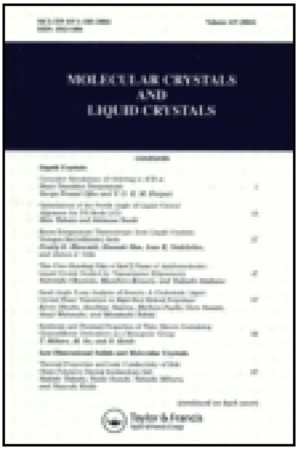

Molecular Crystals and Liquid Crystals

The Dynamics of Some Nematic Liquid Crystals

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Version of record first published: 05 Apr 2011

To cite this article: M. E. Agelmenev, Z. M. Muldakhmetov, S. M. Bratukhin, V. G. Pak, V. V. Polikarpov & O. A. Yakovleva (2008): The Dynamics of Some Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 494:1, 339-352

To link to this article: http://dx.doi.org/10.1080/15421400802430273

Mol. Cryst. Liq. Cryst., Vol. 494, pp. 339–352, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802430273

The Dynamics of Some Nematic Liquid Crystals

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This work shows the results of the computer modelling of some nematic liquid crystals behaviour conducted with the help of GROMACS programme. It shows the influence of different factors 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: arylpropargyl ethers of phenols; molecular dynamics; nematic liquid crystals

1. INTRODUCTION

Nematic liquid crystals based on arylpropargyl ethers of phenols (APEP) are perspective material for improving temperature characteristics of liquid crystal devices [1,2]. Further improving of mezogen properties of the compounds are not possible without detailing of processes happening in the compounds. The attempt to define common appropriateness of interdependence between structure and physical-chemical properties of nematic liquid crystals, based on the APEP [1,2], shows the insufficiency of applying solely quantum-chemical methods. Applying of these methods does not allow learning of the interaction between molecules, which is important in systems where further oriental order appeares. In this case methods of the molecular dynamics, which allow to research behaviour of all molecules of the ensemble, are interesting.

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The presence of a substrate, which exists in the experimental research of electro-physical and optical properties of mezogen compounds, would promote further modelling to real conditions.

For that reason this work represents researches of behaviour of mezogen systems in the presence of a substrate with changing of temperature and composition of the cluster by molecular dynamic methods.

For realization of this work a set of programmes with common name–GROMACS [3,4], 3.2.1 [5] version was used. It is intended for modelling of behaviour of molecular systems with changing of the temperature and pressure. In the calculation standard parameters of calculation GROMOS-96 were used. The given programme was developed by the stuff of BIOSON Research Institute, Dept. of Biophysical Chemistry University of Groningen.

As the object of the researches clusters, which consist of molecules with negative mean dielectric constant anisotropy $\Delta\epsilon < 0$, were used. This model is a compound of 4-methoxybenziliden-4′-butylaniline (temperature of melting 294 K, temperature of bleaching 320 K [6], $\Delta\epsilon = -0,56$ [7]) (MBBA), polar compounds of the phenylpropargyl ethers of p-chlorphenols (melting temperature -338 K, bleaching temperature -390 K, $\Delta\epsilon = -0,81$ [2]) (PEC), the phenylpropargyl ethers of p-iodinephenols (melting temperature -380 K, bleaching temperature -410 K, $\Delta\epsilon = -0,52$ [2]) (PEI), the phenylpropargyl ethers of p-fluorinephenols (melting temperature -306 K, bleaching temperature -326 K, $\Delta\epsilon = -0,19$ [2]) (PEF) and non-polar compound of the phenylpropargyl ethers of p-cresol (melting temperature -333 K, bleaching temperature -351 K, $\Delta\epsilon = -0,35$ [1]) (PEK). For decreasing of impact of the boundary conditions the following sizes of studied cluster: MBBA –($13 \times 13 \times 13$ molecules), PEC, PEI, PEF –($14 \times 14 \times 17$ molecules), PEK –($13 \times 13 \times 17$ molecules) were used.

Taking into account that studied objects are in liquid state forming of the cluster was conducted by putting it in one cell, which eliminated giving periodical border conditions [3–5]. In this case for its forming a special programme was created, which allowed to calculate features of location of molecules in such an ensemble.

In construction of the cluster all experimental and theoretical results of the research were considered [1–2]: antiparallel location of close molecules and characteristic location of liquid crystals in a crystal state ("head to tail") [8] was considered, which in case of translation moving in a liquid state can bring to a parallel location of benzyl rings of close molecules. The distance between atoms of the nearest molecules ∼3–4Å was also accepted, which is typical for liquids [9].

In the clusters group conceptions of construction **T-coupling group** and **Freeze group** [5] 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 molecules that belong to the appropriate border of the initial cluster were used as the substrate. These molecules were chosen as the freeze group. It was assumed that adjoining layer of molecules to the real substrate is the reiteration of its relief.

The dispersion interaction of Lennard-Jones potential and Coulomb interaction were used for modelling [5].

The temperature effect was realized according to Berendsen scheme [5]. In the research a standard set of parameters (input.file) was used [5]. It considered coulon 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 ps.

For getting information about the order a number of programmes were created.

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 lying on their longitudinal axis. In defining a number of molecules N located in a particular angle (10°) 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.

A model of molecule with cylindrical symmetry was used for the calculation of the magnitude of the order parameter [6].

The distribution function $\mathbf{D}(\alpha)$ defines the number of pairs of molecules whose longitudinal axes make an angle α in relation to each other. $\mathbf{D}(\alpha)$ calculation was conducted by giving the radius of the area, in which the studied molecules were located. Analogical calculations were done for all molecules of the cluster. Each pair of molecules is counted only once. 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. The distribution function

D(α) is plotted in polar coordinates. The origin of the angles is taken on the coordinate axis OY: the angle from 0° to 90° was calculated clockwise and from 180° to 90° 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 studied 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_{inf} of the cluster. Knowing the whole distribution of molecule location is can define the magnitude S for each cluster after temperature annealing using Shennon formula [10].

The programme for calculation of cluster compound energy $\mathbf{E}_{\mathrm{b}}$ 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 [5].

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

2. INFLUENCE OF TEMPERATURE ON THE BEHAVIOUR OF MBBA MOLECULES

For optimization of modelling conditions of mezogen compounds in case of temperature annealing clusters with MBBA molecules were used as the object.

The temperature dependence of the volume V(T) is almost insensitive to r_{vdw} ($r_{\mathrm{vdw}} = 0{,}85$; 2; 3; 4; 5 nm) and exhibits an inflexion point at the phase transition temperature (they are shown on the Fig. 1). Negative magnitudes of P(T) in all magnitudes of r_{vdw} were observed only on OZ, that is expanding of the cluster was mainly done in that direction of the substrate.

Decreasing of curves S(T), D(T), N(T), E_{b}(T) is typical with increasing of temperature begining with the temperature close to melting temperature (Figs. 1–3, 5). However for S_{inf}(T) increasing is typical (Fig. 4). At variation of r_{vdw} character of the curves does not have significant changes in the melting temperature area, but in the area of bleaching temperature the additional bends appeare (see Figs. 2, 4).

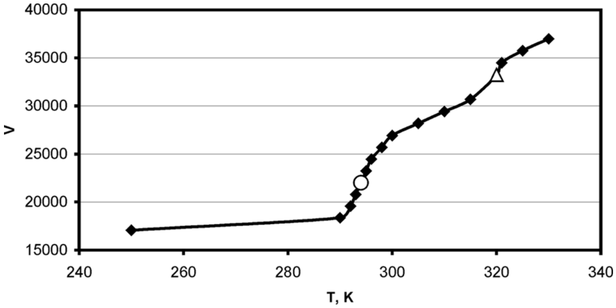


FIGURE 1 Temperature dependence of box with cluster of MBBA. $[V] = {}^{*}10^{27}$ M^3.

On Figure 2A at the parallel annealing, when one and the same initial cluster is heated with different temperatures, S decreases slowly with increasing of temperature in comparison with consecutive annealing (curves **pp-0,85 nm** and **p-0,85 nm** respectively). At the same time the change of orientation affects also the change of S: at

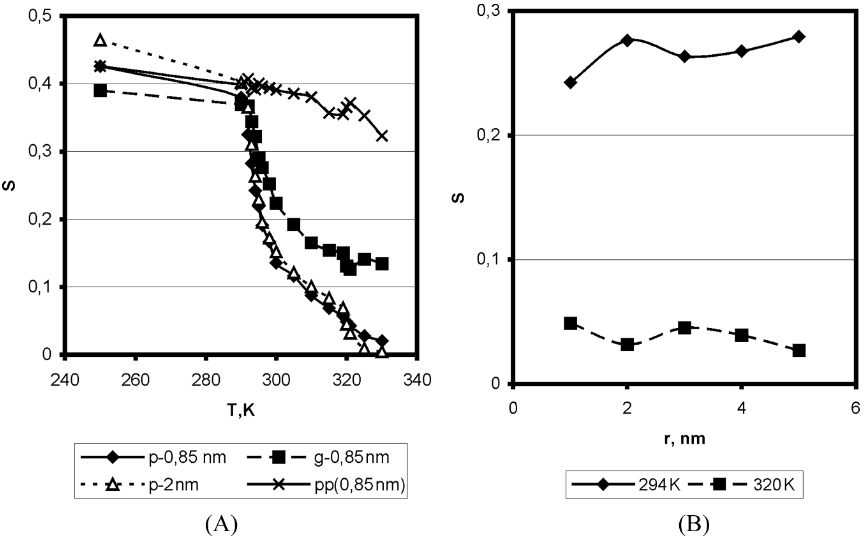
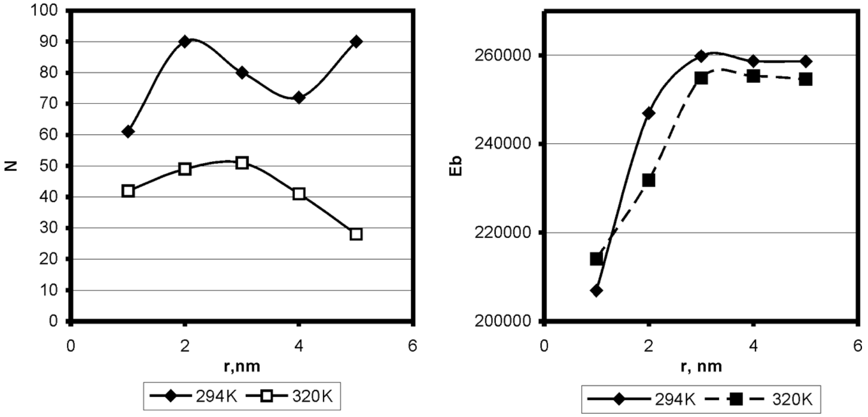


FIGURE 2 Temperature (A) and r_{vdw} (B) dependence of S of MBBA: p and g – planar and homeotropically orientations, pp – planar orientation and parallel annealing. 294 K and 320 K – melting and bleaching temperatures accordingly.



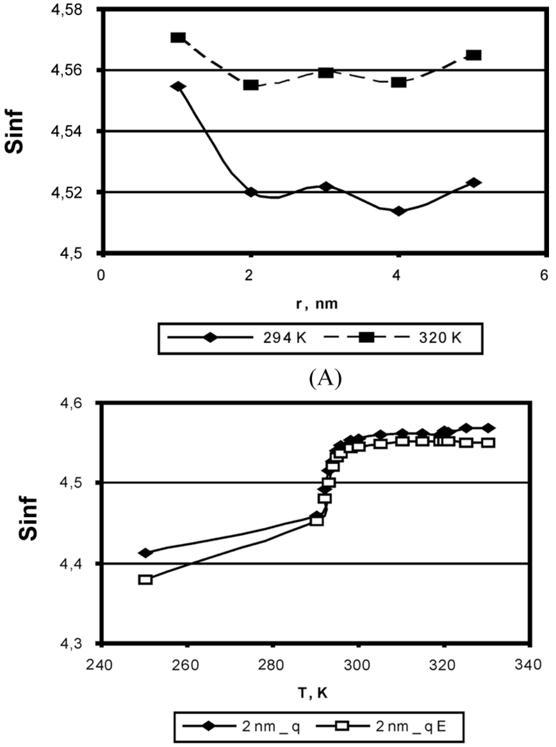
(A) (B)

FIGURE 3 The r_{vdw} dependence of N (A) and Eb (B) of MBBA at melting and bleaching temperatures. $[Eb] = kJ\ mol^{-1}$.

the homeotropical orientation of substrate (curve **g-0,85 nm**) S also changes slowlier in comparison with the case of planar orientation (curve **p-0,85 nm**). The influence of orientation depends on different interaction of molecules with molecules of substrate of the closest molecules of the heated cluster. In case of homeotropical orientation interaction should be stronger because of location of "head to tail" molecules.

In the area of the bleaching (320 K) with increasing of r_{vdw} (curve **p-2 nm** at the Figs. 2A and 2B) more distinguished bend appeares. Such a change (curve **p-2 nm** at the Fig. 2A) happens at the giving of charge distribution on the atoms of molecules in accordance with the given quant-chemical data (MNDO of MOPAC 6.0). As it is shown on Figure 2B the most visible changes happens when $r = 2$ nm, 5 nm. Magnitudes of the N(T), E(T) and S_{inf} from r_{vdw} (see Figs. 3B and 4A) prove it. In that case, as it was emphasised before, at giving of charge distribution to the atoms in the area of the bleaching a visible bend of the curve appeares (curve **q-2 nm** at the Fig. 4B).

For D(T) (see Fig. 5) left and right sides of the curve are not symmetrical. The given curves correspond to all states, which the cluster with molecules MBBA goes through in the annealing process. With increasing of temperature the magnitudes of D(T) with small angles change significantly and form of the curve changes to spherical. Significant meanings at small angles indicate that location of the main part of cluster molecules in relation to OY axis is "herring-bone"



(A)

(B)

FIGURE 4 r_{vdw} (A) and temperature (B) dependences of MBBA Sinf: planar orientation, 294 K and 320 K – melting and bleaching temperature accordingly. q – charge presence, qE – charge and electrostatic field presence ($E_z = 1B$, $E_x = E_y = 0$).

alternating antiparallel layers. It is possible to say about conservation of the main structure of the initial cluster. It is necessary to emphasize presence of intersection points in the left and right sides of the curve. Angular meanings correspond to the meanings of 50 degree area that is number of molecule pairs that have such an angle between longitudinal axes is the same in all the states. It is possible to predict the having embryo of crystal, which is the carcass for the further existence of the long distance orientation order.

Therefore the best approach to the experimental results at the modelling of the behaviour of the nematic liquid crystals cluster with $\Delta\epsilon < 0$ is necessary to conduct when $r_{vdw} = 2\,nm$ at giving of the charge state to neutral molecules in the whole.

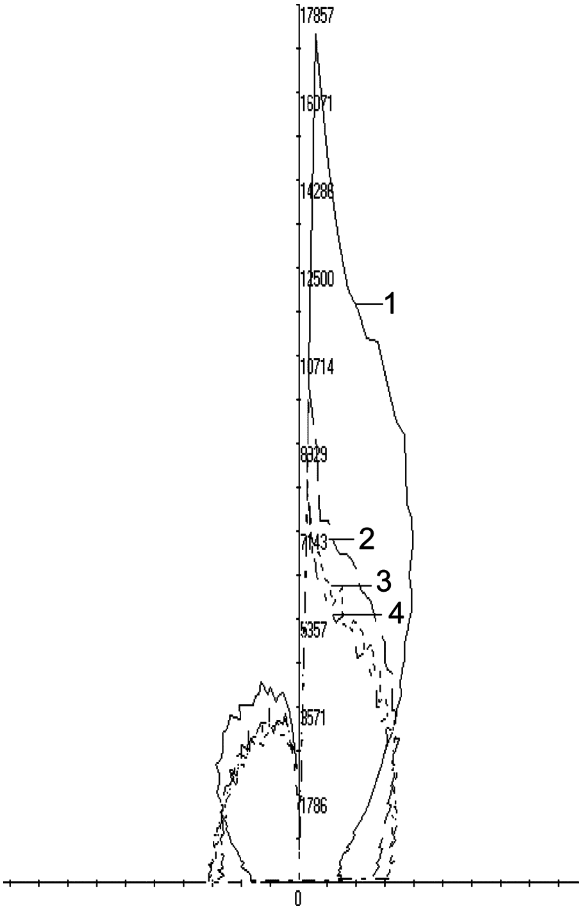
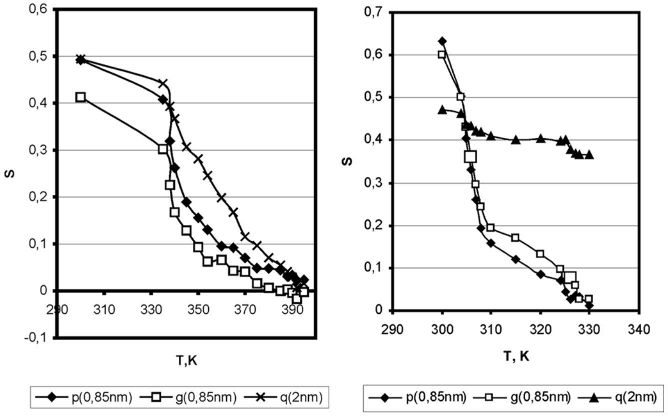


FIGURE 5 Temperature dependence D(T) of MBBA cluster in various conditions: crystal (1), melting (2), liquid crystal (3), and bleaching (4).

3. TEMPERATURE EFFECT ON THE BEHAVIOUR OF (APEP) MOLECULES

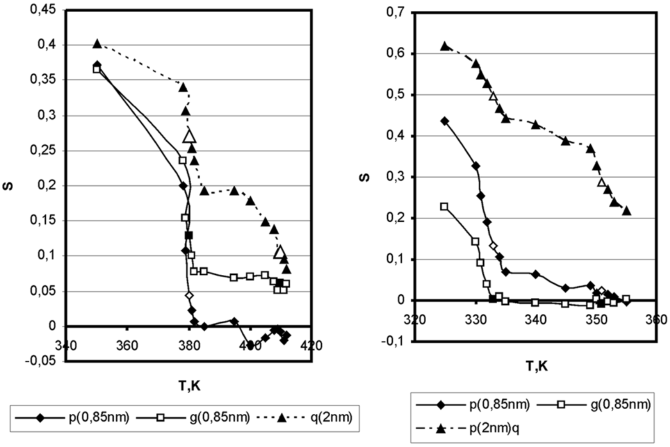
The research results of V(T) dependence for clusters with APEP molecules – PEC, PEK, PEI, PEF – showed that the curve changing is similar to the curve on Figure 1. As it follows from P(T) dependence for these compounds in general they expand in the direction of OX and OZ axes.

Increasing of the radius r_{vdw} to 2 nm brings to increasing of order rate in all clusters by the researched APEP compound, as it is shown



PEC
(a)

PEF
(b)



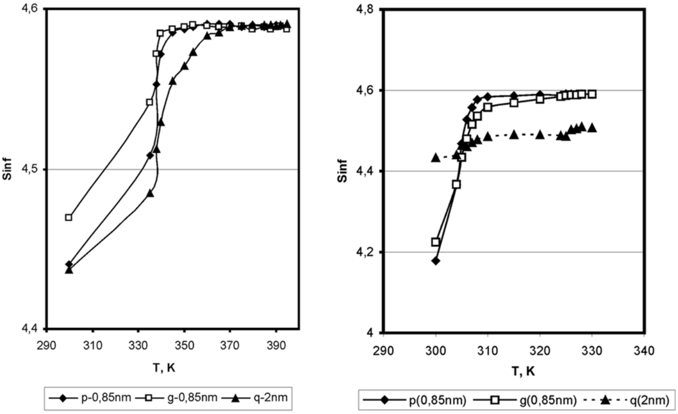
PEI
(c)

PEK
(d)

FIGURE 6 Temperature dependence of some APEP S at planar (p) and (g) – planar and homeotropically orientations.

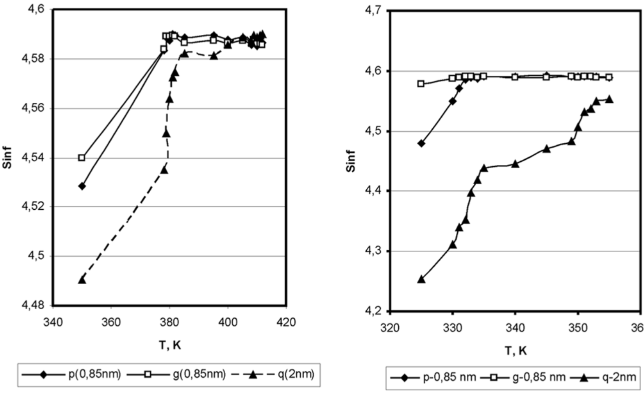
in Figure 6 (curves **q-2 nm**). Influence of substrate orientation is not significant (curves **p-0,85 nm** and **g-0,85 nm**) and in comparison with influence of the radius r_{vdw} and differernce for PEC and PEK compounds S was more at the planar orientation, and less for PEI and PEF. Probably that could be connected with special features of the interaction between molecules.

For compounds PEC, PEF and PEI presence of point of bend in the area of mesophase is typical (see Fig. 6): for PEC it is observed at the temperature of 354 K, for PEFD – 310 K, for PEI – 385 K. The bend on the curve for PEK is observed in the area of the phase changing. It can be connected with dimmers collapse, whose creation is typical for polar compounds, considering their antiparallel location in the initial cluster. For approaching the best correspondence of modelling to the experimental results of the location of the closest layer molecules in the direction OZ in relation to each other for clusters, which consist of PEI and PEK, with $r_{vdw} = 2\,nm$, was changed. In this case the meanings of the PEI molecules of the closest layers were located anti parallelly in relation to each other, and PEK molecules were parallel.



PEC
(a)

PEF
(b)

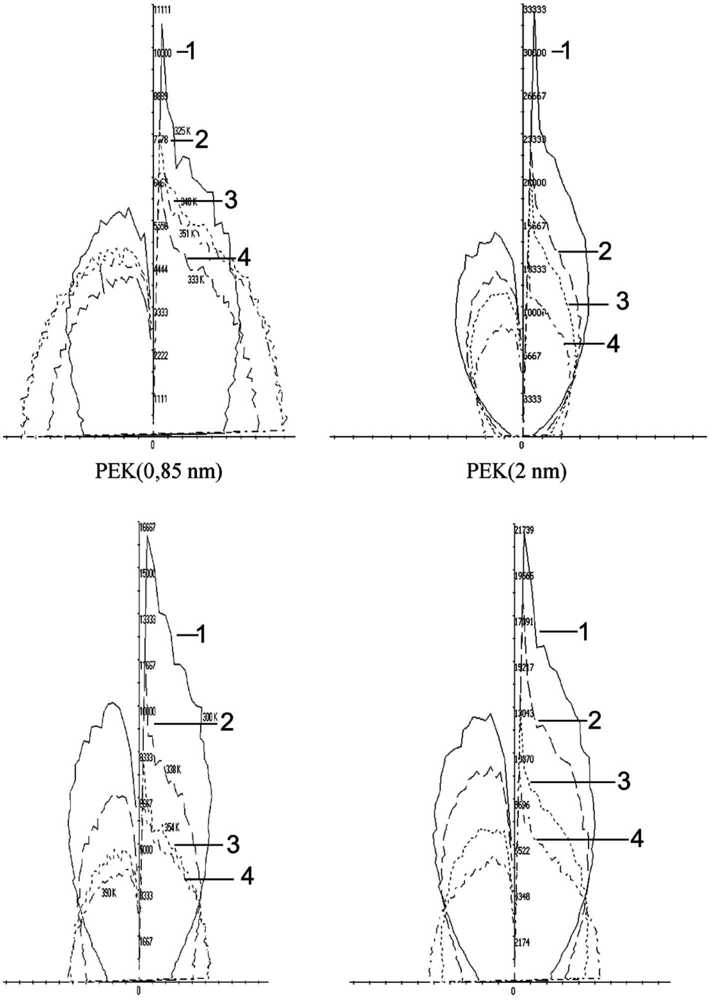


PEI
(c)

PEK
(d)

FIGURE 7 Temperature dependence of some APEP Sinf at planar (p) and (g) – planar and homeotropically orientations.

It is necessary to emphasize, that in case of PEI and PEK compounds r_{vdw} rising brings to a higher S(T) (see curves **q-2 nm** at Figure 6 (PEI, PEK)) correspondence of to the experimental data [1,2]. At the same time we can observe that this magnitude changing for the PEF decreases (curve **q-2 nm** at Fig. 6 (PEF)).



PEK(0,85 nm) PEK(2 nm)

PEC(0,85 nm) PEC(2 nm)

FIGURE 8 Temperature dependence D(T) of some APEP [PEC(300 K, 338 K, 354 K, 390 K), PEK(325 K, 333 K, 340 K, 351 K)] cluster in various r_{vdw} and conditions: crystal (1), melting (2), liquid crystal (3), and bleaching (4).

The $S_{inf}(T)$ research (see Fig. 7) proves the conclusion, that the greatest influence on the system order is realized through r_{vdw} increasing which brings to strengthening of interaction between molecules. Influence of substrate orientation is visible only at the first phase of annealing.

It proves at D(T) dependence for these compounds: at r_{vdw} rising the contraction of the curve shape happenes and the best permission of curves typical to different states is observed. (See Figs. 8, 9). In this

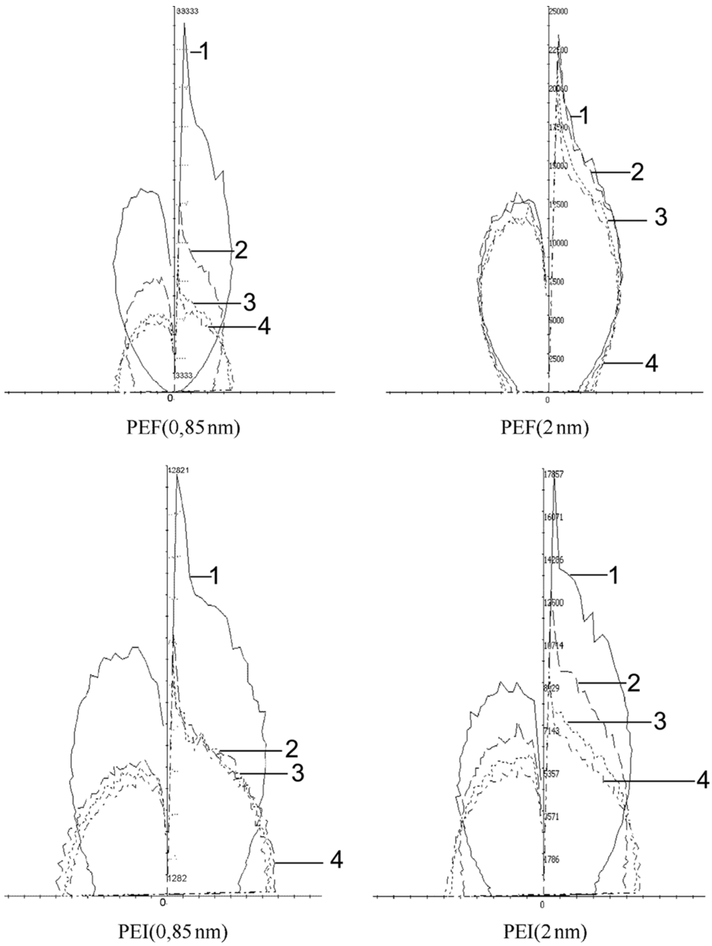


FIGURE 9 Temperature dependence D(T) of some APEP[PEI(350 K, 380 K, 400 K, 410 K), PEF(300 K, 306 K, 315 K, 326 K)] cluster in various r_{vdw} and conditions: crystal (1), melting (2), liquid crystal (3), and bleaching (4).

case the rate of order increases (Fig. 6). In case of cluster with PEF, as it was emphasized before, the order rate changes slightly and does not approach zero in the bleaching point, at the same time S_{inf} and S in this point have the marked bend.

As in the case with MBBA, in the right and left sides of the D(T) of all the curves at the Figures 8 and 9 the common intersection point is observed. It is distinctly shown on the curves which correspond to the highest approach to the experimental data.

The asymmetry of the right and left sides is smaller than in the molecule of MBBA. The ratio of the maximum meanings of this function right and left sides is ~1,7 (APEP) (Figs. 8, 9) and ~3, 9 (MBBA) (Fig. 5). At the disordering these ratios are ~1,4 and ~2, 0 respectively. It is possible to predict that the observed difference depends on the difference in the interaction of the molecules because of specials features in the composition structure of the studied compounds [11–14], which is also proved by entropy data.

As it was emphasized before, the difference between the left and right sides of the $\mathbf{D}(\boldsymbol{\alpha})$ curve depend on the location of the main part of the cluster in type of «herring-bone» with alternating layers of parallel and anti parallel molecules. Decreasing of this ratio for clusters with APEP molecules proves more even distribution in the area of molecules, and therefore it is proves the lower order as well.

Thus the experiments that were conducted on the computer modelling of the nematic liquid crystals behaviour shows the necessity of a correct choice of interaction between molecules. Influence of the molecules location at the initial state on the dynamics of the behaviour at the temperature effect was found.

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