Experimental report

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Proposal: 9-11-2020 **Council:** 10/2020

Title: Adsorbed Polymers under highly viscous flow

Research area: Physics

This proposal is a new proposal

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Samples: PS-d DEP solution

Instrument	Requested days	Allocated days	From	To
D17	0	3	04/06/2021	07/06/2021
FIGARO	3	0		

Abstract:

In this study, we plan to understand the molecular mechanism underlying in the flow of semi-dilute polymer solutions near a solid interface. Thanks to velocimetry techniques based on photobleaching, we measured the slippage of semi dilute polymer solutions as a function of the volume fraction. The scaling law resulting from this measurements is consistent with two mechanisms: either there is a depletion layer, inducing inhomogeneities of concentrations close to the substrate; or polymer solutions are slipping with the same mechanism as melts at the scale of the bulk polymer correlation length. Neutron reflectivity measurements at rest have shown that polymer chains adsorb onto the substrate which play a major role in the stress transmission mechanism. Here we plan to study the influence of the shear of the polymer solution on the conformation of the surface chains. Such in-situ experiment combined with our slippage measurements should highlight the overall behaviour of polymer solutions flowing onto weakly adsorbing surfaces.

Experimental report: Adsorbed polymers under highly viscous flow

Introduction

In a previous experiment performed on the HERMES neutron reflectometer at LLB, we have studied semi-dilute solutions of polystyrene in diethylphtalate on a quartz wafer. The reflectivity curves obtained suggest that polystyrene chains adsorb on the substrate and the extension of the adsorbed layer is of the order of the blob size of the solution. These experiments have been conducted on a static liquid, and we wanted to see the effect of flow on the near-surface concentration profile. To this end, we have upgraded the measuring cell in order to generate flows at high Weissenberg numbers (up to unity). However, for practical reasons, the new experiment has been done on a sapphire wafer instead of a quartz wafer. The results are shown below.

1 Methods

1.1 Cell

The cell is hermetically closed. It is 4 cm large and 8 cm long. The gap h of the cell is 1 mm high, controlled by a rectangular Viton frame. The liquid is injected with a syringe, from bottom to top. The cell is cleaned with toluene and the surface is put under strong UV/light prior to each experiment (except when we want to re-use the surface that has been in contact with the solution before).

1.2 Samples

The solvent is always hydrogenated diethylphtalate (DEP-H) and the solute is polystyrene (PS), either deuterated (-D) or hydrogenated (-H) depending on the desired contrast matching, with various molar masses. All the measurements have been done on a sapphire surface, either freshly cleaned or after contact with a PS-D/DEP-H solution. The solution is always in a semi-dilute regime of concentrations. The details of the solutions are given in Fig.1.

Name	Solvent	Solute	M_n [Mg/mol]	ϕ [%]	τ_{rept} [s]
S	DEP-H	None	/	/	/
D1	DEP-H	PS-D	0.195	3	0.06 ms
D2	DEP-H	PS-D	0.195	6	0.4 ms
D3	DEP-H	PS-D	1.56	3	0.03 s
D4	DEP-H	PS-D	1.56	6	0.2 s
H1	DEP-H	PS-H	0.708	6	0.02 s
H2	DEP-H	PS-H	2.89	6	1 s

Figure 1: **List of samples**. M_n is the molar mass, ϕ the volume fraction and τ_{rept} an estimated reptation time.

1.3 Measurement

Each measurement is done at two angles of incidence $\alpha_1 = 0.5°$and $\alpha_2 = 2.5°$. The acquisition time is 30 min for α_1 et 60 min pour α_2. The injection is done using a Chemyx Fusion 6000 syringe pump. For each system, we do a measurement in a static condition before doing measurements under flow. The flow rate is chosen to reach Weissenberg numbers Wi up to 1. The acquisition time is limited by the quantity of liquid in the injection syringe. For the highest flow rates, we do stroboscopic measurements by alternating between injection and withdrawal of the liquid at the same flow rate. The list of the measurements is shown in Fig.2.

2 Results

2.1 Effect of the molar mass

We first try to compare the concentration profile of solutions of PS-D/DEP with two different molar masses at a given volume fraction $\phi = 6$ %. The results are shown in Fig.3 for $M_n = 195$ kg/mol and $M_n = 1.56$ Mg/mol.

Surface	Sample	Flow rate Q (mL/min)	Weissenberg number Wi
Bare sapphire	S	static	/
Bare sapphire	D1	static	/
Bare sapphire	D2	static ; 0.3 ; 18	/ ; 3.10^{-4} ; 2.10^{-2}
Bare sapphire	D3	static	/
Bare sapphire	D4	static; 0.3 ; 0.9	/ ; 0.1 ; 0.4
Sapphire after D4	S	static	/
Sapphire after D4	H1	static ; 5.0	/ ; 0.3
Sapphire after D4	H2	static ; 0.4	/ ; 1.2

Figure 2: **List of measured configurations.** The apparent Weissenberg number is estimated by $\mathrm{Wi} = \frac{6Q\tau_{\mathrm{rept}}}{lh^2}$ with Q the flow rate, $h = 1$ mm the thickness of liquid and $l = 4$ cm the width of the cell.

In both cases, we obtain a depletion profile of similar sizes (54.4 Å for the 195 kg/mol solution and 63.5 Å for the 1.56 Mg/mol one).

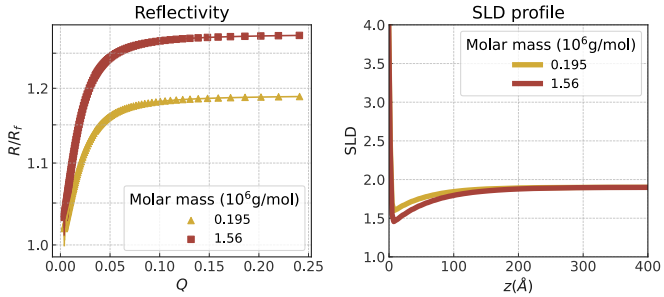

Figure 3: **Effect of molar mass.** Both are done on bare sapphire, without flow. The volume fraction is $\phi = 6$ %. We find a size of the depletion zone $\delta = 54.4$ Å for the 195 kg/mol PS and $\delta = 63.5$ Å for the 1.56 Mg/mol PS.

2.2 Effect of the volume fraction

We compare the density profiles of the solution at two different volume fractions (3 % and 6 %). We find that the thickness of the depleted layer is around 54 Å for $\phi = 6$ % and 103 Å for $\phi = 3$%, which is consistent with de Gennes theory [1], [2] for which the size of the depletion zone δ scales as $\phi^{-3/4}$.

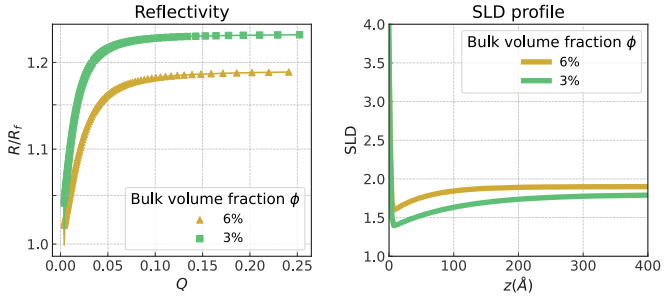

Figure 4: **Effect of volume fraction.** Both are done on bare sapphire, without flow. The molar mass is 195 kg/mol for both. We find a depletion zone of size $\delta = 54.4$ Å for the % solution and $\delta = 103$ Å for the 3 % solution.

2.3 Discussion about adsorption

We have compared the signals for DEP/sapphire interfaces, one with clean sapphire, and the other with a sapphire that has been put in contact with a PS-D/DEP solution (sample D2) during a few hours prior to the experiment, and has been rinsed with DEP. The result is shown in Fig.5.

The first observation is that the reflectivity curves for DEP on bare sapphire and on sapphire which has been in contact with a solution are different. This indicates that some PS chains remain adsorbed on the surface of the sapphire. The curve for DEP/adsorbed sapphire can be fitted by an adsorption model with a typical thickness of adsorbed layer around 5.2 Å. This is *a priori* in contradiction with the results from Fig.3 and Fig.4 for which we observe a depletion of polymer chains near the interface. Our hypothesis is that when the solution is in contact with the sapphire surface, the chains are globally repelled by the interface, but some of them adsorb on preferential sites, which can be inhomogeneities on the solid surface. These adsorbed chains are then visible when the substrate is rinsed and faces only the solvent. The very low amount of adsorbed chains and their large coil size in pure solvent results in a very low contrast. This does not allow us to get a fitted segment density profile in agreement with Guiselin pseudo-brushes as expected [3].

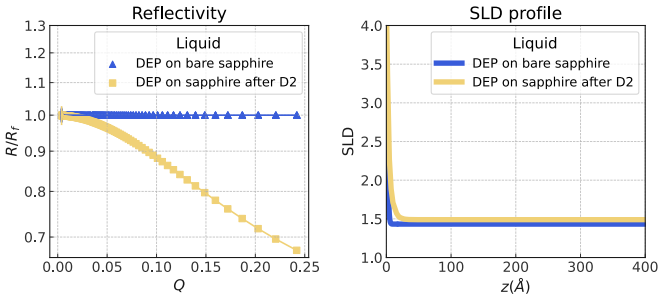

Figure 5: **Effect of contact between the substrate and the PS/DEP solution.** The adsorption profiles have a typical size $\delta = 5.2$ Å for DEP on sapphire after D2.

2.4 Effect of the flow

We have compared the concentration profiles for solutions flowing at different flow rates. The curves shown in Fig. 6 correspond to flow rates which gives Weissenberg numbers up to 0.4. We do not observe any effect of the flow rate on the concentration profile up to these values. The measurements done with flowing H1 and H2 solutions (not shown here) lead to the same conclusions.

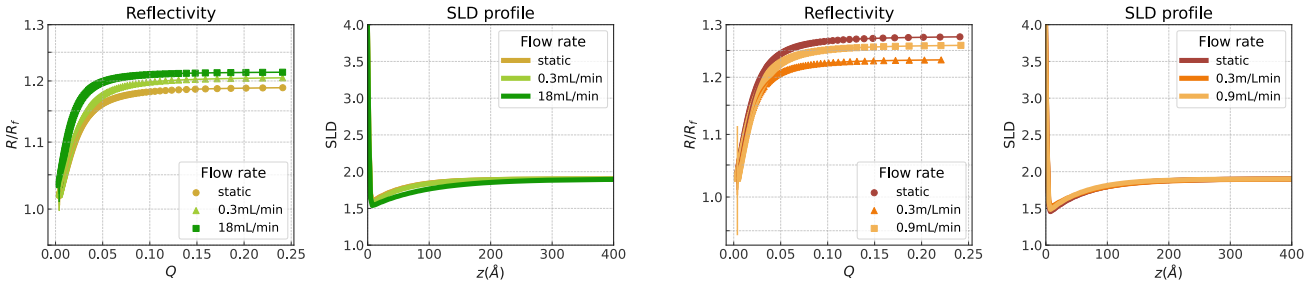

Figure 6: **Effect of flow rate.** The solutions are D2 (left) and D4 (right) on bare sapphire. The curves correspond to Weissenberg numbers of 0, 3.10^{-4} and 2.10^{-2} for D2 and 0, 0.1 and 0.4 for D4.

Conclusion

We evidenced the presence of a polymer depleted layer close to the sapphire interface. The size of the depletion region follows the scaling described by De Gennes. Surprisingly, we notice that even if we observe depletion near the interface, some chains still adsorb on the solid substrate. We think that there are some preferential sites of adsorption due to structural inhomogeneities on the surface. The depleted concentration profiles were found to be insensitive to the flow in the range of flow rates studied, probably because of the small amount of adsorbed chains on the substrate. These results open the question of the effect of high flow rates in the case of highly adsorbing surfaces.

References

[1] P.-G. de Gennes (1981) Polymer solutions near an interface. Adsorption and depletion layers, Macromolecules, 14(6), 1637-1644.

[2] J.-F. Joanny, L. Leibler and P.-G. de Gennes (1979) Effects of polymer solutions on colloid stability, Journal of Polymer Science: Polymer Physics Edition, 17(6), 1073-1084.

[3] O. Guiselin (1992) Irreversible Adsorption of a Concentrated Polymer Solution, Europhysics Letters, 17(3), 225-230.