1. Introduction

Global food crisis with population growth is predicted as one of critical issues in the near future. To overcome this issue, increasing of human-food-production efficiency has been required around the world. Of these, the developments of optically-functionalized films for contribution to photosynthesis promotion are attractive method because expansion of new land for farm is not necessary. Besides, energetic consumption can be reduced compared with cultivation using many light sources or heater equipments.

As the candidates of optical film for photosynthesis promotion, large-area wavelength conversion films composed of organic fluorescence dye is useful for following two reasons. One is that photoluminescence characteristics can be controlled by molecular design of organic fluorescent dye. The wavelength conversion can utilize wasted light to photosynthesis reaction. Another is that attachment to the surface of greenhouse become easy.

Conventionally, K. Kazuki et al. demonstrated that crop yield of basil increased by such wavelength conversion films. However, there are insufficient cases in efficient food production which depends on only wavelength conversion. The leguminous chlorophyl has specific wavelength for photosynthesis reaction and polarization dependence for efficient light absorption, as shown in Fig.1. This property derives from presence of a lot of chlorophyl-a molecules in leguminous leaf and structural isomer by chiral atoms. P. Shibayev et al. reported the growth rate of pea by irradiation of left-handed circularly-polarized light is 1.4-fold faster than that by irradiation of right-handed circularly-polarized light. In addition, chlorophyl-a molecule reflects green-colored light...
light. Therefore, it is necessary to establish a technology for production of large-area wavelength conversion films whose polarized direction can be controlled. Although uniaxially-stretched dye-doped resin has been reported so far, the fluorescent dye is blended into transparent films composed of resin, stretching method is not suitable for low-cost and large-area process. Also, variety of fluorescent materials are limited by concentration quenching effect among dye molecules.

To overcome these issues, we proposed the double-layered coatable optical film which enables both conversion of wavelength and polarized state in this paper. The solution coating process has a potential for manufacturing of low-cost and large-area optical film such as roll-to-roll process. The proposed film is composed of fluorescent-dye doped liquid crystalline (LC) polymer and single-component LC polymer film: detail of the proposed film is explained in the next section. The presence of LC polymer among dichroic dye is expected to suppress the concentration quenching effect.

2. Proposal of Double-Layered Optical Film

2.1. Film Structure

Fig.2 shows schematic of the proposed optical film for photosynthesis promotion. This film is composed of two layers. One is organic fluorescent dye doped LC polymer films, defined as Film A. Another layer is composed of aligned LC polymer, defined as Film B. In this film, dichroic fluorescent dye is expected to align along alignment direction of LC monomer by well-known as guest-host effect between dye and nematic-phase liquid crystal. This alignment structure enables emission of linearly-polarized light along alignment axis due to alignment of optical transition moment (strong light absorption axis). The role of the Film B is that emitted linearly-polarized light from Film A convert to circularly-polarized light. The emitted linearly-polarized and wavelength-converted light from Film A is converted to circularly-polarized light by polymer-based retardation film. This double-layered film can be made by solution process because LC monomer has fluidity.

2.2. Optical principle

When the sunlight (unpolarized light) is irradiated to Film A, there is energy loss caused by surface reflection of 8-10 % within visible light range. This loss is not critical issue for the application of greenhouse farms using large-area vinyl film if the proposed film replaced on their vinyl film. In the incident light to Film A, wavelength of absorbed light is converted to longer wavelength based on fluorescent characteristics of dye molecules. Here, we consider that optical conversion of ultraviolet (UV) and green light only. If suitable fluorescent dye having UV and green light absorption is selected, unpolarized red and blue light is transmitted without optical conversion loss. Therefore, only wasted light for photosynthesis reaction is converted by the proposed film. The light scattering effect in the Film A and Film B will be negligible small because distribution of refractive index become homogeneous due to molecular alignment. The interfacial reflection loss between Film A and B is calculated by following equation (1).

\[ R = \left( \frac{N_1 - N_2}{N_1 + N_2} \right)^2 \]  

where \( N_1 \) and \( N_2 \) are refractive index of Film A and that of Film B, respectively. Assuming \( N_1 \) and \( N_2 \) is 1.64 (liquid crystalline polymer) and 1.59 (polycarbonate), reflectance loss was 0.03 %. The matching between \( N_1 \) and \( N_2 \) This reflectance loss can be suppressed enough by the matching of refractive index. The fluorescent light from parallel aligned dye molecules is isotropically emitted. For this reason, half of fluorescent light returns to the incoming side. In addition, the ideal transmittance of a polarizer is known about 50%. Considering these situations, 20% of wasted green and/or UV light in the sunlight is utilizing for photosynthesis promotion. For efficient utilization of the light, understanding of molecular ordering and fluorescent conversion efficiency in the Film A is

Fig.2 Schematic of proposal of the double-layered optical film for photosynthesis promotion and structure of each films.
important. Therefore, the aim of this paper is clarification of the polarization characteristics of aligned Film A in this paper.

### 3. Experimental

To clarify the principle of optical conversion in the proposed Film A, we used Coumarin 6 molecule (see Fig.3(a)) as a dichroic fluorescent dye. Although this molecule indicates green-colored light emission, its molecular structure is well known as rod-shaped structure and parallel transition moment to molecular long axis. We fabricated mixture films composed of Coumarin 6 and liquid-state LC monomer (UCL-001-AC1, supplied from DIC Corp.), as shown in Fig. 3(b). Prior to fabrication, we confirmed that this LC polymer (after photopolymerization reaction) without dye has parallel-aligned state at air interface. The mixture liquid was coated on glass substrate with photo-alignment film (TO2, Nissan Chemical Corp.) by spin coating method. Then, ultraviolet irradiation (wavelength: 365nm) performed to the coated film in nitrogen-filled environment. Film thickness was 30 µm in order to absorb excitation light enough.

### 4. Results and Discussion

#### 4.1. Concentration effect of fluorescent dye on photoluminescent characteristics

To clarify the concentration quenching in the proposed film, we investigated the optimal concentration of fluorescent dye in the film for efficient photoluminescence. The concentration of Coumarin 6 to monomer was investigated less than 0.9 wt% because dye concentration over 1.0 wt% cannot be solved in LC monomer. In the evaluation of photoluminescence spectra, the wavelength of incident monochromatic light determined 452 nm at maximum excitation wavelength of Coumarin 6. Fig. 4 shows the wavelength-fluorescence characteristics at each dye concentration. For comparison, the photoluminescence spectra of single-component Coumarin 6 film (without monomer) was included in Fig. 4. The maximum fluorescent wavelength of LC polymer/Coumarin 6 films was around 510 nm wavelength. The fluorescence intensity of the films with the LC monomer was drastically improved, compared with Coumarin 6 single-component film. The plotted data of inset shows extracted maximum fluorescent intensity from fluorescent spectra. From dye concentration of 0.1 wt% to that of 0.7 wt%, the fluorescence intensity increases with increasing of concentration. However, fluorescent intensity in dye concentration of 0.9 wt% was decreased significantly. These results indicate that there is the optimal concentration which maximize fluorescence intensity.

The monochromatic light of 450 nm wavelength is extracted by the bandpass optical filter. Fig. 5(b) and (c) shows photograph on the basis of observation system as shown in Fig. 5(a). In the Fig. 5(b), green-colored light emission was observed. This behavior is photoluminescence of Coumarin 6 molecules. The phenomenon indicated that transition moment of Coumarin 6 molecules is aligned along photo-alignment direction. Then, transmittance axis of polarizer was rotated by 90 degree, as shown in Fig. 5(c). In this case, blue-colored light (excitation light) was observed in the most of region. We clarified that molecular long axis of coumarin 6 molecules were aligned along photo-aligned LC polymer. This behavior is similar to guest-host effect. Based on these results, we discuss the suppression of concentration quenching in blend films composed of parallel-aligned Coumarin 6 and LC polymer. Fig. 6 shows schematic illustration of molecular
conformation in the films. The low-concentration Coumarin 6 induced suppression of non-radiative deactivation because intermolecular distance among Coumarin 6 was large, like Fig. 6(a). As the result, energetic transfer among Coumarin 6 molecules was reduced. Alternatively, photoluminescence intensity decreased owing to low abundance ratio of Coumarin dye. In contrast, higher concentration of Coumarin induced non-radiative deactivation by energetic transfer because there is many neighboring Coumarin molecules, as described in Fig. 6(b). Note that simple increasing of film thickness does not increase photoluminescence intensity. The abundance ratio of dye molecules per unit volume is not changed by film thickness. Then, absorbance is saturated by Lambert-Beer's law (see Fig. 7). Furthermore, emitted fluorescent light was reabsorbed by other dye molecules, called as inner filter effect.

Therefore, we found that the optimal concentration of fluorescent dye suppressed concentration quenching in the mixture of fluorescent dye and LC polymer.

4.2. Polarization characteristics

In previous section, we confirmed polarization dependence of the fluorescent dye and LC polymer in addition to wavelength conversion. Here, we evaluated conversion of polarized state in their films.

Fig. 8 shows polarized microscope images of coated films composed of Coumarin 6 and LC polymers. In the condition of 0 degree, bright state derived from light emission of Coumarin 6 was observed, as shown in Fig. 8(a). Rotating a polarizer to 45 degree, illuminance was decreased (Fig. 8(b)). When the polarizer angle is 90 degree, dark state was obtained in Fig. 8(c). In the 135 degree, illuminance increased again. These behaviors
mean similar state of parallel alignment along photolignment direction. Unfortunately, light leakage in the partial region can be seen in Fig. 8(c). This result is attributed to disorder of molecular alignment in dye molecule and LC polymer. Then, we estimated order parameter to the coated Coumarin 6/LC polymer films. In the guest-host interaction model between liquid crystal and dichroic dye, the dichroic ratio $D$ and order parameter $S$ are given by the following equation $^{9,10}$.

$$D = \frac{A_\parallel}{A_\perp}$$  \hspace{1cm} (2)

where $A_\parallel$ and $A_\perp$ are maximum absorbance (polarized direction of incident light is parallel to alignment direction of dye molecules) and minimum absorbance (polarized direction of incident light is perpendicular to alignment direction of dye molecules), respectively.

$$S = \frac{D - 1}{D + 2}$$  \hspace{1cm} (3)

The estimated dichroic ratio $D$ from absorption spectra was 2.11. Calculated order parameter $S$ from this value was 0.27. The typical order parameter of nematic-phase liquid crystal is about 0.4 to 0.7. Compared with this range of order parameter, molecular ordering of fabricated mixture films was poor obviously. There are some possibilities to behind this phenomenon. One is disorder alignment at air interface. The evaluated sample has weak anchoring force from one side. Then, we evaluated the order parameter of mixture films which is sandwiched by two substrates with photoalignment films (cell-type structure). As the results, we obtained order parameter of 0.40. For this reason, presence of air interface is one of causes in poor order parameter. Second is thickness of the sample. In this case, we determined 30-µm thickness. In the thick liquid crystal devices, bulk region without anchoring effect was expanded. As the result, molecular ordering become poor. If thickness become small, molecular design of dichroic dye having large molar absorption coefficient will be important. Other factor is essential issue of liquid crystalline material. The liquid crystalline materials have thermal fluctuation essentially. The temperature control in photopolymerization process might be improvement of molecular ordering. These issues will be next challenges for establishment of the proposed optical films for agriculture application. From these results, we found that emission of linearly-polarized fluorescent is dominated by molecular ordering.

### 4.3. Adoptability to alignment control method of fluorescent dye for photosynthesis reaction

In previous section, we clarified that the operation principle of the proposed film (defined as Film A in the section 2) using fluorescent dye which is revealed direction of transition moment in the molecule. Finally, we show the adaptability of fluorescent dye having absorption characteristics in UV and green light for previous technique.

Fig. 9 shows excitation and photoluminescence spectra of EM-008 (purchased from Yamada Chemical Co.,Ltd) organic fluorescent dye. This fluorescent dye absorbs ultraviolet region around 360 nm wavelength and green-colored region around 550 nm wavelength. These wavelength bands are useless for photosynthesis reaction in leguminous leaf $^6$. For this reason, this fluorescent dye has a potential for agriculture application. To clarify the adaptability of this fluorescent dye to the proposed method, we investigated the angular dependence of a polarizer on coated EM-008/LC polymer films. Fig. 10 shows polarized microscope images of EM-008/LC polymer films. When polarizer angle is 0 degree, bright state was obtained. In contrast, data of 90 degree exhibited dark state. We demonstrated that the alignment control method is adoptable for EM-008. However, light leakage at 90 degree was observed partially. This result was similar behavior with that using Coumarin 6. The evaluated light scattering effect (haze value) of the EM-008/LC polymer mixture film was $2.2 \pm 0.4 \%$. As the reference, haze value of a glass substrate only was $1.3 \pm 0.5 \%$. As mentioned in section 2.2, light scattering effect was very few. The LC polymer and EM-008 dye is aligned in solution-coating films, but molecular fluctuation might be large. In addition, fluorescent conversion efficiency is important factor for emission of linearly-polarized fluorescent is dominated by molecular ordering.
photosynthesis promotion. Then, we evaluated internal and external quantum efficiency of the EM-008/LC polymer mixture films. Fig. 11 shows fluorescent spectra of EM-008/LC polymer films when excitation light of 568 nm wavelength was irradiated. Estimated internal and external quantum efficiency were 31.2 % and 2.45 %, respectively. This efficiency is low due to non-radiative deactivation in solid state. For highly-efficient fluorescence in solid state, molecular design and improvement mechanism have studied11). In order to achieve the improvement of photosynthesis efficiency, both of material development of fluorescent dye and novel solution process leading to highly-ordered molecule will be necessary.

5. Conclusion

In this paper, we have proposed the double-layered optical film for photosynthesis promotion. In this film, we investigated wavelength conversion and polarization characteristics in fluorescent dye-doped liquid crystalline polymer films. We found that there is an optimal dye concentration that maximizes the fluorescence intensity. In addition, we demonstrated that the rod-shaped fluorescent dye is aligned with the liquid crystalline polymer by guest-host interaction and exhibits polarized light emission. Similar effect is obtained in case of using suitable fluorescent dye for photosynthesis promotion. Furthermore, disordered region of dye molecules was also observed in the films. As the next step, we will fabricate a polarization-controllable wavelength conversion film based on the proposed double-layered film including retardation plate for improvement of photosynthetic efficiency.

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