Computer modeling of shear strain in the polymer brushes

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We conducted the modeling of a shear strain in a thin polymer layer (~15 nm) bonded adhesively to a rigid substrate. The discrete-continuous model of a system of chains with given stiffness and polar groups was developed. The polymer chain was considered within Hurst-Harris model. The polar groups were implemented on the base of the tetragonal lattice model. We suppose that a chain with the given stiffness does not extend beyond the limits of a cylindrical region. Its sizes are determined from the condition of a minimum of Helmholtz free energy F. The average elongation of the macromolecule and its entropy depend on the chain bending stiffness and the radius of the tube. The average elongation was computed by random walk method [1]. It was assumed that the potential of polar groups have the main contribution to the energy of interchain interactions (and this energy was calculated using the Metropolis algorithm). The potential of interactions between the nearest polar groups of chains consists of the energy of dipole-dipole (Keesom) interactions and the Lennard-Jones potential. We consider that possible orientations of the polar groups are determined by the average elongation of the chain. The results of modeling showed that the dependence of the free energy on the interchain distance has two minima. The first minimum is characterized by the orientational ordering of the polar groups, the second one by their disordered state. The depth and positions of the minima depend on the temperature, the bending stiffness of chain, the modulus of the dipole moment of the polar groups and the well depth in the Lennard-Jones potential.

Further, the step-by-step modeling of the shear strain in the polymer layer which initially has an orientationally disordered state was conducted. The dependences of the deforming force f on the shear angle γ were obtained. The tangential force was determined as the derivative of the free energy with respect to the shear angle: $f \sim (\partial F/\partial \gamma)_{T,V}$. The $f(\gamma)$ dependences can be divided into three stages of the sample deformation. The first stage is a reversible elastic deformation, obeying Hooke's law and determined by the entropy component of the deforming force. The second stage is a high-strained elastic deformation, characterized by the mutual movement of the segments of macromolecules and the orientation of the polymer molecules along the selected direction. The third stage is the deformation associated with the distortion of valence angles and interatomic distances. The dependences $f(\gamma)$ for polymer systems with different values of chain stiffness are obtained. These stress-strain curves allow us to estimate the value of the elastic limit, as well as to determine the stresses at the points of phase transitions from the disordered state to the orientationally-ordered one.

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