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# Morphology control of liquid crystalline composite gels based on molecular self-assembling kinetics

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Liquid crystalline composite gels consisting of a low molecular mass gelator and a low molecular mass liquid crystal were prepared by two types of gelation method (continuous cooling and isothermal gelating), which provide different molecular self-assembling kinetics of the low molecular mass gelator as gelation proceeds. Optical microscopy and atomic force microscopy revealed that numerous fine strands of the one-dimensionally assembled low molecular mass gelators were formed in the composite gels for both the continuous cooling method and the isothermal gelating method. However, the thinner strands were more homogeneously dispersed in the isothermal gelation product at an appropriate temperature, than in the continuous cooling process. This difference in dispersion state of the strands was shown (by polarizing optical microscopy) to have a significant influence on the molecular alignment of the low molecular mass liquid crystal in the liquid crystalline composite gel. The electro-optical response and light scattering–transmitting switching, of the liquid crystalline composite gel in an applied electric field was extremely dependent on the morphology of the gelators. High contrast light switching was achieved for the composite prepared by isothermal gelation. The response time of electro-optical switching was less than 100 μs under 30 $V_{rms}$.

## 1. Introduction

In recent years, interest in the physical organogel field has increased with the discovery and synthesis of novel molecules which can gelate organic fluids [1–5]. Non-covalent interactions such as hydrogen bonding, metal coordination and van der Waals interaction are the main interactions in maintaining the physical organogel network. Such molecules typically self-assemble into fibrous aggregates through non-covalent intermolecular interactions in an organic solution, leading to a self-supporting physical gel in which an organic fluid is embedded in a three-dimensional fibrous network.

Gelators derived from isoleucine have been found to gelate a wide variety of organic fluids with polar or non-polar characteristics [6, 7]. In this case, hydrogen bonding between the amide groups played a key role in the organo-gelation. It has also been reported that liquid crystal (LC) molecules may be efficiently gelated by self-assembly of low molecular mass gelators through hydrogen bonding [8–10]. On the other hand,

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(polymer/low molecular mass LC) composites have been known since the 1980s to show remarkable switching between the light scattering state and the light transmitting state, upon removal and application of an electric field, respectively [11–20]. The light scattering and transmitting states of these composites are induced, respectively, by the macroscopically random or unidirectional orientation of liquid crystal directors embedded in three-dimensional polymer networks. Hence the (polymer/low molecular mass LC) composites have attracted much attention because of their potential for practical applications, such as large scale displays, switchable windows and light shutters in projection systems. It is reasonable to suppose that a liquid crystalline gel could show a similar electro-optical effect by analogy from a similarity of the aggregation structure to (polymer/low molecular mass LC) composites.

In previous work [21], we found a unique hierarchical aggregation structure, one-dimensional molecular assemblies of nm size, fibrous aggregates composed of bundles of numerous one-dimensional molecular assemblies of order several 100 nm, and spherulite-like aggregates of grown fibrous aggregates of μm size, in the (low molecular mass gelator/LC) composite. The spherulite-like aggregates were shown to be responsible for the light switching contrast in an electro-optical effect. Such morphology of self-assembling gelators in a LC must strongly depend on the kinetics of molecular assembly. Few attempts have yet been made at morphology control based on molecular assembling kinetics. In this study, two types of gelation process, which result in different molecular assembling kinetics of the low molecular mass gelators, were investigated for (low molecular mass gelator/LC) composite systems, in order to develop an electrically responsive soft material showing high contrast light switching.

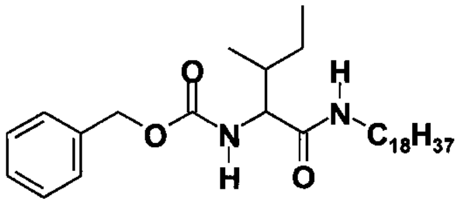
## 2. Experimental

### 2.1. *Materials*

The low molecular mass gelator, *N*-bezyloxycarbonyl-L-isoleucylaminooctadecane **1** used in this study was synthesized by us. The low molecular mass liquid crystal 4-cyano-4′-pentylbiphenyl **2** (Merck Co. Ltd.) was used without purification. Their chemical structures and some physical properties are shown in figure 1. The mixture/solution of (**1**/**2** = 0.5/99.5 mol%) composite in an isotropic state was sandwiched between two indium tin oxide-coated glass plates (10 × 20 mm$^2$) separated by a poly (ethyeleneterephthalate) film spacer of thickness 14 μm. No surface treatment for LC molecular alignment was performed for any cell.

Low molecular mass gelator

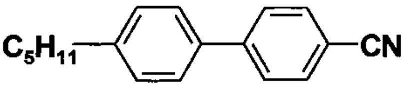
*N*-bezyloxycarbonyl-L-isoleucylaminooctadecane



**1**

Low molecular mass liquid crystal

4-cyano-4′-pentylbiphenyl



$T_{KN}$ = 296 K
$T_{NI}$ = 308 K

**2**

Figure 1. Chemical structures and physical properties of compounds **1** and **2**.

### 2.2. *Preparation of the composite*

The (**1**/**2** = 0.5/99.5 mol%) composite gels were prepared by the two methods as shown in figure 2. First, in

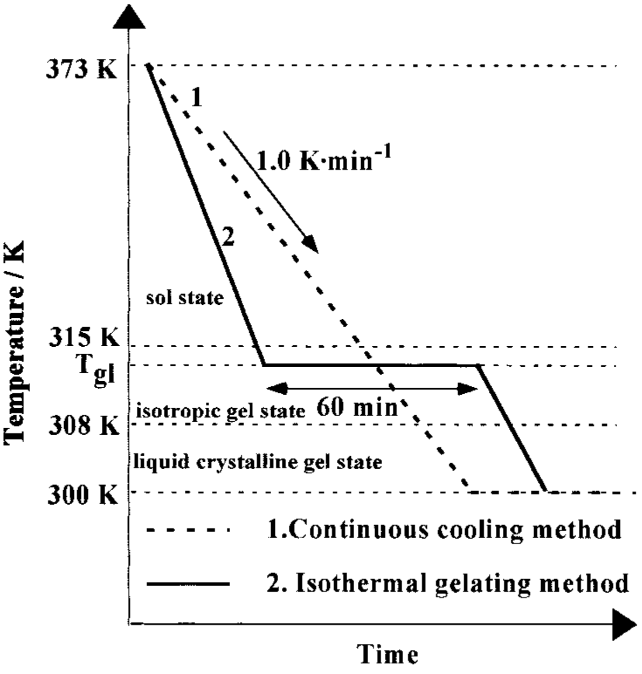


Figure 2. Two gelation processes of the composites: continuous cooling method and isothermal gelating method.

the continuous cooling method, the (**1**/**2** = 0.5/99.5 mol %) mixture/solution was heated to 373 K and held in an isotropic sol state for 1.0 h. The mixture was then continuously cooled at 1.0 K min$^{-1}$ to 300 K, at which temperature **2** is in the nematic state. Secondly, in the isothermal gelating method, the mixture was heated to 373 K, held for 1.0 h, then cooled to a certain temperature, $T_{gl}$, slightly below the sol–gel transition temperature of 315 K, and held for 1.0 h. The mixture was then further cooled to 300 K at which **2** is in the nematic state. The $T_{gl}$ was adjusted with an accuracy of 0.1 K.

### 2.3. *Observation of aggregation structure*

Optical microscopy was carried out at 310 K, at which temperature the composite was in an isotropic gel state, in order to evaluate the aggregation structure of the self-assembled low molecular mass gelator. The reason for optical observation in the isotropic gel state was to avoid light scattering from **2**, with heterogeneous molecular orientation in a nematic phase. The molecular orientational state of **2** in the nematic phase (i.e. the liquid crystalline gel state) was examined by polarizing optical microscopy (POM). The mesoscopic aggregation structure of **1** in the composite gel was observed by atomic force microscopy (AFM) after **2** was extracted from the composite with *n*-hexane.

### 2.4. *Electro-optical measurements*

A He-Ne laser ($\lambda = 632.8$ nm) was used to provide incident light transmitted normal to the cell. An external electric voltage, 0 to 40 V$_{rms}$, was applied across the cell; the transmitted light intensity was measured with a photodiode. The magnitude of the light transmittance of the cell was calibrated by comparing with that of the blank cell. The definitions of two response times are shown in figure 3. The rise time is the time required for a change in light transmittance from 10% to 90% after switch-on; the decay time is the time required for a 90% to 10% transmittance change after switch-off.

## 3. Results and discussion

Figure 4 shows optical micrographs for composites prepared by the continuous cooling (*a*) and isothermal gelating at $T_{gl} = 314.5$ K (*b*) methods. In the case of continuous cooling, a fibrous aggregation texture including spherulite-like structures was formed in the composite, as shown in figure 4 (*a*). The width of the fibre and the diameter of spherulite-like structures were about 1.0 and 20–30 μm, respectively. It has been reported that the (low molecular mass gelator/low molecular mass LC) composite has a hierarchical structure from the one-dimensional molecular assembly to the higher order structure such as spherulite-like aggregation [21]. Therefore, the (**1**/**2**) composite prepared by continuous cooling is likely to form a similar hierarchical structure. However, in the case of the isothermal gelating method at $T_{gl} = 314.5$ K, no morphology was recognized with optical microscopy; that is, no aggregate with a larger dimension than the optical resolution of visible light was present in the composite. This result indicates that the size of molecular aggregation of **1** in the composite prepared by the isothermal gelating method was sub-micrometer.

The optical micrographs of figure 4 conclusively show that the difference in the gelation process had a great effect on the higher order aggregation structure of **1** at an optical size level. The morphology observed with optical microscopy was extremely sensitive to $T_{gl}$. The $T_{gl} = 314.5$ K was a particular temperature of this system because the spherulite-like structure was generated when $T_{gl}$ deviated from 314.5 K even slightly. Thus there is a specific temperature at which the generation and growth of higher order structure such as spherulite-like aggregation could be efficiently suppressed. More details of the mechanism will be discussed later.

Figures 5 (*a*) and 5 (*b*) show AFM images of composites prepared respectively, by the continuous cooling and isothermal gelating methods at $T_{gl} = 314.5$ K. Numerous fine strands were observed in the composite prepared by both gelation processes. Here, let us refer to the terms 'fibre' and 'strand' depending on the width: 'fibre' for μm size and 'strand' for nm size (as

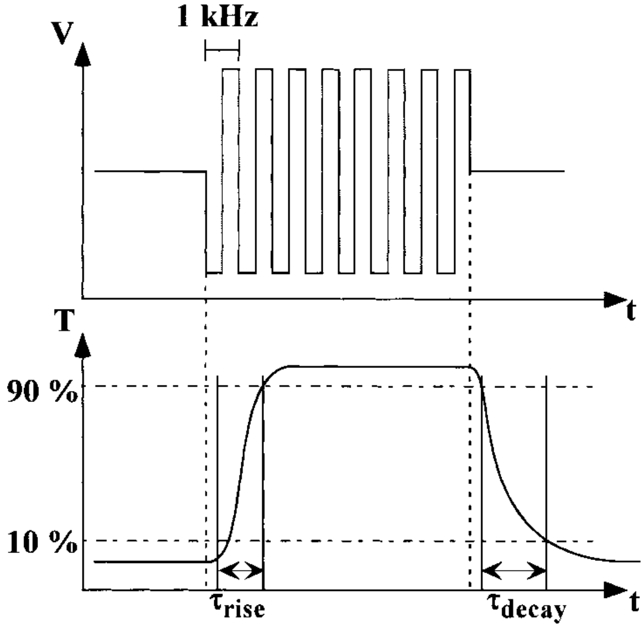
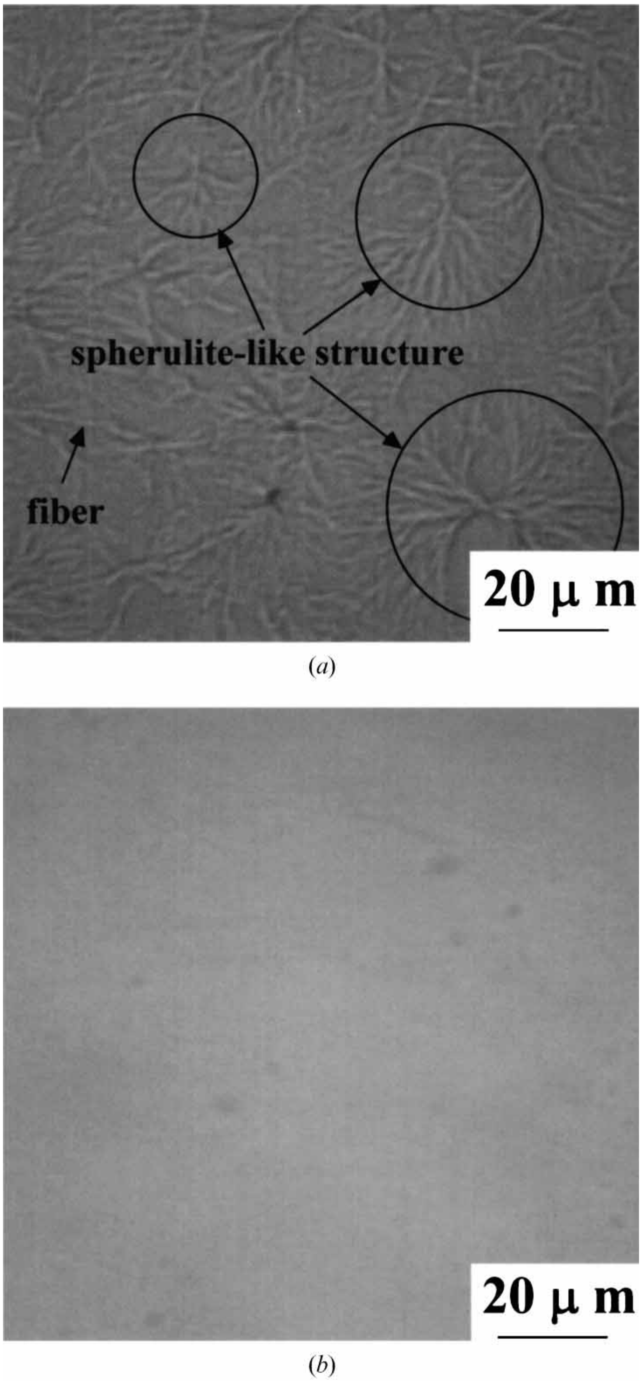


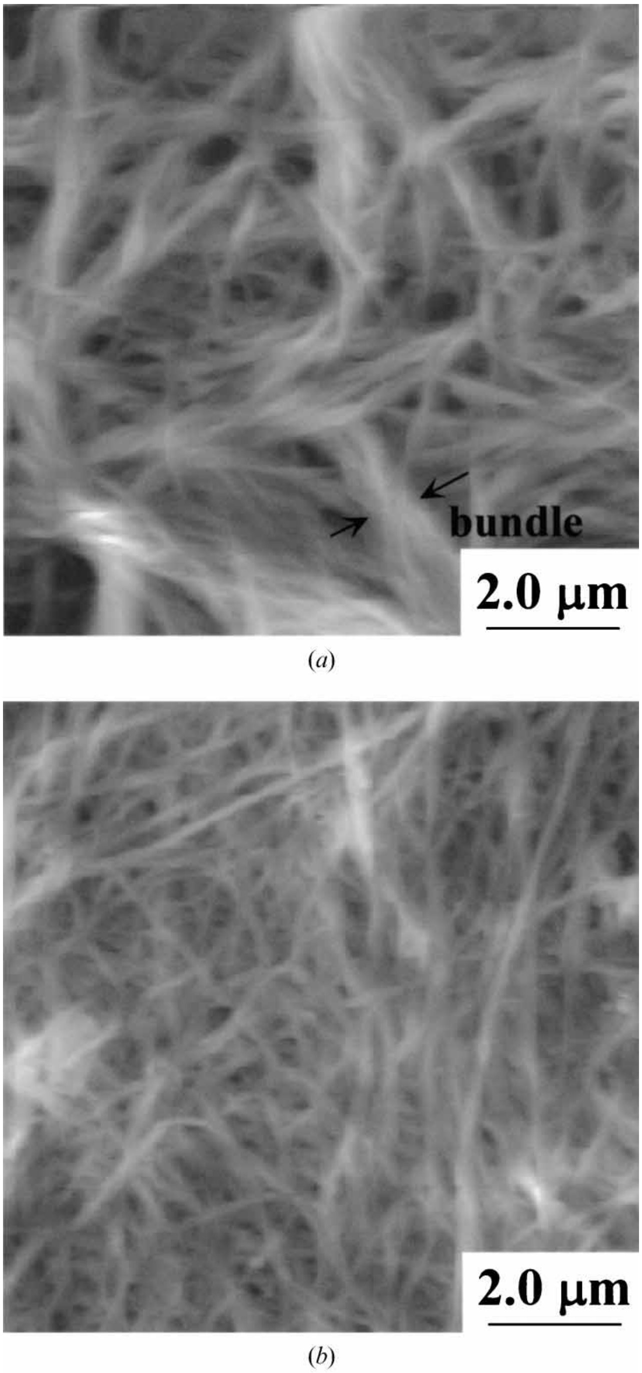
Figure 3. Definitions of rise and decay time on the basis of change of the light transmittance.



(*a*)

(*b*)

Figure 4. Optical micrographs at 310 K for (**1**/**2** = 0.5/99.5 mol%) prepared by (*a*) the continuous cooling method and (*b*) the isothermal gelating method at $T_{gl} = 314.5$ K.



(*a*)

(*b*)

Figure 5. AFM images for (**1**/**2** = 0.5/99.5 mol%) after the extraction of **2** with *n*-hexane: (*a*) continuous cooling method and (*b*) isothermal gelating method at $T_{gl} = 314.5$ K.

mentioned later, a fibre is a bundle of many strands). In the case of continuous cooling, the width of the strands observed was in the range 180–230 nm, which might correspond to 50–70 molecular assemblies of **1**, on the assumption that an extended molecular width of **1** is about 3.5 nm. The width of the bundle was about 1.0 μm, which was in agreement with the fibre width observed by optical microscopy, figure 4 (*a*). This indicates that the fibre observed in figure 4 (*a*) was composed of bundles of many strands.

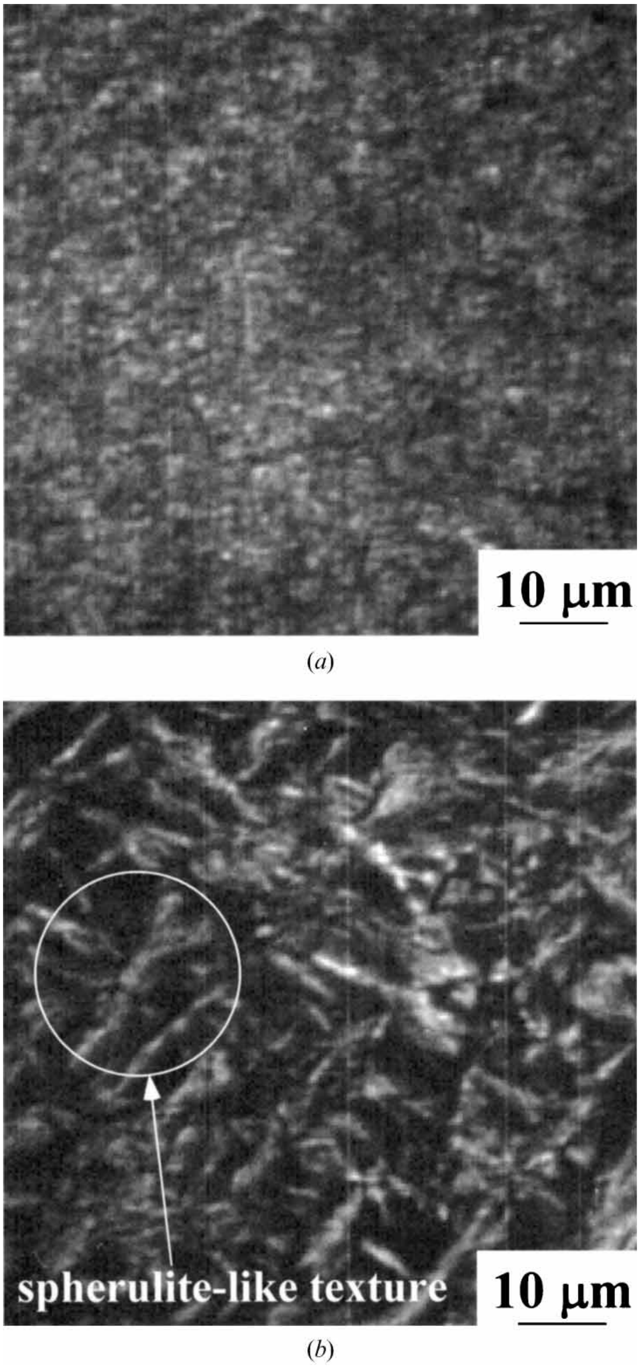


Figure 6. Polarizing optical micrographs for (**1**/**2** = 0.5/99.5 mol%) prepared by the continuous cooling method and under (*a*) 0 and (*b*) 30 $V_{rms}$.

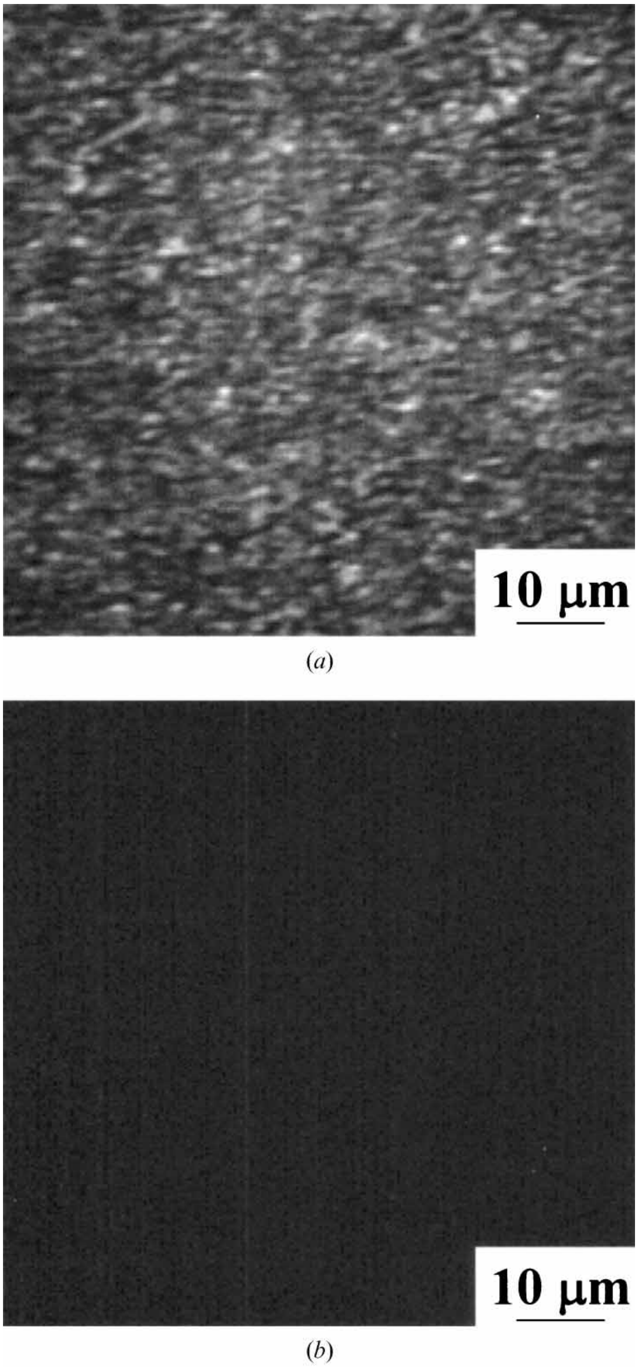


Figure 7. Polarizing optical micrographs for (**1**/**2** = 0.5/99.5 mol%) prepared by the isothermal gelating method under (*a*) 0 and (*b*) 30 $V_{rms}$.

In the isothermal gelating method, finer strands were observed, of width 100–190 nm, which was smaller than that of the strands in the composite prepared by continuous cooling. The width of strands corresponded to 30–60 molecular assemblies of **1**. Also, these fine strands were observed to be homogeneously dispersed in the composite and the number of bundles of fine strands was quite small. This result apparently indicates that the isothermal gelating method suppresses bundling of the strands; that is, cohesion among one-dimensional molecular aggregates in the lateral direction.

Figures 6 and 7 show POM photomicrographs for composites prepared by the continuous cooling and isothermal gelating methods at $T_{gl} = 314.5$ K on application of electric fields of 0 $V_{rms}$ and 30 $V_{rms}$, respectively. As shown in figures 6 (*a*) and 7 (*a*), a sand-like texture was observed for each composite with no electric voltage, indicating that the liquid crystal media formed polydomains. That is, the alignment of the directors of **2** was random in the composite under zero electric field. This might be due to the random dispersion of the fibres or strands in the composite. On application of 30 $V_{rms}$, spherulite-like textures were observed in a dark field for the composite prepared by continuous cooling, figure 6 (*b*). The dark field region resulted from the realignment of **2** along the direction of the applied electric field, i.e. homeotropic alignment. As reported in our previous paper [21], the LC molecules in the spherulite-like structure of the gelator hardly responded to the applied voltage. Only a dark field texture was observed for the composite prepared by the isothermal gelating method at $T_{gl} = 314.5$ K, as shown in figure 7 (*b*). This result suggests that the response of **2** to the applied voltage was homogeneous at an optical size level. Figures 6 and 7 reveal that the response of **2** to an applied voltage is strongly related to the aggregation structure of **1** in the composite.

Figure 8 shows a possible gelation model of the composite for the two gelation processes. In the first stage of the continuous cooling method (*a*) as shown in (1), **1** would begin to form a one-dimensional molecular assembly through hydrogen bonding in a temperature range higher than the sol–gel transition temperature. This molecular assembly was recognized because the intensity of the IR band for the carbonyl group of the amide bond was shifted with the decrease in temperature on moving from an isotropic sol state to an isotropic gel state [10]. In the second stage, the one-dimensional molecular assembly grew along the bonding axis and also aggregated in the lateral direction with decrease of temperature, resulting in the formation of strands, as shown in figure 8 (2). On further continuous cooling (3), the strands aggregated into fibres by bundling in the lateral direction. Depending on the number and position of bundles, a branched structure is created in the fibrous aggregation. As a result, fibre with a dendritic structure is formed in the composite, figure 8 (3), and then a three-dimensional network of fibres with a broad distribution of fibre diameter was formed as shown in (4). In the case of the isothermal gelating method (*b*), growth of a fibril along the bonding axis might be superior to the aggregation of strands in the lateral direction, as shown in figure 8 (5). Therefore, a larger number of fine strands were preferentially formed as shown in figure 8 (6). As a result, fine fibres were homogeneously dispersed in the composite.

Figures 9 (*a*) and 9 (*b*) show the dependence of light transmittance on applied voltage for the composites prepared, respectively, by continuous cooling and isothermal gelation at $T_{gl} = 314.5$ K. Both composites exhibited a strong light scattering state in the absence of an electric field. In the case of continuous cooling (*a*), the light scattering might arise from the heterogeneous aggregation structure of fibres or spherulites of **1** as shown in figures 4 (*a*) and 5 (*a*), and also the random orientation of **2**. Also, in the case of isothermal gelation (*b*), the random orientation of **2** might be mainly responsible for light scattering in the absence of an electric field because the fine sand-like texture in figure 6 (*a*) was observed in the composite at zero voltage, and no heterogeneous aggregation structure such as fibres or spherulite-like structure of **1** with an optical order was observed in the composite, as shown in figure 4 (*b*). The composite prepared by continuous cooling exhibited only 50% light transmittance on the application of an electric voltage of 40 $V_{rms}$ due to the fairly strong light scattering from the aggregation structure of the gelator with an optical order, as shown in figures 4 (*a*) and 5 (*a*). On the other hand, in the case of isothermal gelation, figure 9 (*b*), the composite showed nearly 100% light transmittance on the application of 30 $V_{rms}$. These results indicate that a homogeneous dispersion of the fine strands is important for achieving high contrast light switching between light scattering and transmitting. Moreover, a small hysteresis was observed during the increase and decrease of the applied voltage, as shown in figure 9 (*b*).

Figures 10 (*a*) and 10 (*b*) show the dependence of response time on applied voltage for the composites prepared, respectively, by continuous cooling and isothermal gelation at $T_{gl} = 314.5$ K. In the case of continuous cooling (*a*), the rise time was less than 5.0 ms. The reason for a discontinuous change of rise time between 20 and 30 $V_{rms}$ is still unclear; although the two-step response of **2** to an applied electric field, due to inhomogeneity of the aggregation structure such as the fibre and the spherulite-like structure of **1** in the composite, might be attributed to the dependence of rise time on applied voltage. On the other hand, in the case of isothermal gelation (*b*), rise and decay response times of less than 5.0 ms were attained upon the application of an electric field. The rise time was less than 1.0 ms below 10 $V_{rms}$, and in particular was less than 100 μs on the application of 40 $V_{rms}$ as shown in figure 10 (*b*). The fast response of **2** to an applied electric field might be due to the fairly homogeneous dispersion of domains of **2** in the composite. These results show that the electro-optical properties of the

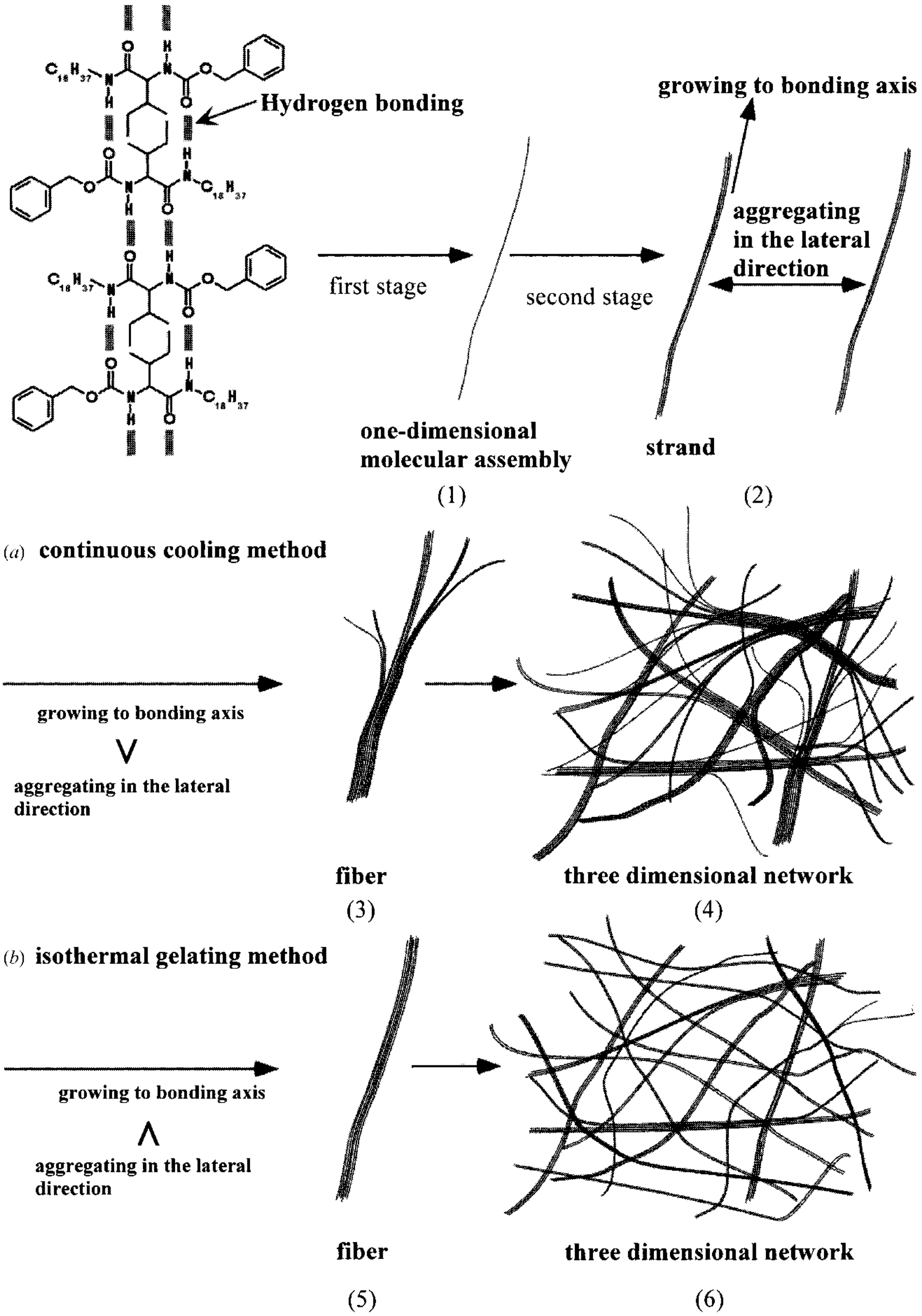
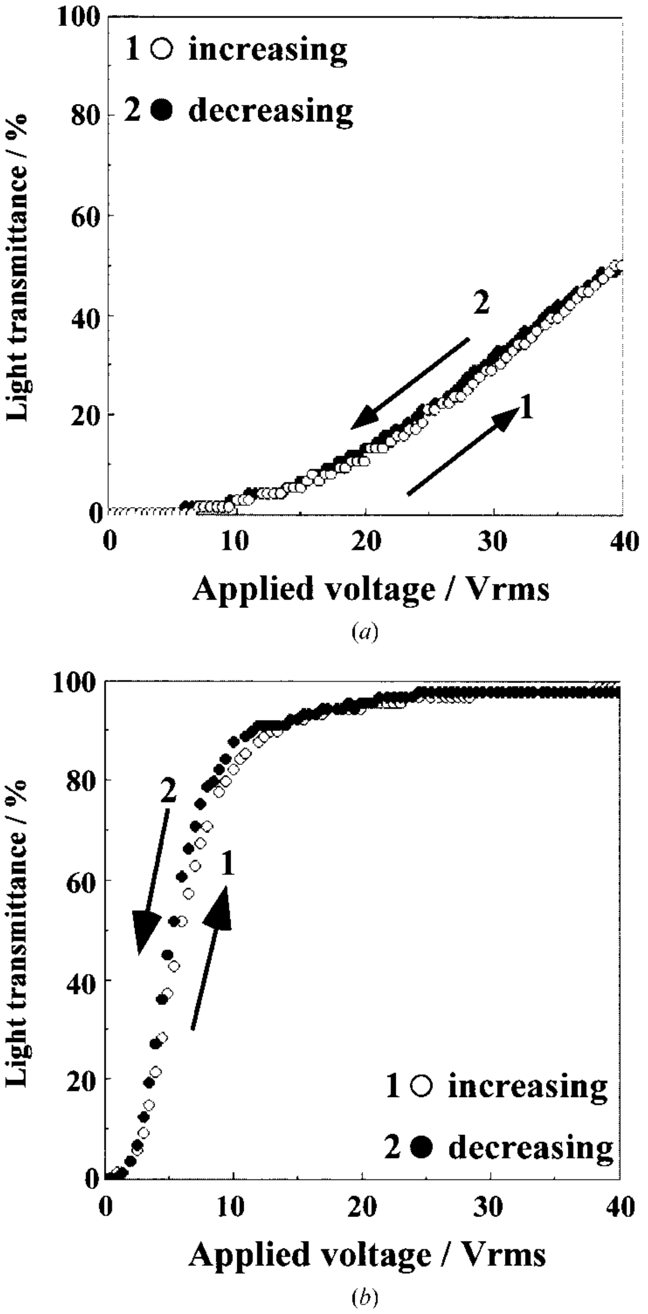


Figure 8. A possible model for the gelation of composites prepared by (*a*) the continuous cooling method and (*b*) the isothermal gelating method at $T_{gl} = 314.5$ K.



(*a*)

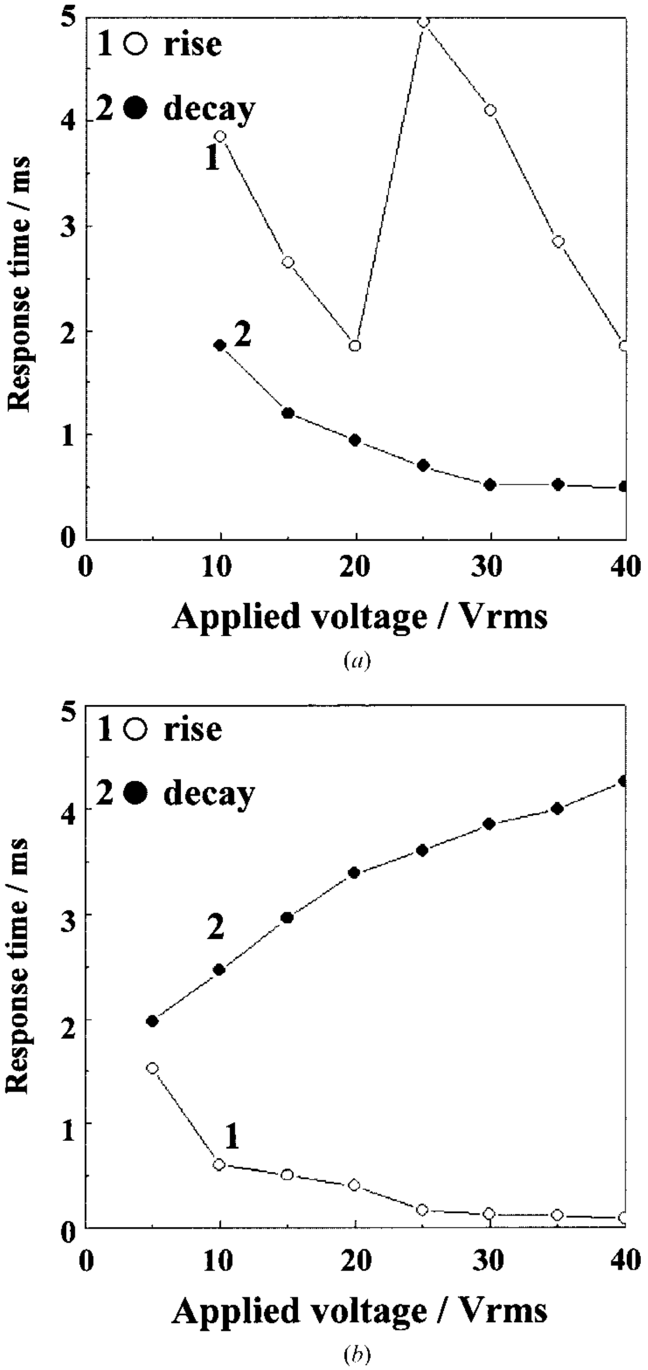
(*b*)

Figure 9. Dependence of light transmittance on applied voltage for (**1**/**2** = 0.5/99.5 mol%): (*a*) continuous cooling method, (*b*) isothermal gelating method at $T_{gl} = 314.5$ K.

composite in a liquid crystalline gel state is strongly dependent on the aggregation structure of **1** in the composite, and indicate that the composite with a dispersion of fine strands of **1** exhibits high contrast and fast light switching.

## 4. Conclusions

The final morphology of the (low molecular mass gelator/LC) composite system was sensitively dependent



(*a*)

(*b*)

Figure 10. Dependence of response time on applied voltage for (**1**/**2** = 0.5/99.5 mol%): (*a*) continuous cooling method, (*b*) isothermal gelating method at $T_{gl} = 314.5$ K.

on the gelation process from sol to gel of the low molecular mass gelator dispersed in liquid crystal. In particular, the formation of an aggregation structure at an optical order was depressed and strands at a mesoscopic order were homogeneously distributed in the composite by controlling the gelation process. This result suggests that the kinetics of molecular self-assembly is responsible for the formation of higher order aggregation of the gelator. The electro-optical properties of the composite in a liquid crystalline gel state were strongly dependent on the aggregation structure of the low molecular mass gelator in the composite. High contrast light switching between light scattering and light transmitting, and fast response to an applied voltage, were successfully achieved for the composite prepared by the isothermal gelating method at a suitable temperature.

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