論文 / 著書情報
Article / Book Information

題目(和文)	光反応性配向膜の光誘起異方性と重合性液晶の配向挙動に関する研究
Title(English)	Studies on photoinduced anisotropy of photoreactive materials in alignment layer and orientation behavior of polymerizable liquid crystals
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Type(English)	Summary

（博士課程）
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論文要旨
THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In this study, the mechanism of photo-induced alignment of polymerizable liquid crystals (PLCs) based on the axis-selective photoreactions of the photoreactive materials and the orientation behavior of PLCs thin film were investigated.

In Chapter 1, the photoalignment of liquid crystalline materials was described in a historical viewpoint and it was pointed out that the photoalignment method is applicable to aligning polymerizable liquid crystals, regardless of low durability and weak anchoring energy of the photoalignment materials. In addition, the objective of the thesis was also expressed.

In Chapter 2, photo-reactive 2,6-bis(4-azidobenzylidene)-4-methyl-1-cyclohexanone (bisABmC) as a bis-azide was blended with a polymer containing acryloyl groups in the side chain (GH-1203). The GH-1203/bisABmC blend was evaluated as a photo-alignment layer for PLCs, and then it was confirmed that it worked well. In this system, in-plane switching of the orientation direction of PLCs was observed, which depended only on irradiation dose of linearly polarized ultraviolet light (LPUVL). The LPUVL irradiation time dependence of FT-IR spectra indicated that the azide group of bisABmC rapidly reacted with the acryloyl group of GH-1203 and gradual reaction of the bisBC unit in the bisABmC also progressed simultaneously. Moreover, the slow axis of retardation of the photo-alignment layer also switched at the same time as the in-plane switching of the orientation direction of PLCs, which means the PLCs aligned along the slow axis of retardation of the photoalignment layer regardless of the in-plane switching. In comparison to the calculated anisotropic polarizabilities of model molecules, it was suggested that photo-reaction of the bisBC led to lower anisotropic polarizability regardless of the photo-isomerization, the photo-dimerization or the other reactions accompanied by the bond cleavage of C=C. Therefore, the reversion of the slow axis of retardation suggested that both the photo-reaction of azide in the early stage of irradiation and that of bisBC unit in the late stage of irradiation dominated the slow axis of retardation.

In Chapter 3, to improve thermal durability of the photo-induced anisotropy in the photo-alignment layer, the photo-reactive polymers containing bisBC unit in the main chain were synthesized by a simple method and evaluated as a photo-alignment layer for the PLCs and a liquid crystalline polymer. These polymers were able to align the PLCs homogeneously and have thermal durability caused by thermal reaction of azide and acrylate at the polymer tail. In these systems, the photodimerization of the bisBC occurred apparently because the polymers after the LPUVL-irradiation was insoluble to cyclopentanone. In addition, the polymers aligned the PLCs perpendicular to the LPUVL eletric field. The orientation direction of the PLCs was also parallel to the slow axis of retardation of the photo-alignment layer and the direction can be explained by the same mechanism described in Chapter 2.

In Chapter 4, to unite photoalignment layer and protection layer by polymer blending for reducing cost and number of processes in manufacuturing, silsesquioxane containing citraconimide (SQ-CI) as a photoalignment material was synthesized and was blended with poly(methyl methacrylate) (PMMA). A photo-aligning material needs to be enriched to the surface of the blend film for aligning the PLCs. In this study, we did not use low surface free energy component for enhancing the surface enrichment because the resultant low surface free energy tends to cause a failure of recoating of PLCs on the film. Thus, we investigated a polymer blend of PMMA and SQ-CI which have similar surface free energy. The blend film of PMMA/SQ-CI prepared from cyclopentanone solution was not able to align the PLCs. However, the blend film prepared from γ-butyrolactone solution enabled to align the PLCs. The SQ-CI was enriched to the surface of the blend film prepared only from γ-butyrolactone solution, although the

SQ-CI has higher surface free energy than PMMA. As a result of evaluation for solubility of PMMA into the solvents and solvent-vapor annealing effect on this system, it was suggested that the difference of affinity between polymer and solvent presumably played important role for surface enrichment of SQ-CI in the blend. This method is simple and useful for surface-segregating any components which do not necessarily show lower surface free energy.

In Chapter 5, a distinctive dewetting phenomenon of the PLCs thin film on the photoalignment layer was found. The thin film of PLCs on the photo-alignment layer anisotropically dewetted at certain film thickness with the shape of elongated ellipse. The edge of long axis of dewetting pattern formed a rim. The rim formation has been also commonly observed in isotropic dewetting of polystyrene and dimethylsiloxane. However, the short axis of dewetting pattern formed comb-like structure. From the polarized UV-vis spectroscopy to determine the orientation direction of PLCs, the PLCs flowed only to the direction of molecular short axis. In the systems of 5CB and 8CB as simple models of nematic and smectic A phase at room temperature, the anisotropic dewetting occurred only in smectic A phase. Based on the dewetting behaviors of 5CB and 8CB, it is considered that the dewetting mechanism of PLC was able to be explained that the flow to the direction perpendicular to the layer spacing in smectic pahse was confined by large restoring force derived from the change of the smectic layer spacing. The spontaneous self-assembly attributed to thin film instability is interesting in fundamental and industrial aspects. Further researches will open the way for controlled anisotropic dewetting available as a bottom-up method for creating fine structures.