Visible-Light-Driven Actuation in Tetra-*ortho*-Fluorinated Azobenzene-Based Liquid-Crystalline Polymer Films

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Photomechanically active polymers are promising materials for soft robotics and responsive systems, particularly when actuated under biologically benign visible light. Here, we report the synthesis, fabrication, and detailed characterization of polymer films polymerized from liquid-crystalline tetra-*ortho*-fluorinated azobenzene mesogens exhibiting reversible (*E*/*Z*)-photoisomerization under irradiation with visible light (415 nm and 530 nm).

The monomer, comprising a rigid tetra-*ortho*-fluorinated azobenzene core, flexible alkyl spacers, and polymerizable acrylate groups, was synthesized in reproducible and scalable yields. Differential scanning calorimetry (DSC) revealed a melting transition at 118 °C and a clearing point at 152 °C. In combination with polarized optical microscopy (POM), these results indicate liquid-crystalline behavior consistent with the formation of a nematic phase. Thermogravimetric analysis (TGA) indicated thermal stability up to 310 °C. UV–vis spectroscopy demonstrated reversible bidirectional photoswitching, with a thermal half-life of the (*Z*)-isomer of 44 d at 25 °C.

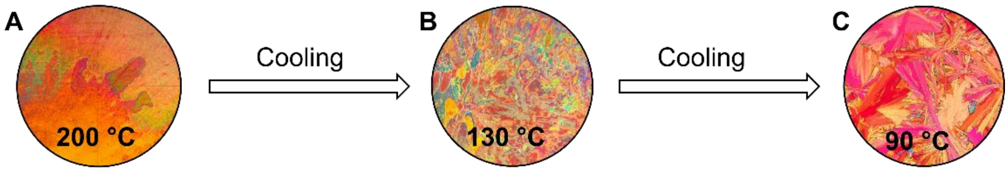

Figure 1. *POM images of the tetra-ortho-fluorinated azobenzene monomer during cooling from 200 °C to 90 °C, showing the isotropic phase (A), the nematic liquid-crystalline phase (B), and the crystalline phase (C).*

Liquid-crystalline polymer (LCP) films were prepared via blue-light-induced photopolymerization at 415 nm, yielding splay, homogeneous, and homeotropic mesogen alignments. A fully documented and reproducible fabrication protocol was established. The resulting crosslinked films exhibited enhanced thermal stability compared to the monomer and a glass transition at 62 °C. Optical and surface characterization by polarized optical microscopy, UV–vis spectroscopy, white-light interferometry, and contact angle measurements confirmed alignment quality and film morphology. Light-induced bending experiments revealed pronounced and reversible macroscopic actuation, strongly dependent on mesogen alignment and film thickness. Splay-aligned films (25 µm) exhibited bending angles of approximately 30° under 530 nm irradiation, whereas thicker homogeneous films showed reduced deformation.

This study establishes a robust fabrication and characterization strategy for visible-light-responsive azobenzene-based LCP films and highlights their potential for applications in soft robotics, bioengineering, and adaptive material systems.

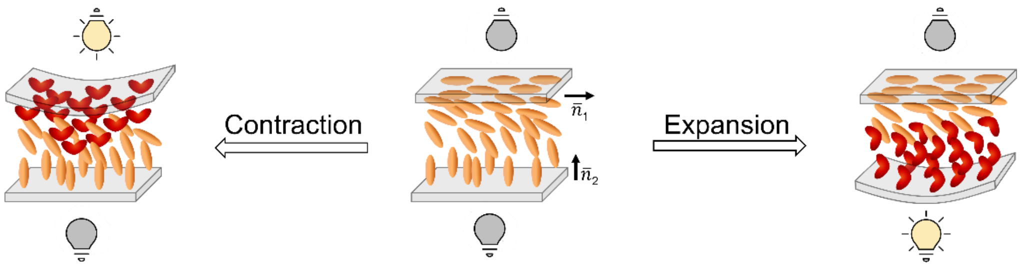

Figure 2. *Schematic representation of light-induced bending in a splay-aligned liquid-crystalline polymer film. The asymmetric mesogen orientation across the film thickness gives rise to differential photoinduced strain and resulting macroscopic deformation upon irradiation.*