Experimental report

15/02/2021

Proposal:	**9-11-1958**	**Council:**	10/2019
Title:	Polyelectrolyte diffusion in layer-by-layer films approaching the glass temperature		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples: thin films of polystyrene sulfonate and polypolydiallyldimethylammonium chloride

Instrument	Requested days	Allocated days	From	To
D17	6	3	28/08/2020	31/08/2020

Abstract:

Center-of-mass diffusion of the polyanion within polyelectrolyte multilayers prepared by Layer-by-Layer technique is measured at different temperatures using neutron reflectometry in the TOF mode. Preliminary experiments suggest that the diffusion constant of the polymers increases by at least four orders of magni-tude on approach of the glass temperature. Furthermore, the influence of the polycation molecular weight and the salt concentration is to be investigated. Temperature equilibration and liquid/liquid exchange will be tested on the first day of experiments. These experiments constitute an essential part of the doctoral theses of Amir Azinfar and Annekatrin Sill.

Experimental Report of Project 9-11-1958: Polyelectrolyte diffusion in layer-by-layer films

University of Greifswald: Annekatrin Sill, Heiko Ahrens, Christiane A. Helm
Local Support: Samantha Miciulla, Philipp Gutfreund (remote experiment)

Up to now, we measured polyelectrolyte diffusion in layer-by-layer films by immersing the film for a defined amount of time into the annealing solution; then the film was dried, and a snapshot was taken [1,2]. For the first time, the dynamics of our films was studied in-situ at D17. To study the vertical polyanion diffusion, we use a slab architecture with selective polyanion deuteration. As polycation linear polydiallyldimethylammonium chloride (PDADMA) is used, polystyrene sulfonate (PSS, PSS-d) is the polyanion. Each film consists of a protonated and a deuterated slab. Two sets of films were examined: (1) films were annealed in 0.1 M NaCl in D_2O at 37 °C, varied was the molecular weight of the polycation (cf. Fig. 1). (2) films were annealed at different annealing temperatures (cf. Fig. 2).

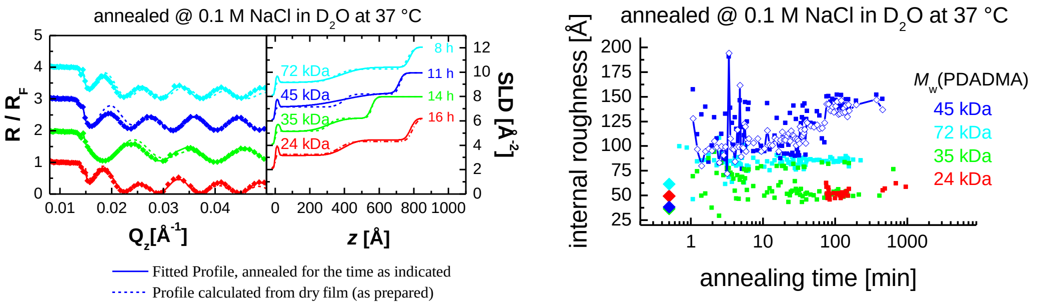

Figure 1. Normalized neutron reflectivity curves (left) measured at D17 and corresponding SLD profiles (centre) of PDADMA/PSS multilayers in D_2O solution built from polycation PDADMA with different molecular weight as indicated. The internal roughness versus the annealing time is shown on the right, for M_w(PDADMA)=45 kDa it increases with time (the large diamonds refer to the internal roughness of freshly prepared films in air, 63 % r.h.; similar values were measured before [1,2].). For clarity, the reflectivity curves are shifted vertically. For the SLD profiles, z = 0 is set to the interface between the oxide layer of the silicon block and film.

The molecular weight of the polycation PDADMA was selected below and above the entanglement limit [2]. PDADMA/PSS multilayers were built from 100 mM NaCl solution, for PSS and PSS-d a molecular weight is 76-81 kDa while the molecular weight for PDADMA is varied (cf. Fig. 1). With increasing annealing time, the width of the internal interface between the blocks increases. From the time dependence of the internal roughness σ_{int} the diffusion constant D_{PSS} is calculated [1,2]. An increase of σ_{int} with annealing time is observed for M_w(PDADMA) = 45 kDa (below the entanglement limit; the polycation also has a slightly lower degree of polymerization than the polyanion). Due to the weak contrast of the reflectivity curves, different constraints of the least square fits led to different values of σ_{int} (indicated in Fig.1, right by different blue symbols).

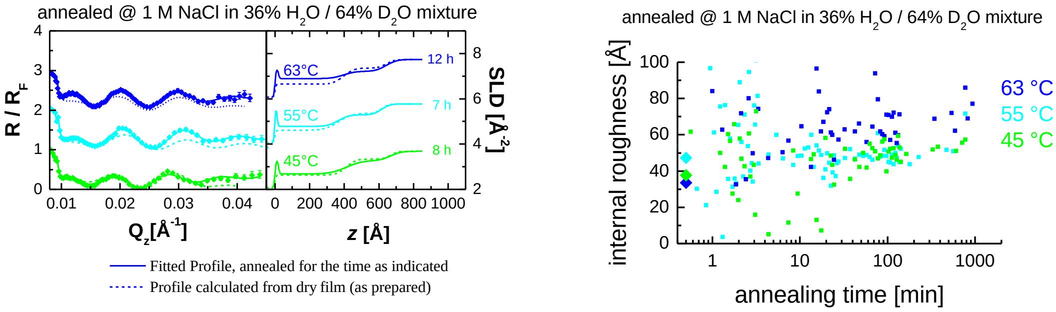

Fig. 2. Normalized neutron reflectivity curves (left) measured at D17 and corresponding SLD profiles (centre) of PDADMA/PSS multilayers in H_2O/D_2O (1:2) with 1 M NaCl at different temperatures (M_w(PDADMA)=117 kDa). The dependence of the internal roughness on the annealing time is shown on the right.

Increasing roughness with annealing time is also observed at different temperatures (cf. Fig. 2). However, due to weak contrast (H_2O/D_2O 1:2), the error bars were even larger. The experiments show that the dynamics of the film can be observed in-situ. However, the contrast must be improved for quantification.

References

[1] Soltwedel O et al., *Macromolecules* **43** (2010) 7288; Sill A et al., *Macromolecules*, **53** (2020) 7107.
[2] Sill A et al., *Macromolecules*, **52** (2019) 9045.