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Cite this: DOI: 10.1039/d0sm02135k

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2. B e i e a l

The LC elastomeric (LCE) monomers used in this study are synthesized following established protocols reported previously.⁶³ Other constituents of the LCE mixture, i.e., the photoinitiator and crosslinker are purchased from Sigma Aldrich and used without further purification (Fig. 1). The chemicals are first dissolved in dichloromethane and then vacuum dried to produce a homogeneous mixture, which are then infiltrated in liquid phase between a glass slide and a cover slip at 85 °C. The inner surfaces of confining glass substrates are spin-coated with PI2555 (HD MicroSystem) or SE5661 (Nissan Chemical) to produce planar (rubbed unidirectionally) or homeotropic (perpendicular) surface anchoring boundary conditions to define the far-field LC molecular orientation θ_0 . The gap between the glass slide and the coverslip is defined by thin films of 20–50 nm thick. Shielded from direct exposure to ambient light, the sample is cooled down to room temperature (25 °C) at a rate of 0.5 °C min⁻¹; we then let it stay overnight to produce a well-aligned LCE mixture in nematic phase over large area. By mixing the two types of monomers, we obtain the mixture in nematic phase at a temperature much lower than that when they are used alone.⁶³ This enlarged thermal range of nematic stability makes such mixtures more suitable for the use in two-photon photopolymerization based fabrication of colloidal particles.

The elastomeric colloidal rings and microstructures are fabricated within the obtained nematic mixture using a home-made 3D microfabrication system²⁵ based on two-photon photopolymerization (Fig. 2a). A femtosecond laser (Chameleon Ultra, from Coherent) operating at 780 nm polymerizes the mixture at the focal point of an objective lens (Olympus UPLFLN 40×

contrast, rings printed in a homeotropic cell where the mesogen's director alignment is perpendicular to the glass substrates simply expand radially (Fig. 5). The rings become larger, but their circular cross-section and aspect ratio defined in this geometry remained the same after heating. Although the thermal response of the two kinds of rings appear differently,

Acknowledgements

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