

THE ROLE OF HYDROGEN BONDING FOR INITIATION OF CHIRALITY, DENDRITES AND PHYSICAL GEL IN NEMATICS WITH SHORT RANGE SMECTIC C ORDER

B. Katranchev*, H. Naradikian, M. Petrov

Laboratory "Optics and Spectroscopy", Institute of Solid State Physics, Bulgarian Academy of Sciences, 72, Tzarigradsko Chaussee Blvd, 1784 Sofia, Bulgaria

The transition from an achiral (racemic) to a chiral liquid crystal (LC) state is studied on microscopic and macroscopic levels. The induced chirality in achiral LC (4,n-alkyloxybenzoic acids – n-OBA, n = homologue number) is explained by symmetry lowering of the liquid crystal system due to breaking of the hydrogen bonds (the transformation of the closed dimers in open dimers) caused by temperature or surface action variations. An oriented dendrite texture appearing at a definite temperature in the nematic phase of 7-OBA and 8-OBA, aligned by rubbed polyimide, is reported. We suggest a possible mechanism for the dendrite growth. A new supramolecular complex: n-OBA and 4-hydroxypyridine (HOPY) is investigated using FT far-IR spectroscopy and polarization microscopy. A mechanism of the complex induction is suggested.

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1. Introduction

Hydrogen-bonded liquid crystals (LC) and their complexes induced by mixtures have interesting properties, due to the intermolecular hydrogen bonds. Typical representatives of the liquid crystal substances constituted by hydrogen bonded in dimer molecules are 4,n-alkyloxybenzoic acids (n-OBAs), where n is the homologue number. The homologues with $7 \leq n \leq 13$ display both smectic C (S_C) and N phases.

n-OBAs show mesomorphic behaviour only because of the presence of a sufficiently high concentration of dimers, formed via hydrogen bonds, and their molecules can not be considered as rigid rods. Monomers and open dimers (in small percentages) also exist in addition to the closed dimers in the N phase of an n-OBA. The dimers can be closed (centrosymmetric, with two hydrogen bonds, symmetry C_{2v}) or open (with just one hydrogen bond) [1,2]. The short range smectic order, as well as the thermodynamic equilibrium between closed dimers, open dimers and monomers in the N phase of an n-OBA, obviously have a strong influence on the microscopic and macroscopic properties of this phase. Due to the temperature variation of the dimer–monomer concentration, different properties of the N phase at high and low temperatures have been reported [3–6]. These experiments demonstrated that in the N phase of 7-OBA and 8-OBA, one temperature exists, usually indicated as T^* , which divides the N temperature range into high temperature N_1 (with macroscopic properties of conventional N, e.g. MBBA, PAA) and low temperature N_2 (with smectic-like character).

The closed dimers may be represented as derivatives of the monomers, which are linked by two linear hydrogen bonds, as in Fig.1. The energy of bonding can be easily destroyed by temperature variation or surface effects. Thus, the closed dimers can be in a stable state, if they are

* Corresponding author: boykopk@issp.bas.bg

isolated from these external effects, which is not case in the LC. The dimerization is a process of minimizing the hydrogen bond energy (on cooling), while the opposite process - monomerization is connected with a high energy state (on heating). Consequently an intermediate process, energetically favourable under external (temperature in our case) effects, is the opening of the closed dimers. This occurs by rotation about one of the hydrogen bond axes, thus forming open dimers or at higher energy, 'free' monomers (Fig.1). The open dimers as well as the 'free' monomers are amphiphilic molecular forms (polar heads and hydrophobic tails). They can participate in H-bonding, thus providing supramolecular forms known as oligomers.

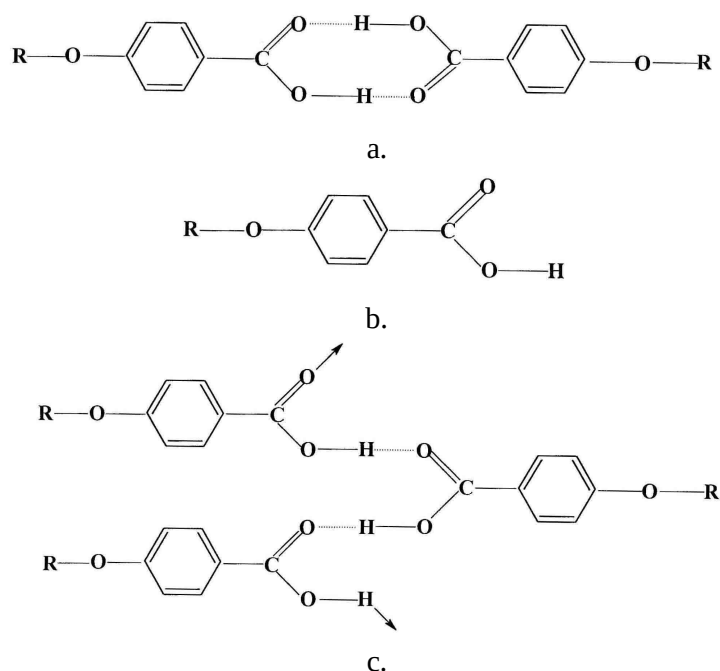


Fig. 1. Oligomer development by temperature variation for 8-OBA. The closed dimer - a; the monomer - b and oligomers - c.

2. Experimental results

Realization of supramolecular LC complexes, using the self-assembly of n-OBA and 4- hydroxypyridine (HOPY) fragments through intermolecular hydrogen bonding, is very important. Such complexes, besides being suitable for applications typical of conventional liquid crystals, also possess better mechanical properties. In such complexes, a n-OBA operates as a H-bonding donor and HOPY serves as a H-bonding acceptor, thus forming a non-ionic electric state, suitable for dielectric reorientation [7].

Using the hydrogen bonding ability of a n-OBA with HOPY, as well as with hydrophilic or hydrophobic orienting surfaces, we explore both by microtextural polarization analysis and FT-IR spectroscopy the macroscopic properties (e.g. dendrite growth) and particularly the chiral characteristics of these complexes. Consequently we expect, by the possible hydrogen bonding between n-OBA and HOPY, to provide building blocks (structure units) of the n-OBA–HOPY complex with underlying amphiphilic properties, implying a majority of polar heads and non-polar tails. We cannot imagine the exact chemical structure of these building blocks, but in any case, due to the amphiphility of the structural units, an aggregation (self-assembling) of the system is expected. The aggregation power of the complex strongly depends on the concentration, thus providing evolution of the complex growth from a pure liquid crystal state (fluid chains) through an intermediate state into a final gel (rigid chains) state. The biphilic dipole (free monomer) can easily be attached with its polar head on a hydrophilic surface (PVA), or be attached by the non-polar chains on a hydrophobic surface (PI).

In the present experiment, the parameters driving the aggregation properties of a n-OBA–HOPY complex are the temperature, the concentration and the surface coating. By their variation, we control the macroscopic properties of the complex. By a phase diagram study, we detect the most suitable concentration in which an effective chirality in the N and S_C states, as well as in the gel state can be obtained.

The important problems of such obtained complexes are the optical anisotropy and induced chirality. The symmetry change (due to deformation of the hydrogen bonding) of the structural units of n-OBA–HOPY results in the chirality. It implies that this structural unit, constituted by n,OBA–HOPY hydrogen bonding, is non-centrosymmetric or an axis of second order is induced - a condition for chirality and ferroelectricity. In respect of the optical anisotropy, we can say that from the underlying birefringence of the liquid crystal state, the system passes into an optical isotropic state-gel.

In this work, we analyze the spectral behavior of the complex expressed by the hydrogen bond state variation. This variation is provided by the induced chirality. In the pure liquid crystal state, the basic vibration deformation is the stretching one, appearing at 87 cm^{-1} . In the mixing process, the pure stretching is depressed and the hydrogen bonding is broken, so that vibration out of the plane of the dimer ring occurs. On a structural level, this is the process of nucleation of the chirality-rotation of the benzene ring parts around the intact hydrogen bond during opening of the closed dimers. Such built-in chiral units serve as nuclei for macroscopic chiralization of the complex n-OBA–HOPY [8].

By FT far-IR analysis, we detect the hydrogen bond variation which follows the process of chiralization, providing a domination of the vibration perpendicular to the dimer axis-s polarization. In such way, we detect the hydrogen bond stretching deformation, expressed in the spectra by corresponding maxima and minima in the trend $I(T)$. By the coordination of the maxima and minima of the spectra with the textures, we found that they indicated both a structural transition between the achiral and chiral states and a transition between the liquid crystal and gel states. Figs.2 and 3 show the chiral 8,OBA–HOPY texture and induced “gel” state respectively.



Fig. 2. Chiral 8,OBA–HOPY texture.

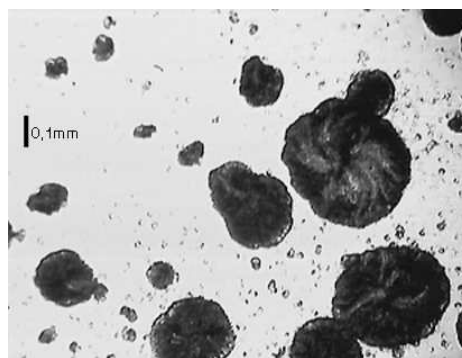


Fig. 3. Induced “gel” state in 8,OBA–HOPY.

We relate the main macroscopic property of the gel observed here to physical gel. Such a gel is characterized by both suppressed fluidity and thermal reversibility.

The local orientation of the assumed building units can more or less provide the selection of the microtextural pattern. We detected such selection, expressed by the growth of the dendrite texture [8]. Thus the role of the hydrogen bonding, besides chirality, is clearly revealed in this macroscopic effect - dendrite formation in the N. Such texture is seen in Fig. 4. The dendrites grow with two main branches, strictly following two directions forming angles of about 30° and 60° with the ‘easy’ direction n_0 ($\mathbf{n}$ is the nematic director).

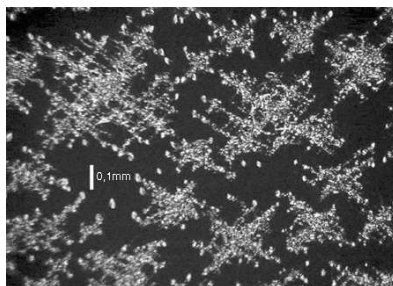


Fig. 4. Dendrite emergence in the nematic state of OOBA, a polyimide well aligned by rubbing.

Considering the phenomenon on the molecular and supramolecular levels, a possible mechanism (on the basis of a hydrogen bonding analysis) for the dendrite growth in the two preferred directions with respect to the ‘easy’ axis could be suggested. This mechanism is similar to that above for the n-OBA-HOPY complex, and consists of aggregation (supramolecular complex formation) caused by the monomer, open dimer and oligomer coalescences, provided by the amphiphility of these molecular forms. The difference between dendrite and n-OBA-HOPY complex formation is, however, that the dendrites grow in two strictly definite directions. Starting with the basic geometry shown in Fig.1, which we used for microstructural analysis of the chiralized, n-OBA-HOPY complexes, one can note two directions in the construction of the building blocks, which resemble the preferred directions of the dendrite growth in respect to the easy ‘axis’, i.e. 30° and 60° . The direction of 60° is half the angle between the C=O and C–O in the dimer ring, thus determining the dendrite growth direction.

3. Conclusions

We assume that the polyimide treatment constrains the ‘rigid’ molecular part, i.e. the benzene rings, to follow the ‘easy’ direction. Besides the molecular structure, the other important parameter controlling the dendrite growth is the surface treatment. To study the role of this, we repeated the experiment with the same substances, changing only the PI (hydrophobic) surface treatment with PVA (hydrophilic) surfaces. We were unable to observe dendrites using these orienting substrates. Therefore, the suppression of hydrogen bonding of the liquid crystal molecules with the hydrophobic PI surface could favour dendrite nucleation.

Finally, the dendrite growth and complex n-OBA-HOPY (or gel) realization are products of the significant role of the hydrogen bonding, providing a distinct class of LC. Furthermore, chirality could be easily induced in achiral LC n-OBAs, even when they are not mixed with chiral dopants (for details see [9]) due to the lowering of the LC system symmetry by surface and bulk deformations.

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References

- [1] R. D. Corsar, C. Atkinson, *J. Chem. Phys.* **54**, 4090 (1971).
- [2] B. Deloche, B. Cabane, *Mol. Cryst. Liq. Cryst.* **19**, 25 (1971).
- [3] M. P. Petrov, P. D. Simova, *J. Phys. D*, **18**, 239 (1985).
- [4] M. Neubert, A. De Vries, *Mol. Cryst. Liq. Cryst.* **145**, 1 (1985).
- [5] S. Frunza, A. Frunza, A. Sparavigna, M. P. Petrov, S. I. Torgova, *Mol. Mater.* **6**, 215 (1996).
- [6] M. Petrov, A. Braslau, A. M. Levelut, G. Durand, *J. Phys. II Fr.* **2**, 1159 (1992).
- [7] T. Kato, T. Uruy, F. Kaneuchi, C. Jin, J. M. Frechet, *Liq. Cryst.* **14**, 1311 (1993).
- [8] J. P. Marcerou, M. P. Petrov, H. M. Naradikian, H. T. Nguyen, *Liq. Cryst.* **31**, 311 (2004).
- [9] S. Torgova, M. Petrov, A. Strigazzi, *Liq. Cryst. (UK)* **29**, 747 (2001).