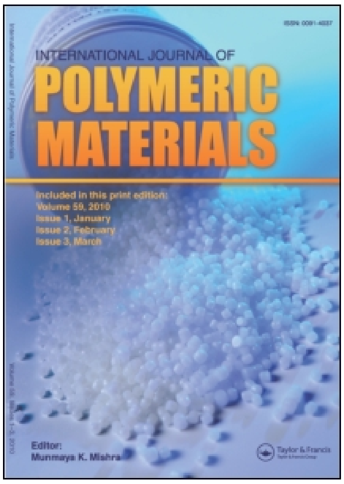

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THE CONFORMATIONAL MECHANISM OF THERMOELASTICITY OF ORIENTED POLYETHYLENE

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Temperature variations of oriented polyethylene (PE) with a draw ratio of ~450% were measured in longitudinal adiabatic tension and compression (along the orientation axis) and transverse compression. Stress-strain curves (for tension and compression) were recorded. Linear thermal expansion coefficients in the longitudinal and transverse direction were measured. Thermoelastic characteristics and also thermal properties of oriented PE were quantitatively analyzed. It has been concluded that conformational dynamics has a dominating influence on these characteristics.

Keywords: polyethylene, thermoelasticity, tension and compression, temperature, isomeric transitions, conformational dynamics

INTRODUCTION

The thermoelastic effect – variations in temperature of a body on its elastic deformation under adiabatic conditions – is a characteristic

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feature of all solids. For a uniaxial deformation, the thermodynamic derivation yields Kelvin formula [1].

$$\frac{\Delta T}{T} = -\frac{\alpha}{C}\sigma \tag{1}$$

where ΔT is the change in temperature T, σ is the uniaxial stress, α is the linear thermal expansion coefficient (LTEC) of a solid along the axis of loading, and C is the specific heat capacity (per unit volume).

Thermodynamic derivation makes expression (1) valid for any nature (mechanism) of elasticity and thermal expansion, which can be different for different solids.

In low-molecular solids, where elastic deformation is associated with deformation of interatomic (intermolecular) bonds and thermal expansion is due to anharmonicity of interatomic interaction, the thermoelasticity mechanism involves redistribution of the kinetic and potential components of the excitation energy of anharmonic oscillators on their loading (deformation) [2,3].

A chain molecular structure of polymeric bodies gives rise to specific features in their elasticity, internal dynamics and energetics:

- deformation of a polymer above the glass transition temperature results from not only deformation of interatomic bonds, but also conformational transitions (whose contribution is typically greater);
- thermal deformation of a polymeric body is due to the influence of transverse vibrations and conformational transitions on the axial length of chain molecules; thus thermal expansion of polymers can include the effects of the nonanharmonic nature, i.e., the effects that are not associated with the anharmonicity of interatomic interaction;
- the anisoenergetic conformational transitions change the heat content and, hence, the temperature of a polymeric body.

In addition, specific features of the supermolecular structure of polymers, such as a pronounced amorphous-crystalline heterogeneity (in crystallizing polymers) and a sharp local anisotropy of mechanical and thermal characteristics of the polymer volume elements, should be mentioned. Of particular interest are uniaxially oriented polymers that exhibit a strong overall anisotropy of properties.

Due to all these features, polymers with different chemical compositions and also polymers of one type, but in different structural conditions, can exhibit greatly differing thermoelastic behavior.

The most comprehensive treatment of the thermoelasticity of polymers was given by Godovsky [4] and in a special issue of

Thermochimica Acta [5]. It was emphasized [4] that further detailing of the mechanism of thermoelasticity of polymers, taking into account their structural condition, is necessary.

This paper describes detailed studies of thermoelastic effects in oriented polyethylene (PE) in longitudinal tension and compression (along the orientation axis) tests and transverse compression tests. Stress-strain curves (for tension and compression) and also LTECs measured in the longitudinal and transverse direction are given. Similar measurements for nonoriented PE are reported. The major goal of the work was to elucidate the mechanism of themoelasticity of oriented PE.

EXPERIMENTAL DETAILS

Objects

The objects were samples of PE with a density of 919 kg/m^3 and crystallinity degree of $\sim$60%. From a plate of nonoriented PE, cylinders 13.4 mm in diameter and 100 mm long were prepared by turning with a lathe. These samples were used to study nonoriented PE.

To obtain oriented samples, the initial cylinders were stretched at room temperature to a draw ratio of 5.5 with a stretching velocity of $\sim$40% per min (with respect to the initial length). Oriented samples were "dogbone"-shaped and had the test section 5.7 mm in diameter. These samples were used for longitudinal tension tests. For longitudinal compression tests, 15-mm–long cylindrical samples of oriented PE were prepared, and transverse compression was studied on bars $\sim 4 \times 4 \times 15$ mm in size, which were put in stacks to reduce heat exchange through contact surfaces (each stack consisted of 3 samples). Temperature was measured at the middle bar.

Procedure of Measurements

To measure temperature effects, a manganin-constantan thermocouple made of a 40-µm-diameter wire was used. One of the junctions of the thermocouple was brought into contact with the sample surface; the other junction was placed into the elements of the loading device (clamps in tension tests and pistons of the press in compression tests). The samples were surrounded with an insulating layer to provide adiabatic conditions of deformation. The sample temperature was measured with an accuracy of 0.01 K. Room temperature was basic.

To load samples and record stress-strain curves (for tension and compression), a UTS 10 machine (Germany) for mechanical tests was employed.

Experiments were carried out in the region of nearly fully reversible deformations (extension of 8–10%, contraction of 2–4%).

The LTECs in the longitudinal and transverse directions were measured while heating unloaded samples from 20°C to 30°C. A vertical IZV-1 extensometer with a scale factor of 1 micron having a heat camera was used. In this narrow temperature range, changes in sizes of oriented samples were reversible (i.e., no noticeable shrinkage and relaxation of orientation of the samples were observed).

RESULTS AND DISCUSSION

Figure 1 shows variations in sample temperature ΔT versus applied stress σ (positive in tension tests and negative in compression).

It is evident that loading along the orientation axis (Figure 1a) causes sample heating in tension and cooling in compression. This temperature variation, which is opposite in sign to the ordinary "solid-state" thermoelastic effect, is a characteristic feature of oriented polymers [4].

When a sample is compressed in the direction perpendicular to the orientation axis, sample heating takes place (Figure 1b, curve 1). For illustrative purposes, Figure 1b repeats the curve for sample cooling in longitudinal compression tests (Figure 1b, curve 2). Therefore, Figure 1b demonstrates anisotropy of the sign of the thermoelastic effect in oriented polymers.

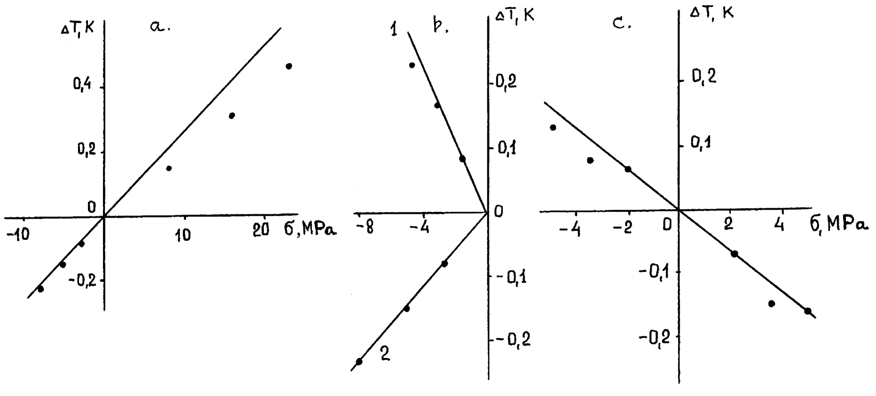

FIGURE 1 Changes in temperature during loading for PE. Points show measured values and lines represent calculations through Eq. (1); a – oriented PE, longitudinal tension and compression; b – oriented PE: transverse compression (curve 1) and longitudinal compression (curve 2); c – nonoriented PE.

For comparison, Figure 1c shows the $\Delta T(\sigma)$ dependence for nonoriented PE. It can be seen that, in this case, the thermoelastric effect of the ordinary "solid-state" sign is observed both in tension and compression.

In all cases the temperature effects are reversible. When the sample is unloaded, the temperature is restored to an almost initial level.

Figure 2 presents relevant stress-strain curves (for tension and compression). The curves demonstrate the range of sample deformations (several percent). Deformations are also nearly reversible.

Figure 3 presents thermal deformations of free (unloaded) samples ε_T as a function of temperature. It can be seen that, as the temperature increases, the oriented sample contracts in the longitudinal direction and expands in the transverse direction, while the nonoriented sample expands. Temperature deformations are also reversible. The LTEC was found from the slopes of the curves given in Figure 3.

The moduli of elasticity ($E = \Delta\sigma/\Delta\varepsilon$) and LTEC ($\alpha = \Delta\varepsilon/\Delta T$) derived from the data of Figures 2 and 3 are summarized in Table 1. In addition to the characteristics of oriented PE, Table 1 gives for

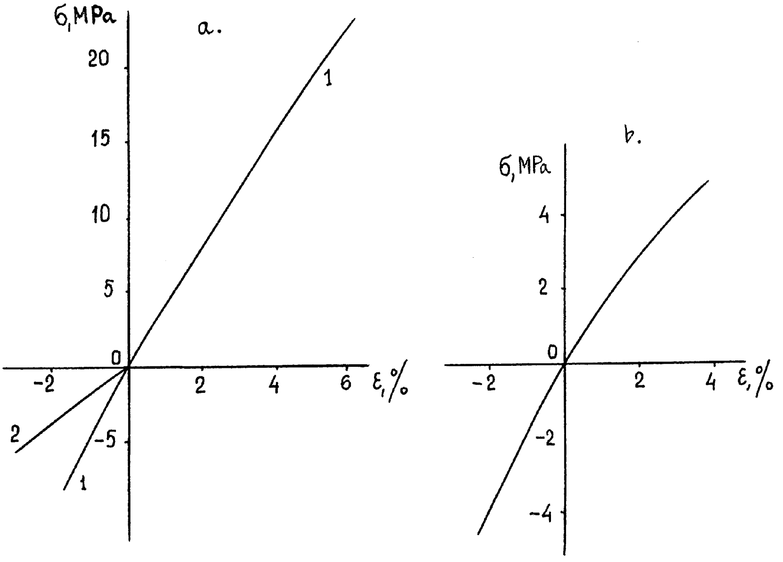

FIGURE 2 Stress-strain curves (for tension and compression) for PE samples. T = 291 K: a – oriented PE, loading in the longitudinal direction (tension and compression) (curve 1) and transverse compression (curve 2); b – nonoriented PE.

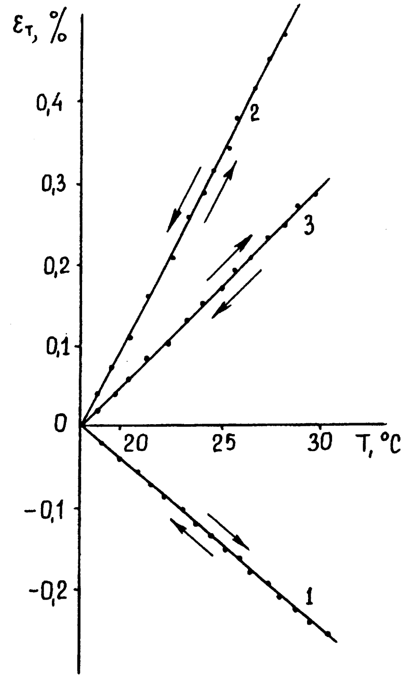

FIGURE 3 Temperature dependence of PE sample sizes. Curve 1 describes longitudinal contraction of oriented PE; curve 2 shows transverse expansion of for oriented PE; and curve 3 is for nonoriented PE.

comparison the data for the PE crystals obtained from X-ray diffraction measurements [6,7].

Note that a crystalline cell of PE exhibits a strong azimuthal anisotropy. For instance, for the equatorial directions 200, 020, and 110 the values of LTEC are $3.5{\cdot}10^{-4}$, $0.7{\cdot}10^{-4}$, and $1.9{\cdot}10^{-4}$ K^{-1}, respectively. For this reason Table 1 gives average values of $\alpha_{\perp}$ for a PE cell.

TABLE 1 Moduli of Elasticity and Thermal Expansion Coefficients of Polyethylene Samples at Room Temperature

	E_1GPa		α, K^{-4}	
Type of PE sample	$E_{\|\|}$	$E_{\perp}$	$\alpha_{\|\|}$	$\alpha_{\perp}$
Crystal [6,7]	~200	~4	$-0.12{\cdot}10^{-4}$	$2.0{\cdot}10^{-4}$
Oriented	0.42	0.19	$-2.1{\cdot}10^{-4}$	$4.8{\cdot}10^{-4}$
Nonoriented	0.18		$2.5{\cdot}10^{-4}$	

Comparison of the moduli of elasticity of oriented PE and crystal reveals the well–known fact that sample deformation is determined almost entirely by deformation of amorphous interlayers, both interfibrillar and intrafibrillar (intercrystallite). Crystallites, which occupy about 60% of the sample volume, are of minor importance for deformation. The same conclusion is valid for nonoriented PE.

Comparison of the LTECs of the oriented sample and crystal points to a significant role of amorphous regoins in thermal expansion of polymers as well. Thus, the thermoelastic effect measured in this work is exhibited by heterogeneous systems with a strong anisotropy, both with overall anisotropy (oriented PE) and anisotropy of volume elements.

Let us analyze the thermoelasticity of PE. The values of LTECs given in Table 1 allow one to see whether the measured $\Delta T(\sigma)$ dependences are consistent with Kelvin formula (1). The measured specific heat capacity of our PE samples was 2.3 MJ $\mathrm{m}^{-3}\mathrm{K}^{-1}$. The $\Delta T(\sigma)$ dependences calculated from Eq. (1) are shown by solid lines in Figure 1a, b, and c. It can be seen that in all the cases experimental and calculated $\Delta T(\sigma)$ dependences are in satisfactory agreement. Thus, the description of thermoelasticity of PE from thermodynamic point of view can be thought to be exhaustive.

However, along with the thermodynamic aspect, there are microscopic aspects or, in other words, the problem of mechanism of thermoelasticity of PE. Of particular interest from this point of view is the cooling of an oriented sample in longitudinal compression and, correspondingly, heating in longitudinal tension.

The thermodynamic reason for such a behavior is a negative LTEC of oriented PE in the longitudinal direction $\alpha_{||}$ (Table 1). Let us discuss the microscopic origin of this phenomenon.

A negative LTEC in the longitudinal direction is a characteristic feature of an oriented system consisting of chain molecules [4]. The most perfect oriented system is a ploymer crystal. Specific features of vibrational dynamics and thermal expansion of a ploymer crystal are determined by a sharp anisotropy of its elastic properties [8,9]. Transverse vibrations of PE molecules (torsional and bending) have characteristic temperatures in the region 200–400 K [4]. Therefore, in the vicinity of room temperature these vibrations are rather strongly excited. Transverse vibrations, by themselves, are anharmonic [9], but transverse thermal expansion of the crystal results from anharmonicity of the intermolecular interaction potential. Longitudinal vibrations in PE molecules have a high characteristic temperature ($\sim$1000 K) [4] because of a high longitudinal rigidity of molecules. Therefore, in the vicinity of room temperature these vibrations are nearly absent (unexcited). So transverse vibrations of the "unstretchable" chain cause reduction in the axial length of molecules, which results in a negative longitudinal LTEC $\alpha_{||}$ [4,9]. Thus, the longitudinal thermal contraction of a crystal is not attributable to anharmonicity of interparticle interaction. This is the geometrical consequence of transverse vibrations (no matter whether they are harmonic or anharmonic). Note once more that a negative longitudinal LTEC of the PE crystal is a result of a strong anisotropy of elastic properties of the crystal [9].

As can be seen from Table 1, anisotropy of the LTEC for the oriented PE sample has features similar to that of the crystal: negative $\alpha_{||}$ and positive $\alpha_{\perp}$ are observed. However, absolute values $\alpha_{||}$ and $\alpha_{\perp}$ and the $\alpha_{||}/\alpha_{\perp}$ ratio are considerably higher than in the crystal. It is quite obvious that these differences are due to the presence of amorphous regions in oriented PE (as noted above). Chain molecules in amorphous regions of PE are, no doubt, oriented, though not to such a high degree and not with such regular ordering in the azimuthal direction as in crystals. Since amorphous regions occupy only a fraction of the sample bulk (about 40%), the value of LTEC of amorphous regions is naturally higher than the LTECs of the whole sample.

It seems unlikely that high LTECs of the samples can be explained only by the usual vibrational dynamics of chains molecules, as in crystals. This would require the assumption of unrealistically large amplitudes of transverse vibrations or a drastic increase in anharmonicity of intermolecular interaction, which also looks doubtful. Let us recall that the studies described in the paper were carried out in the vicinity of room temperature where amorphous regions of PE are in the unglassy state characterized by a sufficiently intense conformational dynamics. In this case the evident reason for, say, longitudinal contraction of oriented regions during sample heating is conformational (isomeric) trans-gauche-transistions in PE molecules [10,4].

Let us derive an approximate expression for longitudinal LTEC of the oriented amorphous region of PE using the statistics of isomers. Since rotational isomers in PE are anisoenergetic (the difference between energies of gauche- and trans-isomers ΔU is 2.1 kJ/mol, which corresponds to $3.5 \cdot 10^{-21}$ J per confromation [4]), increasing temperature will give rise to a decrease in the equilibrium concentration of trans-isomers (and an increase in that of gauche-isomers) and a reduction in the axial molecular length.

Let us introduce the value Δl – the difference between axial lengths of trans- and gauche-isomers. The longitudinal LTEC of an oriented amorphous polymer can be defined as

$$\alpha_{\|}^{am} \approx \Delta l \cdot \frac{dN_{tr}}{dT} \cdot n_s^{-1} \tag{2}$$

where N_{tr} is the number of trans-isomers per unit volume, and n_s is the number of molecules passing through a unit cross section of a sample ($n_s \approx S_M{}^{-1}$, where S_M is the cross sectional area of a chain molecule).

The equilibrium concentration of trans-isomers at temperature T is given by [10]

$$N_{tr}(T) = N \cdot [1 + \exp(-\frac{\Delta U}{kT})]^{-1}$$

where N is the total concentration of isomers.

This expression refers to a free polymer molecule. The oriented state of amorphous regions in PE is preserved owing to a rigid oriented "framework" formed by crystallites. It is obvious that this changes the conditions of equilibrium of chain molecules in amorphous regions. However, since we perform differential treatment, i.e., we consider changes in concentrations of isomers with varying temperature and external stress rather than absolute values of these concentrations, the use of this formula for approximate estimates in justified.

Then it follows from Eq. (2) that

$$\alpha_{\|}^{am} \approx -N \cdot \Delta l \cdot n_s^{-1} \cdot \frac{\Delta U}{kT^2} \cdot \exp(-\frac{\Delta U}{kT}) \cdot [1 + \exp(-\frac{\Delta U}{kT})]^{-2} \tag{3}$$

Thus we have obtained the expression for the longitudinal LTEC of an oriented amorphous polymer by using the statistics of isomeric transitions. Anharmonicity of interparticle interaction does not participate in longitudinal thermal contraction (expansion) here. Below we shall check whether Eq. (3) and measured $\alpha_{\|}$ are quantitatively consistent.

Let us consider now longitudinal elastic deformation of an oriented amorphous polymer by using statistics of isomeric transistions. The field of external force acting along a chain molecule axis changes the difference between energies of trans- and gauche-isomers. For trans-gauche transistions (in compression tests) or gauche-trans transitions (in tension tests) when the isomer axial length changes by Δl, the energy variation under applied stress σ will be

$$\Delta A \approx \sigma \cdot S_M \cdot \Delta l \approx \sigma \cdot n_s^{-1} \cdot \Delta l$$

Then the equilibrium concentration of trans-isomers in a loaded polymer will be given by

$$N_{tr}(T,\sigma) \approx N \cdot [1 + \exp(-\frac{\Delta U + \sigma \cdot n_s^{-1} \cdot \Delta l}{kT})]^{-1}$$

For relatively low σ (similar to those used in this study) the relations

$$\Delta A \ll \Delta U \quad \text{and} \quad \Delta A \ll kT$$

hold.

Then a change in the concentration of trans-isomers under applied stress σ will be given by

$$\begin{aligned} \Delta N_{tr}(T,\sigma) &= N_{tr}(T,\sigma) - N_{tr}(T,0) \\ &\approx N \cdot \frac{\sigma \cdot n_s^{-1} \cdot \Delta l}{kT} \cdot \exp(-\frac{\Delta U}{kT}) \cdot [1 + \exp(-\frac{\Delta U}{kT})]^{-2} \end{aligned} \tag{4}$$

Variation in specific (per unit volume) thermal energy of a given amorphous body resulting from changes in potential energy at aniso-energetic isomeric transitions will then be

$$\Delta Q^{am}(\sigma) = \Delta U \cdot \Delta N_{tr}(T,\sigma) \tag{5}$$

By combining Eqs. (4) and (3), we get from Eq. (5)

$$\Delta Q^{am}(\sigma) \approx -\alpha_{\parallel}^{am} \cdot \sigma \cdot T \tag{6}$$

In oriented PE, the volume of amorphous regions V^{am} constitutes only a fraction of the volume of the solid $V : V^{am} \approx V \cdot (1 - q)$, where q is the degree of crystallinity.

Crystallites play a small role in deformation of the entire PE sample and, hence, in thermoelasticity because of a high longitudinal rigidity of their lattice. Therefore variation in thermal energy per unit volume of oriented PE is $\Delta Q(\sigma) = \Delta Q^{am}(\sigma) \cdot (1 - q)$.

Note that since we perform a rough estimate here and taking into account a relatively low degree of orientation of PE samples used in the experiments (the draw ratio was as small as $\sim 450\%$), we do not separate amorphous regions into intra-and interfibrillar ones and also do not separate the crystallinity degree into volume and linear. Therefore we assume that the longitudinal LTEC of PE samples is $\alpha_{\|} \approx \alpha_{\|}^{am}(1 - q)$. Then we obtain from Eq. (6) for oriented PE

$$\Delta Q(\sigma) = C\Delta T(\sigma) \approx -\alpha_{\|} \cdot \sigma \cdot T \tag{7}$$

Thus by considering only the conformational statistics for thermal and force behavior of oriented chain molecules (above the glass transition temperature of the polymer when isomeric transitions are possible) we obtained the general thermodynamic Kelvin formula (1).

The agreement between experimental data obtained in our experiments and Kelvin formula (Figure 1a,b,c) suggests that anisoenergetic isomeric transitions play a decisive role in the mechanism of thermoelasticity of oriented PE and explains in a most simple and clear fashion why samples are cooled in longitudinal compression and heated in tension.

An important confirmation of this conclusion is also the fact that the thermal energy released during longitudinal tension $\Delta Q = C\Delta T(\sigma)$ considerably exceeds the mechanical work done during tension $\Delta W(\sigma) = \int_0^{\sigma} \varepsilon d\sigma$ calculated from the stressstrain curve (Figure 4). This leads to the conclusion that such factors as entropy effects and internal friction do not significantly affect thermoelasticity of oriented PE, though no doubt they play a role.

We now give some quantitative estimate of the conformational mechanism of thermal expansion of oriented PE.

Eq. (3) allows one to estimate the longitudinal LTEC of oriented PE and to compare it with the measured value. By taking $N \cong 4 \cdot 10^{28}\,\mathrm{m}^{-3}$ (the number of CH_2 groups in unit volume of amorphous PE); $n_s \cong 4 \cdot 10^{28}\,\mathrm{m}^{-2}$; $\Delta l \cong 10^{-10}\,\mathrm{m}$; $T = 300\,\mathrm{K}$, and $q \cong 0.6$, we obtain

$$\alpha_{\|} \approx \alpha_{\|}^{am} \cdot (1 - q) \approx -2.3 \cdot 10^{-4}\,\mathrm{K}^{-1}.$$

As can be seen, the calculated $\alpha_{\|}$ is close to the measured value (Table 1). This result should not be regarded as trivial, even after we have ascertained that Kelvin formula holds because to calculate $\alpha_{\|}$ we

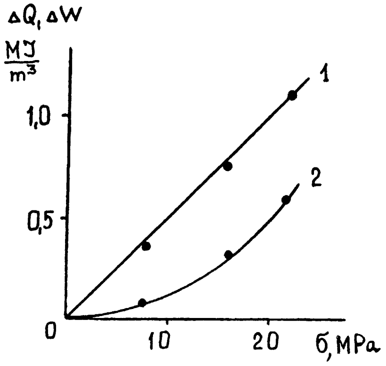

FIGURE 4 Comparison of heat release and mechanical work spent in longitudinal tension of oriented PE. Curve 1 represents specific thermal energy calculated from Figure 1a; curve 2 shows specific mechanical work calculated from Figure 2b.

used the values of N, n_s, Δl, and ΔU, which were not invoked for our quantitative calculations of thermoelasticity above. Therefore the consistency of the calculated (through Eq. (3)) and measured $\alpha_{\|}$ is an independent proof of the correctness of the conformational approach.

Without going into detail, we note that the results obtained in conformational treatment of thermal expansion in the longitudinal direction make it possible to analyze thermal and mechanical behavior of polymers in the transverse direction. These results also allow a quantitative explanation of LTEC and thermoelastic characteristics of nonoriented PE.

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