Experimental report

19/05/2020

Proposal:	**9-11-1928**	**Council:**	4/2019

Title: Co-solvent dependent swelling and switching kinetics of PMMA-b-PNIPAMthin films

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: PMMA-b-PNIPAM

Instrument	Requested days	Allocated days	From	To
D17	5	5	12/09/2019	17/09/2019

Abstract:

It is known that the collapse transition temperature can be tuned by introducing co-solvents into aqueous solutions due to the competitive attachment and detachment of water and co-solvent to the PNIPAM chain. In the present study we increase the complexity by studing block copolymer films. We want to monitor the development of thickness and refractive index whilst investigating morphological changes and the kinetics of individual solvent and co-solvent diffusion into PMMA-b-PNIPAM films. We intend to compare the co-solvents acetone and dimethyl sulfoxide. Both are aprotic yet miscible with water across the whole solvent-co-solvent binary. Moreover, both are available as deuterated derivatives, have suitable vapor pressure and cause a co-nonsolvency based decrease of the LCST at low molar fraction.

Co-solvent dependent swelling and switching kinetics of PMMA-*b*-PNIPAM thin films

(Proposal 9-11-1928)

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The diblock copolymer PMMA-*b*-PNIPAM forms micelles in aqueous solution, which show a shell collapse transition around the lower critical solution temperature of the PNIPAM block (ca. 32 °C). By introducing organic co-solvents, this collapse transition temperature can be tuned due to competitive attachment and detachment of water and co-solvent to the PNIPAM chain [1,2]. In thin film configuration, the cononsolvency effect can be observed as a swelling and collapse of the film as the vapor composition around the sample is changed from water vapor to mixed vapors of water and co-solvent. The swelling and collapse of thin thermo-responsive polymer films has been probed by *in-situ* neutron reflectivity (NR) at the D17 instrument before [3-6], the current investigation however covers a co-solvent stimulus for the first time.

For the **present experiment**, the thermo-responsive polymer PMMA-*b*-PNIPAM poly(methyl methacrylate)-*b*-poly(N-isopropylacrylamide) was spin-coated onto cleaned Si substrates and thermally annealed. *In-situ* NR measurements were performed in time-of-flight (TOF) mode with a wavelength band of 2 to 30 Å at the D17 instrument at the ILL. The sample-detector distance (SDD) was set to 3.1 m. To cover a large q_z range, the reflectivity curves for the films in equilibrium were acquired at two different incident angles (san 0.5° and 2.5°) with a total counting time of 45 min.

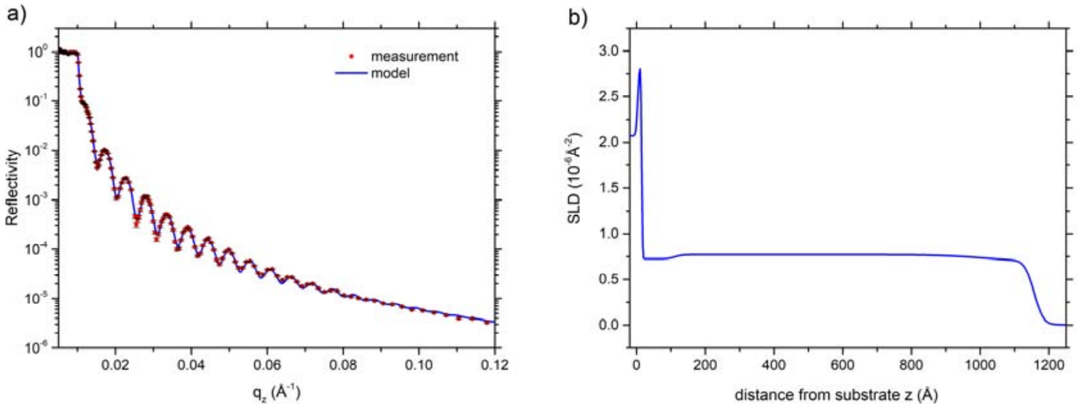

Figure 1. *a) NR curve of the PMMA-b-PNIPAM thin film in the dry equilibrium state (red dots), theoretical NR curve generated by an initial four-layer model (blue line) and the b) corresponding SLD profile (blue line) with Si substrate located at z = 0 Å.*

To follow the kinetics of the thin film during the exchange of atmospheres, reflectivity data was repeatedly recorded at a fixed incident angle (san 1.0°) with a time resolution of 5 s (therefore better by a factor of 2 than anticipated from earlier experiments). This high time resolution allowed the observation of the thin films' response during the hydration and solvent exchange processes. In order to avoid the oversaturation of the detector during the absorption of volatile compounds with high SLD, the count rate was recorded for each kinetic run. If it exceeded the preset value of 15000 c/s, a change in slit width was triggered (S3W 0.8 to 0.2). The reverse of the slit width setting was triggered, if the count rate fell beneath a set value.

The NR data of the dry PMMA-*b*-PNIPAM film in equilibrium (Figure 1a, red dots) exhibits pronounced Kiessig fringes, indicating that the polymer film is homogenous and that the inner micro-phase separation structure is not seen. An initial four-layer model is used to describe the dry film on the Si substrate with a SiO_2 interfacial layer. The theoretical reflectivity curve generated by the model is represented by a blue line in Figure 1a, whereas the resulting SLD profile along the dry films' vertical is shown in Figure 1b. The bottom layer (at the Si/SiO_2 interface) has a thickness of 12 Å and a SLD value of 2.86×10^{-6} Å^{-2}. The second layer has a thickness of 97 Å and a SLD value of 0.72×10^{-6} Å^{-2}. The third layer has a thickness of 930 Å and a SLD value of 0.77×10^{-6} Å^{-2}. The top layer at the air interface has a thickness of 118 Å and a SLD value of 0.68×10^{-6} Å^{-2}. Thus, we see enrichment layers with lower SLD values at the substrate and air interface.

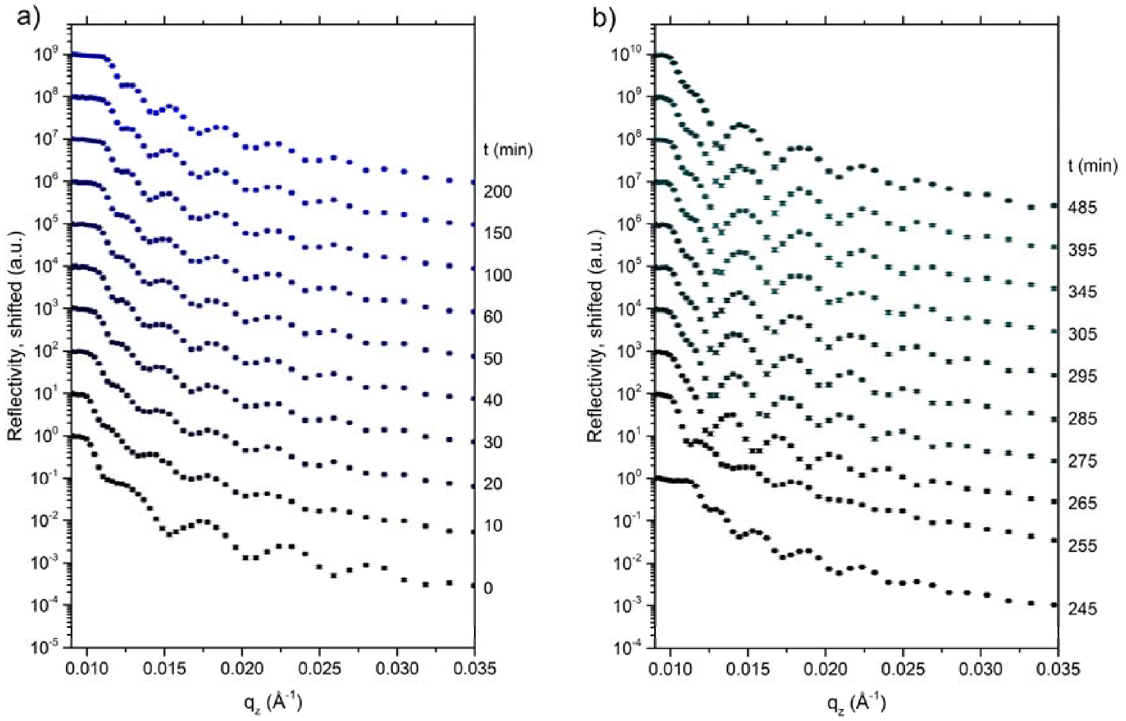

Figure 2. *a) Hydration kinetics of the dry PMMA-b-PNIPAM thin film in D_2O vapor at 18 °C. Selected NR curves from the beginning (bottom) to the end of the hydration process (top). b) Response kinetics to the exchange of D_2O vapor to a mixed D_2O and MeOH vapor at 18 °C. Selected NR curves from the beginning (bottom) to the end (top) as the atmosphere is exchanged and the film collapses as a result of the con-nonsolvency of D_2O and MeOH. The NR curves are shifted vertically for clarity of the presentation.*

The exchange of atmospheres was realized with saturated vapors of D_2O, H_2O, MeOH-d3, MeOH, acetone-d6 and acetone using a N_2 carrier gas flow, thus MeOH replaced dimethyl sulfoxide for safety reasons. We always performed experimental pairs with deuterated and protonated solvents to identify the role of the cosolvent. The thermostat used to equilibrate the vapor generation and sample environment chambers was set to 18 °C, which is below the collapse transition temperature of the PNIPAM block to ensure a full hydration of the film and a collapse transition purely caused by the solvent exchange in the atmosphere surrounding the sample. Selected NR curves from the beginning (bottom) to the end (top) of a hydration process in D_2O are shown in Figure 2a. The distance between the Kiessig fringes shrinks as the films swell in D_2O vapor. The critical edge shifts towards higher q_z values, indicating an absorption of D_2O into the polymer layer. As an example from the big body of co-nonsolvency experiments, selected NR curves from the beginning (bottom) to the end (top) of a collapse process in a mixed atmosphere of D_2O and MeOH are shown in Figure 2b. The Kiessig fringes first shrink as the film swells with increase of absorbed MeOH. They then move apart from each other again, as the film collapses and relaxes into an equilibrium collapsed state due to the con-nonsolvency effect.

Presently, the kinetic data are modelled to determine the development of thickness and refractive index whilst investigating morphological changes and the kinetics of individual solvent and co-solvent diffusion into the PMMA-*b*-PNIPAM films.

Given the high quality of the NR data, we expect publication of the results after careful data evaluation.

References:

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