



Article Enhancement of Polymer Structural Ordering in Polymer-Stabilised Blue Phases for Improved Electro-Optical Properties

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Abstract: Polymer-stabilised blue phase (PSBP) could be employed in novel fast response optical and photonic devices. It is inferred that inside PSBPs, the polymers are selectively aggregated by location in -1/2 disclinations, which are defects coexisting with the blue phase as a periodic lattice, thereby extending the temperature range of the blue phase. The polymer aggregate structure in PSBPs strongly affects their physical properties. In this study, we employed a non-destructive synchrotron ultra-small-angle X-ray diffraction analysis to investigate the effect of polymerisation rates on the polymer aggregate structure in PSBPs prepared with monomers of different polymerisation rates and examined the structure formation process of the polymer during polymerisation. When methacrylate monomers, which exhibit a relatively low polymerisation rate, were used to form polymers in PSBP, the resulting polymer was more selectively aggregated at disclinations in the PSBP. Furthermore, the electro-optical effect in the PSBP was successfully improved by reducing the polymer concentration in the PSBPs prepared with the optimised monomer combinations.

Keywords: liquid crystal; blue phase; polymer-stabilised blue phase; Kerr effect; electro-optics; disclination

1. Introduction

Introducing chiral symmetry into nematic liquid crystals induces twisted molecular arrangements. As the chirality increases, double-twisted arrangements, which cannot continuously fill the three-dimensional space, predominate over simple twists. The cholesteric blue phase, hereafter referred to simply as the blue phase, is a liquid-crystal phase caused by the frustration between double-twisted molecular arrangements and the uniformity of the three-dimensional (3D) space, i.e., defect-free structure of molecular arrangement [1–3]. Since the blue phase is a result of the preference of the double-twisted structure over the uniformity of the 3D space, it necessarily coexists with defects, i.e., -1/2 disclinations. The main feature of the blue phase is that it spontaneously forms a three-dimensional periodic lattice, which has been confirmed by real space observation [4], and thereby defects also form a three-dimensional periodic lattice. The polymer-stabilised blue phase (PSBP) can be obtained by in situ polymerisation of appropriate amounts of monomers in the blue phase, and it is a liquid-crystal phase that dramatically extends the blue phase temperature range without solidification [5]. Unlike ordinary liquid crystals, PSBP is optically isotropic when no electric field is applied, and birefringence occurs when an electric field is applied. The observed electro-optical behaviour is phenomenologically similar to the Kerr effect, although the Kerr coefficient is many orders of magnitude higher than that of ordinary polar liquids due to the cooperative change in molecular orientations, which is a unique property of liquid crystals. In addition, its electro-optical response is much faster than that of ordinary nematic liquid crystals [6–9]. Therefore, PSBP could be good for applications in



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). high-performance displays, high-speed optical modulation devices, photonic devices, etc., which are difficult to achieve with conventional nematic liquid crystals [10–14]. When an electric field is applied to PSBP and removed, the birefringence returns to zero; however, a small residual birefringence is observed sometimes [15,16]. This could be a result of insufficient stabilisation of the blue phase. Because the blue phase is easily supercooled [17], the metastable supercooled state may be misidentified as PSBP, and such a metastable state is prone to residual birefringence. Synchrotron ultra-small-angle X-ray diffraction (USAXD) measurements have revealed that polymers are selectively aggregated by location along disclinations in PSBP [18], and this aggregated structure of polymers is responsible for the stabilisation of PSBPs [19,20]. A truly stable PSBP can be obtained when the polymer correctly fills the disclinations. Controlling the polymer aggregate structure in PSBP is a good technique to improve the performance of PSBP. This study aims to develop a method for selectively aggregating polymers by location along disclinations with high order. As disclinations tend to attract particles [21], herein polymers or oligomers undergoing polymerisation, if the particles are given enough time to diffuse to reach the disclination, they would be properly trapped in the disclination. Here, we focused on the polymerisation rate of monomers and investigated its relationship with the polymer structure in PSBP by synchrotron ultra-small-angle X-ray diffraction analysis.

2. Materials and Methods

The PSBPs were prepared by irradiating a precursor solution with UV light at a temperature that indicates a blue phase. The precursor solution was composed of nematic liquid crystals, a chiral dopant, monomer, and a photoinitiator. We used an equal-weight mixture of 4-cyano-4'-pentylbiphenyl (5CB, Aldrich) and JC-1041XX (JNC Petrochemical Corp.) as the nematic liquid crystals and 2,5-bis-[4'-(hexyloxy)-phenyl-4-carbonyl]-1,4,3,6dianhydride-D-sorbitol (ISO-(6OBA)₂: synthesised) as the chiral dopant. A blue phase was obtained by mixing them in appropriate ratios. In all the samples used in this study, the fraction of the chiral dopant was kept at 3.4 mole per cent of the total precursor solution. An equal-weight mixture of monofunctional nonliquid and bifunctional liquid crystalline monomers was used as the monomer to form the polymers inside the blue phase. The four types of monomers were tagged with iodine to selectively extract only the polymer structure by X-ray diffraction. The iodinated monomers were synthesised according to the procedure in the Supplementary Information of reference [18] (also see Supplementary Materials of this paper). The chemical structures of each liquid crystal and monomer are shown in Figure 1. The molar ratio of the chiral liquid crystal (liquid crystals + chiral dopant) to monomer was 91.6/8.4 in all samples. A photoinitiator of 2,2-dimethoy-2-phenyl acetophenone (Aldrich) was used to photopolymerise the monomers in the blue phase. It was added to the precursor solution at a rate of 0.1 mol% to the total solution.

Well-mixed precursor solutions of liquid crystals/chiral dopant/monomers with 0.1 mol% of photoinitiator were sandwiched between polyethylene terephthalate film substrates at a temperature where the solution is in isotropic phase (60–70 °C), and the cell gaps were fixed by 100-µm-thick film spacers to make the sample cells for X-ray measurements. The cells were irradiated with UV light with an intensity of 1.5 mW cm⁻² and wavelength of 365 nm for 20 min to photopolymerise the monomers within the precursor solutions on a hot stage at a temperature where each solution exhibited a blue phase.

USAXD measurements were performed using a BL40B2 beamline at the synchrotron radiation facility of SPring-8 (JASRI, Hyogo, Japan). The camera length was 4297 mm, and the X-ray wavelength was 0.155 nm. Two-dimensional (2D) diffraction images at small angles were taken using an imaging plate. The diffraction intensity profiles were obtained by circular integration of the 2D diffraction images. Diffuse scatterings by the direct beam of X-ray and polyethylene terephthalate film substrates were subtracted using graphing software.



Figure 1. Chemical structures of materials for preparing PSBPs.

To determine the electro-optical properties of the PSBP, in-plane switching (IPS) cells with a 10-µm cell gap were used. The width and distance of the IPS interdigitated striped electrode were 5 and 10 µm, respectively. The cells were filled with each precursor mixture in an isotropic phase by capillary action. A system composed of a function generator (WF1974, NF Corp., Yokohama, Japan), a high voltage amplifier (2205, Trek Inc., Medina, New York, NY, USA), a differential probe (9322, HIOKI E.E. Corp., Ueda, Japan), and a data logger (GL-900-4, Graphtec Corp.) was used to apply and record an AC voltage of 1 kHz to the PSBP cells mounted on a temperature-controlled stage (10019 Peltier System, Linkam Scientific Instruments Ltd., Tadworth, UK), which was sandwiched between crossed polarisers. The data presented in this paper were measured at 23–25 °C. A white LED light source, LS-L150 (SUMITA OPTICAL GLASS, Inc., Saitama, Japan), was employed, and the changes in transmitted light due to the electric-field-induced birefringence of the PSBP were recorded as colour movies using a colour-high-speed camera (SA4, Photron Ltd., Tokyo, Japan). The transmitted light intensity was calculated using the green brightness component from the colour movie taken by the high-speed camera. The peak wavelength and half-width of spectral sensitivity curve, which is the product of the light source spectrum and the transmission spectrum of the green filter in the colour-high-speed camera, were 545 and 70 nm, respectively.

3. Results and Discussion

3.1. The Monomer Species Dependence of USAXD

Polymerisation rates depend on monomer species, such as acrylate and methacrylate. In general, the radical polymerisation rate is higher for acrylate monomers than for methacrylate monomers. This is also the case even inside PSBPs [22]. PSBPs can be prepared using a mixture of two monomers of monoacrylate with alkyl chains, such as dodecyl acrylate and diacrylate having a mesogenic core such as RM257. In this study, we used two types of monofunctional monomers (iodinated dodecyl acrylate and iodinated dodecyl methacrylate) and two types of difunctional monomers (iodinated RM-257 diacrylate and iodinated RM257 dimethacrylate). Iodine was chemically added to each monomer to increase the X-ray diffraction intensity and enhance the polymer structural contrast in PSBP, according to Reference [18]. The chemical structures of the samples are shown in Figure 1. Five types of samples with different combinations of monomers were prepared for the USAXD measurements. The combinations are listed in Table 1.

Sample No.	Sample Symbol	Mono-Functional Monomer	Difunctional Monomer
1	mA/dA	Dodecyl acrylate	RM257
2	I-mA/I-dA	Iodinated dodecyl acrylate	Iodinated-RM257
3	I-mA/I-dMA	Iodinated dodecyl acrylate	Iodinated-RM257 dimethacrylate
4	I-mMA/I-dA	Iodinated dodecyl methacrylate	Iodinated-RM257
5	I-mMA/I-dMA	Iodinated dodecyl methacrylate	Iodinated-RM257 dimethacrylate

Table 1. Combinations of monomers for preparing PSBPs.

Figure 2 shows the USAXD 2D images trimmed in a small-angle region for PSBPs prepared using (a) mA/dA, (b) I-mA/I-dA, (c) I-mA/I-dMA, (d) I-mMA/I-dA, and (e) I-mMA/I-dMA, which correspond to samples **1**, **2**, **3**, **4** and **5**, respectively. The images were taken at room temperature around 20 °C using an imaging plate. The unexposed circular area at the centre of each image is the shadow of a beam stopper with a diameter of 2 mm. There were only very weak diffractions in sample **1**, as shown in Figure 2a. On the other hand, clear Debye rings were observed in iodinated samples (Figure 2b–e). There were clearer and stronger Debye rings for samples **4** and **5**, whereas, in samples **2** and **3**, the rings were weaker, and large central diffuse scatterings were observed. These results revealed that the polymers in samples **4** and **5** exhibited higher structural order than those in samples **2** and **3**, and a considerable amount of polymers with the nonperiodic structure were present in samples **2** and **3**.



Figure 2. Dependence of monomer combinations in PSBPs prepared using (**a**) mA/dA, (**b**) I-mA/I-dA, (**c**) I-mA/I-dMA, (**d**) I-mMA/I-dA and (**e**) I-mMA/I-dMA, which correspond to samples **1**, **2**, **3**, **4** and **5**, respectively, on a USAXD 2D image.

Figure 3 shows the X-ray diffraction intensity profiles for each sample. In the bodycentred cubic lattice, which is the symmetry of blue phase I, diffractions occur in the order of 110, 200, 211, 220, 310, 222, and 321 from small angles. However, in the disclination lattice within blue phase I, 110, 200, 310, and 222 disappear, according to the extinction law as calculated from its structure factor, and 211, 220, and 321 appear as diffractions. Because the observed diffraction peaks around 0.080–0.085, 0.095–0.100, and 0.125–0.130 Bragg degree are assigned to 211, 220, and 321, respectively, using the same analysis method as in the literature [18], the peaks shown in Figure 3 are attributed to the disclination lattice of blue phase I. This implies that the polymers were selectively aggregated into periodically aligned disclinations within blue phase I. The diffraction peaks of sample **5** are sharper than those of other samples, which implies that highly ordered polymers with an aggregated structure closely fitted in the disclination lattice of blue phase I were formed in sample **5**. Polymers with more than a certain molecular weight are attracted to and trapped in disclination lines [21]. During polymerisation for blue phase stabilisation, an increase in the molecular weight of the polymer and a diffusion of the polymers occur simultaneously. It could take a tangible amount of time for the polymer to reach the disclinations and be trapped there. However, since cross-linking exponentially increases the molecular weight of polymers, if the polymerisation rate is too fast, diffusion will stop before reaching the disclination, resulting in a less ordered polymer structure. The polymerisation rate of acrylate monomers is much higher than that of methacrylate monomers. Therefore, in the methacrylate system, such as sample **5**, the polymerisation speed is low enough; hence, there would be enough time for the polymer to reach disclinations and form highly ordered structures. On the other hand, the polymer isation is too fast in acrylate systems, like sample **2**; thus, the molecular weight of the polymer increases rapidly and the diffusion stops before the polymer reaches disclinations. Polymers that fail to reach the disclinations form less ordered aggregates, which increases diffuse X-ray scattering.



Figure 3. USAXD profiles of PSBPs prepared by using monomers with different combinations.

3.2. Temperature Dependence of USAXD

The temperature dependence of the polymer structure in PSBP was investigated for sample 5. In a blue-phase temperature region (–40 to 46 °C), sample 5 showed a platelet texture with green and blue colours, which is a typical optical texture of the blue phase I, in a polarising optical microscope, as shown in Figure 4a. The texture turns into a dark field when heated above 46 °C due to blue–isotropic phase transition, as shown in Figure 4b. The USAXD images are shown in Figure 4c,d. Although the phases at 43 and 60 °C were completely different, their diffraction images are almost identical. This implies that the polymer structures formed along the disclination lattice in blue phase I were maintained, even after the molecular orientational order completely disappeared in the isotropic phase. This behaviour was reversible and repeatable, i.e., the same phenomenon was observed no matter how many times the phase transition was repeated by increasing and decreasing the temperature between 43 and 60 °C.



Figure 4. Polarizing optical microscope images of PSBP (sample 5) at 43 $^{\circ}$ C (**a**) and 60 $^{\circ}$ C (**b**), and USAXD images of PSBP (sample 5) at 43 $^{\circ}$ C (**c**) and 60 $^{\circ}$ C (**d**).

On the other hand, cooling the sample changed the diffraction intensity. Figure 5 shows the USAXD profiles of sample 5 at 25.5, 0, -10, -20, -30, and -40 °C. As the temperature decreased, the diffraction peaks became smaller. In particular, the peak intensities decreased significantly between -20 and -30 °C. This suggests that the order of the polymer structure was reduced by cooling. However, when the temperature was increased back to 25 °C, the profile almost returned to its original shape. Therefore, the polymer cannot be permanently damaged by cooling, and the order of the polymer is reversibly restored by reheating to room temperature.



Figure 5. USAXD profiles of sample **5** at 25.5, 0, -10, -20, -30, and -40 °C.

3.3. UV Exposure-Time-Dependence of USAXD

The polymerisation of acrylate and methacrylate monomers proceeds with UV-light exposure time. Figure 6 shows the UV-light exposure-time-dependence of the USAXD profiles for sample 5 measured at 32 °C. Almost no diffraction was observed in the initial state (zero exposure time). This means that the monomers were dispersed randomly and uniformly in the blue phase before polymerisation. As the UV exposure started, the intensity of diffraction peaks gradually increased with an increase in the exposure time.



Figure 6. UV light exposure time dependence of USAXD profiles for sample 5.

The changes in diffraction peak areas and peak half widths for 211, 220, and 321 with time during the UV exposure are shown in Figure 7a,b, respectively. Each peak area monotonically increased with exposure time and gradually saturated, whereas the half-width of each peak was almost unchanged. Therefore, we infer that as polymerisation begins, the polymers start to be trapped immediately in the disclinations, forming a highly ordered structure, and as polymerisation progresses, the polymers in the disclinations become highly aggregated, thereby increasing the contrast in the polymer concentration. Figure 8 shows the schematic illustration of a possible monomer distribution state before polymerisation in the initial and aggregated states of the polymers after polymerisation.



Figure 7. The change over time of the diffraction peak areas (**a**) and peak half widths (**b**) for 211, 220, and 321 after the start of UV exposure.



Figure 8. Schematic illustration of a possible distribution state of a monomer before polymerisation in the initial state (**left**) and an aggregation state of a polymer after polymerisation (**right**).

3.4. Mechanism of Polymer-Stabilisation of Blue Phase

In general, the temperature range of a phase is determined by the relative thermodynamic stability of the phase of interest with reference to other phases at the high- and low-temperature sides. In the case of PSBP, since the temperature range on the lowtemperature side is extended, it is considered that the thermodynamic balance with the chiral nematic phase, which is on the low-temperature side, is significantly altered by the presence of a polymer. The blue phase and the chiral nematic phase conflict between double- and simple-twist structures. The blue phase is stable when the double-twist structure, which is a locally stable structure, is dominant at the expense of defect (disclination) generation, and the chiral nematic phase is stable when the simple-twist structure, which is a defect-free state, is dominant at the expense of the locally stable structure. As temperature increases and approaches the isotropic phase, defects exist more easily due to the decrease in the orientational order. Thus, a blue phase generally appears just below the isotropic phase. The experimental results obtained in this study show that when polymers are generated and grown in the blue phase, they aggregate in the disclination, a defect in the blue phase. This implies that the defects are immobilised by filling them with polymers, and the defect-free state, which is the basis of stabilisation in the chiral nematic phase, is lost. Therefore, the equilibrium state between the two phases is greatly disrupted, and the relative stability of the blue phase at lower temperatures would increase. In other words, the chiral nematic phase is replaced by the blue phase because the disadvantage of defects has become a common expense not only in the blue phase but also in the chiral nematic phase due to the immobilisation of defects. It could be inferred that breaking the spatial uniformity destabilises the chiral nematic phase. Because the blue-isotropic phase transition temperature, which is the higher temperature phase, is almost the same with and without the polymer, the polymer does not affect the ordered structure of the blue phase. This fact supports our hypothesis. In other words, the extension of the temperature range of the blue phase is not attributed to the stabilisation of the blue phase but the destabilisation of the chiral nematic phase. This can be expressed in terms of a free energy-based phase transition phenomenon, as shown in Figure 9. That is, the blue phase originally exists in a small temperature range between the chiral nematic and isotropic phases. However, when the chiral nematic phase is destabilised (i.e., the free energy of the chiral nematic phase increases), the transition temperature between the chiral nematic and blue phases shifts to a lower temperature, whereas the blue–isotropic phase transition temperature remains unchanged; thus, the temperature range of the blue phase is extended to the lower temperature side. This agrees well with experimental observations [5].



Figure 9. A possible explanation of expending blue phase temperature range in PSBP based on free energy change.

3.5. Improvement of Electro-Optical Property of PSBP

The blue phases I and II are optically isotropic due to their cubic structure, and when an external electric field is applied, they induce birefringence proportional to the square of the electric field; this is called the electro-optical Kerr effect. Phenomena that can be induced in the blue phases by applying an electric field include (1) phase transition to the chiral nematic phase, (2) lattice rotation, (3) lattice deformation, (4) reorientation of local directors in the lattice, and (5) changes in molecular orientation; (1–3) generally result in responses slower than milliseconds. In PSBPs, such slow responses are suppressed because the lattice is immobilised by the polymer; only fast responses, (4) and (5), occur. Since the change in birefringence resulting from (5) is small, the Kerr effect in PSBPs is mainly attributed to (4). As revealed by the USAXD experiments, inside PSBPs, there are polymers formed in a well-ordered structure along the disclinations and those aggregated in a disordered state. The latter inhibits the electro-optic effect of PSBPs and reduces the induced birefringence. Eliminating the disordered polymer aggregates in PSBPs would reduce the drive voltage, which is a major issue in PSBPs. Simply reducing the polymer fraction in PSBPs would lower the drive voltage, but there is a trade-off below which further reduction would reduce the stability of PSBPs. The decrease in the stability of PSBPs appears as residual birefringence after removing the electric field. It is essential to properly present polymers in the disclinations to prevent a decrease in the stability of PSBPs. As revealed in this study, sample 5 contains the highest ordered polymer structure, which is considered to be properly distributed along the disclinations in the PSBP. Therefore, we investigated the possibility of reducing the driving voltage while maintaining the stability of a PSBP by reducing the polymer fraction in sample 5. Figure 10 shows the polymer-fraction-dependence of applied voltage vs. transmittance curves for PSBP prepared with dodecyl methacrylate and RM257 dimethacrylate (noniodinated). Since the transmittance was obtained by extracting and analysing the data at a wavelength of 545 nm, the transmitted light repeatedly increased and decreased due to the interference with the induced birefringence. Here, the voltage at the first maximum transmittance is defined as the driving voltage. By reducing the polymer fraction by about 13% (from 7.7 to 5.7 wt %), the driving voltage was reduced by about 29%. Almost no residual birefringence was observed in all the samples. This shows that the conventional trade-off can be overcome and the driving voltage can be effectively reduced in PSBP prepared with dodecyl methacrylate and RM257 dimethacrylate (noniodinated) where the polymer should be more properly formed in disclination. Although the measured driving voltage itself is large for a distance of 10 µm between electrodes because we used a general-purpose material as the liquid crystal, the methodology employed in this study can be applied to other liquid crystals. The driving voltage would be sufficiently reduced if a liquid-crystal material with a high Kerr coefficient developed for PSBP is used.



Figure 10. Polymer fraction dependence of the applied voltage vs. transmittance curves for PSBP prepared using dodecyl methacrylate and RM257 dimethacrylate (noniodinated). An electric voltage of 1 kHz was applied between electrodes 10 μ m apart. The transmittance was measured at a wavelength of 545 nm.

4. Conclusions

The aggregation structures of polymers inside PSBPs were evaluated by synchrotron USAXD analyses. The PSBPs were prepared with various combinations of acrylate and methacrylate monomers with high and low polymerisation rates, respectively. Using the methacrylic monomers with low polymerisation rates resulted in the formation of highly ordered polymer aggregates that closely fit the defect lattice in the PSBP. The structure of the polymer inside the PSBP remained almost unchanged even after repeated heating of the PSBP to the isotropic phase and cooling to the original temperature. On the other hand, when the PSBP was cooled to -20 °C and below, the order of the polymer aggregate structure decreased, but when reheated to the original temperature, the polymer aggregate structure also returned to its original state. The driving voltage of the Kerr effect was effectively reduced by reducing the polymer concentration in the PSBPs prepared with methacrylate monomers, which exhibited the highest ordered polymer structure. There was almost no residual birefringence in the PSBP; hence, we conclude that the conventional trade-off between the driving voltage and residual birefringence was successfully overcome.

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