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Morphological studies of a hydrogen-bonded LC polymer obtained by photopolymerization in LC solvents

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Anisotropic morphologies and the phase behaviour of a hydrogen-bonded LC polymer obtained by photopolymerization in two kinds of LC solvent are discussed. The hydrogen-bonded LC monomer, 4-(6-acryloyloxyhexyloxy) benzoic acid (A6OBA), was photopolymerized in 4-cyano-4'-hexyloxybiphenyl (6OCB) and in 4-cyano-4'-undecyloxybiphenyl (11OCB), which show a nematic phase and a smectic A phase, respectively. After photopolymerization, the LC media were removed by extraction and the pure polymer was observed by scanning electron microscopy. SEM images showed that the polymer possessed fibrous morphology with a fibre diameter of a few micrometers, based on polymerization-induced phase separation. The overall geometries reflected typical LC characteristics such as schlieren and focal-conic fan textures. It was found that the hydrogen bond between benzoic acid groups in the monomer was rigid enough to fix the anisotropic phase-separated structure forming during the early stage of phase separation; however, it could not permanently maintain the fibre structure due to dissociation at elevated temperature. X-ray measurements revealed that a well developed layer structure of the hydrogen-bonded mesogen existed in the polymer obtained from the smectic phase of 11OCB, whereas a polymer layer structure could develop only partially from the nematic phase of 6OCB.

1. Introduction

LC polymer networks or LC elastomers have attracted considerable attention because of their unique properties [1–4]. Of particular interest are non-display applications such as second harmonic generation [5, 6], piezoelectricity [7, 8], electrostriction [9], as tunable laser sources [10], and thermally stimulated anisotropic deformation [11, 12]. In order to exploit their properties to the full, it is necessary to align the mesogenic groups macroscopically. In particular, for mechanical properties such as modulus of elasticity and deformation response to stimuli, not only the alignment of the mesogens but also the overall geometry of LC polymer networks is of great importance.

From this point of view, in a previous paper we reported the preparation of LC polymer networks with fibrous morphologies in which the mesogenic group is

also macroscopically aligned [13]. An LC monomer was photopolymerized and crosslinked in liquid crystalline media. Photopolymerization-induced phase separation, which occurred under the liquid crystalline order, endowed the resulting network with anisotropic morphologies. The morphologies were fixed by covalent bonds because a small amount of bifunctional monomer had been added as a crosslinker. The alignment of the mesogens was achieved by the rubbing technique.

In recent years, liquid crystalline polymer networks, crosslinked not by covalent bonds but by hydrogen bonds, have been extensively studied [14–17]. Although the polymer networks have dense hydrogen bonds that form between benzoic acid moieties in the side chain, they can exhibit liquid crystal phases and a reversible LC–isotropic phase transition. Since the benzoic acid of the side chain possesses functionality, as in the formation of a 1:1 hydrogen bond with a pyridyl moiety [18–20], and responds to pH change in aqueous

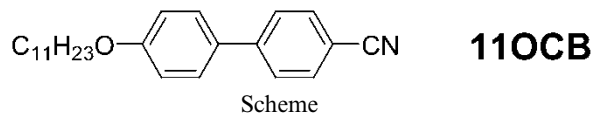
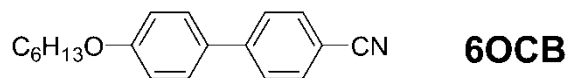
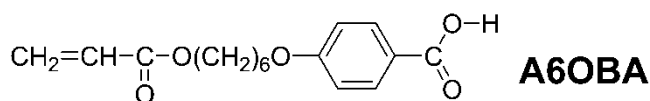
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solution [21, 22], many interesting experiments have been made with these hydrogen-bonded LC polymers.

The polymerization of a hydrogen-bonded monomer having a vinyl group in LC media, was studied by Blumstein *et al.* [23] and Amerik *et al.* [24]. They polymerized *p*-methacryloyloxybenzoic acid in LC phases afforded by *p*-alkoxybenzoic acids and demonstrated polymerization rate, conversion, and the tacticity of the polymer backbone. Phase separation of the polymer from the LC media was not mentioned.

In our current study, we have attempted to prepare LC polymer networks from a hydrogen-bonded monomer without a crosslinker by using photopolymerization-induced phase separation. While a hydrogen-bonded monomer may be expected to act as a crosslinker, it is of considerable interest to know whether it is possible to obtain LC polymers with anisotropic fibrous morphologies forming at the early stage of phase separation, because the hydrogen bond is significantly weaker than the covalent bond. Since hydrogen bonds are dynamic in nature and their strength varies with temperature; it is also interesting to study the temperature dependence of morphology, and the morphological differences between polymer networks resulting from hydrogen bonding and those arising from covalent bonding. Therefore, 4-(6-acryloyloxyhexyloxy) benzoic acid (A6OBA) was synthesized as a hydrogen-bonded monomer and photopolymerized in liquid crystalline media, namely 4-cyano-4'-hexyloxybiphenyl (6OCB) and 4-cyano-4'-undecyloxybiphenyl (11OCB). The resulting polymers have been systematically characterized. The molecular structures of the monomer and the LC media used in this study are shown in the scheme. 6OCB and 11OCB are a nematogen and a smectogen, respectively. Since the cyanobiphenyl mesogen of the LC solvents was quite different from that of the monomer, we anticipated polymerization-induced phase separation. Furthermore, if a blend consisting of A6OBA and 6OCB and a blend of A6OBA and 11OCB exhibit nematic and smectic phases, respectively, we can investigate the effect on morphology of the LC phases in which photopolymerization is conducted.

First, using polarizing optical microscopy (POM) in the presence of the LC solvent, we examined the formation of specific morphologies in hydrogen-bonded polymers and their phase behaviour resulting from photopolymerization. Subsequently, by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD), we investigated the detailed microstructures of the neat polymers obtained after extraction of the LC solvent and unreacted LC monomer. In addition, the phase transition behaviour of the neat polymers was studied by differential scanning calorimetry (DSC).



Scheme

2. Experimental

2.1. Materials

4-Cyano-4'-hexyloxybiphenyl (6OCB), 4-methoxyphenol, and 2,2-dimethoxy-2-phenylacetophenone were purchased from Merck Ltd, Wako Pure Chemical Industries, Ltd, and Tokyo Kasei Kogyo Co., Ltd, respectively. They were used without further purification. 4-Cyano-4'-undecyloxybiphenyl (11OCB) was prepared by etherification from 4-cyano-4'-hydroxybiphenyl and 11-bromoundecane in the presence of K_2CO_3 in a DMF solution. The monomer, 4-(6-acryloyloxyhexyloxy)-benzoic acid (A6OBA), was synthesized as previously described [25].

2.2. Blend preparation

A6OBA and 6OCB (or 11OCB), in a mol ratio of 20/80, were placed in a sample bottle. Chloroform ($CHCl_3$) solutions of 4-methoxyphenol and of 2,2-dimethoxy-2-phenylacetophenone were added to the bottle. They were used as an inhibitor and a photoinitiator. Their concentrations with respect to A6OBA were 3000 ppm and 1 mol%, respectively. The homogeneous $CHCl_3$ solution was air-dried at room temperature. The residual solids were thoroughly dried in vacuum for several hours at 25°C. The thermal properties of the blends and pure compounds are listed in the table. Phase transition temperatures and the types of mesophase were determined from DSC measurements and POM. Although pure A6OBA was thermally polymerized to a large extent during the measurements, the addition of 3000 ppm of 4-methoxyphenol could prevent this. A6OBA containing 4-methoxyphenol showed a smectic A and a nematic phase on heating, and a monotropic smectic C phase on cooling. 6OCB and 11OCB exhibited a nematic phase and a smectic A phase, respectively. Each of the blends, showed a homogeneous and single LC phase. Since the A6OBA/6OCB blend exhibited a

Table 1. Thermal properties of LC compounds and LC blends: transition temperatures ($^{\circ}\text{C}$) and enthalpies of transitions (J g^{-1} , in parentheses). I=isotropic; N=nematic; SmA=smectic A; SmC=smectic C; Cr=crystalline.

Material	Phase transition behaviour ^a															
	Heating								Cooling							
A6OBA ^a	Cr	92 (102.3)	SmA	102 (3.0)	N	109 (5.8)	I	I	108 (6.0)	N	100 (3.6)	SmA	91 (—) ^c	SmC	60 (99.0)	Cr
6OCB	Cr			59 (99.1)	N	77 (1.8)	I	I	75 (2.0)	N	34 (78.4)	Cr				
11OCB	Cr			69 (106.1)	SmA	86 (9.5)	I	I	84 (9.0)	SmA	51 (103.0)	Cr				
A6OBA/6OCB ^b (20/80 mol%)	Cr			56 (96.0)	N	85 (2.2)	I	I	84 (2.1)	N	10 (53.5)	Cr				
A6OBA/11OCB ^b (20/80 mol%)	Cr ₁	59 (36.6)	Cr ₂	65 (67.9)	SmA	86 (8.7)	I	I	84 (8.4)	SmA	42 (—) ^d	Cr ₂	40 (82.4)	Cr ₁		

^a Containing 3000 ppm of 4-methoxyphenol.

^b Containing 3000 ppm of 4-methoxyphenol and 1 mol% of 2,2-dimethoxy-2-phenylacetophenone based on A6OBA.

^c The peak could not be detected.

^d The SmA–Cr₂ peak is overlapped with the Cr₂–Cr₁ peak.

nematic phase and the A6OBA/11OCB blend a smectic A phase, the effect of the types of LC phases on the photopolymerization of A6OBA could be easily investigated using these blends.

2.3. Photopolymerization

The blends were placed between poly(vinyl alcohol) (PVA)-coated glass plates, which were rubbed prior to use if necessary. The temperature of the samples was controlled by a Mettler FP82HT hot stage for investigation of photopolymerization by optical microscopy. UV irradiation (one min; 200 W Hg-Xe lamp; glass fibre lens; 20 mW cm^{-2}) of the A6OBA/6OCB and the A6OBA/11OCB blends was performed at 70°C and 80°C , respectively. These temperatures were selected for investigation as both the blends and their pure components show LC phases in this range. To obtain samples for FTIR, SEM, XRD, and DSC measurements, a Linkam LK-600PH was used for temperature control as it allowed the whole area of the sample to be irradiated. Photoirradiation was carried out for the blends at the same temperatures as those used in optical microscopy. After one min of irradiation, the samples, sandwiched between the glass plates, were placed rapidly in EtOH at 25°C . After the glass plates were separated, most of the samples adhered to one of the plates. The separated plates were extracted with EtOH for 24 h to remove the cyanobiphenyl derivatives and unreacted monomer, and were then dried *in vacuo*. The residual polymers remaining on the plates were used for SEM observation and XRD. The polymer films, which were peeled off from the glass plates in hot water, were

employed for FTIR and DSC measurements after vacuum drying.

Figure 1 shows FTIR spectra of the A6OBA/6OCB blend and of the pure polymer obtained from the same blend after UV irradiation and extraction. In the spectrum of the blend a large, sharp absorption band associated with a cyano group was observed at 2226 cm^{-1} , whereas this band became significantly smaller in the spectrum of the polymer. Furthermore, a small band at 1636 cm^{-1} , corresponding to a vinyl group, in the spectrum of the blend, was no longer visible in the spectrum of the polymer. Similar results were obtained for the polymer prepared from the A6OBA/11OCB blend. These results suggest that almost all the cyanobiphenyl derivatives and unreacted monomer could be removed from the polymer by extraction with EtOH. A carbonyl stretching band observed at 1682 cm^{-1} in the spectrum of the polymer indicates hydrogen bond formation between the benzoic acid moieties [26]. It is noteworthy that the dimer structure of the benzoic acid group was maintained after photopolymerization and extraction.

2.4. Characterization

An Olympus BH2 microscope equipped with a Mettler FP82HT hot stage was used for optical microscopy. Scanning electron microscopy of uncoated samples was conducted in the low vacuum mode using a Philips XL30 ESEM-FEG. FTIR spectroscopy was performed with a Perkin Elmer Spectrum One. Differential scanning calorimetry was carried out using a Seiko

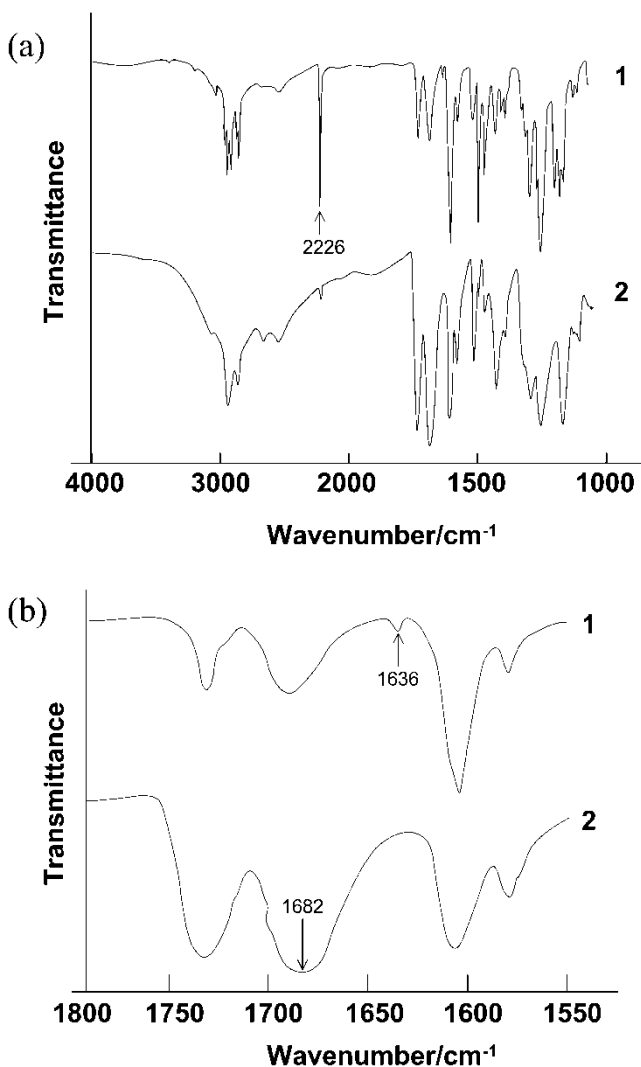


Figure 1. IR spectra of the A6OBA/6OCB blend (curve 1) and poly(A6OBA) (curve 2) in the range (a) 1000–4000 cm^{-1} and (b) 1550–1800 cm^{-1} .

Instruments Inc. DSC 6200. X-ray measurements of the polymers were conducted using a Rigaku Rint2000.

3. Results and discussion

First, we studied the photopolymerizations using POM. Figure 2 shows optical micrographs of the A6OBA/6OCB blend taken before and after UV irradiation. Before UV irradiation, a schlieren texture characteristic of a nematic phase was observed at 70°C when non-rubbed PVA-coated plates were used, figure 2(a). A homogeneous nematic phase displaying uniaxial alignment was successfully obtained using rubbed PVA-coated plates. While retaining the blend in the N phase at 70°C, it was irradiated with UV light for one minute. A POM micrograph of the blend

taken after UV irradiation is shown in figure 2(b). While some fine lines appeared, on the whole the texture hardly changed. The periodic fine lines were evident even when observed in unpolarized light, figure 2(c). This structure may be caused by phase separation between 6OCB and poly(A6OBA).

To investigate the morphological changes of poly(A6OBA) associated with altering temperature, the irradiated sample was heated from 70°C at the rate of 5°C min^{-1} . It exhibited a phase transition at 77°C, corresponding to the nematic–isotropic transition temperature of 6OCB. Figure 2(d) shows a POM micrograph of the irradiated blend taken at 80°C. Whereas 6OCB was in the isotropic phase at 80°C, the blend still exhibited birefringence and the schlieren texture remained. The periodic lines could be seen more clearly under unpolarized light than that observed at 70°C, figure 2(e). This may be because fibrous poly(A6OBA) aggregated. As the irradiated sample was subsequently heated, more and more fibres of poly(A6OBA) aggregated. Once birefringence eventually disappeared at about 180°C, which may correspond to an LC–isotropic transition temperature of poly(A6OBA), the fibres of poly(A6OBA) rapidly agglomerated and a sea–island structure formed. When the sample was cooled from 180°C, the island domain consisting of poly(A6OBA) and the sea part consisting of 6OCB exhibited isotropic–LC phase transitions at 176 and 76°C, respectively. However, the fibrous structure previously obtained just after UV irradiation did not re-appear. A POM micrograph of the irradiated A6OBA/6OCB blend taken at 170°C after cooling from 180°C is shown in figure 2(f). At this temperature, only the island domains consisting of poly(A6OBA) exhibited an LC phase.

It has already been reported that a blend of poly(A6OBA) (prepared from A6OBA by conventional solution polymerization) and 6OCB was immiscible in the range of low polymer concentration [27]. Simply mixing these compounds resulted in a sea–island structure. In this study, however, we were able to obtain the periodic pattern associated with LC phases throughout the photopolymerization-induced phase separation. It is noteworthy that even without a crosslinker, the phase-separated structure with a rather small periodicity was maintained unless the temperature was increased after photopolymerization. This may be attributed to the combined effects of intermolecular hydrogen bond formation between benzoic acid groups, the high glass transition temperature and the viscosity of poly(A6OBA). In an earlier study, we obtained an LC polymer network with an anisotropic phase-separated structure that could maintain its form on account of chemical crosslinking. In contrast, the anisotropic phase-separated structure

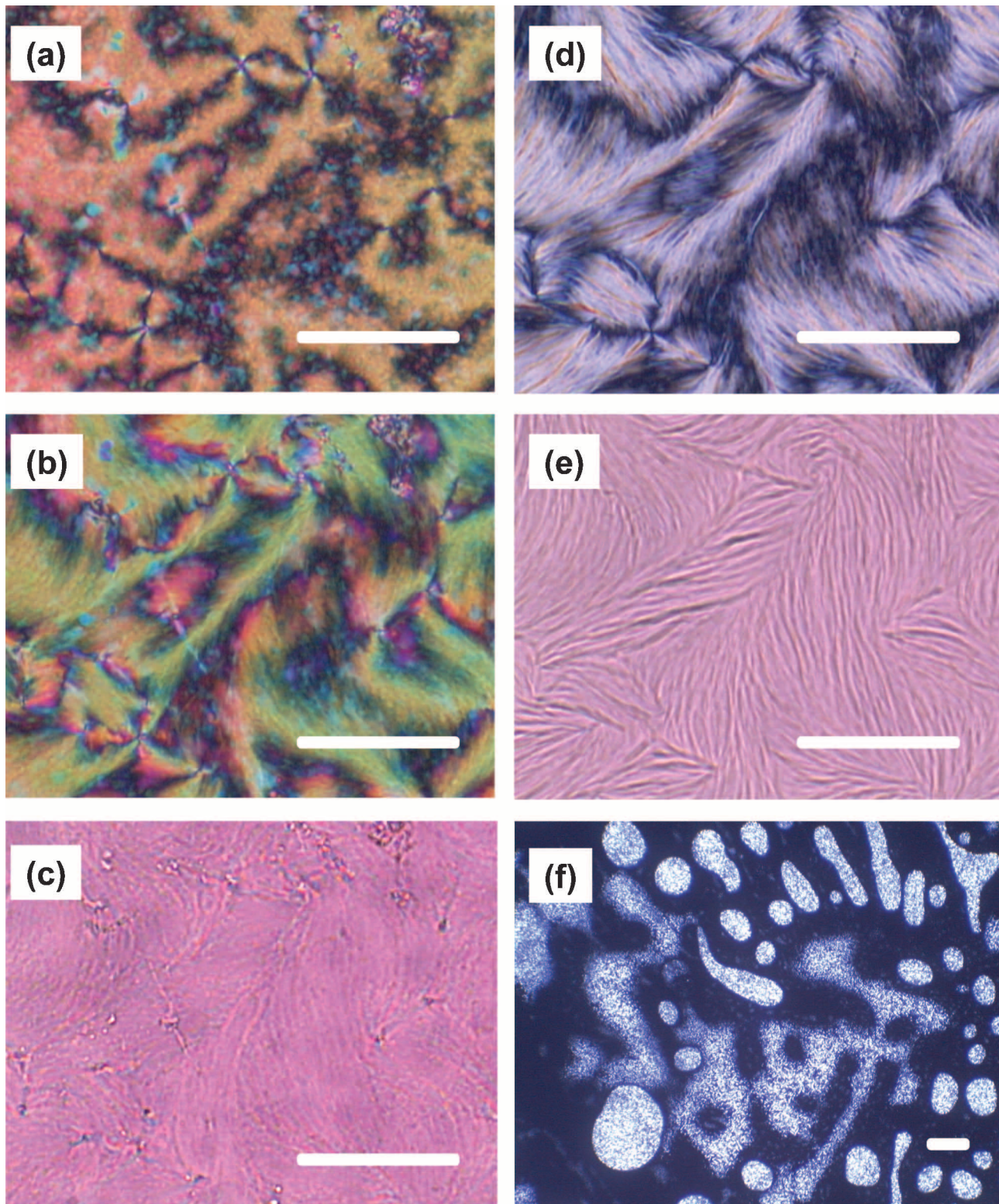


Figure 2. Optical micrographs of the A6OBA/6OCB (20/80 mol%) blend at 70°C under cross-polarized light before UV irradiation (a); at 70°C under crosspolarized light (b) under unpolarized light (c) after UV irradiation at 70°C; at 80°C under crosspolarized light (d) and under unpolarized light (e) after UV irradiation at 70°C; and at 170°C under crosspolarized light after UV irradiation at 70°C and cooling from 180°C (f). Scale bars correspond to 50 μm.

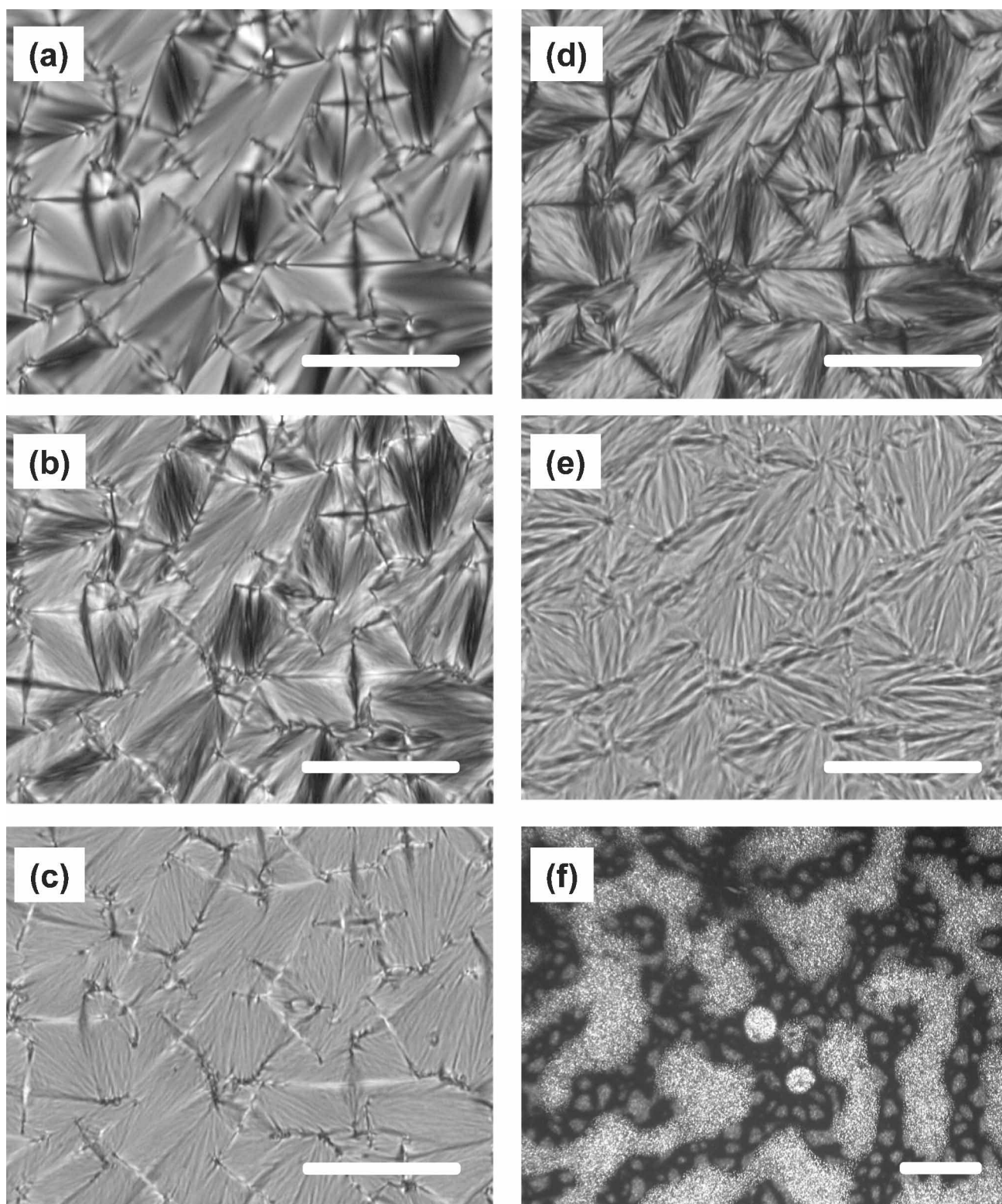


Figure 3. Optical micrographs of the A6OBA/11OCB (20/80 mol%) blend at 80°C under crosspolarized light before UV irradiation (a); at 80°C under crosspolarized light (b) and under unpolarized light (c) after UV irradiation at 80°C; at 90°C under crosspolarized light (d) and under unpolarized light (e) after UV irradiation at 80°C; and at 165°C under crosspolarized light after UV irradiation at 70°C and cooling from 170°C (f). Scale bars correspond to 50 μm.

obtained from the A6OBA/6OCB blend was destroyed at elevated temperature due to dissociation of the hydrogen bonds, and did not re-appear even when the blend was cooled from an isotropic phase to an LC phase when the hydrogen bonds reformed. Abrupt dissociation of hydrogen bonds at the LC–isotropic phase transition in liquid crystalline benzoic acids was reported in a previous paper [26].

Figure 3 shows optical micrographs of the A6OBA/11OCB blend taken before and after UV irradiation. Before UV irradiation, the blend exhibited a focal-conic fan texture characteristic of a smectic A phase at 80°C figure 3(a). While maintaining the blend in the SmA phase at 80°C, UV irradiation was performed for one minute. After irradiation, the LC texture hardly changed, figure 3(b), while the periodic lines, which were composed of poly(A6OBA), could be seen under unpolarized light, figure 3(c).

In order to study the dependence of poly(A6OBA) morphology on temperature, the irradiated sample was subsequently heated from 80°C at the rate of 5°C min⁻¹. It showed the phase transition associated with the LC–isotropic transition of 11OCB at 85°C, but still exhibited birefringence after that. Figure 3(d) shows a polarizing optical micrograph of the blend taken at 90°C. It retained the shape of the same focal-conic fan texture as that observed before UV irradiation. When observed through unpolarized light, figure 3(e), fine lines were clearly seen because the periodicity increased in comparison with that seen at 80°C. On increasing the temperature, the lines progressively gathered together, then eventually lost birefringence and a sea–island structure formed at around 170°C. As the blend was cooled from the isotropic state, the island domains showed a mesophase at 170°C and subsequently the sea part exhibited an LC phase at 84°C. A POM micrograph of the irradiated blend, taken at 165°C after cooling from 170°C, can be seen in figure 3(f). Only the island domains consisting of poly(A6OBA) showed birefringence. The fact that after UV irradiation periodic lines appeared, and two LC–isotropic phase transitions were observed at 85 and 170°C, indicates that the A6OBA/11OCB blend phase separated into 11OCB and poly(A6OBA) as a result of photopolymerization.

Independently of whether a nematic or a smectic A phase is present during UV irradiation, photopolymerization of the blends in the LC phase results in poly(A6OBA) displaying a periodic and anisotropic morphology, in which the geometries reflect the LC textures exhibited prior to UV irradiation. The LC–isotropic transition temperature is higher for the polymer obtained from a nematic phase than from a smectic A phase.

Next, using SEM and XRD, we determined the detailed microstructure of purified polymers showing anisotropic morphology. Figures 4 and 5 show backscattered SEM images of the uncoated polymers obtained from the A6OBA/6OCB blend. The polymers depicted there were prepared using non-rubbed and rubbed PVA-coated plates, respectively. The rubbing direction is indicated in figure 5. It was found that the polymers had a fibrous morphology with a diameter of a few μm and that the fibres extended along the LC direction. The hairpin curves observed in the images of figure 4 are considered to correspond to disclinations of a schlieren texture of a nematic phase.

Backscattered SEM images of the polymer prepared from the A6OBA/11OCB blend are shown in figure 6. The polymer showed a fibrous morphology with fibre diameter of a few μm, similar to the polymer obtained from A6OBA/6OCB. It is interesting that

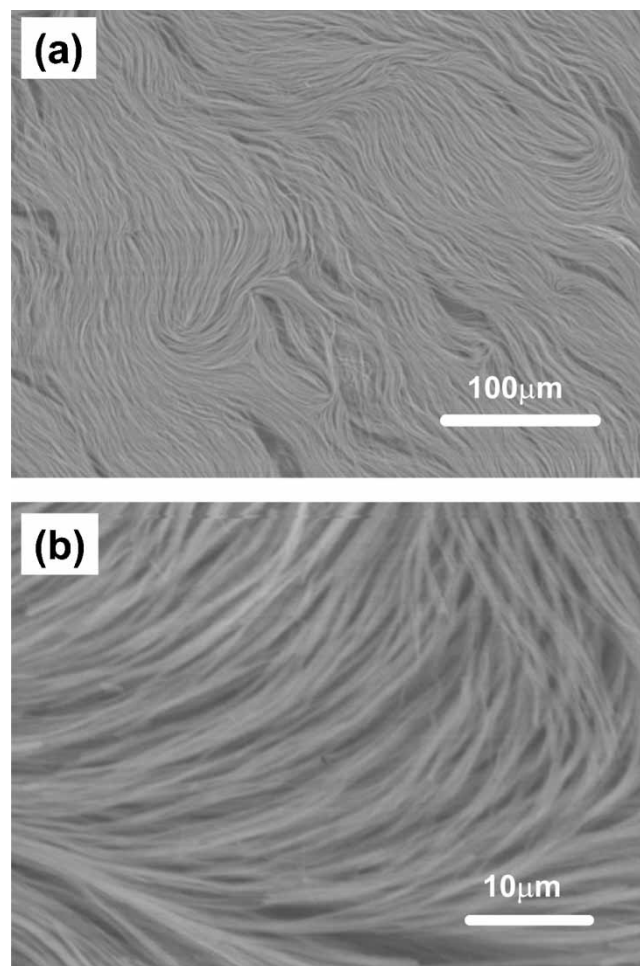


Figure 4. Backscattered SEM images of poly(A6OBA), obtained from the A6OBA/6OCB blend with unrubbed PVA-coated plates, taken at low (a) and high (b) magnification.

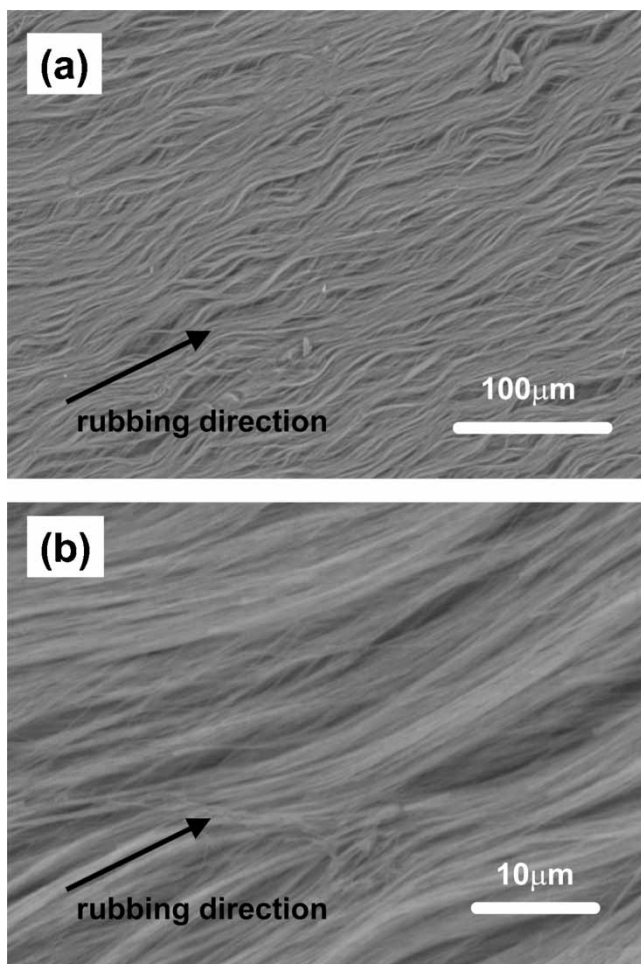


Figure 5. Backscattered SEM images of poly(A6OBA), obtained from the A6OBA/6OCB blend with rubbed PVA-coated plates, at low (a) and high (b) magnification.

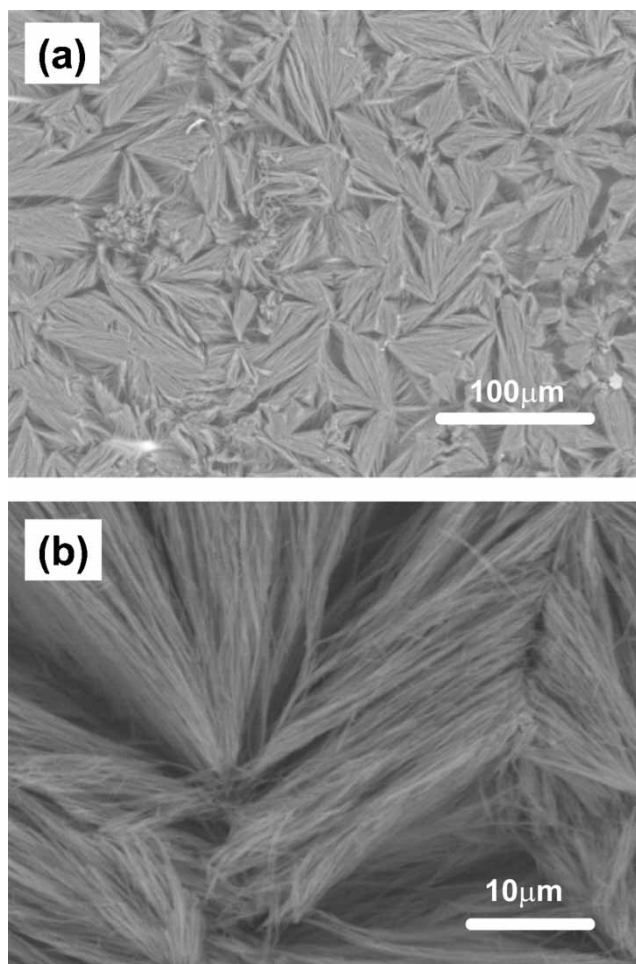


Figure 6. Backscattered SEM images of poly(A6OBA), obtained from the A6OBA/11OCB blend, at low (a) and high (b) magnification.

macroscopically, the polymer displayed rhombic shaped domains with one side *c.* 50 μm long. This macroscopic geometry was thought to be associated with a focal-conic fan texture of a smectic A phase. For a smectic A phase of the A6OBA/11OCB blend, a macroscopically aligned texture was not obtained even when the rubbed PVA-coated plates were used. On the basis of the geometry of a focal-conic domain [28], however, it can be considered that the fibres extended perpendicular to the smectic layer. The fact that anisotropic morphologies with a rather small periodicity were observed for polymers obtained by photopolymerization of the blends suggests that the hydrogen bond between benzoic acid moieties served efficiently to immobilize the phase separation at an early stage and maintain it during extraction.

In order to obtain information on how the hydrogen-bonded mesogen arranges in to the fibrous morphology, we performed XRD measurements on the bare polymers.

Figure 7 shows wide angle X-ray diffractograms of the polymers obtained from the A6OBA/6OCB blend (a) and the A6OBA/11OCB blend (b). A diffuse halo, which is associated with lateral packing of the mesogens, is observed at *c.* 22° in both diffractograms. The packing distance between the mesogens is estimated to be 4.1 \AA . No sharp peak is visible in the wide angle region in either of the diffractograms, which suggests that 6OCB could be removed from the polymer. This fact is consistent with the FTIR results. It is worth noting that sharp but small peaks are observed at 2.6° and 3.5° in the X-ray diffractogram of the polymer from the A6OBA/6OCB blend, whereas a sharp and large peak is seen at 2.5° for the polymer from the A6OBA/11OCB blend. Taking into account the values of distance estimated from these peaks, they appear to be associated with the smectic layers.

We consider that the difference in the small angle region of the diffractograms arises for the following

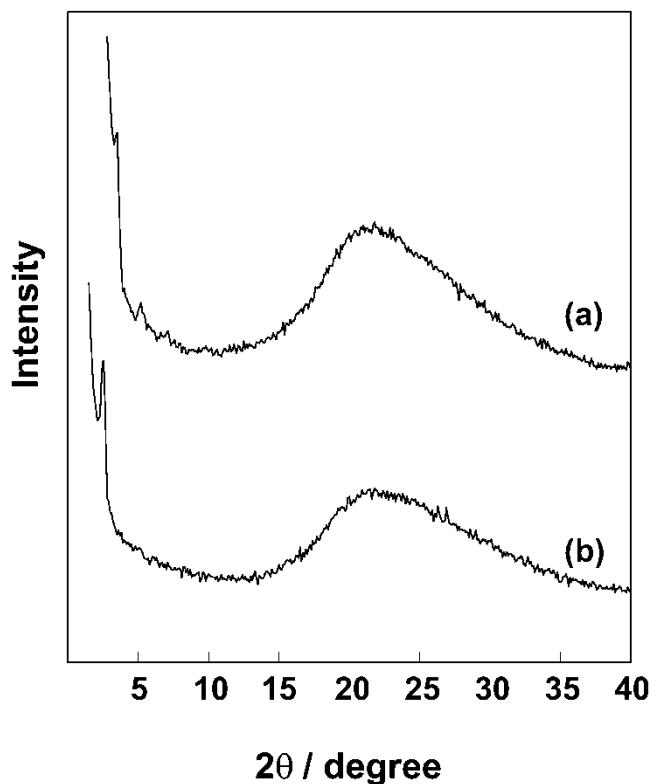


Figure 7. Wide angle XRD patterns of poly(A6OBA) obtained from the A6OBA/6OCB blend (a) and the A6OBA/11OCB blend (b).

reasons. In the case of the A6OBA/11OCB blend, the poly(A6OBA) could readily form a layer structure during polymerization because the smectic layer was present before photopolymerization. In contrast, no layer structure existed in the mesophase of the A6OBA/6OCB blend and photopolymerization progressed too fast for the growing polymer sufficiently to develop a layer structure before the positions of the mesogens were fixed by the formation of a hydrogen-bonded network. From the peak at 2.5° , the spacing of the smectic layer of the polymer obtained from the A6OBA/11OCB blend was estimated to be 35.3 \AA . To compare the layer spacing of the polymer with that of the A6OBA/11OCB blend before UV irradiation, XRD measurement was performed for the blend at 80°C in a smectic A phase using a horizontal sample stage diffractometer (Rigaku RINT-TTR) with a temperature controller. The spacing of the smectic layer of the blend was estimated to be 18.8 \AA . The layer spacing was significantly changed by photopolymerization and subsequent extraction. It may be considered that a H-bonded dimer of A6OBA lies across two layers of 11OCB in a smectic phase of the blend.

On the basis of the results so far discussed, we can schematically illustrate the structures of the polymers

obtained from the A6OBA/6OCB and A6OBA/11OCB blends as shown in figure 8. The length of the fully stretched conformation between two polymer backbones containing the hydrogen-bonded benzoic acid dimer is estimated to be 35 \AA by molecular modelling (figure 8). On comparing the molecular modelling results with X-ray measurements, the hydrogen-bonded mesogens of the A6OBA/11OCB polymer are found to have a smectic A structure. In contrast, in the A6OBA/6OCB polymer, there exist scattered domains consisting of layered structures of the hydrogen-bonded mesogens in the matrix of nematic-ordered mesogens. In addition, the mesogens align parallel to the fibre axis in the both polymers.

DSC thermograms of the polymers obtained after extraction are shown in figure 9. The polymer prepared from the A6OBA/6OCB blend exhibited broad and endothermic peaks at 178°C in both the first and the second heating scans, while the polymer from the A6OBA/11OCB blend showed broad and endothermic peaks at 172 and 171°C on the first and second heating scans, respectively. These results are consistent with the POM results in which the irradiated A6OBA/6OCB blend and A6OBA/11OCB blend lost birefringence at 178 and 172°C , respectively. Since the specific morphologies that had previously formed immediately after UV irradiation, disappeared from the polymers after the first heating, we consider that the difference of isotropization temperatures between the two polymers can be ascribed to differences in the primary structure.

4. Conclusions

A hydrogen-bonded monomer A6OBA, which forms a benzoic acid dimer structure, was photopolymerized in two LC solvents, 6OCB and 11OCB. The A6OBA/6OCB (20/80 mol%) and the A6OBA/11OCB (20/80 mol%) blends, which both contained an inhibitor and a photo initiator, were irradiated with UV in a nematic phase at 70°C and in a smectic A phase at 80°C , respectively. Immediately after photopolymerization, anisotropic phase-separated structures were observed under an optical microscope. Increasing the temperature of the samples resulted in disruption of the anisotropic structures into sea-island structures due to dissociation of hydrogen bonds. The anisotropic phase-separated structures did not recover even after decreasing the temperature to the LC phase. Scanning electron microscopy on the neat polymers, obtained after extraction of the LC solvents and unreacted monomer, revealed fibrous morphologies with a fibre diameter of a few micrometers. The overall geometries reflected the LC textures exhibited by the blends before UV irradiation. The polymer prepared from the N phase of the A6OBA/6OCB blend had a curved

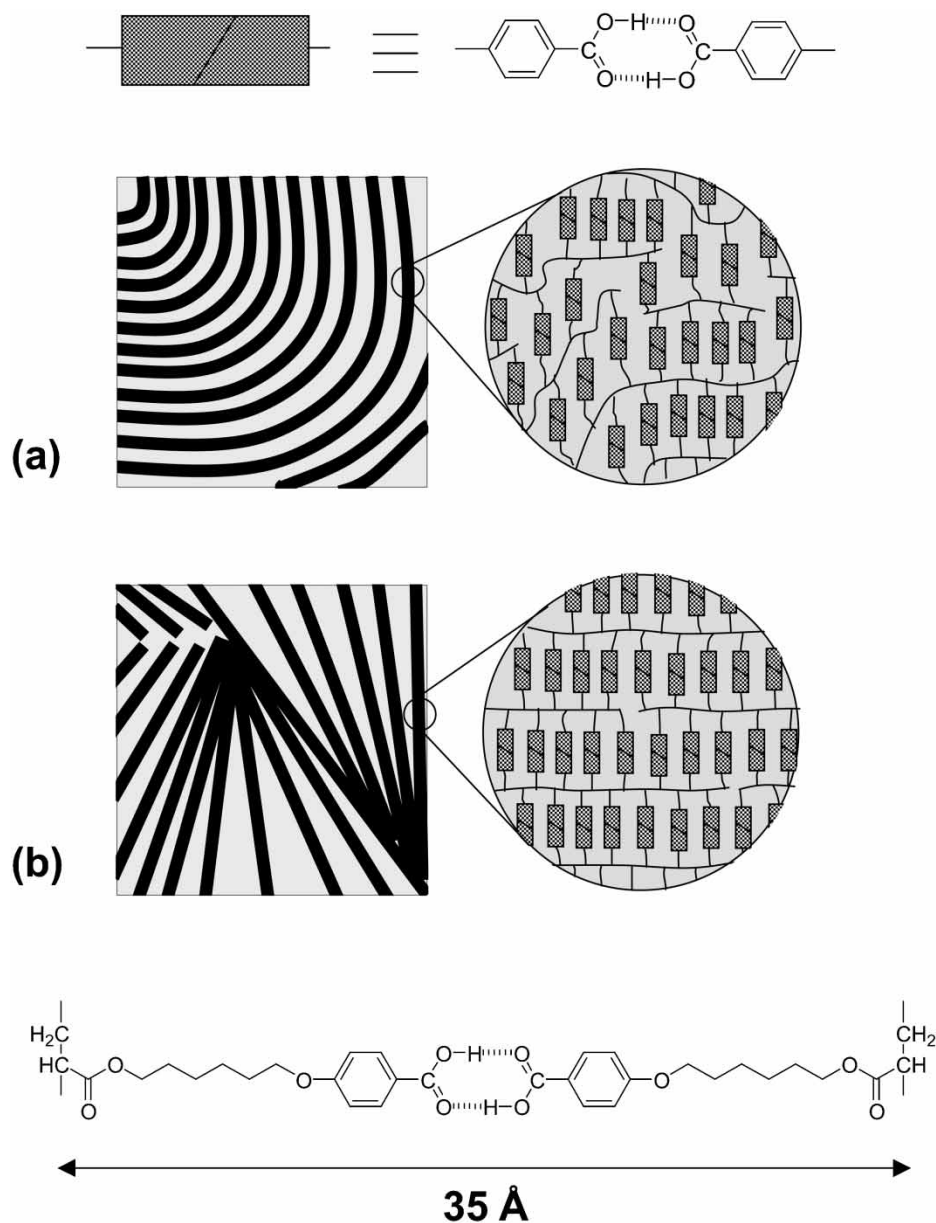


Figure 8. Schematic illustrations of the structures of poly(A6OBA) obtained from the (a) A6OBA/6OCB and (b) A6OBA/11OCB blends.

structure. In contrast, the polymer obtained from the SmA phase of the A6OBA/11OCB blend possessed rhombic shaped domains. They were associated with a schlieren texture and a focal-conic texture, respectively. In the small angle range, XRD patterns of the bare polymers revealed faint diffraction peaks for the A6OBA/6OCB polymer, whereas a large, sharp-shaped peak was seen for the polymer from the A6OBA/11OCB blend. This result suggests that a well developed layer structure of the hydrogen-bonded mesogens existed in the polymer from 11OCB, while a layer

structure could develop only to a certain extent in the polymer from 6OCB.

In this study, it was found that the hydrogen bond between benzoic acid groups of the side chain was rigid enough to immobilize the anisotropic morphology forming at the early stage of phase separation; however, it could not permanently maintain the fibrous morphology because of dissociation at elevated temperature. Furthermore, we found that the nature of the LC phases in which photopolymerization was carried out, not only affected the macroscopic geometries of

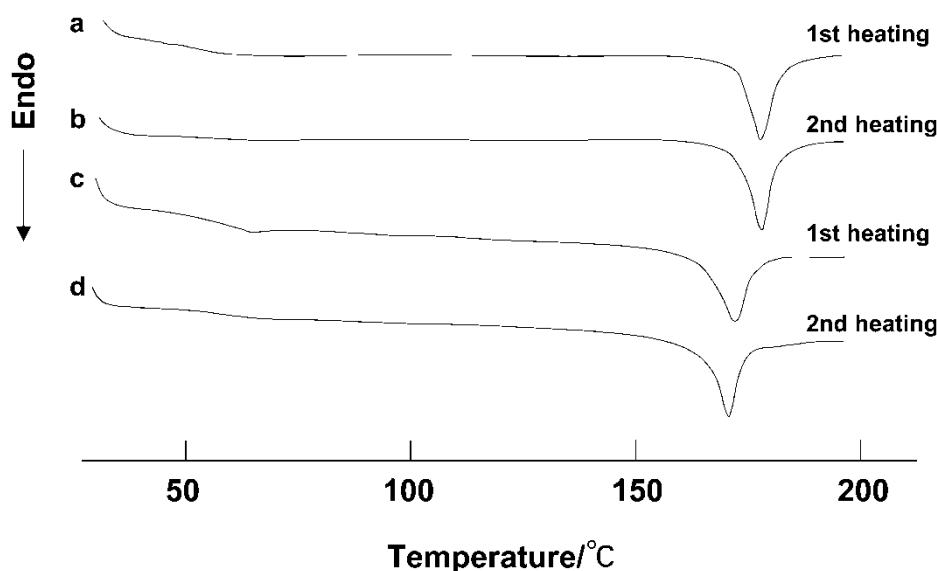


Figure 9. DSC thermograms of poly(A6OBA) obtained from the A6OBA/6OCB blend on the first heating (a) and second heating (b), and from the A6OBA/11OCB blend on the first heating (c) and second heating (d).

the resulting polymers, but also the alignments of the hydrogen-bonded mesogen in the side chain. Studies of hydrogen-bonded polymers with anisotropic morphologies, which are chemically crosslinked, are now in progress.

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