Fabrication of molecularly aligned polymer films by wavelength-selective photopolymerization using acrylate–oxetane crosslinkers and application to thermal actuators

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Crosslinked liquid-crystalline polymers, showing the various stimuli-responsive deformation behavior ruled by the molecular alignment changes, have a great potential for application in soft actuators.[1,2] Precise control of molecular alignment patterns is crucial. Recently, we proposed a novel molecular alignment method using spatiotemporal light exposure, termed scanning wave photopolymerization (SWaP).[3,4] In SWaP, the localized photopolymerization induces molecular diffusion, resulting in molecular alignment along the diffusion direction. However, a remaining challenge is the independent control of molecular alignment and crosslinking density, which are important in determining deformation behavior and high mechanical functions, respectively. Here, we demonstrate SWaP with a heterobifunctional crosslinker containing two different polymerizable functional groups to separate the steps of inducing the molecular alignment and crosslinking polymer networks.

We prepared a sample mixture consisting of an anisotropic monomer, a heterobifunctional crosslinker, and two photoinitiators with different absorption bands. The mixture was filled in a glass cell and irradiated with a scanned patterned blue light to induce molecular alignment (**Figure 1a**), followed by UV light exposure throughout the cell to crosslink the polymer network. The obtained polymer film was observed by polarized optical microscopy (POM), finding that the film has an array of radial molecular alignments (**Figure 1b**). Next, we evaluated the thermal response of the film by POM and confocal laser microscopy. Heating the film above the phase transition temperature resulted in the random molecular alignment, which is repeatedly restored to the initial molecular alignment by cooling. Coincident with the alignment changes, the film shape changed between flat and relief structure, acting as a thermal responsive actuator.

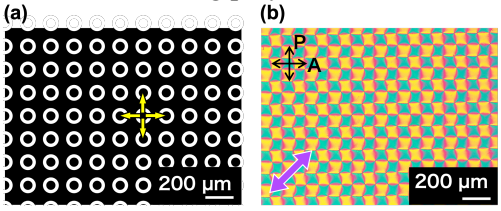

Figure 1. Representative example of molecular alignment induced by SWaP. (a) Irradiation pattern with tetragonally aligned toroids expanding along the yellow arrows. White and black colors indicate the irradiated and unirradiated areas. (b) POM images of the obtained film with a tint plate. Black crossed arrows and a purple arrow show the direction of polarizers and an optical axis of a tint plate with a retardation of 530 nm, respectively.

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