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Relationship between phase and relaxation transitions in partially crystalline polymers based on FAR-IR spectroscopy data

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The IR spectra of partially crystalline polymers polyacrylonitrile (PAN) and polytetrafluoroethylene (PTFE) in the region of manifestation of the spectrum of their crystal lattices ($10-150\,\mathrm{cm}^{-1}$) at temperatures from 4.2 to 300 K are presented and analyzed. The increased sensitivity of the spectral parameters of the bands of these spectra to crystalline effects allows us to trace structural rearrangements at the molecular level. The intensity, half-widths, and position of the maximum of the bands of external translational and rotational modes change especially sharply during phase transitions (PT), indicating a correlation between the PT and the vibrational properties of the external lattice modes. Analysis of these changes shows that during the PT from a low-temperature structure to a more disordered high-temperature structure, conditions arise for the manifestation of relaxation processes (RP) in the system, indicating the relationship between PT and RP, consisting in the fact that the former often precede and are responsible for the manifestation of the latter in the amorphous regions of the polymer.

Keywords: partially crystalline polymers PAN and PTFE, lattice IR spectra, solid-state phase transitions, γ- and β-relaxations, the relationship between PT and RP.

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1. Introduction

The study of relaxation processes in polymers is of constant scientific and technical interest. The practical importance of the subject is evident from the observation that the stiffness of typical thermoplastics can vary with temperature by more than an order of magnitude between low temperatures and temperatures of their usual use.

Such changes have been found to occur in certain temperature regions, each of which is associated with the occurrence of different types of molecular movements [1]. Moreover, the molecular mechanisms of relaxation transitions (units of molecular mobility, their sizes and displacement amplitudes, etc.) are specified in most cases [2]. However, there is still no understanding of the importance of the polymer molecular structure, the specific effect of molecular mobility on mechanical behavior and properties such as aging or viscosity and their temperature dependences.

This is especially true for partially crystalline polymers, which, in addition to the amorphous phase, contain various types of crystalline forms depending on the manufacturing conditions of the sample. That is, in addition to relaxation transitions, thermally induced phase transitions (PT) can also occur in them. The importance of clarifying the nature and specificity of PT, as well as their relationship to relaxation transitions, is quite obvious. Compared with fully amorphous polymers, semi-crystalline polymers have a well-defined melting point, better strength, good chemical resistance, and increased wear resistance due to their ordered structure.

Currently, methods of neutron and X-ray diffraction, Raman and NMR spectroscopy [3,4], as well as methods of differential scanning calorimetry and dynamic mechanical analysis are used to study the structural mechanisms of phase transitions in crystallizing polymers [5]. It has been found that, although the nature of PT is related to the configurational excitation, the thermal motion of atoms also makes a significant contribution to the change in entropy during the phase transition. The thermal initiation of PT (solid-phase and/or order−disorder type) occurs when the ratio of the oscillation amplitude of the atoms of the crystal lattice to the average distance between them reaches a certain value (approximately 10−15%). In other words, unstable higher-amplitude lattice modes are responsible for the instability of the structure during the phase transition.

Vibrational dynamics, as well as static vibrational properties, are very sensitive indicators for determining phases and PT at the molecular level. Such information can be obtained by studying the frequency, intensity, and half-width of absorption bands in the infrared range as a function of temperature and pressure, and low-frequency bands associated with crystal lattice modes are usually more sensitive to PT than high-frequency bands caused by intramolecular vibrations.

The study of low-frequency molecular movements associated with intermolecular degrees of freedom, such as molecular reorientation and libration (hindered rotations), in the frequency range of about $0.1-10$ THz provides valuable information about the structural dynamics of polymers [6].

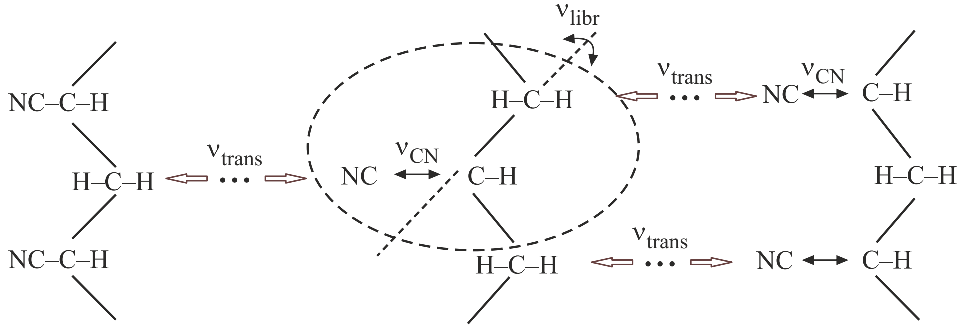

Figure 1. Diagram of oscillatory libration motion in the chain of $CH_2-CH-CN$ group [14], i. e. PAN monounit, on intermolecular bonds.

The purpose of this work was to obtain information from far-infrared (FIR) spectroscopy data on the presence of a crystal structure in atactic polyacrylonitrile (PAN) and the nature of solid-state PT at $\sim -108^\circ C$ [7,8], which initiates the manifestation of γ-relaxation in this polymer. In the case of highly crystalline polytetrafluoroethylene (PTFE) we were interested in the origin of the solid-state PT at 19°C [9], which falls within the temperature range of the useful plastic behavior of this plastic.

2. Methods

FIR spectra were recorded using single-beam vacuum spectrometers with diffraction gratings: from 10 to $50\,cm^{-1}$ — using an instrument developed by LSU and upgraded with an OAP-7 receiver and a new filtration system, and from 50 to $150\,cm^{-1}$ using „Hitachi“ FIS-21 spectrometer. The resolution at a signal-to-noise ratio of about 100 was $1-2\,cm^{-1}$. The accuracy of determining the frequency of the band maximum was $0.1-0.5\,cm^{-1}$. Absorption coefficient $k(v) = \ln(J_0/J)/(t-t_0)$, where J_0 and J is the transmission of samples with a thickness of t_0 and t $(t \gg t_0)$, was measured with an error of 5–10%. Spectra in the temperature range of 155 to 300 K were measured using a cuvette-cryostat with crystalline quartz windows. Its temperature was controlled by changing the flow rate of cold nitrogen in the heat exchanger assembled on the cuvette body. The cuvette was placed in a vacuum for thermal insulation. The temperature on the sample was measured with a copper–constantan thermocouple, its stability was not lower than 2°C. At least three parallel measurements were conducted for each temperature in the range from 50 to $150\,cm^{-1}$. The studied items were the atactic polyacrylonitrile (PAN) and acetonitrile (ACN), similar in structure to the PAN monomer: solid-state transition temperature $(\beta \rightarrow \alpha)$ in acrylonitrile $\sim 175\,K$ [10] and $\sim 205\,K$ [11] in acetonitrile; the average moment of inertia of the acrylonitrile (AN) molecule $\sim 9.5 \cdot 10^{-39}\,g \cdot cm^2$ and $\sim 9 \cdot 10^{-39}\,g \cdot cm^2$ of the acetonitrile molecule. The dipole moments of acetonitrile and acrylonitrile are 4.1 and 4.0 D, respectively. That is, the intensities and positions of the maxima of the libration bands in the PAN and ACN spectra will be almost identical (see below).

3. Results and their discussion

Atactic polyacrylonitrile (PAN) $(CH_2-CH(CN))_n$ is a versatile polymer used for the production of a variety of products, including membrane filters and fibers for the textile industry.

Dielectric measurements reveal three relaxation transitions in the amorphous phase of atactic polyacrylonitrile: α-relaxation in the region of 130°C, attributable to segmental mobility of chains and weakening of van der Waals interactions; β-relaxation at $\sim 100^\circ C$, attributable to local mobility of chain sections and weakening of dipole-dipole interactions between polar nitrile groups of chains, and γ-relaxation in the temperature range from -30 to $-100^\circ C$, attributable to small-angle torsional oscillations (libration) of monomeric PAN units and attenuation of interactions between dipoles of neighboring along the chain $C\equiv N$ groups [8,12]. γ-relaxation is detected not only in the amorphous phase, but also in crystal-like regions of PAN. Therefore, based on the relationship between the crystalline and amorphous phases, it can be expected that phase transition in the crystal structure of this polymer is its precursor and initiator [13].

Figure 1 shows a diagram of oscillatory libration motion in a chain of $CH_2-CH-CN$ group [14], i. e., the PAN monounit, on intermolecular bonds.

Figure 2 shows how the contour of the absorption band in the PAN spectrum changes with temperature at $\sim 127\,cm^{-1}$, which is attributed to the manifestation of libration motion in the chain of the $CH_2-CH-CN$ group [14] on intermolecular bonds (see Figure 1). Full (from 10 to $400\,cm^{-1}$) FIR spectrum of the PAN at 295 K is shown in the insert of Figure 2. In addition to libration absorption, there is a band in the spectrum at $\sim 250\,cm^{-1}$ related to the intramolecular oscillation of the PAN monounit, namely, the deformation of $C-C-CN$ group [15].

Located in the region of manifestation of lattice vibrations of the PAN acrylonitrile monomer (Figure 2), an abnormally

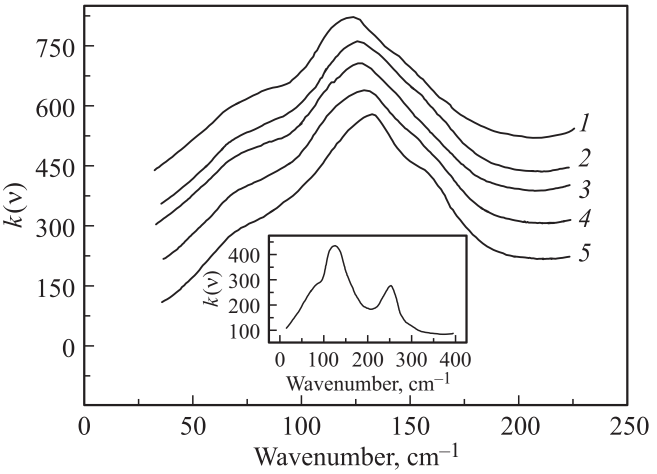

Figure 2. Libration band in FIR spectra of PAN acquired at different temperature T, K: *1* — 295, *2* — 273, *3* — 245, *4* — 205 and *5* — 160. For clarity, the spectra *1–4* are shifted in ordinate relative to the spectrum *5*. The insert shows the PAN spectrum in the range of $10-400\,\mathrm{cm}^{-1}$ at room temperature.

wide libration band at $\sim 127\,\mathrm{cm}^{-1}$, according to Ref. [16] consists of several overlapping bands, the half-width of which is determined by the lifetime of the pseudo-lattice state, equal to the time of dielectric relaxation. Therefore, this lowest frequency band in the polymer spectra is also called „liquid-lattice band“. A similar absorption band exists not only in the spectra of polymers, but also in the spectra of liquids, glasses, and other disordered bodies [17,18]. The spectral characteristics of this absorption are determined by such molecular parameters as the effective dipole moment of the monomer unit and its moment of inertia, i.e. they depend on the non-chemical interactions of the unit with the environment (cohesion energy) and the structure of the link. It is noteworthy that the height of the barrier for monounit libration is close to the value of the potential barrier of displacement of molecular units relative to their neighbors in a condensed medium [19]. This barrier corresponds to the activation energy of low-temperature γ-relaxation in polymers, which allows it to be attributed to the libration motion of the link [20]. The attribution of γ-relaxation to the libration motion of molecules in low molecular weight liquids is also discussed in Ref. [21].

Figure 2 shows that as the temperature decreases, the libration absorption band increases in intensity, narrows, and shifts to high frequencies. The latter is obviously related to a decrease of the amplitude and anharmony of libration oscillations due to increased interchain interactions. The occurrence of an additional peak (arm) in the region of $\sim 150\,\mathrm{cm}^{-1}$ at temperatures below 160 K is of special interest. There is a similar arm in the region of $80\,\mathrm{cm}^{-1}$ in the PAN spectrum in the studied temperature range, which we attribute to the manifestation of the crystal structure of this polymer. Such features of the contour of the libration band are typical for FIR spectra of partially crystalline polymers: PE [22], PTFE [9] and PP [23].

Figure 3 shows, in addition to the FIR spectrum of PAN at 298 K, the spectra of acetonitrile and acrylonitrile, which are similar in chemical structure to the structure of its monomeric unit, in the region of oscillations of their crystal lattices depending on temperature. It can be seen that a phase transition is abrupt at temperatures of ~ 205 K in acetonitrile and at ~ 175 K in acrylonitrile and radically alters their lattice spectrum: the shape, half-width, and position of peaks, clearly indicating a structural reorganization. Let us present the molecular mechanisms and scenarios of these changes using the data studied in detail on the spectrum of the external modes of the ACN molecule [11,25].

The ACN molecule belonging to the point group $C3v$ and crystallizing in symmetry $P2_1/c$ (β-phase) and $Cmc2_1$ (α-phase) has external translational and rotational degrees of freedom: $T_z(A_1)$, $L_z(A_2)$, $T_{xy}(E)$ and $L_{xy}(E)$. They are represented by translational and librational modes in the FIR spectrum of the crystal lattice (Figure 3, *a*): $T_z(A_1)$ at $118\,\mathrm{cm}^{-1}$, $L_z(A_2)$ at $135\,\mathrm{cm}^{-1}$, $T_{xy}(E)$ at $107\,\mathrm{cm}^{-1}$ and $L_{xy}(E)$ at $86\,\mathrm{cm}^{-1}$. Translational modes $T_z(A_1)$ and $T_{xy}(E)$ occur at $\sim 118\,\mathrm{cm}^{-1}$, and librational modes $L_z(A_2)$ and $L_{xy}(E)$ occur at 145 and $90\,\mathrm{cm}^{-1}$, respectively, in the spectrum of the acrylonitrile crystal lattice (Figure 2, *b*).

As can be seen from Figure 3, all these forms of external oscillations are very sensitive to the occurring structural rearrangements from liquid to solid β-phase and from β-phase to α-phase. Moreover, the spectral parameters of the bands in the presented spectra undergo clearly intermittent changes at the phase transition temperatures indicating a correlation between phase transitions and oscillatory dynamics. The mechanisms underlying such changes can be qualitatively understood if we assume that the behavior of oscillatory degrees of freedom in case of phase transitions is associated not only with a change of volume, but also with a sharp change of entropy.

Strong dipole-dipole interactions characteristic of acrylonitrile and acetonitrile lead to the fact that they have highly associated structures with dimers formed by sequential coupling of molecules with each other in the stable α-phase and their parallel coupling in β-phase and liquid phase [26]. In the first case, the orientation of the permanent dipole moment of the dimer leads to the structure of α-phase with macroscopic polarization along the crystallographic axis in an orthorhombic unit cell of symmetry $Cmc2_1$; in the second case, it leads to the structure of β-phase with macroscopic polarization of a permanent dipole the moment along the molecular axis in a monoclinic unit cell of symmetry $P2_1/c$, which is inclined relative to the crystallographic axis [27,28]. That is, the restructuring of the α-phase structure into the β-phase structure is associated with the reorientation or libration movement of dimers at the phase transition temperature.

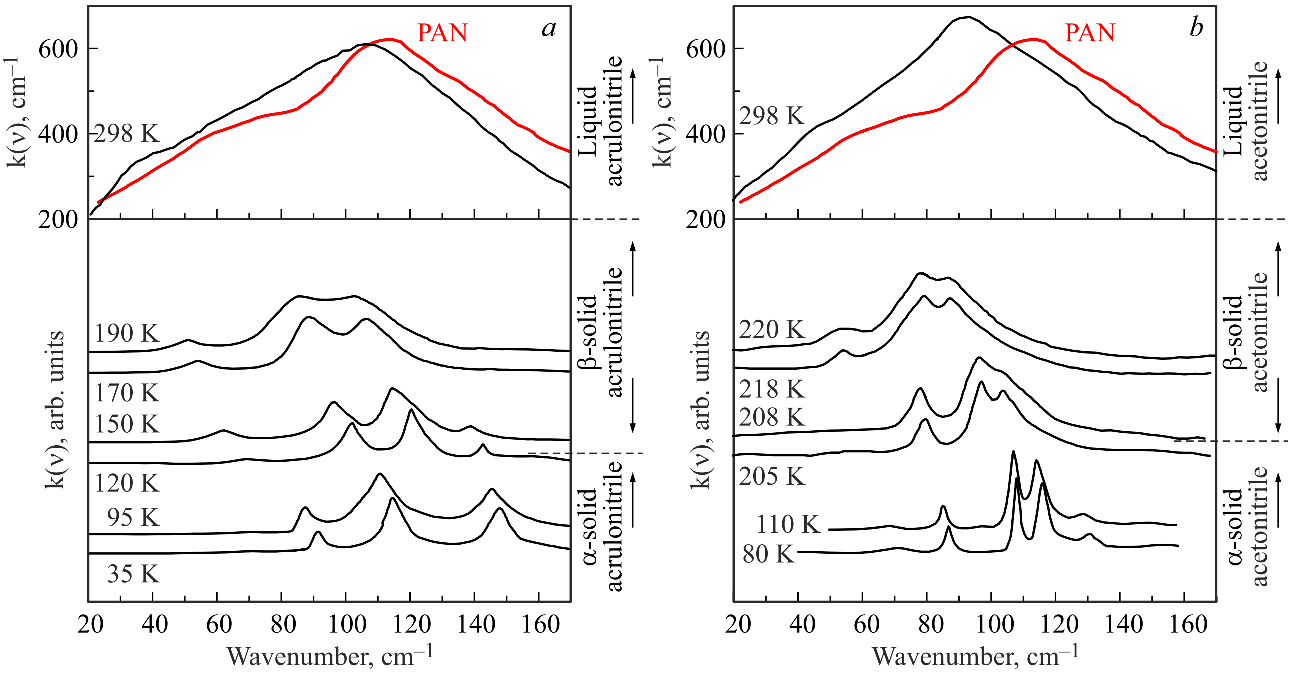

Figure 3. FiR spectra in the region of crystal lattice oscillations of 20−170 cm^{-1} obtained at different temperatures for acrylonitrile (*a*) [24] and acetonitrile (*b*) [11]. For comparison, the upper panel also shows the FIR spectrum of the PAN at $T = 298$ K.

This motion is represented by the mode $L_z(A_2)$ at 145 cm^{-1} and 135 cm^{-1}, respectively, in the low-temperature spectrum of the crystal lattice of AN and ACN (see Figure 3). This degree of freedom is not manifested as a separate band in the spectra of the liquid phase and polymer (PAN) at 298 K, but is part of an abnormally wide absorption band based on the Poley mechanism at ∼ 127 cm^{-1} (Figure 2), attributable to small-angle torsional oscillations (libration) of the $CH_2-CH-CN$ group (monomeric units PAN) [14].

These high-frequency small-angle torsional oscillations of molecular groups generally determine the mechanism of γ-relaxation in low molecular weight liquids and polymers, as already noted above and in Refs. [16,17,21]. Its manifestation and initiation, as we see in the example of a partially crystalline polymer, are associated with PT in the crystalline structures of this polymer.

The scenario for the development of this relationship can be briefly described as follows: the amplitude of oscillations of the crystal lattice increases with the increase of the temperature, as can be seen from the gradual broadening and red shift of bands in the spectrum due to the growth of anharmonicity and dephasing of oscillations. When the amplitude of the most unstable mode, in this case the libration mode $L_z(A_2)$ around the crystallographic axis, reaches a critical value (according to the Lindemann criterion), temperature initiation of the PT occurs (solid-phase or order−disorder type). In the system re-arranged as a result of the PT, the libration degree of freedom is represented by the libration mode $L_{xy}(E)$ around the molecular axis, which is tilted relative to the crystallographic axis.

This mode of the crystal lattice is represented by absorption at ∼ 127 cm^{-1} in the PAN spectrum at temperatures above PT which is caused by molecular torsional oscillation (libration) of PAN monomeric units in amorphous polymer structures. In crystalline regions of the polymer, the $L_{xy}(E)$ mode is represented by an inflection (shoulder) at ∼ 85 cm^{-1} on the low-frequency wing of the absorption band by the Poley mechanism; another libration mode $L_z(A_2)$, as can be seen from Figure 2, is manifested by an arm at ∼ 150 cm^{-1}, but only in the low-temperature FIR spectra of PAN and only up to the PT temperature at ∼ 160 K. It should be noted that a similar low-temperature solid-state PT, due to an unstable libration mode that initiates the transition from an orthorhombic (in this case) to a monoclinic structure, is also observed in other partially crystalline polymers, such as PE and PTFE.

Solid-state PT from an orthorhombic to a monoclinic structure in PE occurs at ∼ 150 K, above which, in addition to the fact that the libration mode B_{3g} ceases to manifest in the Raman spectrum of PE at 108 cm^{-1}, γ-process is „defrosted“ in its amorphous structures, like PAN at ∼ 165 K [29–31]. γ-process in PTFE caused like in PE and PAN, by limited by torsional oscillations (libration) of monomeric units in the amorphous regions of these polymers [20], appears at ∼ 163 K [32].

Let us present the molecular mechanism and the scenario of its initiation by considering the temperature behavior of IR spectra in the region of the external modes of the PTFE crystal lattice like in the case of PAN (Figure 4). As can

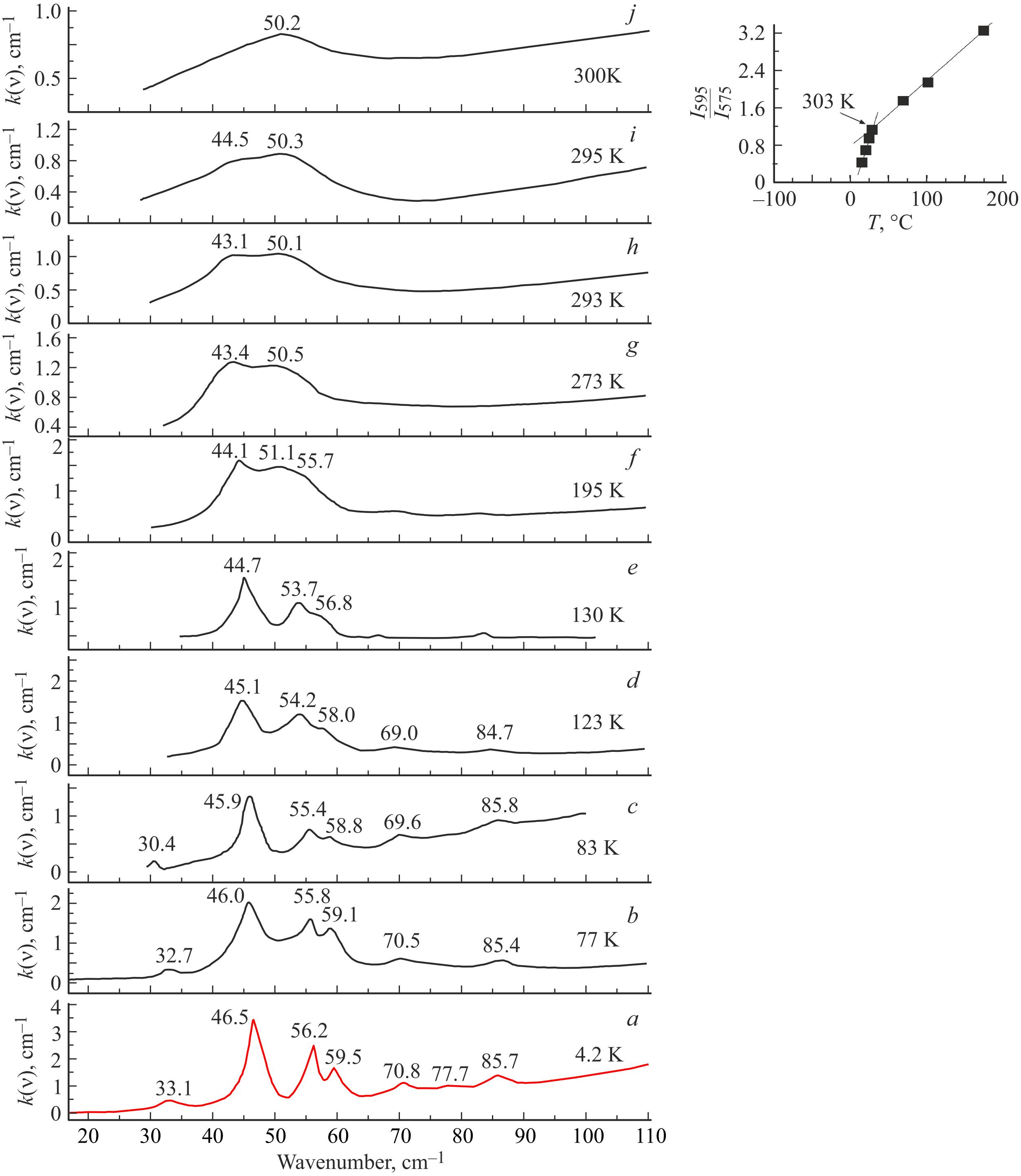

Figure 4. FIR spectra in the region of oscillations of the PTFE crystal lattice as a function of temperature, K: *a* —4.2 [33], *b* —77 [34], *c* — 83 [35], *d* — 123 K [9], *e* — 130 [36], *f* — 195 [34], *g* — 273 [34], *h* — 293 (this work), *i* — 295 K [33], *j* — 300 K [36]. The insert shows the data from Ref. [37,38] on the temperature dependence of the intensity ratio of bands 575 and 595,cm^{-1} in the Raman spectrum of PTFE.

be seen, only a gradual broadening and red shift of the bands occurs with an increase of temperature in the range from 4.2 to 130 K, whereas it is almost impossible to resolve bands in the range of 40–60 cm^{-1} in the PTFE spectrum at 195 K and there are no bands at $\sim$ 70 and 84 cm^{-1}. Such a drastic change of the parameters of the spectrum can only be associated with PT in PTFE at temperatures between 130 and 195 K. The lattice spectrum of PTFE at the PT temperature is not provided in Ref. [9], but it is found that bands in the range of 40–60 cm^{-1} of this spectrum become solvable again at temperatures below 108°C (165 K); the absence of bands in the spectra at ~ 70 and $84\,\mathrm{cm}^{-1}$ after PT is explained by the authors by a decrease of their intensity with temperature.

The assignment of bands in the PTFE oscillation spectrum was performed in Refs. [34,35,39] and is based on the idea that a PTFE lattice cell belonging to a monoclinic crystal system with a spatial group $P2_1$ contains 2 molecular segments at low temperatures. 5 active IR lattice modes provide a complete representation for this spatial group: $\Gamma = A_1 + 2A_2 + E_1 + E_2$, where modes A_1 and A_2 correspond to translational modes $T_z(A_1)$, $T_z(A_2)$ and $T_{xy}(E_1)$, while modes E_1 and E_2 correspond to rotational (libration) modes $L_z(A_2)$ and $L_{xy}(E_2)$. Translational modes include bands at 31.6, 45.8, and $70.2\,\mathrm{cm}^{-1}$, respectively, in the PTFE spectrum at 90 K, and rotational modes include a doublet band at $\sim 56\,\mathrm{cm}^{-1}$ and a band at $85.6\,\mathrm{cm}^{-1}$. The last band, which is not present in the PTFE spectra at temperatures above PT, represents the unstable libration mode $L_z(A_2)$, which initiates a low-temperature solid-state transition. In the system that was rebuilt as a result of the PT, the libration degree of freedom is represented by the mode $L_{xy}(E_2)$ (the band at $\sim 56\,\mathrm{cm}^{-1}$). Now, the limited torsional vibrations of monomeric units, which characterize the band at $\sim 56\,\mathrm{cm}^{-1}$ in the PTFE spectra above PT, will determine the mechanism of γ-relaxation in the amorphous regions of this polymer.

The molecular mobility of PTFE has been studied in detail in Refs. [32,40,41]. Various experimental methods observe several modes of molecular motion in PTFE in the form of relaxation transitions at different temperatures: torsional-oscillatory motion of individual CF_2 groups, manifested, as mentioned, in the form of γ-transition at ~ -100°C; reorientation (conformational) mobility of macromolecules, manifested in the form of so-called „secondary“ β-relaxation at ~ 19°C (also called the crystalline transition, since it manifests itself in the crystalline regions of the polymer) and segmental mobility, that unfreezes in the αtransition at the glass transition temperature of ~ 130°C [42].

The relationship discussed above between solid-state PT and the initiation of γ-relaxation in PAN and PTFE can also be traced in the case of β-relaxation, especially since solid-state PT is well established in PTFE at 19°C (292 K). It was shown that repeating unit of the PTFE polymer chain consists of 13 CF_2 groups in six turns of the spiral below 19°C; the chains form an almost regular triclinic crystal structure. The lattice cell has a hexagonal structure after PT at 19°C; turning by 180° requires 7 turns of the chain and 15 CF_2 groups. The length of such a repeating unit is already close to the size of the statistical PTFE segment in 18 CF_2 groups. The spiral is further unwound above 19°C because of the increase of the amplitude of the torsional-oscillatory motion. It becomes possible to change the confromation of the spiral when 18 CF_2 groups are involved in this movement, and the statistical segment acquires the status of a kinetic unit in the β-relaxation [2]. This transition at 303 K, in contrast to the transition at 292 K, is a type II phase transition [5], it is also called a transition of the type of „orientational melting“ since it precedes the orientational disordering of the crystal lattice.

Spectra of lattice oscillations of PTFE at temperatures of 0, 20, 22 and 27 °C (see Figure 4, g–j) are less intense than low-temperature spectra and are more smoothed. There is only one abnormally wide doublet band in the range of $40-60\,\mathrm{cm}^{-1}$ with a poorly solvable structure. However, it can be seen that the intensity of its low-frequency component corresponding to the translational mode $T_z(A_2)$ decreases more significantly with temperature than the high-frequency component corresponding to the libration mode $L_z(A_2)$. Only librational movement of CF_2 groups is represented with a separate peak in the PTFE spectrum at a temperature of 27°C. The position and, obviously, the half-width of the low-frequency component have changed particularly sharply: its peak has shifted by $0.3\,\mathrm{cm}^{-1}$ in the range of 0–20°C and by $1.1\,\mathrm{cm}^{-1}$ in the range of 20–22°C. Now, an abnormally wide asymmetric band is observed instead of a doublet — this is how the spectrum of the PTFE crystal lattice was affected by a solid-state PT of type I at 19°C. It is impossible to trace the effect of PT of type II on the lattice spectrum, since it leads to the final disordering of the crystal lattice. Indirect spectral confirmations of the generally accepted mechanism of this PT can be obtained using the data from Ref. [37,38] which studied the temperature dependence of bands 575 and 595,cm^{-1} in PTFE Raman spectrum.

Bands 575 and $595\,\mathrm{cm}^{-1}$ in the PTFE Raman spectrum are attributed to deformation oscillations of CF_2 groups attached to trans and gauche sequences of the spiral, respectively. The graph on the inset k in Figure 4 shows that the ratio of the intensities of these bands sharply changes towards an increase of gauche structures at $T \simeq 303\,\mathrm{K}$ because of the onset of conformational mobility in chains after PT of type II.

4. Conclusion

The following general observations can be made based on the results of IR spectroscopy presented here in the field of manifestation of oscillations of the crystal lattice of partially crystalline PAN and PTFE. Firstly, regarding the correlation between the mechanisms of PT and the vibrational properties of the external modes of the crystal lattice, and secondly, regarding the relationship between phase and relaxation transitions, which consists in the fact that the former often precede and are responsible for the manifestation of the latter.

The existence of certain relationships between relaxation transitions and first-order transitions in crystallizing polymers is a well-proven fact. There are many examples of this in the literature, of which the most well-known is that there is a constant ratio between the glass transition temperature and the crystallization temperature. The basis of such associations is the presence of a certain relationship between the crystalline phase and the amorphous one, which manifests itself in the fact that structural changes in the crystalline regions of the polymer are accompanied by changes of the packaging of macromolecules in its amorphous regions [43].

This study illustrates this relationship using data on the temperature dependence of spectral parameters of bands of external vibrational modes of the crystal lattice, which are particularly sensitive to crystal effects. The shape, intensity, half-width, and maximum position of the bands of rotational and translational modes change most dramatically, even abruptly, in case of a structural reorganization. A similar modification of the parameters is observed for the rotational (libration) mode $L_z(A_2)$, which initiates low-temperature solid-state PT at ~ 165 and ~ 163 K in PAN and PTFE, respectively. Thus, the molecular mechanism governing structural rearrangements in PT includes reorientation or librational movement, which is relatively free at temperatures above PT and frozen below this temperature.

Structural transformations in PT contribute to a further increase of the librational degree of freedom, leading to drastic changes of the orientation of the dipole moments of interacting molecules and, as we see from the spectra, to an increase of orientation disorder. γ-process caused by limited torsional oscillations (libration) of monomeric PAN and PTFE units manifests itself in the dielectric loss spectra as a relaxation transition at temperatures of ~ 170 K [8] and 165 K [44], close to low-temperature PT in these polymers.

The relationship between phase and relaxation transitions, which consists in the fact that PT are responsible for the manifestation of RT, can also be traced in the case of high-temperature solid-state PT in PTFE at 19°C (292 K). The ordered triclinic structure of the lattice cell of the crystalline part of PTFE changes to a hexagonal one at this temperature, ensuring a less dense packing of molecules and their „unwinding“ due to thermally activated librational movements of the chain units. When a section of a statsegment-long chain is involved in this movement, the PTFE spiral molecule gains the ability to change its conformation, which corresponds to the activation of β-relaxation mechanism and the onset of local segmental mobility. The graph of the temperature evolution of dynamic losses obtained by dynamic mechanical analysis shows β-transition as a peak at 30°C (303 K) [32].

In general, the presented data show that low-frequency IR spectra in the region of vibrations of crystal lattices of partially crystalline polymers ($10-150\,\mathrm{cm}^{-1}$) at temperatures from 4.2 to 300 K provide useful information about the nature of phase and relaxation transitions and their relationship at the molecular level.

Conflict of interest

The author declares that he has no conflict of interest.

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