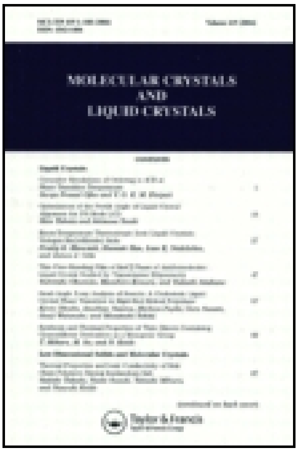

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Theoretical Analysis of Textures SmC on the Basis of C_8H_{17}-Benzylidene-C_6H_{13}-Oxypyrimidine on the Two Polyimides Films Surfaces

V. N. Ryzhov [a] , K. I. Guriev [a] & S. P. Kurchatkin [a]
[a] Saratov State Pedagogical Institute, Saratov, Russia

To cite this article: V. N. Ryzhov, K. I. Guriev & S. P. Kurchatkin (1997): Theoretical Analysis of Textures SmC on the Basis of C_8H_{17}-Benzylidene-C_6H_{13}-Oxypyrimidine on the Two Polyimides Films Surfaces, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 301:1, 169-175

To link to this article: http://dx.doi.org/10.1080/10587259708041763

Mol. Cryst. Liq. Cryst., 1997, Vol. 301, pp. 169–175
Reprints available directly from the publisher
Photocopying permitted by license only

THEORETICAL ANALYSIS OF TEXTURES SmC ON THE BASIS OF C_8H_{17} - BENZYLIDENE -C_6H_{13} - OXYPYRIMIDINE ON THE TWO POLYIMIDES FILMS SURFACES

V.N. RYZHOV, K.I. GURIEV, S.P. KURCHATKIN
Saratov State Pedagogical Institute, Saratov, Russia.

Abstract We have investigated C_8H_{17} - benzylidene - C_6H_{13} - oxipyrimidine- based SmC textures on the surface of two polyimides: I - poly - (4, 4' - oxybiphenylene) piromillitamide acid, and II - poly - 4, 4' - [2, 2'-bis - 4 (4'- aminophenoxy) phenylpropyl] - biphenyloxytetracarbonic acid. Polarized microscopic textures SmC on the above mentioned compounds differ greatly: the texture of SmC on the polyimide I is of "Chevron" type, and the texture of SmC on the polyimide II is of "microfan" type. Calculations of the intermolecular interaction energies enable to determine the nature of texture difference.

INTRODUCTION

Despite great progress in the LCD production technology, the method of liquid cristals' molecules orientation on the base surfaces remain mainly empirical up to now. Therefore an important teoretical problem of electrooptical LC device technology is investigation of LC molecules-substrate surface interaction character, which in most cases determines LCD performance. The aim of this paper is to perform theoretical analysis of two different C_8H_{17}-benzylidene-C_6H_{13}-oxypyrimidine-based SmC textures on two polyimide film surfaces: I - - poly - (4, 4' - oxybiphenylene) piromillitamide acid, II - poly - 4, 4' - [2, 2'-bis - 4 (4'- aminophenoxy) phenylpropyl] - biphenyloxytetracarbonic acid observed by polarizing microscopy.

Theoretical analysis of the SmC textures has been carried out by calculating potential energies of interaction between SmC molecule and molecular polyimide film surfaces, and calculation results have been used to determine preferable SmC molecular alignment on polyimide surface.

SmC TEXTURES

We have examined SmC textures in 1.7 μm flat capillary cells. To the inner surfaces of glass substrates polyimides I and II were applied by solution spinning, followed by imidization at 300°C. The resulting film thickness was 200-300 Å. After the imidization the films were rubbed by a method adopted in LCD technology. Parallel substrate rubbing directions were used. The cells were filled by vacuum or capillary method in isotropic phase, followed by cooling down to room temperature at the rate of 10^{-2} °C per sec.

Polarization microphotographs of SmC textures are shown in Figure 1. Polyimide I (Figure1a) gives an LC alignment with a minimum of textural features; as a rule, these are stripes caused by bulk inclusions (glass fiber spacers). The LC structure is identified as a "chevron"as evidenced by zigzag defects resulting from the cell deformation.

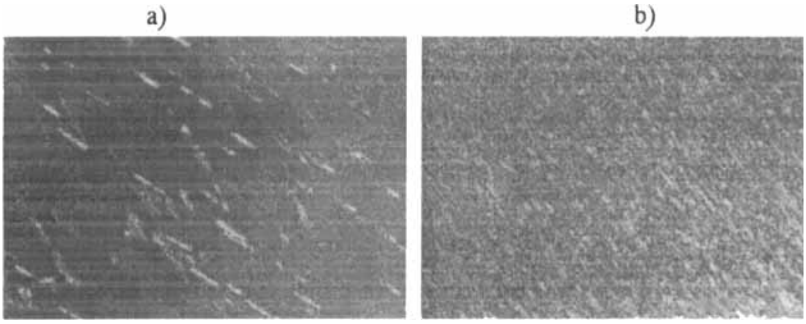

FIGURE 1 Polarized microscopic textures SmC on polyimide I (a) and polyimide II (b).

The texture of LC in contact with polyimide II appears to be essentially different. In this case "microfan" texture is repeatedly observed (Figure 1b). Here, the attempts to produce zigzag defects by mechanical cell deformation fail, hence it may be concluded that within "microfan" nuclei not only azimuthal director alignment, but also the SmC pretilt angle magnitude and direction change significantly. It should be noted that varying the polyimide rubbing force results in no noticeable change of alignment character.

The above evidence indicates the dominant influence of intermolecular interaction mechanism in contrast to viscoelastic mechanism of alignment that results from the surface topographical anisotropy. The role of the intermolecular interaction mechanism in an LC-aligning material system seems likely to be far more important for smectic LC phases owing to the higher ordering of their hypomolecular structure compared to, for instance, the nematic phase. Thus typical nematic (cyanobiphenyl, phenylcyclohexane) textures on the discussed polyimides have essentially the same alignment characteristics.

CALCULATION METHOD

We have calculated energies of interaction between SmC molecule and molecular surface model of polyimides I and II. The intermolecular interaction energy is calculated by the method based on the Rayleigh - Schrödinger perturbation theory [1, 2, 3]. The interaction energy, E_{int}, is approximated by

$$E_{int}=E_{es}+E_{ind}+E_{dis}+E_{rep},$$

where E_{es}, E_{ind}, E_{dis}, E_{rep} are electrostatic, induction, dispersion and valence repulsive energies, respectively. The electron net charges, the atomic dipoles, and the ionization potentials used in the calculation of the first three terms have been approximated by the CNDO/2 molecular orbital method. The valence repulsive energy which is not included in the perturbation theory was estimated from the repulsive part of the Lennard - Jones potential in which the coefficients of the repulsive terms were taken from the literature [4].

Geometrical data of SmC molecule were taken from the standard parameters. The choice of real polyimide conformation has presented the greatest difficulty. Some geometrical figures for the polyimides have been taken from the literature [5].

Electron structure of polyimide I and II monomeric molecular units has been calculated fragment by fragment, since they contain a large number of atoms. Polyimide I molecular fragment contains a rigid diimide fragment having planar structure, and benzylidene rings, rather flexible with respect to single bonds.

Polyimide II molecular fragment appears to be more complex; it has four (three oxygen and one carbon) atoms, around which through single bonds the molecular groups of the fragment can rotate, resulting in different conformations.

In calculating interaction energies we have built up a molecular model of polyimide surface layer of large enough area, above which a SmC molecule with an arbitrary spatial orientation has been placed. For example, polyimide II molecular surface has been presented as three polymer chains, each consisting of two monomers, and spaced at approximately 6Å. Figure 2 schematically presents the model of polyimide II molecular surface, on which SmC molecule with various spatial orientations has been placed.

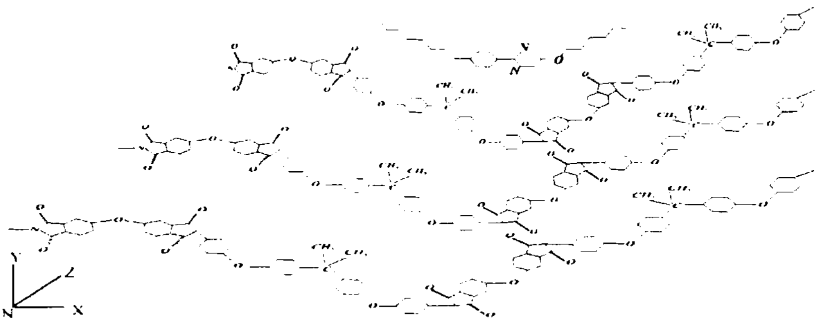

FIGURE 2 Molecular model of surface polyimide II and SmC molecule.

CALCULATION RESULTS AND DISCUSSION

The calculated distributions of electron density over the atoms of C_8H_{17}-benzylidene-C_6H_{13}-oxypyrimidine molecule are given in Figure 3. As seen from Figure 3, considerable negative electron charges are concentrated over nitrogen atoms of pyrimidine ring (-0.23 electron unit) and oxygen atom (-0.26 electron unit). Hence it is mainly these atoms that

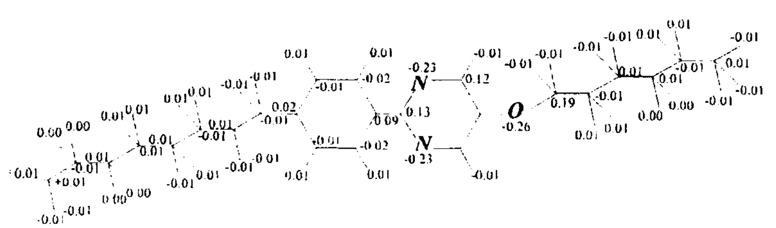

FIGURE 3 Absolute electric charge on the atoms of the C_8H_{17}-benzylidene-C_6H_{13}-oxypyrimidine.

determine the direction and magnitude of the molecule dipole moment, which is aligned with the long axis of the molecule from the pyrimidine ring to the benzylidene one. The contribution from the electron distribution of alkyl groups to the dipole moment is small. Valence electron density of polyimide II monomer is shown in Figure 4. The obtained electron distribution over atoms was then used in calculation of intermolecular interaction energies.

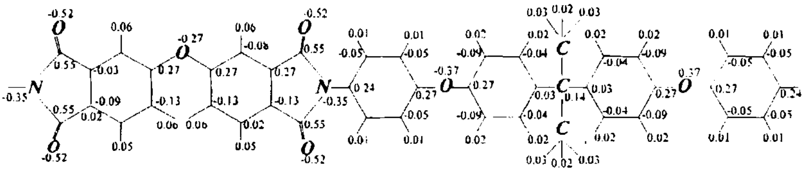

FIGURE 4 Absolute electric charge on the atoms of the polyimide II.

Below we present some results of calculation of SmC molecule-PolyimideII

TABLE I The dependences interaction energy on intermolecular distance along axis OY; other coordinates of molecule center SmC : X=10Å, Z=6.2Å.

Y, Å	E_{dis}	E_{ind}	E_{es}	E_{rep}	E_{int} , kJ mol^{-1}
3	-46.36	-4.63	0.45	53.48	6.65
4	-13.67	-1.75	0.12	2.06	-11.83
5	-5.28	-0.82	0.02	0.19	-5.23
6	-2.41	-0.43	0.00	0.03	-2.46
7	-1.23	-0.24	0.02	0.00	-1.26

molecular surface model interaction energies. In Table I are given dependencies of total potential interaction energies and their components (E_{es}, E_{ind}, E_{dis}, E_{rep}) on spacing for SmC molecule translation over the center polymer chain along 0Y axis. As can be seen from the Table I, the energy minimum corresponds to approximately 4Å, SmC molecule center (the middle of a cross-linking bond) being shifted by 10Å along 0X axis.

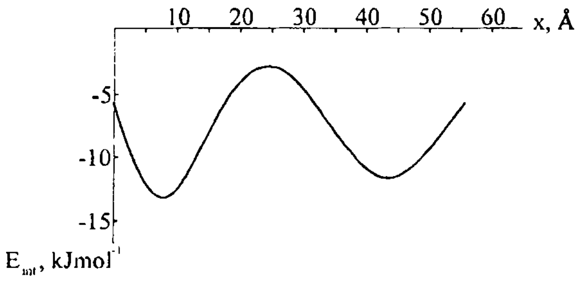

FIGURE 5 The dependencies of total interaction energy from horizontal displacement along of axis OX of the molecule SmC.

In Figure 5 are plotted the dependencies of interaction energies for an average 4 Å spacing between SmC molecule and polyimide II molecular fragment on the molecule center position along OX axis.

Table II lists the calculated interaction energies of the same systems for two different SmC molecule center positions depending on the azimuthal orientation of SmC long axis. From the Table II one can see a distinct energy minimum for about 15° tilt angles. The above results suggest SmC molecular align on polyimide II molecular surface layer with about 15° azimuthal tilt.

Calculations have also shown (the results are not given here) planar alignment of SmC molecule on polyimide I surface. This appears to be responsible for the difference between smectic phase textures on the two polyimide surfaces. The results indicate that in case of a smectic phase the presence of one-dimensional surface topography (microgrooves resulting from rubbing) is not sufficient to eliminate degeneracy in azimuthal orientation on polyimides with long monomers, such as polyimide II.

TABLE II The angle dependencies of the interaction energies from coordinates of molecule center SmC:

angle rotation respective OZ axis	E_{dis}	E_{ind}	E_{es}	E_{rep}	E_{int} , $kJmol^{-1}$
		X=17Å, Y=9Å, Z=6.2Å			
0°	$-13 \cdot 10^6$	-62.63	-2.57	$\sim 10^9$	$\sim 10^9$
5°	$-82 \cdot 10^4$	-31.17	-0.80	$\sim 10^6$	$\sim 10^6$
10°	-373.85	-3.52	-0.33	$\sim 10^5$	$\sim 10^4$
15°	-24.39	-1.83	0.22	9.51	-15.02
20°	-354.73	-7.80	1.11	$\sim 10^5$	$\sim 10^4$
25°	$-14 \cdot 10^5$	-505.14	-4.07	$\sim 10^7$	$\sim 10^6$
		X=15Å, Y=6Å, Z=6.2Å			
0°	-136.67	-4.93	0.59	$\sim 10^7$	$\sim 10^7$
7.5°	-29.32	-1.74	0.42	42.57	13.31
15°	-10.28	-0.84	0.42	1.19	-8.83
22.5°	-678.70	-2.65	0.48	$\sim 10^7$	$\sim 10^7$

We should mention in this connection the study [6] where experimental evidence has led to the conclusion that to obtain a good SmC texture it is essential to choose a polymer with short monomer chains and high degree of crystallinity.

The above analysis of the calculated data and experimental evidence, of course, cannot be considered as absolutely exact, since in our calculations we have used microscopic approximation, only one component of LC-mixture has been chosen, and also certain assumptions regarding polyimide packing conformation have been made. However we believe, such analysis of energy profiles in an LC-aligning material system is useful for predicting alignment effects and selecting alignment material.

REFERENCES

1. R.Rein, P.Claverie, and M.Pollak. Jnt. J. Quantum Chem., 2, 129(1968).
2. W.J.Baran and A.Les. Mol. Cryst. Liq. Cryst., 54, 273(1979).
3. V.N.Ryzhov, T.V.Lipovskay, L.A.Zacharova. J. Phys Chem. (Russia), 61, 1949(1987).
4. F.A.Momany, L.M.Carruther, R.F.McGuire, and H.A.Sheraga, J. Phys. Chem, 78, 1595(1974).
5. Polyimidy - class termostoikih polymerov, ed. H.Bessonov, (Leningrad, 1983).
6. B.O.Myrvold. Ferroelectrics, 85, 25(1988).