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Morphological studies of LC polymer networks prepared by photopolymerization of (LC monomer/LC) blends

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Abstract

The morphology of LC polymer networks prepared by photopolymerization of (LC monomer/LC) blends containing photoinitiator and crosslinker was investigated. For the blends of 4-acryloyloxyhexyloxy-4′-cyanobiphenyl and 4-hexyloxy-4′-cyanobiphenyl, which had the same mesogen, orientation order of LC textures was memorized by photopolymerization, while any structure of LC polymer networks was not observed under an optical microscope because the networks did not phase separate from the low molecular weight LC. However, specific anisotropic phase-separated structures of LC polymer networks were observed for the blends of 4-acryloxloxyhexyloxy-4′-cyanobiphenyl and 4-hexyloxybenzoic acid, which had dissimilar mesogens, on condition that photopolymerization was carried out under the LC phase. If photopolymerization was performed under the isotropic phase conditions, polygonal or continuous phase-separated structures of LC polymer networks were observed for the dissimilar mesogenic blend. These morphologies were strongly dependent on the phase diagrams of (LC monomer/LC) blends and (the corresponding LC polymer/LC) blends. It has been found that the ordering field of LC molecules can give LC polymer networks anisotropic morphologies, which have the long range as the same length scale of LC textures. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: LC polymer network; Phase separation; Anisotropic morphology

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1. Introduction

LC polymer networks, which have the structure of a crosslinked side-chain LC polymer, have attracted much attention because they have unique properties such as second harmonic generation [1,2], piezoelectricity [3,4], electrostriction [5], and thermally stimulated anisotropic deformation [6,7]. It is necessary for optimizing performance of such functions to macroscopically align mesogenic groups of LC polymer networks. Therefore two synthetic approaches have often been employed for preparation of LC polymer networks. In one of the approaches, a difunctional LC monomer or a mixture of monofunctional LC monomer and a crosslinker is macroscopically ordered by external fields or by surface alignment and then polymerization is performed under their LC phases [8–10]. The other is two-step crosslinking reaction. In the first step, a weakly crosslinked LC polymer network is prepared from a solution. After removing solvent, the network is loaded with an external mechanical stress under the LC phase and additional crosslink is carried out [11–13]. LC phase ordering of mesogenic groups can be fixed by these methods; however, it is difficult to go as far as to control morphology of the resulting LC polymer networks.

Morphology of LC polymer networks is worth noting because it is thought to have the same important influence on the properties as the alignment of the mesogenic groups. In particular, the mechanical properties such as modulus of elasticity and contraction/elongation response to stimuli are significantly affected by the morphology. We consider that photopolymerization of (LC monomer/LC) blend is one of the useful techniques to modify morphology of LC polymer networks because the morphology depends to a large extent on miscibility between the polymer network derived from LC monomer and non-reactive LC. Furthermore, compared with a pure LC monomer, the use of LC mixtures has advantages of enlarging LC temperature range and generating other LC phases that did not emerge for a pure LC monomer [14].

In this study, two typical (LC monomer/LC) blends were prepared and photopolymerization was performed for the

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blends containing small amounts of a photoinitiator and a crosslinker. One of the blends consisted of an acrylate monomer bearing a cyanobiphenyl mesogen and an alkoxycyanobiphenyl compound, which possessed the same mesogen. The other was composed of the acrylate monomer and 4-alkoxybenzoic acid which had dissimilar mesogens. Since miscibility of LC polymer and low molecular weight LC depends on their mesogenic groups [15], we chose such two types of blends in this study. In order to predict miscibility between LC polymer networks and the non-reactive LCs, we synthesized linear LC polymer from the LC monomer by solution polymerization and constructed phase diagrams by blending it with non-reactive LCs. On the basis of phase diagrams, we decided photopolymerization conditions and the irradiated blends were investigated by optical microscopy.

2. Experimental

2.1. Materials

The chemical structures of compounds used in this study are given in Fig. 1. 4-Cyano-4′-acryloyloxyhexyloxybiphenyl (A6OCB) having a single acryl group was chosen as a reactive low molecular weight LC. It was synthesized according to a method described in the literature [16]. In order to prepare monomeric blends with A6OCB, 4-cyano-4′-hexyloxybiphenyl (6OCB) and 4-hexyloxybenzoic acid (6OBA) were selected as non-reactive low molecular weight LCs. 6OCB has the same cyanobiphenyl mesogen as A6OCB, whereas 6OBA possesses a different mesogen formed through intermolecular hydrogen bond, as shown in Fig. 1. They are commercially available and were purified by recrystallization before use. Poly(4-cyano-4′-acryloyloxyhexyloxybiphenyl) (P6OCB) used for phase diagrams was prepared by radical polymerization of A6OCB from DMF solution using AIBN as an initiator. M_n and M_w/M_n of the polymer were 2.5×10^5 and 2.4, respectively. LC diacrylate, 1,4-phenylene bis(4-(6-(acryloyloxy)hexyloxy)-benzoate), was synthesized according to a procedure reported previously [17]. It was used as a crosslinker (CL) to avoid hindering the liquid crystallinity of LC blends. Phase transition temperatures of the compounds measured on cooling scans are given in Table 1. The phase diagrams of the blends prepared from these materials were constructed by the results of optical microscopy and DSC measurements on cooling scans.

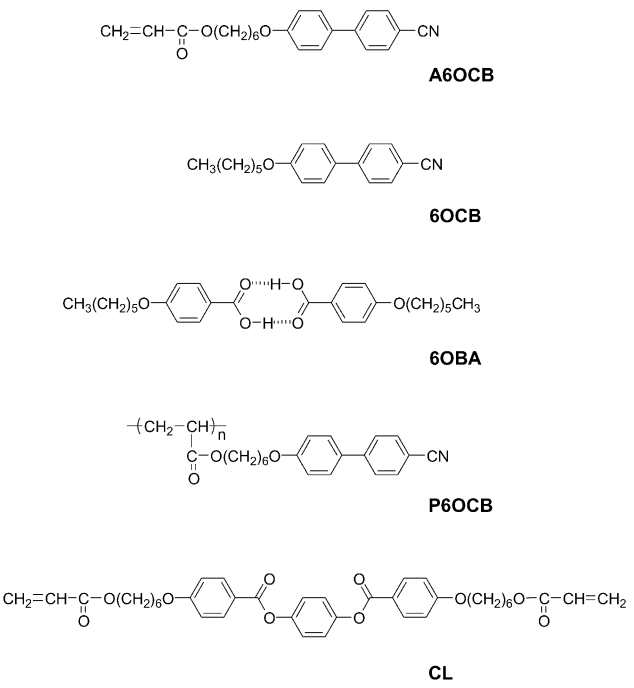

Fig. 1. Structures of LC compounds used in this study.

2.2. Preparation of LC blends

The requisite amounts of the compounds were dissolved in $CHCl_3$ and the solutions were evaporated at atmospheric pressure. The residual solids were thoroughly dried in vacuum for several hours at 25 °C.

2.3. Photopolymerization

2,2-Dimethyl-2-phenylacetophenone was used as a photoinitiator (PI). The LC blends containing CL and PI were placed between the glass slides. All the samples had the thickness of ca. 5–6 μm which was measured after photoirradiation. Using a 200 W mercury–xenon lamp, the samples were irradiated at a certain temperature which was controlled by a hot stage. The irradiation time was 10 min and the intensity was 20 mW/cm^2.

2.4. Characterization

DSC measurements were performed using a Seiko Instruments Inc. DSC 120. Heating and cooling rates of 1 °C/min were used for the measurements. A polarizing microscope (Olympus BH2) equipped with a Mettler FP82HT hot stage was used to observe the LC textures and the morphology of the samples. Fourier transform

Table 1
Phase transition temperatures (°C) of LC compounds

Compound	Phase transition behavior[a]						
A6OCB	I	48	N	46	K		
6OCB	I	76	N	35	K		
6OBA	I	152	N	95	K		
P6OCB	I	128	N	34	g		
CL	I	154	N	88	S_C	71	K

[a] Determined from optical microscopy and DSC measurements on the cooling scans. Abbreviations: I = isotropic, N = nematic, S_C = smectic C, K = crystalline, g = glassy.

infrared spectroscopy was performed with JASCO FT/IR-620.

3. Results and discussion

3.1. Same mesogenic system

First, we prepared A6OCB/6OCB blend and P6OCB/6OCB blend whose components have the same mesogenic moiety (4-cyanobiphenyl group). Phase diagrams of the blends are shown in Fig. 2. Phase transitions were measured on cooling scan. As shown in Fig. 2(A), A6OCB/6OCB blend was completely miscible over the entire ranges of compositions and temperatures. The isotropization temperature of the blend changed linearly with varying compositions. The crystallization temperature exhibited eutectic behavior thereby enlarging the range of nematic phase.

P6OCB used for P6OCB/6OCB blend was synthesized by solution polymerization of A6OCB. The value of mol% of 6OCB in the P6OCB/6OCB blend was based on the side-chain monomer unit of P6OCB. As shown in the phase diagram, the blend exhibited complete miscibility. This result comes from the fact that the compounds had identical mesogenic groups and the length of alkyl chains was adequate. The authors have already showed the phase diagram of the P6OCB/6OCB blend [15]. There is a small difference between the phase diagram of Fig. 2(B) and that of Ref. [15] because phase transition temperatures were determined on the heating scan and plotted as a function of wt% of 6OCB in Ref. [15].

Before photoirradiation was conducted for the A6OCB/6OCB blend, we investigated the effect of CL and PI on liquid crystallinity of the blend. CL and PI were added to the A6OCB/6OCB (12/88 mol%) blend, the amounts of which based on A6OCB were 2.5 and 7.0 mol%, respectively. Phase transition behavior of the A6OCB/6OCB (12/88 mol%) blends with and without CL and PI are shown in Table 2. Compared to the blend without CL and PI, depression of crystallization temperature was observed for the blend containing CL and PI. However, LC phases were the same and the decrease in the isotropic–nematic transition temperature was only 1 °C. This result indicates that the addition of CL and PI has no significant influence on the liquid crystallinity of the A6OCB/6OCB blend.

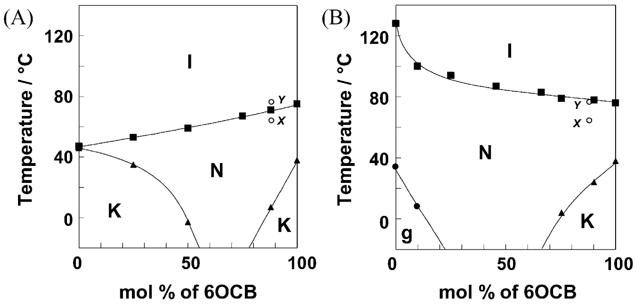

Fig. 2. Phase diagrams of (A) A6OCB/6OCB blend and (B) P6OCB/6OCB blend. X and Y correspond to the points at which photoirradiation was performed for A6OCB/6OCB blend containing CL and PI.

Table 2
Phase transition temperatures (°C) of A6OCB/6OCB blends with and without CL and PI on cooling

LC blend	Mol ratio	Phase transition behavior[a]				
A6OCB/6OCB	12/88	I	71	N	7	K
A6OCB/6OCB/CL/PI	12/88/0.3/0.8	I	70	N	−8	K

[a] Determined from optical microscopy and DSC measurements on the cooling scans. Abbreviations: I = isotropic, N = nematic, K = crystalline.

Using the A6OCB/6OCB (12/88 mol%) blend containing CL and PI, we performed photoirradiation in two different regions of the phase diagrams. In one of the regions, the A6OCB/6OCB blend shows a nematic phase and the P6OCB/6OCB blend also shows a nematic phase (the N → N region). In the other region, the A6OCB/6OCB blend is isotropic while the P6OCB/6OCB exhibits a nematic phase (the I → N region). Since it is of quite interest to investigate the effect of the ordering field of molecules on results of photopolymerization, we chose these conditions.

First, we carried out photoirradiation of the A6OCB/6OCB blend (12/88 mol%) at 65 °C in a nematic phase. This condition is within the N → N region and corresponds to the X point depicted in Fig. 2(A). If the A6OCB/6OCB blend containing only PI is irradiated with UV light, A6OCB will be polymerized and changed into P6OCB. The P6OCB/6OCB (12/88 mol%) blend also exhibited a homogeneous nematic phase at the X point. Fig. 3 shows photomicrographs of the A6OCB/6OCB

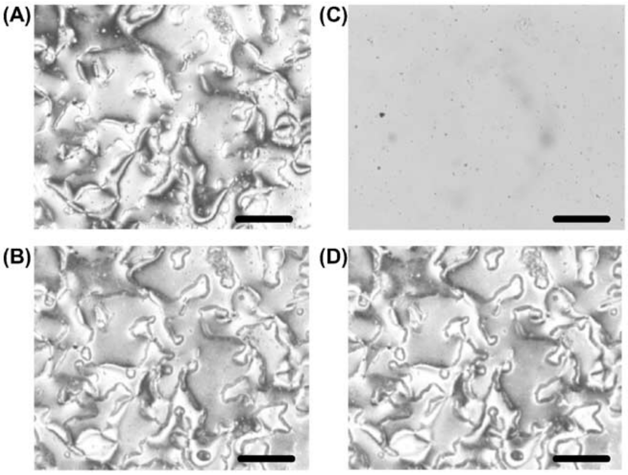

Fig. 3. Optical micrographs of A6OCB/6OCB (12/88 mol%) blend containing CL and PI taken at (A) 65 °C under crosspolarized light before photoirradiation, (B) 65 °C under crosspolarized light after photoirradiation at 65 °C, (C) 86 °C under unpolarized light after photoirradiation at 65 °C, and (D) 70 °C under crosspolarized light after photoirradiation at 65 °C and cooling from 86 °C. Scale bars correspond to 100 μm.

(12/88 mol%) blend containing CL and PI taken before and after photoirradiation. Before photoirradiation, a schlieren texture characteristic of a nematic phase was observed under crosspolarized light (Fig. 3(A)). Even after photoirradiation for 10 min, almost the same texture was seen for the blend, as shown in Fig. 3(B). In order to investigate properties of the irradiated sample, it was heated from 65 °C. The birefringence reduced from 80 °C and disappeared at 85 °C. This result suggests that A6OCB was polymerized and the resulting LC polymer network enhanced liquid crystallinity, because the A6OCB/6OCB (12/88 mol%) blend did not develop a nematic phase over 70 °C. Fig. 3(C) shows a photomicrograph of the blend taken under unpolarized light at 86 °C. A homogeneous isotropic phase without phase separation was observed in Fig. 3(C). Cooling the sample down to 70 °C lead to a nematic phase, as shown in Fig. 3(D). It is noteworthy that the texture of the blend, once heated above the clearing point and cooled, is the same as the texture observed just after photoirradiation. That is to say, the LC texture was memorized in the blend. This memory effect has been ascribed to the polymer network formed in the blend by photoirradiation [18,19]. However, morphology of the LC polymer network was not observed under an optical microscope because it did not phase separate from the non-reactive LC.

According to literatures [17,20,21], photopolymerization of an acrylate group in the LC phases proceeds very fast and to high conversion. In our study, to show validity of comparing the results of photopolymerization with the phase diagram containing P6OCB, we carried out infrared measurements of the non-irradiated and irradiated blends by the KBr disk technique. IR spectra showed that absorption band at 1717 cm^{-1} associated with a carbonyl group of C=C–C=O shifted to 1731 cm^{-1} corresponding to that of C–C–C=O. Moreover, we obtained an insoluble residue by dissolving the irradiated blend with ethanol and unreacted monomer could not be detected by thin layer chromatography from the ethanol solution. These facts indicate that the conversion of photopolymerization in our experiments is high enough to discuss the photopolymerization results on the basis of the phase diagram of P6OCB. We also performed IR measurements and thin layer chromatography for the photopolymerization described later and obtained similar results which show the validity of comparing the photopolymerization results and the phase diagrams containing P6OCB.

In order to eliminate the effect of the ordering field on photopolymerization, we conducted photoirradiation of the A6OCB/6OCB (12/88 mol%) blend at 75 °C in the isotropic phase. This condition is within the I → N region and corresponds to the *Y* point in Fig. 2(A). At the *Y* point, the A6OCB/6OCB blend exhibited a homogeneous isotropic phase. In contrast, as shown in Fig. 2(B), the P6OCB/6OCB blend showed a homogeneous nematic phase at the *Y* point. Fig. 4 shows photomicrographs of the blend taken before and after photoirradiation. Before photoirradiation, a homogeneous isotropic phase was observed under unpolarized light (Fig. 4(A)). A photomicrograph of the texture taken after photoirradiation is shown in Fig. 4(B). Birefringence could be observed under crosspolarized light even at 75 °C, which indicates that the blend exhibited a liquid-crystalline phase. The texture did not develop but showed a bright fine grain texture which was composed of a polydomain of nematic phases. We investigated properties of the irradiated sample by varying the temperature. The birefringence reduced from 83 °C and disappeared at 88 °C on heating. Fig. 4(C) shows a photomicrograph of the blend taken under unpolarized light at 90 °C. In this case, phase separation did not occur and morphology of the LC polymer network could not be observed. Birefringence appeared again in the blend when it was cooled to 75 °C (Fig. 4(D)). Interestingly, the texture of Fig. 4(D) is almost the same as that of Fig. 4(B). Irrespective of photoirradiation conditions, the LC textures observed just after photopolymerization were retained even after the blend was repeatedly heated and cooled.

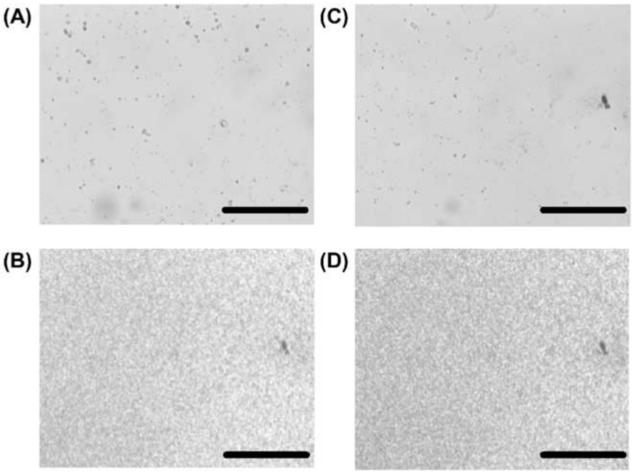

Fig. 4. Optical micrographs of A6OCB/6OCB (12/88 mol%) blend containing CL and PI taken at (A) 75 °C under unpolarized light before photoirradiation, (B) 75 °C under crosspolarized light after photoirradiation at 75 °C, (C) 90 °C under unpolarized light after photoirradiation at 75 °C, and (D) 75 °C under crosspolarized light after photoirradiation at 75 °C and cooling from 90 °C. Scale bars correspond to 100 μm.

In the same mesogenic system, although the LC monomer was converted into the LC polymer network by photoirradiation, morphology of the network could not be observed because phase separation did not take place. LC textures were memorized by the formation of polymer networks.

3.2. Different mesogenic system

Next, we examined the phase behavior of A6OCB/6OBA blend and P6OCB/6OBA blend by constructing their phase diagrams. They consisted of two LC components which had different mesogens, that is, a cyanobiphenyl and a hydrogen-bonded mesogen as show in Fig. 1. A hydrogen-bonded

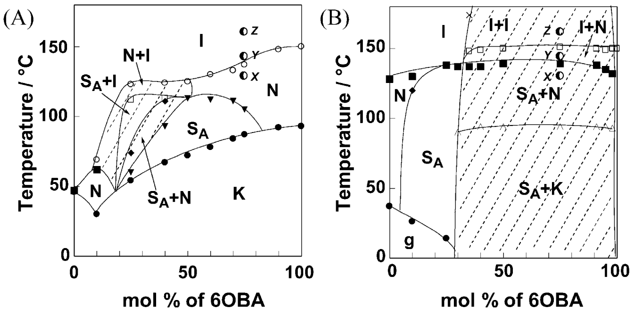

Fig. 5. Phase diagrams of (A) A6OCB/6OBA blend and (B) P6OCB/6OBA blend. The shaded parts indicate two-phase regions. *X*, *Y*, and *Z* correspond to the points at which photoirradiation was performed for A6OCB/6OBA blend containing CL and PI.

dimer of 6OBA has been taken as a single molecule, so that molecular weight of 444.56 calculated from the dimer of 6OBA was used for preparation of the phase diagrams. The phase diagrams of the blends containing 6OBA were quite different from those of the same mesogenic system containing 6OCB. The phase diagram of A6OCB/6OBA blend is depicted in Fig. 5(A). Although phase separation was observed in the shaded part of the phase diagram, the blend exhibited homogeneous phases in wide temperature and composition ranges. Only a nematic phase was observed near both sides of the phase diagram, while in addition an induced smectic A phase was seen around the middle of it. The phase diagram of P6OCB/6OBA blend is shown in Fig. 5(B). Until the composition of 6OBA reached ca. 30 mol%, the blend exhibited a homogeneous phase. At low concentrations, 6OBA was soluble within P6OCB, and this solubility behavior is similar to that of a plasticizer. When the concentration of 6OBA exceeded 30 mol%, however, the blend was divided into two phases, a polymer-rich phase containing ca. 30 mol% of 6OBA and a phase containing almost 100% of 6OBA. Each of the two phases showed phase transitions at its phase transition temperatures. We previously reported similar phase behavior observed for the blend between side-chain LC polymer and low molecular weight LC [15]. In our previous study, we used the side-chain LC polymer having a benzoic acid group as a mesogen and 4-cyano-4′-hexyloxybiphenyl as a low molecular weight LC. Although the mesogens of the SCLC polymer and the low molecular weight LC used in the previous study were the reverse of those in the present study, both of the blends were the same in their general phase behavior.

Before we conducted photoirradiation for the A6OCB/6OBA blend whose mole ratio is 25/75, the effect of CL and PI on phase transition temperatures of the blend was investigated. The results are listed in Table 3. There is no difference in the sequences of LC phases of the blends with and without CL and PI. Phase transition temperatures of the blend with CL and PI are only 1–3 °C lower than those of the blend having neither CL nor PI. It was found that the addition of CL and PI to the blend had no significant effect on the liquid crystallinity of the A6OCB/6OBA blend.

Using the A6OCB/6OBA (25/75 mol%) blend with CL and PI, photoirradiation was carried out in three different regions of the phase diagrams. In the first region, the A6OCB/6OBA blend shows a nematic phase while polymer-rich phase and 6OBA-rich phase of the P6OCB/6OBA blend exhibit a smectic phase and a nematic phase, respectively (the N ⟶ (S,N) region). In the second region, the A6OCB/6OBA blend is isotropic while polymer-rich phase and 6OBA-rich phase of the (P6OCB/6OBA) blend are in the isotropic phase and the nematic phase, respectively (the I ⟶ (I,N) region). In the third region, the A6OCB/6OBA blend is isotropic; moreover, polymer-rich phase and 6OBA-rich phase of the (P6OCB/6OBA) blend are both in the isotropic phases (the I ⟶ (I,I) region). By conducting photopolymerization in these regions, we can investigate the effect of the ordering field, which is present before and/or after photoirradiation, on morphology of the resultant polymer networks.

First, we carried out photopolymerization in the N ⟶ (S,N) region. In this region, the ordering field exists both before and after photopolymerization. The A6OCB/6OBA (25/75 mol%) blend containing CL and PI was irradiated with UV light at 130 °C in the nematic region. This condition corresponds to the *X* point shown in Fig. 5(A) and (B). Photomicrographs of the A6OCB/6OBA blend with CL and PI taken before and after photoirradiation are shown in Fig. 6. Before photoirradiation, a schlieren texture characteristic of a nematic phase could be observed for the blend (Fig. 6(A)). While birefringence and brush lines were maintained as shown in Fig. 6(B), fine lines appeared on the surface of the blend after photoirradiation. In order to investigate properties of the irradiated sample, it was heated from 130 °C. The strong birefringence was lost at 153 °C which corresponds to the clearing point of 6OBA, however a weak birefringence remained, as shown in Fig. 6(C). This weak birefringence reduced from 155 °C and was not detectable at 160 °C. Fig. 7 shows a photomicrograph of the irradiated blend taken at 160 °C under unpolarized light. It is particularly noteworthy that a

Table 3
Phase transition temperatures (°C) of A6OCB/6OBA blends with and without CL and PI on cooling

LC blend	Mol ratio	Phase transition behavior[a]						
A6OCB/6OBA	25/75	I	142	N	106	S_A	88	K
A6OCB/6OBA/CL/PI	25/75/0.6/1.8	I	139	N	103	S_A	87	K

[a] Determined from optical microscopy and DSC measurements on the cooling scans. Abbreviations: I = isotropic, N = nematic, S_A = smectic A, K = crystalline.

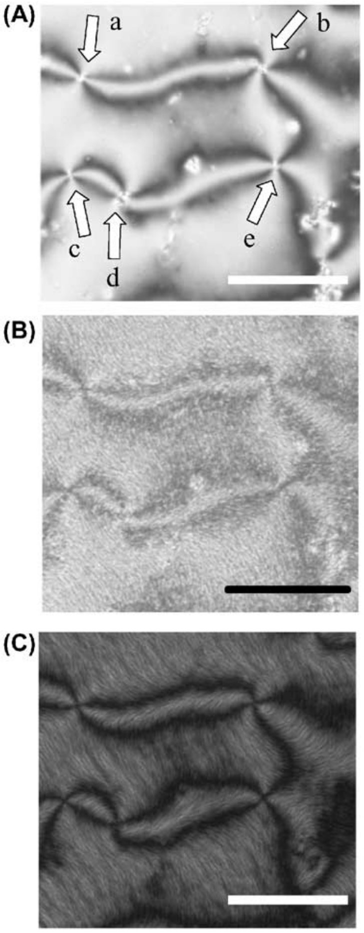

Fig. 6. Polarized optical micrographs of A6OCB/6OBA (25/75 mol%) blend containing CL and PI taken at (A) 130 °C before photoirradiation, (B) 130 °C after photoirradiation, and (C) 153 °C after photoirradiation at 130 °C. The arrows indicate disclinations. Scale bars correspond to 100 μm.

periodic pattern of striations was formed over the whole irradiated area of the surface. The striations were attributable to anisotropic morphology of the resulting LC polymer network because they were observed without polarization. Considering a scale and orientation of the morphology, this may be closely related to the direction field and disclinations of a schlieren texture existed before photoirradiation. Compared the photographs of Figs. 6(A) and 7, the strength S of all the disclinations, namely, a, b, c, d and e, was found to be ±1. However the sign of them cannot be identified at this stage.

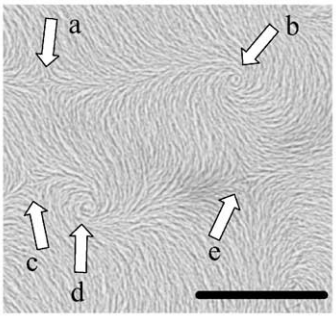

Fig. 7. An unpolarized optical micrograph of A6OCB/6OBA (25/75 mol%) blend containing CL and PI taken at 160 °C after photoirradiation at 130 °C. Scale bar corresponds to 100 μm.

Next, we performed photoirradiation for the A6OCB/6OBA blend in the I → (I,N) region. In this region, the ordering field is generated only after photopolymerization. The A6OCB/6OBA (25/75 mol%) containing PI and CL was irradiated with UV light at 145 °C in the isotropic region. This condition corresponds to the Y point in Fig. 5. The A6OCB/6OBA blend showed a homogeneous isotropic phase whereas the P6OCB/6OBA blend was composed of two phases, which were a polymer-rich isotropic phase and a nematic phase of 6OBA at the Y point. Before photoirradiation, a homogeneous isotropic phase was observed for the A6OCB/6OBA blend containing CL and PI under unpolarized light, as shown in Fig. 8(A). After photoirradiation, a nematic phase could be seen under crosspolarized light (Fig. 8(B)). When it was observed under unpolarized light, we could clearly see the phase-separated pattern which had a polygonal structure, as shown in Fig. 8(C). The nematic phase surrounded by the network changed to an isotropic phase at 153 °C on heating while the network was maintained until decomposition. This result suggests that the LC polymer network, which was derived from A6OCB, phase separated from 6OBA, and 6OBA

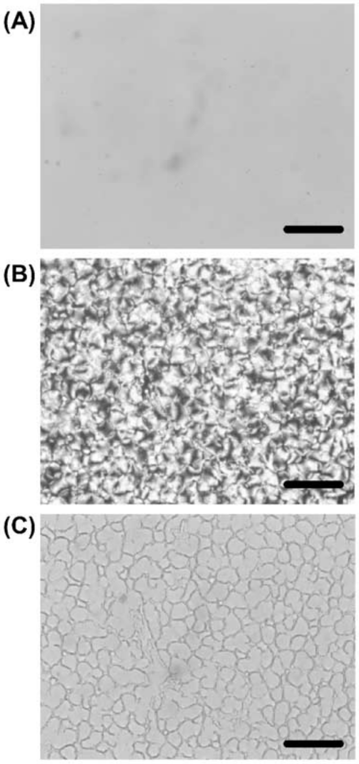

Fig. 8. Optical micrographs of A6OCB/6OBA (25/75 mol%) blend containing CL and PI taken at 145 °C (A) under unpolarized light before photoirradiation, (B) under crosspolarized light after photoirradiation at 145 °C, and (C) under unpolarized light after photoirradiation at 145 °C. Scale bars correspond to 100 μm.

exhibited a nematic phase. This phase-separated structure is analogous to that which has often been observed for polymer-dispersed liquid crystals consisting of a low molecular weight LC and non-LC polymer prepared by the phase separation techniques [22]. Although the morphology of the LC polymer network based on phase separation could be observed, it had no anisotropy due to the lack of the ordering field before photopolymerization.

Finally, we conducted photoirradiation for the A6OCB/6OBA blend in the I ⟶ (I,I) region. In this region, the ordering field is absent from the blend both before and after photopolymerization. The A6OCB/6OBA (25/75 mol%) blend containing CL and PI was irradiated with UV light at 160 °C in the isotropic region. This condition corresponds to the *Z* point in Fig. 5(A). At the *Z* point, the A6OCB/6OBA blend exhibited a homogeneous isotropic phase; moreover, polymer-rich phase and 6OBA-rich phase of the P6OCB/6OBA blend are both isotropic. Photomicrographs of the A6OCB/6OBA blend with CL and PI taken under unpolarized light before and after photoirradiation are shown in Fig. 9. While a homogenous isotropic phase was observed before photoirradiation (Fig. 9(A)), the structure of the LC polymer network associated with phase separation appeared after photoirradiation (Fig. 9(B)). The LC polymer network obtained by photopolymerization in the I ⟶ (I,I) region had a continuous structure without anisotropy.

In the above experiments, photopolymerization of the A6OCB/6OBA blend was carried out without any alignment techniques. It is of particular interest to attempt to control the morphology of phase-separated structures in the long range by means of aligning a nematic phase of the blend. The A6OCB/6OBA (25/75 mol%) blend containing CL and PI was placed between a pieces of glass plates, which were uniaxially rubbed by a polyester cloth and assembled, so that the rubbing directions were the same. Photopolymerization was performed for the blend in the N ⟶ (S,N) region. Fig. 10(A) shows a photomicrograph of the blend taken at 130 °C before photoirradiation. As indicated in Fig. 10(A), the angle between the rubbing direction and polarized direction was 45°. A homogeneous texture of a monodomain nematic phase was successfully obtained even without an alignment film such as a polyimide. Fig. 10(B) shows a photomicrograph of the blend taken at 160 °C after photoirradiation at 130 °C. An anisotropic phase-separated structure ordered in the long range was seen under unpolarized light. A periodic pattern of striations formed along the rubbing direction, that is, the LC polymer network having a fibrous morphology, which aligned parallel to the LC director, was obtained. Therefore, the arrows of a, c, and e in Figs. 6(A) and 7 correspond to disclination with $S = -1$ and those of b and d indicate disclination with $S = +1$ [23]. Surface interaction aligned LC molecules in the same direction to yield the long-range ordered phase-separated structure of the LC polymer network.

We consider that the reason why the LC polymer network having the anisotropic phase-separated structure could be obtained for the A6OCB/6OBA blend at the *X* point of the phase diagrams as follows. As can be seen from the phase diagrams, A6OCB is miscible with 6OBA at mol ratio of 25/75, whereas P6OCB prepared from A6OCB is immiscible with 6OBA at the same mol ratio. Therefore, the polymer derived from A6OCB by photopolymerization phase separated from 6OBA. Since the single phase of the A6OCB/6OBA blend and two phases of the P6OCB/6OBA blend were all liquid crystalline at the *X* point, the phase separation proceeded under anisotropic field and was immobilized by the crosslinker before arriving at a

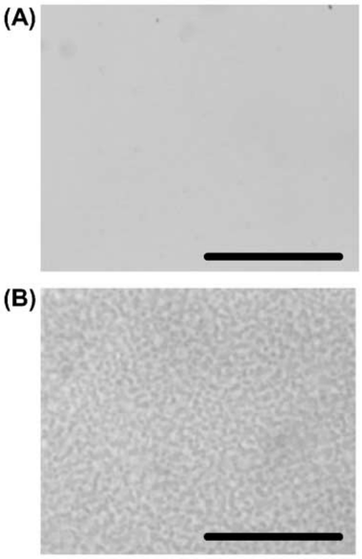

Fig. 9. Unpolarized optical micrographs of A6OCB/6OBA (25/75 mol%) blend containing CL and PI taken at 160 °C (A) before photoirradiation and (B) after photoirradiation at 160 °C. Scale bars correspond to 50 μm.

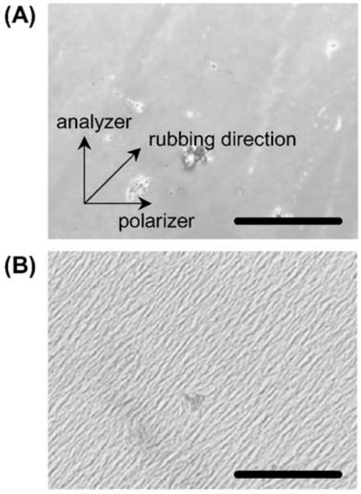

Fig. 10. Optical micrographs of A6OCB/6OBA (25/75 mol%) blend containing CL and PI sandwiched between rubbed glass plates taken at (A) 130 °C under crosspolarized light before photoirradiation and (B) 160 °C under unpolarized light after photoirradiation at 130 °C. Scale bars correspond to 100 μm.

thermodynamically stable state, that is, a sea-island structure [15]. By comparing the results of the *Y* and *Z* points, it is found that phase-separated structures of the LC polymer network also depend to a significant extent on whether one of the two phases induced by photopolymerization is LC phase.

To investigate time-dependence of the phase-separated structures of the LC polymer networks, the (A6OCB/6OBA) blend was irradiated for various time and observed under an optical microscope immediately after irradiation. It was found that the phase-separated structures of the LC polymer networks, which were similar to that obtained by 10 min photoirradiation, formed by irradiation for the time shorter than 10 s. Unlike polymerization-induced phase separation for (monomer/polymer) blend in which the phase-separated structure develops with the elapse of time [24], in our system of (LC monomer/LC) blend containing the crosslinker, it is difficult to follow the time-evolution of phase separation, because crosslinking proceeds as fast as polymerization and the resulting polymer network phase separates from the non-reactive LC even at relatively small molecular weight. Low viscosity of the blend in LC phases may be one of the reasons. If a (LC monomer/LC) blend is obtained, in which polymerization and crosslinking proceed at a slow rate and phase separation occurs under an LC phase, time-dependence of anisotropic phase-separated structures may become apparent.

4. Conclusion

Photopolymerization of (LC monomer/LC) blends containing CL and PI, whose mesogens were the same, yielded the LC polymer networks having no phase-separated structure. In contrast, the LC polymer networks with specific phase-separated structures were obtained by photopolymerization of (LC monomer/LC) blends, whose mesogens were different. The difference results between these two kinds of blends could be explained by comparing the phase diagrams of (LC monomer/LC) blends and (the corresponding LC polymer/LC) blends. Photopolymerization in the region, where the single phase of the (LC monomer/LC) blend and the two separated phases of the (LC polymer/LC) blend are all liquid crystalline, afforded the LC polymer network having the fibrous morphology based on phase separation. The fiber direction was formed parallel to the LC director. The whole phase-separated patterns of the polymer networks were associated with LC textures, such as a schlieren and a homogeneous textures, exhibited by the blend before photopolymerization. We expect that various morphologies would be given to LC polymer networks because it is possible to develop a variety of LC textures from (LC monomer/LC) blends, and novel applications would be developed in LC polymer networks having the specific morphologies.

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