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J. M. Gilli [a] , M. Kamayé [a] & P. Sixou [a]
[a] U.A. 190, Physique de la Matière Condensée, faculté des sciences, Parc Valrose, 06034, NICE Cedex, France
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Quenched Blue Phase, Below the Glass Transition of a Side Chain Polysiloxane: Electron Microscope Studies

J. M. GILLI, M. KAMAYÉ and P. SIXOU

U.A. 190, Physique de la Matière Condensée, faculté des sciences, Parc Valrose, 06034 NICE Cedex, France.

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Blue phases are easily observed over an extended temperature range with an oligomer, side chain, cholesteric copolysiloxane. The use of four different samples of variable copolymerisations allows the observation of the progressive disappearance of the blue phases when the pitch increases. The shorter pitch sample shows the well known sequence of three blue phases when temperature is decreased from the isotropic phase. Some characteristic coloured platelets are easily supercooled below the glass transition temperature of this material and a simple microtome and resin inclusion technique allows the observation of these quenched blue phase domains with a transmission electron microscope.

Keywords: blue phase, side chain, cholesteric

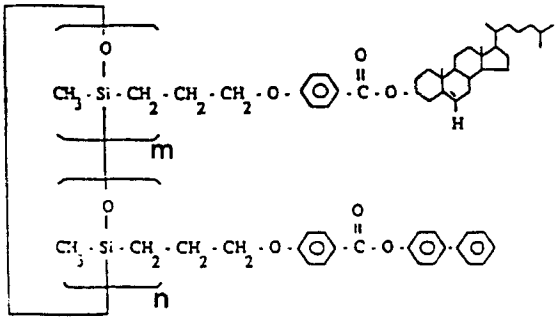
INTRODUCTION

Recent experimental work on small pitch cholesteric monomer material, allowed the understanding of the cubic structure of BPI and BPII,[1,2,3] the two lowest temperature blue phases. But many questions remained open concerning BPIII and transitional behaviours between the five different phases present in a narrow temperature range.

The oligomeric nature of the cholesteric material investigated gives us the opportunity of an easier observation of these small-pitch cholesteric behaviours, with an extended temperature range and slower kinetics. Moreover, this last fact, and the existence of an above room temperature glass transition with this material allowed us to easily quench a three dimensional periodic structure probably intermediate between BPI and the cholesteric one dimensional periodic one.

MATERIAL

The considered industrial oligomers are described in the following formulae.



Each sample is in fact a polydisperse blend with $1800 < Mn < 2200$, $3 < n + m < 7$ and $Mw/Mn < 1{,}3$. Four different statistical copolymerisation rates were available corresponding to cholesteric pitches of about 290 nm (A), 315 nm (B) 345 nm (C), 370 mn (D), measured near the transition to BPI. The electron micrography studies are concerned with the A sample only.

EXPERIMENTAL

Reflexion and transmission textures from glass slide samples were obtained with polarising optical microscopy. Light wavelengths under normal incidence were measured by the use of a computer-driven monochromator associated to the microscope.

The glass slide samples with blue phase platelets were quenched by a simple contact with a metallic plate at room temperature. The polymeric samples with glittering blue phase platelets quenched at room temperature and directly visible, by naked eye on the glass slides, or with the polarising microscope, were scratched and included in a resin, before microtome cutting and observation with an electron microscope used in transmission mode.

OPTICAL MICROSCOPY AND SPECTROSCOPIC RESULTS

As shown in Reference 4, we studied the normal incidence reflection wavelengths of the four samples versus temperature T given in Figure 1. The blue phase reflections were studied with a slow decrease (O, 1°C/mn) of temperature T. The cholesteric reflections were obtained with a slow increase of T. The textures were observed simultaneously. Far from the cholesteric appearance easily detected with birefringence the behaviours obtained are very comparable to the monomers ones.[5] With the A sample we observed successively in reflection a poorly reflecting "blue fog" from which single coloured platelets are nucleating. These blue platelets are

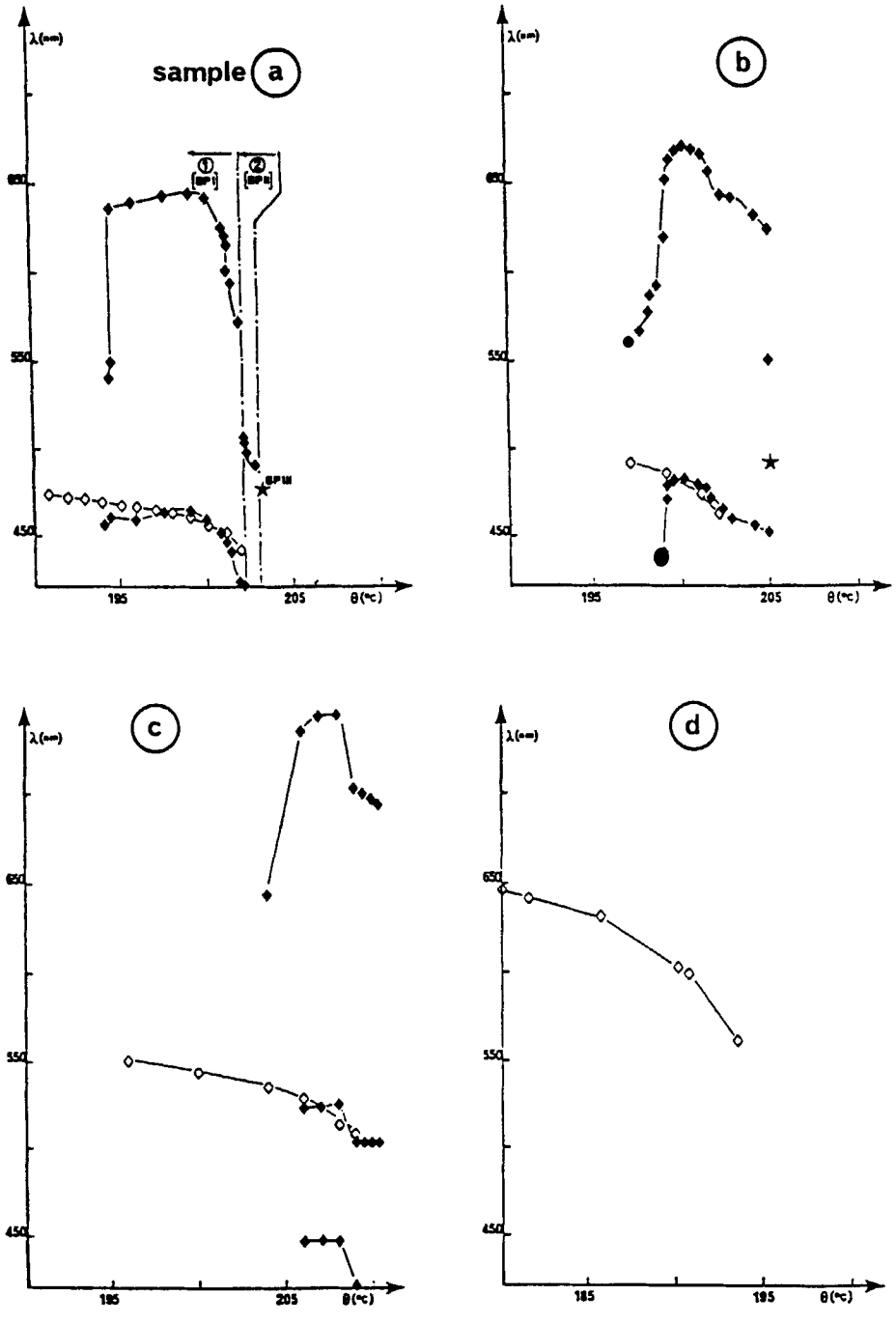


FIGURE 1 Wavelength reflected between crossed polars under normal incidence, with A, B, C, D samples versus temperature. Black diamonds; slow decrease of the temperature (5°C/h) from the isotropic phase. White diamonds; increase of the temperature in the cholesteric phase, up to the appearance of the first blue phase platelets. Stars; broad peak reflection near the isotropic phase (BPIII).

in their turn undergoing a first order transition, shifting strongly their colour to the red and being striated by a dislocation process. All through this process the reflection wavelength undergoes a red shift, which is discontinuous at the BPIII-BPII and BPII-BPI transitions. At BPII-BPI transition some other bright platelets, coloured with a shorter wavelength are also appearing. The wavelength ratio of these different simultaneously observed platelets allows us to identify the presence of 200, 110, and 211 reticular reflections as in monomer materials.[6] The 211 is only observable with the C sample, due to the red shifted pitch.

EFFECT OF THE PITCH INCREASE

As in some monomer materials[6,7] the increase of the pitch as we go through A to D samples shifting the obtained blue phases reflections to the red is also responsible of the progressive disappearance of these phases in the same pitch range: A and B samples allowed the full observation of the three different blue phases, with a reduced temperature extent for BPII and III in the B case, while with C, only BPI is observed and with D no more blue phases are observed.

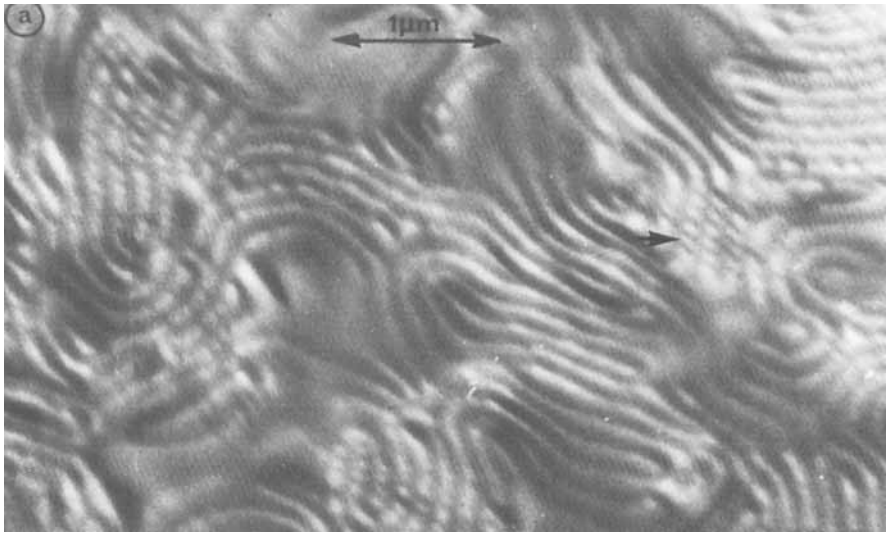
ELECTRON MICROSCOPY

Up to now, the rare existing studies of blue phases[8,9] and cholesteric phases[10] by electron microscopy were made by a "fast freeze"—"freeze fracture" and "metal replica" heavy technique, just allowing very few texture observations. In this case the contrast obtained is related to the fracture plane relief, enhanced by the shadowing of the oblique incidence platinium evaporation. On another hand, the freeze fracture planes observable by this method are only the low Miller index ones, easily recognised by their simple plane symmetry characteristics.

We present here observations of cholesteric and BPI quenched phases obtained by transmission on the chiral material itself. On one hand, the cuts realised at room temperature, with a soft material are made along random reticular planes as demonstrated by the very different symmetry aspects of the obtained textures (photomicrographs c, Plate 1 and d, e, f, g, h, i, Plate 2). On the other hand the origin of the electronic contrast obtained here remains an open question: the electron beam propagation being probably related to the local anisotropic biaxial tensorial order parameter integrated through the thickness of the cuts.

It is here important to remark that the obtained contrast is strongly dependent of the thickness of the cut: the thinner ones giving the better contrast. In the absence of a sophisticated model describing the interaction of the beam with our material, we can imagine that a thickness (typically 0.1–0.2 μm) less than the repeat unit of the probable quenched cubic phases obtained, leads to a non-averaged director orientation seen by the electrons, and consequently to plane periodic differences for their propagation.

Plates 1 and 2 shows examples of the different numerous textures observed by our simple experimental method:



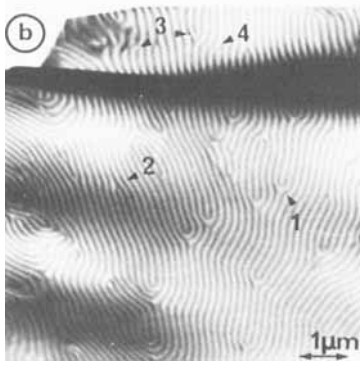
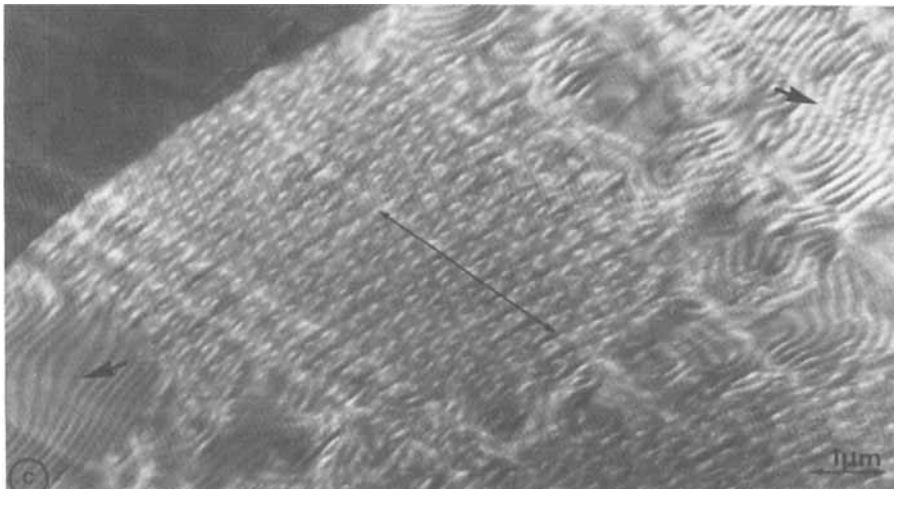


PLATE 1 Photomicrographs obtained with a direct electron transmission microscope observation of quenched A type cooligosiloxane cuts a few tenths of micrometer thick; a), b) observation of the layered cholesteric texture with an in-plane optical axis: the thin arrows of b indicate different identifiable defects of the structure; c) coexistence of probable cubic and cholesteric organisation. The large arrow up and right on the photomicrograph indicate a regular striation of the cholesteric layers probably reminiscent of BPI (see also the arrow of a). The other large arrow indicates a cholesteric region with optical axis perpendicular to the cut. The thin arrow shows lines originating from the cutting knife.



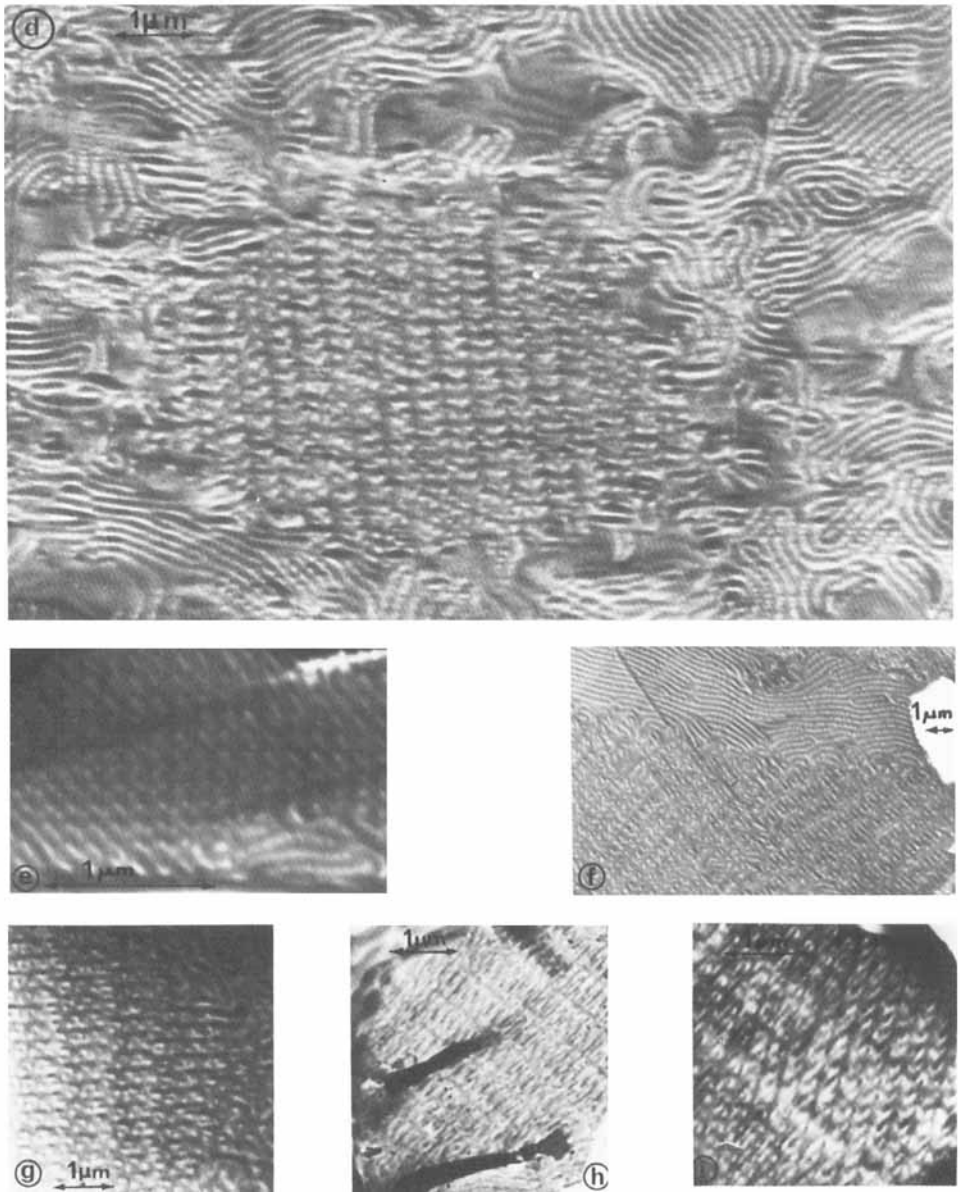


PLATE 2 Photomicrographs obtained with a direct electron transmission microscope observation of quenched A type cooligosiloxane cuts a few tenths of micrometer thick; d), f): coexistence of the classical layered cholesteric textures with probable indifferent orientation O^{8+} planes allowing observation of interfacial region undergoing the spatial transition between these two phases; e), g), h), i): examples of the in plane bidimensional textures probably corresponding to a quenched O^{8+} organisation.

In photomicrographs a and b, Plate 1, we see domains transformed from the blue phase to the cholesteric one and the minimal spacing period between the layers is in complete agreement with the half pitch of the cholesteric phase measured by spectroscopic method ($\lambda = Pn$). The quality of the obtained cholesteric organisation is extremely variable from one domain to the other as seen in the different photomicrographs. The photomicrograph b Plate 1 is particulately useful for the observation of the edge dislocations of the cholesteric layers[11] and the high frequency of the "1" type with a P Burger vector is probably associated with a $\lambda^-\lambda^+$ type (without director singularity in the core). It seems possible on this ground, to associate the white regions of the photomicrograph (and the black ones on the negatives, corresponding to the irradiated regions) with a director orientation perpendicular to the plane of the Figure. Other $P/2$ Burger vector dislocations are also observed on the same photomicrograph, the "2" type being probably a $\tau^-\lambda^+$ and the "3" ones a $\tau^+\lambda^-$ ($\tau^+\tau^-$ and other high strength dislocations are observed elsewhere). The "4" arrow shows the presence of a probable $\chi_{1/2}$ line. The cholesteric regions, also observable in photomicrographs a, b, Plate 1 and photomicrographs d, f, Plate 2 allowed to observe that the white lines are frequently regularly striated, (see for example the up and right arrow of photomicrograph c): we suppose that this strange texture correspond to a quenched intermediate situation between N* and BPI.

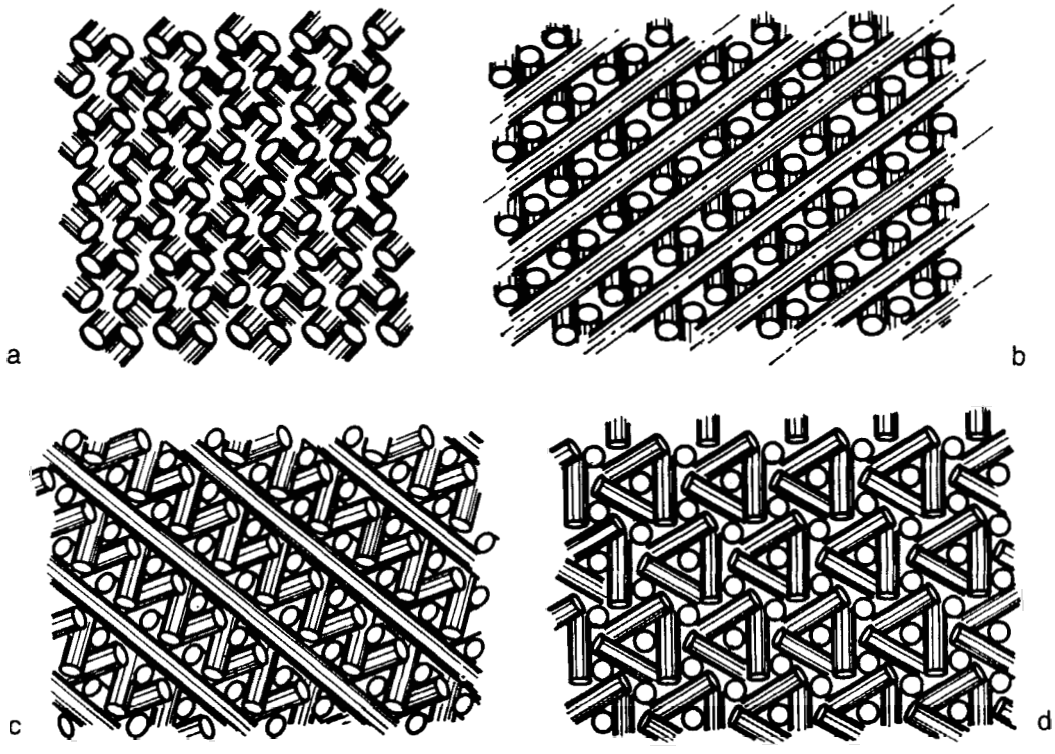


FIGURE 2 A naive representation of cuts along low Miller index reticular planes based on the classical O^{8+} tube model describing BP1: a) 100, b) 110, c) 211, d) 111.

In the photomicrographs c, Plate 1, d, f Plate 2, we see that single period cholesteric domains are coexisting with other biperiodic textures and interfacial zones between these two situations undergoing the transformation are clearly observed. Different types of biperiodic textures are shown, associated in the plane of the cut, to rectangular, square or hexagonal symmetries, this last case being rarely observed. As previously mentioned, these biperiodic texture symmetries are not identifiable with the simplest low Miller index ones, shown on Figure 2 on the naive base of the classical tube O^{8+} model.

The identification of the O^{8+} high Miller index reticular plane probably observed here, associated to the observation of interfacial region between the defect-free cholesteric domains and the quenched BPI ones would open us the possibility of a new understanding of the disclination recombination process involved at the BPI-N* transition. The major difficulties for such an indexation of the observed reticular planes are associated to the smoothness of our material at room temperature and to the small scale direction variation of the cut relative to the cubic structure. The use of an image analysis technique, allowing for an accurate choice of small homogeneous domains and for an investigation in the reciprocal space is actually in progress and would probably lead us to this interesting possibility.

CONCLUSION

These preliminary observations in the small-pitch cholesteric to isotropic phase transition with oligomeric side-chain material give us the opportunity of a better understanding of the complex blue phase structures, up to now only studied with monomer material in a very narrow temperature range. Moreover, the possibility of easy quenching of some 3-dimensional blue phase organisation enhances these investigation possibilities and opens a new application field for this state of matter.

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