Chemistry–A European Journal

Supporting Information

The Interplay between Different Stimuli in a 4D Printed Photo-, Thermal-, and Water-Responsive Liquid Crystal Elastomer Actuator

Alessio Cremonini, Jeroen A. H. P. Sol, Albert P. H. J. Schenning, Stefano Masiero, and Michael G. Debije*

Video S1. Actuation of LC elastomer on PI substrate in air exposed to UV light from the left.

Video S2. Actuation of LC elastomer on PI substrate in 30 °C water exposed to UV light from the left.

Video S3. Actuation of LC elastomer on PI substrate in 40 °C water exposed to UV light from the left.

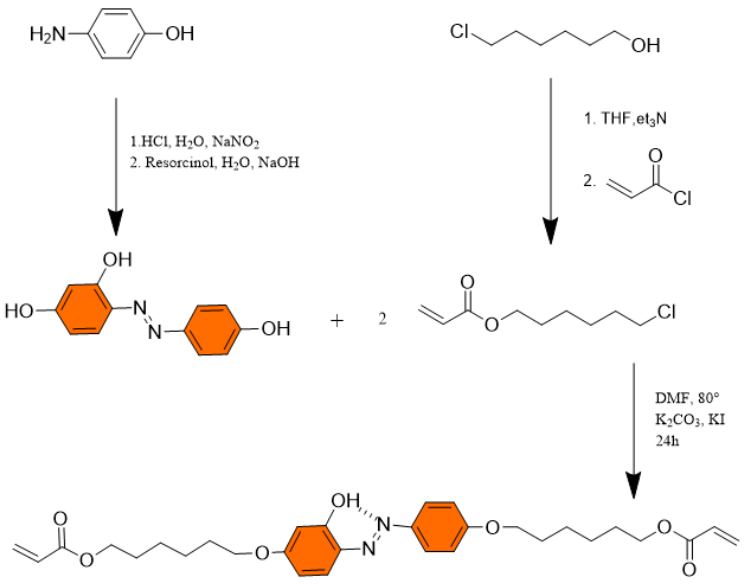

Figure S1. Synthesis scheme of (E)-6-(4-((4-((6-(acryloyloxy) hexyl)oxy)-2 hydroxyphenyl)diazenyl)phenoxy)hexyl acrylate.

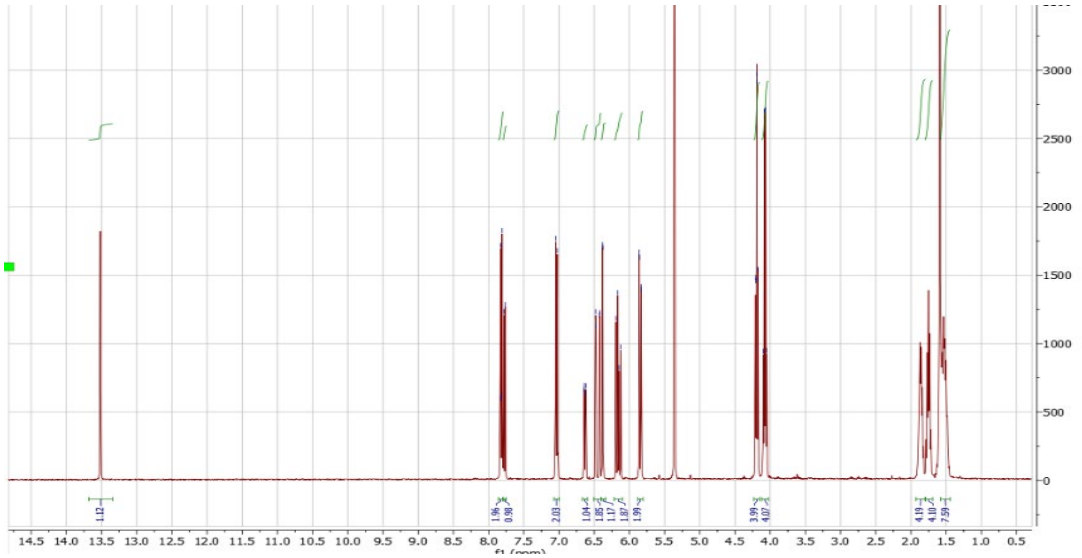

Figure S2. (E)-6-(4-((4-((6-(acryloyloxy) hexyl)oxy)-2-hydroxyphenyl)diazenyl)phenoxy)hexyl acrylate H1 NMR spectrum. 1H NMR (400 MHz, CD_2Cl_2): δ (p.p.m.) = 13.51 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 1H), 7,06 (d, *J* = 8.8 Hz, 2H), 6.58 (dd, *J* = 8.8 Hz, *J* = 2.6 Hz, 1H), 6.40 (m, 3H), 6.12 (dd, *J* = 17.3 Hz, *J* = 10.4 Hz, 2H), 5.82 (dd, *J* = 10.4 Hz, *J* = 1.5 Hz, 2H), 4.18 (m, 4H), 4.02 (m, 4H), 1.83 (m, 4H), 1.72 (m, 4H), 1.50 (m, 8H).

Figure S3. (Top) Oligomer H1 NMR spectrum; (bottom) the same spectrum focusing on a narrower range. The signals around 8.15 ppm correspond to the aromatic protons of **1**. The signals around 7.68 ppm correspond to the aromatic protons of **2**. The integral around 6.29 ppm is set as 2.0 (proton terminated acrylic groups). The repeat unit and number average molecular weight:

n (**1**) = 25.95 /4 = 6.49

n (**2**) = 2.83 /3 = 0.94

The average chain's length is 6.49+0.94 = 7.43 di-acrylates units. Average molecular weight Mn = Mn (1) + Mn (2) – Mn (DODT) = 855.07 x 7.59+ 704.94 x 0.81– 182.30 = 6878.7 g/mol.

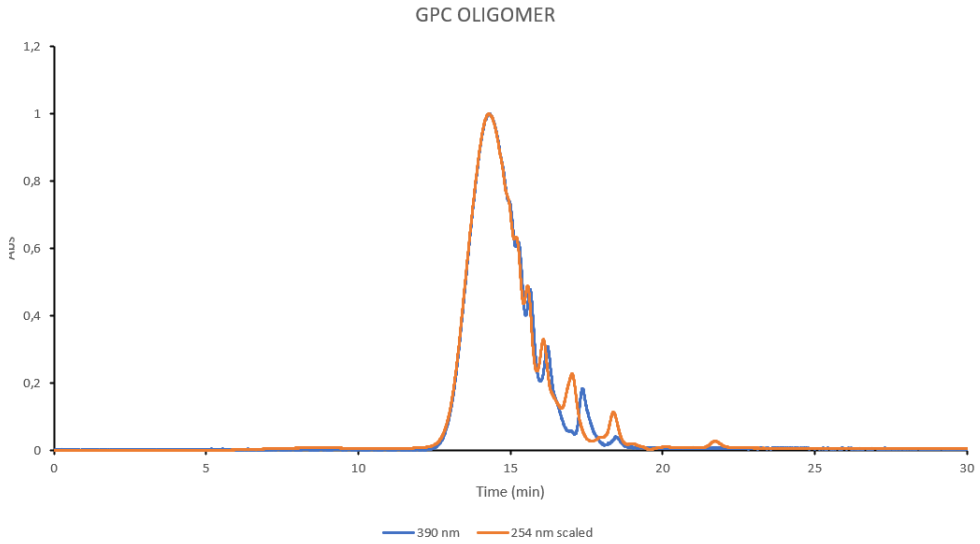

Figure S4. Oligomer gel permeation chromatography (GPC) plot of the oligomer synthesized using DMP as catalyst. The eluent was tetrahydrofuran.

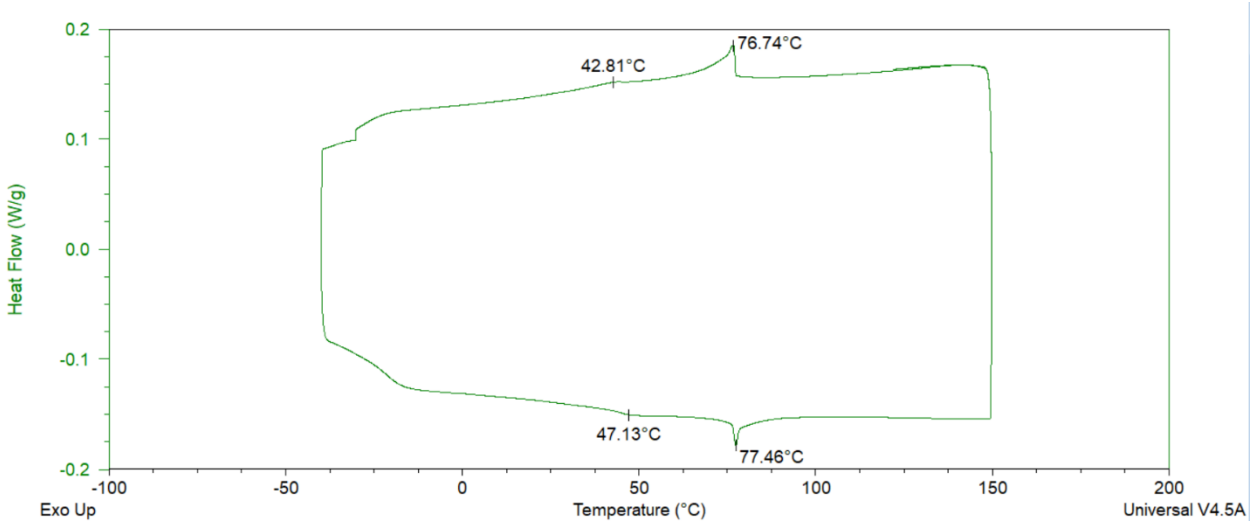

Figure S5. DSC traces from the ink used for DIW. Exotherm. Scan speed: 5 °C/min. Estimated smectic to nematic transition = 42 °C, nematic to isotropic transition = 77 °C.

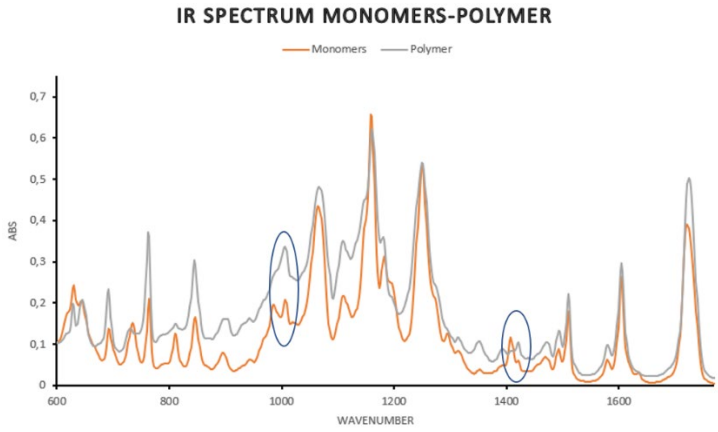

Figure S6. FT-IR spectroscopy of monomers (orange line) and polymer (grey line) N.B. 985, 1410 cm^{-1}, change in acrylate bending and stretching peaks).

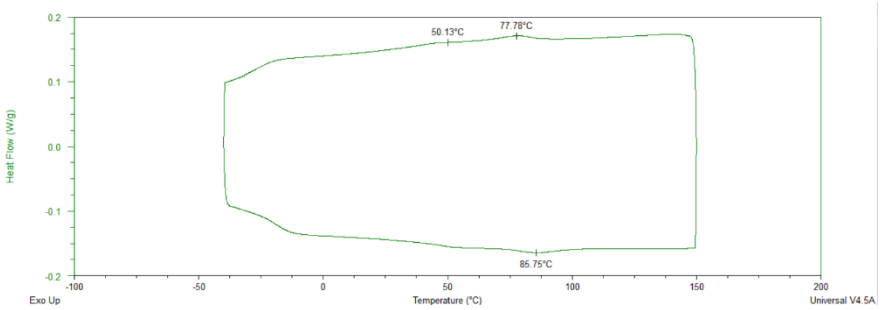

Figure S7. DSC traces from the LCE obtained from DIW. Exotherm. Scan speed: 5 °C/min. Estimated smectic to nematic transition = 50 °C, nematic to isotropic transition = 78 °C.

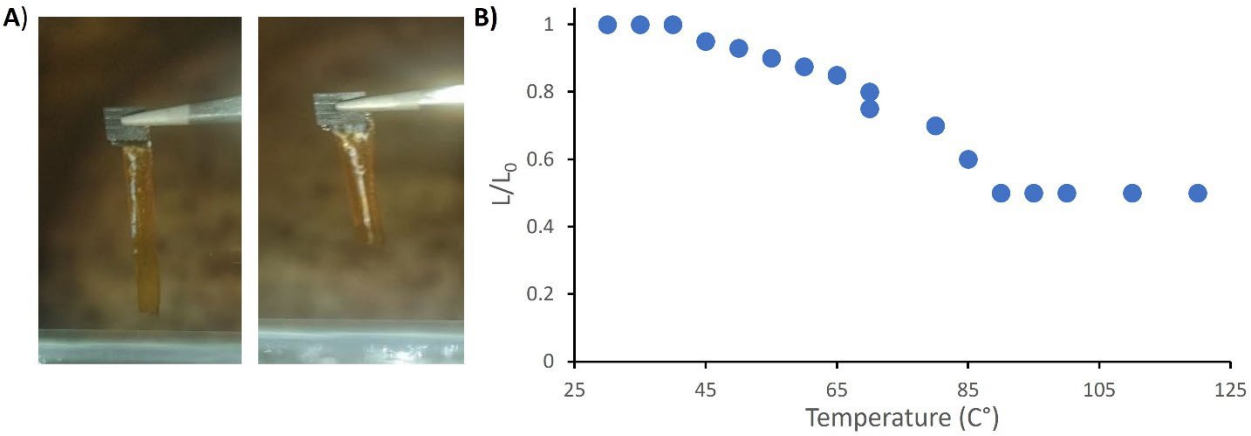

Figure S8. Photographs of the A) freestanding film at (left) 30 °C and (right) 100 °C, showing the contraction of the film along its long axis and expansion along its width. B) Longitudinal shrinkage ratio (L/L_0) of the freestanding film as a function of temperature. L represents the length of the film at a given temperature and L_0 the length at 30 °C. Below 45 °C (the smectic to nematic transition temperature) a minimal contraction was detected, followed by a significant decrease in length until the isotropic phase was reached at about 85 degrees.

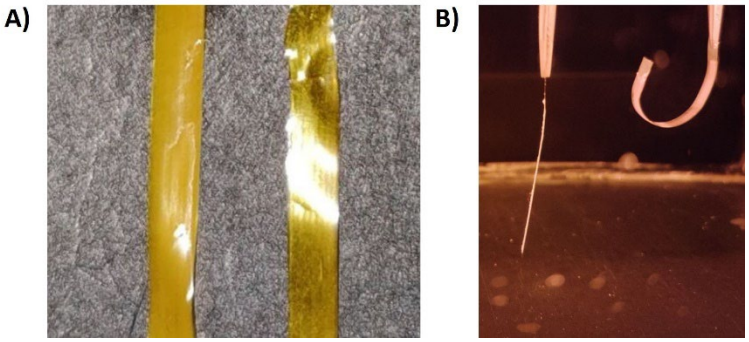

Figure S9. A) Photograph of freestanding films containing (left) (4,4'-bis(6-acryloyloxyhexyloxy)azobenzene) and (right) **2** after removal from water immersion. B) Photograph of substrate-bound films of (left) (4,4'-bis(6-acryloyloxyhexyloxy)azobenzene) and (right) **2** upon submersion in water at RT.

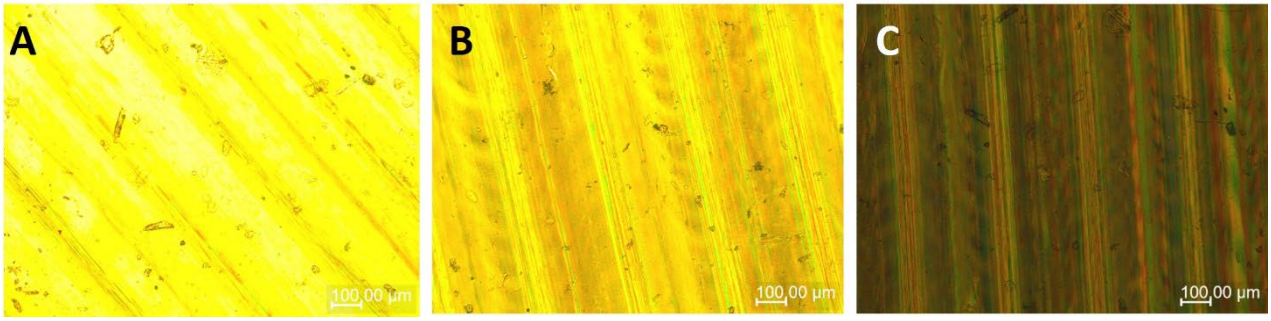

Figure S10. POM images of the polymer rotated A) at 45° B) at 30° and C) parallel to the polarizer.