Dual thermo-responsive polyzwitterionic copolymers in solution and thin films

Polyzwitterions bear the same number of cationic and anionic groups within their constitutional repeat unit. One class of polyzwitterions are polysulfobetaines (PSBs), which contain a cationic quaternary amine and an anionic sulfonyl group in every monomeric unit. Since they feature high biocompatibility and chemical stability, they are promising candidates for antifouling materials. Furthermore, their zwitterionic nature is stable over a broad pH range (≈ 2 – 14), which leads to various attractive and repulsive interactions of the charged groups with each other and with water molecules. Thus, PSBs exhibit an upper critical solution temperature (UCST) in aqueous solution [1]. By combining a suited zwitterionic UCST-type homopolymer with a nonionic lower critical solution temperature (LCST) type homopolymer (e.g., PNIPAM or PNIPMAM), dual thermo-responsive diblock copolymers (DBCs) are generated. In aqueous solution, they self-assemble into micelles with a hydrophobic core and a hydrophilic shell [2]. Since the two polymer blocks feature the inversed response to temperature change, a structural inversion of the micellar system is enabled. This special behavior is called 'schizophrenic' micellar self-assembly and is schematically shown in Figure 1. Depending on the relative positions of the clearing point (CP_{UCST}) and cloud point (CP_{LCST}), the DBCs are either fully miscible (regime II) or immiscible (regime II') with water. By adding salinity as a second stimulus, the system gains even more flexibility. Now the micellar inversion can be realized via the fully immiscible regime (Fig. 1a), the fully miscible regime (Fig. 1b), or directly (Fig. 1c) [3-7]. Hence a broad range of switchable micellar solutions is provided, which is promising for 'smart' applications, in which a controlled uptake, transport and release is needed.

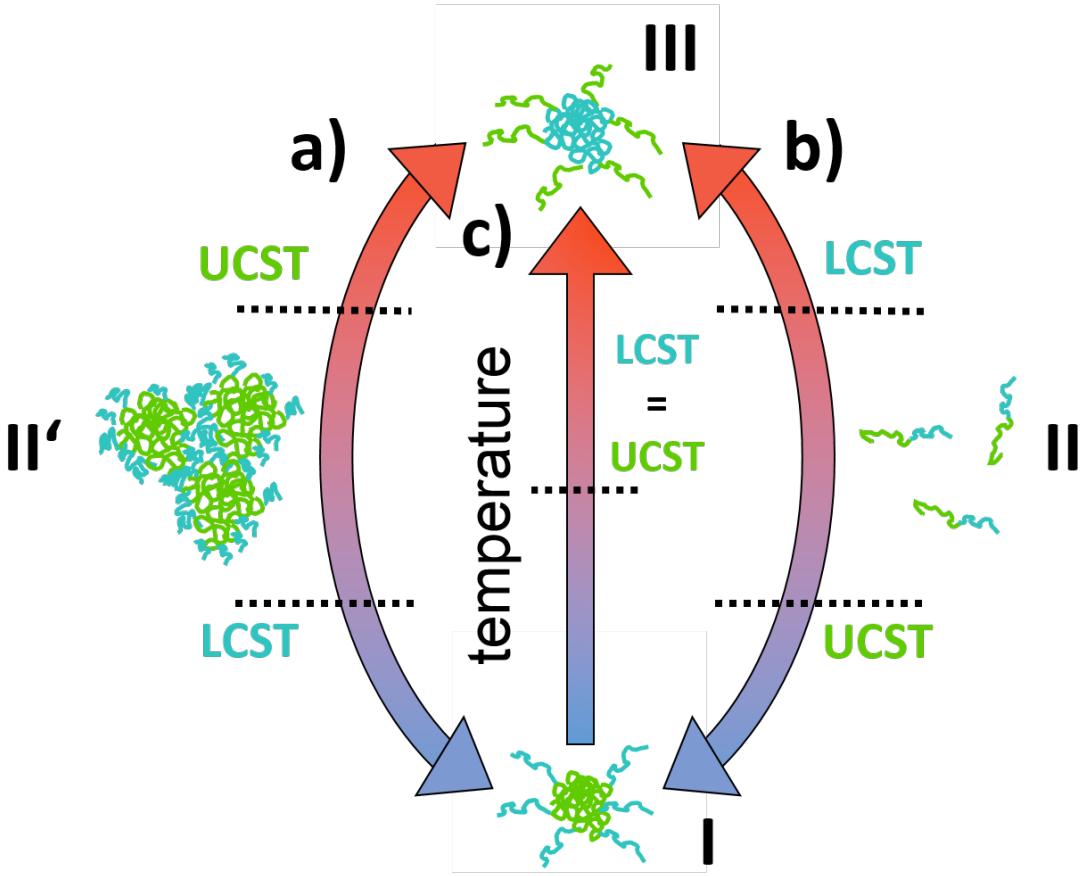

Figure 1: Schematic overview of the 'schizophrenic' behavior of a zwitterionic, and dual thermo-responsive DBC in aqueous solution. The dashed black lines denote the clearing point of the zwitterionic block (CP_{UCST}) and the cloud point of the nonionic block (CP_{LCST}), respectively. The resulting regimes are labeled with I, II, II', and III. Regime II and II' are present if (a) $CP_{UCST} < CP_{LCST}$ or (b) $CP_{UCST} > CP_{LCST}$, respectively. Case (c) indicates the direct transition from regime I to III if $CP_{UCST} = CP_{LCST}$.

By transferring 'schizophrenic' DBCs from aqueous solution to thin-film geometry, the situation gets more complex. [8] The DBC in thin films is subject to geometrical restrictions and the behavior is mainly governed by polymer-polymer interactions. Also, interfacial effects (substrate-polymer and polymer-air) have a serious impact on diffusion or exchange processes. Therefore, the behavior of a thin film cannot be predicted from the corresponding bulk DBC in aqueous solution.

For a first fundamental understanding of the behavior of such thin films, we exposed a PSB-*b*-PNIPAM thin film to pure H_2O or D_2O vapor, which was then exchanged by the corresponding other water species (H_2O with D_2O and vice versa). The thin films featured a higher affinity to H_2O than to D_2O, which is mainly addressed to the isotope sensitivity of the PSB, and results in a faster and larger H_2O adsorption. Since this behavior is already known from solution, a deviating thin-film behavior in H_2O or D_2O vapor has been expected, however not to such a significant level. [9]

A follow-up study focused on the swelling behavior in pure water vapor (H_2O and D_2O) and the exchange behavior in mixed water/methanol vapor (H_2O/CD_3OH and D_2O/CH_3OH) of PSB-*b*-PNIPMAM thin films. While the thin films featured a strong swelling behavior in water vapor, they exhibited two individual contraction processes in mixed water/methanol vapors. We were able to address these two contractions to the individual PSB (first contraction) and PNIPMAM block (subsequent second contraction), respectively. Interestingly, the swelling degree in pure methanol vapor was slightly higher than in mixed water/methanol vapor, which indicates a co-nonsolvency-type behavior. Overall, the investigated system enabled five distinct thin-film regimes (dry, water-swollen, after the first PSB and the second PNIPMAM contraction, and methanol-swollen). By using different water and methanol isotopes, these thin film regimes can be further tuned [10,11].

Further studies focused on the temperature-dependent behavior of these dual thermo-responsive thin films. In contrast to aqueous solution, the transition temperatures of both polymer blocks (PSB and PNIPMAM) in thin film geometry were strongly shifted. Furthermore, a changing thin-film morphology upon increasing temperature was found. However, the observed changes were very slow (in the order of hours) and small. A structural inversion, as is known from aqueous solution was not observed, which was mainly referred to the low polymer chain mobility in the thin-film geometry [12,13].

Very recently, the response of dual thermo-responsive PSB-b-PNIPMAM thin films towards two stimuli (temperature and ionic strength via the addition of salt to the thin films) was investigated. The salt addition led to an increased water adsorption and a decreased transition temperature of the PSB block. Both effects originate from the zwitterionic and salt-sensitive nature of the PSB. Generally, the application of two external stimuli results in a highly tunable, but simultaneously a very complex thin-film system [14] .

In summary, these zwitterionic and dual thermo-responsive materials feature a versatile behavior, which can be tuned significantly by applying different stimuli, e.g., temperature, salt,

different solvents. Furthermore, the sample geometry (solution or thin film) has an enormous impact on behavior of the DBC. While the 'schizophrenic' solution behavior is promising for applications in the fields of rheology or drug delivery, the DBC in thin-film geometry can be used as nano-sensors and switches, or as functional surfaces.

Featured publications:

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