoid carbon chain (*t*-chain) are formed.

To verify the hypothesis as for the chaotic arrangement of terminal groups in the interval  $\Delta T_{1m}$ , we obtained the Raman spectra at temperatures of  $-75$ ,  $-25$ ,  $0$ , and  $20$  °C (Fig. 2). The spectra were registered by a spectrometer DFS-24 with the use of an Ar-laser as an exciting source (the line with  $\lambda=488$  nm).

It is known that the Raman spectra of crystalline hydrocarbons in the region below  $600$   $\text{cm}^{-1}$  contain bands, whose wave numbers are reciprocal to the length of a *t*-chain [20]. These bands are caused by longitudinal acoustic oscillations (LAO), during which the constriction and the tension of the transoid carbon skeleton occur.

In work [21], the dependence of the wave number of a LAO band for paraffins on the length of a *t*-chain was constructed. For octadecane ( $C_{18}H_{38}$  with  $n=18$ ) in the crystalline state, the Raman spectra contain a band at  $132.5$   $\text{cm}^{-1}$ . In the Raman spectra obtained by us for 1-octadecene (Fig. 2), we observe the bands  $133.2$   $\text{cm}^{-1}$  at  $-75$  °C,  $137.8$   $\text{cm}^{-1}$  at  $-25$  °C, and  $133.1$   $\text{cm}^{-1}$  at  $0$  °C, whereas no band is observed at  $20$  °C. By analogy with paraffins, this fact allows us to determine the length of a regular *t*-chain in crystals of 1-octadecene. From the data given in [21], we get that the number of carbon atoms in a *t*-chain is between 17 and 18 at various temperatures. It is not amazing because 1-octadecene has a double bond ( $\text{C}=\text{C}$ ) in the *t*-chain, whose length is less than that of a single bond ( $\text{C}-\text{C}$ ). On this basis, we may conclude that the molecule of

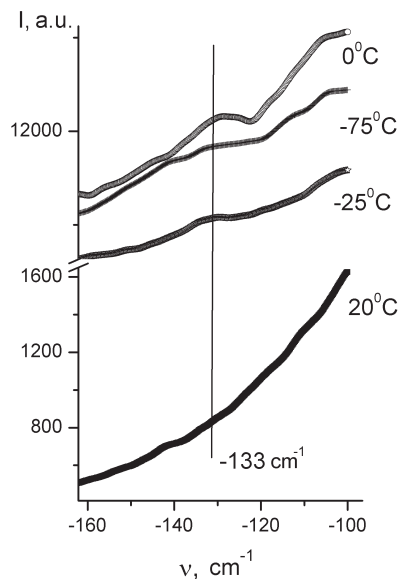
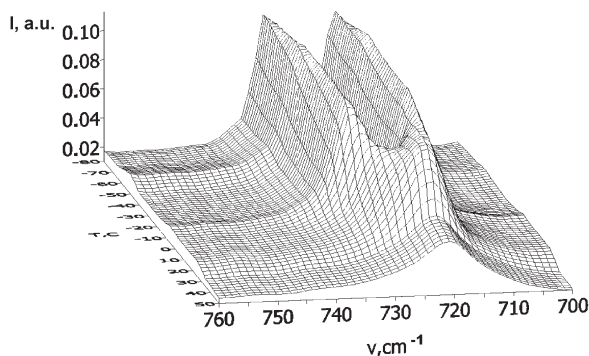


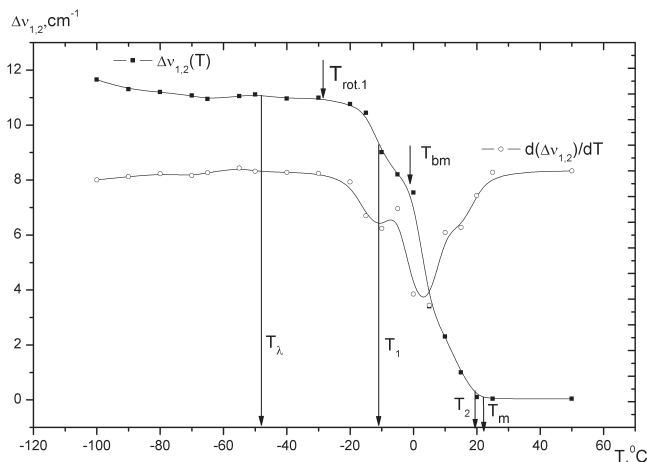
Fig. 2. Raman spectra for 1-octadecene at various temperatures

Fig. 3. Dependence of the intensity of the IR-spectra for 1-octadecene on the temperature  $T$  and the wave number  $\nu$  in the region near  $\nu=720\text{ cm}^{-1}$ 

1-octadecene in the crystalline state has a  $t$ -chain elongated along the  $c$ -axis, in which gauche-isomers are absent. Further at the heating, the length of a  $t$ -chain remains invariable up to the beginning of the melting ( $T_{\text{bm}} = 0\text{ }^{\circ}\text{C}$ ). In the process of melting, the length of a  $t$ -chain decreases because gauche-isomers are created.

This indicates the ordered arrangement of terminal groups in crystallites of 1-octadecene before the beginning of the melting ( $T_{\text{bm}} = 0\text{ }^{\circ}\text{C}$ ), i.e. the existence of gauche-isomers is possible only above  $T_{\text{bm}} = 0\text{ }^{\circ}\text{C}$ .

A change of the type of subcells of the molecular crystals of olefins on phase transitions can be registered with the help of X-ray diffractograms obtained at various temperatures, but it is a difficult problem in the case of the polycrystals under study [2]. Therefore, in order

Fig. 4. Dependences of the Davydov splitting  $\Delta\nu_{1,2}(T)$  and the derivative  $d(\Delta\nu_{1,2})/dT$  on the temperature for 1-octadecene

to obtain a comprehensive explanation of both the structure of 1-octadecene and the molecular nature of the relevant processes, we measured the IR-spectra with an IR Fourier spectrometer Nicolet-Nexus at various temperatures. Structurally sensitive is the band in the IR-spectra of similar specimens which is related to rocking vibrations of  $\text{CH}_2$  groups in aliphatic chains near  $\nu=720\text{ cm}^{-1}$ . At temperatures lower than those of the phase transitions, we observe the splitting  $\Delta\nu_{1,2}(T)$  of this band which is named the Davydov splitting (it is inherent only to the orthorhombic subcell of a crystal) [3]. In Fig. 3, we present the dependence of the absorption intensity  $I$  in the IR-region for 1-octadecene on the temperature  $T$  and the wave number  $\nu$  near  $\nu=720\text{ cm}^{-1}$ . With increase in the temperature, we observe that the two peaks approach each other and unite into one peak in the vicinity of the phase transition. In order to separate two maxima and to determine the value of  $\Delta\nu_{1,2}(T)$  in the region near  $\nu=720\text{ cm}^{-1}$ , we approximated the profiles of the peaks with the Voigt distribution according to [3].

The temperature dependence of the Davydov splitting  $\Delta\nu_{1,2}(T)$  for 1-octadecene is given in Fig. 4.

It is seen that, in the interval of temperatures  $-100 \div -20\text{ }^{\circ}\text{C}$ ,  $\Delta\nu_{1,2}(T)$  is almost invariable. But, at approaching the beginning of the phase transition ( $T_{\text{rot1}} = -30\text{ }^{\circ}\text{C}$ ), the splitting decreases sharply in two stages from  $T_{\text{rot1}} = -30\text{ }^{\circ}\text{C}$  to  $T_{\text{bm}} = 0\text{ }^{\circ}\text{C}$  and from  $T_{\text{bm}} = 0\text{ }^{\circ}\text{C}$  to  $T_2 = 18\text{ }^{\circ}\text{C}$ . We may conclude that, on the cooling down to  $-100\text{ }^{\circ}\text{C}$ , 1-octadecene is crystallized with the orthorhombic symmetry of subcells  $Or_{\text{cryst}}$ . The splitting  $\Delta\nu_{1,2}$  is inversely proportional

to  $R^3$ , where  $R$  is the distance between the axes of molecules in the orthorhombic subcell [3]. Therefore, Fig. 4 allows us to conclude that, in the vicinity of the phase transition ( $T_{\text{rot1}} = -30$  °C), the distance between the axes of molecules increases significantly in two stages, and the azimuth reorientation of a chain molecule becomes possible. This confirms the existence of the orthorhombic rotation-crystalline phase  $Or_{\text{rot1}}$  in 1-octadecene.

The splitting disappears at  $T_2 = 18$  °C, which testifies to the absence of the azimuth correlation between molecules. Therefore, 1-octadecene in the interval  $18 \div 21$  °C is in the hexagonal rotation-crystalline modification  $Hr_{\text{rot2}}$ .

The decrease in the splitting indicates the transition from the orthorhombic modification of subcells of the crystal in the plane  $ab$  to the orthorhombic rotation-crystalline one. That is, it indicates the possibility of the azimuth reorientation of molecules around the  $c$ -axis of a subcell at  $T > T_{\text{rot1}}$ . We refer such a reorientation to the appearance of topological solitons which correspond to the constriction of a zigzag-like chain by a half-period and are accompanied by a rotation by  $180^\circ$  [15–17]. The generation of a soliton occurs on a methyl group ( $-\text{CH}_3$ ) of 1-octadecene. But we are faced with the question why the distance between the axes of molecules increases significantly in two stages on the azimuth reorientation of the chains of molecules by topological solitons, rather than in one stage, as it happens for  $n$ -paraffins [3, 8].

It is known [22] that the bands of IR-absorption in the liquid state expand with increase in the temperature, and the integral intensity decreases simultaneously. According to the theory developed in [22], the broadening of the IR-absorption band is caused by the Brown rotational motion of molecules and, respectively, is related to the mean lifetime of a molecule between two reorientations  $\tau_{\text{or}}$ :

$$\delta - \delta_0 = 1/\pi c \tau_{\text{or}}, \quad (1)$$

where  $\delta_0$  is the “residual” half-width of the absorption band which is independent of the temperature, and  $c$  is the light velocity.

According to the Frenkel theory, the mean time of relaxation of a molecule varies with the temperature by the exponential law

$$\tau = \tau_0 \exp(U_{\text{or}}/kT), \quad (2)$$

where  $\tau_0$  is the half-period of rotational vibrations of a molecule, and  $U_{\text{or}}$  is the potential barrier which should be overcome by a molecule on the reorientation.

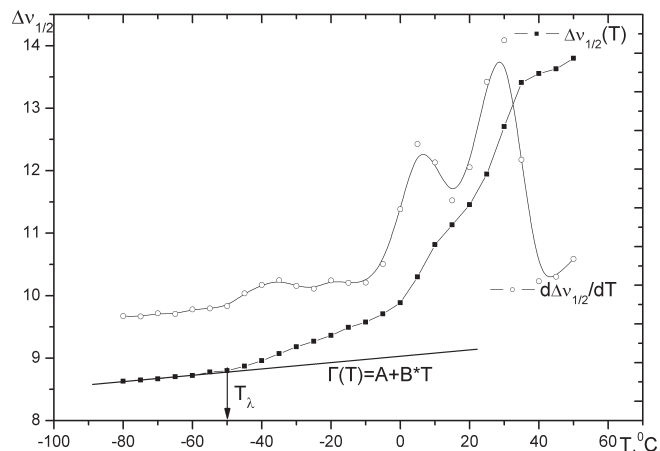


Fig. 5. Temperature dependences of the half-width  $\Delta\nu_{1/2}(T)$  of the band at  $996\text{ cm}^{-1}$  of the IR-spectrum and the derivative  $d(\Delta\nu_{1/2})/dT$  for 1-octadecene

It was determined [23] that the bands at  $996$ ,  $912$ , and  $635\text{ cm}^{-1}$  caused by deformational vibrations of atoms of a terminal vinyl group are most suitable to study the character of the molecular motion in  $\alpha$ -olefins. These bands have dispersive form and are distinguished by their position and intensity. In particular, the broadening for these bands is not related to planar vibrations of hydrogen atoms in the vinyl group.

We measured the temperature dependence of the half-width of the band at  $996\text{ cm}^{-1}$   $\Delta\nu_{1/2}(T)$  of the IR-spectrum for 1-octadecene (Fig. 5).

The dependence  $\Delta\nu_{1/2}(T)$  indicates that the half-width depends weakly on the temperature in the interval  $-80 \div -48$  °C. It is known [3] that the contribution of an anharmonism of the potential energy in a crystal to the broadening of a band depends linearly on the temperature  $\Gamma(T) \sim T$ . In view of this fact, this contribution can be separated, by approximating  $\Delta\nu_{1/2}(T)$  by a linear function  $\Gamma(T) = A + BT$  at  $T < T_\lambda$  (Fig. 5). Starting from  $T_\lambda = -48$  °C, the half-width grows with the temperature. Moreover, the growth rates are different in the intervals  $-48 \div 0$ ,  $0 \div 18$ , and  $18 \div 35$  °C. After  $35$  °C, the half-width monotonously increases with a constant rate.

In order to comprehensively study the behavior of a broadening of the  $996\text{-cm}^{-1}$  band related to deformational vibrations of the hydrogen atoms of a vinyl group  $\chi_{\text{CH}}^{\text{=CH}_2}$ , we constructed the dependence  $\ln(\delta - \delta_0)$  on  $1/T$  (Fig. 6) by relations (1) and (2).

To determine the energy of the potential barrier  $U_{\text{or}}$ , we set  $\delta_0$  to be equal to the half-width of the  $996\text{-cm}^{-1}$  band in the spectrum of the orthorhombic crystalline

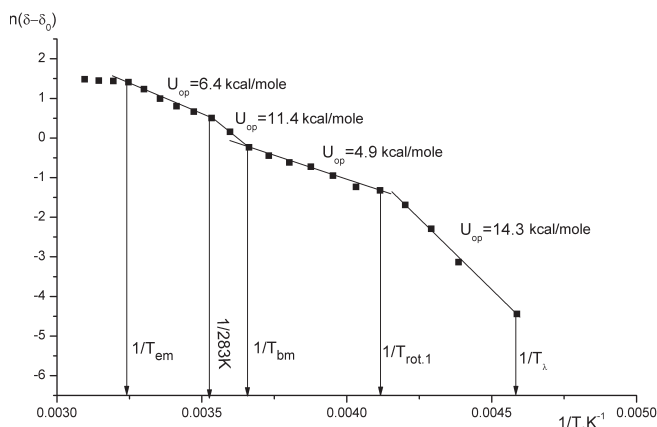


Fig. 6. Dependence of  $\ln(\delta - \delta_0)$  on  $1/T$  for the  $996\text{-cm}^{-1}$  band of the IR-spectrum of a molecule of 1-octadecene

modification at  $T = -80$  °C according to [3], by subtracting the contribution of an anharmonism of the potential energy in a crystal to the broadening (Fig. 5).

It is seen from Fig. 6 that the dependence is not linear but has only separate linear sections, for which we can determine the energies of potential barriers for the reorientation of the dipole corresponding to the vibration of  $\chi_{-\text{CH}}^{\text{CH}_2}$ . By analyzing these barriers, we can assert that, in the orthorhombic crystalline phase near  $T_\lambda = -48$  °C, there appears the possibility for the dipole to reorient itself, and the corresponding value of the potential barrier is  $U_{\text{or}} = 14.3$  kcal/mole. At the temperature  $T_{\text{rot}1} = -30$  °C, there appear the topological solitons which are generated on terminal methyl groups. By passing along a carbon chain, solitons are reflected from a vinyl group, by transmitting some energy to it and, in this case, by decreasing a height of the potential barrier down to  $U_{\text{or}} = 4.9$  kcal/mole for the dipole. At the temperature  $T_{\text{bm}} = 0$  °C, where the melting begins, topological solitons acquire the energy sufficient for the reorientation of vinyl groups with the simultaneous translation of a molecule along the  $c$ -axis into the interlayered space, where the potential barrier  $U_{\text{or}}$  is due to the adjacent layers and equals 11.4 kcal/mole. This is related to the two-stage increase in the distance between the axes of a molecule in the phase  $Or_{\text{rot}1}$ . Further, near  $T = 10$  °C, the interface between the layers of crystallites erodes, and, respectively, the barrier height decreases down to  $U_{\text{or}} = 6.4$  kcal/mole. At  $T_{\text{em}} = 35$  °C, the specimen becomes a melt.

The reorientation of dipoles in the vicinity of  $T_\lambda = -48$  °C is possible with increase in the free volume near vinyl terminal groups of 1-octadecene in two cases: 1 –

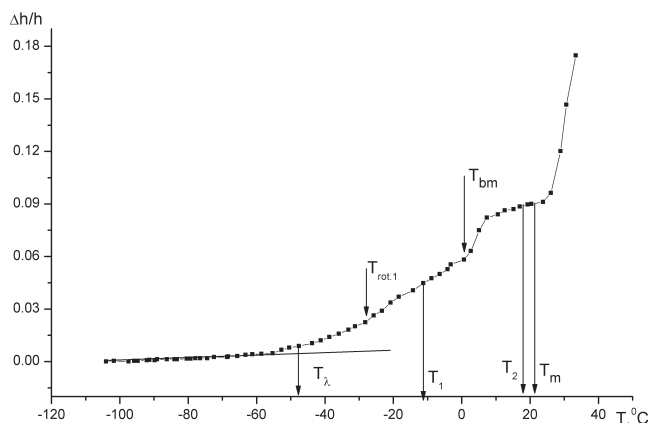


Fig. 7. Linear expansion  $\Delta h/h(T)$  versus the temperature for 1-octadecene

on the alignment of the  $c$ -axes of molecules relative to the plane of the intercrystalline space; 2 – with increase in the volume of the intercrystalline space. It was shown for 1-eicosane [4] that the  $c$ -axes of molecules are perpendicular to the plane of the intercrystalline space in all crystalline phases. Therefore, situation 1 is unlikely. It is more probable that the increase in the free volume is related to the realization of the second case associated with a change of the density of a polycrystal as a whole.

In order to clarify such a possibility, we determined the dependence of the linear expansion  $\Delta h/h(T)$  for 1-octadecene on the temperature (Fig. 7). The curve  $\Delta h/h(T)$  was obtained with the use of a method developed by us earlier [24] for liquids in a wide interval of temperatures which covers the range of phase transitions, including the melting. This method was realized on an automated setup which includes a computer-based ac bridge R5083. In this case, we used a 4-electrode temperature-controlled measuring cell which allows one to measure the thickness of a polyethylene capsule with the specimen. The use of a hermetic capsule with the specimen prevents the oxidation of the specimen on both the heating and the corrosion of electrodes and allows one to observe changes of  $\Delta h/h$  in the process of melting.

On the curve  $\Delta h/h(T)$  (Fig. 7), we see the manifestation of the thermal expansion in the region  $-105 \div -55$  °C. Beginning from  $T = -55$  °C, we observe the intervals of temperatures  $-55 \div 0$ ,  $0 \div 9$ , and  $9 \div 22$  °C, where the growth rates of linear expansion are different. Starting from  $T_m = 22$  °C, the growth is related to the thermal expansion of liquid 1-octadecene.

The results obtained allow us to propose the following sequence of phase transitions which are observed in polycrystalline 1-octadecene with increase in the temperature.

At  $T < -55$  °C, crystallites of 1-octadecene have the orthorhombic subcell, and the  $c$ -axes of molecules are perpendicular to the plane of layers. On the heating up to  $T = -55$  °C, a phase transition occurs. In this case, both the distance between the  $c$ -axes of neighboring molecules and the length of  $t$ -chains are not changed, but the density of the polycrystalline specimen begins to decrease due to an increase of the volume of unordered layers between crystallites. As a result, there appears the possibility for the dipole associated with a terminal vinyl group to reorient itself at  $T_\lambda = -48$  °C.

Further, as the temperature  $T_{\text{rot1}} = -30$  °C is attained, topological solitons are generated on methyl groups. By passing along a molecule, the solitons are reflected from the double bond of a vinyl group without its reorientation. While approaching  $T_{\text{bm}} = 0$  °C, the phase transition (melting) starts. In our opinion, it is related to the fact that topological solitons at  $T = T_{\text{bm}}$  possess the energy sufficient for the reorientation of vinyl groups with the simultaneous translation of a molecule along the  $c$ -axis. With increase in the concentration of topological solitons in the vicinity of  $T_2 = 18$  °C, the azimuth correlation between the planes of molecular chains disappears, and 1-octadecene passes into the hexagonal rotation-crystalline phase. At  $T_m = 21$  °C, the melting begins.

### 3. Conclusions

A change of the structure of the crystal lattice on the phase transitions in polycrystalline 1-octadecene is related to the generation of topological solitons in molecular  $t$ -chains due to the increase in the amplitudes of torsional vibrations of terminal methyl groups with increase in the temperature. The further heating induces an increase in the concentration of solitons, which leads firstly to the disappearance of the azimuth correlation of molecules in the lattice and then to the melting as a result of the passage of a soliton along the molecule.

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ФАЗОВІ ПЕРЕТВОРЕННЯ В ЛАНЦЮГОВИХ  
МОЛЕКУЛЯРНИХ ПОЛІКРИСТАЛАХ 1-ОКТАДЕЦЕНУ

*О.М. Алексеев, С.О. Алексеев, Л.А. Булавин,  
М.М. Лазаренко, О.М. Майко*

Резюме

Теплофізичними, діелектричними та спектроскопічними методами досліджено фазові перетворення в полікристалах 1-октадецену. Показано, що в 1-октадецені при  $-55\text{ }^{\circ}\text{C}$  відбувається уширення міжшарового простору. В околі  $-30\text{ }^{\circ}\text{C}$  з'являються топологічні солітони типу стиснення на одну лан-

ку з переорієнтацією на  $180^{\circ}$ , які зароджуються на кінцевих метильних групах та, проходячи вздовж молекули, відбиваються від подвійного зв'язку вільних груп. При цьому кристали 1-октадецену переходять в орторомбічну ротаційно-кристалічну фазу. При досягненні  $0\text{ }^{\circ}\text{C}$  енергія топологічних солітонів стає достатньою для переорієнтації вільних груп з одночасною трансляцією молекули 1-октадецену вздовж осі *c*. Зі збільшенням концентрації топологічних солітонів в околі  $18\text{ }^{\circ}\text{C}$  зникає азимутальна кореляція між площинами молекул і кристали 1-октадецену переходять в гексагональну ротаційно-кристалічну фазу. За температури  $21\text{ }^{\circ}\text{C}$  розпочинається плавлення кристала.