

Electronic supporting information for:

Strain-induced macroscopic magnetic anisotropy from smectic liquid-crystalline elastomer-maghemite nanoparticle hybrid nanocomposites

Johannes M. Haberl,^a Antoni Sánchez-Ferrer,^a Adriana M. Mihut,^{b†} Hervé Dietsch,^{b‡} Ann M. Hirt,^c and Raffaele Mezzenga^{*a}

Preparation of the liquid-crystalline elastomer nanocomposite

The NP volume content was calculated based on the density of maghemite (5.0 kg·dm⁻³) and silica (2.0 kg·dm⁻³), and the average particle core-shell volume determined from TEM experiments.¹ Thus, the average particle density was estimated to be 2.9 kg·dm⁻³. The preparation of the LCE nanocomposite involved 3 steps: i) the magnetic NPS synthesis, ii) the liquid-crystalline polymer synthesis, and iii) the LCE nanocomposite synthesis.¹ Anisotropic hematite nanoparticles were synthesized based on the method described by Ocaña et al.² In a typical synthesis procedure, a 2 L glass bottle was charged with Fe(ClO₄)₃·6H₂O (92.4 g, 200 mmol, 0.047 eq), NaH₂PO₄·H₂O (1.3 g, 9.4 mmol, 1 eq) and urea (NH₂)₂CO (12 g, 200 mmol, 1 eq) in ultra-pure water (2.0 L), and then sonicated until a homogeneous solution resulted. The solution was kept in a preheated oven at 98 °C for 24 h. A brown precipitate was obtained from the solution. The supernatant was decanted, and the precipitate was cleaned by five successive cycles of washing with pure water and centrifugation at 13,000 rpm for 10 min to remove the impurities. Hematite NPs (2 g) were recovered and dispersed into pure water (40 mL).² One gram of spindle-type hematite NPs was dispersed in Milli-Q water (354 mL), and PVP (24.6 g) was added to the solution, and the mixture was stirred overnight.³ The excess of the PVP was removed by five successive cycles of washing with pure water and centrifugation at 10,000 rpm for 10 min. The PVP-stabilized hematite NPs were dispersed in water (30 mL). For a typical 20 nm thick silica coating, PVP-stabilized hematite particles (1 g) were dispersed in a mixture of water (169 mL) and ethanol (2 L) and were stirred mechanically at 400 rpm in a plastic bottle. Tetramethyl ammonium hydroxide (892 g, 25 w/w%) was added, and then a solution of TEOS (9.2 g) in ethanol (11.7 mL) was added in four portions within 2 h to the stirred suspension and stirring continued overnight. The coated NPs were cleaned by three successive cycles of washing with ethanol and centrifugation at 10,000 rpm for 15 min. The recovered NPs were dispersed in ethanol (30 mL). The resulting silica-coated NPs were dried in an air oven at 90 °C for 24 h. In order to control the oxidation state of iron, the NPs were annealed at 360 °C in a H₂-gas flow. Finally, the powder was exposed to air, and the furnace temperature decreased to 240 °C for 2h. The obtained maghemite NPs had an iron core composition of 70/30 w/w% maghemite/hematite, which was determined by XRD data based on the Rietveld method. The silica-coated ellipsoidal magnetic NPs had an aspect ratio of 5.6, with a major core axis of 310 nm,

a minor core axis of 55.2 nm, and a shell thickness of 22 nm and 18.5 nm, respectively. In a typical example of surface functionalization, silica-coated maghemite NPs (1 g) were suspended in an ethanol/water solution (1 L/0.3 mL), and APTES (23.6 g) was added to the mechanically stirred suspension under sonication for 2 h at 20 °C. After stirring the suspension overnight, the obtained amino-functionalised silica coated magnetic NPs were centrifuged at 10,000 rpm for 15 min, redispersed in ethanol and the process was repeated five times. Afterwards, the mixture was dispersed in 30 mL of dichloromethane (DCM). The surface functionalized NPs (6.55 mg, 1 w/w%) were transferred into dichloromethane (0.2 mL), added to a solution of Basonat HI-100 (1, 66.0 mg, 0.130 mmol, 1.0 eq) in DCM (2 ml, absolute), and kept for 2 h. The liquid-crystalline polymer was synthesized from dimethyl biphenyl-4,4-dicarboxylate (10.0 g, 37 mmol, 1 eq) and triethylene glycol (6.1 g, 41 mmol, 1.05 eq) catalysed by titanium (IV) isopropoxide (4.2 mg, 15 μmol, 0.04%) at 200 °C for 6 h under nitrogen atmosphere. The mixture was kept at 230 °C during 1 h at reduced pressure. Triethylene glycol (150 mg, 1 mmol, 0.027 eq) was added and the process was repeated twice. The liquid-crystalline polymer **2** was reprecipitated from DCM by adding methanol, and dried under high vacuum (10.9 g, 70%). A portion of **2** (571 mg, 0.391 mmol, 1 eq) was redissolved in a solution of dibutyltin dilaurate (8.2 mg, 13 μmol, 10%) in DCM (1 mL). Finally, the polymer solution and the particle mixtures were merged and casted onto a Petri dish. The obtained film was allowed to dry within 24 h at room temperature by controlling the DCM partial pressure in the atmosphere, and was then put in an oven at 70 °C for 2 days. In order to determine the gel content and the swelling ratio, the soluble fractions of the films were extracted three times with chloroform.

Supporting figures:

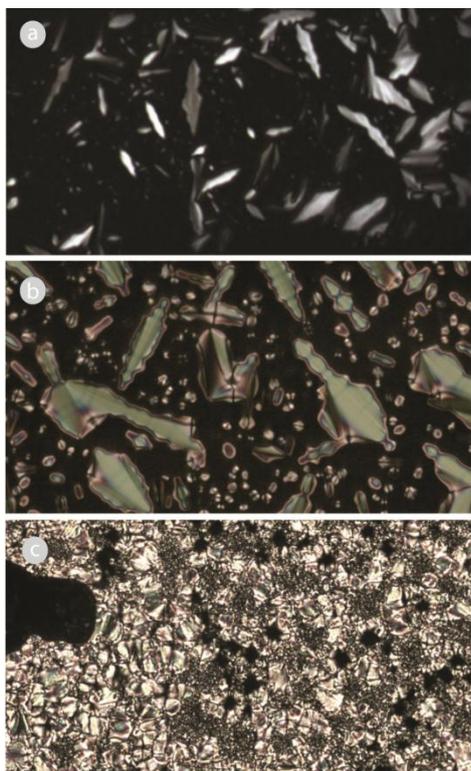
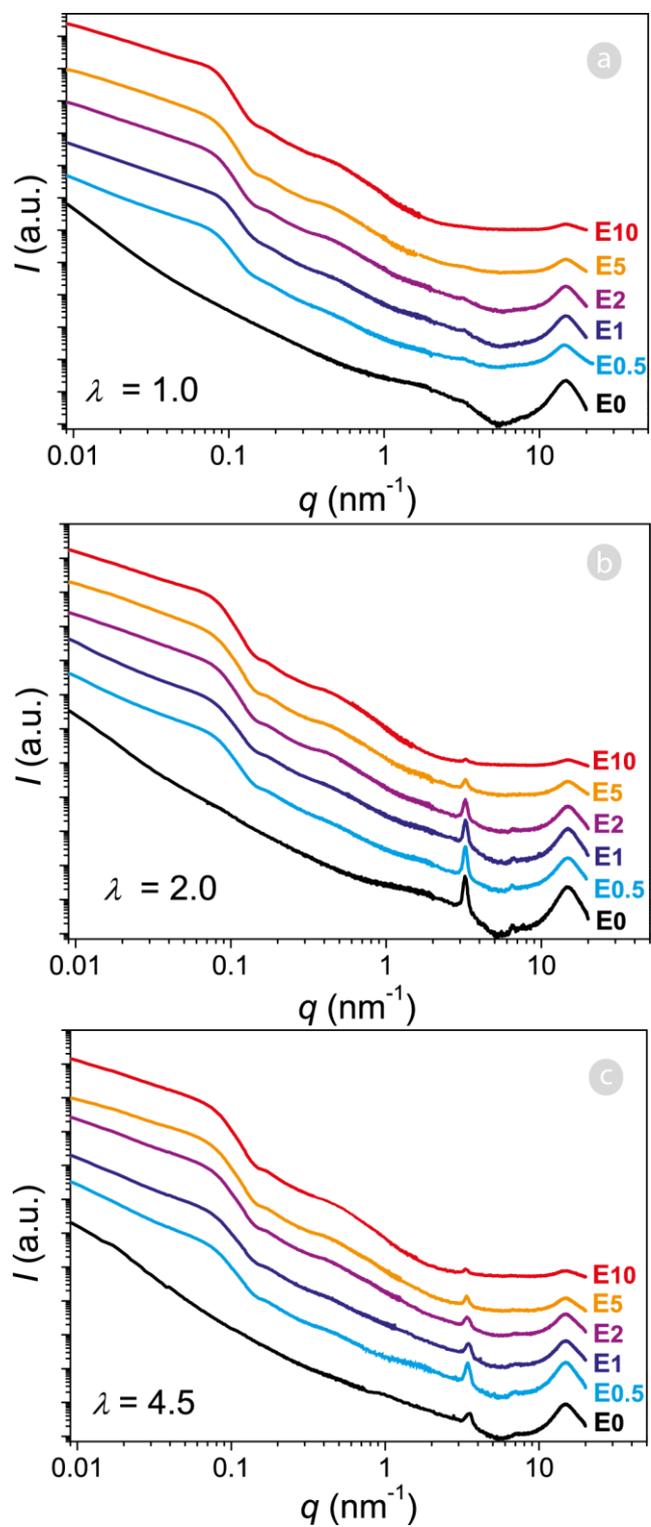


Fig. ESI-1. Polarized optical microscopy (POM) images of the liquid-crystalline polymer P0 at (a) 105 °C, (b) 100 °C after 2h of annealing, and (c) 35 °C.



5 Fig. ESI-2. 1D X-ray scattering intensity patterns for the LCE E0 and the nanocomposites E0.5, E1, E2, E5 and E10 at (a) $\lambda = 1.0$, (b) $\lambda = 2.0$, and (c) $\lambda = 4.5$. Curves are shifted for better readability.

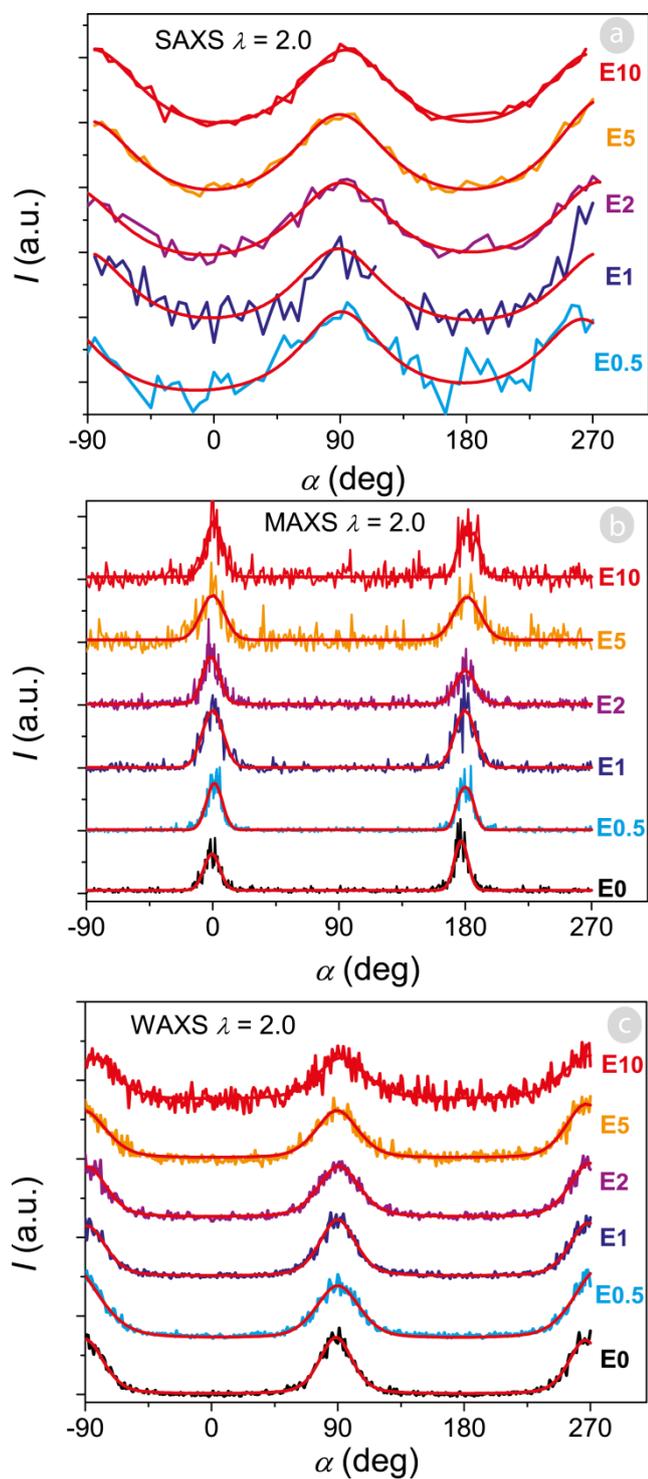


Fig. ESI-3. Azimuthal X-ray scattering intensity distribution for the LCE E0 and the nanocomposites E0.5, E1, E2, E5 and E10 at $\lambda = 2.0$ at the scattering wave-vector (a) $q_p = 0.153 \text{ nm}^{-1}$, (b) $q_l = 2.7\text{-}3.7 \text{ nm}^{-1}$, and (c) $q_m = 14.4 \text{ nm}^{-1}$. Curves are shifted for better readability.

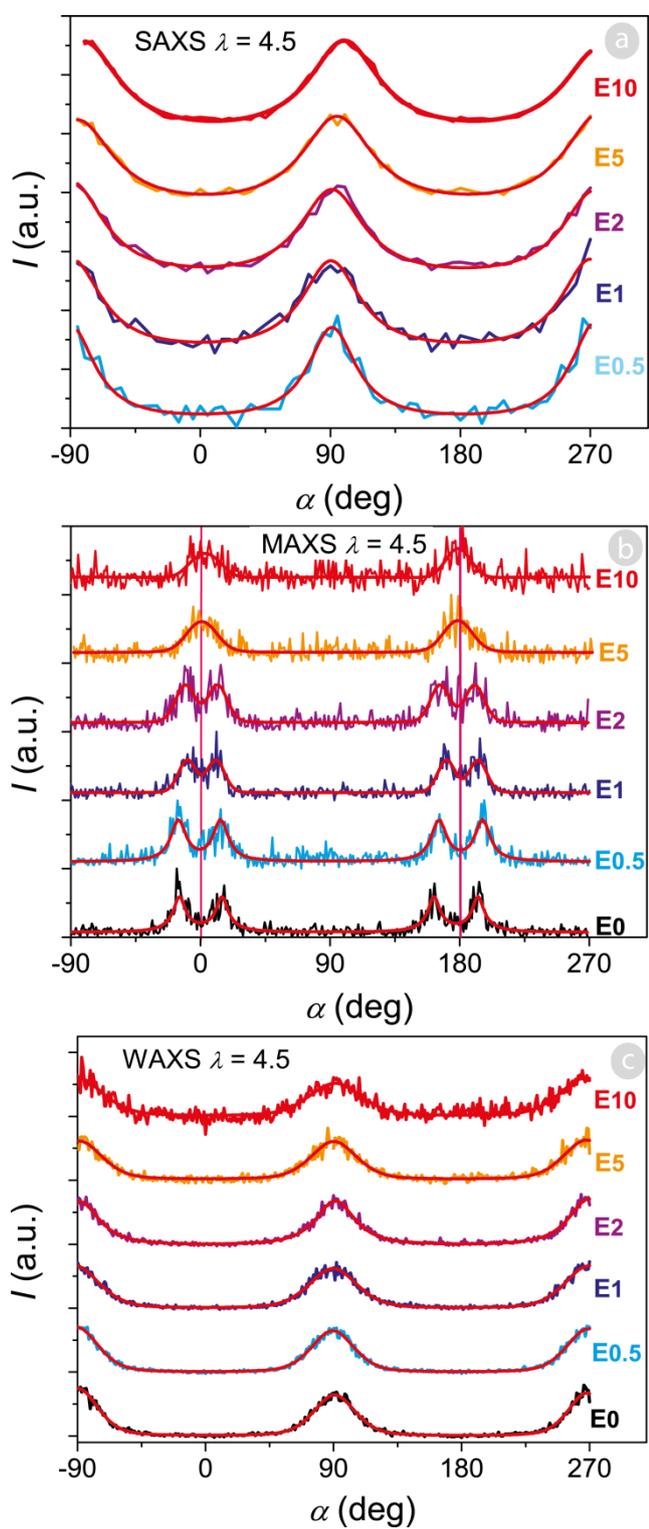


Fig. ESI-4. Azimuthal X-ray scattering distribution of the liquid-crystalline elastomer E0 and the nanocomposites E0.5, E1, E2, E5 and E10 at $\lambda = 4.5$ nm at the scattering wave-vector (a) $q_p = 0.153 \text{ nm}^{-1}$, (b) $q_l = 2.7\text{-}3.7 \text{ nm}^{-1}$, and (c) $q_m = 14.4 \text{ nm}^{-1}$. Curves are shifted for better readability.

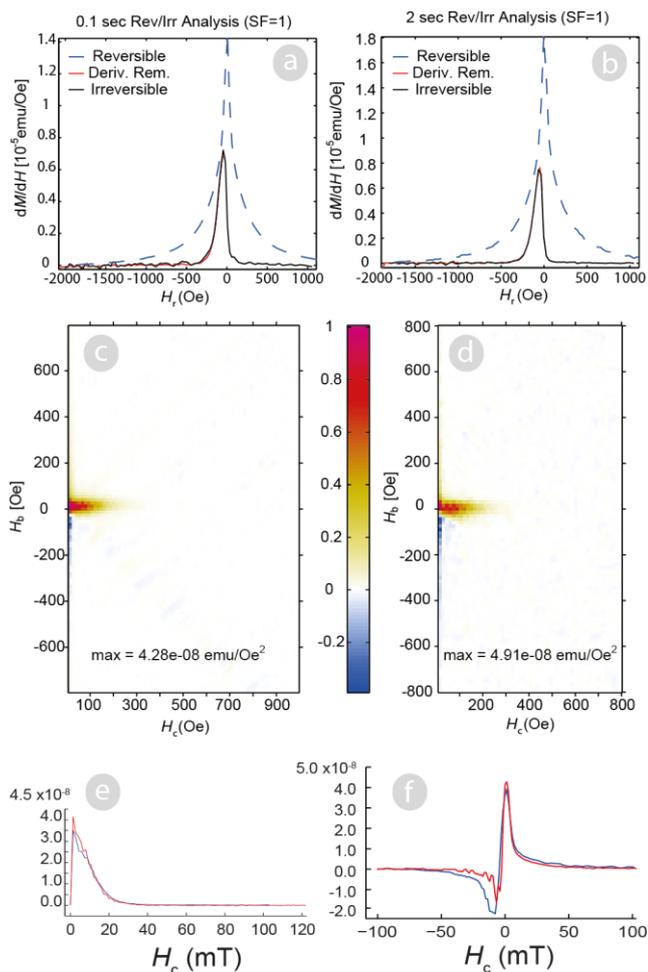


Fig. ESI-5. FORC Measurements of LCE10 with 0.1 (a,c) and 2.0 s (b,d) relaxation time. The difference in the FORC profiles (e) and the interaction fields (f) of the 0.1 s measurement (red) and the 2.0 s measurement (blue) is negligible.

Notes and references

^a *ETH Zürich, Department of Health Science and Technology, 8092 Zürich, Switzerland. Fax: +41 44 632 16 03; Tel: +41 44 632 91 40; E-mail: raffaele.mezzenga@hest.ethz.ch*

^b *Adolphe Merkle Institute and Fribourg Center for Nanomaterials, University of Fribourg, 1723 Marly, Switzerland*

^c *ETH Zürich, Department of Earth Science, 8092 Zürich, Switzerland*

† *Present Address: Physical Chemistry, Department of Chemistry, Lund University, 22100 Lund, Sweden*

‡ *Present Address: BASF SE, Formulation Platform, 67056 Ludwigshafen am Rhein, Germany.*

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