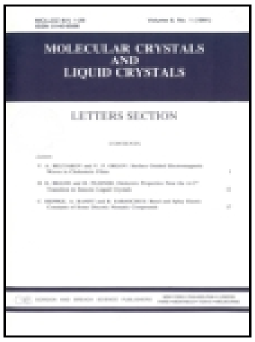

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Blue Phase Range Widening Induced by Laponite Nanoplatelets in the Chiral Liquid Crystal CE8

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We report on the widening of blue phase range induced by surface-functionalised laponite nanoplatelets dispersed in a chiral liquid crystal. The results are obtained by means of high-resolution ac calorimetry and optical microscopy and they are reproducible upon heating and cooling, identifying thermodynamically stable blue phases. It is shown that nanoplatelets target mostly the cubic structure of blue phase I and increase its temperature stability range by a factor of two. The present results are in agreement with recent findings that anisotropic nanoparticles tend to effectively stabilise blue phase I.

Keywords liquid crystals; laponite; nanoplatelets; blue phases; heat capacity.

1. Introduction

Among the first successful experimental approaches for extending the temperature range of liquid-crystalline blue phases (BPs) one can mention the polymer-induced stabilization [1] or the use of doping agents [2]. More recently, spherical [3–8] or anisotropic nanoparticles [8–10] have been exploited as stabilisation agents. In all these cases nanoparticles are surface-functionalised in order to achieve a homogeneous dispersion in the liquid crystal hosts [4–6].

Recently, it has been shown that the geometry of nanoparticles plays an important role in the BP stabilization. In particular, the spherical nanoparticles have a tendency to increase the stability range of *BPIII* [4, 5], whereas the anisotropic ones target mostly the ordered structure of *BPI* [9, 10]. Here we report that a small amount of anisotropic laponite

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nanoplatelets can effectively increase the temperature stability range of *BPI* of a chiral liquid crystal.

2. Samples and Experimental Methods

The chiral liquid crystal compound 4-octyl-biphenyl-4-carboxylic acid 4-(2-methylbutyl)-phenyl ester (CE8) was purchased by Merck, stored carefully and used without any further treatment. It exhibits all three blue phases in a temperature regime of almost 5 K [4]. The nanoplatelets (NPs) consist of a laponite RD clay core with dimensions of 25 × 1 nm [11, 12]. The organically functionalised laponite was prepared according to the following procedure. A quantity of 1 g of laponite RD was swollen in 100 ml of deionised water at 80°C for 2 h. After the complete exfoliation of laponite disks, a hot solution of hexadecyl-trimethyl-ammonium bromide in 100 ml of deionized water was added drop-wise to the clay dispersion, and the mixture was stirred vigorously for the next 3 h at 80°C. 50% excess of the ammonium cations to cation exchange capacity of laponite was used for the cation exchange reaction. The organically modified laponite was recovered by centrifuging. To remove the non-reacted ammonium salts, the product was washed twice with 100 ml of water and then a couple of times by absolute ethanol in order to remove water. The purified product was dried from ethanol at ambient conditions and re-dispersed in high-purity toluene.

A mixture of CE8 and laponite NPs with concentration $\chi = 0.02$ was prepared, where χ is defined as the mass of NPs over the total mass of the sample. The protocol of mixture preparation has been described in detail elsewhere [4, 9]. After preparation the sample was immediately placed in a high-purity silver cell.

A high-resolution ac-calorimeter, at Jožef Stefan Institute, has been employed in order to derive the accurate heat capacity temperature profiles $C_p(T)$ of the mixture. The setup is home-made and fully-automated, operating in both ac and relaxation modes [13]. The samples are placed in silver cells of flat cylindrical geometry, with a heater and a thermistor attached on the two sides. The contributions of each component (cell, heater, thermistor) are subtracted, yielding the net heat capacity of the sample.

3. Results and Discussion

After being mounted on the calorimeter, the sample was heated to temperatures corresponding to the isotropic (*I*) phase of pure CE8. Then it was cooled down to the smectic-A phase with a scanning rate of 250 mK/h. Afterwards, it was again heated up to isotropic phase with the same scanning rate. As shown in Figure 1, on cooling we observe three heat capacity anomalies between the *I* and chiral nematic (N^*) phases, i.e., all three blue phases, *BPIII*, *BPII* and *BPI* appear. On the contrary, upon heating we see two anomalies. Hence, in this case only *BPI* and *BPIII* appear. The total BP range is fully reproducible between cooling and heating. The characteristic optical textures of each phase were also confirmed by means of polarising optical microscopy in 20 μm thick cells (no orientation imposed on glass surfaces).

The $C_p(T)$ profiles demonstrate that the mixture with laponite NPs exhibits a slightly increased total blue phase range of 6 K with respect to the 5 K of pure CE8 [4]. Although the effect on the total BP range is mild, it is noteworthy that the *BPI* range is increased by a factor of two (5 K for the present mixture with respect to the 2.5 K for pure CE8). The cubic structure of *BPI* is favored by the presence of laponite NPs with respect to *BPIII* and *BPII* that appear in a narrower range with respect to pure CE8.

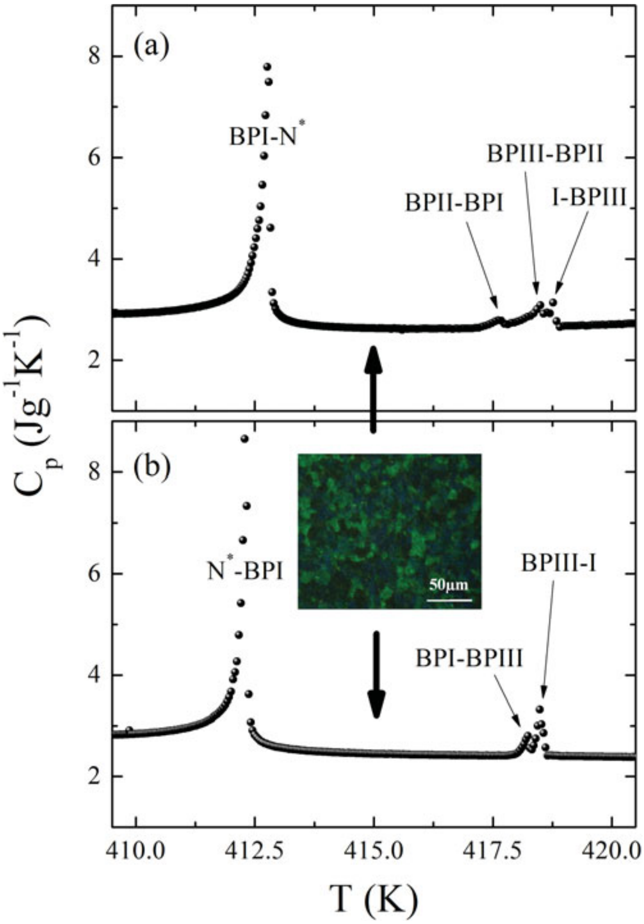

Figure 1. The temperature profiles of heat capacity $C_p(T)$ are shown here for the mixture of CE8 and laponite nanoplatelets, on cooling (a) and heating (b). The inset shows the characteristic texture of *BPI* obtained by means of polarising optical microscopy at 415 K.

The present results are in agreement with recent findings in mixtures of CE8 with molybdenum sulfide nanoplatelets [9] and graphene nanosheets [10]. It has been shown that spherical quantum dots of similar surface coating stabilise mostly the macroscopically amorphous *BPIII* [4, 5], whereas the anisotropic ones (nanoplatelets) affect mainly *BPI* [9, 10]. The relatively large surfaces of nanoplatelets induce some ordering of liquid-crystalline molecules when cooling from the *I* phase, favoring the faster appearance of the more-ordered structure of *BPI* and reducing the stability range of *BPIII* and *BPII*. In addition, the small spherical nanoparticles have been shown to induce a twist-grain boundary phase (*TGBA*) at lower temperatures [14], whereas the larger nanoplateles and nanosheets do not show such an effect [9, 10]. A possible explanation for the latter stabilisation selectiveness is as follows. The key feature behind the stabilisation of various defect lattices is attributed to the elimination of the defect core, referred to as the *Defect Core Replacement* (DCR) mechanism [14]. This mechanism is effective if a nanoparticle is adaptive, i.e., it does not significantly elastically disrupt the local liquid-crystalline environment. In BPs a trapped nanoplatelet (or nanosheet) is expected to orient with its characteristic surface's normal perpendicular to the dislocation direction in order to maximise the DCR effect. However, in the presence of smectic layers there might be a tendency of platelets to be inserted between the adjacent smectic layers. This is expected if the entropic interactions are stronger than the enthalpic ones. The latter are considered of being relatively weak due to the required adaptive character of NPs. However, in this case the platelets normal is roughly along a screw dislocation in the *TGBA* phase. Consequently, due to this competing tendency the effectiveness of DCR mechanism might be reduced in comparison with BP structures.

Note that nanosheets and nanoplatelets resemble two-dimensional shapes. We anticipate that one of future aspects can be the effect of one-dimensional objects, such as nanorods, in the stabilization of liquid-crystalline blue phases. In the last 10 years, several theoretical works have focused on the theoretical study of liquid-crystalline structures stabilised by topological defects, as well as on the effective trapping (of nanoparticles) in defect lattices of disclination lines, screw and edge dislocations [15–20].

4. Conclusions and Perspectives

The present high-resolution calorimetric results demonstrate that a small quantity of surface-functionalised laponite NPs influences the temperature stability range of blue phases of CE8. In agreement with recent studies, it is shown that the nanoplatelets target mostly the cubic structure of *BPI*, increasing its temperature stability range by a factor of two.

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References

[1] Kikuchi, H., Yokota, M., Hisakado, Y., Yang, H., & Kajiyama, T. (2002). *Nat. Mater. 1*, 64.

[2] Nakata, M., Takanishi, Y., Watanabe, J., & Takezoe, H. (2003). *Phys. Rev. E 68*, 041710.

[3] Yoshida, H., Tanaka, Y., Kawamoto, K., Kubo, H., Tsuda, T., Fujii, A., Kuwabata, S., Kikuchi, H., & Ozaki, M. (2009). *Appl. Phys. Express 2*, 121501.

[4] Karatairi, E., Rožič, B., Kutnjak, Z., Tzitzios, V., Nounesis, G., Cordoyiannis, G., Thoen, J., Glorieux, C., & Kralj, S. (2010). *Phys. Rev. E 81*, 041703.

[5] Cordoyiannis, G., Losada-Pérez, P., Tripathi, C.S.P., Rožič, B., Tkalec, U., Tzitzios, V., Karatairi, E., Kutnjak, Z., Muševič, I., Glorieux, C., Kralj, S., & Thoen, J. (2010). *Liq. Cryst. 37*, 1419.

[6] Wang, L., He, W., Xiao, X., Meng, F., Zhang, Y., Yang, P., Wang, L., Xiao, J., Yang, H., & Lu, Y. (2012). *Small 8*, 2189.

[7] Sharma, A., Worden, M., & Hegmann, T., (2012) *Ferroelectrics 431*, 154.

[8] Dierking, I., Blenkhorn, W., Gredland, E., Drake, W., Kociuruba, R., & Kayser, B. (2012). *Soft Matt. 8*, 4355.

[9] Lavrič, M., Cordoyiannis, G., Kralj, S., Tzitzios, V., Nounesis, G., & Kutnjak, Z. (2013). *Appl. Opt. 52*, E47.

[10] Lavrič, M., Tzitzios, V., Kralj, S., Cordoyiannis, G., Lelidis, I., Nounesis, G., Georgakilas, V., Amenitsch, H., Zidanšek, A., & Kutnjak, Z. (2013). *Appl. Phys. Lett. 103*, 143116.

[11] Nikolai, T., & Cocard, S. (2000). *Langmuir 16*, 8189.

[12] Datta, K. K. R., Achari, A., and Eswaramoorthy, M. (2013). *J. Mater. Chem. A 1*, 6707.

[13] Yao, H., Ema, K., & Garland, C.W. (1998). *Rev. Sci. Instrum. 69*, 172.

[14] Cordoyiannis, G., Jampani, V.S.R., Kralj, S., Dhara, S., Tzitzios, V., Basina, G., Kutnjak, Z., Nounesis, G., Tripathi, C.S.P., Losada-Pérez, P., Jesenek, D., Glorieux, C., Muševič, I., Zidanšek, A., Amenitsch, H., & Thoen, J. (2013). *Soft Matt. 9*, 3956.

[15] Cieśla, M., & Longa, L. (2004) *Phys. Rev. E 70*, 012701.

[16] Rožič, β., Tzitzios, V., Karatairi, E., Tkalec, U., Nounesis, G., Kutnjak, Z., Cordoyiannis, G., Rosso, R., Virga, E. G., Muševič, I., & Kralj, S. (2011). *Eur. Phys. J. E 34*, 17.

[17] Draper, M., Saez, J. M., Cowling, S. J., Gai, P., Heinrich, B., Donnio, B., Guillon, D., & Goodby, J. W. (2011). *Adv. Funct. Mater. 21*, 1260.

[18] Fukuda, J. (2012). *Phys. Rev. E 86*, 041704.

[19] Coursault, D., Grand, J., Zappone, B., Ayeb, H., Lévi, G., Félidj, N., & Lacaze, E. (2012). *Adv. Mater. 24*, 1461.

[20] Thanassoulas, A., Karatairi, E., Cordoyiannis, G., Kuntjak, Z., Tzitzios, V., Lelidis, I., & Nounesis, G. (2013). *Phys. Rev. E 88*, 032504.