

## FIGURE 2 README FILE

### Description of data:

Differential scanning calorimetry trace of pure unpolymerised monomer A6OCB and pure unpolymerised monomer RM82.

### Equipment used:

TA Q-20 DSC

### Experiment settings:

Experimental settings can be found in metadata in .txt or .0001 files. Also described in the main text.

### Analysis conducted:

Fitting of phase transitions conducted in software TA Universal Analysis (<https://www.tainstruments.com/>)

## FIGURE 3 README FILE

### Description of data:

Experimental differential scanning calorimetry traces for unpolymerised monomer mixtures with varying ratio of A6OCB to RM82.

Sample labels corresponding mixture parameters can be found in Figure3\_ExperimentalPlottedData.txt.

Predicted transition temperatures for binary mixtures of A6OCB and RM82, obtained as described by Harrison et al (DOI: 10.1039/C39740000098) can be found in Figure3\_TheoreticalPlottedData.txt

### Equipment used:

TA Q-20 DSC

### Experiment settings:

Experimental settings can be found in metadata in .txt or .0001 files.

### Analysis conducted:

Fitting of phase transitions conducted in software TA Universal Analysis (<https://www.tainstruments.com/support/software-downloads-support/downloads/>).

## FIGURE 4(a) README FILE

### Description of data:

Differential scanning calorimetry traces for polymerised LCEs with varying ratio of A6OCB to RM82.

Sample labels corresponding mixture parameters can be found in Figure4(a)\_ExperimentalPlottedData.txt.

### Equipment used:

TA Q-20 DSC

### Experiment settings:

Experimental settings can be found in metadata in .txt or .0001 files.

### Analysis conducted:

Fitting of glass transition conducted in software TA Universal Analysis

(<https://www.tainstruments.com/support/software-downloads-support/downloads/>).

## FIGURE 4(b) README FILE

### Description of data:

Glass transition temperatures and degree of polymerisation for fully atomistic MD simulations with varying concentration of crosslinker (RM82) and also different initial configurations (Nematic, Isotropic, Limited-Isotropic).

Glass transitions were determined by fitting density versus temperature as described in the manuscript.

Degree of polymerisation was obtained from the cumulative count of the number of new bonds formed during the simulation.

## FIGURE 6 README FILE

### Description of data:

Glass transition temperatures and degree of polymerisation for fully atomistic MD simulations with varying concentration of crosslinker (RM82) and also different initial configurations (Nematic, Isotropic, Limited-Isotropic).

Glass transitions were determined by fitting density versus temperature as described in the manuscript.

Degree of polymerisation was obtained from the cumulative count of the number of new bonds formed during the simulation.

## FIGURE 7 README FILE

### Description of data:

Experimental order parameter measurements conducted on LCE samples at room temperature using Raman spectroscopy.

Raw D-RatioData included for each sample in subfolder (Figure7\_Raw\_Raman\_Data\), with depolarisation ratio data given in "D-ratio data for Raman Temperature Scans.xlsx".

Sample labels corresponding composition can be found in Figure7\_ExperimentalPlottedData.txt.

Order parameters of simulations were calculated via the Q-tensor approach as implemented in MDtraj version 1.94, with data presented in

Figure7\_TheoreticalPlottedData.txt.

### Equipment used:

Renishaw inVia confocal Raman microscope in reflection geometry. 532nm solid-state laser. 50x objective. Linkam TMS93 hotstage.

### Analysis conducted:

Analysis conducted using WiRE data acquisition software.

## FIGURE 8(a) README FILE

### Description of data:

Experimental order parameter measurements conducted on LCE samples using Raman spectroscopy.

### Equipment used:

Renishaw inVia confocal Raman microscope in reflection geometry. 532nm solid-state laser. 50x objective. Linkam TMS93 hotstage.

Sample labels corresponding RM82 concentration can be found in the header from Figure8(a)\_DataPlot.txt.

### Analysis conducted:

Analysis conducted using WiRE data acquisition software.

## FIGURE 8(b) README FILE

### Description of data:

Order parameters of simulations with varying composition and at varying temperature were calculated via the Q-tensor approach as implemented in MDtraj version 1.94. Errors are given as one standard deviation from the mean. Data are presented in

Figure7\_TheoreticalPlottedData.txt.



## FIGURE 9 README FILE

### Description of data:

Anisotropic thermal expansion measurement. Measurement split across 3 experiments labelled 010221, 150121, and 200121.

Calibration images for each image sequence are included.

Relating sample to images can be found in - SampleLabels\_raw.txt. The samples are labelled from left to right upon opening the raw images.

Sample labels corresponding mixture composition can be found in SampleLabels\_raw.txt.

### Equipment used:

Imaged using a NikonD7100 whilst using a UniTemp GmbH HP-220 hotplate for temperature control.

### Analysis conducted:

Analysis conducted using ImageJ software. Linear fitting of expansion (at greater than  $T_g$  as measured by DSC) conducted using linear fit in OriginPro.

## FIGURE 10 README FILE

### Description of data:

Experimental complex Young's modulus measurements conducted on LCEs samples with varying mol% of RM82 using dynamic mechanical analysis (DMA).

Measurements performed at 1hz frequency at a temperature of  $T_{\text{(glass transition)}} + 30 \text{ K}$  as determined by DSC.

Data included the storage modulus ( $E'$ ), loss modulus ( $E''$ ) and  $\tan(\delta)$ .

### Equipment used:

Rheometrics Solid Analyser II using the film tension clamp attachment with TA Orchestrator.

## FIGURE 11 README FILE

### Description of data:

Experimental dynamic mechanical analysis temperature sweeps performed on LCEs with varying mol% of RM82.

Measurements performed at 1hz frequency with a temperature range of 30 - 140 deg C.

Data included the storage modulus ( $E'$ ), loss modulus ( $E''$ ) and  $\tan(\delta)$ .

### Equipment used:

Rheometrics Solid Analyser II using the film tension clamp attachment with TA Orchestrator.