Elastic strain energy behavior in the polymer nanocrystals

Alexander I. Slutsker[a], Yuri I. Polikarpov[b,*], Dmitry D. Karov[b]

[a] Ioffe Physical Technical Institute of RAS, 26 Politekhnicheskaya St., St. Petersburg 194021, Russian Federation
[b] Peter the Great St. Petersburg Polytechnic University, 29 Politekhnicheskaya St., St. Petersburg 195251, Russian Federation

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Abstract

In the paper, the changes in axial and contour lengths of skeletal interatomic bonds in the chain molecules of polyethylene nanocrystals have been measured using X-ray diffractometry and Raman spectrometry. In the course of the measurements the samples were subjected to stretching and heating (mechanical and thermal actions). The measured force and temperature dependences were analyzed and the calculated description of the polymer nanocrystal strain was inferred from them. In so doing the original results were obtained for the thermal action. The potential energy components related to both the skeletal bond stretching and the chain molecule bending were determined for the strained polymer crystal. The sharp distinction between the ratios of these components for the object under mechanical and thermal actions was found.

1. Introduction

The polymer crystals are formed from the stretched parts of chain molecules stacked parallel along the direction of the orienting force [1]. The linear size of these parts ranges from 20 to 100 nm [2], so, these crystalline objects are nanocrystals. Their distinctive feature is the sharp anisotropy of mechanical and thermal properties in the longitudinal (along the axes of stretched molecules) and in the transversal (orthogonal to the molecular axes) directions. E.g., the rigidity of crystalline lattice and the characteristic temperatures of vibrations are substantially higher in longitudinal direction than in transversal one [3]. This fact determines certain features of the deformation response of the polymer crystals to mechanical and thermal effects. Moreover, the chain structure of macromolecules leads to specific types of stiffness of polymeric material: the stretching hardness (an increase in contour length of molecules) and flexural rigidity (the "curvature" change of segments of chain molecules, leading to a change in its axial length). However, despite the large number of studies [1] considering the description of the polymer nanocrystal deformation response to the mechanical (stretching) and thermal (heating) effects, a number of issues need further clarification. In particular, the behavior details of skeletal interatomic bonds of macromolecular segments forming nanocrystals when subjected to the actions mentioned remain

* Corresponding author.
E-mail addresses: Alexander.Slutsker@mail.ioffe.ru
(A.I. Slutsker), yuryi.polikarpov@yandex.ru (Y.I. Polikarpov),
dmkarov@yandex.ru (D.D. Karov).

unclear. To obtain the necessary information it is advisable to use such methods to study molecular dynamics as diffraction (X-ray, electron, neutron) and Raman spectroscopy. The latter is known to be sensitive to the influence of various effects on the skeletons of polymeric molecules [4,5]. The combination of Raman and X-ray methods of investigation leads to a clarification at the molecular level of the mechanics and energetics of polymer nanocrystals subjected to these conditions.

2. Objects and methods of study

The studies have been carried out for oriented samples of crystallizing polymers – polyethylene (PE), polypropylene (PP), polycaproamide (nylon 6). This paper presents the results obtained for PE only, as for the other two polymers they were the same.

The PE samples were acted upon two types of effects:

  (1) tensile stress along the orientation axis at $T = 90$ K;
  (2) heating of unloaded samples from $T = 90$ K to $T = 300-350$ K.

The choice of the temperature value of 90 K was due to the fact that the thermal molecular dynamics of PE nanocrystals remains virtually unexcited at this temperature. It is also unexcited at lower temperatures but more complicated equipment is then required for measurements.

The angular shift of (002) reflection patterns to smaller angles was recorded upon elastic tensile stress at $T = 90$ K by X-ray diffractometry. The increase of the distance between the skeletal carbon atoms along the molecular axis in PE was determined using the values of measured angular shift [6]. The low-frequency shift $\Delta \nu$ of the band $\nu = 1130$ cm^{-1} $\approx 3.4 \cdot 10^{13}$ Hz responsible for the valence vibrations of (C–C)-bonds in PE was recorded by Raman spectroscopy. It is important to note that the variation of the vibration frequency is caused only by the change in the contour length of skeletal bonds, while the variation of the valence angle does not affect the results. Hence, the relative change of the vibration frequency $\varepsilon_\nu = \Delta \nu / \nu$ in PE with tensile stress reflects the relative change of the (C–C)-bonds contour length $\varepsilon_C = \Delta l_C / l_C$ under stress. Since the relation between these changes has the form

$$\varepsilon_C \approx -0.3\varepsilon_\nu, \qquad (1)$$
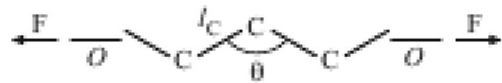

Fig. 1. A scheme of a stretched PE molecule. O–O is the molecule axis; l_C is the C–C-bond contour length; F are stretching forces.

according to [8], the measured linear dependence of frequency relative decrease ε_ν on tensile stress σ in the range from 0.4 to 1.8 GPa (coefficient is $\sim 5 \cdot 10^{-3}$ (GPa)$^{-1}$) shows the contour stretching of C–C-bonds under stress with the same proportionality factor.

3. Experimental results and discussion

It is known [7] that the carbon skeleton of a straightened PE molecule has a form of a plane zigzag (Fig. 1). Here the O–O line is the molecular axis; $l_C = 0.154$ nm is the C–C-bond contour length; $\theta = 109°$ is the valence angle between C–C-bonds. The projection of a (C–C)-bond onto a molecule axis (the axial length of a (C–C)-bond) is

$$l_{ax} = l_C \sin \theta / 2$$

at $T = 90$ K $l_{ax} = 0.127$ nm.

So, both axial and contour lengths of molecules in PE crystals increase upon longitudinal elastic tensile stress.

When heated, the axial length of C–C-bond decreases with temperature as it was found from the temperature dependence of (002) pattern shift measured by the X-ray diffractometry. The axial length relative change is described by

$$\varepsilon_\Sigma = \Delta l_\Sigma / l_\Sigma$$

Where l_Σ and Δl_Σ are the C–C-bond length and its change respectively.

The use of new symbols is due to the change of the molecule axial tilt under heating, and this change causes the change of the C–C-bond projection onto the PE orientation axis. We emphasize that at $T = 90$ K the equation

$$l_\Sigma = l_{ax} = l_c \sin \theta / 2$$

is true.

By means of Raman spectrometry using Eq. (1), the contour length of a C–C-bond was found to increase under heating.

So, when heated, the changes of axial and contour lengths of PE molecules in crystals have the opposite signs in contrast to the changes under tensile stress.

The experimental data obtained on the deformation (the changes of axial and contour lengths) of the chain