Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

Two-dimensional pH-responsive printable smectic hydrogels

Ivelina Shishmanova, [a] Cees W.M. Bastiaansen, [a, b] Albertus P.H.J. Schenning [a] and Dirk J. Broer [a*]

[a] Dept. Functional Organic Material and Devices, Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands. Fax: +31 (0) 40 243 6999; Tel: + 31 (0) 40 247 5875; E-mail: d.broer@tue.nl.

[b] School of Engineering and Materials Science, Queen Mary, University of London, Mile End Road, London E1 4NS, UK. Fax: +44 (0)20 7882 3390; Tel: + 44 (0) 20 78828865

Experimental section

Materials and hydrogel preparations:

Monomer **1** and **2** were custom made by Synthon, Germany. The experiments employed blend of monomer **1** and **2** in 90/10 w/w ratio. In order to make the mixtures accessible for photopolymerization, 2wt % 1-hydroxycyclohexylphenylketone (Irgacure 184, Ciba Specialty Chemicals) was added as photoinitiator and for stabilization 100ppm of p-methoxyphenol was used. Mixtures were made by dissolving the compounds together in dichloro methane, which was subsequently evaporated.

Films with a thickness that varied between 5 and 20µm were made by processing the mixtures in the melt by capillary suction between two accurately spaced glass plates, either non-coated, coated with 3-methacryloxypropyltrimethoxysilane or spincoated with AL1021 polyimide (JSR Corporation, Tokyo, Japan) and rubbed with a velvet cloth. The photopolymerization in the Smectic A state of the monomers was performed at 104 °C by exposure with a mercury lamp (OmniCure S1000) that emitted at 365nm at the intensity of approximately 5mW/cm2 at the sample surface. The samples were illuminated for 5 min, followed by an additional heat treatment at 120 ^{o}C, but well below the temperature at which the hydrogen bridges break (around 170 ^{o}C), to ensure maximum conversion of the acrylate groups.

The monomeric mix was printed from a mixture of monomer **1** with 10wt% **2** dissolved in DMF to a solid content of 50 wt% using a commercial Fuji Dimatix printer. The nozzle was heated to 50° C and the substrate was kept at room temperature. After printing and evaporating of the solvent the pattern was UV cured under nitrogen flow in the smectic phase of the liquid crystals.

For the mask photolithography thin films of monomer are formed by capillary filling of cells of which the glass plates are coated with 3-methacryloxypropyltrimethoxysilane or rubbed polyimide. Polymerization takes place by exposure through a hole mask. After polymerization the unexposed areas were removed by washing with dichloromethane.

Sample characterization:

DSC measurements were performed on Q1000 from TA instruments. The thickness measurements were done on a Fogale 3D zoomsurf Interferometer.

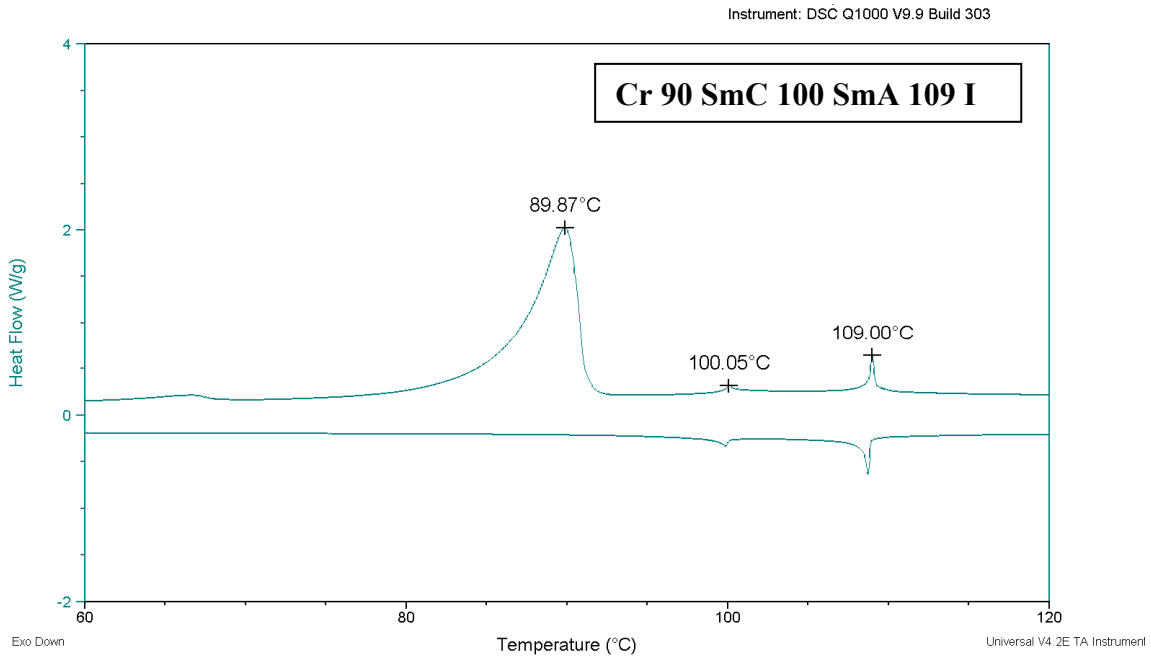

Figure S1. DSC of the mixture monomer **1** with 10 wt % monomer **2**; scan rate 5°C/min, second heating cycle

Inkjet printed structures:

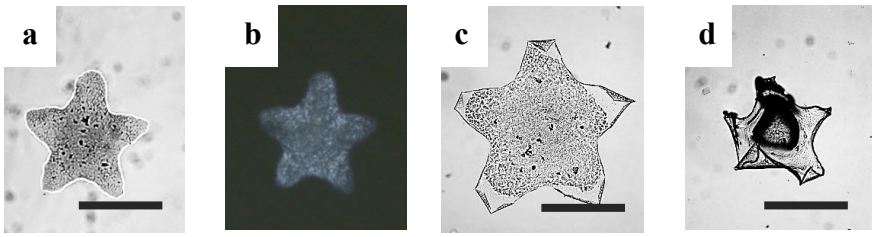

Figure S2. Polarizing optical microscope image of a homeotropic oriented inkjet printed star pattern before (a, b), after swelling (c) in a high pH solution and deswelling (d) in low pH solution (scale bar - 500µm)

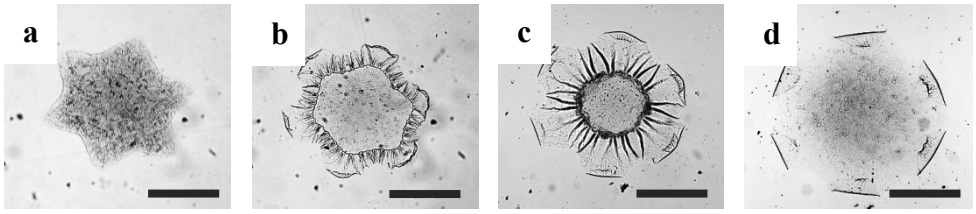

Figure S3. Polarizing optical microscope image of a homeotropic oriented inkjet printed star pattern before (a), in the intermediate state (b, c) and after swelling (d) in a high pH solution (scale bar - 500μm)

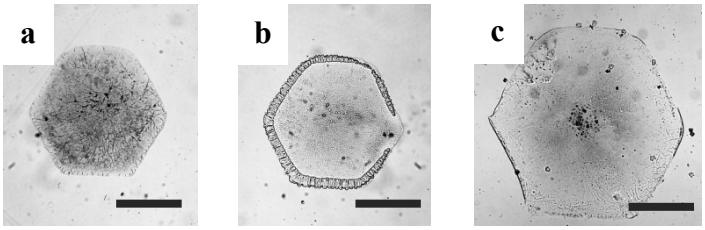

Figure S4. Polarizing optical microscope image of a homeotropic oriented inkjet printed hexagonal pattern before (a), in the intermediate state (b) and after swelling (c) in a high pH solution (scale bar - 500μm)