Near Surface Crystallization of Pluronic P123

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Abstract. On a hydrophilic substrate the growth of a Bragg peak was observed at $Q \approx 0.05 \ \AA^{-1}$ which we attribute to a layering of micelles. This ordering is destroyed when the system is sheared. When shear is removed, it builds up and reaches equilibrium at ambient temperature after approximately 700s. However, there is a waiting time of 200s before any structure becomes visible again. When lower shear rates are applied the ordering recovers more quickly, but it does not build up to the same extent.

1. Introduction
Aqueous solutions of tri-block copolymers PEO-PPO-PEO are well-known for the reduction of surface tension and friction at an interface. For these reasons they are used in many washing agents or lubricants [1, 2, 3, 4, 5]. In medical applications tri-block copolymers are used as drug delivery agents, wound stabilizers or structural gels [6, 7, 8, 9]. At low temperatures PPO and PEO show good solubility in water. With increasing temperature, however, especially the PPO block undergoes a distinct dehydration, accompanied by an increase in hydrophobicity. Above the critical micellization temperature (CMT), micelles are formed with a hydrophobic core (PPO) surrounded by a hydrophilic shell (PEO). This makes the surfactants an excellent model system for the study of crystallization in soft matter [10].

Different chemical surface treatments influence the near-interface ordering. In particular crystal growth is preferred at an interface which is attractive for the micelles [11]. Then, coming from a liquid state, micellar layers may build up at the interface driven by an increased polymer concentration even if the bulk concentration is too low for bulk crystallization.

2. Sample and Methods
Our interest focuses on Pluronic P123 (purchased from Sigma Aldrich and used without further purification), which has a central part of 70 propylene oxide (PO) units and two end groups of 20 ethylene oxide (EO) units (EO$_{20}$–PO$_{70}$–EO$_{20}$). It readily forms stable micelles [1, 12, 13, 14]. In concentrated bulk solutions (above 27 weight percent (wt-%)) the micelles self-assemble into crystalline structures at intermediate temperatures [15, 16]. This study focuses on the near surface crystallization of diluted Pluronic P123 below the concentration regime for bulk micelle crystallization with particular emphasis on the effect of shear on agglomerated polymers near an interface. A cone-plate shear device suitable for in-situ neutron reflectometry was built with
a cone angle of 4°. To assure a constant shear rate the servo\(^1\) controls a motor\(^2\) coupled with a gear transmission ratio of 1:25 to the shear cone. Thus, the shear rate is calculated to

$$\dot{\gamma} = \frac{2\pi \cdot n_{\text{rpm}}}{25 \cdot 60 \tan 4^\circ}.$$ 

It is important to control both the sample and the shear cone temperature to minimize the heat transfer to the sample due to friction at the sealing between sample and cooling liquid (see figure 1). The neutron path goes through a silicon crystal plate above which the liquid of interest and the shear cone are located. More details will be given in a forthcoming publication.

![Figure 1](image1.png)

**Figure 1.** Schematic drawing of the shear cell (left), and a picture of the cell (right) with the motor on the top and the tubing system for the cooling water. The neutron entrance window is visible at the bottom of the shear cell.

The pluronic is dissolved in D\(_2\)O to enhance the neutron scattering contrast to the protonated polymer chains and to achieve total reflection at the solid-liquid interface. Taking the density differences for H\(_2\)O and D\(_2\)O in account, the P123 concentration (in wt-%) for a heavy water solutions is

$$c_{\text{D}_2\text{O}} = \frac{1}{1 + \left(\frac{1}{c_{\text{H}_2\text{O}}} - 1\right) \frac{\rho_{\text{D}_2\text{O}}}{\rho_{\text{H}_2\text{O}}}}.$$ 

Thus, the number density of polymers in the solvent is the same as in light water and a comparison with phase diagrams from literature is readily possible.

Reflectometry is the method of choice for the investigation of adsorbates at a molecular scale at a buried solid-liquid interface [17, 18, 19]. The measurements were done at the PLATYPUS reflectometer [20, 21] at ANSTO\(^3\) in Australia. This is a vertical time of flight reflectometer with the capability of scattering downwards to \(Q_{\text{max}} = 0.4 \text{ Å}^{-1}\). The time of flight option is valuable for analyzing the adsorption kinematics because all Q-points are measured simultaneously, in contrast to a monochromatic angular dispersive reflectometer.

\(^1\) Schneider Electric Lexium 05
\(^2\) Schneider Electric BSH0552T01A2A
\(^3\) Australian Nuclear Science and Technology Organization
3. Results
The adsorption kinetics of 2 wt-% P123 dissolved in D$_2$O were investigated after the cessation of shear at a temperature of 68 °C on a hydrophilic silicon substrate. No bulk crystallization occurs in this temperature and concentration regime. Every single reflectivity profile has been accumulated for a period of 60 s. In figure 2 example datasets are shown after the cessation of a shear rate of 50 s$^{-1}$ and 400 s$^{-1}$.

![Figure 2. Comparison of successive reflectivity profiles measured for 60 seconds each after the cessation of a shear rate of 50 s$^{-1}$ (left) and 400 s$^{-1}$ (right).](image)

![Figure 3. Integrated intensity of the Bragg peak after the cessation of different shear rates. The solid lines represent a fit for the model of a logistic function.](image)

The reflectivity profiles were multiplied by $Q^4$ to compensate for the Fresnel reflectivity. A linear function was subtracted to account for background and the oscillation originating from the thin silicon dioxide. The intensity of the Bragg peak was integrated to characterize the recovery.
process. A logistic function was used for refinement of the inflection time $t_0$, the extent of the recovery of the Bragg peak $I_{\text{max}}$ and the growth rate $r$ defined by $I(t) = I_{\text{max}} \left( \frac{1}{1 + \exp(-rt-t_0)} \right)$. This function models an exponential growth in the initial stage combined with a saturation when half of the surface is covered. The inflection time $t_0$ corresponds to the point of inflection of the growth process.

Fit parameters are shown in table 1 and plotted in figure 4. It is remarkable that after a shear rate of $50 \text{ s}^{-1}$ and $100 \text{ s}^{-1}$ the integrated intensity is about equal. After shearing with higher rates the intensity increases linearly. The inflection time seems to increase and the growth rate to decrease with the shear rate.

| Applied shear rate [s$^{-1}$] | $I_{\text{max}}$ [a.u.] | $t_0$ [s] | $r \times 10^{-3} \text{ s}^{-1}$ |
|-----------------------------|----------------|---------|-----------------|
| 50                          | 5.14 ± 0.11 | 70.97 ± 7.16 | 37.8 ± 10.4 |
| 100                         | 4.74 ± 0.12 | 100.7 ± 9.68 | 24.6 ± 5.86 |
| 200                         | 9.24 ± 0.13 | 204.4 ± 5.67 | 19.8 ± 1.94 |
| 400                         | 18.1 ± 0.10 | 576.2 ± 3.20 | 12.4 ± 0.43 |

Figure 4. Inflection time $t_0$, integrated intensity of the Bragg peak $I_{\text{max}}$ and growth rate $r$ plotted as a function of the applied shear rate.

4. Conclusion and Outlook

We have constructed a compact cone-plate shear cell for inverse geometry with temperature stabilization and an encapsulated volume for long time measurements.

The recovery of an adsorbed micellar layer was observed in dependence of the previously applied shear rate. A 2 wt-% solution of P123 dissolved in D$_2$O was measured at 68 °C to emphasize the effect of the interface. It has to be noted, that in this concentration and temperature regime no bulk crystallization occurs as observed in small angle X-ray scattering measurements and rheometry data [16]. Therefore, the ordering (figure 2) is only induced from the hydrophobic interface. Using hydrophobic interfaces, no ordering is observed at all.

The integrated intensity is about the same after stopping the shear rate of 50 s$^{-1}$ and 100 s$^{-1}$. The growth rate $r$ decreases as a function of the previously applied shear rate. The integrated intensity is increased after the cessation of shear with rates above 100 s$^{-1}$. This could be due to a shear induced ordering within the liquid. Also the inflection time of the recovery changes quadratically with the applied rotation speed of the cone. Maybe this is due to the low damping of the rotation of the liquid after stopping the shear cone, a topic which needs further attention in the future. Alternatively, it could also be attributed to shear induced ordering of the polymer within the liquid. The polymer chains may be entangled on the surface and as soon as the shear
rate reaches a critical value, they become free yielding an improved ordering. This would cause a depletion like zone at the interface as a function of the applied shear rate and thus a change in the inflection time and the growth rate. Below this critical shear rate the polymer chains stay entangled close to the interface and the ordering after stopping the shear remains unchanged.

References
[1] Loh W 2002 *Encyclopedia Surface Colloid Sci.* 8 802–813
[2] Alexandridis P and Hatton T 1995 *Colloids and Surfaces A* 96 1–46
[3] Förster S and Konrad M 2003 *J. Mater. Chem.* 33 2671–2688
[4] Bahadur P and Riess G 1991 *Tenside Surf. det.* 28 173
[5] Schmolka I 1977 *J. Am. Oil Chem. Soc.* 54 110
[6] Lin S and Kawashima Y 1985 *Pharm Acta Helv.* 60 339
[7] Yokoyama M 1992 *Crit. Rev. Therapeutic Drug Carrier Syst.* 9 213
[8] Gunzman M, Garcia F, Molpeceres J and Aberturas M 1992 *Int J. Pharm.* 80 119
[9] Kabanov A, Bartakova E, Melik-Nubarov N, Fedoseev N, Dorodnich T, Alakhov V, Chekhonin V, Nazalova I and Kabanov V 1992 *J Controlled Release* 22 141
[10] Mortensen K 1996 *J. Phys.: Condens. Matter* 8 A103–A124
[11] Wolff M, Scholz U, Hock R, Magerl A, Leiner V and Zabel H 2004 *Phys. Rev. Lett* 92 255501
[12] Sasanuma Y 1995 *Macromolecules* 28 8629–8638
[13] Guo C, Wang J, Liu H and Chen J 1999 *Langmuir* 15 2703–2708
[14] Guo C, Liu H and Chen J 1999 *Colloid Polym Sci* 277 376–381
[15] Wanka G, Hoffmann H and Ulbricht W 1994 *Macromolecules* 27 4145–4159
[16] Walz M, Wolff M, Voss N, Zabel H and Magerl A 2010 *Langmuir* 26 14391–14394
[17] Tolan M 1999 *X-ray scattering from soft-matter thin films* (Springer tracts in modern physics vol 148) (Springer-Verlag Berlin)
[18] Als-Nielsen J and McMorrow D 2001 *Elements of Modern X-Ray Physics* (John Wiley & Sons, Ltd)
[19] Daillant J and Gibaud A 1999 *X-Ray and Neutron Reflectivity: Principles and Applications* (Springer)
[20] James M, Nelson A, Holt S, Saerbeck T, Hamilton W and Klose F 2011 *Nuclear Instruments and Methods in Physics Research A* 632 112–123
[21] Nelson A 2010 *Journal of Physics: Conference series* 251 012094