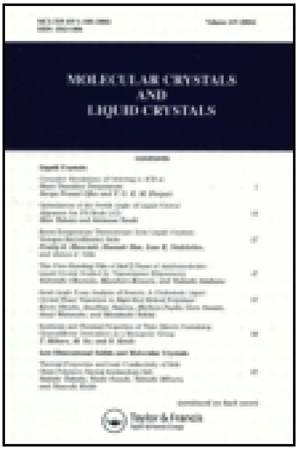

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Pressure Induced Mesophases in Side-Chain Polymer Liquid Crystal Revealed by Neutron Diffraction

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To cite this article: G. Pépy, L. Noirez & P. Baroni (2001): Pressure Induced Mesophases in Side-Chain Polymer Liquid Crystal Revealed by Neutron Diffraction, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 279-285

To link to this article: http://dx.doi.org/10.1080/10587250108025305

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 279-285
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Gordon and Breach Science Publishers imprint,
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Printed in the USA

Pressure Induced Mesophases in Side-Chain Polymer Liquid Crystal Revealed by Neutron Diffraction

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We report here pressure studies on a side-chain liquid crystalline polymer which exhibits a reentrant nematic phase at atmospheric pressure. It reveals that the two nematic transitions behave differently.

The N-S_{Ad} transition is shifted towards higher transition temperatures whereas the S_{Ad}-N_{Re} transition remains invariant with increasing pressure. In the smectic phase, a significant increase of the order parameter and of the correlation length of the smectic layers is observed. The results are obtained using a pressure cell specifically designed for neutron diffraction.

Keywords: Pressure liquid crystals; polymers; neutron diffraction

INTRODUCTION

In side-chain liquid crystal polymers (LCPs) the mesogen field acts as a stress competing with the main chain entropy. A reference model had been proposed by Wang et Warner (W&W) [1]. It foresees a wide variety of mesophases sensitive to the competing interactions within the polymer. Experimentally, all the LCPs studied up to now, display only a narrow succession of phases and conformations which correspond mainly to conventional nematic and smectic phases and to oblate and prolate main-chain conformation [2,3]. Therefore it appears interesting to understand the behaviour of LCPs submitted to an external stress as **pressure**, which is a continuous variable (in contrast with for instance the spacer length) supposed to extend the phase diagram.

TECHNOLOGY

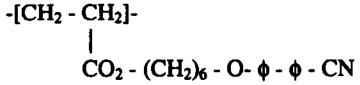
A simple Zircalloy cell has been built, allowing to reach a nominal pressure of 400 bars and a temperature of 150°C. The polymer sample is encapsulated under vacuum in an internal container with a flexible wall made of Kapton (from Dupont de Nemours). In the pressure cell, this container is surrounded by D_2O, the pressure transmitting medium. Zircalloy is a high strength alloy, transparent to the neutron beam.

THEORETICAL APPROACH

An analytical theory has been proposed by W&W for nematic side-chain liquid crystal polymers. It is based on five interaction forces between the components of the LCP, and the occupancy ratio for the side-chain mesogens. It foresees three main nematic phases. Taking in account sub order parameters for the main chain and the mesogens, more phases are predicted, with either strong or poor ordering of the main chain. LCP smectic phases have also been predicted by F. Dowell [3], from molecular calculations. However they are based on specific cases and no generic theory was proposed for smectic LCP phases.

POLYMER LIQUID CRYSTAL SAMPLE

The first sample chosen was a liquid crystal polymer assumed to be rather sensitive even to a moderate pressure. This LCP, noted PA-CN, consists in a polyacrylate main chain to which is linked a mesogen terminated by a cyano group.



$$\begin{array}{l} -[CH_2 - CH_2]- \\ \qquad | \\ \qquad CO_2 - (CH_2)_6 - O - \phi - \phi - CN \end{array}$$

This polymer exhibits a reentrant behaviour [5] :

$$T_g - 35°C - N_{Re} - 83°C - S_{Ad} - 112°C - N - 122°C - I$$

The reason of this peculiar behaviour is probably a competition between the strong electric dipolar momentum due to the cyano group and the attraction between the aromatic rings of neighbouring mesogens. These arrangements are spatially incompatible. In this case it leads to a frustration which is revealed at low temperature by the appearance of a reentrant nematic phase below the smectic phase. The application of an external pressure should displace this equilibrium.

EXPERIMENTAL RESULTS

The measurements have been performed using the LLB 3T1 diffractometer at the Orphée reactor, Saclay. The sample container has been filled under vacuum with PA-CN, then put inside the pressure cell. Along the experiment the pressure cell was kept in the gap of a 1.5T electromagnet in order to align the mesophases.

The neutron scattering measurements have been focussed on the 001 smectic reflection. The scattering angle was scanned over its position, through the full temperature range for a set of pressure values. The shape of the peak was automatically fitted to a gaussian curve, which provided the peak position, intensity and full width at half maximum.

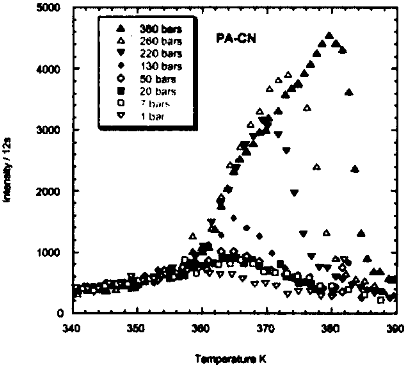


FIGURE 1, Maximum intensity of the 001 peak versus temperature, for various pressures. See Color Plate XI at the back of this issue.

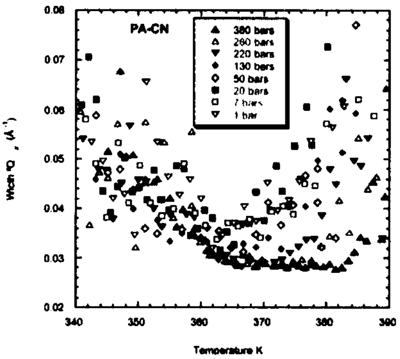


FIGURE 2, Width of the 001 peak. This width is minimum in the smectic temperature range. Since smectic fluctuations exist in the nematic regions, a peak with a broader width can also be observed there. The experimental resolution determines a minimum width. See Color Plate XII at the back of this issue.

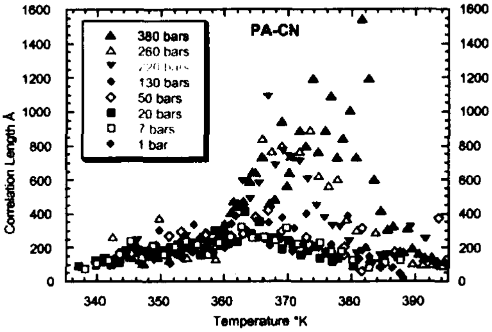


FIGURE 3, Correlation length calculated as $(\Delta_{obs})^2 = (\Delta_{inst})^2 + (\Delta_{int})^2$
The correlation length is limited to a few smectic layers at atmospheric pressure. It diverges when the pressure is increased. The instrumental resolution limits its measurement to about 1500Å. See Color Plate XIII at the back of this issue.

The correlation length, $L=1/\Delta_{int}$, has been deduced from the intrinsic width Δ_{int}, assuming that the spectrometer instrumental width Δ_{inst} corresponds to the bottom plateau displayed Fig 2 and that the instrumental Δ_{inst} and intrinsic Δ_{int} widths are added as

$$(\Delta_{obs})^2 = (\Delta_{inst})^2 + (\Delta_{int})^2$$

where Δ_{obs} is the observed width.

DISCUSSION

We have measured evolution of the 001 reflection of the S_{Ad} phase of PA-CN versus pressure and temperature. We have observed four major changes :

a) the 001 intensity increases strongly (up to sevenfold) with increasing pressure, which implies an increase of the smectic order parameter. Another explanation might be linked to a sliding of the 001 reflection position out of a minimum of the form factor; such an assumption may be ruled out, since the 001 position scarcely moves with pressure.

b) the S_{Ad}-N transition temperature increases with increasing pressure: the pressure transforms the smectic fluctuations in a long range modulation, producing the early S_{Ad} phase appearance at higher temperature,

c) in contrast, the N_{re}-S_{Ad} transition temperature remains invariant whatever the pressure. Moreover the intensity seems to reach an asymptotic limit as the pressure increases. The fluctuations associated to this transition are not sensitive to the increase of the pressure,

d) the 001 peak width (along the director) presents a minimum, (Fig 2); the higher the pressure the lower this minimum; the pressure increases the smectic layers correlation length. At atmospheric pressure the correlation length (Fig 3) corresponds to a few smectic layers, while at 400 bars it extends up to 30 layers.

High pressure studies of small molecules of reentrant liquid crystals [6] have shown that the N-S_A separation line is an ellipse, which implies an upper pressure limit for the existence of the smectic phase. For PA-CN the variation of the S_A-N transition temperature with pressure is compatible with the above observation. It is however not the case for the N_{Re}-S_A transition which seems invariant.

CONCLUSION

We have shown that pressure has a strong effect on the structure of the phase of a reentrant polymer liquid crystal, enhancing the ordering of the mesogens. Higher pressure studies will show whether a pressure limit exists for the smectic phase. An other phase transition in the S_A-N region is also expected.

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