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To cite this version:

J. Gilli, M. Kamaye, P. Sixou. BIPHASES, BLUE PHASES, AND SHAPES OF NUCLEATION. Journal de Physique Colloques, 1990, 51 (C7), pp.C7-183-C7-188. <10.1051/jphyscol:1990718>. <jpa-00231117>

HAL Id: jpa-00231117
https://hal.archives-ouvertes.fr/jpa-00231117
Submitted on 1 Jan 1990

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BIPHASES, BLUE PHASES, AND SHAPES OF NUCLEATION

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Résumé- Nous avons étudié les phases bleues obtenues avec un oligomère mésomorphe polydisperse à chaînes latérales et nous pensons qu'elles peuvent être décrites à partir d'un modèle de type "microémulsion": la tendance connue de ce genre de matériau impur à former une biphase conduit probablement ici à la ségrégation des deux composantes isotrope et anisotrope en deux sous-réseaux imbriqués. Ce type de modèle conduit à se poser le problème plus général de la forme de nucléation de la phase cholestérique: dans le cas de ce même matériau chiral en solution, cette dernière s'opère par l'intermédiaire d'une très grande variété de formes géométriques.

Abstract- We have studied blue phases with a side chain polydisperse cholesteric oligomer and we think they can be described by a "microemulsion" model: the known tendency of this kind of impure material to form a biphase brings probably here to the separation of the isotropic and anisotropic phases in two associated networks. This kind of model is related to the more general problem of the cholesteric shape of nucleation: in the case of a solution of this same material, the nucleation is operated with a great number of different geometrical shapes.

INTRODUCTION

Many recent experimental works have described the blue phases behaviours of small molecules liquid crystals, in a narrow temperature range, between the small pitch cholesteric and isotropic phase.

For a strong enough chirality, three different blue phases, BP III, II and I are successively observed when temperature is decreased from the isotropic phase. Microcalorimetric measurements have shown (1) four peaks in this case, demonstrating the thermodynamic stability of these five different phases, separated by first order transitions. The observation of Kossel lines associated to convergent light diffraction in the visible domain (2) allows the identification of the $O^8$ and $O^2$ cubic symmetries of the BP I and BP II lowest temperature blue phases. Concerning BP III (blue fog) observed as a strongly light diffusing fog between microscope slides, no satisfactory description exists at the present time.
**Theoretical model**

From a theoretical point of view, a Landau-Ginzburg approach allows the prediction of this kind of tridimensional phases without being able to describe their favoured symmetries and their sequence with temperature.

A more geometrical approach, points out the double twist tube as an alternative to the classical frustrated cholesteric structure (3): a cylinder of this kind allows an elastic energy gain if its radial extent does not overstep a critical value of the order of the half cholesteric pitch. The geometrical stacking of these tubes needs the presence of elastically distorted connecting domains and above all, of singular lines with undefined director orientations (3).

These two models are consistent if we associate these connecting unfavourable regions with a decrease to zero of the local order parameter in the core of disclinations. But, and we think this particularly pertinent in the case of polydisperse polymeric material, a discontinuous core singular line model brings us to prefer a microemulsion model, for blue phase constituted by polydisperse compounds. In this model, two phase separated by a sharp interface, in a thermodynamic equilibrium, are coexisting in a temperature dependent proportion.

**Biphase**

It is well known in the case of mesomorphic polymeric materials generally constituted of coexisting slightly different molecular species associated to different transition temperatures, that anisotropic-isotropic first order transitions are performed by the intermediate of large temperature extent biphases (4). The first anisotropic component is enriched in high transition temperature \( T_c \) species, the isotropic one is enriched in low \( T_c \) species (we can note here that the same kind of process is unvolved in the case of very pure components in solutions). Cooling down from the homogenous phase, the occurence of the physical structure of this kind of biphase is generally operated through a classical process of nucleation, growth and coalescence associated to the possibility of minimising total free energy of the system by a decrease of the ratio of interface extent to anisotropic volume: this brings to the macroscopic separation of the two components. In some particular cases, however, the nucleating objects can undergo the necessity of limiting their growth to a critical size, this being associated to a complex volume and surface topological structure. (this is the case for the radial extent of a double twist tube). This kind of situation is probably able to describe the large temperature blue phase domain obtained by us (5) with a side chain cholesteric oligomer and in particular of BP III: as developed in the following, this model allows the understanding of the transition from the \( O^2 \) simple cubic symmetry to the \( O^8 \) centered cubic (BP II- BPI) with the decrease of temperature.
The shape of the nucleating objects

In the case of liquid crystal mediums, energetical contributions arise from the topological necessity of volume and/or surface defects or distortions and the nucleation problem is hugely more complex than the simple liquid one (case of smectics): a very thin energetic equilibrium exist here, between volume and surface contributions.

Two different extreme hypothesis have been proposed (6) to define the shape of the anisotropic objects constituting the first appearance of the first order transition isotropic- BP III.

- a spherical or quasi spherical form favourable by its lowered surface extent.
- an elongated one, as the double twist cylinder, whose volume elastic energy is now favourable.

Concerning the second hypothesis, it is necessary to limitate the tube longitudinal extent and to introduce point singular and/or curvature defects constituting connexion locus with other tubes by anihilation. The radial calibration phenomena is here clearly understandable but we don't think that nucleation of tubes of uncorrelated spacial orientations can easily give rise to a regular cubic network (an hexagonal or quadratic one being more probable).

The first hypothesis of globular objects is for us a better candidate and we can try to built such an object from a limited number of 3D oriented tubes along various symmetries axes (fig. 1). In this case the surface defects connectivity becomes tridimensional and able to bring to the BP II and I organisations (see fig. 2). The temperature dependent calibration is simply explained here by the constituting tube properties.

FIGURE1: the nucleating quasispherical objects are built as an association of a limited number of double twist tubes. (a): association of three cylinders, analogue of an O² node. (b and c): two different drawings of a possible dodecaedral node model for the BPlll nucleation.
FIGURE 2: a naive geometrical model for BPIII (a), and BPI (b), showing the possible relation between sphere and cylinders organisations: surface singular point defects being the possible connection locus between nucleating calibrated objects. The tube higher compacity network is constituted of tubes nodes that are the topological analogue of the nucleating globules.

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Table 1 gives the optimal compacities (% of tube volume/total volume) obtained with both hypothetical objects and seems to strongly suggest the observed phase behaviour: blue fog constituted of isolated "quasi spherical" globules, followed, for a 52% ratio, by a simple cubic network of spheres, the connexion of defects allowing now the 58% ratio for the sc cylindrical structure. The following sc-cc transformation BPIII-BPI is obtained through the occurrence of new diagonal defect connections between the cubic network nodes (~68%). We can also see that the validity of the spherical model decreases as the cholesteric phase is approached and it seems to predict more compact quadratic (78%) and hexagonal (90%) bidimensional tubes packing: it is interesting to remark that experimental observations of the first birefringent texture obtained from BP I seem to reveal an hexagonal character (see photo. a).

We give here briefly a few experimental results related from our point of view, to this "nucleation shape" problem: 
- We think that the progressive disappearance of blue phase when chirality decreases is probably associated to the geometrical and topological shape change of the nucleating objects.

- In the thermotropic main chain polymers case, the splay exclusion predicted by some authors (7) possibly favour a double twist tube nucleation and this is a possible explanation of the absence of blue phase behaviour in this case even when the cholesteric pitch is low enough.

- It is also known in some cases of diluted chiral polymeric main chain systems (probably able to undergo more easily splay distortions), that a physical gel can be obtained in the neighbouring of Ch - iso transitions (cf. biological systems as cellulosic derivatives (8)). We observed a comparable behaviour with an oligometric side chain polymer diluted in different particular solvents: few corresponding textures observed with a polarising microscope are associated here, with an elongated nucleation and the entanglements of these disordered tubes probably induce the anomalous viscosity and the strong optical diffusion observed.

- The use of this same diluted material with variable cooling kinetics, concentrations, etc, allowed us to observe a large variety of macroscopic nucleation shapes and the objects (see photomicrographies) are more or less calibrated.

PHOTOMICROGRAPHIES: Gr=700, taken with a polarising microscope in transmission for a,b,c,d,e and in reflexion for f. (a): an "hexagonal" texture obtained after 12 hours annealing of BPII. (b,c,d,e): elongated, disc like, torus like, and helicoidal shaped nucleating objects obtained with variable temperature kinetics, and concentration, of a side chain cholesteric polymer in solution, cooling down from the homogenous isotropic phase. (f): at a higher polymer concentration, star shaped Bragg reflecting objects are obtained.
Conclusion:

The unlarged observation of blue phase temperature domain with polydisperse polymers, solutions, and more generally with cholesteric impure material have brought us to describe blue phases in term of two phase microemulsion equilibrium. This kind of approach put forward the general opened question of the chiral nematic shape of nucleation and the problem of surface/volume topology of finite chiral objects.

From another point of view, these reflexions associated to the possibility of supercooling tridimensional organisations under the glass transition of our polymeric material strongly suggest diffraction experiments able to reveal the exact features of the repeat units of the blue phase "crystals".

REFERENCES:


