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High-Temperature Quasi-Hexagonal Phase
in the Simplest Model of a Polymer Crystal

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Polymorphism and structural phase transitions in polymer crystals have been extensively studied for many years. However, even in polyethylene (PE), a model polymer, the molecular mechanisms of structural transitions are still unclear. Several types of crystallites, including orthorhombic and quasi-hexagonal (packing of round cylinders), have been found in PE. The transition of the orthorhombic phase to the quasi-hexagonal one occurs upon heating at high pressure [1] or when geometric constraints are imposed on the sample [2]. The structure of this phase has not been determined thus far. Most popular is the model of a conformationally disordered (condis) crystal [3] in which chains are, on average, parallel but the fraction of *gauche* conformations in them is very large. A model was also proposed in which long sequences of *trans* conformations are separated by short sequences composed of a few *gauche* conformations and flat chain segments can rotate as a whole like chains in paraffins [4]. Another model [5] implies that the orthorhombic cell locally (within short segments of several neighboring chains) persists in the crystal, which is a mosaic of differently oriented pieces of the orthorhombic structure. All these models predict the existence of a hexagonal lattice in the crystal.

This work deals with the transition to the high-temperature quasi-hexagonal phase in the simplest molecular dynamic model of a polymer crystal, PE composed of united atoms (CH$_2$ groups are modeled by atoms with the mass $m = 14$ amu) [6]. A three-dimensional crystal was assembled from parallel infinite macromolecules having an all-*trans* conformation. The calculated cell was a rectangular parallelepiped that accommodated 30 molecules containing 800 atoms. Periodic boundary conditions were imposed in all three directions, which excludes all boundary effects. In such a model, the low-temperature phase has a monoclinic

crystallographic cell (Fig. 1) [7]. To study the orientational order in the chain, let us introduce the local setting angle α for each atom. For each bond angle formed by three neighboring atoms in the chain, a bisector vector is constructed, which is multiplied by $(-1)^n$ (n is the number of an atom in the chain). In the ideal *trans*-zigzag conformation, all constructed vectors point in the same direction. The angle α is the angle between the a axis and the projection of this vector onto the cross-section plane of a sample.

It is reasonable to begin the study of the mechanism of thermally induced orientational disordering in a polymer crystal consisting of flexible chains with this simplest model. In this model, we may expect a pure structural transition to the quasi-hexagonal phase in the premelting region.
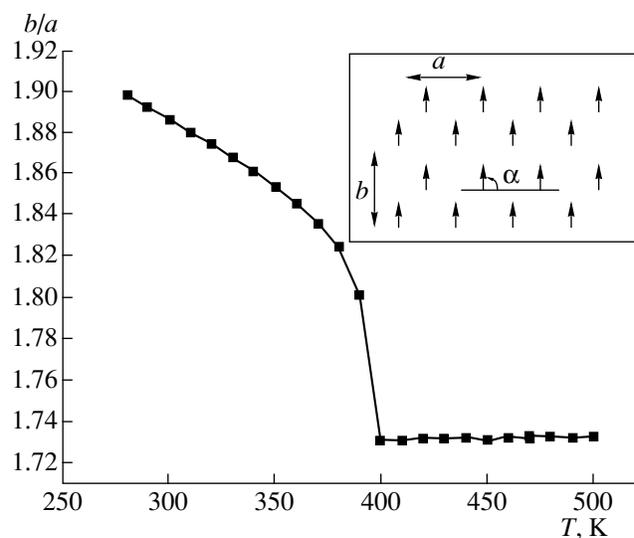

Fig. 1. Temperature dependence of the b/a ratio. The inset shows the cross-section plane at zero temperature. The arrows show the direction from the nearest atom of the chain under the plane to the nearest atom above the plane.
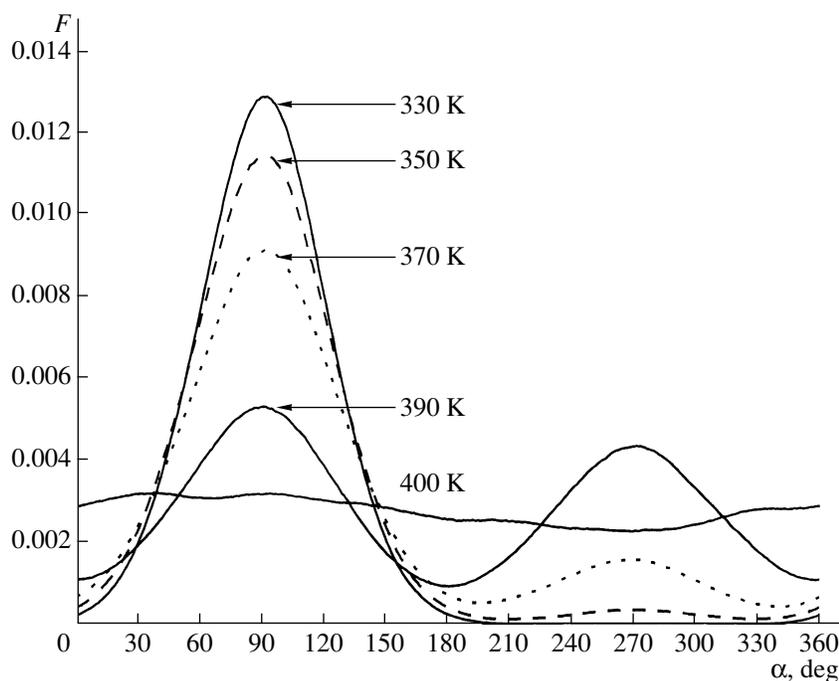
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Fig. 2. Local setting angle α distribution function F (see Fig. 1) at different temperatures.

The numerical parameters of the model were chosen in the following way. The energy of the covalent bond between neighboring atoms was taken to be

$$U_b(l) = k_b(l - l_0)^2,$$

where l is the distance between these atoms, $l_0 = 1.53$ Å, and $k_b = 250$ kcal mol^{-1} Å^{-2}.

The bond angle distortion energy was taken to be $U_\theta(\theta) = k_\theta(\theta - \theta_0)^2$, where $\theta_0 = 1.972$ rad (113°) and $k_\theta = 40$ kcal mol^{-1} rad^{-2}. The torsion angle energy was taken to be $U_\tau(\varphi) = [1.99 + 1.60\cos(3\varphi) + 0.39\cos(\varphi)]$ kcal mol^{-1}. The interaction of atoms separated by more than two neighbors or belonging to different chains was described by the cutoff Lennard-Jones potential

$$U_{nb}(r) = \begin{cases} U_{LJ}(r) - U_{LJ}(R_{cut}), & r < R_{cut} \\ 0, & r \geq R_{cut}, \end{cases}$$

where $U_{LJ}(r) = \varepsilon\left[\left(\dfrac{r_{min}}{r}\right)^{12} - 2\left(\dfrac{r_{min}}{r}\right)^{6}\right]$, r is the distance between atoms, $\varepsilon = 0.12$ kcal mol^{-1}, $r_{min} = 4.2654$ Å, and $R_{cut} = 10.5$ Å. The equations of motion were integrated using the velocity Verlet algorithm [8] with the step $\Delta t = 1$ fs. To maintain the temperature, a collisional thermostat [9, 10] was used with the parameters $m_0 = 1$ amu and $\lambda = 5.5$ ps^{-1}, and a Berendsen barostat was used for maintaining pressure [11]. Measurements were carried out after the system had been relaxed for at least 1 ns, when the size of the calculated cell

achieved equilibrium. The crystallographic unit cell parameters at 280 K were $a = 8.00$ Å, $b = 4.22$ Å, and $c = 2.50$ Å.

At $T = 400$ K, the crystal undergoes a first-order phase transition (0.47% density jump). In the temperature range 380–400 K, the $\dfrac{b}{a}$ ratio decreases (see Fig. 1) to 1.73, which is typical of the quasi-hexagonal packing. This is accompanied by a complete loss of the regular arrangement of atoms along chains and of the peak of the local setting angle α distribution density (Fig. 2). On the other hand, the order in the arrangement of projections of the centers of mass of the chains onto the cross-section plane persists and the axes of molecules remain parallel. Thus, in our model, a transition to the quasi-hexagonal phase is observed. However, the structure of this phase turned out to be rather unexpected.

First of all, *gauche* conformations in molecules are virtually absent at all temperatures up to 510 K. It is evident that the periodic boundary conditions prevent the conformational chain disorder. Whereas the α angles of the atoms of all molecules in the monoclinic phase are close to the average setting angle, the molecules in the quasi-hexagonal phase are chains with smooth (wide) torsions and form "effective cylinders" without conformational defects (Fig. 3). As far as we know, such a structure of chains in the quasi-hexagonal phase of polymers has never been suggested as a possible one.

The dynamics of the transition to this phase is also rather unexpected. At $T = 350$ K, there appear chain segments rotated through 180° with respect to the other
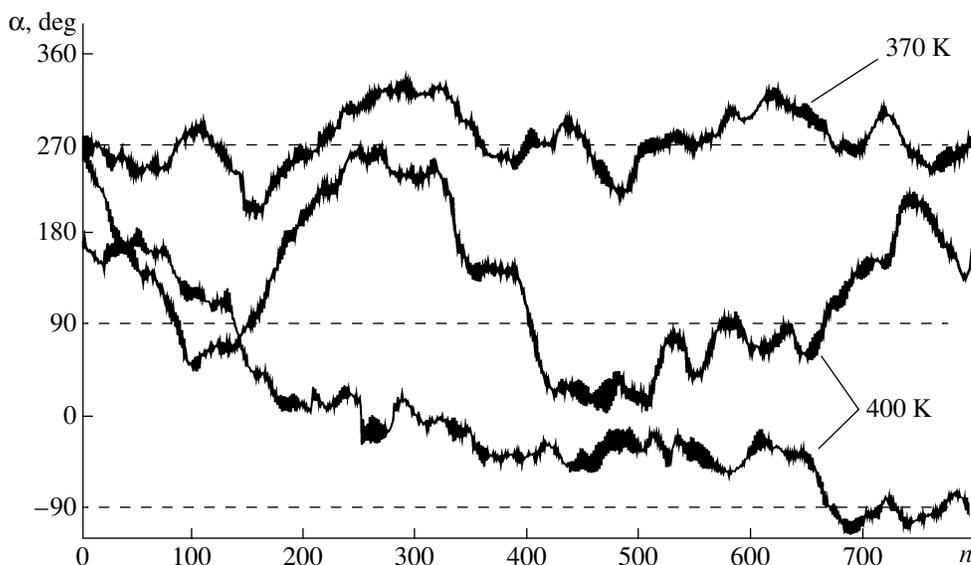
Fig. 3. Comparison of characteristic conformations of molecules in the monoclinic (at 370 K) and quasi-hexagonal (immediately after the transition at 400 K) phases of a polymer crystal. The local setting angle α (see Fig. 1) of an atom as a function of its number along the chain is shown for three different molecules for which the atomic coordinates were averaged over a 1-ps interval.
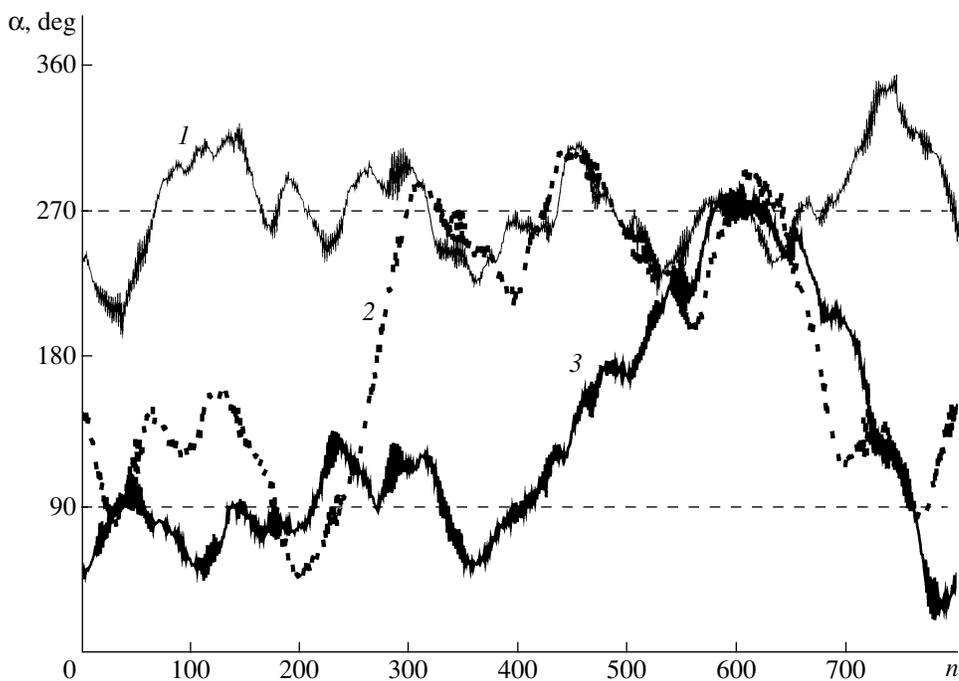

Fig. 4. Characteristic conformations of molecules before the transition (390 K). The α angles along three different molecules are shown. The α angle was calculated for the atomic coordinates averaged over a 1-ps interval; 70% of molecules (24 of 30 molecules in the sample) are in the type *1* state, 13% of molecules (4 molecules) are in the type *2* state, and 7% of molecules (2 molecules) are in the type *3* state.

segments (Fig. 2). The number of such segments increases with temperature. Near the transition point ($T = 390$ K), a noticeable fraction of local setting angles of atoms falls between the initial and new peaks of virtually the same height. This means that, before transi-

tion, molecules have regions of rotations through 180°, although the orientation of their planes is, on average, retained. Localized soliton-like twist defects (twistons) have been known for a relatively long time. To retain crystallographic order outside the defect region in the

PE crystal, rotation through 180° should be accompanied by local tension or compression by half the chain period (see, e.g., [12]). For the topological charge in an infinite chain to persist, twistons can appear only in pairs: twist-tension plus twist-compression defects. Such pairs appear on chains long before the transition but rapidly annihilate. Twistons appear more often with an increase in temperature; therefore, some twiston pairs annihilate after they have traveled the full length of the chain and thereby shift it by a half period and rotate it by 180°; as a result, the plot of local setting angles shows a new peak near 270°. Strictly speaking, the peak near 270° arises from the atoms of molecules rotated by such twiston pairs an odd number of times, whereas the peak at 90° is due to the atoms of chains rotated an even number of times. These atoms are from the chain segments that retain the orientation order of the initial monoclinic unit cell. The atoms for which the local setting angles are between these peaks are located in the region of twistons or torsions and disturb the crystallographic order.

Figure 4 shows characteristic conformations of chains before transition. The main state of molecules corresponds to vibrations of their atoms near equilibrium positions. In addition, there is some number of twiston pairs (for example, in molecule *2*, in the region of 250–300 and 650–700 atoms). On the other hand, the sample contains molecules in states close to the quasi-hexagonal phase. Indeed, molecule *3* (Fig. 4) shows two wide chain torsions that rotate it first through 180° and then back. These torsions have a considerably larger width (more than 200 atoms) than twistons (no more than 50 atoms) and an irregular shape. It is likely that they formed as a result of "spreading" of twistons in the region of local weakening of the substrate potential. The defect chain segment stimulates spreading of emerging twistons on neighboring chains and can serve as a nucleus of a new quasi-hexagonal phase. Simulation using the explicit atom model, which takes into account chain ends, will show whether a real PE crystal can contain the phase obtained by us in a model crystal composed of united atoms.

ACKNOWLEDGMENTS

REFERENCES

1. Langen, M. and Prins, K.O., *Chem. Phys. Lett.*, 1999, vol. 299, pp. 195–200.
2. Pennings, A.J. and Zwijnenburg, A., *J. Pol. Sci.: Pol. Phys. Ed.*, 1979, vol. 17, pp. 1011–1032.
3. Noid, D.W., Sumpter, B.G., and Wunderlich, B., *Macromolecules*, 1990, vol. 23, no. 2, pp. 664–669.
4. Kuwabara, K. and Horii, F., *Macromolecules*, 1999, vol. 32, pp. 5600–5605.
5. Auriemma, F., Rosa, C.De., and Corradini, P., *Adv. Polym. Sci.*, 2005, vol. 181, pp. 1–74.
6. Balabaev, N.K., Gendel'man, O.V., Mazo, M.A., and Manevich, L.I., *Zh. Fiz. Khim.*, 1995, vol. 69, no. 1, pp. 26–29.
7. Zubova, E.A., Balabaev, N.K., and Manevich, L.I., *Zh. Éksp. Teor. Fiz.*, 1999, vol. 115, pp. 1063–1069.
8. Allen, M.P. and Tildesley, D.J., *Computer Simulation of Liquids*, Oxford: Clarendon, 1987.
9. Lemak, A.S. and Balabaev, N.K., *Mol. Simul.*, 1995, vol. 15, no. 4, pp. 223–231.
10. Lemak, A.S. and Balabaev, N.K., *J. Comput. Chem.*, 1996, vol. 17, no. 15, pp. 1685–1695.
11. Berendsen, H.J.C., Postma, J.P.M., Gunsteren, W.F., DiNola, A, and Haak, J.R., *J. Chem. Phys.*, 1984, vol. 81, pp. 3684–3690.
12. Zubova, E.A., Balabaev, N.K., Manevich, L., and Tsygurov, A.A., *Zh. Éksp. Teor. Fiz.*, 2000, vol. 118, no. 3(9), pp. 592–601.