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***(Late-News Paper)***

# Resettability of Cholesteric Liquid Crystal Helix Pitch Using Self-Assembled Dendrimer with Lysine Groups

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## ABSTRACT

*For the exploration of the applications using cholesteric liquid crystals, we attempted to control their helix pitch by the addition of self-assembled dendrimers into cholesteric liquid crystals. Consequently, we realized the stabilization and resettability of the helix pitch by the molecular interaction between the dendrimer and cholesteric liquid crystals.*

## 1. INTRODUCTION

Cholesteric liquid crystals with helix structure have the specific characteristics of selective light reflection based on Bragg reflection, in which the reflective wavelength strongly depends on the average refractive index of the liquid crystal and the helix pitch length. This unique property has been adapted to various applications such as wavelength-tunable lasers [1], optical recording materials [2], optical shutters [3], and electronic paper [4] so far. However, helix pitch cannot be stabilized by environmental temperature changes. Therefore, the development of a precise control technique of the helix pitch has a possibility of the exploration of the novel device application based on the cholesteric liquid crystals.

To stabilize the helix pitch of cholesteric liquid crystal, polymer-stabilized cholesteric liquid crystals have been reported so far [5]. In this stabilization technique, monomer molecules that are blended into cholesteric liquid crystal are photopolymerized by ultraviolet irradiation. The constructed polymer network in cholesteric liquid crystal stabilizes the helix pitch by anchoring force in polymer interface. However, the reset of helix pitch length in the polymer-stabilized cholesteric liquid crystal is difficult extremely because the construction mechanism of polymer network is based on the irreversible reaction of photopolymerization. Any controllable technique of helix pitch length is one of the important challenges for the structurally-stabilized cholesteric liquid crystal.

To overcome this problem, we proposed self-assembly dendrimer-doped cholesteric liquid crystal in this paper. The self-assembly dendrimer can be reconstructed aggregation structure by temperature control. The conventional photo-polymerized network structure has not this unique feature. The details of the proposed method are explained in the next section. Here, we report on the helix pitch stabilization effect and helix pitch resettability to demonstrate the proposed dendrimer-doped cholesteric liquid crystals.

## 2. PROPOSAL OF THE METHOD

The dendrimers with lysine groups (POSS-Lys) have hydrogen-bonding functional groups on their side chains and spontaneously form an aggregated fibril-like structure [6] (see Fig.1). We have previously reported that this dendrimer can be formed a nano-sized network structure composed of self-aggregated dendrimers in nematic-phase liquid crystals and stabilize the molecular alignment of LC [7]. This experimental fact means exist of molecular interaction between POSS-Lys and LC. For

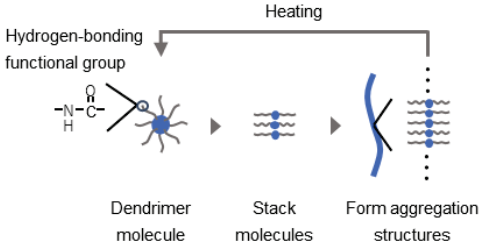


**Fig. 1 Schematic illustration of self-aggregation process of lysine-based dendrimers.**

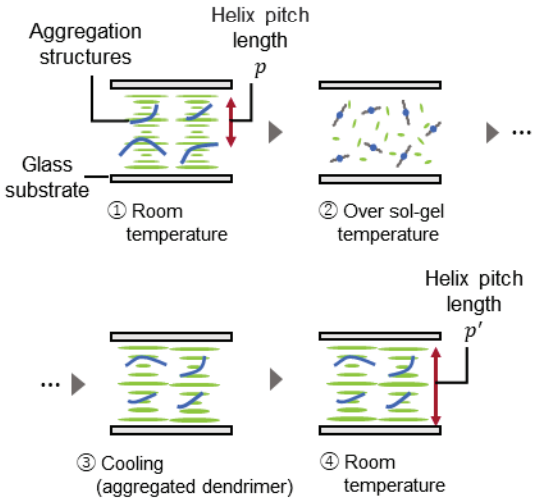


**Fig.2 Schematic illustration of proposed control method of helix pitch length using self-alignment of that liquid crystals assembled dendrimer.**

this reason, it is expected that the aggregated fibril structure can penetrate among helical structure and stabilize the helix pitch length due to its anchoring effect.

Furthermore, the self-assembled dendrimer can be dispersed on the individual molecular level by thermal treatment. The heating over gel-sol transition temperature (from aggregated state to dispersed state) of LC/dendrimer mixture leads to individually-dispersed dendrimer molecules in LC. After that, the cooling process induces the reconstruction of the aggregated fibril or network structure. This intermolecular reaction is reversible. Therefore, if the helix pitch length is changed by unintentional temperature and external mechanical stress, resettable pitch length by only changing of temperature is expected. This is based on the reconstruction of the aggregation structure in POSS-Lys molecules (see Fig. 2).

## 3. EXPERIMENTAL

### 3.1. Evaluation Method of Helix Pitch Length

In this study, we used a wedge cell to evaluate the helix pitch length of cholesteric liquid crystal, as a reference to the literature [8]. Fig. 3 shows the structure of the wedge-type cell. A mylar film with a thickness of several tens' micrometer was used as a spacer on only one side of the glass substrate. As a result, the upper glass substrate is tilted and the thickness of the liquid crystal layer is distributed. When the cholesteric liquid crystal is injected into the cell, disclination lines appear where the helix angle changes by 180°. The ratio of the distance $\Delta x$ between the disclination lines and the half-pitch $p/2$ of the cholesteric liquid crystal is equal to the ratio of the distance $L$ from the junction point of the glass substrate to the spacer and the thickness $d$ of the spacer. Therefore, the helix pitch length can be evaluated by Equation (1).

$$p = 2\frac{d\Delta x}{L} \tag{1}$$

In equation (1), since $d$ and $L$ are known from the cell fabrication conditions, it is possible to evaluate the helix pitch length $p$ by measuring the distance $\Delta x$ between the disclination lines.

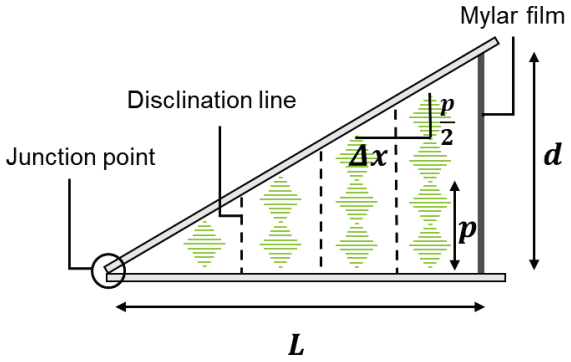


**Fig. 3 Schematic of the wedge-type cell structure.**

## 4. OBSERVATION OF PITCH-LENGTH STABILITY

### 4.1. Investigation of the Effect of Cholesteric LC on Doping Dendrimer

In this study, POSS-Lys (synthesized from Nard institute ltd.) was used as a dendrimer that has been reported to be capable of constructing and reconstructing aggregate structures [9]. The molecular structure of POSS-Lys is shown in Fig. 4. We have reported that doping POSS-Lys of 0.50 wt% to a nematic-phase liquid crystal with a cyano group causes a random alignment of the liquid crystal by gelation [7]. However, to form a helical structure, keeping the molecular alignment of the liquid crystal is necessary. Therefore, we investigated the additive amount of dendrimer for alignment control of cholesteric liquid crystal. The used nematic liquid crystal was E-7 (purchased from LCC corp.) which is terminally modified with a cyano group and the chiral dopant was DDS-1015L (purchased from LCC corp.). The amount of chiral dopant was uniformly set to 6 wt% regardless of the amount of POSS-Lys added, and the prepared liquid crystals were injected into the wedge cell and observed under a polarizing microscope. The results are shown in Fig. 5.

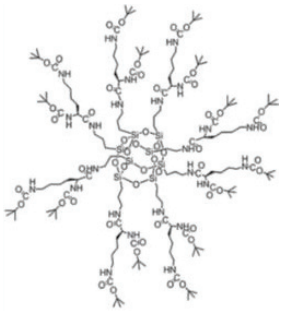

**Fig. 4 The molecular structure of POSS-Lys.**

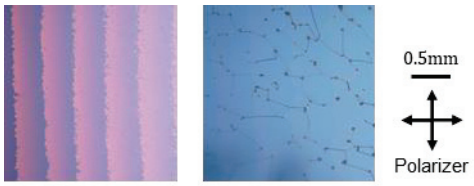


**Fig. 5 Crossed-Nicols photograph of the wedge-type cholesteric liquid crystal cell.**
**(a) concentration of POSS-Lys: 0.01wt%**
**(b) concentration of POSS-Lys: 0.50wt%**

When 0.50 wt% of POSS-Lys was added to the cholesteric liquid crystal, the liquid crystal was not oriented and no disclination lines could be observed. Afterward, the amount of POSS-Lys was gradually reduced to 0.01 wt%, and the disclination line could be observed. It was found that the alignment of the liquid crystal was maintained at 0.01 wt% addition. The concentration of 0.01wt% might be not forming a

sufficient network to prevent the alignment of the liquid crystal due to extremely few concentrations.

### 4.2. Helix Pitch Stabilization by Dendrimers

The addition of dendrimers to the cholesteric liquid crystals may inhibit the change in helix pitch with temperature change due to the aggregation structure. Here, we investigated the stabilization effect of doping POSS-Lys of 0.01wt% concentration on the helix pitch length in cholesteric liquid crystal. A cholesteric liquid crystal containing 0.01 wt% of POSS-Lys was injected into the wedge-type cell at 150°C. The POSS-Lys have a dispersed state under individual molecules at this temperature. Then, we cooled to room temperature in order to prompt aggregation among the POSS-Lys molecules. After that, the temperature was increased to the evaluation temperature and evaluated the temperature dependence of the helix pitch length along the process as shown in Fig. 6. Cholesteric liquid crystals are known to change the helix pitch length when other impurities are doped to that LC. Therefore, we adjusted the doped amount of chiral dopant to cholesteric liquid crystal for comparison with the changes in helix pitch length. Here, we determined the amount of chiral dopant the same as that at 10 ºC. The purpose of this determination is to standardize the start time of changes in helix pitch length.

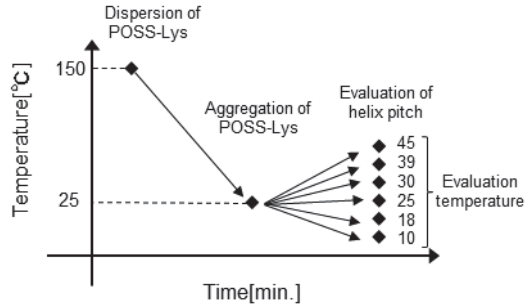


**Fig. 6 Schematic diagram of the temperature changing process for evaluation of the helix-pitch stabilization.**

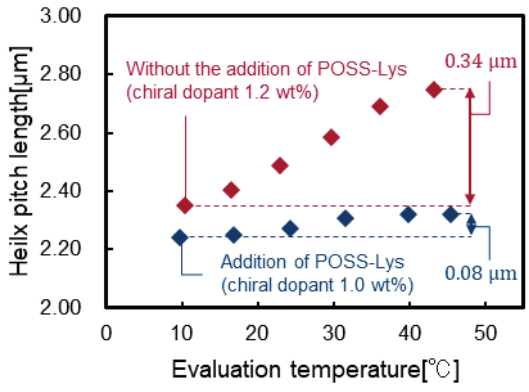


**Fig. 7 Dependence of helix pitch length on evaluation temperature changes under different concentration of chiral dopant. (concentration of dendrimer: 0.01wt%)**

Fig. 7 shows the results of the temperature dependence of the helix pitch length. In the case of data with POSS-Lys, the difference of helix pitch length between at 10 ºC and 45 ºC was 0.08 um. In the case of without POSS-Lys, the difference of helix pitch length between 10 ºC and 45 ºC was 0.34 um. Compared with the data without POSS-Lys, the changes in helix pitch length could be significantly suppressed. These results indicate that the dendrimers have a stabilizing effect on the helix pitch, as the temperature variation of the helix pitch varies with the presence of dendrimers. When POSS-Lys was added with 0.01 wt% concentration, it is presumed that a short aggregation structure was constructed and its alignment control force acted on the liquid crystal molecules, resulting in the stabilization of the helix pitch.

## 5. REALIZATION OF PITCH-LENGTH RESETTABILITY

### 5.1. Evaluation of Fixed Helix Pitch Length by Aggregation Temperature Change

Since the aggregation structure of POSS-Lys can be reconstructed by hydrogen bonding [6], changing the aggregation temperature ($T_{Ag}$) may cause a change in the fixed helix pitch length. Therefore, we evaluated the fixed helix pitch length at different $T_{Ag}$. After heating the cell to 150°C to separate the dendrimer molecules, the

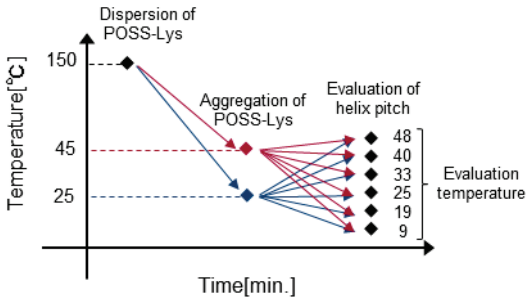


**Fig. 8 Schematic diagram of the temperature changing process for evaluation of the helix-pitch resettability.**

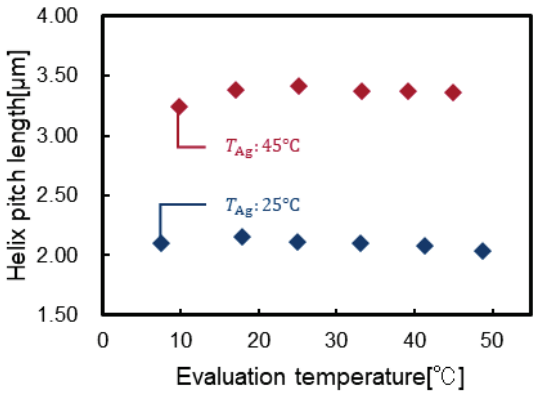


**Fig. 9 Comparison of fixed helix pitch length with changes in aggregation temperature.**

cells were cooled to $T_{\mathrm{Ag}}$(25°C,45°C), and the temperature dependence of the helix pitch length was evaluated (see Fig. 8). The results are shown in Fig. 9.

As shown in Fig. 9, the fixed helix pitch length varies depending on $T_{\mathrm{Ag}}$. It is known that the helix pitch length of a cholesteric liquid crystal varies depending on the temperature. Since the helix pitch is fixed when the aggregation of POSS-Lys is completed, the change in the fixed helix pitch length likely occurred when $T_{\mathrm{Ag}}$ was changed. From Fig. 7, we can see that the helix pitch length extends with increasing in the evaluation temperature. Since the helix pitch is fixed at the $T_{\mathrm{Ag}}$, it is assumed that the longer helix pitch is fixed at the higher $T_{\mathrm{Ag}}$.

From these results, it was shown that changing the aggregation temperature of POSS-Lys causes a change in the fixed helix pitch length. We assumed that this study can bring tuning capabilities to cholesteric liquid crystal lasers that can be driven at low threshold voltages.

## 6. CONCLUSION

In this study, we have proposed a method to control the helix pitch of cholesteric liquid crystals doped with dendrimers. We have shown that the helix pitch length can be fixed by the molecular interaction between dendrimer and cholesteric LC including the chiral dopant. We also show that the helix pitch can be freely selected by varying aggregation temperature of the dendrimers.

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