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Norihiro Mizoshita [a], Yuki Suzuki [a], Kenji Kishimoto [a], Takashi Kato [a] & Kenji Hanabusa [b]

[a] Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Tokyo, Japan

[b] Department of Bioscience and Textile Technology, Graduate School of Science and Technology, Shinshu University, Ueda, Nagano, Japan

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LIGHT SCATTERING ELECTROOPTIC BEHAVIOR OF LIQUID-CRYSTALLINE PHYSICAL GELS — EFFECTS OF MICROPHASE-SEPARATED MORPHOLOGIES

*Norihiro Mizoshita, Yuki Suzuki, Kenji Kishimoto, and Takashi Kato**
Department of Chemistry and Biotechnology,
School of Engineering, The University of Tokyo, Hongo,
Bunkyo-ku, Tokyo 113-8656, Japan

Kenji Hanabusa
Department of Bioscience and Textile Technology,
Graduate School of Science and Technology, Shinshu University,
Ueda, Nagano 386-8567, Japan

Light scattering electrooptic behavior has been examined for liquid-crystalline physical gels consisting of a room temperature nematic liquid crystal and amino acid gelators. Electrooptic properties of the gels depend on the morphologies of the hydrogen-bonded aggregates. We show that liquid-crystalline gels comprising of randomly dispersed networks have potentials for light scattering electrooptic materials.

Keywords: electrooptic properties; liquid crystal; microphase separation; physical gel; self-assembly

INTRODUCTION

Room temperature nematic liquid crystals have been used as electrooptic materials on twisted nematic (TN) mode [1–3]. TN liquid crystal display devices have complicated structures. The existence of polarizers lowers the brightness of the displays. Electrode surfaces are coated with liquid crystal alignment layers that require rubbing processes. As an approach

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*Corresponding author.

to liquid crystal displays showing high brightness and high contrast, light scattering electrooptic materials have been fabricated by the composition of liquid crystals and non-liquid-crystalline components [4–15]. A number of studies have focused on polymer-dispersed and polymer-stabilized liquid crystals [4–8], filled nematics [9–11], and chemical anisotropic gels [12,13].

Recently, we have developed liquid-crystalline (LC) physical gels as a new class of electrooptic materials [14–24]. Those gels consist of liquid crystals and hydrogen-bonded gelators. Low molecular weight gelators for common organic solvents have attracted attention from the view of supramolecular chemistry, materials science, and industrial application [25–29]. Fibrous aggregation of such low molecular weight compounds in nematic liquid crystals leads to the formation of nematic LC gels [14–23]. We have reported that the nematic LC gels containing an L-isoleucine-based gelator exhibit faster electrooptic responses than neat liquid crystals in TN cells [19,22,23]. In those cases, the LC gels containing 0.5–0.7 wt% of the gelator are applied to TN displays. When the LC gels contain more than 1.0 wt% of the gelators, the gels cannot be used on TN mode because of the occurrence of light scattering [22,23]. Such light scattering is caused by the formation of LC polydomains due to the existence of the aggregates of the gelator. This indicates the LC gels containing more than 1.0 wt% of gelators are applicable to light scattering displays if we could control the electrooptic response of the LC molecules as schematically shown in Figure 1. We reported that LC gels formed by an oligo(amino acid) gelator showed significant light scattering electrooptic properties [15]. Here we

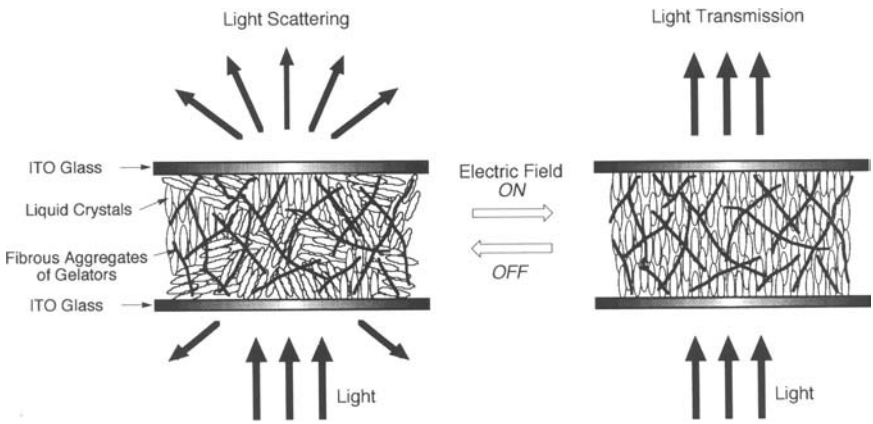
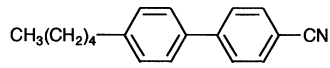
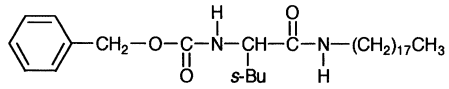


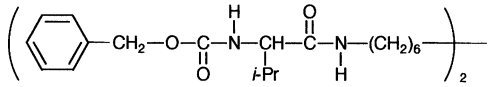
FIGURE 1 Schematic illustration of electrooptic switching as light scattering materials of LC physical gels.



5CB



ZI18



$(ZV)_2$12

FIGURE 2 Molecular structures of the liquid crystal and the gelators used in this study.

report on the light scattering electrooptic behavior of the LC gels consisting of a nematic liquid crystal and L-amino acid derivatives (Fig. 2). We show that the electrooptic behavior is greatly dependent on the microphase-separated structures of the LC gels.

EXPERIMENTAL

4-Cyano-4′-pentylbiphenyl (5CB, nematic-isotropic transition temperature (T_{NI}): 35°C, refractive anisotropy (Δn): 0.184) was used as a room temperature nematic liquid crystal. The gelators derived from L-amino acids, ZI18 and $(ZV)_2$12, were used for the preparation of anisotropic gels [19,27,28]. The LC physical gels were prepared by mixing the liquid crystal and the gelators, heating to isotropic states, followed by cooling to required temperatures.

The electrooptic effects of the LC gels were measured with ITO (indium tin oxide) glass sandwich cells (1 cm × 1 cm × 16 μm). The mixtures in the isotropic states were introduced into the cell, then cooled to room temperature. A He–Ne laser (632.8 nm) was used as an incident light source. AC electric fields (300 Hz) were applied for the cells. The transmitted light

intensity was measured with a photodiode. The light intensity for the ITO cell filled with toluene was assumed to be full-scale intensity. The rise and decay times of the samples were measured at 100 V. They were evaluated as the time periods required to reach 90% and drop 10% of the maximum transmittance by the application and removal of electric fields, respectively.

For atomic force microscope (AFM) observation, samples were prepared by immersing the LC gels in hexane for two days to remove the LC components and finally drying at room temperature. All tapping-mode AFM measurements were performed with a commercial AFM (Digital Instrument Inc., Santa Barbara, CA, Nanoscope IIIa) equipped with a cantilever (NCH-10-T) at room temperature in air.

RESULTS AND DISCUSSION

The electrooptic measurements for the LC gels formed by ZI18 and $(ZV)_2$12 show that the electrooptic behavior is greatly dependent on the chemical structures of the gelators. The 5CB/ZI18 gels show electrooptic switching between light scattering and light transmission states, while the 5CB/$(ZV)_2$12 gels do not function as electrooptic materials. As for the 5CB/ZI18 gels, the relationships between transmittance and applied voltage are shown in Figure 3. The transmittance in the electric field off-states becomes higher with the decrease in the concentration of the gelator from 5.0 to 0.5 wt% and the driving voltages become lower. For example,

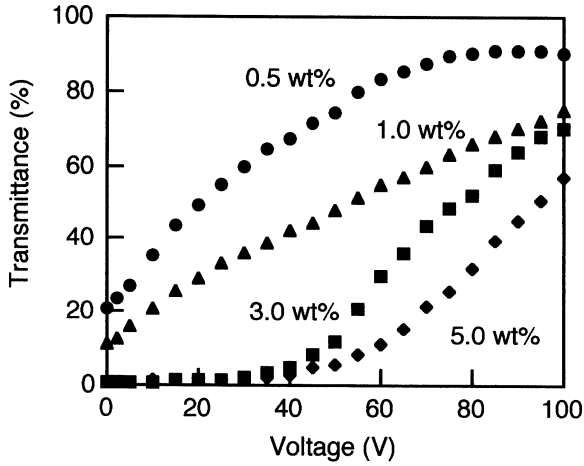


FIGURE 3 Relationships between transmittance and applied voltage for the 5CB/ZI18 gels in 16 μm-thick cells.

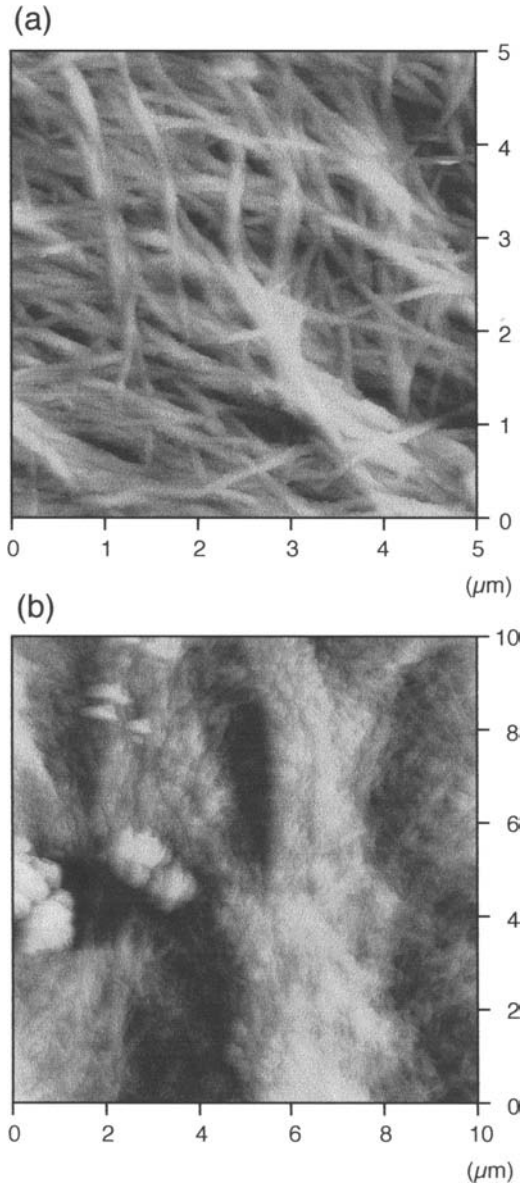


FIGURE 4 AFM images of the xerogels obtained from the 5CB/ZI18 gel (a) and the 5CB/$(ZV)_2$12 gel (b).

the light transmittance in the off-state is 1.0 and 11.0% for the gels containing 3.0 and 1.0 wt% of ZI18, respectively. The application of electric fields induces the homeotropic alignment of 5CB, leading to the increase in the transmittance. The transmittance of the 5CB/ZI18 gel containing 3.0 wt% of ZI18 at 100 V is 70%, which means the contrast ratio for the gel is 70. On the other hand, the 5CB/$(ZV)_2$12 gels show poor electrooptic switching due to the low transmittance in the electric field on-states. For example, the transmittance for the 5CB gel containing 1.0 wt% of $(ZV)_2$12 is 1.1% before the application of electric fields. However the LC gel shows no response up to 40 V, and even at 100 V, the transmittance is only 25%.

AFM observation indicates that the different electrooptic behavior of the LC gels is closely related to the microphase-separated structures of the LC gels, that is, the morphologies of the aggregates of the gelators. Figure 4 shows the AFM images of the hydrogen-bonded aggregates formed in the liquid crystal cells. We can see that gelator ZI18 forms randomly dispersed fibrous aggregates (Fig. 4a). Those network aggregates induce the formation of LC polydomains, leading to electrooptic switching on light scattering mode as shown in Figures. 1 and 3. In contrast, thick aggregates of $(ZV)_2$12 are observed for the xerogel obtained from the 5CB/$(ZV)_2$12 gel (Fig. 4b). The poor response of the 5CB/$(ZV)_2$12 gel may be due to the strong interactions between the thick aggregates of $(ZV)_2$12 and the LC molecules. Previously similar poor response behavior of the 5CB/$(ZV)_2$12 gel was also observed for TN cells [19].

We have measured the response times of the gels. For the 5CB/ZI18 gel containing 1.0 wt% of ZI18, the rise and decay times are 0.5 and 1.0 ms, respectively. The decrease in the concentration of the gelators leads to longer decay times as similarly observed for the liquid crystal/polymer composites [4–8]. For example, the decay time of the 5CB/ZI18 gel containing 0.5 wt% of ZI18 is 36 ms.

CONCLUSIONS

We have shown that the LC physical gels have potentials for light scattering electrooptic materials. The electrooptic properties are greatly dependent on their microphase-separated structures. In order to improve the electrooptic behavior of the LC gels, it is required to optimize the chemical structures of the gelators and their amounts, maintaining the existence of the dispersed fibrous aggregates that effectively induce light scattering in the off-states. The selection of the components and tuning of the microphase-separated structures of the anisotropic gels will lead to the fabrication of a new type of light scattering displays.

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