EFFECT OF WATER ON THE MODULAR STRUCTURE
CONFORMATION OF "POLIKON K" MATERIAL

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This paper presents the developed probabilistic spatial model fragments of the structure of polyacrylonitrile fiber, the monomerization composition (condensing components of the polymer matrix), and "Polikon K" – "Polikon K_{1a}" material. The dynamic contact angle of the investigated material was experimentally determined, and the work of adhesion (1.154 mJ/m^2) and wetting (73.855 mJ/m^2) of the surface material was calculated. The model of the structure of the "Polikon K_{1a}" material indicates the most likely point of interaction of copolymer polyacrylic fiber with reactive CH_3- groups of the polymer matrix, namely, the interaction with the $C\equiv N$ group, by breaking one bond and forming a methylene bridge. The size of the unit cell of the model was estimated: $10.6 \times 10.3 \times 9.7$ Å. The dependence of the torsion angle near the methylene bridge on the concentration of water molecules was investigated.

The work described in this paper is a continuation of the previously published comprehensive studies [1-3], and is devoted to investigating the methods of molecular mechanics of one embodiment of polycondensation filling in the system monomerization composition – polyacrylonitrile (PAN) fiber, the experimental study of the wettability of the material surface by the method of droplet spreading, and the influence of water molecules on the conformation of the model structure of the "Polikon K" material.

Based on the chemical composition and structure of the composition, a flat model of its macromolecules was created. The authors consider the simplified flat models with the extreme end methyl groups and the lowest possible degree of polymerization of the given microstructure.

In polycondensation filling after impregnation of PAN fibers with monomers, polycondensation of temperature reactive oligomers occurs in the structure and on the surface of the fibers at elevated temperature and normal pressure.

We studied the wetting of the material surface by the method of droplet spreading (Fig. 1) using a precision optical tensiometer "Theta Lite Optical Tensiometer TL100" [4], which allows real-time measurements of the dynamic contact angle (Fig. 2). The resulting images (Fig. 1b) were processed using a special computer program that automates the process of approximation of the experimental curves by the Young – Laplace equation. Individual contact angles were determined with an accuracy of ± 0.1 ° in the range of 0-180 °. A schematic representation of a liquid droplet on a horizontal, solid, rough surface, according to [5], is shown in Fig. 1a.

For the test samples, the work of adhesion and surface wetting with water were calculated, with the surface tension of 72.7 mJ/m^2:

Work of adhesion, mJ/m^2	1.154
Work of wetting, mJ/m^2	73.855

The most likely point of interaction of the copolymer PAN fiber with the reactive CH_3- groups of the polymer matrix is the interaction with the Ca"N group, breakage of one bond and the formation of a methylene bridge.

The plane model of the "Polikon K_{1a}" material contains a fragment of the PAN fiber consisting of elementary units of acrylonitrile, methyl acrylate, and sodium itaconate, a monomerization composition and an

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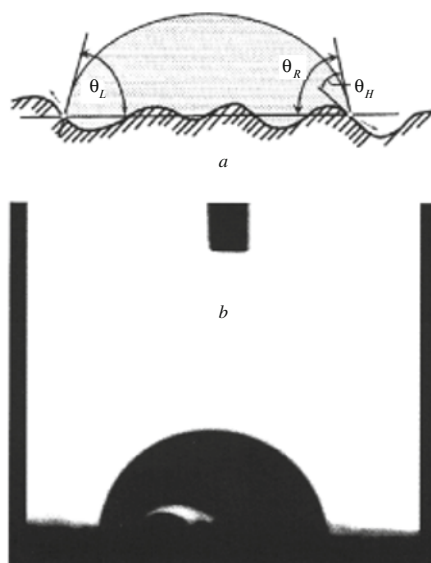
Fig. 1. Schematic representation of the shape of a liquid droplet on a horizontal rough surface of "Polikon K" (*a*) and an image of the contact angle θ of a liquid droplet (of water) on the surface of the material, obtained on a precision optical tensiometer Theta Lite Optical Tensiometer TL100 (*b*).
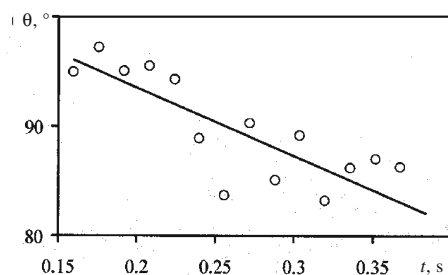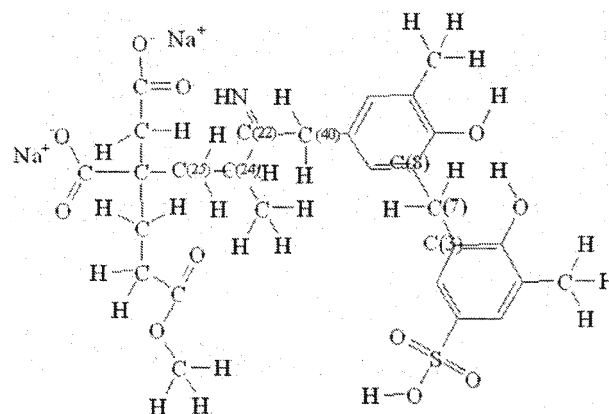

Fig. 2.

Fig. 3.

Fig. 2. Dynamic changes of the contact angle of the "Polikon K" material.

Fig. 3. Model of the "Polikon K" – "Polikon K$_{1a}$" structure.

elementary unit (Fig. 3). The size of the unit cell of the "Polikon K$_{1a}$" material model is as follows: length 10.6, width 10.3, and height 9.7 Å.

Molecular mechanics suggests that the spatial (steric) energy of the molecule arises from a few interactions. These interactions include various deformations of bonds and angles, torsional effects of twisting around single bonds, Van der Waals attraction or repulsion of the atoms in proximity to each other, and the electrostatic interaction between the partial charges in the molecule due to polar bonds. For quantitative evaluation of the contributions to the total energy, the interactions can be represented with the aid of the potential function given by the energy of the interaction depending on the distance, angle, or charge. In this paper, the most likely model is developed, and the energy of an elementary unit of the "Polikon K" material is obtained by the MM2 method [6, 7].
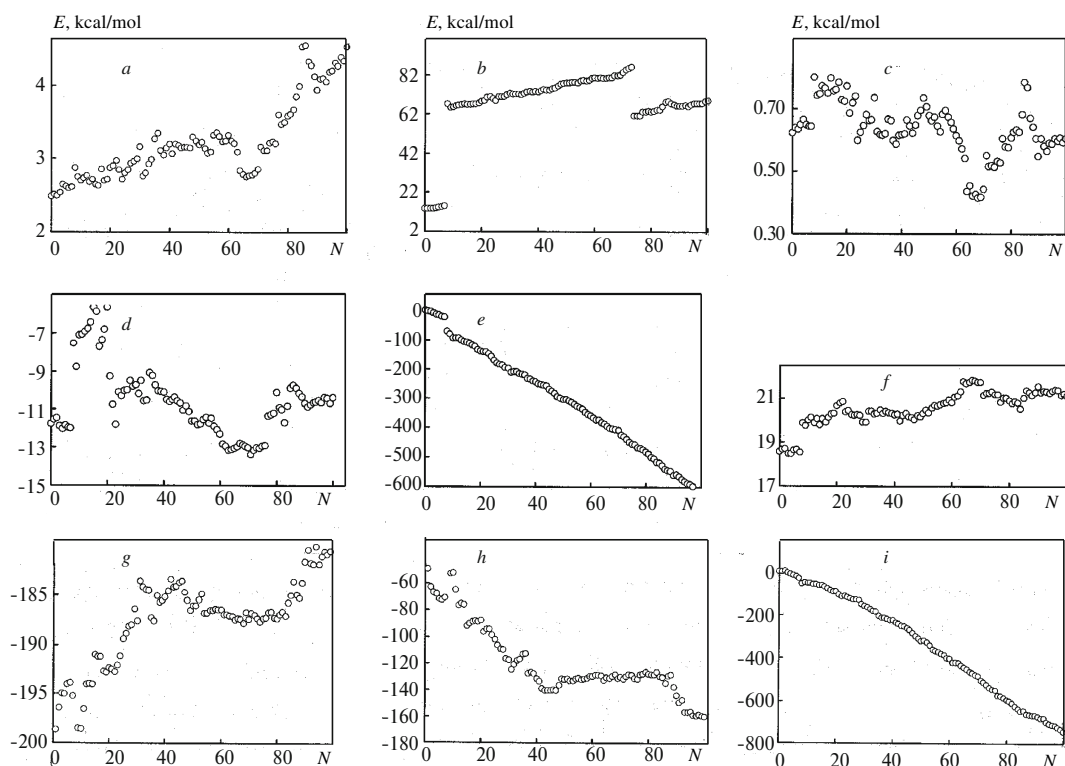
Fig. 4. Dependence of the components of steric energy on the concentration of water molecules: *a* – bond stretching; *b* – bending of bond angles; *c* – bending – stretching corrections; *d* – internal rotation; *e* – non-Van der Waals interactions; *f* – Van der Waals interactions; *g* – ion – ion; *h* – dipole – ion; *i* – dipole – dipole.
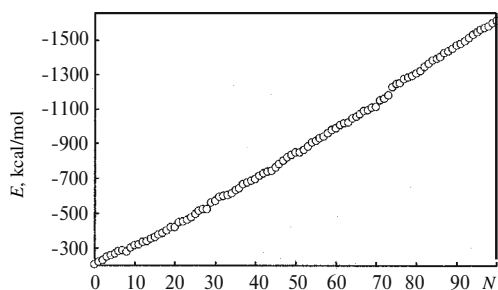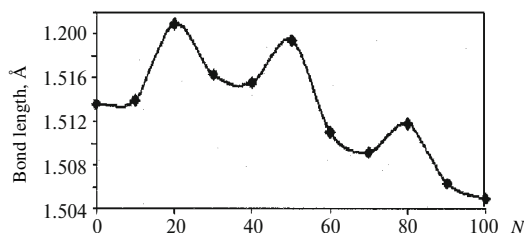

Fig. 5.

Fig. 6.

Fig. 5. Dependence of the total steric energy of the "Polikon K_{1a}" molecular model structure on the concentration of the aqueous solution.:

Fig. 6. Change in C(22)–C(24) bond length with water molecule concentration (Å).

After obtaining the molecular model of the elementary unit, a study was conducted in which the effect of water on the conformation of this unit was considered. The concentration of water molecules was varied from 1 to 100 in increments of one molecule (Fig. 2). From the obtained concentration dependences of the contributions to the total steric potential energy, the predominant influence of electrostatic components was found (Fig. 4, g-i). With increasing concentration of water molecules, steric energy decreased.

Also considered in detail were the bond length where bonding occurs between the PAN fiber and the phenol formaldehyde resin [C(22)–C(24)], three valence angles [C(22)–C(24)–C(25), C(40)–C(22)–C(24), C(3)–C(7)–C(8)], and a single torsion angle [C(40)–C(22)–C(24)–C(25)] (Figs. 6-9).
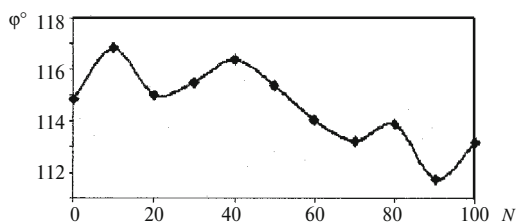
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Fig. 7.   Fig. 8.

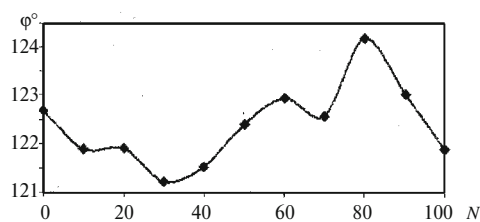Fig. 7. Change in C(22)–C(24)–C(25) bond angle with water molecule concentration (in degrees).

Fig. 8. Change in C(40)–C(22)–C(24) bond angle with water molecule concentration (in degrees).
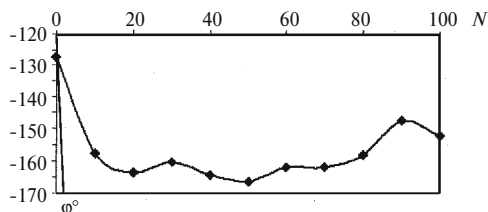

Fig. 9. Change in C(3)–C(7)–C(8) bond angle with water molecule concentration (in degrees).

It should be noted that the most important results of the study are as follows:

– increasing the concentration of water molecules changes the overall conformational spatial structure of the material, which is reflected in a significant decrease in total steric energy from –218 to –1385 kcal/mol;

– bond angles and bond lengths vary little, unlike the torsion angles, especially when the water molecule enters the space between the PAN fiber and the phenol formaldehyde resin near the methylene bridge, which may considerably influence the macroproperties of the "Polikon K" material;

– it was found that the torsion angle dependence on the concentration of water molecules near the methylene bridge [(C(40)–C(22)–C(24)–C(25)] is the most likely to influence the overall conformation of the spatial model with a subsequent change of macroproperties in the presence of an aqueous colloidal solution;

– methylene bridge [C(22)–C(24)] length and bond angles near the methylene bridge [C(22)–C(24)–C(25) – C(40)–C(22)–C(24)] and between the benzene rings [C(3)–C(7)–C(8)] have no significant dependence on the concentration of water molecules.

In the future, a detailed study is required of all the most probable variants of chemical interaction of a PAN fiber with a monomerization composition to optimize the process parameters in the preparation of the "Polikon K" material to improve its sorption characteristics.

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