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Morphological studies of a (self-assembling oil gelator/liquid crystal) composite system

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The aggregation structure of a novel (self-assembling oil gelator/liquid crystal) composite was investigated using light scattering studies and morphological observations. The oil gelator forms a self-assembled-networks aggregate in an organic solvent with a low molecular weight liquid crystal (LC). It became apparent from Hv light scattering patterns and polarizing optical microscopy that two types of LC molecular alignments exist in the composite: a random orientation and a spherulite type one in a nematic gel state. Also, optical and atomic force microscopic observations revealed that fibrils which formed bundles in the fibre-like and spherulite-like aggregates, were formed in the composite. The alignment of the liquid crystal molecules was related to the aggregation structure of the self-assembling oil gelator in a liquid crystal gel state.

1. Introduction

Many low molecular mass organic compounds have been found to be applicable as gelators for oils or organic fluids [1–8]. These compounds self-assemble in organic solution and form elongation fibre-like aggregations due to non-covalent intermolecular interactions such as hydrogen bonding, coordinating bonding, van der Waals interactions, etc. The fibre-like aggregation structure forms an extended three-dimensional network in organic fluids through non-covalent interaction, so these gelators can form thermoreversible physical gels in organic fluids. It has been reported by one of the authors (K.H.) that derivatives of amino acids or cyclohexanediamine can form organogels induced by hydrogen bonding [4–6]. *Trans*(1*R*, 2*R*)-1,2-bis(undecanoylamino)cyclohexane (Cy(11)$_2$) can also gelate various kinds of organic fluids and low molecular mass liquid crystals (LCs) [9, 10]. The composite gel containing a self-assembling oil gelator and a low molecular mass LC exhibited various kinds of temperature-dependent aggregation states, such as an isotropic liquid, an isotropic gel, a liquid crystalline gel, and a crystal. Since the end of the 1970s, the novel (polymer/liquid crystalline polymer and low molecular mass LC) composite materials have been intensively studied in order to extend unique LC functions in a self-supported flexible film [11, 12]. The (polymer/low molecular mass liquid crystal) composite film can be switched between light scattering and light transmitting states upon removal and application of an electric voltage, respectively. The light scattering and transmitting states are respectively induced by (a) the macroscopically random orientation and (b) the unidirectional orientation of LC directors embedded in the three-dimensional polymer network. Therefore composite films have attracted much attention because of their potential for practical applications, such as large scale displays, switchable windows and light shutters in projection systems [13–22]. The liquid crystalline gel may also be applicable to new types of electric-optical devices because it is an optically

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anisotropic material, responsive to external stimuli such as an electric voltage, magnetic field, mechanical force, etc. However, the kinds of aggregation structure formed in the LC crystalline gel have not been sufficiently clarified. In this paper, the aggregation structure of the LC gel is investigated by light scattering, polarizing optical microscopy (POM) and atomic force microscopy.

2. Experimental

2.1. *Samples*

The self-assembling oil gelator, *trans*(1*R*, 2*R*)-1,2-bis-(undecanoylamino) cyclohexane ($Cy(11)_2$) used in this study has been previously synthesized [9, 10]. The LC molecule was 4-cyano-4′-pentylbiphenyl (5CB) (Merck Co. Ltd.). Their chemical structures and phase transition temperatures are shown in figure 1. The sample cell of the ($Cy(11)_2/5CB = 0.5/99.5$ mol %) composite was prepared as follows. $Cy(11)_2$ and 5CB were mixed at 373 K with stirring for 24 h. The mixture in the isotropic state was sandwiched between two indium tin oxide (ITO)-coated glass plates (10 mm × 20 mm) which were separated by a poly(ethyleneterephthalate) film spacer (4.5 μm). No surface treatment for LC molecular alignment was performed for any cell. The cell was cooled to a nematic gel state and held at 303 K for more than 30 min. The ($Cy(11)_2/5CB = 0.5/99.5$ mol %) composite thus prepared shows a sol–gel transition at 334 K and isotropic–nematic transition at 308 K.

2.2. *Polarizing light scattering measurement*

Figure 2 shows a schematic illustration of the experimental set-up for polarizing light scattering measurement. The linearly polarized He-Ne laser ($\lambda = 632.8$ nm) was incident on the sample cell upon application of an a.c. voltage of 0 or 60 V_{rms}. The scattered light passing through the sample was projected onto a screen through an analyser. When the polarization directions of the polarizer and the analyser are crossed, the observed light scattering pattern is called an Hv pattern. The position of the scattered reflection is denoted by the two angles, θ and μ, as shown in figure 2; θ is the polar scattering angle with respect to the direct beam axis, and μ is the azimuthal scattering angle in the screen plane. A photograph of the Hv light scattering pattern projected on the screen was taken with an electric voltage applied perpendicular to the cell substrate surface.

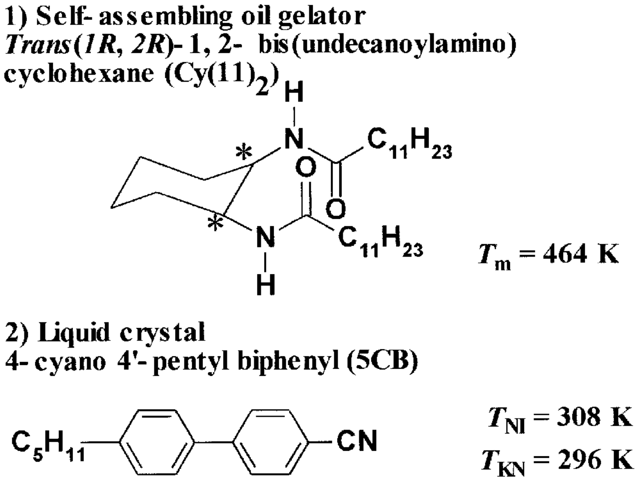


Figure 1. Chemical structure and transition temperatures of self-assembling oil gelator and liquid crystal.

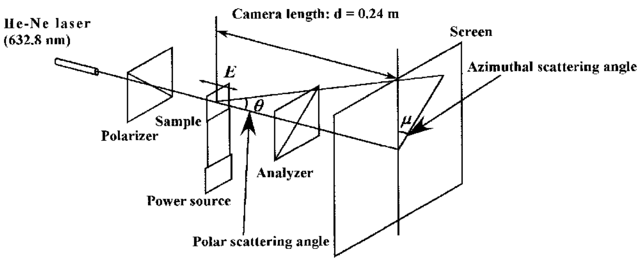


Figure 2. Schematic illustration of the measurement system for the Hv light scattering pattern observation.

2.3. *Optical, polarizing optical and atomic force microscopy observations*

The optical texture of the composite in a liquid crystalline state was observed with a polarizing optical microscope upon the application of an a.c. voltage from 0 to 60 V_{rms} under crossed Nicols. The direction of the liquid crystalline directors in the observed texture was decided by means of a colour-sensitive plate (optical retardation, $R = 530$ nm) placed between the sample cell and the analyser.

The microscopic and mesoscopic morphologies of $Cy(11)_2$ molecular aggregates formed in the composite were studied with optical and atomic force microscopies, respectively. Since the composite shows a sol–gel transition at 334 K, $Cy(11)_2$ molecular aggregates were formed in the isotropic state of 5CB. In order to carry out these observations, 5CB was extracted from the sample with *n*-hexane for 1.0 h, then dried in a vacuum for 24 h at 298 K.

3. Results and discussion

3.1. *Light scattering measurements*

Figure 3 shows Hv light scattering patterns for the ($Cy(11)_2/5CB = 0.5/99.5$ mol %) composite in a nematic gel state at 298 K (*a*) in the absence of an electric voltage, and (*b*) upon the application of 60 V_{rms}. If optically anisotropic aggregates with a larger size than $\lambda/20$ (λ = wavelength of incident light) exist in the sample, some scattering patterns can be observed.

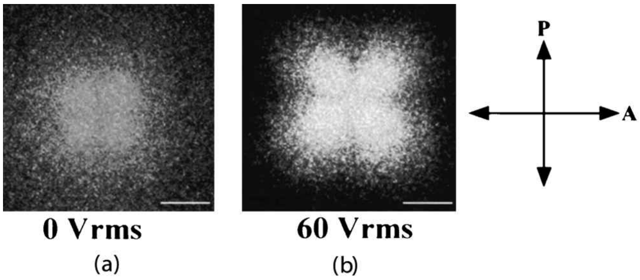


Figure 3. Hv light scattering patterns for ($Cy(11)_2/5CB = 0.5/99.5$ mol%) composite under (*a*) $0\ V_{rms}$ and (*b*) $60\ V_{rms}$ at 298 K. A bar corresponds to $0.5\ \mu m^{-1}$.

Figure 4 is a schematic illustration of typical Hv light scattering patterns for two typical assemblies of molecular aggregates with (*a*) random and (*b*) spherulite-like orientations [23–27]. When the orientation of the molecular aggregates is random, the Hv pattern is isotropic about the angle μ; that is, circular symmetry exists, exhibiting the maximum intensity at the centre. In the case of a spherulite-like orientation, the Hv pattern shows a four-leaf clover type as shown in figure 4 (*b*).

The Hv light scattering pattern observed for the composite under $0\ V_{rms}$ at 298 K (liquid crystalline gel state) may correspond to the overlapping of circular symmetric and four-leaf clover patterns, as shown in figure 3 (*a*). Since the Hv scattering pattern disappeared upon heating above 308 K, at which 5CB was isotropic, it seems reasonable to conclude that the light scattering patterns observed for the composite at 298 K, figure 3 (*a*), might arise from the 5CB molecular aggregates with nematic alignment.

If an electric voltage of $60\ V_{rms}$ was applied to the composite, the four-leaf clover pattern became more distinct, as shown in figure 3 (*b*), because the circular symmetry pattern became weaker. That is, the 5CB molecular aggregates with random director orientation under $0\ V_{rms}$ rearranged their director orientations along the direction of the electric voltage. However, the 5CB molecules with spherulite orientation did not respond to the electric voltage. As shown in figure 3 (*b*), in the case of the sperulite-like aggregation structure, the maximum intensity of the Hv light scattering pattern appeared at an azimuthal scattering angle, $\mu = 45°$ to both the polarizer and the analyser [23]. The characteristic Hv light scattering pattern can be determined theoretically by the shape factor, $U = 4\pi nR/\lambda \sin(\theta/2)$, where R, n and λ are the average radius of the spherulite-like aggregate, refractive index of the material, and the wavelength of incident light, respectively. The maximum shape factor is given by equation (1)

$$U_{\max} = \frac{4\pi nR}{\lambda} \sin\left(\frac{\theta_{\max}}{2}\right) = 4.09 \qquad (1)$$

where $\theta_{\max}$ is the scattering angle at which the intensity maximum appeared, therefore R can be experimentally determined from $\theta_{\max}$. In the case of the composite system in a liquid crytalline gel state, the average refractive index of 5CB, 1.61, can be applied as the magnitude of n because the fraction of $Cy(11)_2$ was sufficiently small. Then, the average radius of the spherulite-like aggregation structure can be determined to be about $10\ \mu m$.

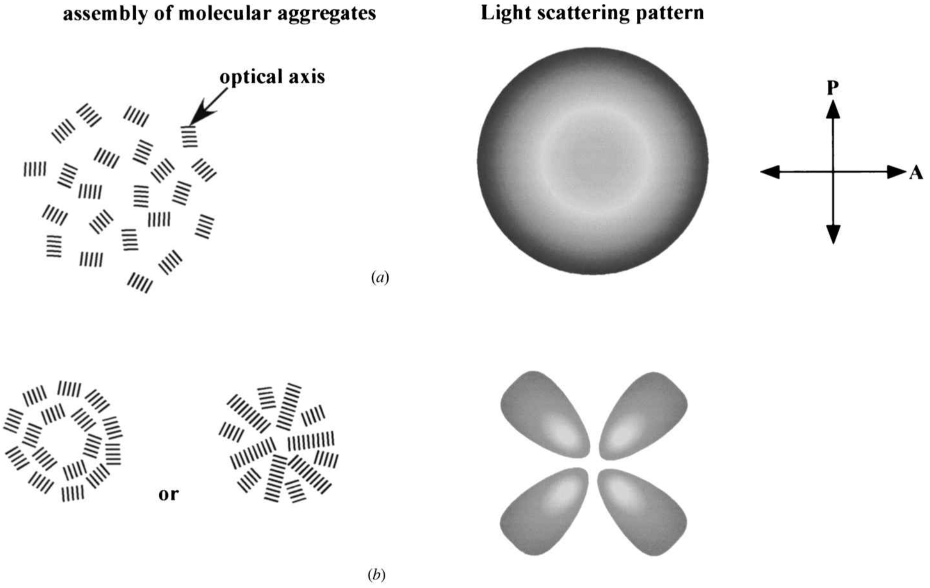


Figure 4. Illustration of the relationship between optical orientations and Hv light scattering patterns: (*a*) random orientation, (*b*) spherulite-like orientation.

3.2. *Polarizing optical microscopy*

Figures 5(*a*) and 5(*b*) show the polarizing optical micrographs photographs for the (Cy(11)$_2$/5CB = 0.5/99.5 mol %) composite at 298 K under 0 and 60 V$_{rms}$, respectively. Since, as shown in figure 5(*a*), a multidomain texture was observed in the composite under 0 V$_{rms}$, it is reasonable to consider that the orientation of 5CB was fairly random at an optical wavelength order. This conclusion is supported by the circular light scattering pattern shown in figure 3(*a*). When a voltage of 60 V$_{rms}$ was applied to the composite cell, a large number of the spherulite-like textures with Maltese-cross shapes were observed in the dark-field as shown in figure 5(*b*). It seems reasonable to conclude that in the region of the dark-field, which appeared upon the application of 60 V$_{rms}$, the 5CB molecules could easily realign to the direction of an applied voltage; furthermore, 5CB molecules in the spherulite-like texture could not realign, even upon the application of 60 V$_{rms}$. Also, the average radius of the spherulite-like aggregation structure observed in POM was about 10 µm, which coincided with the radius estimated by means of the light scattering measurement. Furthermore, polarizing optical observation through a colour-sensitive plate under 60 V$_{rms}$ revealed that the alignment of 5CB molecules was radial in the spherulite-like aggregation structure; that is, 5CB molecules aligned along the direction of the spherulite radius.

3.3. *Optical microscopy*

In order to investigate the optical-scale morphology of Cy(11)$_2$ in the composite, optical microscopic observation without polarizers was carried out. Figure 6 shows the optical micrograph for the (Cy(11)$_2$/5CB = 0.5/99.5 mol %) composite after 5CB was extracted from the composite with *n*-hexane; fibre-like aggregates were observed in the composite, forming a spherulite-like aggregation. Since the sol–gel transition of the composite occurred at 334 K, the molecular aggregation of Cy(11)$_2$ proceeded in the isotropic state of 5CB, whose nematic–isotropic transition temperature is 308 K. Therefore, the morphology observed in figure 6 is not dependent on the nature of the nematic phase, but on the growth mechanism of the Cy(11)$_2$ aggregates. The diameter of fibre-like aggregates was about 1 µm.

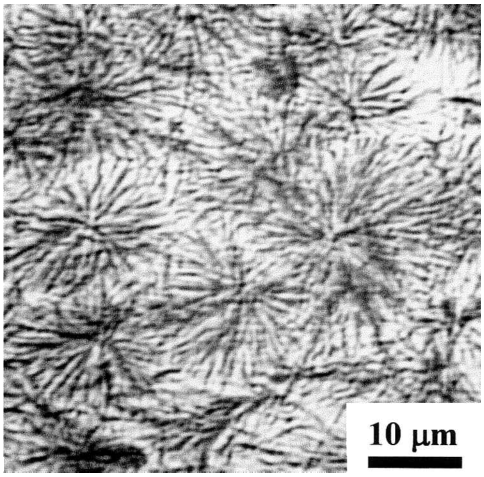
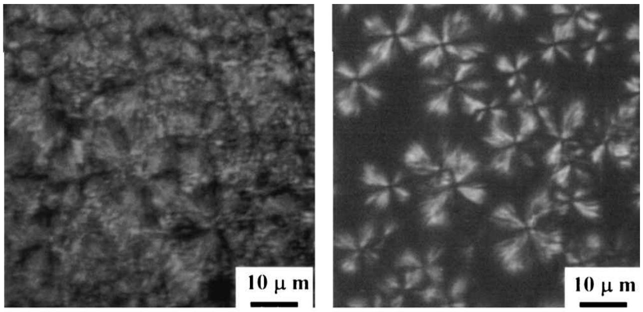


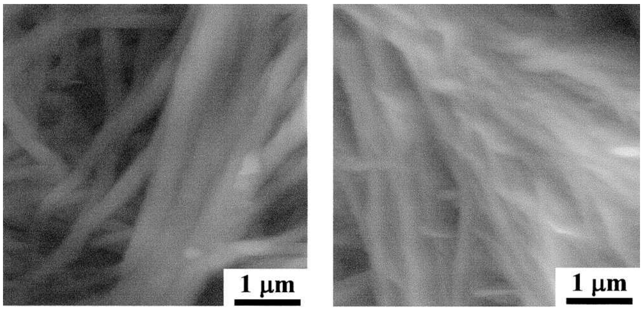
Figure 6. Optical micrograph of (Cy(11)$_2$/5CB = 0.5/99.5 mol %) composite after the extraction of 5CB from the composite with *n*-hexane.

In the spherulite-like aggregation, the bundles of fibre-like aggregates of 20 µm diameter extended radially. The composite was composed of heterogeneous assemblies of the fibre-like and spherulite-like aggregates of Cy(11)$_2$ in the µm range. Therefore, the heterogeneous assemblies of Cy(11)$_2$ aggregates might induce inhomogeneous alignments of 5CB molecules and their inhomogeneous response upon application of an a.c. voltage, as discussed above. That is, in the region of low density fibre-like aggregates, 5CB molecules were weakly anchored to Cy(11)$_2$ aggregates, resulting in the response to an electric field. On the other hand, in the region of high density fibre-like aggregates (i.e in the spherulite-like aggregate),



0 Vrms (a) **60 Vrms** (b)

Figure 5. Polarizing optical micrographs of (Cy(11)$_2$/5CB = 0.5/99.5 mol %) composite under (*a*) 0 V$_{rms}$, (*b*) 60 V$_{rms}$ at 298 K.



(a) **(b)**

Figure 7. AFM images for (Cy(11)$_2$/5CB = 0.5/99.5 mol %) composite after the extraction of 5CB from the composite with *n*-hexane.

5CB molecules were strongly anchored by Cy(11)$_2$ spherulite-like aggregates, resulting in the non-response to an electric field.

3.4. *Atomic force microscopy*

In order to obtain a more detailed morphological insight into Cy(11)$_2$ aggregates, AFM observations were made. Figure 7 shows AFM images for the (Cy(11)$_2$/5CB = 0.5/99.5 mol %) composite after 5CB was extracted with *n*-hexane. Fine fibrils of 180 ~ 460 nm width were observed in the composite. It seems reasonable to consider that from the mean width of the fibrils, one fibril might be composed of about one hundred one-dimensional molecular associates of Cy(11)$_2$, as shown in figure 8 (*c*), assuming that fully extended Cy(11)$_2$ is aligned perpendicular to the fibre axis. One of the authors (K.H.) reported that the one-dimensional molecular associate was formed via hydrogen bonding between the amide bonds of Cy(11)$_2$ [5].

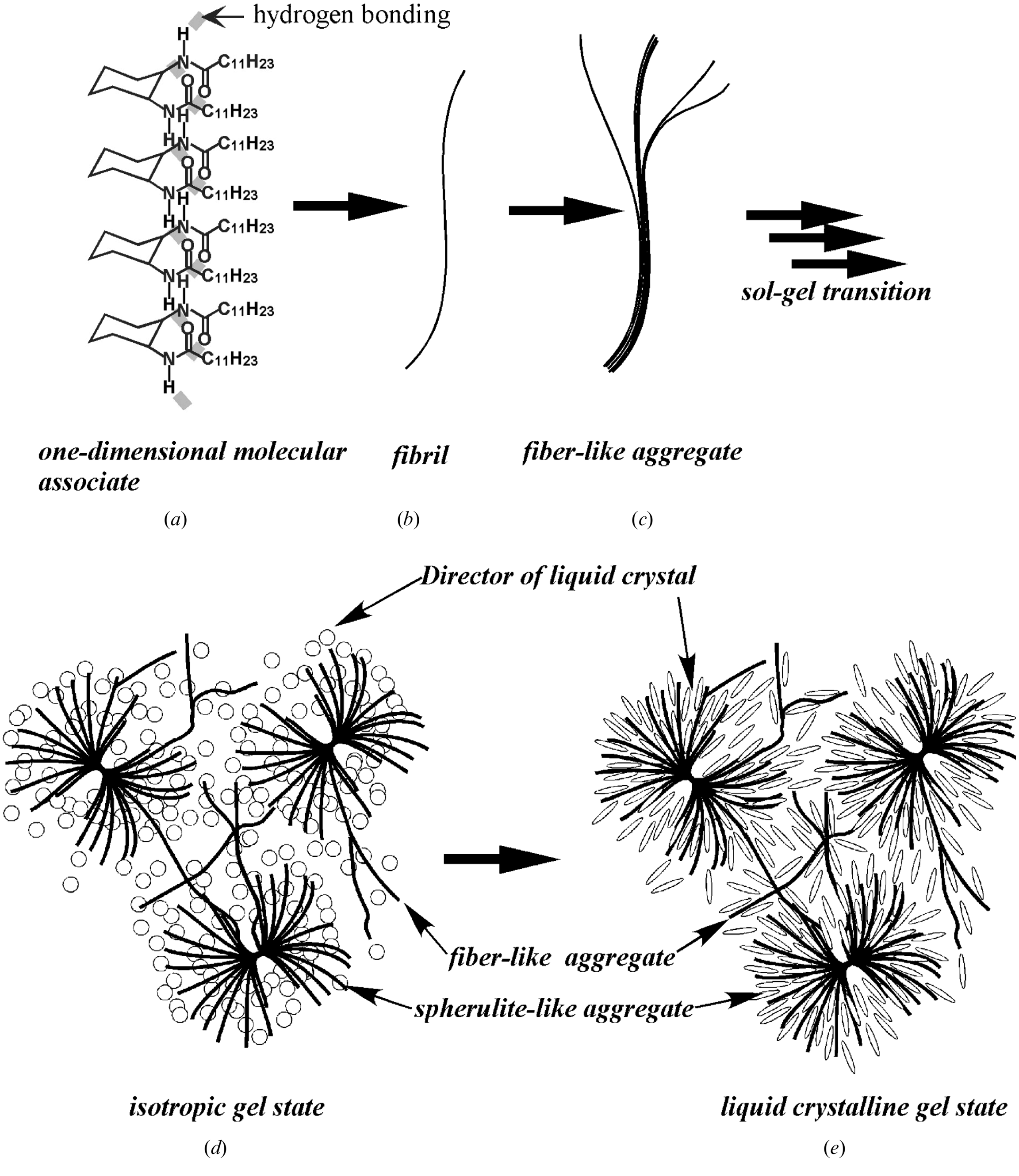


Figure 8. A possible model for the aggregation process of a (self-assembling oil gelator/liquid crystal) composite.

Bundling or intertwining of several fibrils was observed for the composite as shown in figures 7(*a*) and 7(*b*). Although the gelation mechanism in the composite has not been investigated extensively, it is reasonable to consider that the case of the composite is similar to that of an organogel, being composed of a common organic solvent and a self-assembling oil gelator; bundling or intertwining of several fibrils, similar to our observation in figures 6 and 7, have also been reported in the case of some organogels.

3.5. *Possibility of molecular aggregates in the composite*

Figure 8 shows a possible model for the molecular aggregation process in the (Cy(11)$_2$/5CB) composite. In a sol–gel transition process, firstly, the one-dimensional molecular associate is formed through hydrogen bonding, as shown in figure 8(*a*). An elongated fibril is then built up by the one-dimensional molecular association of a number of Cy(11)$_2$ molecules, figure 8(*b*). The fibrils then begin to assemble along their lateral directions with lowering temperature, resulting in the formation of a fibre-like aggregate of several hundreds nm in diameter, as shown in figure 8(*c*). With further lowering of temperature, the composite is composed of a mixture of the (fibre-like Cy(11)$_2$ aggregates/5CB) phase and the (spherulite-like Cy(11)$_2$ aggregates/5CB) phase, as shown in figure 8(*d*); the composite then exhibits the gel state as well as the organogel, being composed of the gelator and the common organic solvent. When temperature is lower than its isotropic–nematic transition temperature, 5CB molecules in the composite have anisotropic orientation; however the orientation of 5CB director is strongly dependent on the Cy(11)$_2$ aggregation structure, as shown in figure 8(*e*).

4. Conclusion

The aggregation structure of a (self-assembling oil gelator/liquid crystal) composite was investigated using light scattering studies, optical microscopy and AFM; it was revealed that a three-dimensional network consisting of fibre-like and spherulite-like aggregates was formed in the composite. The composite had a hierarchical-structure, from the one-dimensional molecular associate to fibre-like or spherulite-like aggregate. The alignment and response of the 5CB molecules to an a.c. voltage were strongly dependent on the Cy(11)$_2$ aggregation state in the composite.

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