Experimental report

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Proposal: 9-11-2101 **Council:** 10/2022

Title: Study of the crystallisation underflow of star-polymer in the flow direction to probe bcc-to-fcc transition

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: 1,4-polybutadiene star polymers

Instrument	Requested days	Allocated days	From	To
D22	2	2	24/05/2023	26/05/2023

Abstract:

Star polymers are ultrasoft colloidal particles obtained by tethering a number f of linear polymer chains (arms) to a common center. It has been shown that the application of shear promotes cooperative rearrangements of the star polymer and arm disengagement leading to crystal formation.
RheoSANS experiment using a common cop-and-bob geometry has shown that the softness and morphology of the object apparently play an important role on the nucleation process and crystallisation kinetics [Phys. Rev. Lett. 120, 078003 (2018)]. Furthermore, computer simulations has shown that a bcc-to-fcc transition is promoted under constant flow. To further investigate this phenomenon, here we propose to use the 1,2 shear cell only available on D22 to measure the behaviour of star polymers with different softness under flow. As indicated by computer simulated scattering patterns, the emergence of the bccc-to-fcc transition can be detected only in the flow plane.

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The beamtime was dedicated to the investigation of crystallization under shear of dense suspensions of multi-arm star polymers. Indeed, while these dense suspensions typically form amorphous glass states in quiescent conditions, application of shear, that promotes cooperative rearrangements and arm disengagement, can induce glass melting and crystallization. Furthermore, shear can also induce crystal-crystal transitions. In particular, the goal of the SANS experiments was that of providing clear evidence of a shear-induced bcc crystal-fcc crystal transition that is supposed to occur in a limited range of packing fractions, applied shear rates or oscillation frequencies and is a signature of the ultrasoft nature of star polymers. For the planned experiment the 1,2 shear cell available on D22 is an ideal tool, since it allows to measure the sample structure in the velocity-gradient plane, where the structural variations due to crystallization are maximal.

The sample investigated was a dense suspension of a f = 122 arm polybutadiene (PB) star. The original concentration prepared was c = 1.52c*, being c* the polymer overlap concentration, corresponding to a packing fraction $\eta \approx 0.155$. The packing fraction was chosen according to previous investigations indicating shear-induced crystallization at this value. After loading the sample in the 1,2 cell, continuous shear at increasingly large shear rate was imposed to the sample, and the scattered intensity I(Q) was collected every 30 minutes. The measured I(Q) indicates an amorphous structure of the sample: unfortunately, no evidence of significant structural variations indicating the onset of crystallization was observed, as shown in Fig.1a. Since oscillatory shear is typically more effective in inducing crystallization of dense colloidal suspensions, we subjected the sample to oscillatory shear with an amplitude $\gamma_0 \approx 13.6\ \%$ and a frequency equal to 0.8 Hz. The scattered intensity I(Q) measured every 20 minutes for a total of 3 hours did not show indications of crystallization, rather suggesting the onset of some aggregation in the sample associated with the increase of the forward scattering (Fig.1b). Due to the lack of shear-induced crystallization, we decided to dilute the sample with the aim of accessing the region of the state diagram where the bcc-to-fcc transition should be observed. The sample was diluted to c = 1.36c* ($\eta \approx 0.137$), where crystallization could also be expected from previous work. The sample was subjected again to oscillatory shear with $\gamma_0 \approx 13.6\ \%$ and a frequency equal to 0.8 Hz. The I(Q) measured at different times after application of shear indicated a progressive shift of the structure factor peak to larger Q values, and an increase in its intensity, indicative of a progressive structuration of the sample. While this evolution suggested the possible tendency to a crystalline state, no lattice peaks and Bragg reflections in the 2D detector pattern could be observed after 13h of measurements (Fig.1c). As a last attempt we also modified the oscillation frequency to 1.6 Hz, however the I(Q) did not show additional evolution (Fig.1d).

In conclusion, while we could obtain preliminary indications of a shear-induced partial ordering of the system, no clear evidence of shear-induced crystallization could be obtained. Fine tuning of the packing fraction and shear protocol might be necessary in future experiments to observe the expected structural transition.

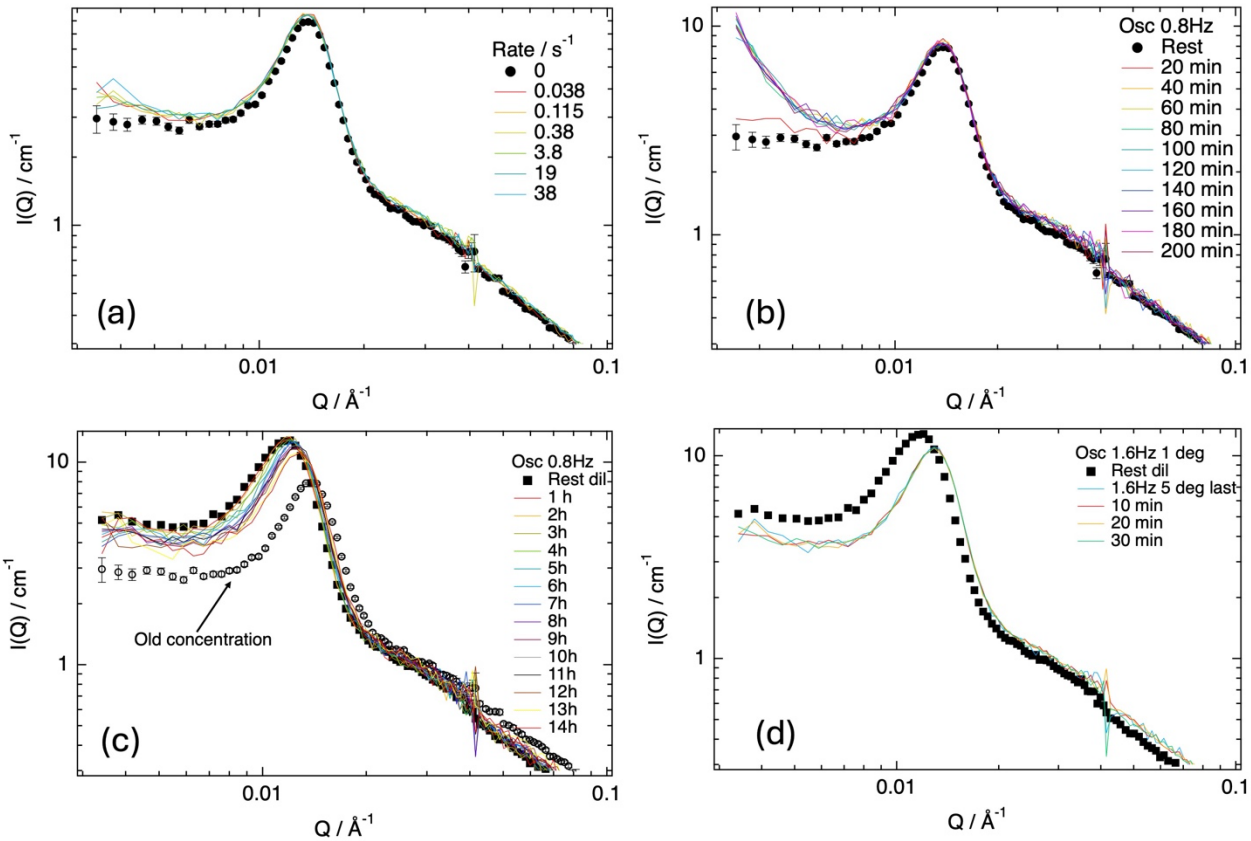

Figure 1: SANS scattering intensities I(Q) measured for (a) $\eta \approx 0.155$ and different shear rates $\dot{\gamma}$ (as indicated) under continuous shear (b) $\eta \approx 0.155$ and different times after application of oscillatory shear at $\gamma_0 \approx 13.6\ \%$ and a frequency equal to 0.8 Hz. (c) $\eta \approx 0.136$ and different times after application of oscillatory shear at $\gamma_0 \approx 13.6\ \%$ and frequency equal to 0.8 Hz (d) $\eta \approx 0.136$ and different times after application of oscillatory shear at $\gamma_0 \approx 13.6\ \%$ and frequency equal to 1.6 Hz.