

Photo-patterned e-wave polarizer

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Abstract

In this paper, we report our development in the photo-patterned e-wave polarizer. This polarizer is prepared from amphiphilic dye molecules, which self-assemble and stack up to form the hexagonal complexes of lyotropic liquid crystals (LLC) under certain conditions. As a result, it gives rise to a high order parameter and a cylindrical symmetry. Along the *c*-axis of these complexes most of the e-wave is transmitted, whereas the o-wave, which propagates on the plane orthogonal to this *c*-axis, can be absorbed effectively. However, the methods usually used to manufacture the e-wave polarizer are based on the mechanical shear flow, which causes unpleasant visual defects and has limited resolution. Therefore, we propose and demonstrate two novel fabrication methods to both photo-align and photo-pattern these e-wave polarizers. The first method consists of transferring a well-prepared LLC polarizing film onto the substrate using the photo-curing glue. The second method consists of applying a photo-alignment layer to induce a preferential orientation of the LLCs. The *c*-axis in this case is determined by the polarization vector and the incidence plane of the actinic radiation. Since the local structure is patterned optically, the multi-axes and multi-colour polarizers can be prepared cost-effectively. In addition, this photo-patterned polarizing film, which is about 0.3–0.7 μm , can be coated on the internal or external substrate surfaces of a liquid crystal display (LCD). For the TN-LCD with the internal polarizers, we find that the electro-optic characteristics are basically similar to those with the external polarizers. This is central to the internal polarizer development since the STN-LCD is sensitive to any voltage and thickness variations. © 2001 Published by Elsevier Science B.V.

Keywords: Photo-alignment; Lyotropic liquid crystal; Polarizer

1. Introduction

Light-polarization films or polarizers are the major components of the liquid crystal displays (LCDs) and other liquid crystal (LC) devices. Common polarizers are based on polyvinyl-alcohol (PVA)-iodine films of 30–50 μm thickness. These polarizers are generally laminated on the external glass surfaces of the LCD and consist of a stack of thin films for the scratch protection, anti-glare, anti-reflection, phase and chromatic compensations, anisotropic absorption, etc. The fabrication of this stack structure is complicated and expensive. The external placement of the polarizers results in the additional reflections and parallax effect, which affect the LCD contrast, optical performance and viewing angles [1]. So, thin internal polarizers are very desirable. Yet, this can hardly be achieved on the basis of the conventional polarizing film technology.

The patent of France 2,186,165 suggested that the internal polarizer could be fabricated by dyeing a sheared polymer

film. A polymeric solution was first dispersed on the substrate and then subjected to a linearly mechanical shear deformation using a rubber rod. This gave rise to a preferential direction parallel to the shear direction, and led to an ordering of the long polymeric molecules along this direction when the solvent had evaporated. The final polarization film was obtained by a volume impregnation of the iodine vapour or iodine solution. This method is complicated, unreliable and inefficient for LCD manufacturing processes. One of the disadvantages of this method is the diffusion of the iodine molecules into the bulk of the LC. Consequently, it results in reduced resistivity, increased power consumption and shortened LCD lifetime.

Amphiphilic dye molecules such as sulphonated chromogens can be used in place of the PVA-iodine for the preparation of thin polarizing films. These molecules are usually water-soluble and at a wide range of concentrations, temperatures and pH-values, they self-assemble and stack up to form hexagonal complexes. This is usually referred to as the lyotropic liquid crystalline phase. By mechanical shear stress, an orientation of the lyotropic liquid crystal (LLC) is induced along the shear flow direction. When the solvent has evaporated, the molecular order is maintained in the LLC solid film. As a result, it gives rise to a high order

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parameter and a cylindrical symmetry. Along the c -axis of these complexes most of the e -wave is transmitted, whereas the o -wave, which propagates on the plane orthogonal to this c -axis, can be absorbed effectively. These dye molecules are also stable against UV-radiation and thermal treatment (up to 230°C), and have good colourfastness [2,3]. These properties make them attractive for the replacement of iodine-based external polarizers in the LCD production.

However, there are problems associated with the shear-flow-induced alignment of the LLC. The first is the visual defects, which are in the form of horizontal stripes of several to 10 μm wide. The defects divide the area with different molecular orientations, which are clearly seen in a polarized light as vertical bands. These are due to the non-uniform LLC flow gradients, which are sensitive to the shear speed, LLC viscosity and temperature. The second is the particulate contamination, which is transferred from the substrate to the rollers and back onto another substrate. This is a serious problem since the stringent particle control and frequent cleaning otherwise slow down the throughput and add a new cost.

A shear-flow free method was described in US patent No. 5,739,296, which might help to solve these problems. The isotropic solution of the LLC was dispersed onto a brushed or rubbed surface of the flexible polymer film. At an optimal thermal condition, a highly ordered solid polarizing film of the LLC was formed with a good extinction ratio. The typical thickness of the LLC polarizing film prepared by this method is 0.3–0.7 μm , which is tolerable for the LCD fabrication. The rate of evaporation is a critical factor. The rapid evaporation rate at high temperature results in spoiling of the molecular order, while a slow evaporation rate at low temperature leads to the formation of randomly oriented poly-crystals. In both cases, the optical quality of the polarization film is affected. In addition, the polarization axis cannot be made arbitrary to follow a specific local distribution, for example, to follow the mosaic picture with the characteristic size of tens of microns or less. This limitation is due to the poor spatial resolution of this method.

In this paper, we continue our pioneering development [4] and describe the results and the fabrication methods of the e -wave polarizer. The first method is to transfer a well-prepared LLC polarizing film onto the substrate using the photo-curing glue. The second method is to apply the photo-alignment layer to induce a preferential orientation of the LLC. The c -axis in this case is determined by the polarization vector and the incidence plane of the actinic radiation. Since the local structure is patterned optically, the multi-axes and multi-colour polarizers can be prepared cost-effectively. In addition, the second is a non-contact method, which minimizes the particulate contamination and defect generations. This polarizing film, which is about 0.3–0.7 μm , can be placed on the internal or external substrate surfaces of an LCD. We shall discuss these methods in Section 3 and the optical characteristics of the photo-aligned polarizer in Section 4. The electro-optic characteristics of

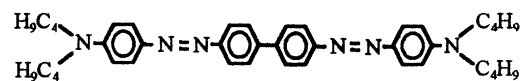


Fig. 1. The chemical structure of the azodye AD-1.

the TN-LCDs with the internal and external polarizers will be compared in Section 4.3. For the TN-LCD with the internal polarizers, we find that the electro-optic characteristics are basically similar to those with the external polarizers. This is central to the internal polarizer development since the STN-LCD is sensitive to any voltage and thickness variations. In other words, we have laid down a stepping stone for the manufacturing of advanced LCD structures.

2. Experiment

The LLC Crystal Ink™ was provided by Optiva, Inc. and the neutral mixture LCP.N was used for the following experiments. The UV-glue Norland 65 was purchased from Norland, Inc. for the photo-transfer method. On the other hand, an azodye AD-1 with the chemical formula shown in Fig. 1 was synthesized for the photo-alignment method. To prepare the photo-alignment layer, a 0.5-wt% solution of AD-1 in chlorobenzene was spin-coated on a glass substrate at room temperature. This solid dye film was then irradiated with polarized UV light using a 1000-W Oriel Xenon arc lamp. The UV sheet polarizer was purchased from Oriel Instruments. The intensity of the polarized UV light at 365 nm was about 6 mW/cm².

The dichroism was measured using a Perkin–Elmer lambda 20 UV–VIS spectrometer, whereas the polarized transmission spectra were obtained using our HKUST cell gap measurement system. For the TN-LCD fabrication, rubbed polyimide PIA3744 from Chisso, Corp. was used as the alignment layer and the nematic liquid crystal mixture MLC6621 from Merck KGaA was doped with 0.5 wt% chiral CB15. The cell gap was about 7.2 μm for the test cells coated with and without an internal polarizing film. Commercial dichroic polarizer samples such as those provided by Nitto Denko were used for the following comparisons. The electro-optic properties were characterized in Autronic-Melchers display measurement system DMS 501.

3. Fabrication methods of e -wave polarizer

3.1. Photo-transfer method

The first method of the polarizer fabrication is outlined in Fig. 2. According to the technology described in US patent No. 5,739,296, a good polarizing film is prepared by shearing the LLC on a polyethylene-terephthalate (PET) film. For

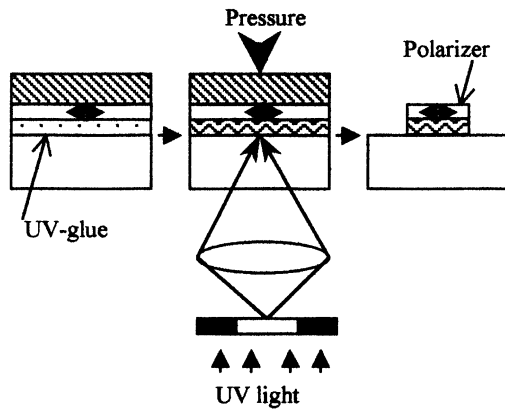


Fig. 2. The photo-transfer method to fabricate the e-wave polarizer.

the photo-pattern transfer, a thin layer of the UV photo-polymerizable glue is first cast on a glass substrate before it is laminated with this polarizing film. This laminated structure is exposed using a photolithographic projection system. Those regions exposed to the UV light will be photo-hardened, whereas those regions not photo-hardened will be removed by an organic solvent. Then, the PET film can be detached from the substrate so that only regions of the polarizing film as a replicate of the mask pattern can be photo-transferred onto the substrate. The same procedure can be repeated with other masks to generate the desired local orientations of the principal absorbing axes. Since the voltage and thickness are likely affected, this method is more appropriate for the external applications. Nevertheless, this is one of the simplest solutions to mount a fine e-wave polarizer for the LCDs.

3.2. Photo-alignment method

The second method of the polarizer fabrication is based on the photo-alignment technology (Fig. 3). This is a non-contact proven technique to align the thermotropic LCs [1], and we find that it is also possible to align the LLCs. In the

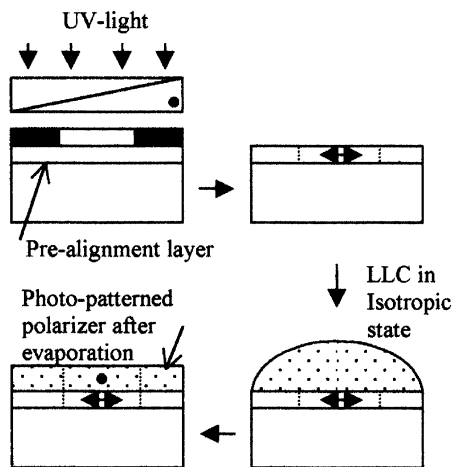


Fig. 3. The photo-alignment method to fabricate the e-wave polarizer.

first fabrication stage, an azodye layer AD-1 of about $0.1 \mu\text{m}$ thickness is spin-coated on a glass substrate. It is then illuminated with a shadow mask using the polarized UV light to form the photo-alignment layer. In the second fabrication stage, few drops of an isotropic LLC solution are dispersed onto the photo-alignment layer. When the solvent has evaporated, the LLC is oriented preferentially along the photo-induced axis, where the absorption axis of the LLC is parallel to that of the photo-alignment layer in this case. Therefore, the light leakage of the LLC at the blue regime can be reduced anisotropically and the polarization efficiency can be enhanced.

In addition, since the azodye is photo-chemically stable, the degree of LLC ordering is stable against further UV and thermal exposure, which is important for the display applications. It is also noted that numerous photolithographic stages can be minimized and the photo-alignment pattern can be generated in a single exposure by using an alignment master [5].

4. Results and discussion

4.1. Photoisomerization of azodye AD-1

Azobenzene derivatives have two geometric isomers: the *trans* and the *cis* forms. The isomerization reaction is a light- or heat-induced transformation between these two isomers. Two mechanisms may occur during the photoisomerization of the azobenzene derivatives: one from the high energy $\pi-\pi^*$ transition, which leads to the rotation around the nitrogen double bond; and the other from the low energy $n-\pi^*$ transition, which induces the isomerization by means of the inversion through one of the nitrogen nuclei. Both mechanisms give rise to the same conformational molecular change, although the physical processes are different. The experimental results of the azobenzene derivatives are in favour of the theory that the conformational molecular change induced by the polarized light is due to the photoisomerization [6–8]. When the azodye molecules are optically pumped by a polarized light beam, the energy absorbed for the transformation is proportional to the square of $\cos \theta$, the angle between the transition dipole moments of the molecules and the direction of the polarized light. In other words, the azodye molecules that have their transition dipole moments parallel to the direction of the polarized light will probably undergo the *trans* to *cis* isomerization. Since the *cis* isomer is not thermally stable and will relax to one of the *trans* forms, a rotation to the conjugated position is energetically favourable. Therefore, the anisotropic dichroism is photo-induced and the associated order parameter, which can be deduced from Fig. 4, is given by

$$S = \frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + 2D_{\perp}} \quad (1)$$

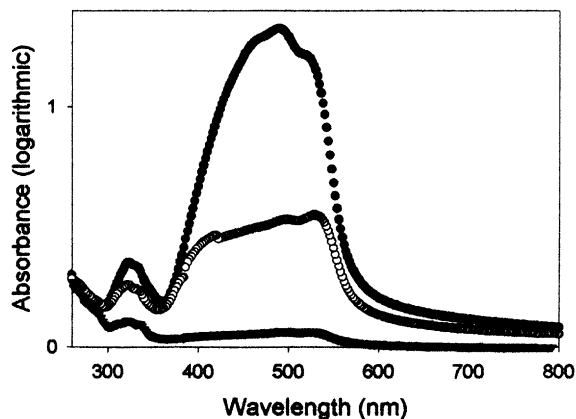


Fig. 4. The spectroscopic absorbance of the azodye AD-1 parallel (solid circle) and perpendicular (solid triangle) to the absorption axis. The initial absorbance is represented by the hollow circle.

where D_{\parallel} and D_{\perp} are the dichroism parallel and perpendicular to the absorption axis, respectively. In the case of AD-1, S is greater than 0.86 since the dichroic ratio at 490 nm is equal to 20.4. Such large anisotropic absorption dichroism is obvious when viewing with a linear polarizer (Fig. 6). In Fig. 5, the difference of transmittance according to Eq. (2) is plotted,

$$\delta T = T_p - T_0 \quad (2)$$

where T_p and T_0 are the transmittance along the direction of the polarized pumping beam and at the initial state, respectively. More than 50% change in transmittance is noticed at both pumping wavelengths in less than 2 J/cm^2 . The probing beam at 632.8 nm falls in the same line with the pumping beam at 488 or 514 nm, and they have the same direction of polarization. A laser line filter differentiates the probing signal from the pumping and the background. The saturation

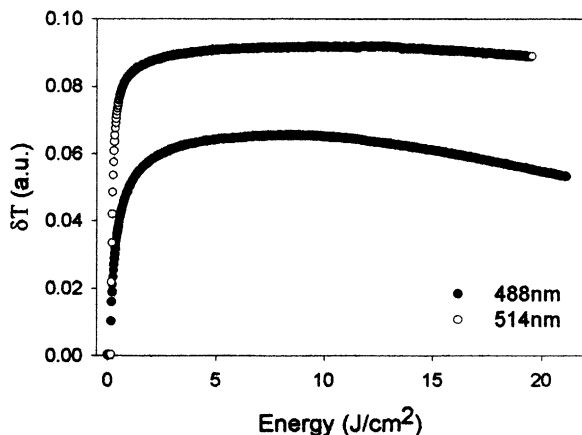


Fig. 5. The transmittance change of the azodye AD-1 induced by a polarized pumping beam at 488 nm (solid circle) and 514 nm (hollow circle). These changes are measured by another linearly polarized probing beam at 632.8 nm and the direction of polarization is parallel to that of the pumping.

at 488 nm begins to fall after about 10 J/cm^2 . This can be attributed to the two competitive processes associated with the conformational molecular changes since the kinetics of photoisomerization depends on the free-volume distribution of the azodye molecules. For the photoisomerization of azobenzenes it has been shown that the free volume required for inversion is smaller than that for rotation.

4.2. Transmission spectrum of photo-aligned polarizer

The photo-induced anisotropy and the absorption dichroism are formed in the alignment layer as a result of the reversible (photochromic) or irreversible (photochemical) reactions. When the molecules absorb either polarized or non-polarized quanta of light, a molecular order is formed on the surface and in the bulk of such a photo-alignment layer. The molecular order depends on the exposure energy, while the direction of the preferred molecular orientation is induced by the polarization vector and the plane of light

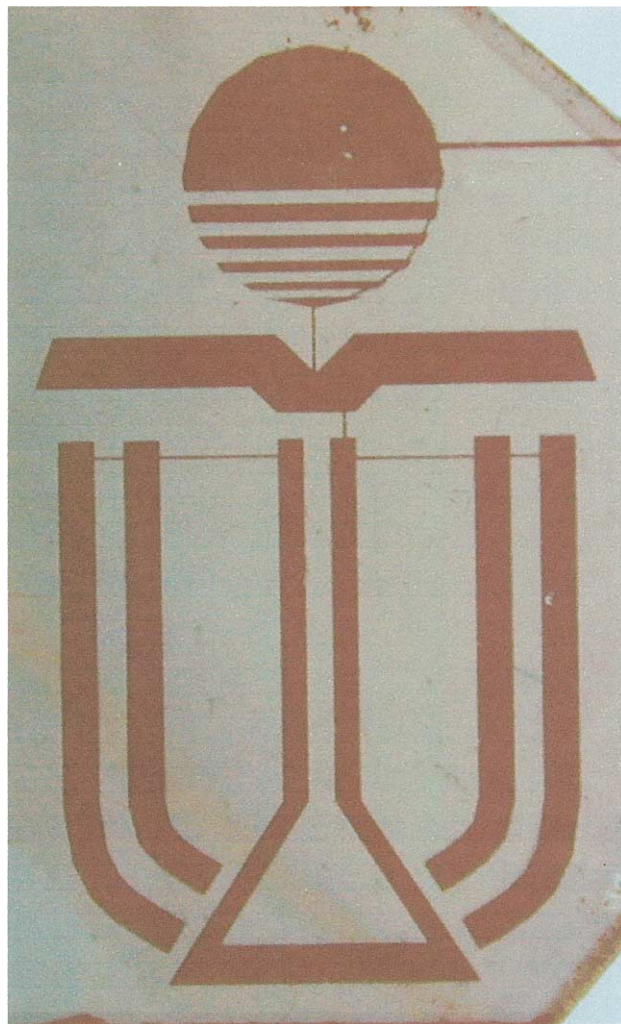


Fig. 6. The photo-induced pattern of HKUST logo viewed with a polarizer, where the polarization axis is perpendicular to the absorption axis of the azodye AD-1. The exposure energy of the polarized UV light is $25 \text{ J/cm}^2 @ 405 \text{ nm}$.

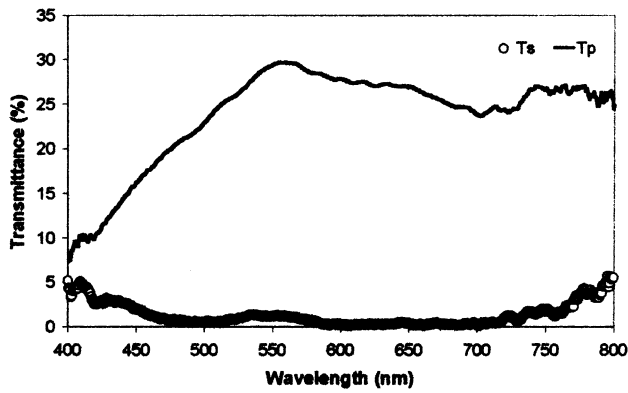


Fig. 7. Polarized transmission spectra of the photo-aligned LLC polarizer. T_p and T_s represent the transmission spectra parallel and perpendicular to the direction of the polarized UV light, respectively.

incidence. Due to the molecular dispersion forces between the photo-aligned azodye and the LLC, a homogeneous orientation of the whole lyotropic layer can occur. We discover that certain organic photochemical stable substances such as AD-1, illuminated by a polarized or non-polarized light, show a much higher degree of induced molecular order than that found in an active photochemical molecular layer. We also find that it is possible to align the LLC, using the obliquely incident non-polarized light. In this case, the molecular order in the photo-alignment layer increases with the exposure energy. The preferred orientation of the lyotropic molecules is parallel to the plane of oblique incidence and depends on the interaction between the lyotropic and dye molecules. Thus the expensive UV polarizers can be eliminated and the whole production process of thin internal polarization films can be considerably simplified.

The polarized transmission spectra of the lyotropic polarizer aligned by AD-1 are shown in Fig. 7. The polarization efficiency is calculated using the following equation.

$$E_p = \frac{T_p - T_s}{T_p + T_s} \quad (3)$$

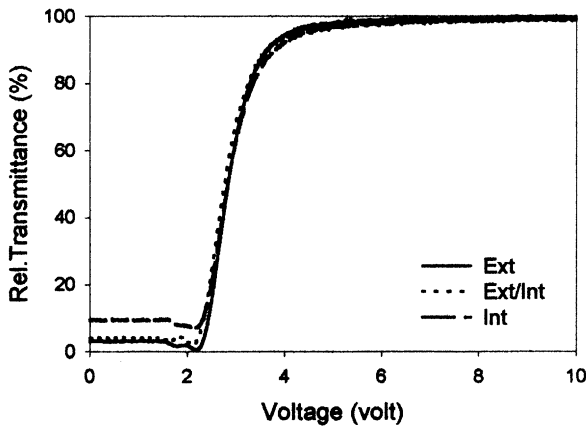


Fig. 8. Transmission-voltage curves of the TN-LCDs with both external (solid), internal and external pair (dot), and both internal (dash) polarizers.

where T_p and T_s are the transmittance parallel and perpendicular to the direction of the polarized pumping light, respectively. At the peak transmission wavelength 559 nm, the polarization efficiency is equal to 92.2% and the transmittance is 29.7%.

4.3. Comparison of TN-LCDs with internal and external polarizers

The electro-optic characteristics of the TN-LCDs (normally black) with internal and external polarizers are compared. In Fig. 8, the transmission-voltage curves of both external (solid), internal–external pair (dot) and both internal (dash) polarizers are measured using a diffused white light source. There is no noticeable voltage shift and the steepness is not affected. The minimum transmissions in the latter cases are higher, though. In Fig. 9, the rise and fall times are measured for these three cases and again the differences are negligible. These imply that the electrical characteristics of the polarizing film do not hammer against the internal polarizer applications which, however, are not the same case as reported in Ref. [9]. Nevertheless, the iso-contrast of the e-wave (internal) and o-wave (external) polarizer pair in our case is about 30 head-on and has a wide plateau of 20. This is our best result so far but the effort to improve it is still going on.

5. Conclusions

We have reported our pioneering development in the fabrication of a photo-patterned e-wave polarizer, which can have different local axis orientations and absorption spectra. The polarizing material is based on the LLC and its homogeneous orientation can be induced by the mechanical shear flow and the photo-alignment material. The former will cause visual defects and particulate contamination problems, whereas the latter is a non-contact method and can be applied directly for the fabrication. We have synthesized an azodye for this non-contact technique and

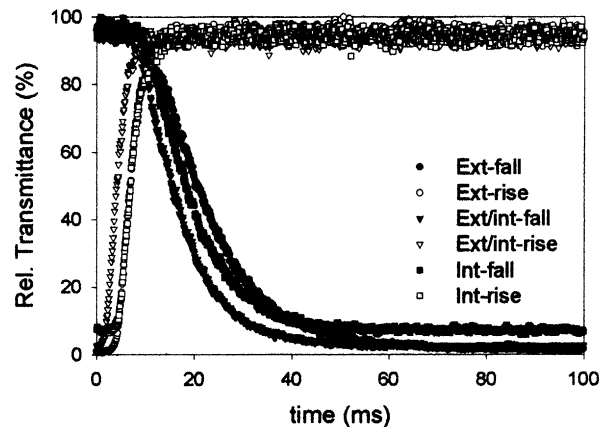


Fig. 9. Temporal responses of the TN-LCDs with both external (circle), internal and external pair (triangle), and both internal (square) polarizers.

this dye exhibits a high photo-induced order parameter after the absorption of a linearly polarized or non-polarized light. We have also cited the fact that to obtain the multi-axes polarizer in a single exposure, the alignment master that has local light-guiding properties can be used. In addition, the electro-optic characteristics of the TN-LCDs with the internal and external polarizers are compared and the results show that the change in voltage and temporal responses are negligible. The stepping stones have been laid down for the STN-LCD and other LCD fabrications.

Acknowledgements

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