Molecular Alignment and Nanostructure Formation of Liquid-Crystalline Block Copolymers during Spatially Selective Photopolymerization

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Block copolymers, composed of covalently bonded multiple polymer chains, spontaneously form periodic nanostructures by microphase separation. These nanostructures have attracted great attention owing to their potential applications, including microfabrication templates, ionic conductive films, and highly selective filter membranes, leveraging their regularity and anisotropy.[1] To enhance the functionality of these materials, controlling the alignment of nanostructures is crucial, as they typically exhibit random alignment. Alignment control is conventionally conducted after polymerization, but the low mobility of polymers poses a challenge.[1,2] Recently, we found that spatially selective photopolymerization induces the alignment of molecules and polymer chains during polymerization.[3] We hypothesize that this system enables the precise alignment control of nanostructures in a highly fluidic state. In this study, we synthesized block copolymers by spatially selective photopolymerization and investigated their molecular alignment and microphase separation behaviors.

A photopolymerizable sample was prepared by mixing an anisotropic monomer, a photoinitiator, and a macromolecular chain transfer agent. The mixture was injected into a glass cell and irradiated with a scanned ultraviolet slit light or uniform light throughout the cell (Figure 1). Size exclusion chromatography revealed that both photopolymerization processes produced polymers with narrow molecular weight distributions. Polarized optical microscopy of the film obtained by spatially selective photopolymerization showed uniaxial molecular alignment parallel to the light scanning direction. The formation of periodic nanostructures was confirmed by atomic force microscopy. In contrast, the film obtained by uniform photopolymerization showed random molecular alignment and no clear periodic nanostructure. These results suggest that spatially selective light irradiation plays an indispensable role in the spontaneous formation of microphase-separated structures during photopolymerization.

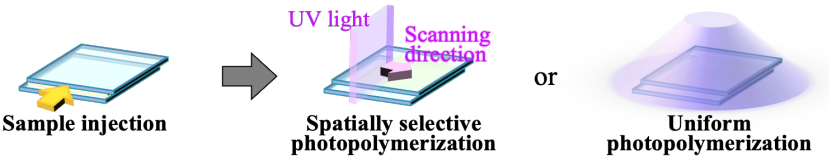

Figure 1. Schematic illustration of the photopolymerization process.

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