Experimental report

23/01/2024

Proposal:	**9-11-2093**	**Council:**	10/2022
Title:	Investigation of the Influence of Salts on the Co-Nonsolvency Effect of Poly(sulfobetaine)-Based DiblockCopolymer Thin Films in Mixed Water		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples: PSBP-b-PNIPMAM

Instrument	Requested days	Allocated days	From	To
D17	5	4	14/04/2023	18/04/2023

Abstract:

We will study salt-loaded thin films of a doubly thermo-responsive diblock copolymer (DBC). The DBC consists of a thermo-responsive UCST¿type zwitterionic polysulfobetaine (PSBP) block and a LCST-type nonionic poly(N-isopropylmethacrylamide) (PNIPMAM) block. To study the influence of different potassium salts on the solvation behavior in mixed water/methanol vapors, salt-loading used KCH3COOH, KCl or KI. Considering the salt-sensitive nature of the zwitterionic PSBP block and the salt solvation effect, a comprehensive mechanism of salts influencing the co-nonsolvency effect of the DBC in mixed water/methanol vapors is expected. The vapor-sensitive different film thicknesses of the DBC thin films make this DBC an excellent candidate for applications in the field of sensors, soft robotics, tissue engineering, implantable electronics, etc. By performing in situ neutron reflectometry (NR) measurements in time-of-flight (ToF) mode at D17 (time resolution of 5 s), we elucidate the solvent distribution over the swelling and exchange time and the swelling behavior of each thin film. A high neutron scattering contrast between polymer and solvents results from deuterated water and methanol.

Investigation of the Influence of Salts on the Co-nonsolvency Effect of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films in Mixed Water/Methanol Vapors (Proposal 9-11-2093)

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Thermo-responsive polymers display a sudden change in solubility and conformation in a well-defined temperature regime. Their possible applications are multiple, ranging from viscosity control to controlled wettability, and are further of great importance in many biomedical applications.[1,2] Besides temperature-responsiveness, it has been demonstrated that the aqueous solution stability of such macromolecules can be tuned by the addition of different salts, an effect generally recognized as the specific ion effect. [3] This behavior is more pronounced for anions than for cations and the typical order for the anion series is as follows:

$$CO_3^{2-} > SO_4^{2-} > PO_4H^{2-} > F^- > CH_3COO^- > Cl^- > Br^- > I^- > NO_3^- > ClO_4^- > SCN^-.$$

Ions on the left are called kosmotropes, which tend to precipitate proteins from solution and prevent protein unfolding, whereas ions on the right are chaotropic, which increase the solubility and promote the denaturation of proteins. Chloride is usually considered the dividing line between these two types of ions.

In our previous NR studies on thermo-responsive polymer thin films, it was found that the phase transition behavior, including swelling degree, absorbed solvent content, and volume phase transition temperature, can be modulated by the addition of salts. [4-6] Furthermore, the cononsolvency effect on thermo-responsive thin film was also investigated previously. [7,8] Based on these studies, the following questions arise. First, is the cononsolvency behavior in thermo-responsive polymer thin films maintained upon the addition of salts? Second, what is the influence of salt on the aforementioned cononsolvency effect? Finally, does this effect follow the Hofmeister series?

Based on these questions, the cononsolvency behavior of salt-loaded diblock copolymer (DBC) thin films was investigated by ToF-NR measurements at the D17 instrument. The selected DBC consisted of a thermo-responsive UCST–type zwitterionic polysulfobetaine (PSBP) block and a LCST-type nonionic poly(*N*-isopropylmethacrylamide) (PNIPMAM) block. We studied the influence of different potassium salts on the solvation behavior of the salt loaded DBC thin films in mixed water/methanol vapors. The ToF-NR measurements were performed with the following vapor protocol at 18 °C. Firstly, the film was dried under an N_2 flow for 1h and a static ToF-NR measurement was conducted at two incident angles of $\alpha_i = 0.5°$ (20 min) and $\alpha_i = 2.5°$ (70 min) to obtain a large q_z range. Then, *in situ* ToF-NR measurements were performed at two incident angles of $\alpha_i = 1.0°$ and $\alpha_i = 1.5°$ to trace the evolution of the D_2O swelling process over 8 h under a saturated D_2O vapor atmosphere. Once an equilibrium in swelling was reached a second static measurement was performed. Next, a saturated mixed vapor (D_2O/methanol-d_3 = 6/4) was introduced into the environment of the sample and again *in situ* measurements were performed. Finally, a last static measurement was conducted to investigate the equilibrated state in a mixed vapor atmosphere.

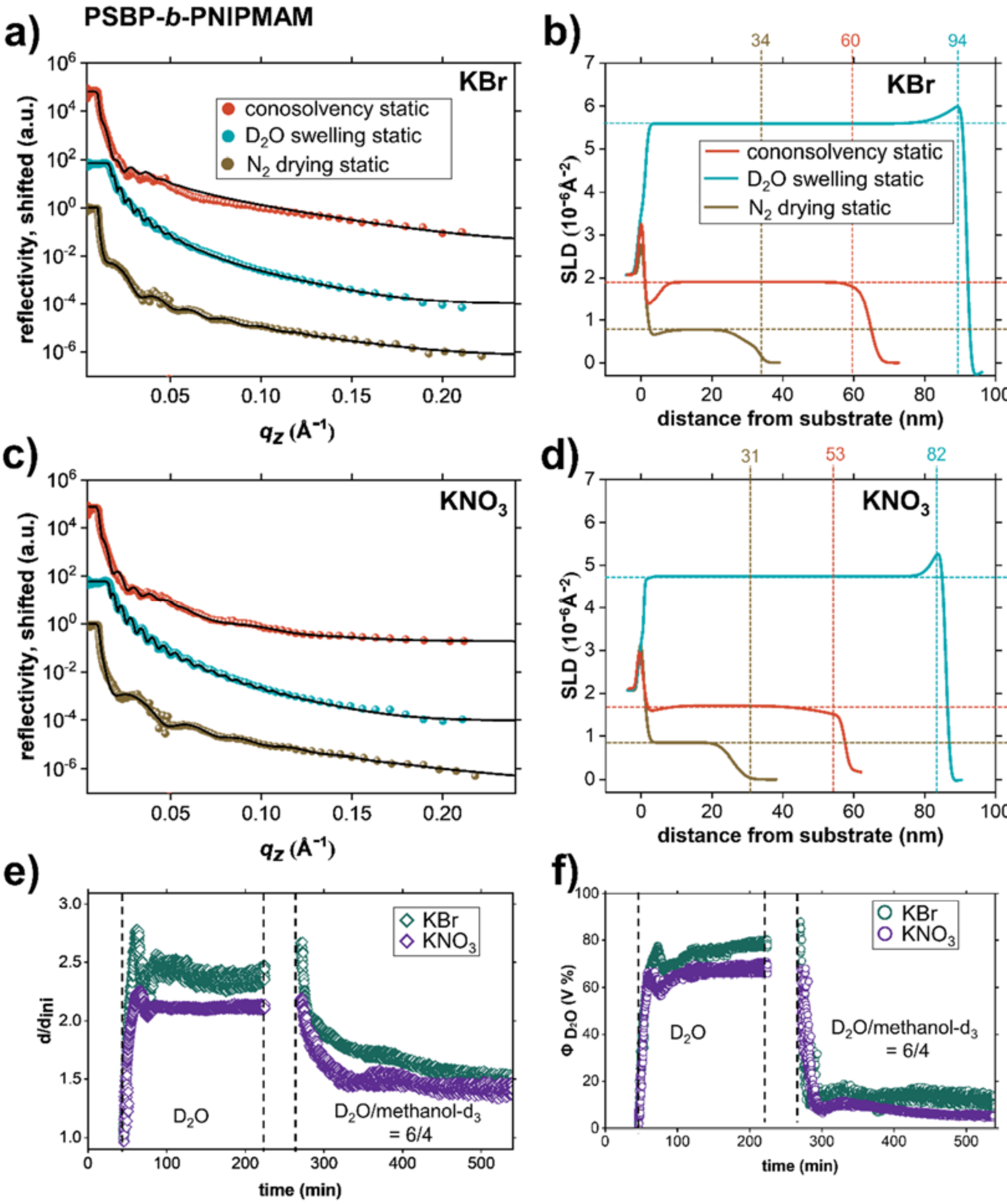

Figure 1: (a,c) Fitted static ToF-NR data (raw data as symbols) and (b,d) determined SLD profiles of KBr and KNO_3-loaded PSBP-*b*-PNIPMAM thin films. Evolution of the (e) swelling ratio d/d_{ini} and (f) calculated solvent contents obtained from ToF-NR data as a function of time for KBr (green) and KNO_3-loaded (purple) PSBP-*b*-PNIPMAM films.

A three-layer model is used to fit the static NR data, which includes a substrate-polymer interface layer, a bulk polymer layer, and a polymer-air interface layer. The static NR curves with the best fits and the corresponding SLD profiles are shown in Figure 1a-d. For the static ToF-NR curves of each sample, the Kiessig fringes spacing decreases and the critical edge shifts towards higher q_z values in the case of the D_2O swollen static state compared with the N_2 drying static state. These observations illustrate the increase in film thickness and SLD values (i.e., the incorporated D_2O molecules), visualizing in the marked values in corresponding SLD profiles. Analogously, the reversed changes occur upon the vapor atmosphere switching process, demonstrating a decrease in thickness and SLD values. Comparing the SLD profiles of the two salt-loaded DBC films, it was found that the KBr-loaded film reaches a higher swelling ratio and a larger SLD values (i.e., D_2O absorption) than the KNO_3-loaded film at both D_2O swollen static state and cononsolvency static state. Moreover, there occur differences in the water enrichment layers depending on the salt loading.

Figure 1e and f present the results of the *in situ* ToF-NR investigation of both DBC samples. As expected, a higher swelling ratio, SLD values and D_2O content are observed for the KBr-loaded DBC film, compared to the KNO_3-loaded DBC film, which correlates with the observations from the static NR measurements. Besides, upon D_2O hydration, a synchronous fluctuation that appears in the swelling ratio and D_2O content, is ascribed to the rearrangement of polymer chains induced by a rapid water absorption. Once the mixed D_2O/methanol-d_3 vapor replaces the D_2O vapor, a fast release of D_2O molecules is observed for both samples in 10 -15 min.

A further data analysis is progressing, including the KCH_3COO and KI-loaded samples, especially concerning the methanol-d_3 content for all samples. The results will be published after finishing the data analysis.

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