Shear-induced macroscopic “Siamese” twins in soft colloidal crystals

Supporting Information

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Scanning Rheo-SANS

Fig. S1: Rheo-SANS scattering patterns of a shear-oriented FCC twin phase of a 13%wt PI(62)-PEO(193) solution in D₂O, presheared at 500 s⁻¹. (A) Measured scattering pattern in the “radial” beam position probing the [111]-direction. (B, C) Measured scattering patterns in the “tangential” beam position probing the [110]-direction at two different positions x₂ and x₃ in the gap. The distorted hexagonal array of the first-order reflections in (B) indicates the presence of twin “B” at the outer position x₃ of the gap of the Searle cell. The measurement at x₂ was taken close to the inner rotor of the cell and indicates the position of the twin boundary layer. The corresponding model calculations are shown in the lower panel.

Fig. S1 shows measured rheo-SANS patterns of a 13% PI(62)-PEO(193) solution after shearing at 500 s⁻¹ and sudden cessation of shear. Fig. S1A displays the measured scattering pattern in the radial sample position, probing the [111]-direction of the lattice. A calculated scattering pattern is shown in Fig. S1D. The model calculation using Eq. (1) allows one to obtain the characteristic structural parameters of the FCC crystal. We observe a unit cell dimension of a = 70 nm (mean displacement σₐ = 0.03) and

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micellar core radius of $R = 12$ nm (mean rel. std. dev. $\sigma_R = 0.07$). The peak shapes can be well described by an anisotropic Gaussian peak shape with longitudinal coherence lengths of $l_{120} = l_{110} = 200$ nm and $l_{111} = 90$ nm as derived from the Gaussian peak widths $\sigma_{210}$, $\sigma_{110}$, and $\sigma_{111}$ via Eq. (15). The calculated scattering patterns in Figs. S1E,F are calculated for the [110]-direction assuming nearly exclusively twin “B” ($r=0.1$, S1E) and twin coexistence ($r=0.5$, S1F) using the same structural parameters as in Fig. S1D.

Fig. S2: Rheo-SANS scattering patterns of a shear-oriented FCC twin phase of a 15% wt PI(55)-PEO(170) in D$_2$O, presheared at 500 s$^{-1}$ (A) Measured scattering pattern in the “radial” beam position probing the [111]-direction. (B, C, D) Measured scattering patterns in the “tangential” beam position probing the [110]-direction at three different positions $x_1$ – $x_3$ in the gap. The distorted hexagonal array of the first-order reflections in (B) indicate the presence of twin “B” in the outer region (position $x_3$) of the gap of the Searle cell. The measurement at $x_2$ (C) was taken in the middle of the gap indicating the position of the twin boundary layer. The measurement at $x_1$ (D) was taken close to the inner rotor in the gap indicating the presence of twin “A”. The corresponding model calculations are shown in the lower panel (E, F, G, H).

Fig. S2 shows measured rheo-SANS patterns of a 15% PI(55)-PEO(170) solution after shearing at 500 s$^{-1}$ and sudden cessation of shear. Fig. S2A shows the measured scattering pattern in the radial sample position, probing the [111]-direction of the lattice.

A calculated scattering pattern is shown in Fig. S1D. The model calculation using Eq. (1) allows one to obtain the characteristic structural parameters of the FCC crystal. We observe a unit cell dimension of $a = 70$ nm (mean displacement $\sigma_a = 0.03$) and micellar core radius of $R = 12$ nm (mean rel. std. dev $\sigma_R = 0.07$).

The peak shapes can be well described by an anisotropic Gaussian peak shape with longitudinal coherence lengths of $l_{210} = l_{110} = 200$ nm and $l_{111} = 90$ nm as derived from the Gaussian peak widths $\sigma_{210}$, $\sigma_{110}$, and $\sigma_{111}$ via Eq. (15). The calculated scattering patterns in Figs. S2F-H are calculated for the [110]-direction assuming twin “B” ($r=0.0$, S1F), twin coexistence ($r=0.5$, S1G), and twin “A”-dominance ($r=0.8$, S1H) using the same structural parameters as in Fig. S1E.
Fig. S3: Rheo-SANS scattering patterns of a shear-oriented FCC twin phase of a 16%wt PI(55)-PEO(170) in D_{2}O, presheared at 200 s^{-1} (A) Measured scattering pattern in the “radial” beam position probing the [111]-direction. (B, C, D, E) Measured scattering patterns in the “tangential” beam position probing the [110]-direction at four different positions x_{1} - x_{4} in the gap. The distorted hexagonal array of the first-order reflections in (B) indicate the presence of twin “B” at the outer position x_{4} of the gap of the Searle cell. The measurement at x_{3} (C) was taken further in the middle of the gap. We observe Debye-Scherrer rings indicating an irregular arrangement of twinned domains. In the subsequent position x_{2} (D) both twins are observed in their oriented state. Close to the inner rotor (E) at position x_{1} we observe twin “A”. This measurement shows that high pre-shearing rates of > 200 s^{-1} are required to induce macroscopic twin growth.

Fig. S4: Rheo-SANS scattering patterns of a shear-oriented FCC twin phase of a 16% wt PI(55)-PEO(170) in D_{2}O, presheared at 1000 s^{-1} (A) Measured scattering pattern in the “radial” beam position probing the [111]-direction. (B, C, D, E) Measured scattering patterns in the “tangential” beam position probing the [110]-direction at four different positions x_{1} - x_{4} in the gap. The distorted hexagonal array of the first-order reflections in (B) and (C) indicate the presence of twin “B” at the outer positions x_{1} and x_{4} of the gap of the Searle cell. The measurement at x_{3} (D) was taken in the middle of the gap indicating the position of the twin boundary layer. The measurement at x_{1} (D) was taken close to the inner rotor in the gap indicating the presence of twin “A”.

Fig. S4 displays measured rheo-SANS patterns of a 16% PI(55)-PEO(170) solution after shearing at 1000 s^{-1} and sudden cessation of shear. Fig. S4A shows the measured scattering pattern in the radial sample position, probing the [111]-direction of the lattice. We observe the presence of twin “B” at the outer and central gap positions x_{2} - x_{4} (S4B,C,D), whereas at the inner position x_{1} close to the rotor we observe a regular hexagon with the coexistence of both twins.
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Fig. S5 shows measured rheo-SAXS patterns of a 13% PI(62)-PEO(193) solution in H2O after shearing at 500 s⁻¹ and sudden cessation of shear. Here we show the scattering pattern measured in the radial sample position (Fig. S5A) and all eleven positions (Fig. S2B – K) in the tangential sample position. We observe twin “B” on all positions x₃ – x₁₁ in the outer region of the gap. At position x₂ the scattering pattern is symmetric, containing the twin boundary surface, and at location x₁ we observe twin “A”.

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**Fig. S5**: Synchrotron rheo-SANS scattering patterns of a shear-oriented FCC twin phase of a 13%wt PI(62)-PEO(193) in H2O, presheared at 1000 s⁻¹. (A) Measured scattering pattern in the “radial” beam position probing the [111]-direction. (B - L) Measured scattering patterns in the “tangential” beam position probing the [110]-direction with a complete scan over eleven different positions x₁₁ – x₁ through the gap of the Searle cell. The distorted hexagonal array of the first-order reflections in (B - J) indicates the presence of twin “B” at the outer position x₁₁ until position x₃ in the gap of the Searle cell. In the subsequent position x₄ (K) both twin are observed in their oriented state. Close to the inner rotor we observe the presence of twin “A”.

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