# 論文 / 著書情報
# Article / Book Information

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Precise control of molecular alignment is crucial for fabricating functional materials with great potentials applicable in soft robotics, photonics, and electronics. Among various alignment techniques, the photoalignment process has attracted significant attention due to its ability to precisely control molecular alignment through a non-contact process. Recently, a novel alignment method, termed scanning wave photopolymerization (SWaP), has been proposed, which utilizes flow fields induced by a polymer concentration gradient under spatiotemporal polymerization. Although various functional materials have been developed, the alignment and polymerization behavior under the photo-induced molecularly flow remains unclear. The influence of external flow fields on synthesized polymers has been extensively studied, including intriguing phenomena such as polymer scission and the emergence of specific functionalities. In contrast, SWaP induces the flow field by the polymerizing molecules themselves. Such a unique environment could cause entirely specific polymerization behaviors. In this thesis, the author investigated molecular alignment mechanism and polymerization behaviors under photo-induced molecular flow. Furthermore, SWaP was applied to various polymerization systems, including controlled polymerization and the synthesis of polythiophene, to fabricate optical materials.

In **Chapter 2**, the molecular alignment mechanism driven by photo-induced flow fields generated through SWaP was investigated in terms of polymer concentration and the LC phase SWaP experiments conducted under varying exposure energies. The change of exposure energy altered the temporal polymer concentration during polymerization, revealing that a certain threshold of polymer concentration is necessary for the induction and stabilization of molecular alignment. Based on the analysis of (1) the phase diagram to elucidate the relationship between polymer concentration and LC phase, and (2) real-time POM observations during SWaP, the author has found that the emergence of the LC phase with increasing polymer concentration plays a crucial role in inducing molecular alignment.

In **Chapter 3**, the polymer growth behavior under photo-induced flow fields was investigated. The polymerization efficiency was enhanced by 90%, yielding a high-molecular-weight polymer when utilizing SWaP, compared to the results achieved through spatially uniform polymerization. The polymer concentration gradient formed during spatiotemporal photopolymerization, which promotes molecular diffusion of the growing polymers. Consequently, polymerization proceeds in dark regions with very low radical concentrations, significantly reducing termination reactions and enabling the efficient production of high-molecular-weight polymers.

In **Chapter 4**, RAFT polymerization was explored using SWaP, and fine molecular alignment induced by reversible bond cleavage of RAFT was investigated. Spatiotemporal RAFT photopolymerization simultaneously controlled molecular alignment and molecular weight distribution in low-energy photoirradiation. Moreover, by incorporating RAFT agent in crosslinked points of the molecularly aligned polymer films via SWaP, a precise molecular alignment pattern was achieved through a light-induced chain reshuffling reaction. The films functioned as phase-modulated holograms.

In **Chapter 5**, the scope of SWaP was extended to encompass non-LC polymers. Various commodity polymers were synthesized via SWaP, yielding high-molecular-weight polymers with up to 23 times greater molecular weight with high efficiency. Moreover, polythiophene, a material with exceptional electrical and optical properties that has attracted considerable interest for practical applications, was synthesized via patterned light, facilitating the fabrication of an aligned polythiophene film.

The author believe that SWaP will bring a revolutionary transformation to polymer synthesis and the development of functional materials.