Polymer-stabilized liquid crystal blue phases

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Published online: 2 September 2002; doi:10.1038/nmat712

Blue phases are types of liquid crystal phases that appear in a temperature range between a chiral nematic phase and an isotropic liquid phase. Because blue phases have a three-dimensional cubic structure with lattice periods of several hundred nanometres, they exhibit selective Bragg reflections in the range of visible light corresponding to the cubic lattice. From the viewpoint of applications, although blue phases are of interest for fast light modulators or tunable photonic crystals, the very narrow temperature range, usually less than a few kelvin, within which blue phases exist has always been a problem. Here we show the stabilization of blue phases over a temperature range of more than 60 K including room temperature (260–326 K). Furthermore, we demonstrate an electro-optical switching with a response time of the order of 10^{-4} s for the stabilized blue phases at room temperature.

Composite systems consisting of polymers and low-molecular-weight liquid crystals have provided a new field of liquid crystal science and technology. The polymer/liquid crystal composites giving rise to a bicontinuous phase separation of a polymer and a liquid crystal have been studied for their application to gas-permeable membranes for molecular separations and large-area flexible display materials[1–5]. The composites in which isolated liquid crystal droplets are dispersed in a polymer matrix, the so-called polymer-dispersed liquid crystal, have been applied to light shutters and displays[6–8]. In the polymer-stabilized liquid crystal[9] or polymer-stabilized cholesteric texture[10], a desired macroscopic orientation of liquid crystal directors can be stabilized by a crosslinked network dispersed within a liquid crystal. Also, permanent stabilization of blue phases (BPs) by *in situ* photopolymerization has been reported[11]. In those conventional cases, the polymers play a role in controlling the aggregation structure of liquid crystal domains, stabilizing the orientation of liquid crystal directors or freezing the ordered structure of liquid crystals. Here, we show a marked expansion of the temperature range of a liquid crystal blue phase achieved by a new type of polymer-stabilization effect, in which an equilibrium phase is thermodynamically stabilized by coexistence with a polymer. This is essentially unlike the conventional polymer-stabilization effect.

The nature of blue phases have been a subject of considerable interest in the field of condensed matter because blue phases are very different from all other materials: that is, they have a fluid lattice whose structure is stabilized by lattice defects[12,13]. The exotic structure is based on a delicate balance between the intermolecular interaction and the topological requirement, resulting in a frustrated system. From the viewpoint of practical applications, blue phases possess great potential because of their unique characteristics, such as electrically controllable Bragg diffraction of visible light[14–17] and a photonic band. However, the limitation of the available temperature range—only a few kelvin—of blue phases has always been a problem. This paper is the first, to our knowledge, to report that a temperature range of blue phases can be successfully extended to more than 60 K.

The polymer/liquid crystal composites were prepared by *in situ* photopolymerization of acrylate monomers in monomer/photoinitiator/liquid crystal mixtures in a blue phase state (see Methods). The constituent fractions of the samples reported here are shown in Table 1.

Table 1 Chemical composition of samples and phase-transition temperatures of N*–BP and BP–isotropic liquid, and the temperature range of BP, determined by polarizing optical microscopic studies. See Methods for full names of chemicals.

	Monomer (mol%)		Initiator (mol%)	Liquid crystal (mol%)		Chiral dopant (mol%)	Transition temperature (K)		
Sample no.	EHA	RM257	DMPAP	JC-1041XX	5CB	ZLI-4572	N*–BP	BP–Iso	ΔT[a] (K)
1	0	0	0	48.19	47.37	4.44	330.7	331.8	1.1
2	2.37	1.51	0.19	45.08	45.79	5.06	319.5	326.3	6.8
3	3.99	2.60	0.33	44.74	43.44	4.89	<260	326.4	>60
4	5.76	3.66	0.47	42.73	42.54	4.85	<260	326.4	>60
5	6.81	4.33	0.58	39.73	43.69	4.87	<260	327.0	>60
6	4.11[b]	2.00	0.38	44.40	43.89	5.22	<260	326.2	>60
7	4.00[c]	2.03	0.34	44.12	44.32	5.17	318.0	326.2	8.2
8	3.60[d]	0.19	0.19	46.64	44.37	5.01	329.0	330.8	1.8
9	2.76[d]	1.14	0.20	46.18	44.67	5.01	327.7	329.8	2.1
10	1.16[d]	2.67	0.21	45.58	45.35	5.04	328.2	329.9	1.7

[a] ΔT is the temperature range of BP. [b] TMHA used as monomer. [c] HA used as monomer. [d] 6CBA used as monomer.

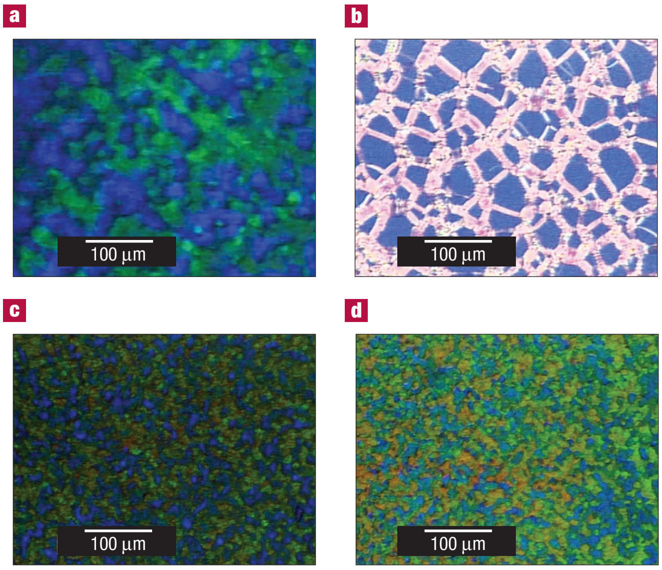

Figure 1 **Polarizing optical micrographs obtained using crossed Nicole polarizers.** **a**, **b**, Sample 1. BP I at 331.5 K (**a**) and N* at 330.3 K (**b**). **c**, **d**, Sample 3. BP I at 319.3 K (**c**) and BP I at 296.9 K (**d**).

Polarizing optical microscope observations can show characteristic textures apparently associated with different kinds of liquid crystal phases. Fig. 1a and b shows the optical textures for sample 1, in which no polymer component was included. On cooling gradually from the isotropic phase, a platelet texture, which is a peculiar optical texture of a blue phase, was observed in a temperature range 330.7–331.8 K (Fig. 1a). A brightly coloured texture with oily streaks, which is a typical texture of a chiral nematic phase (N*), was observed on further cooling below 330.7 K (Fig. 1b). It is well known that there are three thermodynamically stable blue phases, BP I, BP II and BP III, occurring in that order with increasing temperature. BP I and BP II exhibit a three-dimensional periodic structure in the director field, having body-centred and simple cubic symmetry, respectively. The lattice periods are comparable to the wavelength of visible light, resulting in the selective Bragg reflection of visible light. BP III is seemingly amorphous with a cubic local structure. Figure 2a and b shows the reflection spectra obtained for sample 1. The reflection peak appeared in a narrow temperature range around 331 K at about 550 nm (Fig. 2a), which could be assigned to be the Bragg diffraction from the (110) plane of the cubic lattice in BP I. A platelet texture was observed over the same temperature range with a polarizing optical microscope (Fig. 1a), and therefore could be of BP I. The shoulder around 410 nm in Fig. 2b, which corresponds to the selective diffraction of N*, overlapped with the peak base of the xenon emission. Every texture change with temperature was reversible on cooling and heating. Therefore, the phase transitions of sample 1 were clearly determined to be N*–blue phase (probably BP I) at 330.7 K and blue phase–isotropic phase at 331.8 K.

On cooling sample 3 from the isotropic phase, a dark field changed into a platelet texture at 326.4 K. The phase transition between the blue phase and the isotropic liquid phase occurred reversibly for sample 3 on cooling and heating. The platelet texture was observed in a temperature range of 260–326.4 K. Examples of the optical textures are shown in Fig. 1c and d at different temperatures. Figure 2c–e shows the reflection spectra obtained for sample 3. The reflection peak at approximately 540–550 nm corresponding to (110) diffraction of BP I was seen below about 330 K (Fig. 2c). The peak was seen on even further cooling down to 260 K (Fig. 2d). However, no peak was found at around 400 nm (Fig. 2e), where the selective reflection must occur if the N* was present. These results are conclusive proof that the blue phase occurred in a broader temperature range than 60 K for sample 3, including room temperature, in marked contrast to the 1.1 K range for sample 1. The transition temperatures that were determined from the studies with the polarizing optical microscope and the reflection spectra measurements for all the samples are summarized in Table 1. It is clear from the results of samples 1–5 that the amount of EHA had a significant influence on the temperature range of the blue phase, that is, the stabilized temperature was extended by more than 50 K by an increase of only 1.6 mol% in EHA content between samples 2 and 3. When photopolymerization was carried out in phases without a blue phase—for example, an isotropic phase of the initial mixture solution—little expansion of the temperature range where the blue phase occurred was observed. Therefore, a special network structure of polymer chains constructed in the blue phase is suggested to have a dominant influence on its stabilization as discussed below.

Blue phases are known to be frustrated phases resulting from the competition between the chiral forces and the packing topology[18–21]. In the cubic lattice of blue phases, the basic unit is the double-twist cylinder (DTC) in which the director is parallel to the axis at the centre, and rotates spatially about any radius. The DTC has been shown theoretically

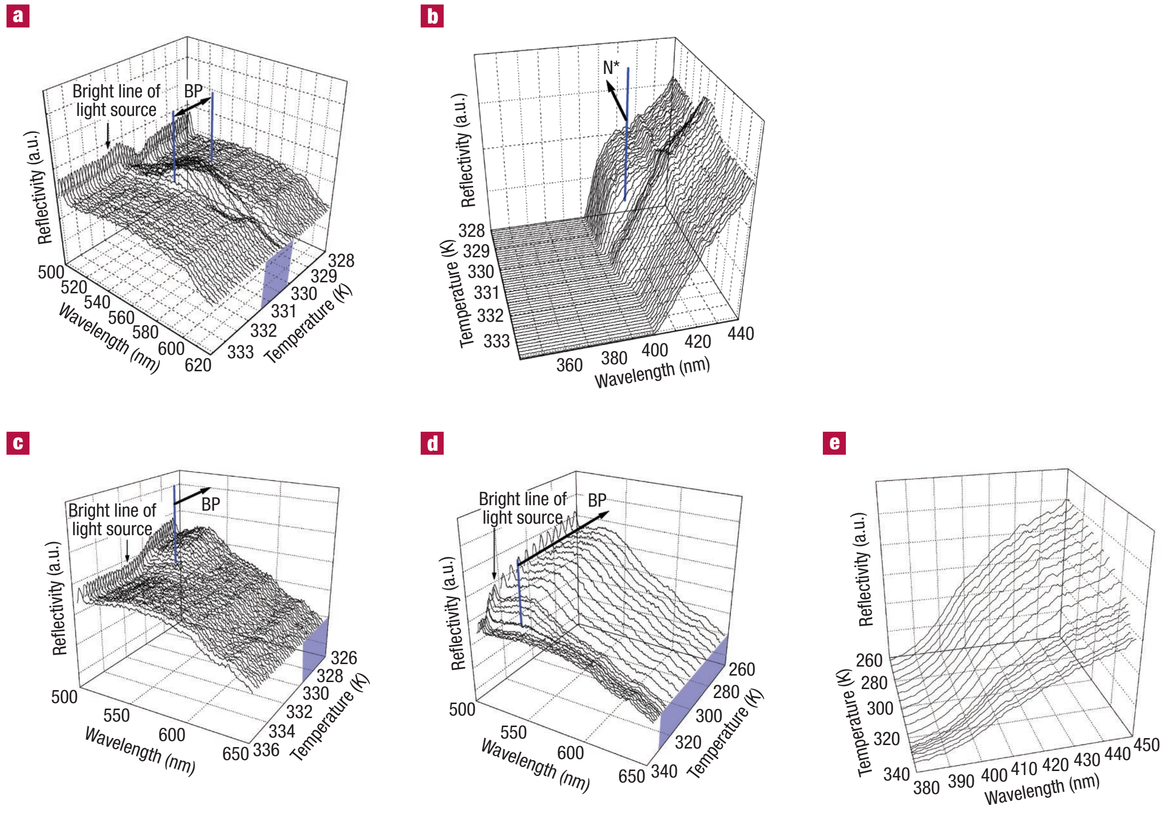

Figure 2 Reflectivity versus temperature and wavelength. a, **b**, Sample 1. (110) diffraction of BP I (**a**), selective reflection of N* (**b**). **c**, **d**, **e**, Sample 3. (110) diffraction of BP I near T_{iso} (**c**), (110) diffraction of BP I in a wide temperature range (**d**), wavelengths around 400 nm where the selective reflection must occur if the N* was present (**e**).

to be more stable locally than the single-twist structure of N*. However, the DTCs cannot fill space uniformly and completely so that the directors match everywhere, and hence disclination lines—lines of singularity in the molecular alignment—are formed. In other words, the structure of the blue phases is stabilized by its coexistence with disclination lines. Schematic illustrations of the proposed arrangement of DTCs in BP I, and the corresponding arrangement of disclination lines are shown in Fig. 3a and b, respectively[13]. The cores of disclination lines are assumed to be isotropic liquid.

The free energy per unit length of a single disclination line F for a lattice of defects is expressed by four terms[18]:

$$F = a(T_{iso} - T)\pi R^2 + 2\sigma\pi R + \tfrac{1}{4}\pi K \ln(R_{max} / R) - \pi(K_{22} + K_{24}), \quad (1)$$

where a is the constant including the Boltzmann constant, T_{iso} is the phase-transition temperature between the blue phase and the isotropic phase, T is a temperature near T_{iso}, K is the Oseen–Frank elastic constant concerning the splay, twist and bend distortions of the director (the single constant simplification is taken), σ is the surface tension of the disclination core, R is the radius of the disclination core, R_{max} is the cut-off radius, and K_{22} and K_{24} are the elastic constants of the twist and saddle-splay distortions, respectively.

Energy is required to make the core of the disclinations isotropic below T_{iso}. The first term in equation (1) represents the excess free energy of the disclination core below T_{iso}. The second term is an interfacial energy between the core and the external chiral material. The third term is derived from calculating the elastic free energy outside a disclination core but inside R_{max}. The last term, which makes F below zero, is an elastic term associated with the interface between the core and the external chiral material. When T is suitably less than T_{iso}, the magnitude of F increases above zero, and a blue phase becomes unstable. Usually, because the effect of the first term is large, the temperature range of a blue phase is very narrow.

In the case of the polymer/BP composites, polymerization proceeded in a template of the cubic lattice formed in the blue phase. Because the Bragg reflection of the blue phase was maintained after polymerization, the lattice structure of the blue phase was not destroyed by the polymerization of the monomer molecules in it. It is well known that the miscibility of a polymer with a liquid crystal is dependent on the degree of orientational order of the liquid crystal molecules. In general, a polymer is more miscible with an isotropic phase than a liquid crystal phase. Therefore, it is reasonable to assume that the polymer chains are selectively

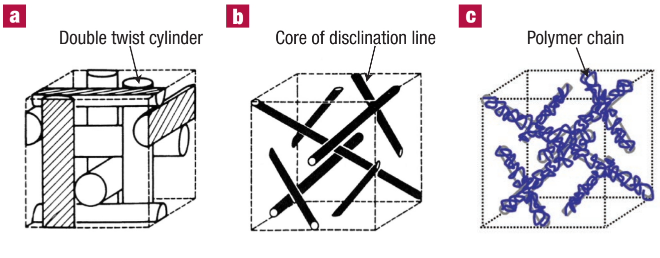

Figure 3 Possible models of unit cells in BP I. a, Arrangement of double-twist cylinders. **b**, Corresponding disclination lattices. **c**, Possible aggregation state of polymer chains in a polymer-stabilized blue phase.

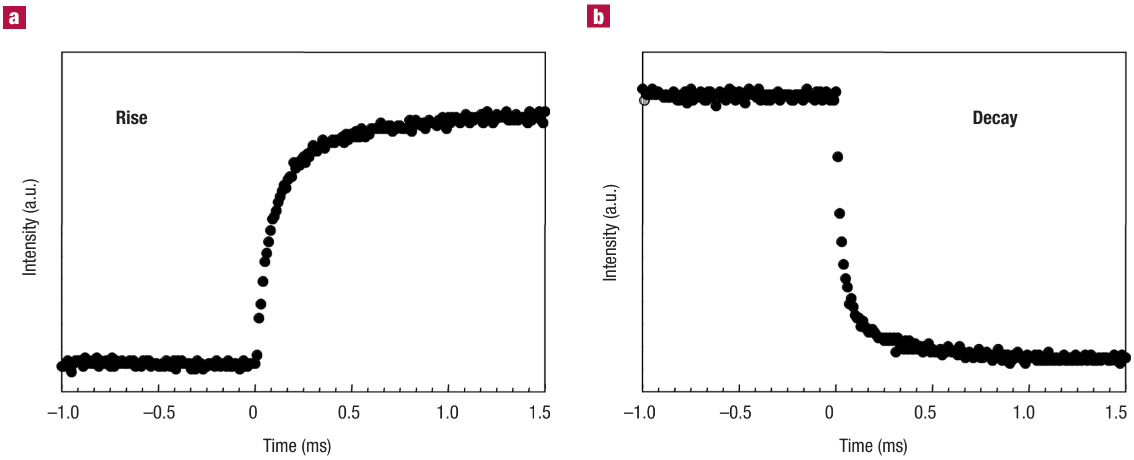

Figure 4 **Electro-optical response curves of sample 3 in the rise (a) and decay (b) processes on application of 57 V.**

concentrated in the disclination core, being in an isotropic state, rather than in the DTC. A possible model structure is illustrated in Fig. 3c.

The most stable steric conformation of flexible polymer chains dissolved in a liquid is a random coil. Therefore, the polymer chains localized in the disclination core should be in a random coil conformation, which contributes to disturbing the orientational order of the liquid crystal molecules. The blue phase of the composite therefore does not require thermal energy to keep the disclination core isotropic at a temperature below T_{iso}. This leads to a reduction of the first term of equation (1), resulting in thermodynamically stabilizing the blue phase even for T far below T_{iso}. A marked expansion of the temperature range of the blue phase in the composite was therefore achieved because the presence of the disclination lines, which although undesirable for an ordered phase, were stabilized by the amorphous polymer chains localized within them. The important point to note is that the physical mechanism of this polymer-stabilized blue phase is essentially different from the conventional polymer-stabilized liquid crystal or polymer-stabilized cholesteric texture, in which the direction of liquid crystal directors is stabilized by a polymer network that was formed with a desired orientation in the liquid crystal.

By using TMHA instead of EHA, a distinguished stabilization effect of the blue phase was also obtained (sample 6 in Table 1). However, the use of HA did not give a significant stabilization effect of the blue phase (sample 7 in Table 1). These results suggest that the polymer-induced stabilization effect of the blue phase might be associated with a branched structure of the side alkyl group in the polymer. When a liquid crystalline monomer, 6CBA was used instead of a non-liquid crystalline monomer such as EHA and TMHA, no stabilization effect was seen (samples 8–10 in Table 1). This is because poly(6CBA) chains could be homogeneously dispersed in a whole region of the blue phase, the miscibility of poly(6CBA) with liquid crystals being much higher than poly(EHA) or poly(TMHA).

Figure 4 shows the optical switch-like response curves of the transmitted light intensity through the cell of sample 3 (49 μm thick) on the application of a 20 kHz a.c. electric voltage of 57 V at 293 K. The change in the transmitted light intensity results from the rotational change in the polarizing direction of the incident light, owing to an electric field-induced distortion of the cubic lattice. The response time of the electro-optical performance was found to be about 100 μs for both the rise and decay processes at room temperature. The intensity of the transmitted light was proportional to the square of the applied voltage, which coincides well with the characteristics of a pure blue phase. This result indicates that the liquid crystal molecules in the composite are able to respond easily to an external field in spite of the presence of the polymer network. It is significant to discuss whether the electro-optical response of the polymer-stabilized blue phase is caused by changes in the refractive index or a change in the lattice constant. The latter effect would probably result in a larger shift of the wavelength of the reflection band, and its response to an electric field would be much slower (with time constants in the range of seconds). Therefore, it seems that the fast electric field effect reported here corresponds to a local director orientation within the unit lattice, caused by a change in refractive index.

Frustrated phases such as blue phases and twist grain boundary phases, which are found in chiral smectics, have attracted scientific interest because of the unique phase that appears, caused by a delicate balance between a structure with a local energetic minimum and defects[22,23]. Because these defects tend to make the global structure less stable, frustrated phases are energetically favourable only in a narrow temperature range. The limitation of the temperature range of occurring phases is a major obstacle in putting them to practical application. Our achievement will be useful for overcoming this obstacle, and open new perspectives in liquid crystal technologies.

METHODS

The monomers used were: 2-ethylhexyl acrylate (EHA, Aldrich), 1,3,3-trimethylhexyl acrylate (TMHA, Aldrich), *n*-hexyl acrylate (HA, Aldrich), 6-(4′-cyanobiphenyl-4-yloxy)hexyl acrylate (6CBA, mesogenic monomer synthesized by ourselves) and a diacrylate monomer (RM257, Merck). For the liquid crystal material, an equimolar mixture of a nematic mixture (JC-1041XX, Chisso) and 4-cyano 4′-pentyl biphenyl (5CB, Aldrich) was used. A chiral dopant, ZLI-4572 (Merck), was used to induce blue phases and helical phases such as N*. We added 2,2-dimethoxy-2-phenyl acetophenone (DMPAP, Aldrich) to the solution as a photo-initiator.

Samples of a homogeneous mixture of a photopolymerizable monomer and a low-molecular-weight liquid crystal was filled into glass cells. The cell thickness was adjusted to 15 μm by poly(ethylene terephthalate) film spacers. Each sample (Table 1) was irradiated with UV light of 1.5 mW cm^{-2} (measured at 365 nm) in a temperature range where a blue phase would form. The light source used in the photopolymerization experiments was a metal halide lamp (Hamamatsu Photonics L2859-01). Because the temperatures of N*–BP and BP–isotropic phase transitions are likely to shift, especially in the early stages of polymerization, the conditions were carefully controlled to avoid phase transition during polymerization. The cell was exposed to ultraviolet radiation stepwise, while checking the optical texture with a polarizing optical microscope. The temperature of the cell was carefully changed so as to keep the same texture and colour as at the initial state of each exposure step. The optical textures of the cells were observed by a polarizing optical microscope (Nikon) equipped with a hot stage calibrated to an accuracy of ± 0.1 K (Linkam LK-600PM). The reflection spectra of the cells were measured with a multichannel photodetector (Hamamatsu photonics C4564-010G). A xenon lamp was used as the light source for the reflection spectra measurements. In our electro-optical measurements, the sample cell was placed between two polarizers, and the mutual polarizing directions were adjusted to give the maximum contrast between on and off electric voltages. A He–Ne laser was incident to the sample cell at the angle of 45°. The transmitted light was detected by a photodiode (New Focus 1621M), and recorded with a digital storage oscilloscope (LeCroy WP950).

Received 6 June 2002; accepted 29 July 2002; published 2 September 2002.

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Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas B from the Ministry of Education, Science, Sports and Culture of Japan.
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Competing financial interests

The authors declare that they have no competing financial interests.