Experimental report

01/09/2022

Proposal:	**9-11-2054**	**Council:**	4/2021
Title:	In-situ observation of polyelectrolyte diffusion		
Research area:	Chemistry		

This proposal is a continuation of 9-11-1958

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Samples: PSS, PDADMA, H2O, NaCl

Instrument	Requested days	Allocated days	From	To
D17	4	3	14/09/2021	17/09/2021

Abstract:

Diffusion of the polyanion within polyelectrolyte multilayers (PEMs) is probed in-situ. The PEMs consist of a deuterated and a protonated slab prepared by selectively deuterated polyanions. Annealing in high salt solution causes interdiffusion which broadens the internal interface between the two compartments and allows to calculate the diffusion constant D. Preliminary experiments indicate a glass transition temperature at 50 - 60°C. The dependence of the diffusion constant on (i) the temperature approaching the glass transition and (ii) the salt concentration at an elevated temperature will be studied systematically. This series of experiments will be explored with a system slightly below the entanglement limit; for better understanding few exploratory experiments substantially above and below the entanglement limit will be performed. These experiments are an essential part of the thesis of Annekatrin Sill and Peter Thran (support by SFB 1270, project A04).

Proposal 9-11-2054. In-situ observation of polyelectrolyte diffusion

Layer-by-layer films (LbL films) are composed of alternating layers of oppositely charged polyelectrolytes (PEs) (synthetic PEs, proteins, DNA or nanoparticles), which are formed by sequential adsorption of oppositely charged polyelectrolytes [1]. LbL films have stimulated great interests from both academic researchers and industry due to their potential applications. Yet, it remains a challenge to control the position and mobility of the molecules within the film for selected applications such as drug delivery.

PDADMA/PSS LbL films formed at 0.1 M NaCl are one of the standard systems, [2-8]. As polycations linear polydiallyldimethylammonium chloride (PDADMA) is used, polystyrene sulfonate (PSS) is the polyanion. We studied *D*(PSS), the diffusion constant of the polyanion, by using a slab architecture: the multilayer consists of selectively deuterated slabs. Previously we exposed the LbL film to an annealing solution for a defined time. Then, the film was dried and investigated by monochromatic neutron reflectometry [3, 5, 9]. To obtain a diffusion constant, LBL-films from the same batch were annealed for individual times, giving a snapshot of the frozen-in polymer movement. Now we went further. We used a single film, annealed it in 1 M NaCl solution, and observed the polymer diffusion in situ (cf. Figure 1), employing neutron time of flight reflectometry. The film consists of a deuterated and a protonated slab. The silicon block was functionalized with a polyethylenimine (PEI) layer. The polycation is PDADMA with M_w(PDADMA) = 44 kDa as polyanions PSS with M_w(PSS) = 75.6 kDa and PSSd with M_w(PSSd) = 80.8 kDa were used. The multilayer (in total 16 bilayers) is built from deposition solutions containing 1mM/Monomer of the respective polyion and 100 mM NaCl.. The resulting film thickness in air was 500 Å (confirmed by in-house XRR). The PEM was measured in D_2O as prepared (black curve) and after the post-treatment in 1 M NaCl (pink curve) with TOF-NR. Measurements in 1 M NaCl solution at 20 °C are shown in Fig. 1 at indicted annealing times. To fit the data and determine a diffusion constant, our approach [5 Soltwedel et al.] was further developed to better model the low-contrast data. Additionally, appropriate constraints were introduced. A PEI slab (with a thickness of 3 nm and a roughness σ_{PEI}) describes the high intensity R/R_F of about 0.5 at large Q_z-values. Its thickness is based on the molecular structure of PEI, since the Q_z-range is not sufficient for an unambiguous fit. This constrain describes the immobile PEI/PSSd layer on the silicon surface, and arouses due to the high charge density of branched PEI.

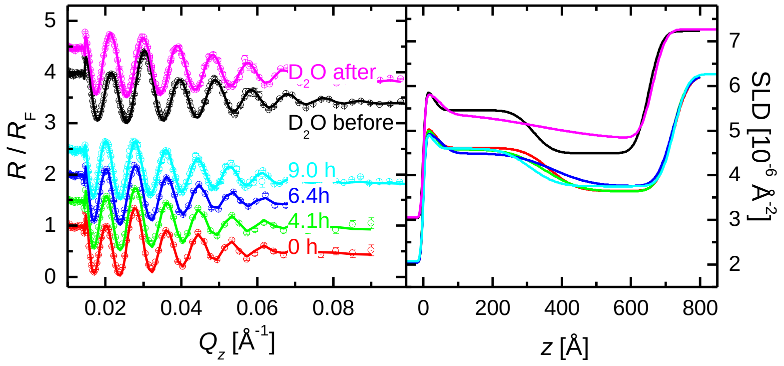

Fig. 1: Annealing of a polyelectrolyte multilayer film in 1 M NaCl solution at 20 °C: neutron reflectivity curves normalized with respect to the Fresnel reflectivity R_F of an ideally flat surface (left) and corresponding SLD profiles (right). The layer sequence is (PEI/PSSd)/(PDADMA/PSSd)$_9$/(PDADMA/PSS)$_6$. For the SLD profiles, z = 0 is set to the interface between the silicon substrate and the deuterated slab. For clarity, both the reflectivity curves and the SLD profiles are shifted vertically.

The aim of the experiments is to determine the diffusion constant of PSS from the widening of the internal interface between the slabs over the diffusion/annealing time. The first challenge was to determine the time 0 of the diffusion when D_2O is exchanged to 1 M NaCl solution. We figured out that looking at the raw data was the best way to see if there was any development over time. We fitted the positions of the first minima and maxima in the Fresnel normalized data. If the thickness of the multilayer changes, there Q_z-positions shift. This is shown schematically in Fig. 2, left. Furthermore, if the internal roughness between the slabs increases (due to the exchange/diffusion of PSS and PSSd), the intensity of the first maximum (blue) should increase and the intensity of the second maximum (red) should decrease. This is shown schematically in Fig. 2, right. We were able to determine these described changes for the film under investigation and were then able to determine the development of the internal roughness between the slabs over the diffusion time (Fig. 3).

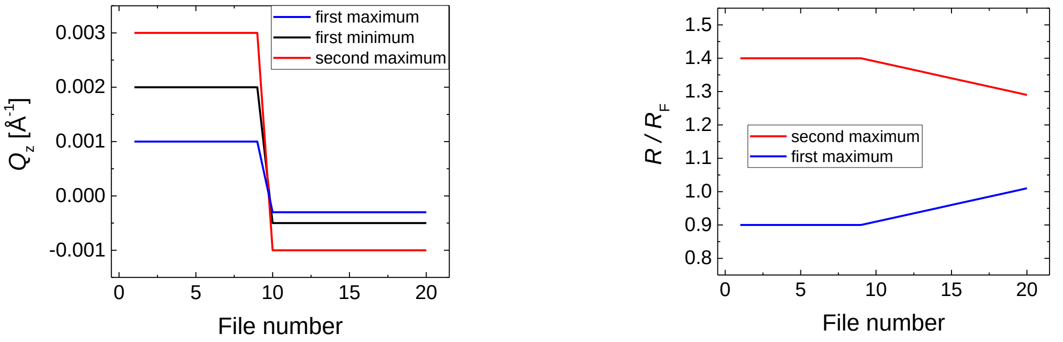

Fig. 2: Simplified representation of the changes during solvent exchange of D_2O to 1 M NaCl solution. Left: Difference in Q_z-values of the first two maxima and the first minimum of the normalized neutron reflectivity curves. Right: Peak intensity of the first and second maximum.

Looking at the internal roughness over the square root of the annealing time, we can assume that two diffusion processes are taking place, one fast and one slow (see Fig. 3). We have already shown the diffusion of a fast and a slow PSS fraction in another system (72 kDa PDADMA, high annealing temperatures; see Sill et al. 2021). The diffusion constant of the fast process fits well with the determined diffusion constant of the same system via a snapshot experiment [9]. Further measurements are needed to make more precise conclusions. It was also unexpected that the thickness increase of the films depends on the salt concentration in the solution (see Fig. 4). To our knowledge, this salt-dependent swelling was described in the literature for the first time in April of this year [10]. We plan to quantify the swelling of the films in solutions with in-situ ellipsometry [3, Sill et al. 2020]. Then we will have a measure of whether a solvent exchange was successful.

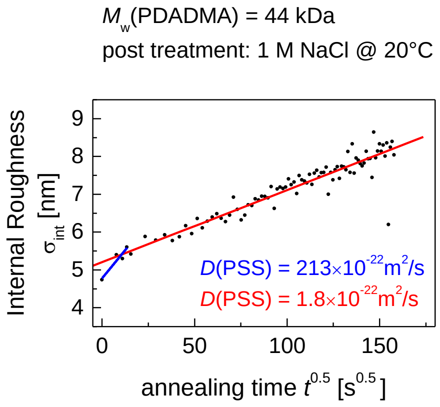

Fig. 3: Internal roughness vs square root of annealing time. Two diffusion constants were determined.

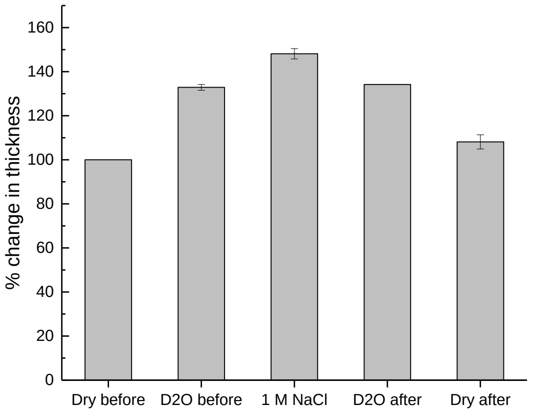

Fig. 4: Percent change in film thickness determined from two films post-treated in 1 M NaCl solution.

We were able to show that our idea of in-situ measurements works in general. However, the system behaves differently in aqueous solutions than we had expected. . The crucial parameter to trigger and adjust the diffusion is the salt concentration in the LbL-film, which might be altered by the swelling history of the film as well. Compared to a dry LbL-film, the lower osmotic pressure of an already swollen LbL-film might lead to a lower salt concentration in the film, upon direct exposure to an annealing solution. Further experiments are necessary to optimize the method and to better understand the system.

References

1 Decher G, *Science* (1997) 277, 1232.; Von Klitzing R, *PCCP*, (2006) 8, 501; Costa RR, Mano JF (2014) *Chemical Reviews* 43 (2014) 3453.

2 Lavalle P, Gergely C, Cuisinier FJG, Decher G, Schaaf P, Voegel JC, Picart C.*Macromolecules* 35 (2002) 4458.

3 Nestler P, Paßvogel M, Helm CA, *Macromolecules* 46 (2013) 5622; Paßvogel M, Nestler P, Köhler R, Solltwedel O, Helm CA, *Macromolecules* 49 (2016) 935; Sill A, Nestler P, Weltmeyer A, Paßvogel M, Neuber S, Helm CA *Macromolecules* 53 (2020) 7107; Sill A, Nestler P, Thran P, Helm CA, *Macromolecules*, 54 (2021) 9372.

4 Selin V, Ankner JF, Sukhishvili SA, *Macromolecules* 48 (2015) 4983.

5 Nestler P, Paßvogel M, Ahrens H, Köhler R, Helm CA, *Macromolecules* 48 (2015) 8546; Soltwedel O, Ivanova O, Nestler P, Müller M, Köhler R, Helm CA *Macromolecules* 43 (2010) 7288.

6 Selin V, Ankner JV, Sukhishvili SA, *Macromolecules* 50 (2017) 6192.

7 Lalwani SM, Eneh CI, Lutkenhaus JK, *Physical Chemistry Chemical Physics* 22 (2020) 24157.

8 Mueller R, Köhler K, Weinkamer R, Sukhorukov G, Fery A, *Macromolecules*, 38 (2005) 9766.

9 Sill A, Nestler P, Azinfar A, Helm CA, *Macromolecules*, 52 (2019) 9045.

10 Eneh CI, Kastinen T, Oka S, Batys P, Sammalkorpi M, Lutkenhaus JL *ACS Polymers Au*, 2 (2022) 287.