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SOME PROPERTIES OF THE MEZOGEN ARYLPROPARGYL ETHERS OF PHENOLS

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This work presents the results of experiments on computer modeling of behaviour of clusters consisting of nematic liquid crystals on the basis of the arylpropargyl ethers of phenols (APEP) with the help of GROMACS programme and of them IR absorption spectrum. It shows the influence of fluorine atom on properties which happen as a result of temperature annealing to the processes of disordering. The given experiments demonstrate the necessity of a correct choice of interaction between molecules. The influence of location of molecules at the initial state to the behaviour dynamics was found.

Keywords: computer modeling, clusters, nematic liquid crystals, disordering, temperature influences.

Background

Nematic liquid crystals based on APEP offer promise for the improvement of the temperature characteristics of liquid crystalline devices [1-3]. There were received liquid crystal mixtures with the melt temperature equal to 20 ^{0}C, the temperature interval of mesomorphic phase existence equal to 90 ^{0}C with positive $\Delta\varepsilon$ on the basis of which it is possible to receive LC materials perspective from the commercial point of view [3]. The perfecting of the mesogenic properties of compounds cannot be accomplished without detailed information about processes in them. Statistical theory methods are most often incapable of visualizing the results of changes in many-particle systems. The cooperative features of molecular processes are often obscured by the assumptions made. In this respect, molecular dynamics methods are of interest. They allow the behavior of all ensemble molecules to be visualized. It is only in the last few years that real progress has been made towards accurate atomistic simulations and the use of simulation methods to obtain material properties [4-7].

It is necessary to note, that the connections of APEP with fluorine with r_{vdw} increase become inertial in relation to temperature influences [8]. This result requires additional researches, as fluorine influence often appears determining the order of liquid crystal systems [9]. Thus with participation of this connection high parameters of meanings of temperature intervals of mesomorphic phase existence in binary mixes with participation APEP were received [3]. It is also known that the connection with the fluorine atom results in reduction of viscosity.

Having the purpose to reveal features of disordering processes that occur at temperature influences in such a system, the experiments on computer modeling of cluster behaviour with PEF with r_{vdw} variation in the interval from 0.85 nm up to 2 nm were carried out.

Results and Discussion

The modeling by GROMACS

For realization of the given work the set of programs under the general name GROMACS [10-11] version 3.2.1 [11] was used. It is intended for modeling behaviour of molecular systems at temperature and pressure change. In calculation GROMOS-96' standard parameters of calculation were used.

For realization of the analysis of the experimental results the software package was created [12]. The comparative analysis of the research results of changes of volume, pressure, binding

energy, distribution function of molecules, degree of order, information entropy, self-diffusion coefficient is carried out.

This model is a compound of the phenylpropargyl ethers of p-fluorine-phenols (melting temperature – 306 K, bleaching temperature – 326 K [2]) (PEF), the phenylpropargyl ethers of o-nitro p-fluorine-phenols (melting temperature – 352 K, bleaching temperature – 393 K [3]) (PEoF). For decreasing of impact of the boundary conditions the following sizes of researching cluster: PEF – (14x14x17 molecules), PEoF – (13x13x18 molecules) were used.

Taking into account that researching objects are in liquid state forming of the cluster was conducted by putting it in one cell, which eliminated giving periodical border conditions [10-11]. In this case for its forming a special programme was created, which allowed calculating features of location of molecules in such an ensemble.

In construction of the cluster all experimental and theoretical results of the research were considered [12].

In the clusters group conceptions of construction T-coupling group and Freeze group [11] were realised**.** The first one had correspondence to the basic part of the cluster suited to which had undergone the temperature effect, the second one- molecules of the substrate which did not move during the experiment (external border of the cluster YOX – planar orientation, ZXO – homeotropically, in all the cases in the initial state longitudinal axes of molecules were located parallelly to OY axis).

The temperature effect was realized according to Berendsen scheme [11]. In the research a standard set of parameters (input.file) was used [11]. It considered coulomb and disperse interaction (maximal radius of interaction, radius of «cutoff», $r_{coulomb}$ and r_{vdw} respectively).

After construction the cluster represented a cube with the total atom number about 100000. The calculation was done with the version for two processor computer. Annealing of the cluster was conducted through consecutive increasing of temperature: moreover case the final cluster at some temperature became initial for the next annealing. Time of annealing at a particular temperature was $10*10^{-12}$ s.

The direction of molecules in space in all the programmes was given by with the help of single vectors, which are defined by 2 atoms laying on their longitudinal axis. In defining a number of molecules N located in a particular angle (10^0) relative to this axis of primary initial location of molecules OY, comparison of the given angle and the angle between longitudinal axis of the particular molecule and OY axis was used.

In calculation of the magnitude of the order power S was used as a model of molecule cylindrical symmetry [13].

Function of **D(α)** distribution corresponded to the number of couple molecules in the given angle **α** in relation to each other. **D(α)** calculation was conducted by giving the radius of the area, in which the researched molecules were located. Analogical calculations were done for all molecules of the cluster. The repeating of including of the same couple was eliminated. It is necessary to emphasize that further working up of the angle dependence of this function was done by special programme, which was created on Delphi 7.0. Curve lines of dependence were represented in polar coordinates. Axis of the angle calculation was the coordinate axis OY: the angle from 0^0 to 90^0 was calculated clockwise and from 180^0 to 90^0 anticlockwise. In this work the results of **D(α)** curves for the radius in 32 angstrom area which is compared to longitudinal length of the researched molecules. In general the curves, constructed for different radiuses represent features of changing dependences given in the work. In case when radius is 4 angstroms the curves are represented as broken curves.

As far as the number of molecules in the cluster was final, the next programme calculated the magnitude of information entropy S of the cluster. Knowing the whole distributions of molecule location are can define the magnitude S for each cluster after temperature annealing using Shennon formula [14].

The programme for calculation of cluster compound energy $\mathbf{E_b}$ was created. It was calculated as a difference between the sum of energy of separated molecules and total energy of the cluster. Apart from the created programmes in Gromacs, there was a possibility to calculate energy of the cluster, volume and distribution of pressure inside the cluster [11].

Comparative analysis of research results of changing in volume V, pressure, energy of the compound $\mathbf{E}_b$, distribution of molecules **D,** magnitudes of the order power S, information entropy Sinf, N of consecutive annealing for clusters, which have different structures.

The modeling of IR absorption spectra by LADY

Elementary unit cell in accounts of IR spectra of APEP crystals: space symmetry group I- 11; a=20 Å, b=40 Å, c= 10 Å $\alpha=\beta=\gamma=90^0$ was used. In Fig. 1 the structural formulas of PEF and PEoF is shown.

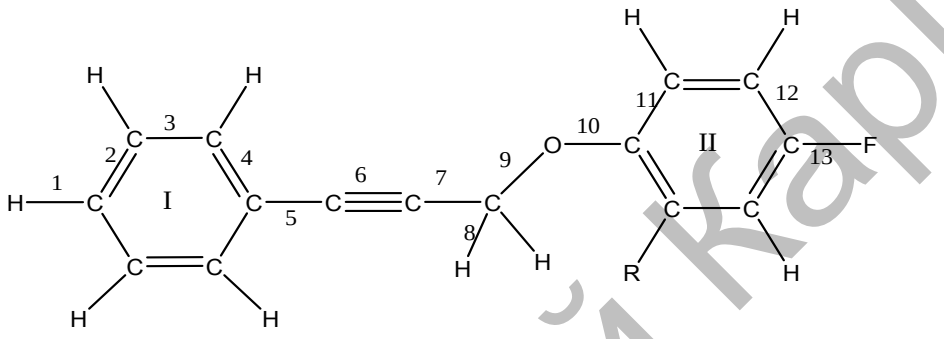
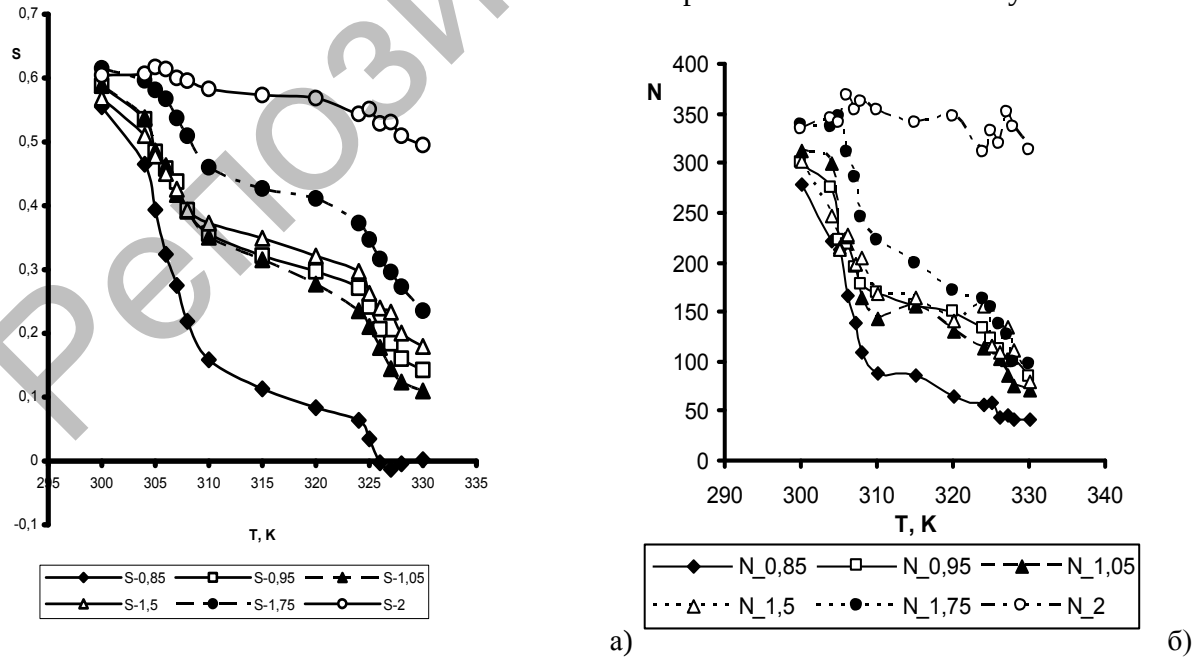


Fig. 1 Structure of molecules PEF (R=H) and PEoF (R=NO_2)

LADY (Lattice Dynamics) – software for lattice dynamics calculation [15]. This program LADY is capable of simulating different crystal properties depending on the adiabatic potential function such as IR, Raman spectra. Valence force field model and inter-atomic potentials for 1-4 interactions was used.

Results

The curve of S (T) order degree becomes flatter with radius growth (Fig. 2A). In the interval from 0.95 nm up to 1.5 nm S (T) curves do not strongly change in comparison with cases of r_{vdw} = 0.85 and 2 nm. Characteristic excesses in the field of phase transitions are everywhere observed.



а) б)

Fig. 2 Temperature dependences of the order degree S(A) and N (B) for the PEF cluster at different cutoff

radiuses (planar orientation of a substrate)

Apparently, the tendency of a more "crystal" condition should be also observed and on N (T) curves (Fig. 2B): a sharp change of a curve after 1.75 nm cutoff radius is observed.

The increase of interaction radius results in preservation of a greater order a cluster at temperature annealing and thus in entropy reduction as a measure of disorder in the system (Fig. 3). Like in Fig. 2, the appreciable distinctions in curves are observed at the meanings of the radius exceeding 1.5 nm. Apparently, at such distances specific interactions with fluorine atom participation are shown.

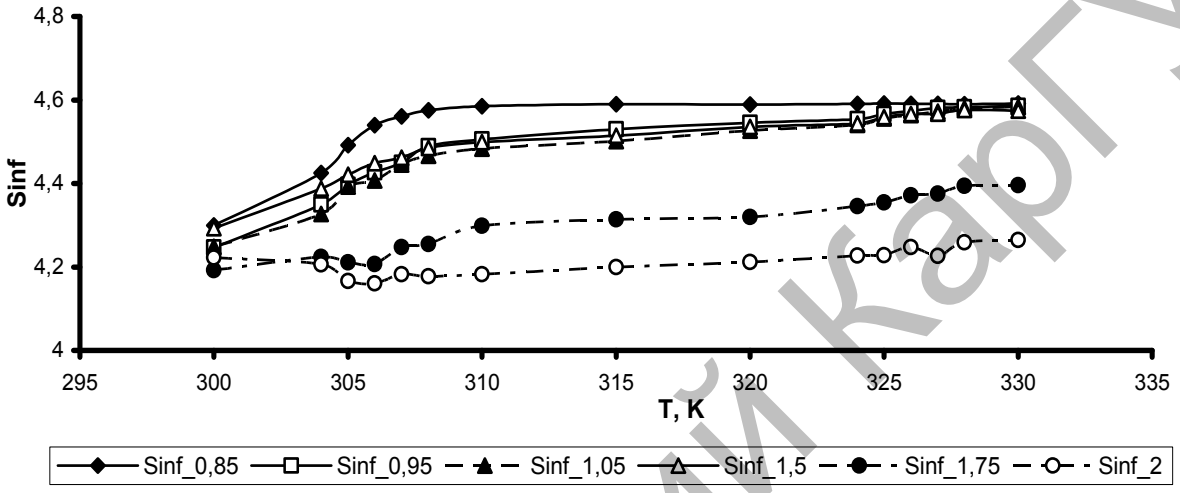


Fig. 3 Temperature dependences of informational entropy S_{inf} for the PEF cluster at different cutoff radiuses (planar orientation of a substrate)

It is necessary to expect, that "crystal" strengthening will result in the increase of intensity in a crystal, and also in the growth of the cluster energy. The similar tendency is shown in the change of connection energy determined as difference between the sum of energy of separate molecules of a cluster and the whole cluster energy. At the excess of 1,5 nm cutoff radius there is a sharp Eb reduction, and at 2 nm radius its size becomes negative.(see Fig. 4).

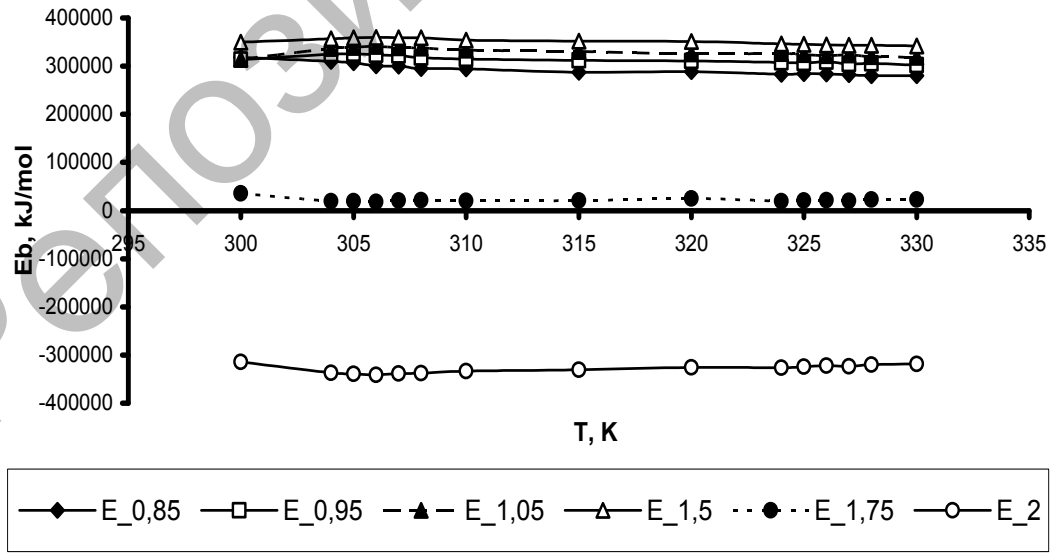


Fig. 4 Temperature dependences of bond energy E_b for the PEF cluster at different cutoff radiuses

It is obvious, that the “crystal” strengthening at the growth of interaction radius of should result in reduction of molecules mobility in the cluster.

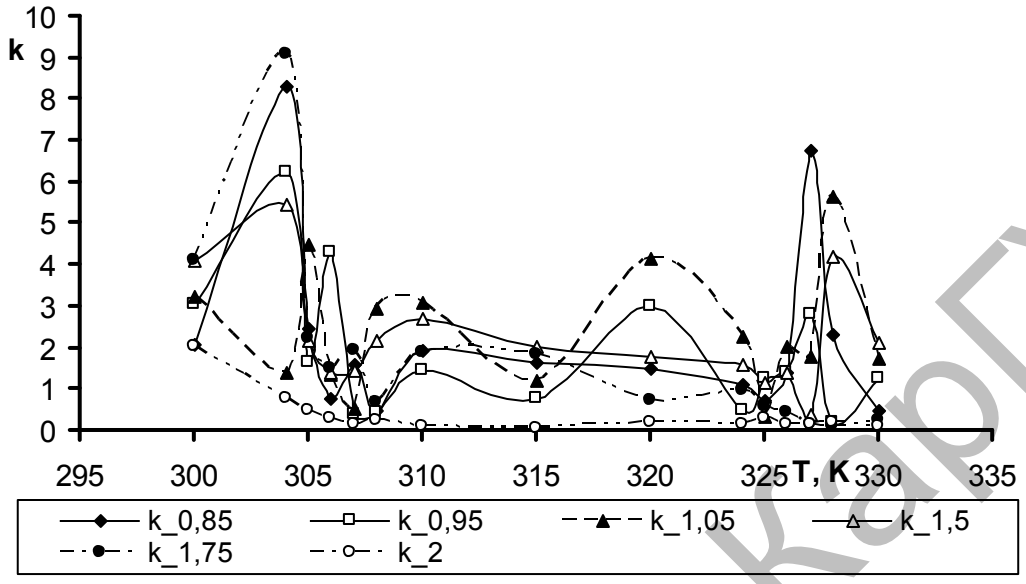
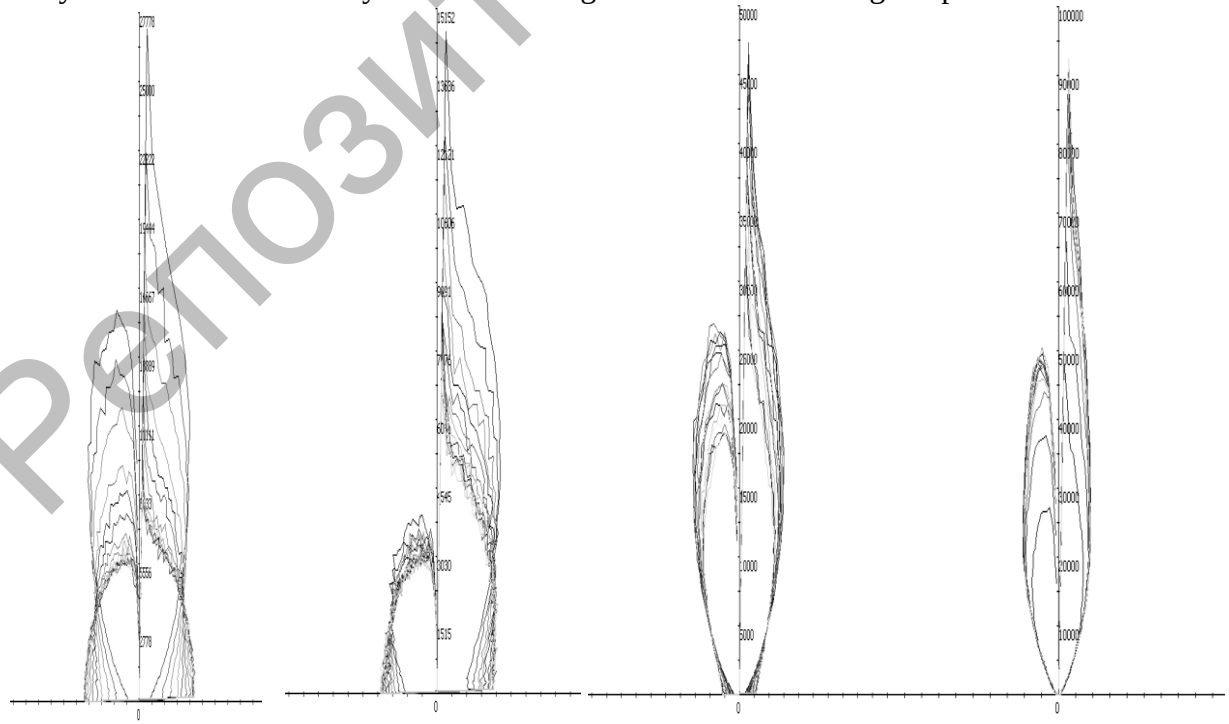


Fig. 5 Temperature dependences of the self diffusion coefficient for the PEF cluster at different cutoff radiuses. [k] =*10^{-6} м^2/с. (planar orientation of a substrate)

The research of the self diffusion coefficient of the central molecule of the cluster at various cutoff radiuses shows, that at r_{vdw}=2 nm the molecule practically becomes motionless in area mezophase (see. Fig. 5). As it is clear from Fig. 5, the high mobility in the beginning of the annealing and after the enlightenment point is observed at all other r_{vdw} meanings. In the mesomorphic phase an appreciable mobility is also observed, except the case, when radius is equal 2 nm. A compound character of the change in this area is apparently connected with the molecule polarity that can result in decay of dimers with growth of the annealing temperature.



planar PEF(0,85nm) sMBBA (2nm) PEF(2nm) PEF(2nm)homeotropical

Fig. 6 $D(\alpha)$ distribution functions for PEF at different cutoff radiuses r_{vdw} and orientation of a substrate

As Fig. 6 shows the increase of the radius results in an essential change of the form of D (T) curves. Here with the increase of temperature D (α) meanings grow, that is opposite to the results received on MBBA [12], that testifies to the increase of the order in a cluster at the increase of the cutoff radius. In case of planar orientation of a substrate D function increases with the growth of temperature for a MBBA molecule, and in case of PEF - in the beginning it grows up to 308 K, and then it decreases (see Fig. 6). At homeotropical of orientation the quantity of pairs of molecules having small meanings among themselves, grows with the growth of temperature.

Deterioration of simulation takes place with occurrence of nitro group in an orto-position, however striving for "crystallization" is kept (see Fig. 7-9, 11).

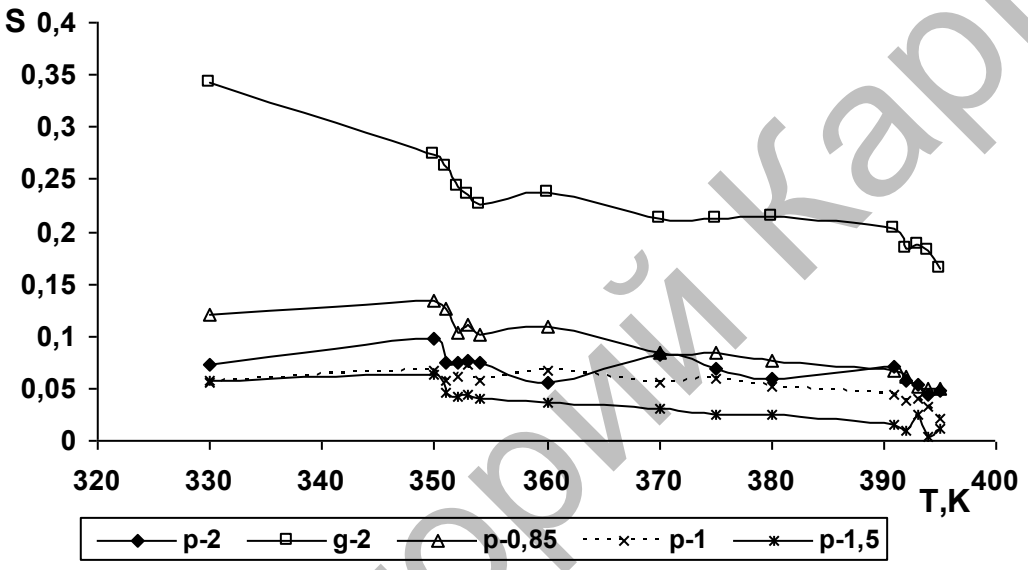


Fig. 7 Temperature dependences of the order degree S for the PEoF cluster at different cutoff radiuses r_{vdw} and orientation of a substrate (planar – p, homeotropical – g)

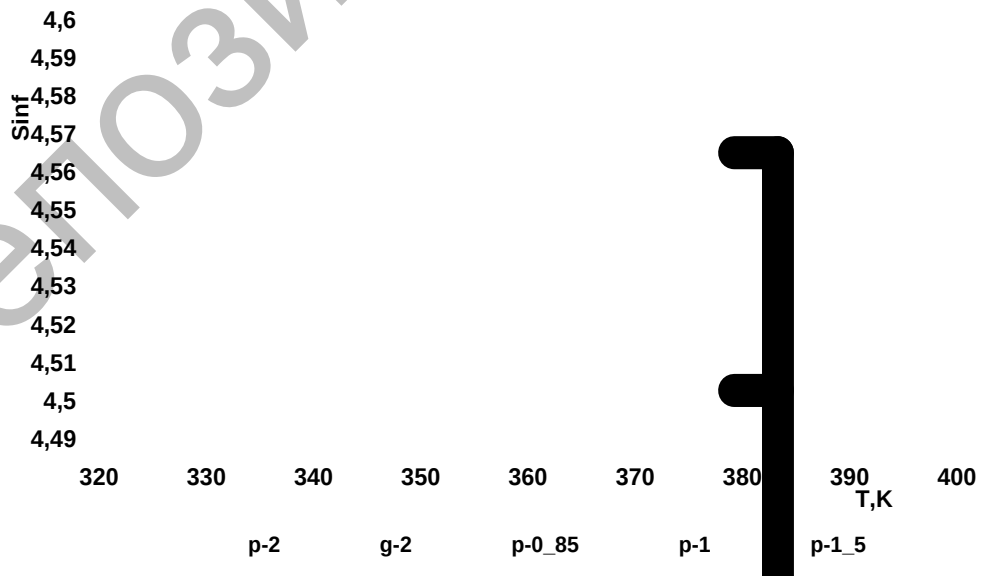


Fig. 8 Temperature dependences of informational entropy S_{inf} for the PEoF cluster at different cutoff radiuses r_{vdw} and orientation of a substrate (planar – p, homeotropical – g)

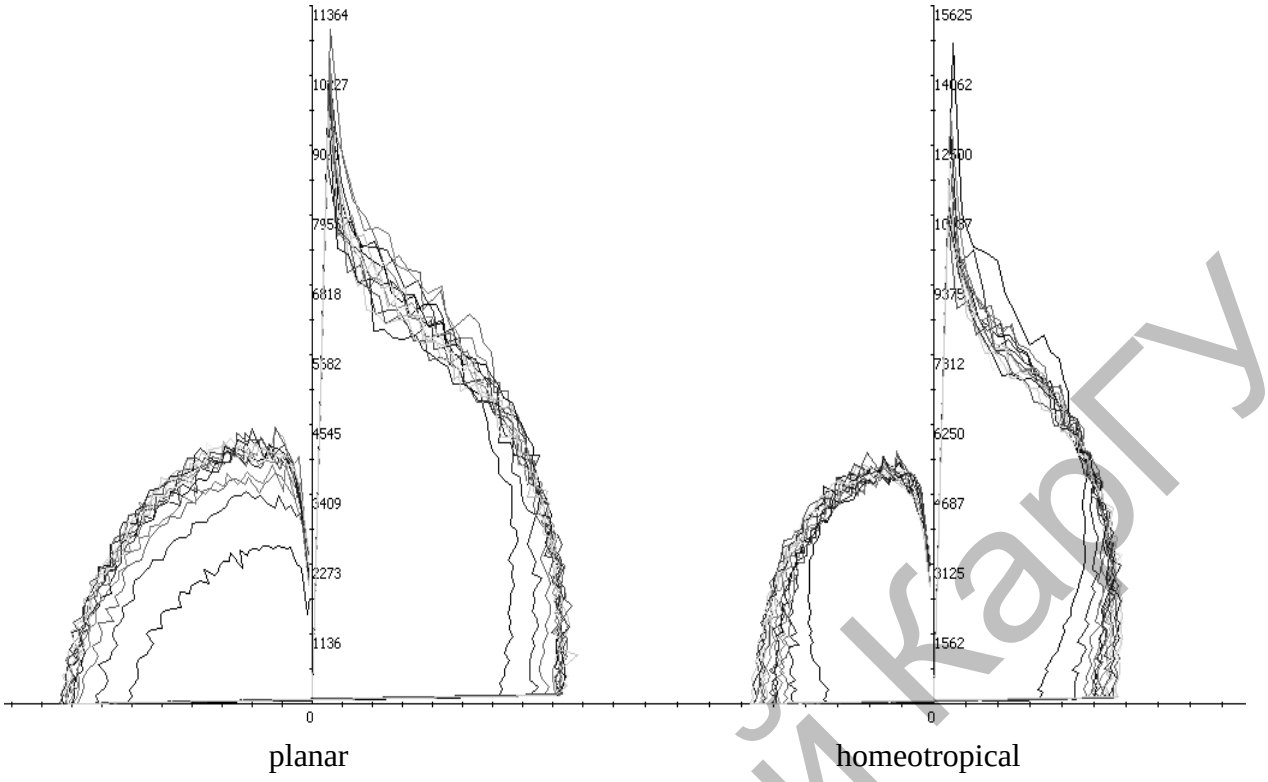
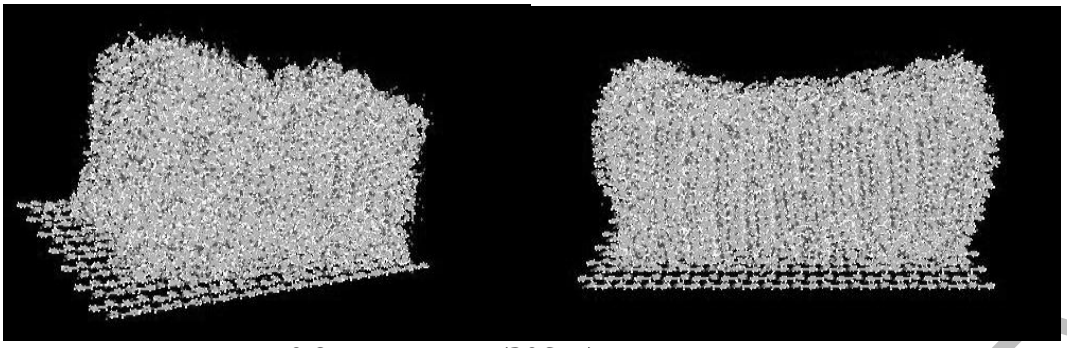


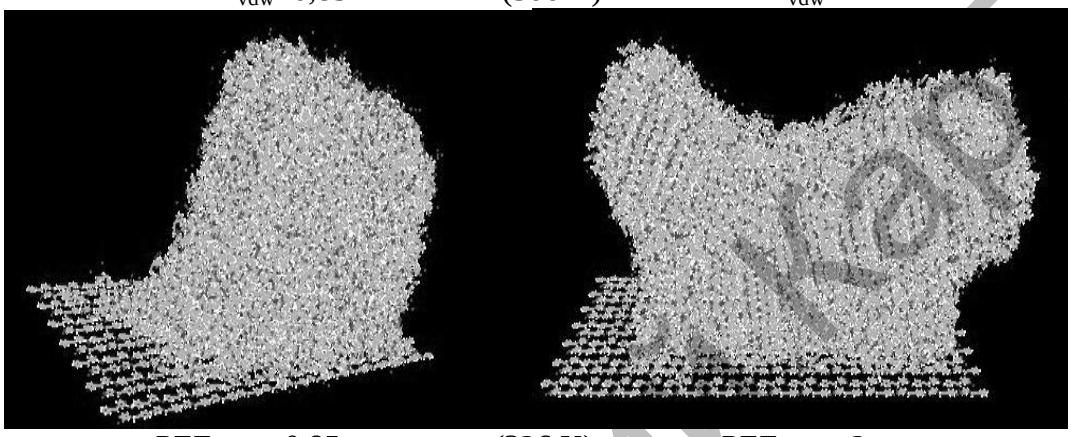
Fig. 9 $D(\alpha)$ distribution functions for PEoF at r_{vdw} =2 nm and different orientation of a substrate

From the Fig. 7, the given temperature dependents of the degree of order for the PeoF molecule shows, that the S(t) curve with rise of the temperature becomes more gradual, like it was observed for the PEF. Such a tendency could be found in curves of change of the entropy from the temperature with different radius of cutoff (Fig. 8): by increasing of radius the value of the entropy decreases. The lowest values of the entropy could be observed at homeotropical orientation of the base. That is probably related with taking off the movement restriction of molecules in the OZ axis direction. The types of curve functions of D(T) distribution (Fig. 9) show the increase of number of the molecule couples, which is located with angle of 900 between each other. That is probably related to the increasing of disorder processes with appearing of nitro-group in orto location. Despite to the mentioned differences, the ftor atom also in this case increases the tendency of crystallinity growth at the increase of values of the cutoff radius. That also proves the visual observations of clusters (Fig. 10-11), in which shape of clusters and existence of the characteristic lines indicate it.

Thus the increase of the cutoff radius of dispersion interaction up to 20 Å allows the cluster with PEF molecule to show a high level of the order at temperature annealing. It points to the fact the account of Lennard-Jones potential within the limits of 20 Å between the cooperating atoms in this case is sufficient for manifestation of the long-distance orientation order. It is obvious, that the possible intermolecular interaction determining a mesomorphic phase nature has the same potential as dispersion interaction.

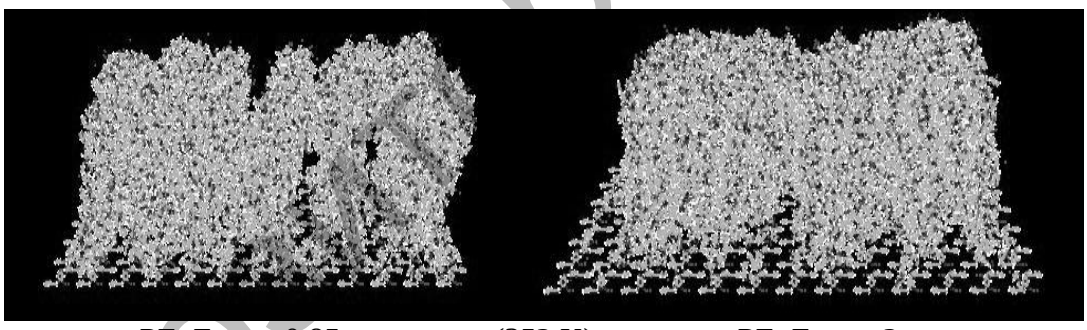


PEF r_{vdw}=0,85 nm (306 K) PEF r_{vdw}=2 nm

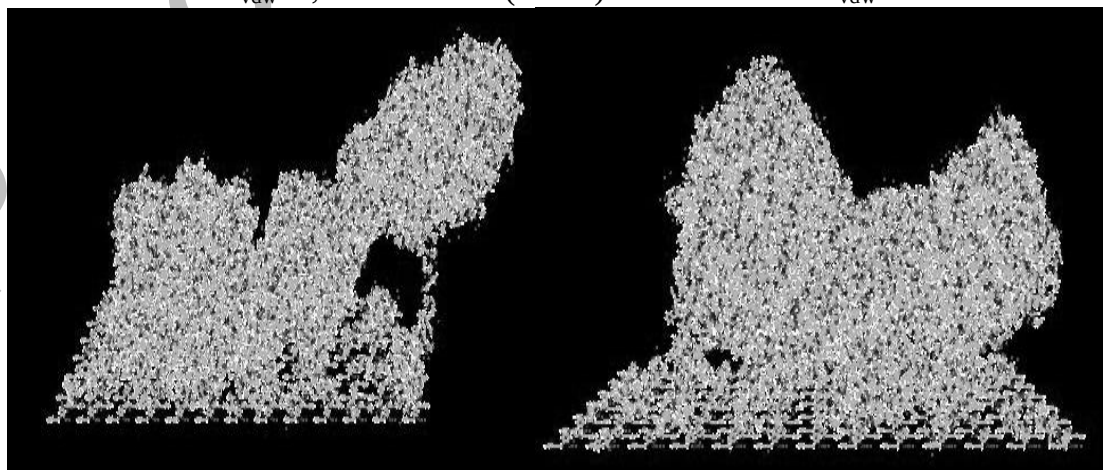


PEF r_{vdw}=0,85 nm (326 K) PEF r_{vdw}=2 nm

Fig 10 Picture of the PEF cluster



PEoF r_{vdw}=0,85 nm (352 K) PEoF r_{vdw}=2 nm



PEoF r_{vdw}=0,85 nm (393 K) PEoF r_{vdw}=2 nm

Fig 11 Pictures of the PEoF cluster

Analysis of IR absorption spectra of PEF and PEoF

With the help of the program LADY [15] the calculation and analysis of IR absorption spectra of APEP is executed. The type of symmetry determining an arrangement of molecules in a cluster is established. Here are received the meanings of force constants, potentials of interatomic interaction of atoms which are not bound in valency satisfactorily describing experimental IR spectra. In the table 1 the interpretation of the appropriate strips of the absorption spectra is given. The influence of such a substitution on a force field of separate APEP molecules is clarified.

Table 1. The experimental and calculated frequencies of IR absorption spectra

PEF		
$\nu_{exp.}$ (cm^{-1})	$\nu_{calc.}$(cm^{-1})	Reference *
3080 – 3050	3060-3050	$\nu CH_{I\ and\ II}$ (100)
2910	2910	$\nu CH_{CH2\ antisym.}$ (100)
2860	2860	$\nu CH_{CH2\ symm.}$ (100)
2230	2229	νCC_6(79), νCC_7(11), νCC_5(10)
1600 – 1540	1591 1578 1553	νCC_I (79), νCC_5(8) νCC_{II} (100) νCC_I (98)
1540-1500	1508 1503	νCC_{II} (86), νCO_{10}(7) νCC_{II} (52), δCCH_{II} (17), νCO_{10}(14), νCF (10)
1475-1415	1471 1451	δCHH_{CH2}(72),δCCH_{78} (16), νCC_I (6), νCC_{II} (6) νCC_I (48), δCCH_I (32), δCCC_I (10), νCC_5(10)
1390-1340	1386 1373 1332	νCC_I (48), δCCH_I (36), δCCC_{45}(8), δCCC_I (7) νCO_9(33), νCO_{10}(17), νCC_{II} (17), δCCH_{78}(12), δHCO (10) νCC_{II} (67), δCCH_{II} (12), δCCF(12), δCCC_{II}(9)
1240-1110	1214 1197 1188 1131	δCCH_I(93) δCCH_{II}(41), νCF(18), νCO_{10}(14), νCC_{II}(10), δCCC_{II}(8) δCCH_{II}(75) δCCH_{78}(80), δHCO (20)
1080	1074	νCO_{10}(29), δCCH_{II}(12), δOCC_{79}(11), δCOC (9)
1040-960	1066 1037 1036 1005 986	δCCH_I(69), νCC_I (10) νCC_I (25), δCCH_{II}(25), νCC_{II} (15), νCC_7(16) δCCH_{II}(27), νCC_I (14), νCC_{II} (14), νCO_9(10) δCCH_I(50), νCC_I (36), δCCC_I (8) νCC_I (41), δCCH_I(28), δCCC_I (18)
910	944 942	νCC_{II}(25), δCCC_{II}(20), δCCH_{II}(20), δCCC_I(19),νCC_I (9) δCCC_I(36), δCCC_{II}(14), δCCH_I(13), νCC_{II}(14), νCC_I (12), δCCH_{II}(8)
	861	νCC_{II}(46), δCCF(15), δCCC_{II}(13), νCF(11), νCO_{10}(10), δCOC(5)
800-700	770 764 703	δCCC_{II}(20), δHCO(14), νCF(12), νCC_{II}(11), δCOC(7), δCCH_{78}(5), δOCC_{79}(5) δHCO(71), δCCH_{78}(22) δCCC_I(31), νCC_5(12), νCC_I (10), δCCH_I(7)
700-575	601 598 590	δCCC_{II}(56), δCCH_{II}(17), νCC_{II}(10) δCCC_{56}(20), δCCC_{67}(20), δCCC_{45}(18) δCCC_I(54), δCCH_I(14), δCCC_{56}(6), δCCC_{67}(5)
560	559	δCOC(16), δCCC_{II}(16), δOCC_{79}(8), δCCF(6)
530	476	δOCC_{79}(19), δCCF(23), δCCC_{45}(15), δOCC_{II}(14)

445-400	410 404	δCCF(28), δCCC_{II}(14), νCC_5(7), δCCC_{45}(6), δCCC_I(8) δCCF(26), δCCC_I(9), νCC_5(8), δCOC(7)
PEoF		
3090 – 3070	3075-3060	ν$CH_{I\ and\ II}$ (100)
2920	2920	ν$CH_{CH2\ antisymm.}$ (100)
2860	2860	ν$CH_{CH2\ symm.}$ (100)
2230	2227	νCC_6(79), νCC_7(11), νCC_5(10)
1580 – 1500	1575 1562 1542 1522 1505	νCC_I (100) νCC_{II} (100) νCC_I (96) ν$NO_{NO2\ antisymm.}$ (100) νCC_{II} (90)
1500-1450	1476	νCC_{II} (50), δCCH_{II} (20), δCCC_{II}(15), νCF (11)
1450-1410	1444 1436	δCHH_{CH2}(38), νCC_I (31), δCCH_{78} (10) δCHH_{CH2}(50),νCC_I (25), δCCH_I (16), δCCH_{78} (6)
1380-1350	1368 1355	νCC_I (55), δCCH_I (30), δCCC_{45}(9), δCCC_I (6) νCN(36), ν$NO_{NO2\ symm.}$ (36), νCC_{II} (20)
1350-1300	1341 1317	νCO_9(31), νCC_{II} (19), νCO_{10}(19), δCCH_{78}(11) νCC_{II} (48), νNO_{NO2} (29), δONO (12), δCCF(11)
1300-1200	1273 1229	νCC_{II} (20), νCF(15), νCO_9(11), δCCH_{78}(10), νCO_{10}(7) δCCH_I(16), νCC_5 (16), νCC_I (14), νCF(9), νCO_9(8)
1200-1140	1187 1186	δCCH_{II}(35), νCO_{10}(12), δCCC_{II}(9),δCCH_{78}(8), δHCO(5) δCCH_I(88)
1130	1137	δCCH_{II}(58), νCC_{II}(14), δCCC_{II}(10)
1070-1030	1067 1059 1047 1045 1040	δCCH_{II}(46), νCN (16), νCC_{II}(14), νCF(8) δCCH_I(86), νCC_I (6) δCCH_{78}(81), δHCO(16) δCCH_I(75), νCC_I (12) δCCH_{II}(52), νCC_{II}(18), δCCC_{II}(9), νCN (6)
1010	1016	νCC_I (52), νCC_7 (21)
1000-950	990 976 967	δCCH_I(52), νCC_I (32), δCCC_I (8) δCCH_{78}(18),νCO_9(15),δHCO(15), νCC_I(11),δCCH_{II}(11) δCCH_I(20), νCC_I (19), νCC_7 (15), νCO_9(14)
920	932	δCCC_I(58), δCCH_I(20), νCC_I (7)
880	893	νCC_{II}(39), νCF(19), δCCF(15), δCCH_{II}(12)
800	813	δCOC(23), νCC_{II}(19), δHCO(15), νCO_{10}(14)
750	741	δONO (38), δCNO (32), νCN (9), νNO_{NO2} (8)
695	697	δCCC_I(37), νCC_5 (14), νCC_I (12), δOCC_{79}(10)
665	678 659	δHCO(36), δCCC_{II}(10), δOCC_{79}(6), δCCC_{67}(6) δCCC_{II}(38), δONO (11), νCC_{II}(7), νCF(5)
600-495	583 543 530 490	δCCC_{56}(18), δCCC_{67}(12), δOCC_{79}(12), δCCC_{45}(11), δHCO(10) δOCC_{II}(23), δCCF(15), δCCC_{45}(9), δOCC_{79}(8), δCCN(6) δCNO (88) δOCC_{79}(19), δCCC_{45}(15), δCCF(7), δHCO(6), δCCC_{II}(6)
450	456	δCCF(31), δCCC_{II}(18), δCOC(10), δCCN(7), δHCO(6)

Note νAB – stretching of A-B bond, δABC – bending of a A-B-C valence angle; the contributions (in percentage) of deformations of an appropriate coordinate in distribution of

potential energy of the given fluctuation are specified in brackets. Indexes I and II specify are belonging of the given bond or angle to the first or second benzene ring.

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