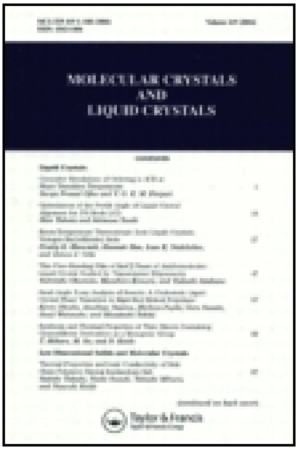


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

# Blue Phase in Liquid Crystal Polymer Mixtures

J. F. D'allest [a] , J. M. Gilli [a] & P. Sixou [a]
[a] U.A. 190, Physique de la Matière Condensée Pare Valrose, 06034, Nice, Cédex, France

Version of record first published: 13 Dec 2006.

To cite this article: J. F. D'allest , J. M. Gilli & P. Sixou (1988): Blue Phase in Liquid Crystal Polymer Mixtures, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 155:1, 571-579

To link to this article: http://dx.doi.org/10.1080/00268948808070397

*Mol. Cryst. Liq. Cryst.*, 1988, Vol. 155, pp. 571–580
Photocopying permitted by license only




# BLUE PHASE IN LIQUID CRYSTAL POLYMER MIXTURES

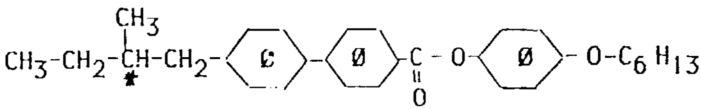
J.F. D'ALLEST, J.M. GILLI, P. SIXOU
U.A. 190, Physique de la Matière Condensée
Parc Valrose, 06034 Nice Cédex. France.

Abstract Blue phases are observed in mixtures of a low molecular weight cholesteric and a nematic polymer. Phase diagrams, optical properties and textures of these mixtures are reported and compared to the case of low molecular weight cholesteric-low molecular weight nematic mixtures.

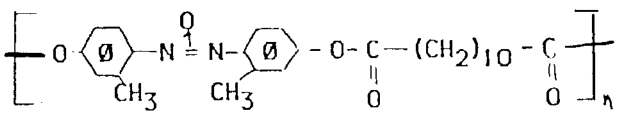
Blue phases, in conventional liquid crystals, are phases which exist in a narrow range of temperature (a few degrees) near the cholesteric-isotropic transition [1]. The BP1 and BP2 blue phases have a cubic crystalline structure with a giant unit cell. The structure results from a competition between local geometry and the global properties of space. The favorable local structure is globally unfavorable, in other words there is "frustration of the cholesteric phase"[2]. An abundant literature exists on this subject, describing results from experiments[3,16] as well as theory[17-21]. The main experimental studies concern pure cholesterics or mixtures with nematics and treat thermodynamical properties and phases diagrams[12,13,14] as well as elastic[10,11] or electric properties[7,9]. The most important effort was made on the optical properties of these materials in connection with their cristallinity[4,5,6,15,16]. To our knowledge, no study has been carried out on liquid crystal polymers. We present here the first results on the blue phase of a polymer mixture. Our approach is simple : it consists of considering a mixture of a conventional cholesteric in a conventional nematic, which shows blue phase in a certain range of temperatures and after, replacing the conventional nematic by a nematic polymer of a relatively large degree of polymerization. We study then the resulting modifications of the phase diagrams, of the optical properties of the blue phases in connection with the cholesteric pitch, of the crystalline growth properties and more generally of the textures.

EXPERIMENTAL

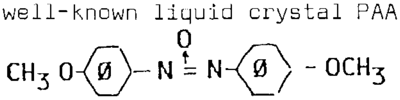
The conventional cholesteric compound which was chosen is the CE3 which general formula is :



The cholesteric - BP1 transition temperature of this compound is 164.5°C . The main chain nematic polymer used is named DDA-9 *. They are of the spacer-mesogen type :



The polymer sample used is a fraction obtained from rough synthesis of the polymer using the method of solvent addition. Its polydispersity is between 1.2 and 1.4. For the fraction selected for further studies Mn = 3400. The nematic-isotropic biphase of this fraction ranges from 113°C to 132°C. In order to carry out some comparisons we also have used a well-known liquid crystal PAA.



* We are grateful to Profs R.B.and A.Blumstein for supplying the sample of DDA-9.

The nematic-isotropic transition temperature of this compound is 135°C.
The samples were studied with an Olympus BHP polarizing microscope equiped with a Metler FP 82 hot stage and examined by reflection microscopy between crossed polarizers.

PHASE DIAGRAMS

Figure 1 shows the phase diagrams of CE3 in PAA and in DDA-9 3400. The concentrations correspond with the molar fractions of repeating units. In both cases, the blue phases extend over a large range of concentration. In the case of the polymer mixture the temperature of appearance of the blue phase is lower. This is related to the relative values of the isotropic-nematic transition temperature of the poly-

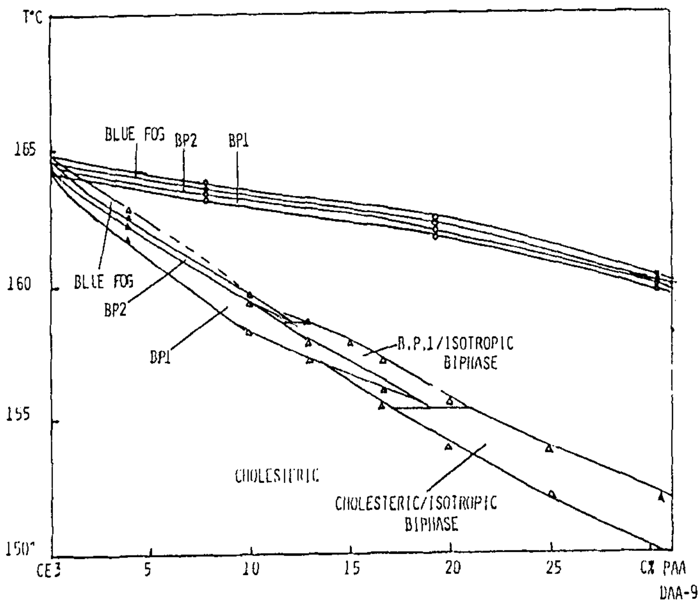



FIGURE 1. ○ Phase diagram of CE3/PAA
△ Phase diagram of CEA/DDA-9 ($M_n$ = 3400)

mer and of the small molecule liquid crystal.On another hand the temperature range of the blue phase is greater in the case of the CE3/DDA-9 mixture. One possible cause of this broadening is the polydispersity of the samples. In the polymer mixture one can also observe very clearly a bi-phasic zone (BP1-Isotropic).

## CHOLESTERIC PITCH

Fig. 2 shows the cholesteric pitch as a function of temperature for different mixtures of CE3 with DDA-9 3400. Numbers above each curve indicate the percentage (molar fraction of repeating units) of the nematic compound in the mixture. Pure cholesteric CE3 shows the usual decrease of the reflection color with temperature.

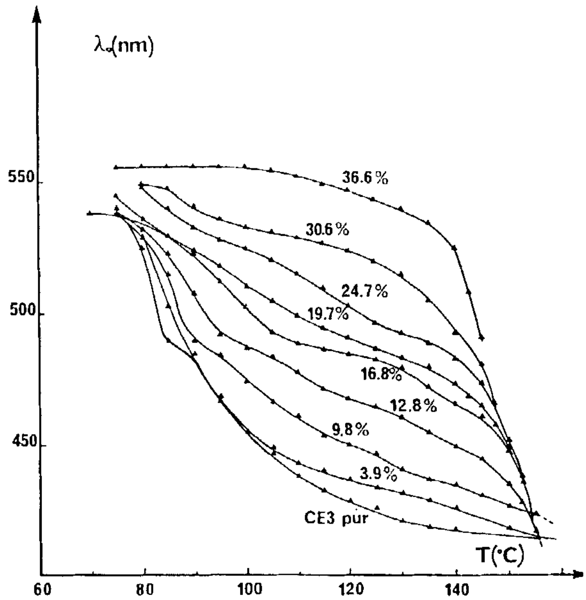



FIGURE 2. Cholesteric pitch for CE3/DDA-9 ($M_n$ = 3400) mixtures.
Numbers indicate the concentration of DDA-9

Mixtures show different behaviour if the temperature of the experiment is close to (or not) the anisotropic-isotropic transition. Near the transition the pitch decreases more rapiedely with temperature.

Figure 3 compares, at 120°C the cholesteric pitch as a function of the concentration of the nematic diluent for both CE3/PAA and CE3/DDA-9 3400 mixtures. No significant varition of the value of the cholesteric pitch is observed.

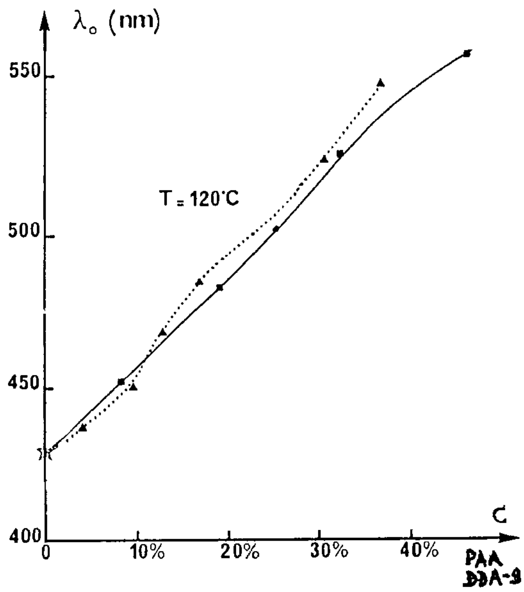



FIGURE 3. Cholesteric pitch as a function of concentration.

■ 120°C CE3/PAA Mixtures

▲ 120°C CE3/DDA-9 ($M_n$ = 3400) Mixtures

## OPTICAL PROPERTIES

The most interesting property of the blue phases is the reflection of light for the individual platelets of a polycristalline blue phase texture which fulfills the Bragg equation for normal incidence.

$$\lambda_{(h,K,l} = 2\ na/(h^2 + k^2 + l^2)^{1/2}$$

= Reflection wavelength

h, k, l = Miller indices

n = refractive index

a = cubic lattice parameter

As shown by Pieransky and al the direct observation of fa-

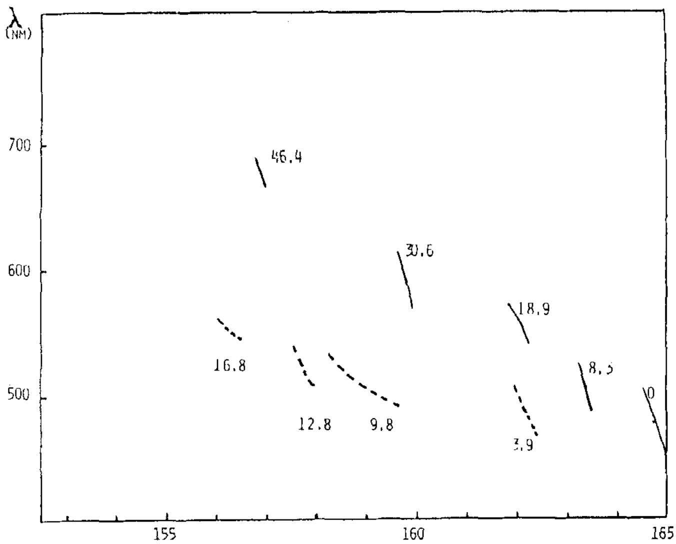


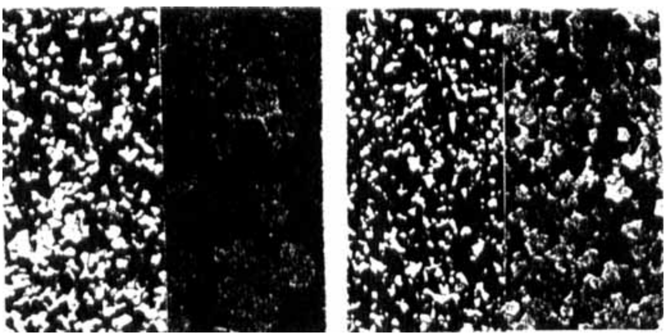

FIGURE 4. Bragg reflection wavelength for BP1 in the case of
(—) CE3/PAA Mixtures (molar fraction)
(---) CE3/DDA-9 (Mn = 3400) Mixtures (molar fraction of repeating units)

cetting in large crystals demonstrates that the symmetry of BP1, in small molecule liquid crystal blue phases, is center cubic.

Figure 4 shows the BP1 Bragg reflection :of the CE3-PAA mixture as a function of temperature for different concentrations. A quasi linear variation is obtained. The cholesteric-nematic CE3-DDA9 3400 system is also shown for comparison. (dashed line).It can be noticed that two closed concentrations (for example : 18.9% for the CE3-PAA mixture and 16,8% for the CE3-DDA-9 mixture) give approximatively the same reflection wave lengths.

TEXTURES

Platelet polycristalline textures are a function of the nature and the concentration of the nematic polymer and of the temperature. As qualitatively expected :



a b c d

FIGURE 5. Textures for the biginning and the end of BPI

a, b CE3/PAA Mixture C(PAA) = 11,9%
c, d CE3/DDA-9 3400 Mixture
C (DDA-9) = 10%

- For a given concentration of nematic solvent the size of platelets increases with temperature.

- For a given nematic solvent the size of platelets decreases when the concentration of nematic component increases.

- At the same weight (or molar) concentration the size of platelets decreases when considering the CE3/polymer mixture compared to the CE3/low molecular weight mixture. These results are related to a slower growth of crystallites when the polymer molecular weight increases. Figure 5 shows the characteristic platelets for a CE3/PAA mixture and a CE3/DDA-9 mixture.

## CONCLUSION

Blue phase can be observed in a mixture of conventional cholesterics with mesomorphic polymers. The characteristic of these phase seems directly related to the phase diagram. Other examples can be studied ; studies of blue phase in pure polymers are in progress.

## ACKNOWLEDGMENT

We are very grateful to Pawell Pieranski for fruitful discussions.

## REFERENCES

1. H. Stegemeyer, Th. Blumel, K. Hiltrop, H. Onusseit, F. Porsch, Liquid Crystals, 13-26, (1986).
2. P. Pieranski, P.E. Cladis, Euro Phys. Lett. 17, 113, (1986).
3. K. Bergmann, Ber Bunsen, Stegemeyer, Chem. 82, 1309, (1978).
4. H. Stegemeyer, K. Bergmann, Liquid Crystals of one and two dimensional order W. Helfrich, G. Heppke, p. 161 Springer, Berlin 1980.
5. S. Meiboom, M. Sammon, Phys. Rev. Let., 44, 882, (1980).

6. J.H. Flack, R.P. Crooker, Phys. Lett. 82 A, 247, (1981).
7. D. Armitage, R.J. Cox. Mol. Cryst. Liq. Cryst., 64, 41, (1980).
8. M. Marcus, J. Phys. 42, 61, (1981).
9. E.G. Heppke, M. Krumrey, F. Destreicher, Mol. Cryst. Liq. Cryst., 99, 1983.
10. N.A. Clark, S.T. Vohra, M.A. Handschy, Phys. Rev. Lett. 52, 57, (1984).
11. P.E. Cladis, P. Pieranski, M. Joanicot, Phys. Rev. Lett. 52, 542, (L984).
12. Th. Blumel, P.J. Collings, H.Onusseit, H. Stegemeyer, Chem. Phys. Lett., 116, 529, (1985).
13. K. Bergmann, H. Stegemeyer, Z. Naturforch, 34a, 251, (1979).
14. P.L. Finn, P.E. Cladis, Mol. Cryst. Liq. Cryst. 84, 159, (1982).
15. R. Barbet-Massin, P. Pieranski, J. de Phys. 46, 61, (1985).
16. P. Pieranski, P.E. Cladis, Phys. Rev. A, 35, 355, (1987).
17. M. Marcus, Mol. Cryst. Liq. Cryst. 82, 167, (1982).
18. R.M. Hornreich, M. Kluger, S. Shtrikman, Phys. Rev. Lett. 48, 1404, (1982).
19. H. Grebel, R.M. Hornreich, S. Shtrikman, Phys. Rev. A, 28, 1114, (1983).
20. H. Grebel, R.M. Hornreich, S. Shtrikman, Phys. Rev. A, 30 3264, (1984).
21. J.P. Sethna, Phys. Rev. B 31, 6278, (1985).