Experimental report

22/01/2024

Proposal: 9-11-2130 **Council:** 4/2023

Title: Investigation of the Influence of Salts on the Co-nonsolvency Effect of Thin Polymer Films in Mixed Water/Dimethyl Sulfoxide Vapors

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: poly(N-isopropylmethacrylamide) (PNIPMAM)

Instrument	Requested days	Allocated days	From	To
FIGARO	0	0		
D17	5	4	26/09/2023	30/09/2023

Abstract:

The influence of salts with different anions and cations on the swelling and phase transition behavior in water and water/dimethyl sulfoxide (DMSO) mixtures of poly(N-isopropylmethacrylamide) (PNIPMAM) thin films will be studied. The vapor sensitive PNIPMAM thin films are excellent candidates for applications in the field of sensors, soft robotics, tissue engineering, and implantable electronics. Polymer-based sensors are generally used to detect specific vapors in the surrounding atmosphere and are an alternative to rather expensive techniques like gas chromatography devices. Among these, sensors to detect DMSO are of special importance in quality control measure in foods and beverages as well as in the assessment of sea life health. To tune the responsiveness of these nanodevices, additives such as salts can be used. In this study we aim to elucidate the influence of the cation and anion species by varying the salt composition of Mg(NO3)2, Mg(ClO4)2, or NaClO4 in PNIPMAM thin films. By performing in situ neutron reflectometry measurements at D17 with a high time resolution of ¿t = 5 s, we want to elucidate the solvent distribution during the swelling and exchange process.

Investigation of the Influence of Salts on the Co-nonsolvency Effect of Thin Polymer Films in Mixed Water/Dimethyl Sulfoxide Vapors

(Proposal 9-11-2130)

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Vapor sensitive thermo-responsive thin films are excellent candidates for applications in the field of sensors, soft robotics, tissue engineering, and implantable electronics. In general, polymer-based sensors are used to detect specific vapors in the surrounding atmosphere and are an alternative to rather expensive techniques like gas chromatography devices. Among these, sensors to detect dimethyl sulfoxide (DMSO) are of special importance for quality control measure in foods and beverages as well as in the assessment of sea life health.[1,2] Accordingly, the coil-to-globule transition of responsive polymer thin films has gained increasing attention. These smart systems adapt to external stimuli, such as temperature, pH, or co-solvent addition, which is expressed by their capability of reversibly undergoing coil-to-globule transitions. [3,4] Furthermore, additives can be used to tune the transition behavior. [5] Therefore, it is pivotal to elucidate the underlying mechanism, which in turn will enable the rational design of new functional materials and additives to be used in these applications. In the realm of possible additive, salts provide a unique opportunity due to their easy incorporation in the device fabrication and the relatively low substance demand. For this purpose, poly(*N*-isopropylmethacrylamide) (PNIPMAM) thin films have proven to be an ideal lower critical solution temperature-type (LCST-type) model system due to the known excellent water uptake capability and the already proven responsiveness to salt addition. So far, the influence of the cation and anion species on the mechanism of the film swelling process in water vapor atmosphere, and of the coil-to-globule phase transition, induced by the co-nonsolvency effect (mixture of two solvents turns into a non-solvent) in mixed solvent vapors, has not been investigated.

For the **present experiment**, the thermo-responsive polymer PNIPMAM was mixed with different salts in solution and then was spin-coated onto pre-cleaned Si substrates. It was decided to use specific salts to study the influence of different anions (NO_3^- vs. ClO_4^-) and cations (Na^+ vs. Mg^{2+}). Namely $NaClO_4$, $Mg(ClO_4)_2$ and $Mg(NO_3)_2$ were investigated. *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. 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 TOF count of 10 s. 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.

In Figure 1, NR curves and their corresponding fits and scattering length density (SLD) profiles of the PNIPMAM thin film without the addition of salt in the equilibrated dry (top) and the D_2O swollen state (bottom) are shown. It can be seen, that for both states pronounced Kiessig fringes were observed. In general, 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. For the equilibrated dry state, the NR pattern was fitted with a four-layer model consisting of silicon, native SiO_2, polymer bulk and air. Whereas the equilibrated swollen state had to be fitted with two additional interface layers to describe solvent enriched layers at the interfaces.

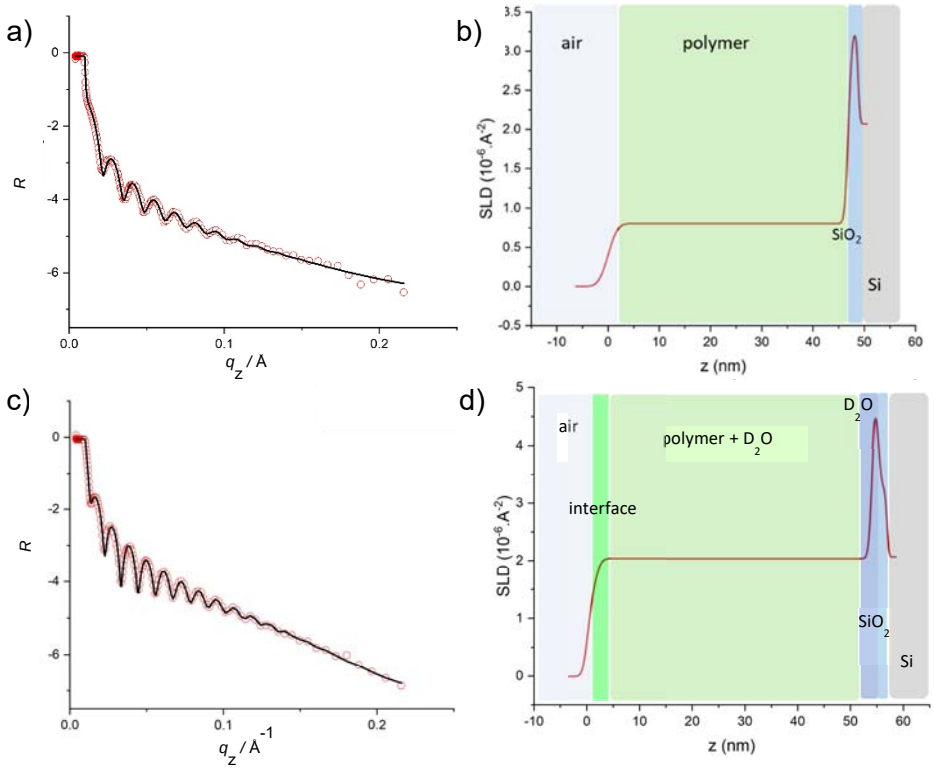

Figure 1: *NR curve of the PNIPMAM thin film without the addition of salt in the dry (a) and swollen equilibrated state (c), theoretical NR curve generated by an initial four-layer model (black line). b) and d) corresponding SLD profiles (red line).*

The exchange of atmospheres was realized with the use of saturated vapors of D_2O, H_2O, DMSO-d6 and DMSO using a N_2 carrier gas flow. The thermostat used to equilibrate the vapor generation and sample environment chambers was set to 25 °C, which is above the melting temperature of DMSO (19 °C) and is below the collapse transition temperature of PNIPMAM to ensure a full hydration of the film and a collapse transition purely caused by the solvent exchange in the atmosphere surrounding the sample. Presently, the in-depth analysis of the kinetic and static ToF-NR data is ongoing. Since the experiments worked out very well, we expect to publish the results with the local contact as coauthor after having finished the data analysis.

References:

[1] Pirsa, S., Alizadeh N. A selective DMSO gas sensor based on nanostructured conducting polypyrrole doped with sulfonate anion. *Sensors and Actuators B: Chemical* **2012**, 168, 303-309.

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[3] Geiger, C., Reitenbach, J., Kreuzer, L. P., Widmann, T., Wang, P., Cubitt, R., Henschel, C., Laschewsky, A., Papadakis, C. M., Müller-Buschbaum, P. PMMA-*b*-PNIPAM Thin Films Display Cononsolvency-Driven Response in Mixed Water/Methanol Vapors. *Macromolecules* **2021,** 54, 3517–3530.

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