Journal of Thermal Analysis, Vol. 38 (1992) 1031-1045

THERMOPHYSICAL PROPERTIES OF MACROMOLECULES IN THE BLOCK STATE
Spectroscopic investigation

V. I. Vettegren, L. S. Titenkov and S. V. Bronnikov***

A. F. IOFFE PHYSICAL- TECHNICAL INSTITUTE, ACADEMY OF SCIENCES OF RUSSIA, 194021, ST. PETERSBURG, RUSSIA
* MOSCOW TEXTILE INSTITUTE, MOSCOW, 117918, RUSSIA
**INSTITUTE OF MACROMOLECULAR COMPOUNDS, ACADEMY OF SCIENCES OF RUSSIA , 199004, RUSSIA

The macromolecules of linear polymers usually consist of regular helices. The paper presents the results of investigation of the concentration, thermal expansion coefficient and vibration amplitude of such helices at different temperatures. These parameters were determined from temperature dependences of the intensity, frequency and halfwidth of regular bands in IR and Raman spectra of polymers.

Keywords: IR spectroscopy, macromolecules of linear polymers, Raman spectroscopy, thermal expansion coefficient, vibration amplitude

Introduction

It is well known that the macromolecules of linear polymers consist of regular helices, N_m, and their repeat unit consists of N monomer fragments in m coils. In recent years, investigation of thermal properties, such as the thermal expansion coefficient of its length and vibration amplitude ash acquired a great importance. It was found that these parameters are closely related to temperature and time dependences of polymer strength and elasticity. They may also be used to predict both polymer fracture and deformation over wide temperature ranges [1–3].

It is possible to determine these parameters both in crystal and amorphous regions by IR and Raman spectroscopy. These methods are based on the presence of regular bands in optical spectra. These bands are responsible for vibrations of the helix N_m with length of l_{opt}. The latter is related to the run distance, Λ_{opt}, for an optical phonon: $l_{opt} = \Lambda_{opt}$. The phonon decay is caused by the nonlinearity of interatomic forces, and during the phonon lifetime, τ_p it runs the distance

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

$\Lambda_{opt} = S_p \tau_p$ (S_p is the phonon group velocity). The quantum of incident light, the photon, interacts with the helix as with a single oscillator. The integral absorbance coefficient, A, is proportional to the helix concentration, C_H in a sample: $A = kC_H$ where k is the absorbance coefficient for a sample that completely consists of helices.

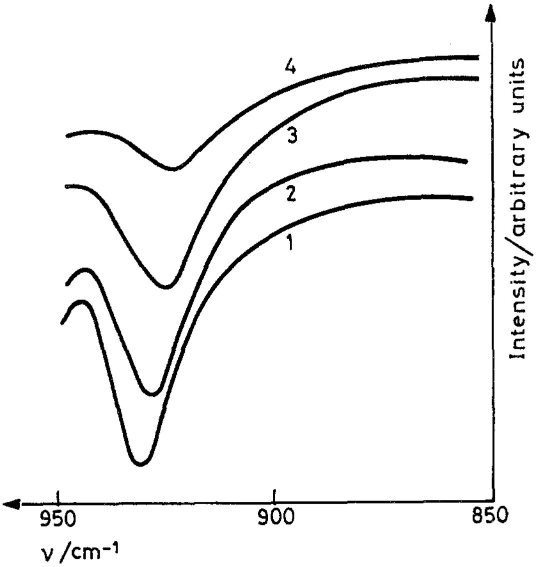

Fig. 1 930 cm^{-1} band in the IR spectrum of Nylon 6 at temperatures: (1) 100, (2) 300, (3) 430 and (4) 480 K

Hence, it is possible to determine a relative concentration, C_H, for regular helices, N_m, in a sample if the parameter A is known. The regular band broadening with increasing temperature is known to be caused by the phonons decay [4]. Part of band halfwidth depending on temperature, $\Delta\Gamma(T)$ is proportional to the mean-square amplitude of acoustic vibration, $\langle \Delta a^2 \rangle$. Hence, it is possible to investigate the amplitude of acoustic vibrations by IR or Raman spectroscopy.

The shifts of regular bands are caused by thermal expansion of axis length of the helix N_m [5]. Hence it is possible to investigate the axial thermal coefficient of the helices.

Experimental and discussion

Investigation were carried out in the temperature range form =100 K to above T_{melt} where T_{melt} is the melting temperature. Changes of the regularity band

930 cm^{-1} with increasing temperature are demonstrated for Nylon 6 in Fig. 1. It can be seen that with increasing temperature the band shifts to lower frequency, its intensity decreases and its width increases. Similar results were obtained for other regularity bands.

1. Temperature dependences of the integral absorbance coefficient, A, for Nylon 6 (the 930 cm^{-1} band) are demonstrated in Fig. 2. The coefficient, A, decreases with increasing temperature, and the slope of the $A(T)$ dependence at specific temperatures T_t and T_b changes. For comparison, the temperature dependence of the NMR second moment, $<\Delta B^2(T)>$, is shown in Fig. 2. It can be seen that both dependences, $A(T)$ and $<\Delta B^2(T)>$, have similar peculiarities at approximately the same temperatures.

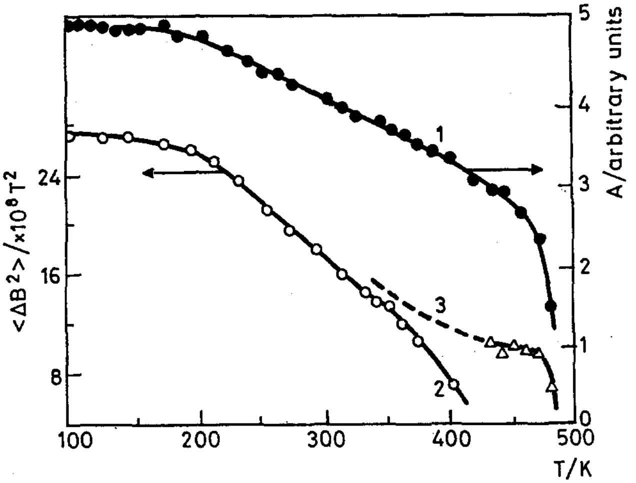

Fig. 2 Integral absorbance coefficient of (1) the 930 cm^{-1} band, (2) and (3) the second moment of NMR spectrum of Nylon 6 *vs.* temperature: (2) narrow and (3) wide bands

Similar results are obtained for regularity bands of PET and isotactic PP: $A(T)$ dependences change their slopes at temperatures T_t and T_b for these polymers. The peculiarities of the $A(T)$ dependences have previously been described in [69]. Significant changes in $<\Delta B^2>$ are due to the 'freezing out' of a new thermal motion mode. Consequently it can be suggested that the similarity of specific temperatures for $A(T)$ and $<B^2(T)>$ dependences is not accidental. Indeed, temperature increase causes disturbance in chain regularity. This disturbance leads to a decrease of the integral absorbance coefficient for regular bands [10].

Polymers are known to consist of alternating crystalline and amorphous regions. At low temperatures, the intensity of the thermal motion is low and therefore the disturbance of helices occurs in the zones with the lowest weak intermolecular interactions. The intensity of thermal motion increases with temperature and the zones with disturbed helices are broadened.

It is known that the integral absorbance coefficient, A, for regularity bands is proportional to the concentration, C_H, for helices within both crystalline and amorphous regions. Assuming the lack of conformational disturbance within crystallites ($C_{cr} = C_H$) one obtains

$$A = kC_H = k\ (C_{cr} + C_{am.H.})$$

If one divides and multiplies the right side of the above equation by the integral concentration of helices both in amorphous and crystalline regions, C_o, one obtains

$$A = kC_o\cdot\frac{C_{cr}}{C_o} + \frac{C_{am}}{C_o} = k'\cdot\frac{C_{cr}}{C_o} + \frac{C_{amH}}{C_{am}}\cdot\frac{C_{am}}{C_o}$$

where ($C_{am,H} / C_{am}$) is the concentration of helix within amorphous regions.

Since the degree of the crystallinity is $\chi = (C_{cr} / C_o)$, and near the melting temperature all helices within amorphous regions are destroyed ($\eta = C_{am.H.}/C_{am} = 0$), one obtains [10]

$$\eta = \frac{\chi}{1-\chi}\cdot\left(\frac{A(T)}{A_{melt}} - 1\right) \tag{1}$$

where A_{melt} is the value A at $T = T_{melt}$.

This equation permits us to estimate the degree of conformational regularity for amorphous regions, η, on the basis of the temperature dependence of the integral absorbance coefficient.

For films under investigation the degree of crystallinity was about 40% for Nylon 6 and 50% for isotactic PP. It was found that for Nylon 6 and PP the concentration of the helices in amorphous zones at 100 K varied from 60% to 90%. At room temperature the helix concentration is 1.5 to 2.0 times lower than at 100 K [10]. These results demonstrate that the molecular regularity in amorphous regions greatly depends on the temperature.

2. There are two reasons for the shift of the regularity bands [11, 12]. The first reason is the thermal expansion of the helix axis length and the change in intermolecular forces. Regular bands corresponding to the valence backbone vibrations were investigated. The shift of these bands under intermolecular forces usually is negligible. The shift value for the i-th vibrational mode, $\Delta\nu_i$, is determined by the thermal expansion ε of the helix axis according to the equation

$$\frac{\Delta\nu_i}{\nu_i(0)} = -G_i\,\varepsilon \tag{2}$$

where $\Delta\nu_i = \nu_i(T) - \nu_i(0)$, $\nu_i(T)$ and $\nu_i(0)$ are the vibrational frequencies at temperatures T and 0 K; G_i is the Grüneisen mode parameter.

The second reason for the band shift is the decay of the optical phonon. To realize which reason gives the greater contribution we compare spectroscopic data with wide-angle X-ray data. Let us suppose that a helix N_m in crystal is the main diagonal of a parallelepiped formed by a, b and c axis of crystallographic lattice, and the deformation of helix length with increasing temperature may be calculated as the relative increase of this diagonal. The a, b and c axis values at different temperatures are listed in [13, 14]. Calculated ε values were substituted into Eq. (2). Then the $\Delta\nu_i$ values were determined and compared with the measured shift values. The G_i parameters were determined as described in [15].

It was found that for the 1130 cm^{-1} band in the Raman spectrum of PE, the 1146 cm^{-1} band in the IR spectrum of PVA and the 930 cm^{-1} band in the IR spectrum of Nylon 6, the calculated $\Delta\nu_i$ values coincide with the measured values within experimental error.

Hence, for these regular bands, the thermal expansion of helix axis provides the main contribution to the shift.

It is suggested that this is justified for other regular bands corresponding to valence backbone vibrations.

This conclusion makes possible to determine the expansion, ε, of the helix axis length with increasing temperature

$$\varepsilon = \frac{-\Delta\nu_i}{\nu_i(0)\cdot G_i} \tag{3}$$

and, hence, to determine the thermal expansion coefficient

$$\beta = \frac{d\varepsilon}{dT} = -\frac{1}{G_i \cdot \nu_i(0)} \cdot \frac{d\nu_i}{dT} \tag{4}$$

For this purpose the temperature dependences of the band shift were measured and then ε and β were calculated with the aid of Eqs (3) and (4).

Figures 3 and 4 show $\nu_i(T)$, $\varepsilon(T)$ and $\beta(T)$ dependences. One can see that at low temperatures ($T<T_t$) the helix expansion, β, is small ($\beta<10^{-6}$ K^{-1}), at $T = T_t$ β increases rapidly, attains the β_t value and at $T_t < T < T_b$ β undergoes little change. Furthermore, at $T = T_b$ the thermal expansion coefficient increases again to the β_b value and does not change from $T>T_b$ up to the melting temperature.

This character of the $\varepsilon(T)$ and $\beta(T)$ dependences is typical for all polymers under investigation.

The calculeted β_t, β_b, T_t and T_b values are listed in Table 1. To elucidate the nature of these dependences, the theory of the thermal expansion for chain molecules [16, 17] was used.

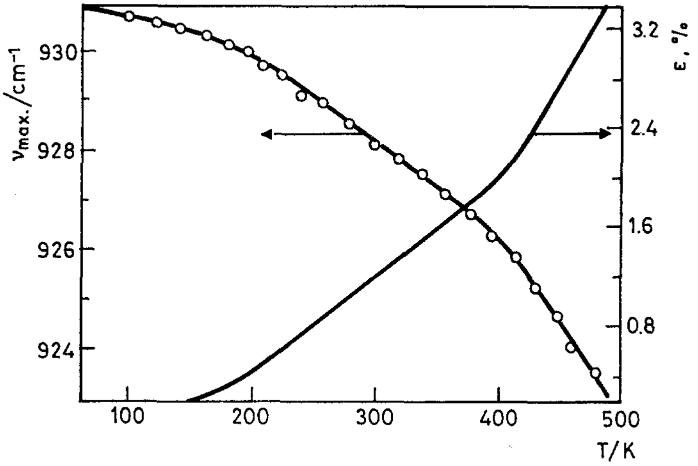

Fig. 3 Maximum position of the 930 cm^{-1} band and the thermal expansion of helix axis for the macromolecule Nylon 6 *vs.* temperature

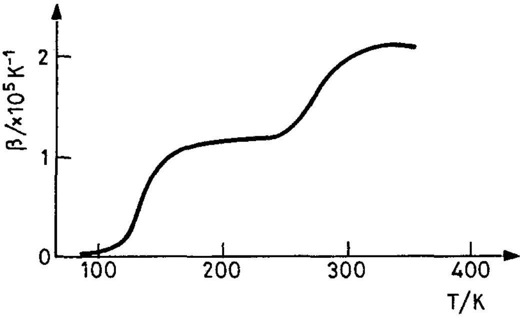

Fig. 4 Thermal expansion coefficient of the PE helix axis *vs.* temperature

The free energy of solids, F, is related to the deformation tensor ε_{lk}, by the equation

$$\varepsilon_{lk} = \frac{\partial F}{\partial \sigma_{lk}} \tag{5}$$

where σ_{lk} is the stress tensor.

The free energy is expressed by the equation

$$F = U + \sum_{i} \left\{ \frac{h\nu_i}{2} + kT \ln \left[1 - \exp\left(- \frac{h\nu_i}{kT} \right) \right] \right\} \tag{6}$$

The substitution of Eq. (6) in (5) results

$$\varepsilon = \sum_{m,n} G_{m,n} \cdot S^T \cdot \left\{ \frac{h\nu_{m,n}}{2} + \frac{h\nu_{m,n}}{\exp[(h\nu_{m,n}/kT) - 1]} \right\} \tag{7}$$

where S^T is the isothermal compliance (l and k indices have been omitted since the axis deformation was measured by the spectroscopic method), $G_{m,n}$ is Grüneisen parameter.

Table 1 Characteristic temperatures for twisting (T_t) and bending (T_b) vibrations and expansion coefficients of helix axis

No.	Polymer	Characteristic temperatures / K		Thermal expansion coefficients / K^{-1}	
		T_t	T_b	β_t	β_b
1.	Poly(etylene)	120	250	1.2	2.1
2.	Poly(etylene terephthalate)	240	390	1.3	2.0
3.	Nylon 6	200	400	1.5	3.1
4.	Nylon 66/6	220	310	2.1	3.8
5.	Nylon 610	200	320	1.4	2.2
6.	Poly(vynil alcohol)	230	370	1.7	—

In future discussion the summation of the total number, i, is replaced by that over n, within vibrational modes, and over m, by the vibrational modes.

Differentiation of Eq. (7) by temperature gives the equation for the thermal expansion coefficient β

$$\beta = \frac{S^T}{V} \cdot \sum_m C_m G_m = \sum_m \beta_m \tag{8}$$

where β_m is the contribution of the m-th vibrational mode to the thermal expansion

$$\beta_m = \frac{S^T}{V} \cdot \sum_m C_m G_m \tag{9}$$

G_m is the average Grüneisen parameter and C_m is the contribution of the m-th vibrational mode in capacity

$$C_m = k \cdot \sum_n \left(\frac{h\nu_{m,n}}{kT} \right)^2 \cdot \frac{\exp - \frac{h\nu_{m,n}}{kT}}{1 - \exp(-\frac{h\nu_{m,n}}{kT})} \tag{10}$$

where V is the volume of the crystallographic unit.

The Debye mode temperature, θ_m, may be determined by the equality $h\nu_{m,max} = k\theta_m$ where $\nu_{m.max}$ is the maximal frequency of the m-th mode.

The analysis of Eq. (10) shows that $C_m = 0$ at $T<(\theta_m/3)$ and $C_m=k$ at $T \geq (\theta_m/3)$. Therefore, $\beta_m = 0$ at $T < (\theta_m/3)$ and

$$\beta_m \simeq \frac{S^T k}{V} \cdot G_m \tag{11}$$

at $T \geq (\theta_m/3)$.

The polymer molecule in helix conformation is known to participate in three vibrational modes: twisting, bending and stretching ones. The mode temperatures, θ_m, for these vibrations usually differ by several hundred degrees. This difference permits us to separate the contributions of twisting and bending modes to the thermal expansion of the helix axis.

For instance, for PE the maximum frequency of twisting vibration, $\nu_{t,max} =$ 240 cm^{-1} [18], the Debye mode temperature, $\theta_t = (h\nu_{t,max}/k) = 340$ K. Therefore, at $T < (\theta_t/3) = 110$ K $\beta = 0$, whereas at $T \geq 110$ K β increases and attains the value: $\beta_t = 1.2 \cdot 10^{-5}$ K^{-1} (Fig. 4).

The coefficient β does not change its value to $T \geq T_b = (\theta_b/3) = (h\nu_{b,max}/3k)$ where $\nu_{b,max}$ the bending vibration frequency ($\nu_{b,max} = 520$ cm^{-1}) [18]. At this temperature β increases rapidly attaining the value $2.1 \cdot 10^{-5}$ K^{-1}.

In the temperature range under investigation $T < T_{melt} < T_s = (\theta_s/3)$ the value $\beta_s = 0$.

At T 0 K, $\beta = 0$, but $\varepsilon > 0$ (Eq. (7)). It is known that $\sum_m h\nu_{m,max} = k(\theta_m/4)$. Therefore, at T 0 K Eq. (7) may be rewritten as

$$\varepsilon_o = \beta_t (k\theta_t/4) + \beta_b (\theta_b/4) + \beta_s (k\theta_s/4) = \varepsilon_{ot} + \varepsilon_{ob} + \varepsilon_{os}$$

where ε_t, ε_b and ε_s are the contributions to the expansion caused by the zero twisting, bending and stretching zero phonons respectively.

The $\nu_i(T)$ dependences (Fig. 3) permit us to calculate the contributions of twisting and bending vibrations to ε_o. Let us extrapolate the linear parts of the $\nu_i(T)$ dependence at $T_t < T < T_b$ and at $T < T_t$ to the frequency axis and designate the intersection part by $\Delta\nu_{ot}$. The expansion, ε_{ot}, may be determined from the equation

$$\varepsilon_{ot} = -[\Delta\nu_{ot}/\nu_i(0) \cdot G_i] \tag{12}$$

Let us consider the $\nu_i(T)$ dependence at $T > T_b$. It is extrapolated to the frequency axis and the intersection part is designated by ν_{ob}. The intersection

$\Delta\nu_{ob} = \nu_{ob} - \nu_i\,(T)$ permits us to find the expansion, ε_{ob} caused by zero bending phonons: $\varepsilon_{ob} =-[\,\Delta\nu_{ob}/\nu_i\,(0)\cdot G_i]$

It was found that the values ε_{ot} and ε_{ob} for most investigated polymers were close to the value of the thermal expansion of the helix length at room temperature.

3. It was found that the increase of the regular band halfwidth related to the valence bonds vibrations in the backbone with increasing temperature caused the decay of the optical phonons [4, 12]. According to the theory [12] the regular band halfwidth, $\Delta\Gamma_a$, is related to the average numbers of acoustical (n_{ac}) phonons by the equation

$$\Gamma_a = \Gamma_a\,(0)\cdot(\,n_{ac} + 1) \tag{13}$$

where $\Gamma_a\,(0)$ is the halfwidth at T 0.

The average phonon number, n, is related to the temperature by the equation

$$n = (\exp\frac{h\nu}{kT} - 1\,)^{-1} \tag{14}$$

The mean-square amplitude of atomic vibrations, $<\Delta a^2>$, is related to n by equation

$$<\Delta a^2> = B\,(\,n + 1/2\,) \tag{15}$$

where B is a constant depending on the atom mass and the stiffness of interatomic bonds.

If Eq. (15) is substituted in Eq. (14), one obtains

$$\Gamma_a \simeq \Gamma_a\,(0)\cdot\left(\frac{<\Delta a^2>}{B} + 1\right) \tag{16}$$

Figure 5 demonstrates the dependences of some regularity bands halfwidths on the mean-square vibrational amplitude $<\Delta a^2>$ determined by X-ray scattering. One can see that the band broadening increases proportionally to the mean-square value of the vibration amplitude.

Equation 15 can be written in the following form

$$\Gamma_a = \Gamma_a\,(0)\cdot\left[1 + \left(\exp\frac{h\nu_{ac}}{kT} - 1\right)^{-1}\,\right] \tag{17}$$

where ν_{ac} is the average frequency of acoustic phonons which interact with optical phonons. At $T \geq (\,\theta_m/3)$ Eq. (17) may be replaced by the approximate equation

$$\Gamma_a \cong \Gamma_a(0)\cdot\frac{kT}{h\nu_{ac}} \tag{18}$$

Figure 6 shows that at $T \geq T_t$ the halfwidth actually increases linearly with temperature. Let us extrapolate the linear parts of the $\Gamma(T)$ dependence to the ordinate (Fig. 6). The interval cut off by the line is assumed to be the approximate $\Gamma_a(0)$ value, i.e., the broadening caused by the optical phonon decay at $T=0$ Eq. (17) may be rewritten in form

$$\ln\left(\frac{\Gamma(T)}{\Gamma(0)}-1\right)=-\frac{h\nu_{ac}}{kT} \tag{19}$$

Figure 7 shows that at $T < T_b$ the experimental data are actually described by Eq. (19). The ν_{ac} values may be determined from the slopes of straight lines. For example, the value $\nu_{ac} = 250$ cm^{-1} was found for PE. This value is in a good agreement with the 240 cm^{-1} value corresponding to the maximum frequency of twisting phonons [18].

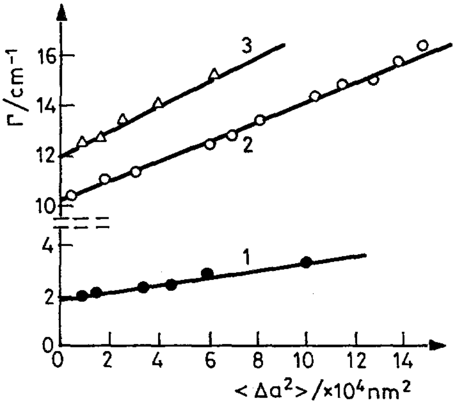

Fig. 5 Regular band halfwidth *vs.* mean-square amplitude of atomic vibration: (1) the 1130 cm^{-1} band for PE, (2) the 1146 cm^{-1} band for PVA and (3) the 930 cm^{-1} band for Nylon 6

Figure 5 shows that at $T > T_b$ the slope of the $\Gamma(T)$ dependence increases. This fact may be explained by the contribution of the bending phonons to the process of decay of the optical phonons.

One may determine the values of temperatures θ_t and θ_b from the $\Gamma(T)$ dependence it changed slope at temperatures $=T_t=(\theta_t/3)$ and $T_b=(\theta_b/3)$. The calculated values of θ_t and θ_b coincide with the same parameters determined from the temperature dependences of the coefficient of thermal expansion (Table 1).

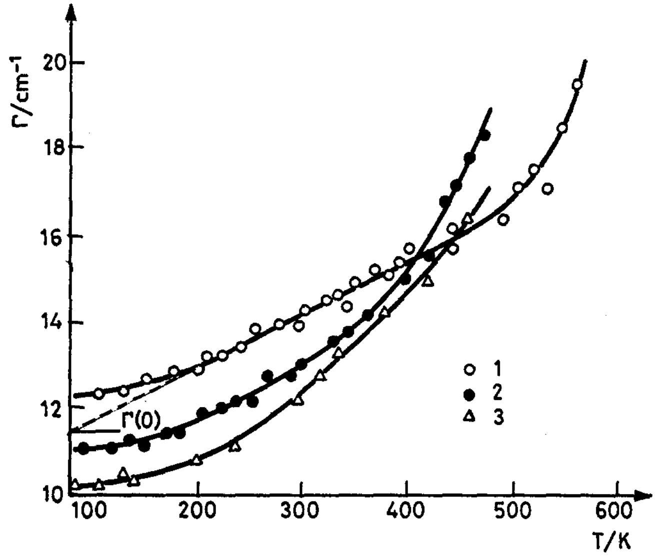

Fig. 6 Reguler band half width *vs.* temperature: (1) the 976 cm^{-1} band for PET, (2) the 930 cm^{-1} band for Nylon 6 and (3) the 1146 cm^{-1} band for PVA

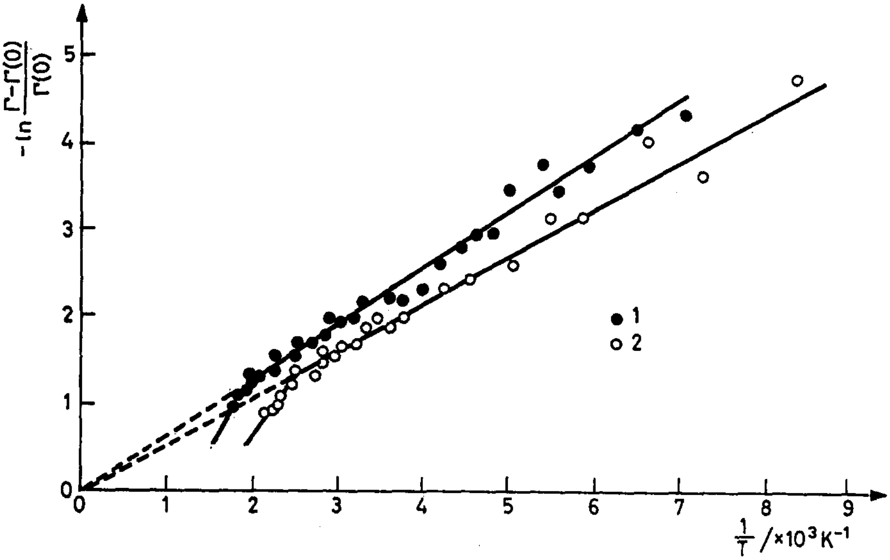

Fig. 7 Plot used for ν_{ac} determination: (1) the 976 cm^{-1} band for PET and (2) the 930 cm^{-1} band for Nylon 6

4. It was discovered that the equilibrium interatomic distance in helices and atomic vibration amplitude were correlated with the longitudinal dimensions of the crystallite. This effect has been investigated for PE [19].

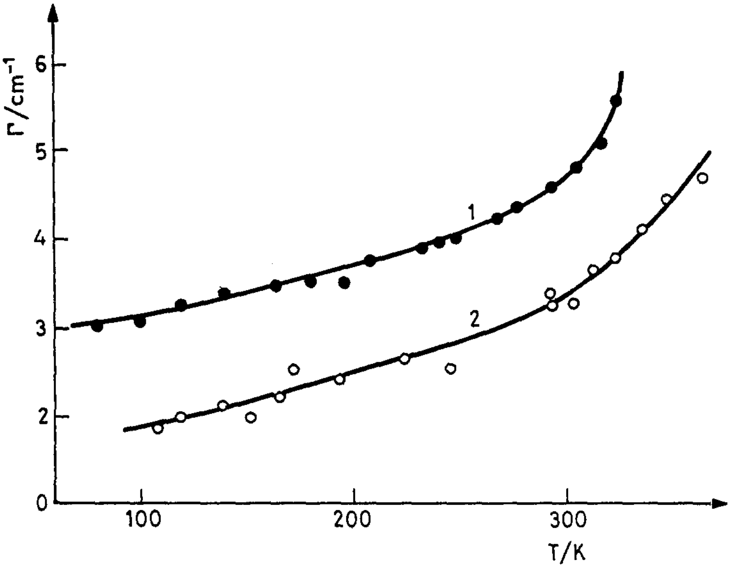

Fig. 8 1130 cm^{-1} band halfwidth in the Raman spectrum of PE with crystallite size of (1) 10 and (2) 100 nm *vs.* temperature

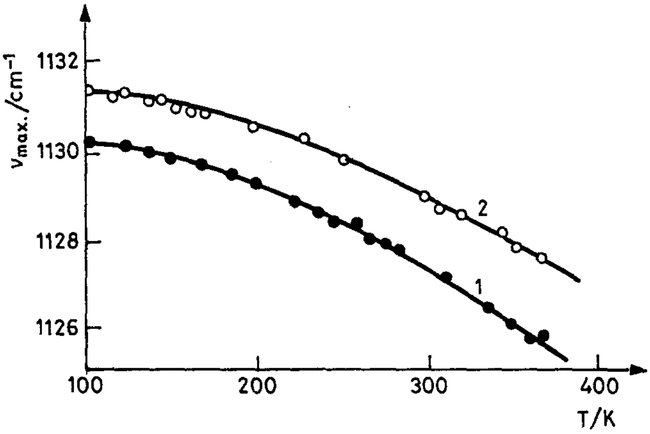

Fig. 9 Maximum position of the 1130 cm^{-1} band for PE with crystallite size of (1) 10 and (2) 100 nm *vs.* temperature

Figure 8 shows the temperature dependences of the 1130 cm^{-1} regularity band halfwidth in Raman spectra for crystallite sizes of 10 and 100 nm. One can see that at all temperatures the halfwidth for the first sample is =1 cm^{-1} greater than that for the second sample. Hence, the mean square amplitude of atomic vibrations in helices for the sample with crystallite dimensions of 10 nm are greater than for the sample with crystallite dimension of 100 nm.

Figure 9 demonstrates the temperature dependences of the maximum position of 1130 cm^{-1} band in the Raman spectrum of PE samples.

The frequency of the maximum in the spectrum of the first sample is =1.5 cm^{-1} higher than for the second sample. Hence, the length of the helices in the sample with 10 nm crystallites is greater by= 0.2% than in sample with crystallite dimensions of 100 nm.

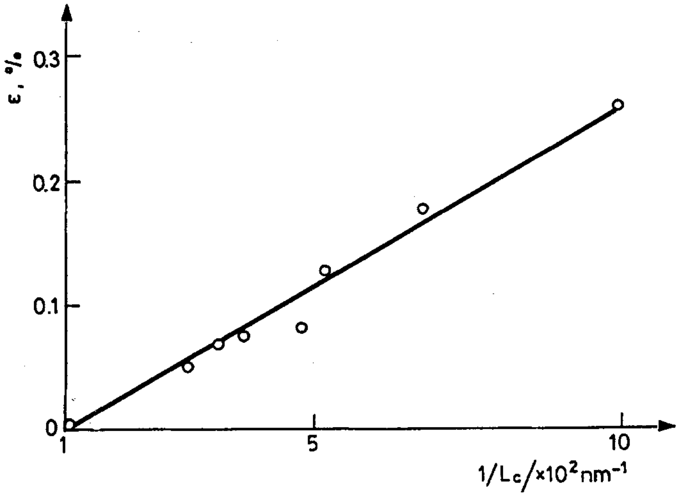

Fig. 10 Helix axis expansion of PE molecule *vs.* $1/L_c$

To interpret these results, the mean-square amplitude of atomic vibrations and expansion for the model of a linear atomic chain were calculated by fluctuation-dissipation theorem [20]. It is shown that the contribution caused by zero phonons with maximum frequency $\nu_{max} > (kT/h)$ in the mean square amplitude is

$$<\Delta a_0^2> \simeq \frac{h\nu}{2\pi^2 \Lambda E a^3} \cdot \ln\left(\frac{2\pi\nu_{max}\Lambda}{v}\right) \tag{20}$$

where Λ is the run distance of the phonons, *E* is the Young modulus, *a* is the interatomic distance and v is the sound velocity. The expansion caused by zero phonons is

$$\varepsilon_0 \simeq G < \Delta a_0^2 > \tag{21}$$

where G is the average Grüneisen parameter.

It is possible to evaluate the value of Λ by the equation

$$\Lambda \cong \frac{Ea^4}{e^{1/2} k \theta G^2} \cdot \exp \frac{\theta}{2T} \tag{22}$$

where θ is the Debye temperature. Let us use Eq. (22) applying the following parameters $G = 2$, $a = 0.127$ nm, Young's modulus along the c axis = 300 GPa, along the a axis = 4 GPa and along b axis = 5 GPa [21].

According to calculations at 100 K for stretching phonons $\Lambda_s = 1200$ nm, for bending phonons $\Lambda_b = 100$ nm and for twisting phonons $\Lambda_t = 40$ nm. Hence, the stretching phonons have the longest run distance. These results suggest that the $< \Delta a_o^2 >$ (or ε_o) depedences on the longitudinal dimensions of L_c of the crystallite are caused by the stretching zero phonons scattering at crystallite boundaries.

Taking into account this scattering one can obtain

$$< \Delta a_o^2 > = A/L_c \, ; \qquad \varepsilon_o = B/L_c \tag{23}$$

where $A \equiv \frac{h\nu}{2\pi^2 E_c a^3} \cdot \ln \left(\frac{2\pi\nu_{\max}}{\nu} \right)$, $B \equiv GA$.

Eq. (23) is confirmed experimentally (Fig. 10). The A and B parameters in this equation coincide numerically with the slopes of the ε_o $(1/L_c)$ and $< \Delta a_o^2 >$ experimental dependences. These results make it possible to interpret the discovered effect by the zero stretching phonons scattering on the crystallite boundaries.

References

1 S. V. Bronnikov, V. I. Vettegren, L. N. Korzhavin and S. Ja. Frenkel, Mech. Kompoz. Mater., No.5 (1983) 920.

2 V. I. Vettegren, S. O. Lasarev and V. A. Petrov, Physical Foundations of Materials Fracture Kinetics, A. F. Ioffe Physical-Technical Institute Academy of Sciences of the USSR, Leningrad (1989) p. 73.

3 S. V. Bronnikov, V. I. Vettegren, L. N. Korzhavin and S. Ja. Frenkel., Vysokomol. Soed., (A), 30 (1988) 2115.

4 V. I. Vettegren and V. A. Kosobukin, Opt. a. Spectroscopy. 31 (1971) 589.

5 L. S. Titenkov, V. I. Vettegren, S. V. Bronnikov and Ju. V. Zelenev, Vysokomol. Soed., (B) 27 (1985) 857.

6 A. Anton, J. Appl. Polymer Sci., 12 (1968) 2117.

7 H. Hannon and J. Koenig, J. Polymer Sci., 2 (1969) 1085.

8 Y. Huang and J. Koenig, J. Appl. Polymer Sci., 15 (1971) 1237.

9 O. A. Nikitina, N. A. Slovokhotova and V. A. Kargin, Vysokomol. Soed., (B), 10 (1968) 458.

10 V. I. Vettegren, L. S. Titenkov, Ju. V. Zelenev, V. V. Zhizhenkov and E. A. Egorov, Vysokomol. Soed., (A), 22 (1980) 2101.

11 M. A. Ivanov, M. N. Krivoglaz, D. N. Mirlin and I. I. Reshina, Phyz. Tverd. Tela, 8 (1966) 192.

12 A. I. Gubanov and V. A. Kosobukin, Mech. Polym., 1 (1975) 33.

13 G. Dodobaev and A. I. Slutsker, Phys. Tverd. Tela, 23 (1981) 1936.
14 G. Dodobaev and A. I. Slutsker, Vysokomol. Soed., (A) 24 (1982) 30.
15 V. I. Vettegren, Phys. Tverd. Tela, 26 (1984) 1699.
16 I. M. Lifshits, J. Exp. a Theor. Phys., 22 (1952) 475.
17 Yu. K. Godovsky Heatphys. Polymers, Chemistry, Moscow 1982 p. 85.
18 M. Tasumi and T. Shimanouchi, J. Chem. Phys., 43 (1965) 1245.
19 L. S. Titenkov, V. I. Vettegren, A.A. Kusov and Ju. V. Zelenev, Vysokomol. Soed., (A) 16 (1974) 1681.
20 L. D. Landu and E. M. Lifshitz, Statistics Physik, Nauka, Moscow 1976 p. 463.
21 I. Sakurada, T. Ito and K. Nakamae, J. Appl. Polymer Sci., 15 (1966) 75.

Zusammenfassung — Die Makromoleküle linearer Polymere zeigen gewöhnlich Helixstruktur. Es wurden Konzentration, Wärmeausdehnungskoeffizient und Schwingungsamplitude derartiger Helizes bei verschiedenen Temperaturen untersucht. Diese Parameter wurden anhand von Intensität, Frequenz und Halbwertbreite der Normalbanden in IR- und Raman-Spektren von Polymeren bestimmt.