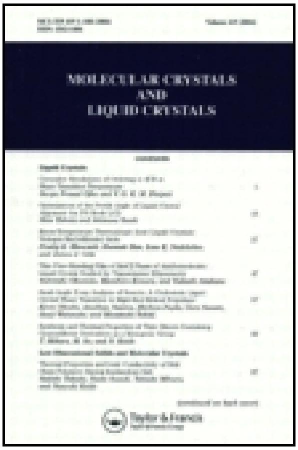

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IMPROVEMENT OF LIGHT SWITCHING CONTRAST OF LIQUID CRYSTALLINE COMPOSITE GEL BY ADDING POLAR ORGANIC SOLVENT

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The aggregation structure and electro-optical properties were investigated for novel liquid crystalline composites composed of a low molecular weight gelator and a low molecular weight liquid crystal. The gelator spontaneously aggregated through intermolecular hydrogen bonding and formed spherulite-like and fiber-like aggregation structures in the composite. By the addition of a solvent with a high dielectric constant and a large dipole moment, such as dimethyl sulfoxide, the number of the spherulite-like structures in the composite decreased strikingly due to affecting the hydrogen bonding of the self-assembling gelators in the composite, resulting in a higher light transmission state upon an application of an a.c. electric field. Dimethyl sulfoxide was found to be an effective agent for improving the electro-optical properties of (gelator/liquid crystal) composite gel.

Keywords: light switching; light scattering; gel; hydrogen bond

INTRODUCTION

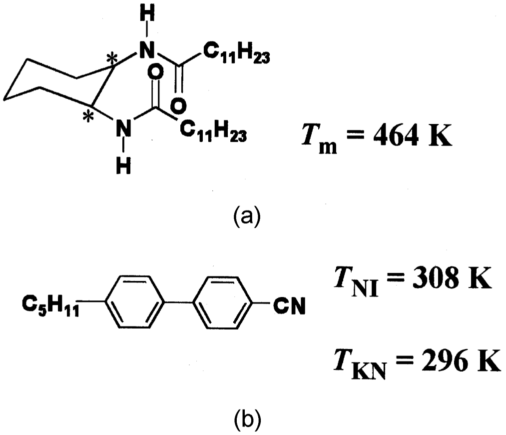
New gelators such as organic fluids have recently attracted much attention because these gelators form a three-dimensional network of interconnected fibrous aggregates, which can immobilize various organic solvents [1–7]. The gelators form molecular associations through noncovalent interactions such as hydrogen bonds, van der Waals interaction, and coordinating bonds. Hanabusa et al. reported that *trans(IR, 2R)*-1,2-bis (dodecanoylamino)cyclohexane could gelate various organic fluids from nonpolar to polar solvents through intermolecular hydrogen bonding between the two amide bonds [6]. Kato et al. found that the gelator could gelate some liquid crystals in the nematic or smectic liquid crystalline phase [8,9]. The (gelator/liquid crystal) composite exhibited various temperature-dependent aggregation states, such as an isotropic sol, an isotropic gel, and a liquid crystalline gel. The composite maintained liquid crystalline characteristics such as birefringence or anisotropy of dielectric permittivity even after the gelation. Also, Kajiyama et al. developed (polymer/liquid crystal) composites and applied them as permselective molecular filtration membranes [10–13] and large flexible films for light scattering-light transmittance switching [14–18]. Recently, Abe et al. reported that the (gelator/liquid crystal) composite formed a hierarchical structure from the one-dimensional molecular associate to the fiber or spherulite-like formation and, furthermore, the electro-optical response of liquid crystalline molecules was strongly dependent on the aggregation state of the gelator in the composite [19].

In this article, the influence of the addition of organic solvents to the (gelator/liquid crystal) composite was investigated in regard to the aggregation structure and the electro-optical properties.

EXPERIMENTAL

Samples

The self-assembling oil gelator, ***trans(IR, 2R)***-1,2-bis(dodecanoylamino) cyclohexane ($Cy(11)_2$), used in this study was synthesized by one of the authors (Hanabusa). The liquid crystal (LC) of 4-cyano-4′-phentylbiphenyl (5CB) (MERCK Co., Ltd., Japan) was used without purification in this study. Their chemical structures and some physical properties are shown in Figure 1. In order to change the hydrogen bonding strength of the the gelator in the liquid crystal media, some polar organic solvents were selected to add into the composite because the hydrogen bonding plays an important role in the formation of the aggregation structure of the gelator. The dielectric constant and the dipole moment of several organic solvents added to the composite are shown in Table 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 and then the mixture was stirred at 373 K for 24 h. The mixture in an 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 of 4.5 μm thick. No surface treatment for LC molecular alignment was done on any of the cells. The cell was cooled to a nematic gel state and held at 303 K for more than 30 min. The fraction of polar organic solvent was 2.0 mol%.



(a)

(b)

FIGURE 1 Chemical structure and physical properties of low molecular weight gelling agent, liquid crystal, and organic solvent. (a) Low molecular weight gelator *Trans*(1R, 2R)-1, 2-bis(undecanoylamino) cyclohexane ($Cy(11)_2$). (b) Liquid crystal 4-cyano-4′-pentylbiphenyl (5CB).

TABLE 1 Dielectric Constant and Dipole Moment of the Organic Solvents, and Light Transmittance of the Composite Upon Application of 75 V and Sol-Gel Transition Temperature of the Composite

Organic solvent	Dielectric constant	Dipole moment/ debye	Decrease in $T_{\text{sol-gel}}$	Transmittance of composite including organic solvent upon 75 V/%
dimethylsulfoxide	48.9	4.30	2.1	98
N, N-dimethylformamide	36.7	3.86	1.4	31
cyclohexanone	18.3	3.01	0.8	21
ethylene glycol	37.7	1.66	0.7	20
propanol	15.0	2.20	1.3	10
toluene	2.2	0.37	1.3	10

Also, the sol-gel transition temperature of the composites was determined by the test tube tilting method, whereby a test tube containing the gel was immersed inversely in a water bath with a thermostat [20].

Morphological Studies

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. electric voltage from 0 to 75 Vrms under crossed Nicols.

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

Light Transmittance Measurement

Figure 2 shows the measuring system for the light transmittance intensity. An He-Ne laser ($\lambda = 632.8$ nm) was used as incident light being transmitted normal to the cell, and the transmitted light intensity was measured with a photodiode (detectable area: $3.0 \times 3.0\,\text{mm}^2$). The light transmittance intensity of the cell was evaluated in comparison with that of the blank cell. An external a.c. electric voltage from 0 to 75 Vrms was applied across the cell.

RESULTS AND DISCUSSION

In order to investigate the effect of the addition of an organic solvent on the morphology of the composite, optical microscopic observation was carried out. Figures 3a and 3b show the photographs of optical microscopy

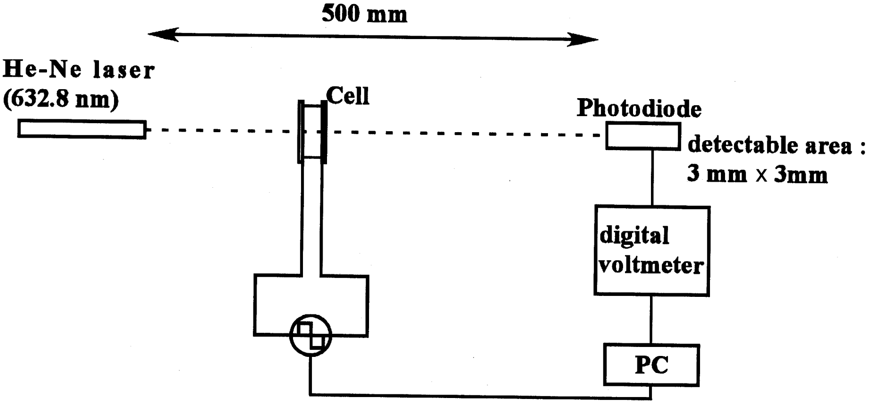


FIGURE 2 Schematic illustration of measuring system for the intensity of light transmittance.

for ($Cy(11)_2$/5CB = 0.5/99.5 mol%) and ($Cy(11)_2$/5CB/DMSO = 0.5/97.5/2.0 mol%) composites after 5CB was extracted with *n*-hexane, and Figures 3c and 3d show the schematic illustrations of the morphology observed by optical microscopy. As shown in Figures 3a, fibrous aggregates were observed in the ($Cy(11)_2$/5CB = 0.5/99.5 mol%) composite and they also took the shape of spherulite-like formations. The average diameter of the fibers was about 1 μm. The spherulites, sphere-shaped crystalline structures, are the most obvious of the observed structures when crystalline polymers are crystallized from the bulk. The spherical shape originates from the diverging growth of the crystal outward in a splaying motion. In the spherulite-like formations, the aggregation of fibers extended radially, as shown in Figure 3c. Thus, the ($Cy(11)_2$/5CB = 0.5/99.5 mol%) composite was composed of heterogeneous assemblies of the dispersed fibers and the spherulite-like formations of $Cy(11)_2$ with μm order. On the other hand, in the case of the ($Cy(11)_2$/5CB/DMSO = 0.5/97.5/2.0 mol%) composite, only the dispersed fibers of the $Cy(11)_2$ were observed without the spherulite-like formation, as shown in Figure 3b. Therefore, it is apparent that DMSO had the remarkable effect of suppressing the spherulite-like formation. This effect will be discussed later.

Figures 4a and 4b show the AFM images for ($Cy(11)_2$/5CB = 0.5/99.5 mol%) and ($Cy(11)_2$/5CB/DMSO = 0.5/97.5/2.0 mol%) composites, respectively, after 5CB was extracted with *n*-hexane. As shown in Figure 4a, fine fibrils about 300 nm wide were observed in the ($Cy(11)_2$/5CB = 0.5/99.5 mol%) composite. Also, the bundles of several fibrils were observed in the composite. In the case of the ($Cy(11)_2$/5CB/DMSO = 0.5/97.5/2.0 mol%) composite, although the morphology of the fibrils was basically similar to

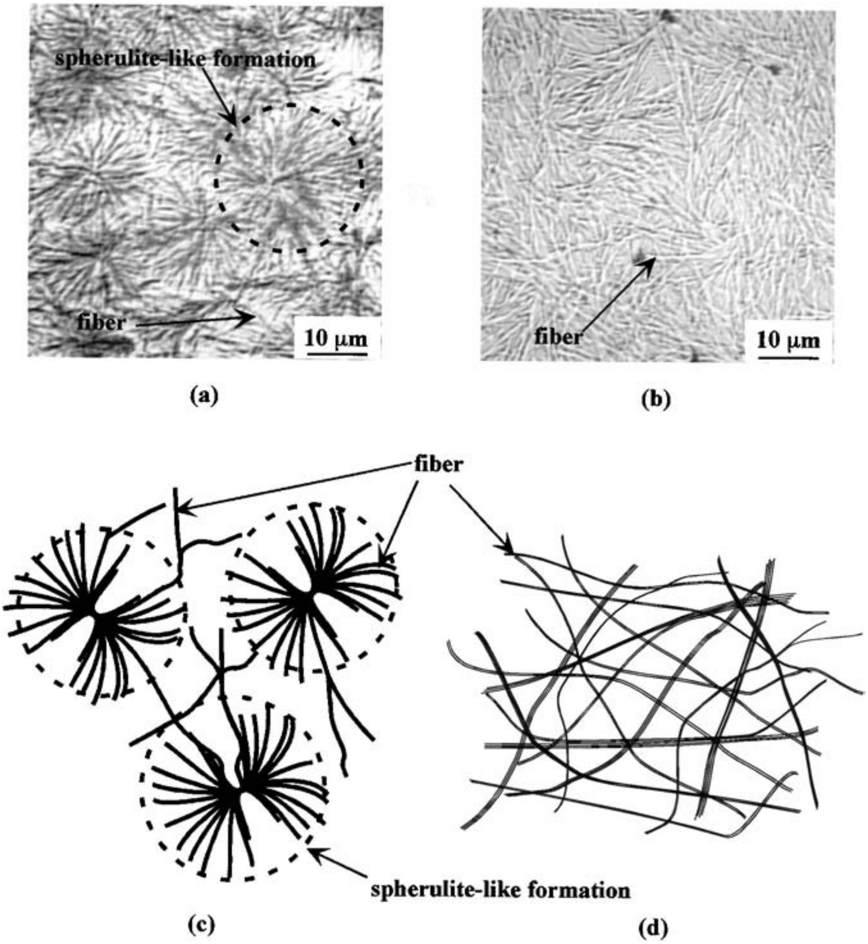


FIGURE 3 (See COLOR PLATES V and VI) Optical microscopic photographs for (a) ($Cy(11)_2/5CB = 0.5/99.5\,mol\%$) and (b) ($Cy(11)_2/5CB/DMSO = 0.5/97.5/2.0\,mol\%$) after the extraction of 5CB with *n*-hexane from the composites and schematic illustration of the morphology observed by optical microscopy. (c) and (d) are the schematic illustrations of the aggregation structure for (a) and (b), respectively.

that of the fibrils of the ($Cy(11)_2/5CB = 0.5/99.5\,mol\%$) composite, the width of fibrils was larger and there were more open spaces among them. It has been reported that a solvent has a strong effect on the aggregation structure, such as molecular packing or a higher-order structure, through intermolecular hydrogen bonding of the amide bond because the hydrogen bonding of the amide bond is sensitive to characteristics of the solvent,

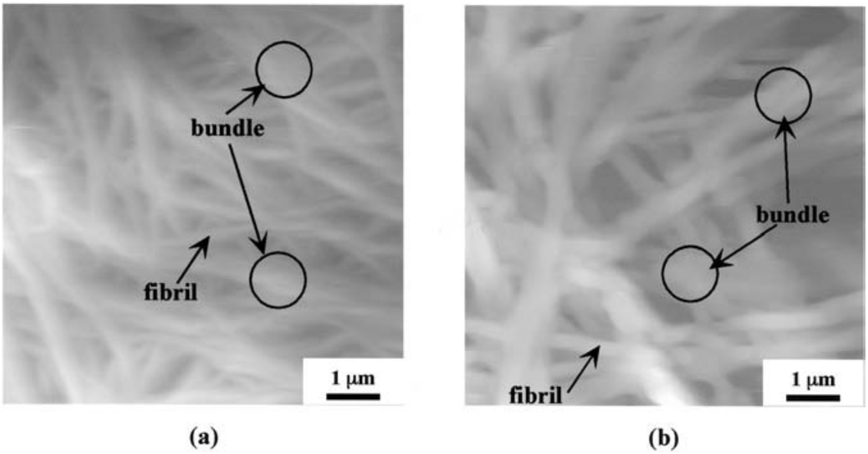


FIGURE 4 (See COLOR PLATES VII and VIII) AFM images for (a) ($Cy(11)_2/5CB = 0.5/99.5$ mol%), (b) ($Cy(11)_2/5CB/DMSO = 0.5/97.5/2.0$ mol%) after the extraction of 5CB with *n*-hexane from the composites.

such as polarity, being the donor or acceptor for hydrogen bonding, and the dielectric constant [21,22]. In our system, the addition of DMSO had an influence on the fibrous aggregation structure of the $Cy(11)_2$ which self-assembles via intermolecular hydrogen bonding.

Figure 5 shows polarizing optical microscopic photographs for the ($Cy(11)_2/5CB = 0.5/99.5$ mol%) and the ($Cy(11)_2/5CB/DMSO = 0.5/97.5/2.0$ mol%) composites upon the application of 60 Vrms. It is reasonable to

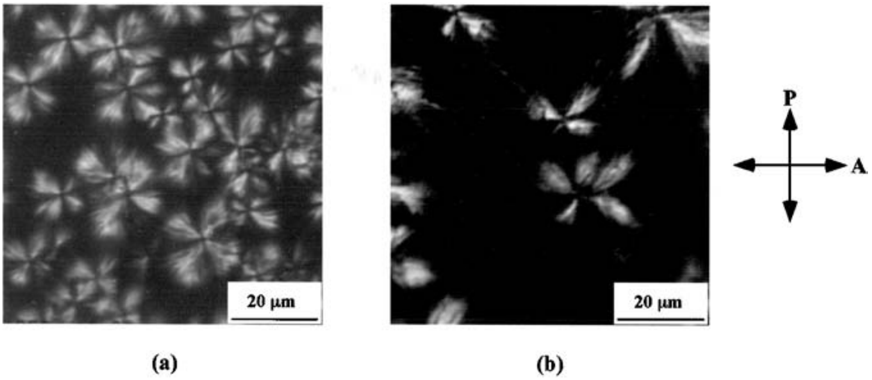


FIGURE 5 (See COLOR PLATES IX and X) POM photographs upon the application of 60 Vrms: (a) ($Cy(11)_2/5CB = 0.5/99.5$ mol%), (b) ($Cy(11)_2/5CB/DMSO = 0.5/97.5/2.0$ mol%).

conclude from the region of the dark-field, as shown in Figures 5a and 5b, that the 5CB molecules responded to an a.c. applied electric field and aligned their directors parallel to the direction of an applied electric field, that is, perpendicular to the cell substrate. Also, the spherulite-like textures with the so-called Maltese-cross was observed as a bright area in the dark-field for both composites. This indicates that it was difficult for the 5CB molecules existing in the spherulite-like structure to align responding to the applied a.c. electric field, owing to strong anchoring of the 5CB molecules in the $Cy(11)_2$ aggregates. However, by the addition of DMSO into the composite, the number of the spherulite-like structures remarkably decreased, as shown in Figure 5b, in comparison with Figure 5a. As stated in our previous report [19], the 5CB molecules in the spherulite-like formation could scarcely respond to an electric field. Therefore, it was easily expected that the responsive characteristic of the 5CB molecules to the applied a.c. electric field in the composite must be remarkably improved due to decreasing the number of spherulite-like formations of $Cy(11)_2$ by the addition of DMSO into the composite.

In order to evaluate the electro-optical property of the composites, the light transmittance intensity was measured upon the application of an a.c. electric field from 0 to 75 Vrms. Figures 6 shows the applied voltage

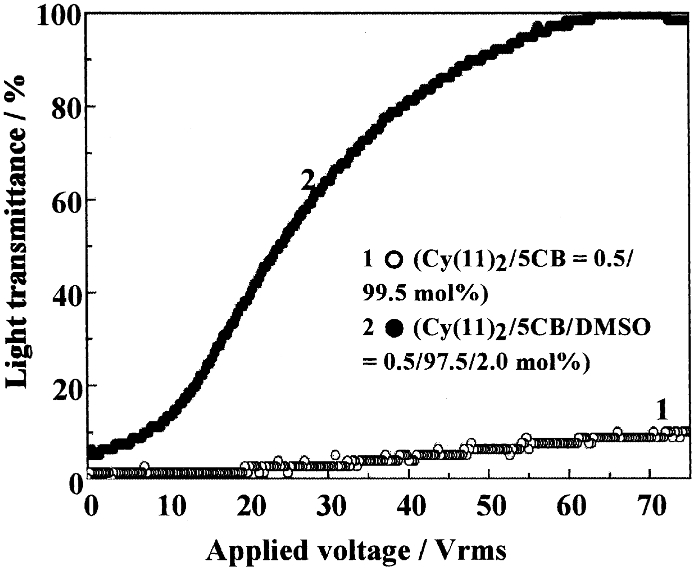


FIGURE 6 Applied voltage dependence of light transmittance for (curve 1) ($Cy(11)_2$/5CB = 0.5/99.5 mol%), (curve 2) ($Cy(11)_2$/5CB/DMSO = 0.5/97.5/2.0 mol%).

dependence of the light transmittance intensity for the ($Cy(11)_2$/5CB = 0.5/99.5 mol%) and ($Cy(11)_2$/5CB/DMSO = 0.5/97.5/2.0 mol%) composites. The light transmittance in the absence of an electric voltage was nearly zero for both composites because of strong light scattering. The strong light scattering was due to the distributed orientation of 5CB nematic directors with an optical wavelength order and also the existence of the spherulite-like formations of $Cy(11)_2$ molecules in the composite. As shown in Figure 6, the light transmittance of both composites increased with an increase of an a.c. electric field. However, the light transmittance of the ($Cy(11)_2$/5CB = 0.5/99.5 mol%) composite was less than 15% upon application of 75 Vrms, that is, the ($Cy(11)_2$/5CB/ = 0.5/99.5/ mol%) composite exhibited strong light scattering even if an electric field was applied. This might arise from the tight anchoring of 5CB molecules in the spherulite-like formations of $Cy(11)_2$, as shown in Figures 3a and 5a. On the other hand, the ($Cy(11)_2$/5CB/DMSO = 0.5/97.5/2.0 mol%) composite exhibited a high transmission state under 75 Vrms. This is responsible for a decrease in the number of the spherulite-like formations of $Cy(11)_2$ in the composite by the addition of DMSO. Therefore, the addition of DMSO into the composite was extremely effective for the improvement of the electro-optical property of the composite.

The electro-optical properties were examined for the composite, including organic solvents other than DMSO. Table 1 shows the dielectric characteristics of the solvents and the light transmittance upon application of 75 V. DMSO is shown to prominently give an excellent electro-optical effect to the composite. DMSO has a higher dielectric constant and a higher dipole moment compared to other solvents. Also, the composite including DMSO exhibited a lower sol-gel transition temperature, as shown in Table 1. Therefore, the $Cy(11)_2$ could be depressed, affecting the higher-order structure of the ($Cy(11)_2$.

CONCLUSION

By the addition of a polar organic solvent, the aggregation state of the gelator in the liquid crystalline media changed and the electro-optical properties based on the light scattering of the (gelator/liquid crystal) composite gel were improved. In particular, by the addition of DMSO with a large dielectric permittivity and dipole moment into the composite, the formation of the higher-order structure of $Cy(11)_2$, such as the spherulite-like formation, was suppressed because DMSO could strongly interact with the hydrogen bonding of $Cy(11)_2$. As a result, the addition of DMSO into the composite was very efficient in improving the electro-optical properties.

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