

# Unsymmetric Main-Chain Liquid Crystal Elastomers with tunable Phase Behaviour: Thermal Properties

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## I Preparation of the liquid crystal elastomers

The reactions were performed in a customised centrifuge (Hettich, Universal 32R) equipped with a custom-made stainless steel rotor, which contained a Teflon cell with dimensions 49 mm of diameter and 20 mm height. The inner wall of the cell was coated with Teflon film. The centrifuge was heated by a water-bath circulator (Julabo, MP-5) equipped with an immersion pump. The sample environment within the centrifuge was heated to a temperature of 60 °C, which was maintained constant.

The proportion between the vinyl groups and the hydrogen of the silane was stoichiometric, with 10% of cross-linker used for all the elastomers. In this way, when the functionality of the cross-linker was four (**C1**), the mesogenic unit (2 mmol), cross-linker (0.2 mmol, % related to the mmol of mesogenic unit) and spacer (1.6 mmol) were solubilised in toluene (2 cm<sup>3</sup>). For functionality of three, the proportions were mesogenic unit (2 mmol), cross-linker (0.2 mmol, % related to the mmol of mesogenic unit) and spacer (1.7 mmol) in dry toluene (2 cm<sup>3</sup>).

Table S1. Amounts of monomer, spacer and cross-linker used for the family of **C1** elastomers

Monomer / g (mmol)	Spacer			Cross-linker C1 / g (mmol)
	S1 / g (mmol)	S2 / g (mmol)	S3 / g (mmol)	
<b>M1</b>	0.732 (2)	0.332 (1.6)	0.362 (1.6)	0.048 (0.2)
<b>M2</b>	0.872 (2)	0.332 (1.6)	0.362 (1.6)	0.048 (0.2)
<b>M3</b>	0.928 (2)	0.332 (1.6)	0.362 (1.6)	0.048 (0.2)

Table S2. Amounts of monomer, spacer and cross-linker used for the family of **C2** elastomers

Monomer / g (mmol)	Spacer			Cross-linker C2 / g (mmol)
	S1 / g (mmol)	S2 / g (mmol)	S3 / g (mmol)	
<b>M1</b>	0.732 (2)	0.353 (1.7)	0.385 (1.7)	0.052 (0.2)
<b>M2</b>	0.872 (2)	0.353 (1.7)	0.385 (1.7)	0.052 (0.2)
<b>M3</b>	0.928 (2)	0.353 (1.7)	0.385 (1.7)	0.052 (0.2)

The components were mixed in toluene and placed inside the Teflon cell. To this, a solution of [PtCl<sub>2</sub>COD] in dichloromethane (30 µl, 1% w/w) was added before the polymerisation started. The cell was sealed and placed inside the centrifuge. The reaction was carried out for between 2 and 6 hours at 5000 rpm. Once the reaction was finished, the cell was removed from the centrifuge, allowed cool to room temperature and the swollen network was removed from the Teflon cell. From the network film, a part was cut and deswollen on a water surface to avoid mechanical deformation to form polydomain networks. The rest of the film was hung at one end with a clamp and the other free end of the film was loaded in order to form aligned, monodomain networks. In these conditions, the solvent slowly evaporated from the film during 24 h. The film was then placed in an oven at 30 to 50 °C, depending on the clearing temperature, and the cross-linking reaction was allowed to complete during 48 h. Polydomain networks were placed in the oven without a load, while for monodomain films, the cross-linking reaction was finished under load.

## II Thermal behaviour of the monomers and elastomers

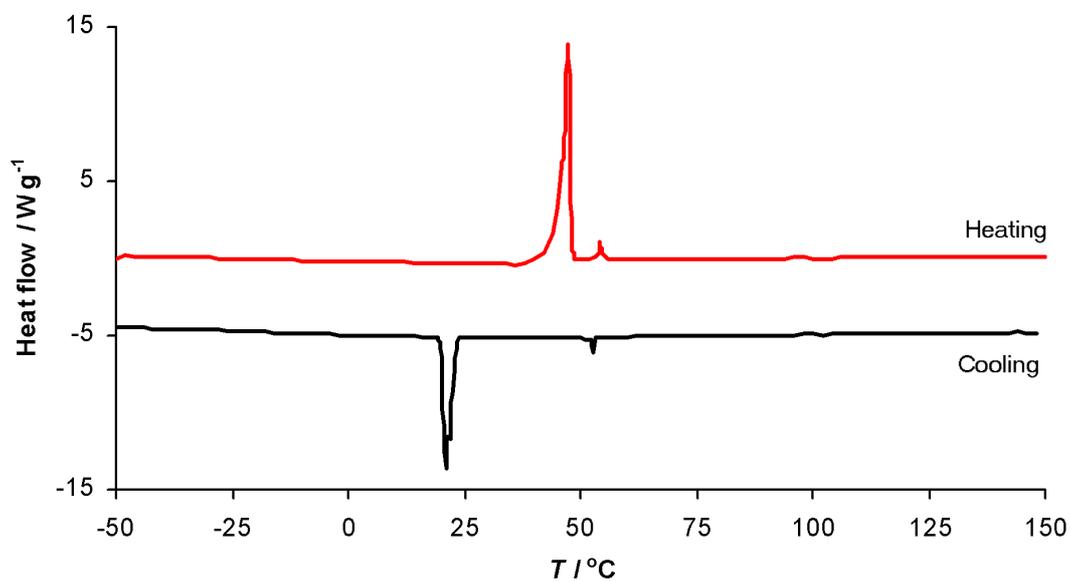


Figure S1. DSC traces of the mesogenic monomer M1

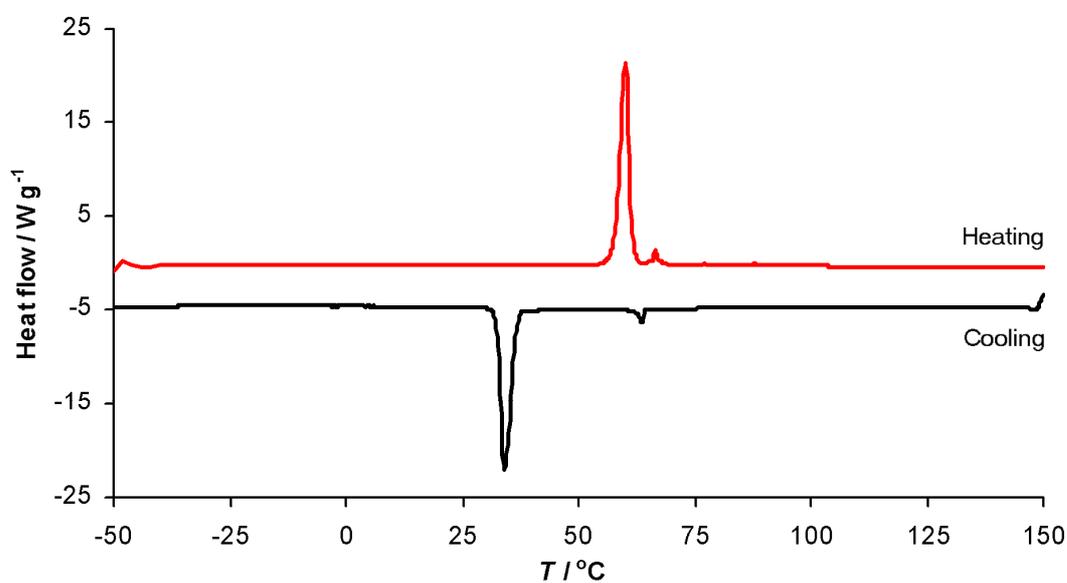


Figure S2. DSC traces on heating and cooling cycles for monomer M2.

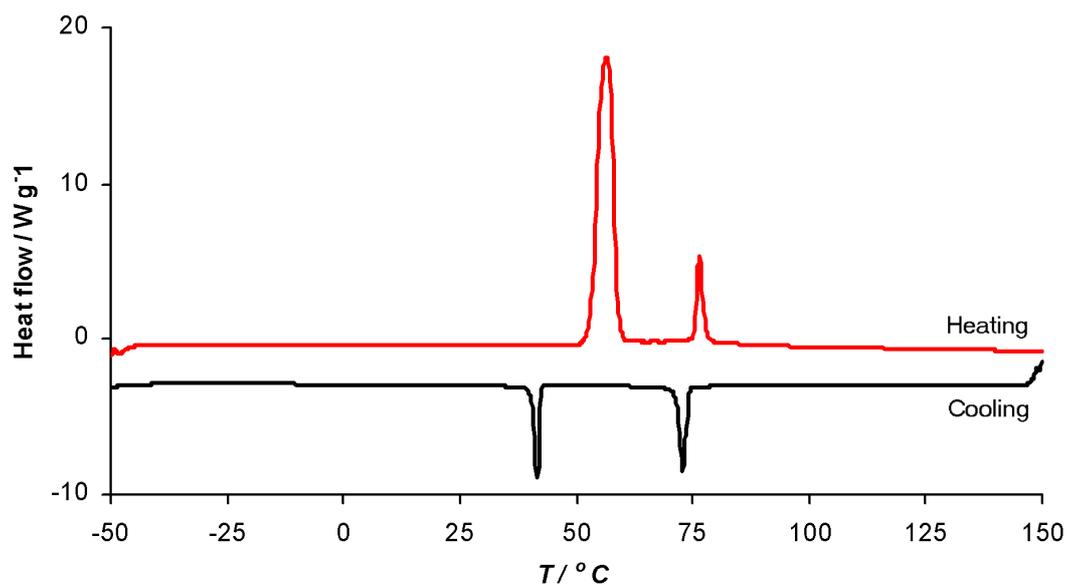


Figure S3. DSC traces of the mesogenic monomer M3.

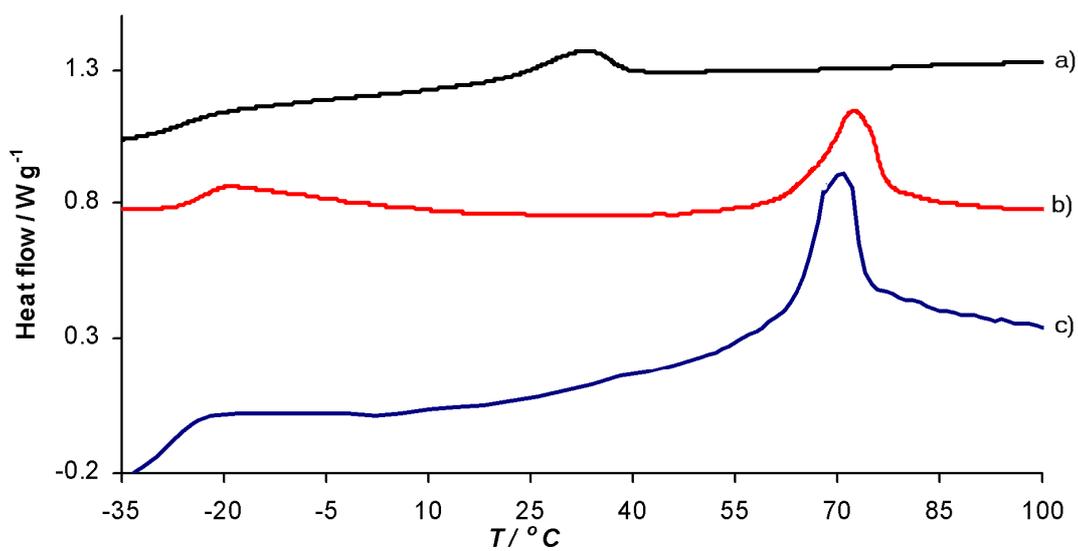


Figure S4. DSC thermograms for elastomers containing spacer S1 and mesogenic monomers a) MA, b) M2 and c) M3.

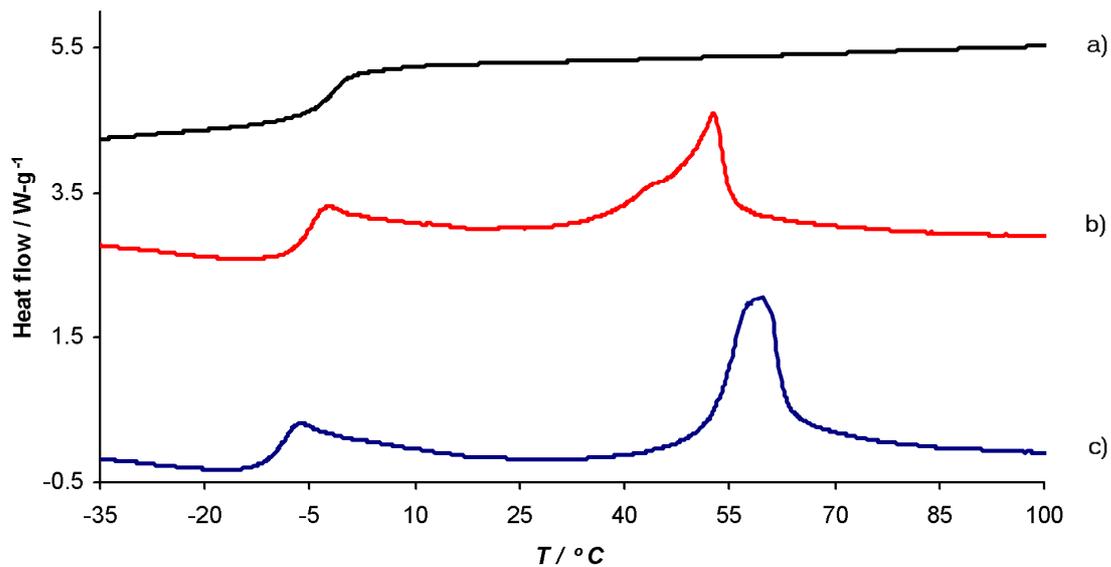


Figure S5. DSC thermograms for elastomers containing spacer S2 and mesogenic monomers a) M1, b) M2 and c) M3.

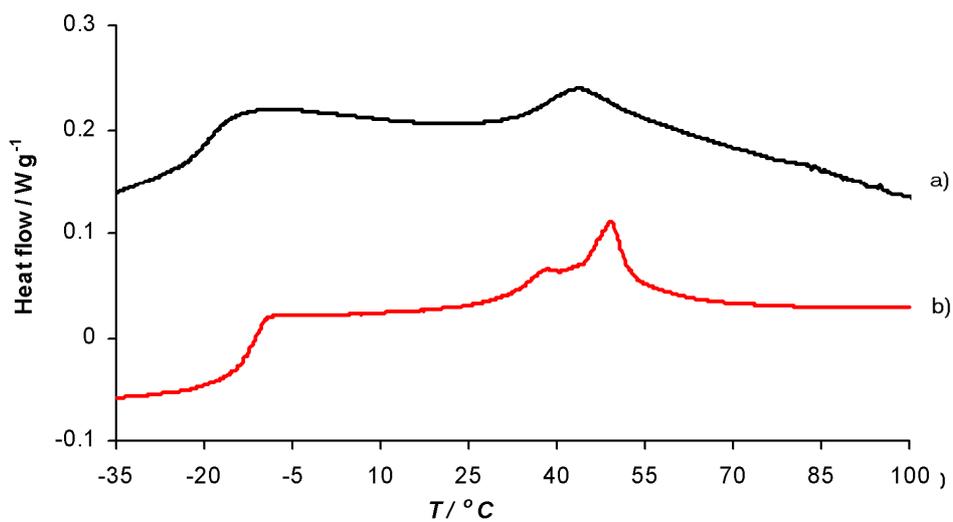


Figure S6. DSC thermograms for elastomers containing spacer S3 a) M1 and b) M2.

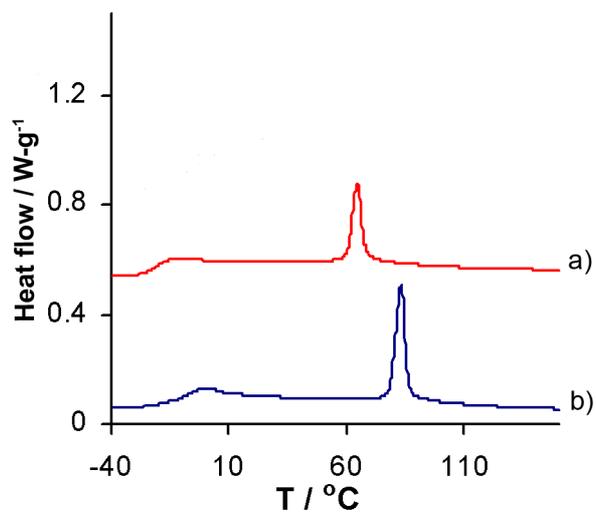


Figure S7. DSC thermograms for the elastomers containing spacer S1 a) M1, b) M2 and c) M3.

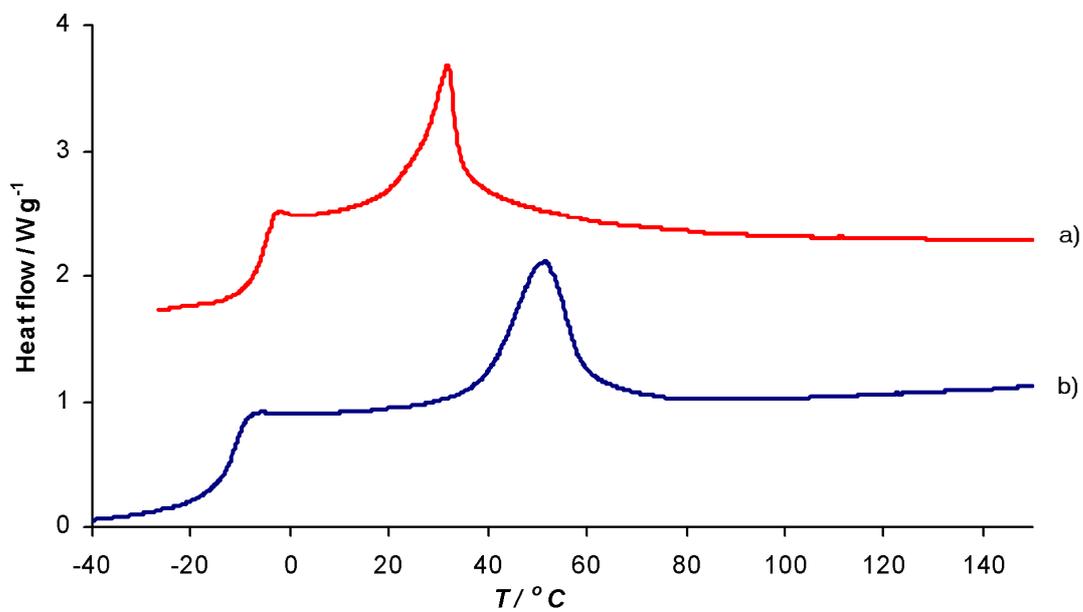


Figure S8. DSC thermograms for the elastomers containing spacer S2 a) M2 and b) M3.

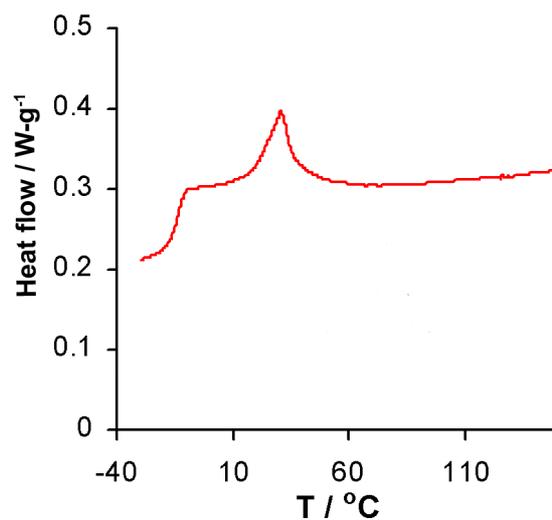


Figure S9. DSC thermogram for the elastomers containing spacer S3 and monomer M2

### III X-Ray diffraction of elastomers

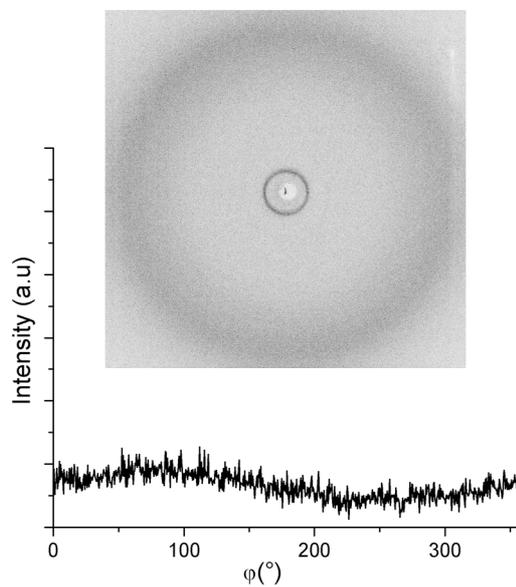
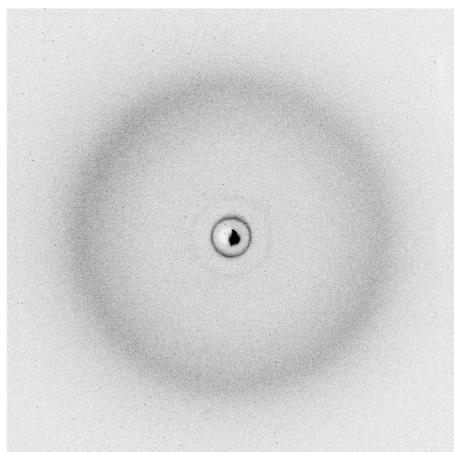
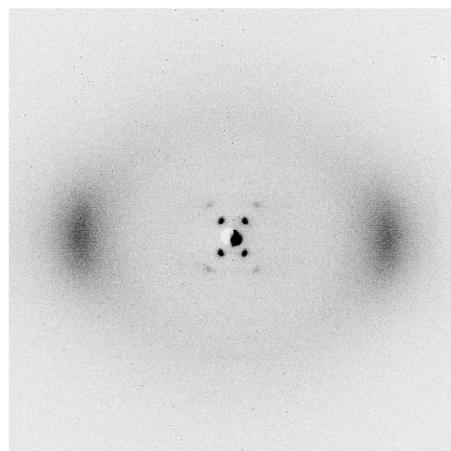


Figure S10. X-Ray pattern of polydomain E5 at room temperature and wide angle reflection graph

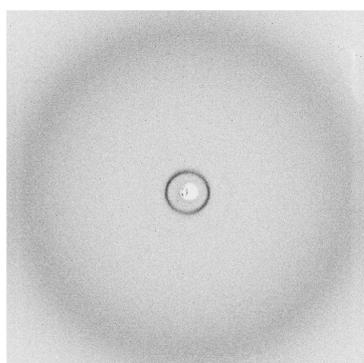


polydomain SmC T = 25 °C

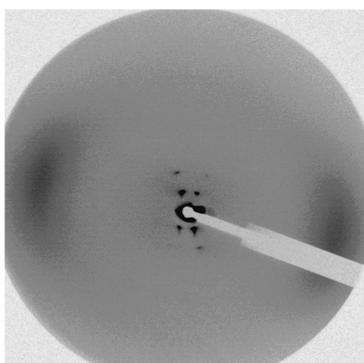


monodomain SmC T = 25 °C

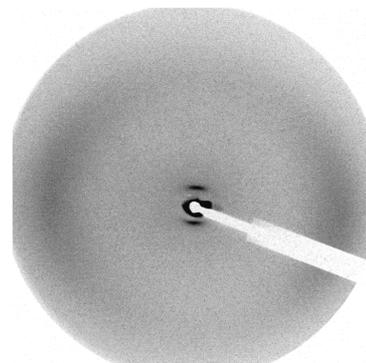
**Figure S11. W-Ray patterns of elastomer E6**



polydomain SmC T = 25 °C

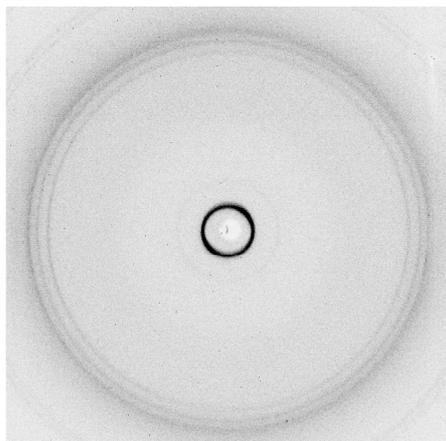


monodomain SmC T = 25 °C

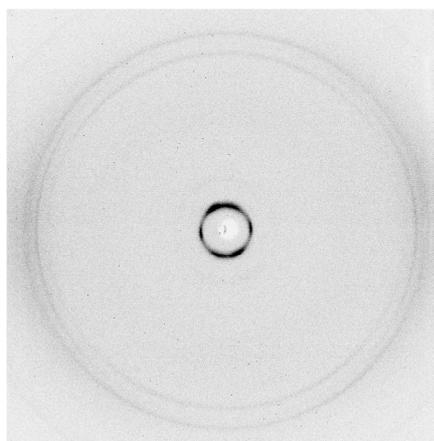


Nematic T = 45 °C

**Figure S12. X-Ray patterns of elastomer E8**

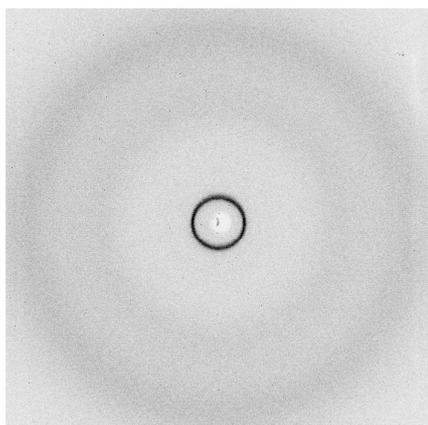


**polydomain T = 25 °C**

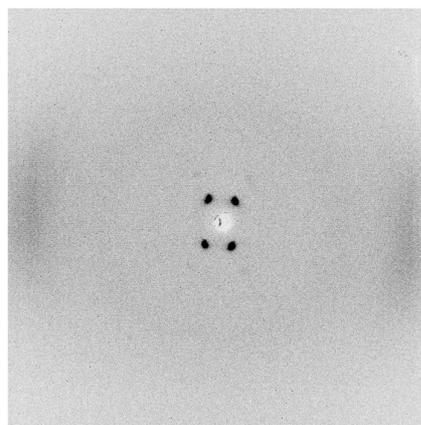


**Crystalline phase T = 25 °C**

**Figure S12. X-Ray patterns of elastomer E9**

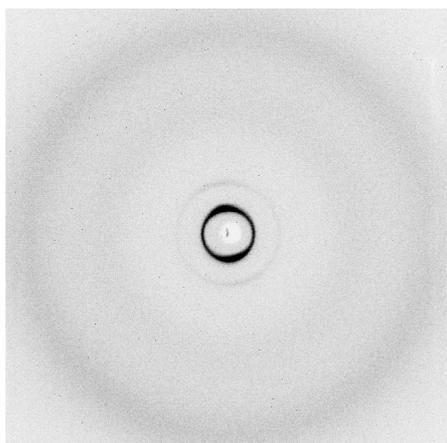


**Polydomain T = 25°C**

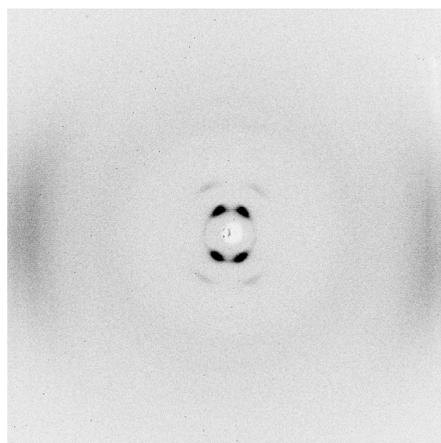


**Monodomain T = 25°C**

**Figure S13. X-Ray patterns of elastomer E2**

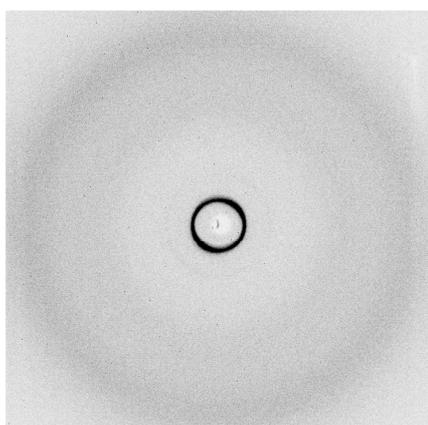


**Polydomain SmC T = 25 °C**

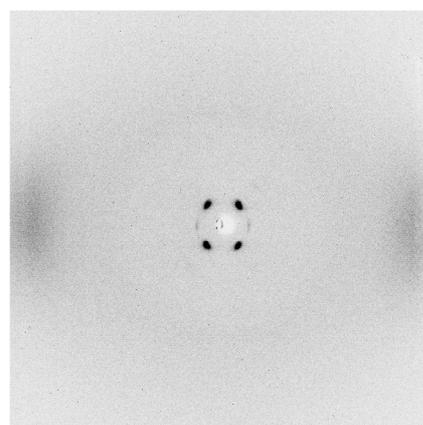


**Monodomain SmC T = 25 °C**

**Figure S14. X-Ray patterns of elastomer E3**

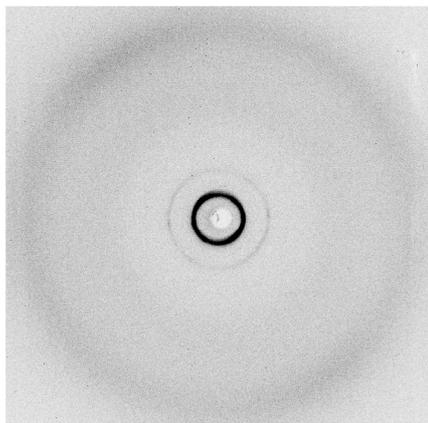


**polydomain SmC T = 25 °C**

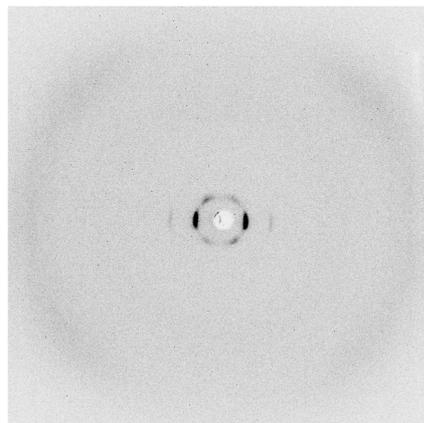


**monodomain SmC T = 25°C**

**Figure S15. X-Ray patterns of elastomer E10**



polydomain T = 25 °C



crystalline phase T = 25 °C

**Figure S16. X-Ray patterns of elastomer E11**