論文 / 著書情報
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題目(和文)	表面状態と高分子構造に着眼した動的光重合の分子配向メカニズム
Title(English)	Molecular alignment mechanism of scanning wave photopolymerization in terms of surface conditions and polymer structures
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The purpose of this study is to investigate the molecular alignment mechanism of the recently developed scanning wave photopolymerization (SWaP) method, which aligns molecules by molecular diffusion caused by photopolymerization. The author revealed that SWaP could generate molecular alignment regardless of surface anchoring layers. The author also explored the effect of molecular structure on SWaP, and discovered that side chain mesogen alignment direction depended on the side chain spacer length. Moreover, the detailed structural analysis of the fabricated films revealed that SWaP could also align polymer main chains and self-organized nanostructures.

In **Chapter 2**, the effect of surface conditions of substrates on the results of SWaP was investigated by comparing the bare glass cell, glass cell with an unrubbed polyimide layer and the cell covered with an alignment layer made of a rubbed polyimide layer. It was revealed that the key for SWaP is the initial alignment state of monomers prior to photopolymerization. Randomly oriented monomers could be aligned by photopolymerization with the scanning light. Of particular interest is that SWaP for isotropic monomers resulted in molecular alignment along the light scanning direction regardless of the surface anchoring from substrates covered with an alignment layer that is vital to conventional alignment methods.

In **Chapter 3**, the author explored the effect of the side chain spacer length on SWaP. Monomers with various alkyl spacer lengths were photopolymerized by SWaP, and resultant alignment was evaluated by polarized UV-vis spectroscopy. As a result, alignment direction of mesogenic moieties depended on the spacer length. The monomers with longer spacers in the side chain resulted in mesogen alignment parallel to the light scanning direction. On the other hand, a rigid monomer with the shortest spacer with no alkyl chain resulted in orthogonal alignment to the other monomers.

In **Chapter 4**, the author further investigated the effect of the side chain spacer length in detail in terms of polymer structure. Characterizations by polarized IR spectroscopy firstly revealed that the polymer main chains were aligned along the light scanning direction by SWaP for both the rigid monomer with the shortest side chain spacer and the monomers with flexible side chains. Based on the results, the author hypothesized that the shear stress due to molecular diffusion during photopolymerization aligns main chains, and as a result, the side chain mesogens are aligned according to both the main chain orientation and shear stress from diffusion depending on the flexibility of side chains. Moreover, the grazing incidence small angle X-ray scattering (GI-SAXS) analysis revealed that anisotropic nanostructure composed of smectic layers were also aligned by SWaP, showing that the SWaP could also regulate the orientation of self-organized nanostructure.

In this study, the author investigated the molecular alignment mechanism of SWaP to ensure and extend the versatility of this method. It is significant that SWaP could align molecules regardless of surface anchoring, which allows aligning anisotropic materials over various substrates with any surface boundary conditions. The investigation on the effect of the side chain spacer length revealed the role of the flexibility of side chains in SWaP process, which would help one to design a chemical system for fabricating a new functional film. The ability to align main chains and nanostructures would offer a simple powerful pathway to achieve high resolution two-dimensional main chain alignment and sophisticated orientation of self-organized structure that would provide new optical, mechanical and energy converting materials that have not ever seen. The author anticipates that further investigation of the SWaP in terms of both fundamental mechanism and development of materials and devices would achieve a breakthrough in materials science.