Experimental report

23/02/2016

Proposal:	**9-11-1745**	**Council:**	4/2015
Title:	Stick-Slip transition of polymer solutions on polymer brushes		
Research area:	Soft condensed matter		

This proposal is a continuation of 9-11-1683

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Local contacts:	Philipp GUTFREUND

Samples:	Polystyrene solution Polymer brush

Instrument	**Requested days**	**Allocated days**	**From**	**To**
FIGARO User-supplied	4	3	20/10/2015	23/10/2015

Abstract:

From rheology it is known that entangled polymer melts or solutions do not obey the stick boundary condition at a solid wall when exposed to high shear stress. This may display an interfacial stick-slip transition (SST) where the apparent flow rate jumps discontinuously due to a massive wall slip. Although this phenomenon is frequently observed in polymer tribology and several theoretical models exist to describe it, a direct experimental observation of its origin is still lacking. In our experiment we will use in situ shear neutron reflectometry to record the theoretically proposed structural change during SST.

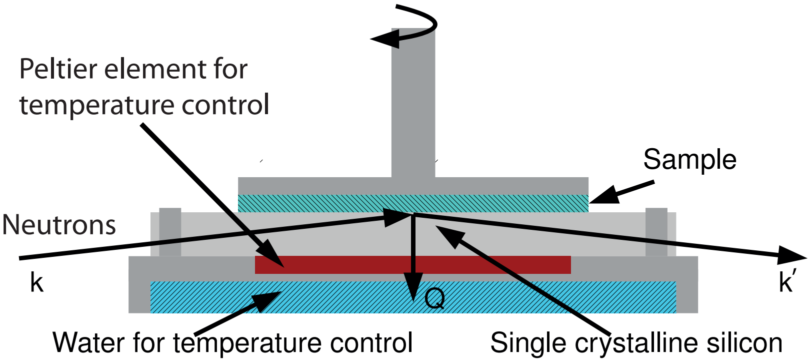


FIGURE 1. Schematic drawing of the rheo-reflectometry set-up. The neutrons are impinging through the silicon and are reflected at the solid/liquid interface.

A combined Small Angle Neutron Scattering (SANS) and Grazing Incidence Transmission SANS (GT-SANS) study of sheared polystyrene (PS) solutions was performed on FIGARO by using the *Anton Paar MCR 501* rheometer recently purchased by the PSCM in a plate/plate set-up [**1**]. The scattering geometry with downward reflection of the neutrons impinging through a silicon wafer is shown in fig. 1.

The aim of this series of experiments was to measure the form and structure factors of the polymer coils under shear. Tube theory predicts an alignment of the tubes at shear rates Wi >1. A deformation of the polymer coils is predicted at a shear rate Wi $>\mathrm{N}/\mathrm{N}_e$ where N/N_e denotes the number of entanglements per chain [**2**].

1. 22wt% 600k dPS in DEP solution

First GT-SANS was performed on a solution of deuterated PS chains (575 kg/mol (N=5127), PDI = 1.09, Polymer Source) solved in diethyl phtalate (DEP, good solvent) at 22 wt% concentration. Those measurements were performed at about 48°C. The shear rates were up to 300 s^{-1} in plate-plate geometry which were still in the Newtonian regime for this solution. The viscosity was 4.7 Pas. Consequently no detectable SANS intensity was observed.

2. 27vol% 600k dPS in DEP solution

A higher concentration of deuterated PS chains (575 kg/mol (N=5127), PDI = 1.09, Polymer Source) was solved in diethyl phtalate (DEP, good solvent) at 27 vol% concentration. Those measurements were performed at about 45°C. The shear rates were up to 1090 s^{-1} with shear-thinning starting between 3-10 s^{-1}. The zero-shear viscosity was 290 Pas and the longest relaxation time was measured at about 0.25 s. The SANS intensity started to rise slightly at about 10-40 s^{-1} ($4<\mathrm{Wi}<10$) and significantly at about 70-100 s^{-1} ($18<\mathrm{Wi}<25$). This was observed no matter whether oscillatory shear (up to 30 Hz) or steady shear was applied. The intensity rise was not instantaneous, but equilibrated after approximately 5 min. After stopping shear most of the SANS intensity vanishes after some minutes but macroscopic motion persists (recoil) which could be observed by the normal force leading to SANS signal being present up to 8 h after the intentionally stopped flow. The integrated GT-SANS intensity can be directly correlated to the viscosity as can be seen in fig.2. *In situ* shear NR measurements were performed as well in order to verify the

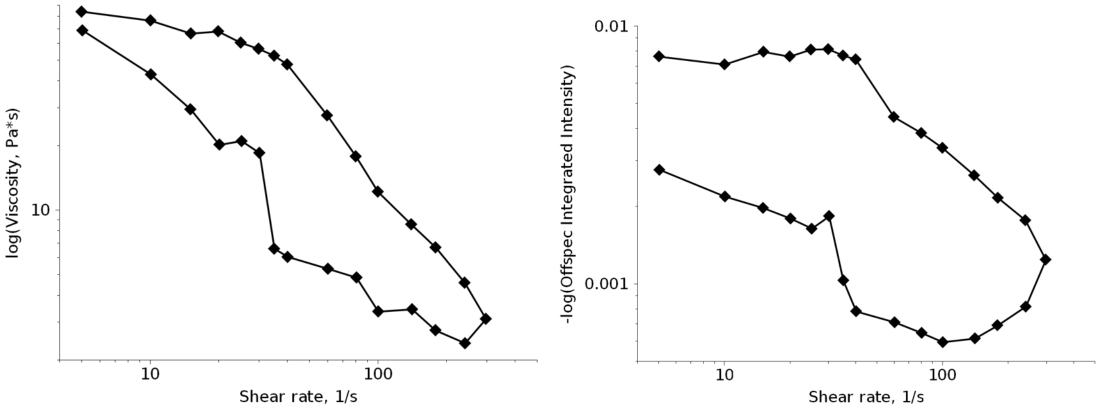


FIGURE 2. Left: Viscosity on a logarithmic scale versus shear rate in a loop of first rising and then falling shear rates. Right: The inverse of the integrated SANS signal on a log-scale versus the same shear rate as on the left.

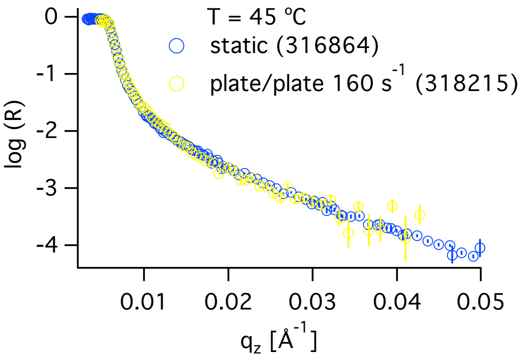


FIGURE 3. Left: NR of a silicon surface in contact with 27% solution of deuterated PS (575 kg/mol) in DEP.

correct polymer concentration in the bulk and to watch for any change at the silicon/liquid interface. As can be seen in fig. 3 the reflectivities show no change with shear stress if the SANS scattering is subtracted from the specular signal. The full GT-SANS pattern can be observed in fig. 4. It can be seen that the SANS signal is highly asymmetric mostly scattering in the direction of shear gradient. Interestingly even when the q_y-vector was set to be parallel with the neutral or vorticity direction the pattern was unchanged meaning that the scattering is exclusively along the shear gradient direction in this q-range.
We have integrated those patterns along the q_z direction and fitted them with the following equation

$$I(q) = \frac{A}{(1 - q^2\zeta^2)^2}. \tag{1}$$

The results are summarised in table 5. One can see that the correlation length seems to diminish along the shear gradient direction with increasing shear.

In an additional experiment on the SNS Liquids Reflectometer with the same dPS solution in DEP in a cone/plate set-up showed the same effect as can be seen in the raw detector images in fig. 6 showing that cone/plate geometry also leads to the same signal.

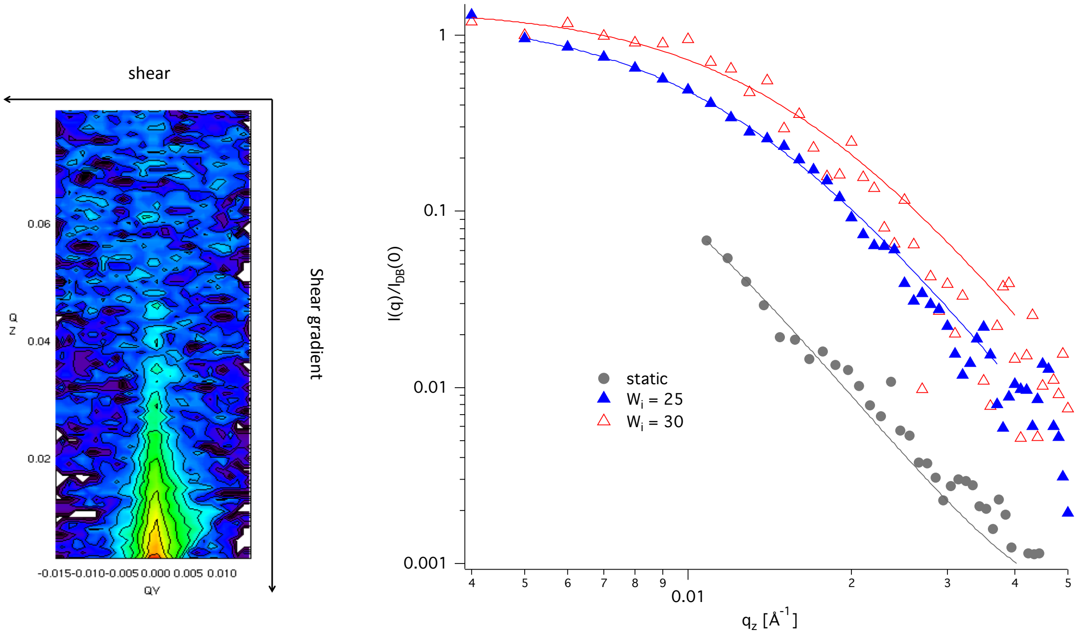
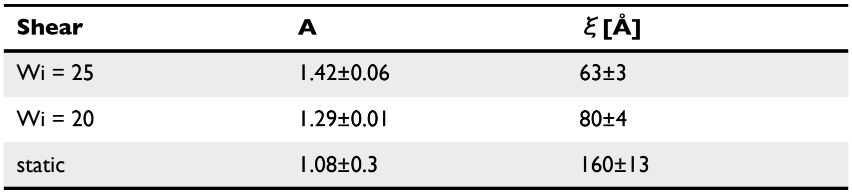


FIGURE 4. Left: GTSANS pattern of a silicon surface in contact with 27% solution of deuterated PS (575 kg/mol) in DEP. Right: q$_z$-integrated intensity of the GT-SANS patterns for different shear rates. The solid lines are Debye-Bueche Fits.



Shear	A	ξ [Å]
Wi = 25	1.42±0.06	63±3
Wi = 20	1.29±0.01	80±4
static	1.08±0.3	160±13

FIGURE 5. Fitting results of the GT-SANS curves with eq. 1.

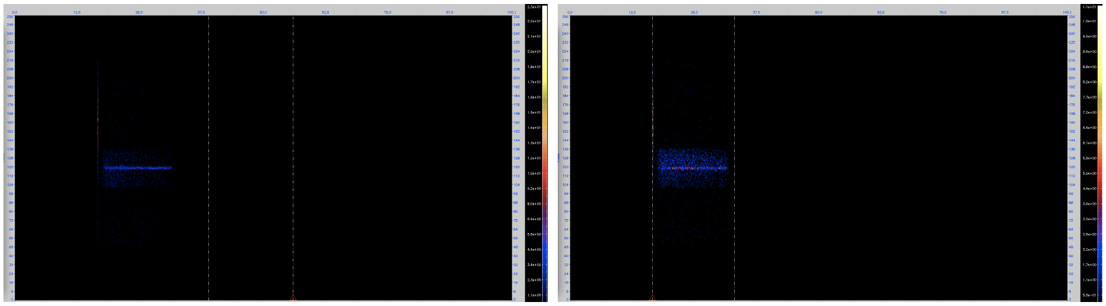


FIGURE 6. Raw NR data of a silcon wafer covered by an initiator SAM in contact with 30% solution of deuterated PS (575 kg/mol) in DEP under static (left) conditions and steady cone-plate shear of 1000 s^{-1} (right).

References

[1] Wolff, M., Kuhns, P., Liesche, G., Ankner, J. F., Browning, J. F., and Gutfreund, P. *Journal of Applied Crystallography* **46**(6), 1729–1733 Dec (2013).

[2] Cates, M. E., McLeish, T. C. B., and Marrucci, G. *Europhysics Letters* **21**(4), 451 (1993).