Supplementary information for:

New insights into the nature of semi-soft elasticity and "mechanical-Fréedericksz transitions" in liquid crystal elastomers

Devesh Mistry[1], Philip B Morgan[2], John H Clamp[3] and Helen F Gleeson[1]

[1] School of Physics and Astronomy, University of Leeds, Leeds, LS2 9JT, UK
[2] Eurolens Research, University of Manchester, Manchester, M13 9PL, UK
[3] UltraVision CLPL, Commerce Way, Leighton Buzzard, LU7 4RW, UK

A full copy of the dataset used in this work can be found at the following DOI: http://doi.org/10.5518/131 (prior to publication please use the following link:

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Cell fabrication

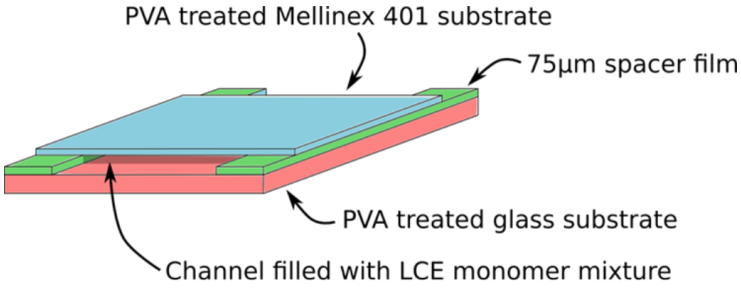

FIGURE S1 diagram of cell construction

Cells described by the simplified diagram in figure S-1 were made according to the following procedure:

- Cells were made with one glass and one 100µm thick Melinex® substrates. A Melinex substrate was used due to its flexible nature. This aided when opening the cells as it was easily peeled away. In all cases, the polymerised LCEs were left on the glass substrates.
- Glass microscope slides, 25x75mm were used as glass substrates. These were cleaned by:
    - Sonication for 20 minutes in DI water + soap,
    - Rinsed several times in DI water,
    - Sonicated in DI water for 20 minutes,
    - Dried using an air gun,
    - Sonicated in Acetone for 20 minutes,
    - Dried using an air gun.

- Melinex substrates (cut to 60x15mm) than the glass were cleaned more gently by immersing in methanol for 5 minutes and were then dried using an air gun.
- Substrates were spin coated using an alignment layer of 2% by wt. PVA dissolved in DI water (filtered). PVA solution was placed on the substrates with care to ensure the whole of the surface was covered and was left for 30 seconds. The spin speed was then gradually increased to 1500rpm, then increased to 4000rpm for 30 seconds. This was enough to coat and dry the substrates.
- The alignment layers were then rubbed uniaxially at the desired angle using a rubbing machine built in house. Briefly, the rubbing machine consists of a vacuum plate which holds the samples and moves under the roller. The roller was covered in a velvet cloth and rotated to brush the surfaces.
- Spacer strips of 75µm thick Melinex were cut and cleaned. Cells were constructed by applying a thin lines of Norland Optical Adhesive NOA61 down each side of the Melinex substrate (on the PVA coated side). The 75µm spacers were placed on top of the glue and another layer of glue was placed on top of the spacers. The glass substrate was then placed to form the top of the cells, being careful to align the rubbing directions accurately in an antiparallel fashion. The cells were then placed on a flat metal block and masses were placed on top of centres of the cells to compress the glue with an even pressure. The cells were then place under a low-intensity UV fluorescent source for 30 minutes for the glue to cure.

LCE synthesis

LCEs were synthesised using the materials:

- 2-Ethylhexyl acrylate (EHA),
- 6-(4-Cyano-biphenyl-4'-yloxy)hexyl acrylate (A6OCB),
- 1,4-Bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (RM82),
- 4-Cyano-4'- hexyloxybiphenyl (6OCB) and
- methyl benzoylformate (MBF).

Using a balance with an accuracy of 0.3mg, dry materials were measured into a 4ml sample vial containing a small magnetic stirring bead. This was then heated to 100°C and stirred at 60rpm on a magnetic stirring heat plate for 5 minutes. The liquid materials were added to this using Eppendorf pipettes and the vial was placed on a separate stirring plate held at 40°C and stirred at 60rpm for a further 5 minutes. As EHA and HDDA are volatile materials, this stirring should be performed for no longer than 5 minutes to minimise the quantity of these materials lost.

The mixtures were then filled in the isotopic phase at 40°C C (the nematic to isotropic transition temperature (T_{NI}) was found to be 36.6 ± 1.0°C via DSC) into the cells previously prepared via capillary action and left for approximately half an hour to cool to ambient temperature and the nematic phase for alignment with the rubbing direction. Once aligned, the cells were placed under a low intensity UV fluorescence light source (intensity of 2.5 mW cm^{-2}) for two hours to cure. Radical polymerisation is a fast process for thin films of material, however we used an exposure time of 2 hours to ensure complete polymerisation. After curing, the cells were opened by carefully prising away the Melinex substrate using a scalpel. In all cases then polymerised sample remained on the glass substrate. A sharp blade was then used to trim approximately 0.5mm from the edges of each film and the spacers were removed using the scalpel. By placing the glass substrate with exposed sample in a petri dish of methanol, the sample began to swell slightly and delaminate at the edges. For small samples, the sample of could be left to lift away from the glass, however for large samples the sample would often end up tearing in some areas. Therefore for larger samples the film was carefully prised away using large flat tipped tweezers. Once separated, the film was washed in dicholormethane (DCM) by slowing

adding DCM stepwise to about 30% concentration. Solvents were exchanged several times to ensure all waste materials were removed before deswelling the LCE films by adding methanol stepwise. This process took 24 hours to prevent it tearing itself apart from fast sewlling. Next the films were left to dry fully overnight before tested on.

Equipment specification for mechanical tests

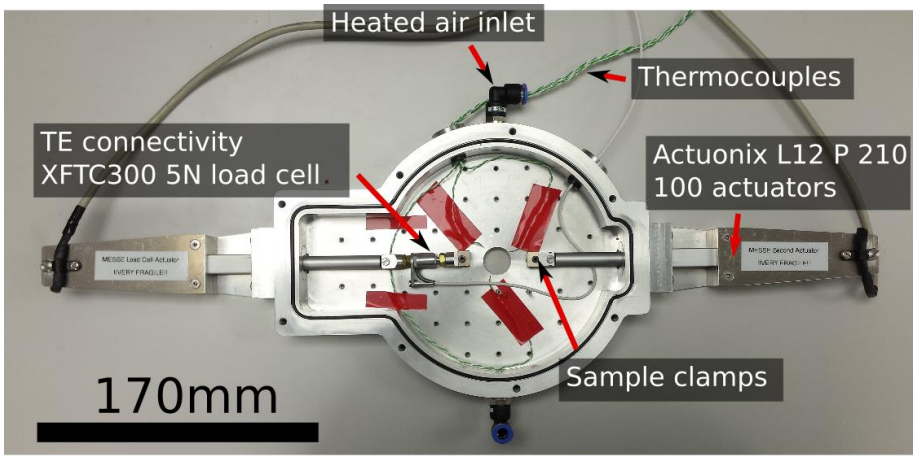

FIGURE S2a Photograph of mechanical testing enclosure

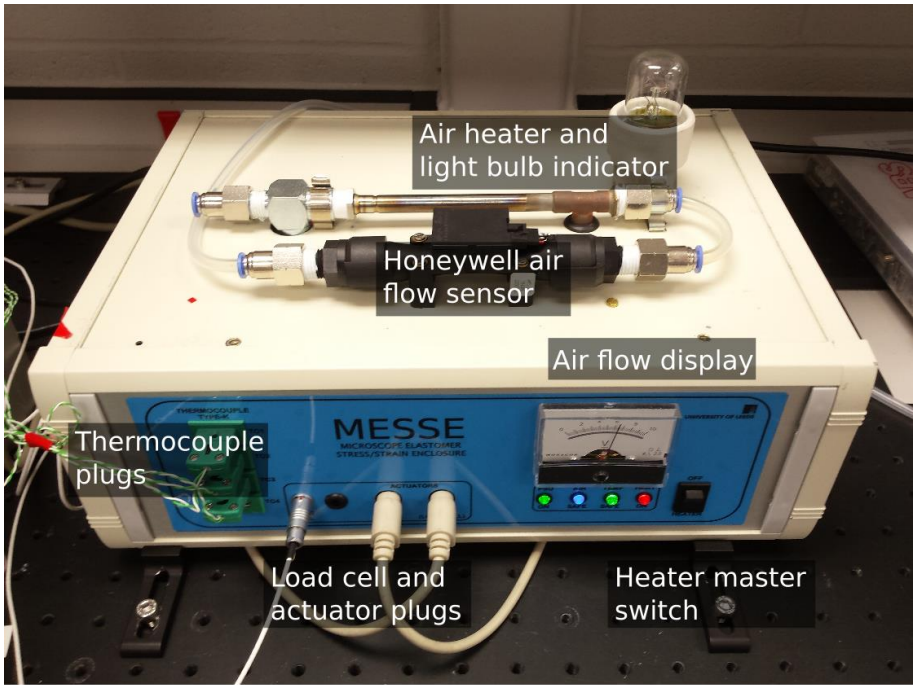

FIGURE S2b Photograph of mechanical testing control box

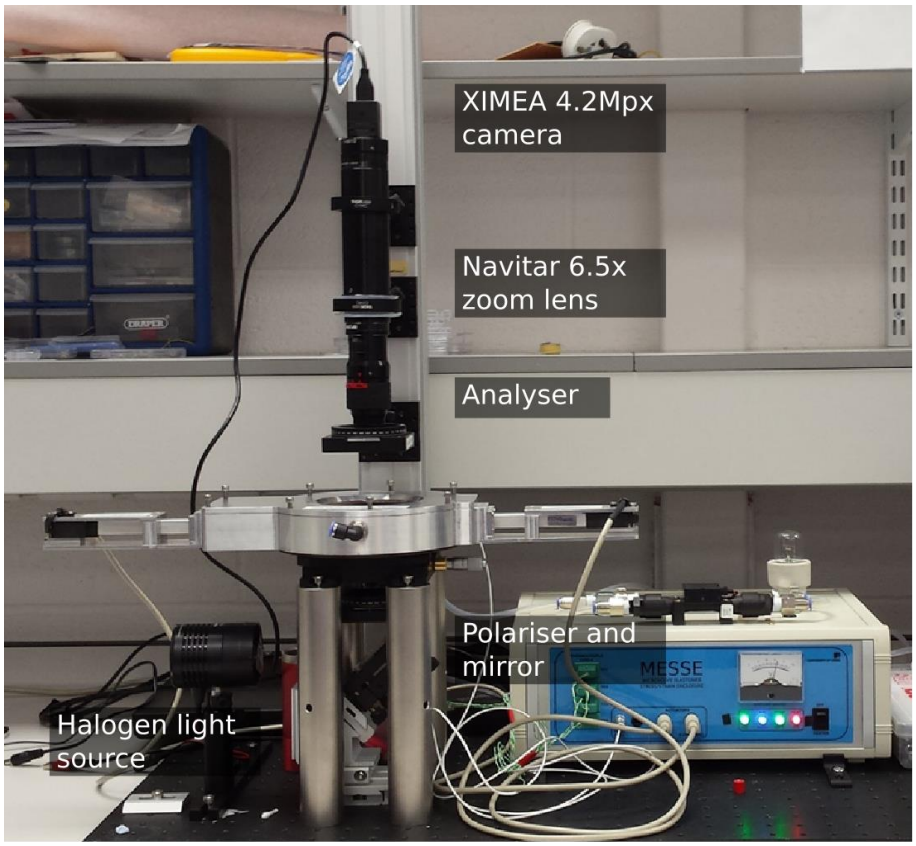

FIGURE S2c Photograph of complete equipment set up used for mechanical tests

For mechanical tests, bespoke equipment was built in house for allowing accurate mechanical tests to be performed while viewing the sample via polarising microscopy. The aluminium sample chamber (figure S3a) supports the two opposing linear actuators which strain the sample mounted. Samples can be stretched with any position maintained over the central viewing hole. On one actuator, a load cell is mounted in series. The load cell is calibrated by removing the right hand actuator and hanging calibration masses off the load cell.

The chamber can be filled with a variety of gases including heated air, nitrogen or humidity controlled air. Two through ports for instrumentation cables allows various measurements to be performed although currently we only measure the load cell output and temperature values from three thermocouples distributed around the window. The average thermocouple value is used to set the temperature of the heated air via a PID control loop in the control software. The base is tapped with an array of holes for extra instrumentation to be installed, for instance and adapter to allow an approximation of radial stretching of the sample.

The electronics control box (figure S3b) contains several pieces of equipment:

- Pico TC-08 for logging the thermocouple readings and load cell value (using an additional extension board),
- Two actuator control boards,
- Arduino and Kirda electronics Triac board (designed for dimming AC incandescent lamps via the arduino) for controlling the heater output, and
- A power supply and circuit board for powering the devices and providing safety controls for the heater.

All equipment connects via a USB to a computer which controls the equipment via a custom LabVIEW program. This software allows programmed actuation sequences to extend and retract the actuators at various rates for extensive testing of materials. All data is logged to text files for later analysis.

Examples of particle tracking and director angle monitoring

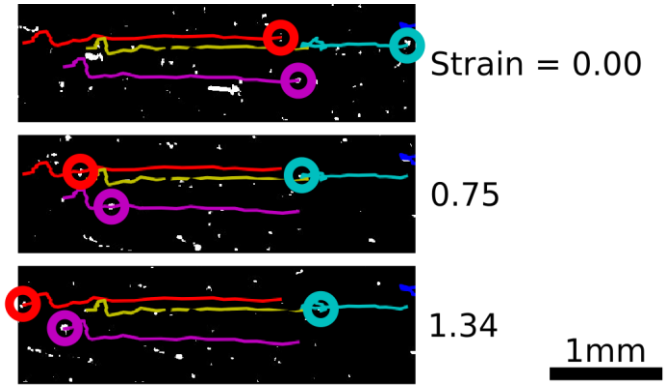

FIGURE S3 Example of particle tracking output for 89° sample

Trackpy (http://soft-matter.github.io/trackpy/v0.3.2/) was used to track the movement of particles embedded within the films of LCE as they were strained. This allowed localised strain to be easily calculated between many different points. Photographs sometimes required pre-processing such as histogram equilization (using OpenCV) prior to tracking with trackpy. Figure S4 shows a crop of some of the data from the 88° sample with tracked points highlighted.

Examples of data used for fitting for director orientation angle

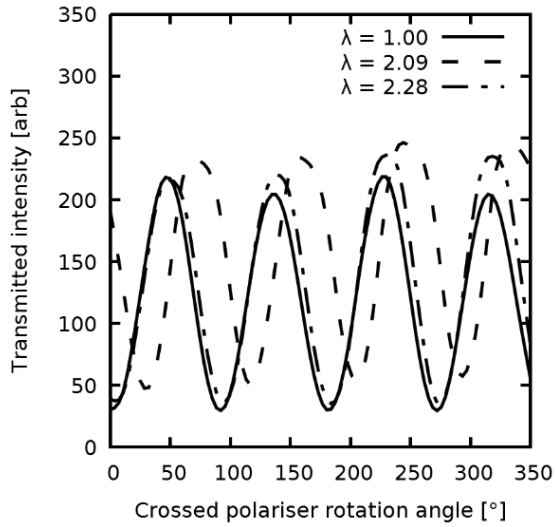

FIGURE S4

Figure S5 shows the transmitted intensity of the 88deg sample as a function of polariser rotation angle for various extensions of the sample, λ. The sine-squared shape and contrast in transmitted intensity is indicative of the high quality monodomain alignment. The director alignment was found by fitting

$$I = I_0 \ sin^2\left(\frac{b\pi \times (\theta - c)}{180}\right) + d$$

to these datasets results. In the above equation I_0, b, c and d are fitting parameters and c gives the value of one of the minima of the curve from which the director angle is deduced.

DSC results

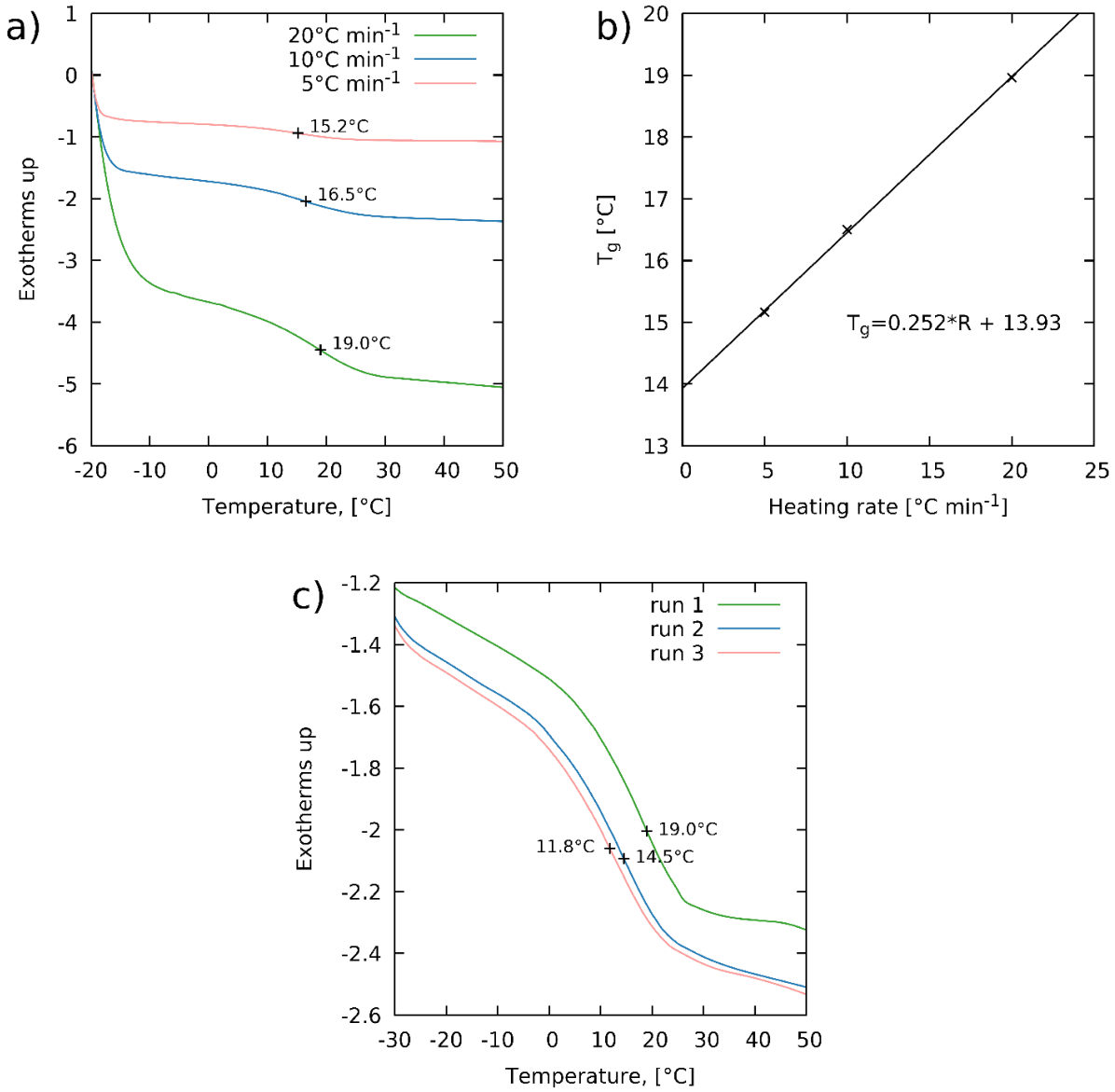

FIGURE S5 Results from DSC tests. a) Curves for sample of LCE thrice cycled between -20 and 150°C at heating rates shown. Inflection points determined by fitting using TA universal analysis. b) Inflection points extrapolated to a heating rate of 0°C min^{-1}. The intercept of 14°C gives the LCE's T_g. c) A second sample of LCE first cycled between -40 and 120°C gave a constant inflection point of 19.0°C. Two subsequent cycles from -40 to 330°C led to a decrease in the inflection point to 11.8°C. This decrease in inflection point was used to assess the effect of thermal degradation and generate the error contribution for determining the nematic to isotropic transition temperature of the LCE.

Structure of full dataset

A full copy of the dataset used in this work can be found at the following DOI: http://doi.org/10.5518/131

'…\figure 1 example of SSE\'

Plotting file for generating example semi-soft elastic load curve based on equations given in the book by Warner and Terentjev[1]

'…\figure 2 chemical diagrams\'

Contains .cdx (for ChemDraw (PerkinElmer, UK) software) and .eps files of the chemical structures of the chemicals used for the synthesis of liquid crystal elastomers (LCEs) used in this dataset. Also contains the Inkscape .svg and .png versions of figure 2 from the paper.

'…\figure 3 polarising microscopy images\'

Full resolution polarising microscopy images used to demonstrate the quality of monodomain alignment. Photos taken with director parallel and at 45° to the polariser

'…\figure 4 and 5 opto-mechanical data\'

Contains the raw data measured during opto-mechanical tests including polarising microscopy images of the samples throughout deformation used in figure 6.

Also contains:

- Analysis files for determining the extension using trackpy and director angle.[2]
- Summary data files and plotting files used to generate figures

'…\figure 6 order investigations\'

Contains copies of the polarising microscopy images used to assess the state of order within the 89° sample of LCE throughout the deformation. Plotting files included

'…\figure 7 birefringence on heating\'

Contains the data recorded for the sample's geometry and retardance as it was heated. Analysis deduced the birefringence of the sample at each temperature. Plotting and fitting files used to deduce a value for the step length anisotropy included.

'…\figure 8 in plane polymer conformation evolution \' and *'…\figure 9 LC-backbone coupling types \'*

Respective folders containing illustration diagrams for figures 8 and 9.

'…\Supplementary figures\'

Contains:

- the differential scanning calorimetry data used to calculate the LCE glass transition and monomer mixture T_{NI} and also for studying the effects of thermal degradation. Details are given of the calibration procedure along with the .001 files which are the native files of the machine. These files can be opened using TA universal analysis (free available from the TA instruments website).
- Files for figures contained within this supplementary information

References

1. Warner, M., Terentjev, E. M. Liquid Crystal Elastomers, Clarendon Press, 2013.
2. Allan, D., Caswell, T., Keim, N., Van Der Wel, C. 2016.