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Morphology of a hydrogen-bonded LC polymer prepared by photopolymerization-induced phase separation under an isotropic phase

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Abstract

A hydrogen-bonded LC polymer was prepared by photopolymerization of an LC blend composed of 4-(6-acryloyloxyhexyloxy)benzoic acid (A6OBA) and 4-hexyloxy-4′-cyanobiphenyl (6OCB), containing small amounts of an inhibitor and photoinitiator, at two different temperatures in an isotropic phase. To elucidate the factors determining the morphology of the obtained polymer (poly(A6OBA)), we chose two irradiation temperatures: one in the LC temperature range of the polymer, the other in the isotropic range. We investigated structures of the polymers by optical microscopy and scanning electron microscopy. SEM images showed that the film obtained at the lower temperature consisted of randomly extended fibers having a diameter of ca. 1.0 μm and some branches, whereas the film prepared at the higher temperature was composed of polymer particles with a diameter ca. 1.5 μm. By comparing these results with those of an earlier experiment in which we obtained macroscopically oriented LC fibers by photopolymerization under the LC phase of the blend, we infer the following; (i) the presence of an LC phase in the resulting polymer itself during photopolymerization is necessary for it to form fibrous morphology and (ii) the LC ordering field present prior to photopolymerization is not indispensable for the fibrous morphology but it is for the macroscopic orientation and reduction of the branches in the fibers.

Keywords: LC polymer; Photopolymerization-induced phase separation; Fiber

1. Introduction

Synthetic polymer fibers with nanometer-sized diameters have attracted much attention because of their potential for many important applications, which are associated with their specific characteristics such as large surface area to volume ratio and superior mechanical performance. In recent years, polymer nanofibers have been successfully fabricated by template synthesis [1], self-assembly [2,3], electrospinning [4,5], and so on.

In addition, it has been known for some time that LC polymers or networks having fibrous morphology are formed as a component of polymer-stabilized liquid crystals (PSLCs) [6–9], and the factors controlling the fibrous morphology have been intensively studied. While the kinds of the phases (liquid-crystalline or isotropic) exhibited by the polymers during the polymerization process probably have a significant influence on the morphology, a clear understanding of their relationship is still not available.

We have recently synthesized LC polymers, having diameters from a few micrometers down to hundreds of nanometers, by photopolymerization-induced phase separation [10–12]. The LC polymer fibers were prepared by photopolymerization of (LC monomer/low-molar-mass LC) blends. Their macroscopic structures are representative of the LC textures exhibited by the blend before photopolymerization. We have used various LC textures as templates for preparation of such LC polymer films.

In our previous paper [12], in order to elucidate a relationship between the phases exhibited by the phase-separated polymer and its morphology, we carried out photopolymerization of an LC blend at two specific temperatures in the LC state of the blend. In Fig. 1(a), the phase transition behaviour of the blend and the phase-separated polymer are compared; the two polymerization temperatures are indicated by the arrows. One of them (arrow A) was in the LC temperature range of the phase-separated polymer, while the other (arrow B) was in the isotropic range of the polymer.

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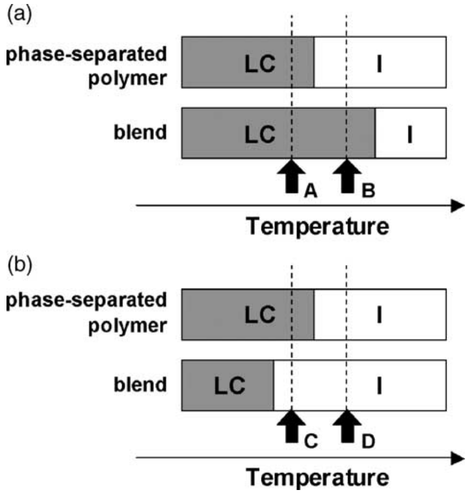
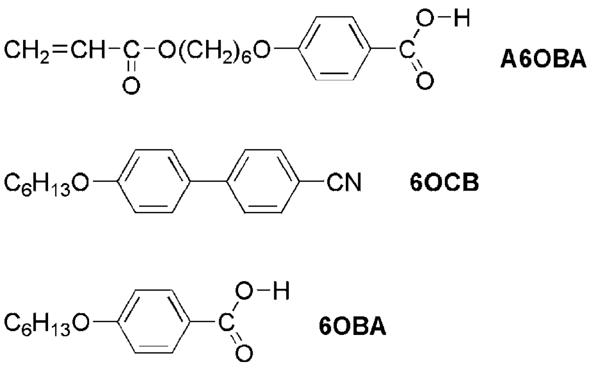


Fig. 1. Schematic representations of the relationship between the phase behaviour of the blend and the phase-separated polymer, and photopolymerization temperatures for (a) our previous study and (b) the present study. Abbreviations: I, isotropic; LC, liquid-crystalline.

We studied the morphology of the polymers by SEM and found that the presence of the LC phase of the phase-separated polymer during photopolymerization was necessary to form the fibrous morphology.

In the present study, to examine the necessity of the inherent LC phase of the phase-separated polymer to the formation of fibrous morphology and to clarify the role of the LC ordering field present prior to photopolymerization, we have prepared an LC blend from A6OBA and 6OCB (Scheme 1), and performed photopolymerization of the blend at two different temperatures (see arrows in Fig. 1(b)) in the isotropic state of the blend. At the lower temperature (arrow C), the phase-separated polymer, that is poly(A6OBA), shows an LC phase, while at the higher temperature (arrow D), poly(A6OBA) exhibits an isotropic phase. Morphological study of the polymers obtained from the two different conditions will enable us to understand the effect of an LC phase of the phase-separated polymer under conditions in which the LC ordering field is absent before photopolymerization. Consequently, the result ought also clarify the role of the LC ordering field in the morphology formation.

Moreover, by studying photopolymerization of an LC blend composed of A6OBA and 4-hexyloxybenzoic acid (6OBA) (Scheme 1), we demonstrate that polymerization-induced phase separation is essential for the LC polymer to take on fibrous morphology.



Scheme 1.

2. Experimental

2.1. Materials

6OCB was purchased from Merck Ltd and used as received. 6OBA was obtained from Tokyo Kasei Kogyo Co. Ltd and recrystallized from acetone before use. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone and the inhibitor, 4-methoxyphenol were purchased from Wako Pure Chemical Industries and Tokyo Kasei Kogyo Co. Ltd, respectively. They were used without further purification. A6OBA was synthesized as described in the literature [13].

2.2. Blend preparation and photopolymerization

The A6OBA/6OCB blend and the A6OBA/6OBA blend, in a mol ratio of 1/4, containing small amounts of inhibitor and photoinitiator were prepared by a procedure outlined in a previous paper [10]. Photopolymerization of the blends was also carried out following the previous technique. After photopolymerization, the blends were extracted with ethanol to remove soluble fractions. The insoluble polymers were investigated using SEM.

2.3. Characterization

An Olympus BH2 microscope equipped with a Mettler FP82HT hot stage was used for the optical microscopy. Scanning electron microscopy was carried out in a low vacuum mode using a Philips XL30 ESEM-FEG. Differential scanning calorimetry was performed using a Seiko Instruments Inc. DSC 6200.

3. Results and discussion

In Fig. 2, we compare LC temperature ranges of the A6OBA/6OCB blend, 6OCB, and the polymer poly(A6OBA) synthesized from A6OBA by solution polymerization in DMF. 6OCB showed a nematic phase from 35 to 76 °C and poly(A6OBA) exhibited an LC phase between 70 and 176 °C. Strictly speaking, the solution-polymerized poly(A6OBA) might be different from the photopolymerized one. However, since photopolymerization of an acrylate group in LC phases proceeds rapidly, and conversion and molecular weight are very high [13–16], the phase behaviour of the photopolymerized poly(A6OBA) may be similar to that of the solution-polymerized one. Therefore, we discuss photopolymerization conditions based on the solution-polymerized poly(A6OBA). In addition, we have already investigated the phase diagram of the blend between the solution-polymerized poly(A6OBA) and 6OCB [17], and mentioned the thermal behavior of the A6OBA/6OCB blend before and after UV

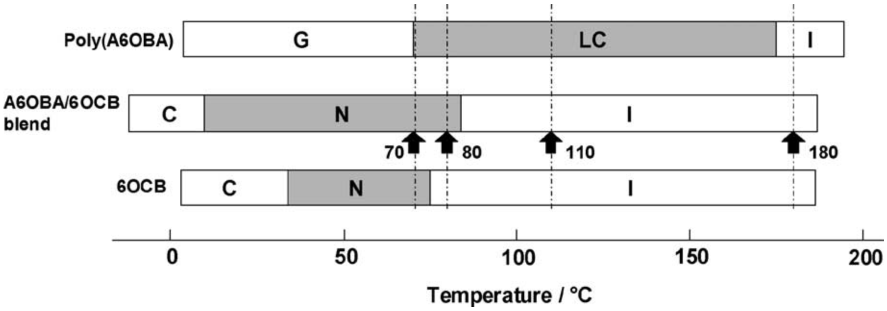


Fig. 2. Comparison of the LC temperature ranges of the A6OBA/6OCB blend, 6OCB, and poly(A6OBA). Abbreviations: I, isotropic; N, nematic; LC, liquid-crystalline; C, crystalline; G, glassy.

irradiation [10]. The results from these previous papers also support the validity of using the comparison in Fig. 2.

We previously carried out photopolymerization of the A6OBA/6OCB blend at 70 °C [10]. At this temperature, all the blend, phase-separated 6OCB, and poly(A6OBA) exhibited LC phases as shown in Fig. 2. After photopolymerization, we obtained a polymer film consisting of oriented fibers and a macroscopic structure, which reflected the 'Schlieren' texture present before photopolymerization.

In the present study, to investigate the effect of the LC phase of the phase-separated polymer without the influence of the LC ordering field present before photopolymerization, we irradiated the A6OBA/6OCB blend with UV light at 110 °C. At this temperature, the blend and 6OCB show the isotropic phases, whereas poly(A6OBA) exhibits the LC phase.

Polarizing optical micrographs of the blend taken before and after UV irradiation at 110 °C are shown in Fig. 3. Although the whole view was black before UV irradiation (Fig. 3(a)), mesh-like birefringence was observed after irradiation as shown in Fig. 3(b). This result indicates that the A6OBA/6OCB blend that had showed a homogeneous isotropic phase was divided into 6OCB and poly(A6OBA), which exhibited an isotropic and an LC phase, respectively, due to photopolymerization-induced phase separation.

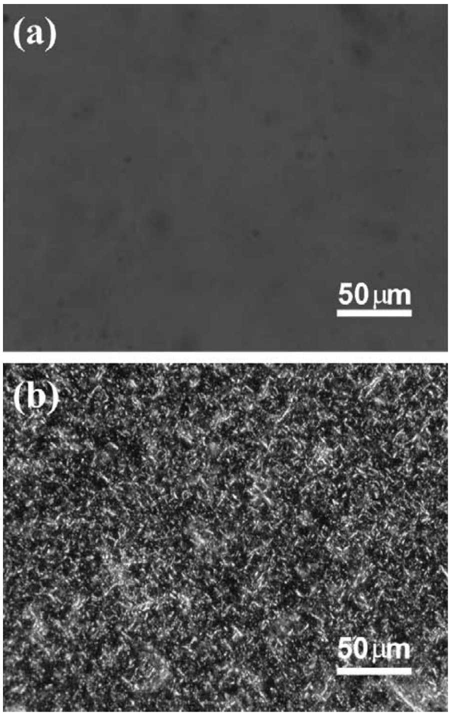


Fig. 3. Polarizing optical micrographs of the A6OBA/6OCB blend taken before (a) and after (b) UV irradiation at 110 °C.

Immediately after photopolymerization, we immersed the irradiated sample in ethanol, extracted the soluble fractions, and then obtained a polymer film as the insoluble fraction. We observed the morphology of the obtained polymer by scanning electron microscopy. The SEM image reveals that the polymer had fibrous morphology with a diameter ca. 1.0 µm wide, as shown in Fig. 4. The polymer fibers seem to extend randomly and possessed many branches. In contrast, the polymer fibers, which were previously prepared by photopolymerization-induced phase separation with the LC ordering field present before UV irradiation, had orientation and less branches than those obtained from the isotropic phase.

Next, we conducted the photopolymerization of the A6OBA/6OCB blend at 180 °C, at which both the blend and poly(A6OBA) exhibited isotropic phases (Fig. 2). Whereas optical microscopy gave a low-contrasted image, we could obtain an insoluble polymer film resulting from photopolymerization-induced phase separation after extraction of the irradiated sample with ethanol. The SEM image of the polymer film is depicted in Fig. 5. We could see polymer particles with a diameter about 1.5 µm instead of fibers. The spherical shape was formed probably because interfacial tension predominantly governed the polymerization process.

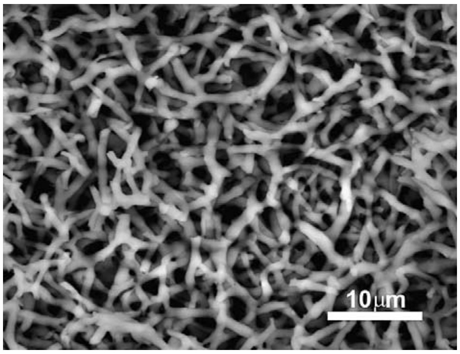


Fig. 4. SEM image of poly(A6OBA) obtained by photopolymerization of the A6OBA/6OCB blend at 110 °C.

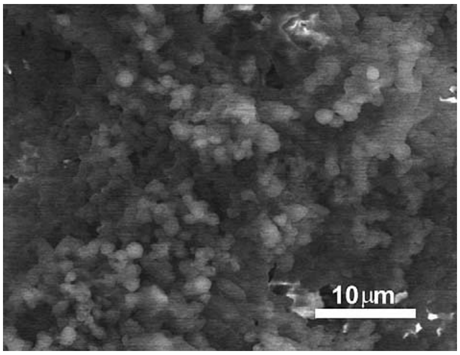


Fig. 5. SEM image of poly(A6OBA) obtained by photopolymerization of the A6OBA/6OCB blend at 180 °C.

These results suggest that, even if the blend showed the isotropic phase before photopolymerization, the phase-separated polymer had fibrous morphology as long as it exhibited the LC phase at the photopolymerization temperature. However, the fibers obtained from the isotropic phase of the blend were randomly extended and possessed many branches. In contrast, the fibers from the LC phase of the blend had only few branches and were oriented. Therefore, we conclude that the LC ordering field present prior to photopolymerization plays an important role in reducing the number of branches and determining the orientation of the fibers.

When the A6OBA/6OCB blend was photopolymerized at 70 °C in the LC phase, 6OCB still showed a nematic phase after phase separation (Fig. 2). It is interesting to reflect that the blend exhibits an LC phase before photopolymerization whereas 6OCB shows an isotropic phase after phase separation because isotropic-phased 6OCB cannot play a role in orienting the phase-separated polymer. Therefore, we carried out photopolymerization of the blend at 80 °C in the LC phase (Fig. 2). Polarizing optical micrographs taken before and after UV irradiation at 80 °C are shown in Fig. 6. While the birefringence and Schlieren texture seemed to be maintained after UV irradiation (Fig. 6(b)), the appearance was quite different from that taken before UV irradiation (Fig. 6(a)). When the irradiated blend was cooled at the rate of 5 °C/min, the appearance abruptly changed at 75 °C. This is consistent with the I–N transition temperature of 6OCB (Fig. 6(c)). This result indicates that photopolymerization at 80 °C induced the blend to phase separate into poly(A6OBA) showing an LC phase and 6OCB exhibiting an isotropic phase. The appearance change at 75 °C occurs at the phase transition of 6OCB from an isotropic to a nematic phase.

To investigate the morphology of the polymer obtained at 80 °C, we extracted the blend with ethanol immediately after UV irradiation and observed the insoluble fraction by SEM. As shown in Fig. 7, the polymer had a fibrous structure and the fibers showed a definite orientation. The orientation was attributed to the LC ordering field, which existed during polymerization and phase separation. Hence we conclude that, in the case of UV irradiation at 80 °C, phase separation and the formation of the fibers took place in advance of the isothermal transition of 6OBA from a nematic to an isotropic phase.

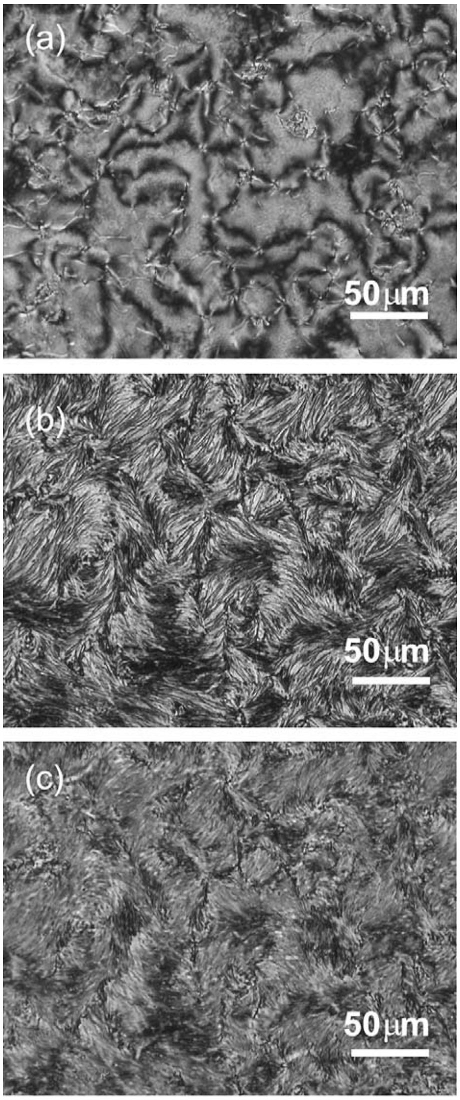


Fig. 6. Polarizing optical micrographs of the A6OBA/6OCB blend taken at 80 °C before (a) and after (b) UV irradiation, and taken at 75 °C after UV irradiation at 80 °C (c).

In polymer-dispersed liquid crystals (PDLCs), which consist of amorphous polymers and low-molecular-weight liquid crystals, we often see the polymers take fibrous morphology. In addition, it was theoretically demonstrated

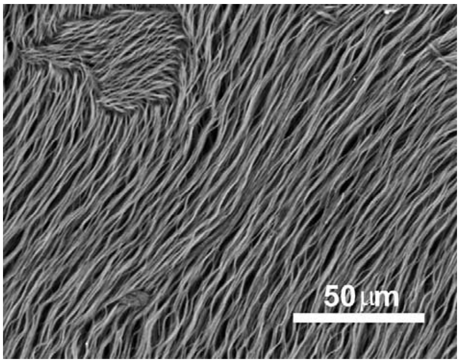


Fig. 7. SEM image of poly(A6OBA) obtained by photopolymerization of the A6OBA/6OCB blend at 80 °C.

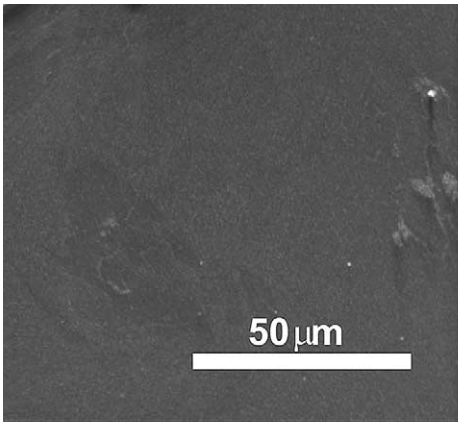


Fig. 8. SEM image of poly(A6OBA) obtained by photopolymerization of the A6OBA/6OBA blend at 130 °C. Without polymerization-induced phase separation, no fibrous structure was obtained.

that flexible polymers transiently form the fibrous structure during the phase separation process in the mixtures of the flexible polymers and rigid LC polymers [18]. Although these fibrous structures are similar to that observed in Figs. 4 and 7, they are essentially different. This is because, in PDLCs and flexible/rigid polymer blends, LC phases are matrices and the flexible polymers form the fibrous structures, whereas in our systems the polymers exhibiting LC pahses take the fibrous structures and the matrices are isotropic phases.

The morphology of a polymer obtained by photopolymerization of an (LC monomer/ low-molar-mass LC) blend is strongly affected by the miscibility between the polymer and the low-molar-mass LC. Further, it is known that the miscibility is significantly influenced by the sort of mesogens [17,19]. Therefore, we next performed photopolymerization of a blend containing A6OBA and 6OBA, which have the same mesogen (Scheme 1). The A6OBA/6OBA (1:4 molar ratio) blend showed a nematic phase from 67 to 141 °C. Unlike the blend composed of the different mesogenic compounds, we could not observe phase separation of the A6OBA/6OBA blend on photopolymerization at any temperature, instead, the irradiated sample showed a homogeneous nematic phase up to 156 °C on heating, which is 15 °C higher than that of the non-irradiated blend. Fig. 8 shows a SEM image of the polymer obtained by UV irradiation of the A6OBA/6OBA blend at 130 °C and after extraction. The polymer had no fibrous structure and its surface was quite smooth. This result reveals the importance of phase separation process in the formation of fibrous structures.

4. Conclusions

We conducted photopolymerization of two blends consisting of (i) an LC monomer and a low-molar-mass LC having differing mesogens and (ii) an LC monomer and a low-molar-mass LC having the same mesogen. By photopolymerization under various conditions, we could infer the following. Photopolymerization-induced phase separation in the blends is essential for the resulting polymer to possess fibrous morphology. In addition, for the formation of fibrous morphology it is necessary that the polymer shows the LC phase immediately after photopolymerization. On the other hand, the LC ordering field existing before photopolymerization does not play a crucial role in forming a fibrous structure. It does, however, serve to give orientation to the fibers.

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