

Conformational Induced Behaviour of Copolymer-capped Magnetite Nanoparticles at the Air/Water Interface

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Stimuli-responsive behavior and conformational changes of copolymers are topics of high scientific interest for both theoretical and practical reasons. Stimuli-responsive polymers containing oligo or poly(ethylene glycol) are especially interesting for biomedical applications due to their resistance to protein adsorption. Consequently, nanoparticles (NPs) coated with ethylene glycol polymers can improve the biocompatibility of the NPs and prolong their in vivo circulation time for different biological applications. The present work belongs to a series of studies dedicated to the interfacial behaviour of Fe₃O₄ NPs capped with a biocompatible and stimuli-responsive copolymer containing ethylene glycol units. Fe₃O₄@MEO₂MA₉₀-co-OEGMA₁₀ NPs are able to form Langmuir and Gibbs layers which are energetically and kinetically long-time stable up to the critical surface pressure of the film [1, 2]. The current study presents new experimental evidence to the antagonistic interfacial behavior of the Fe₃O₄@MEO₂MA NPs at the air/water interface below and above the lower critical solution temperature (LCST).

The X-ray reflectivity data for the Fe₃O₄@MEO₂MA NP layers formed on a liquid subphase and compressed to different pressures, below and above the critical pressure of the monolayer, were obtained at the liquid-surface beamline BW1 of HASYLAB. Figure 1A shows the X-ray reflectivity curves normalized by the Fresnel reflectivity. The contrast is obviously not good enough to observe pronounced maxima and minima. One reason is the low particle density in the monolayer and the smooth decay of the electron density of spherical particles immersed into the subphase, and the other reason is that the electron density of strongly hydrated and in water dispersed polymer chains is close to that of water. Therefore, mainly the less hydrated polymer chains adsorbed at the air/water interface contribute to the reflectivity signal.

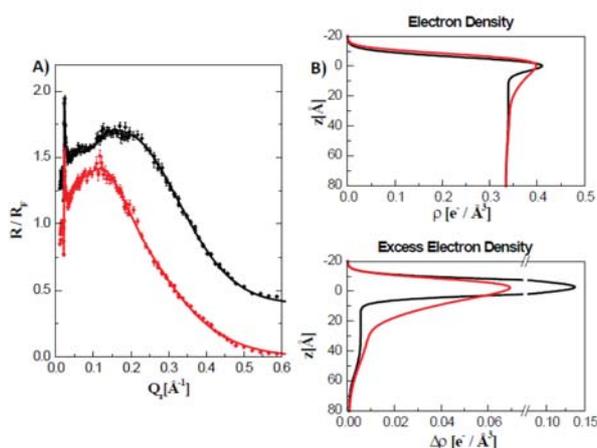


Figure 1: A) Measured reflectivity (symbols) and fits (lines) of the Fe₃O₄@MEO₂MA NP layers on a water subphase at 20 °C (15 mN/m – black curve (shifted for clarity), 29 mN/m – red curve) and B) the respective electron density profile (top) and the excess electron density profile (bottom) of the NP layers.

The derived electron density profile (Figure 1B) shows a clear maximum at the interface. The electron density achieves values which are close to the ones found for the crystalline phase of poly(ethylene oxide) (PEO) ($0.403 e^-/\text{\AA}^3$) [3]. The adsorption layer is with $\sim 12 \text{\AA}$ rather thin.

The adsorbed polymer chains are stretched and tightly packed in a pancake-like conformation. The main contribution for the second layer underneath this polymer layer comes from the NPs which have a low number density. The layer thickness of only 50 Å is 20% smaller than the particle diameter. The hydrated and dispersed polymer chains are completely invisible.

Above the critical pressure (29 mN/m), the observed layer thickness is only slightly larger than that at lower pressure. The maximum of the electron density profile is lower, which could be an indication of losing the stretched and well-packed conformation of the polymer chains at the surface by compression of the film. The excess electron density profile shows a higher electron density over the whole thickness because of the higher number density of NPs in the compressed state. The results are in perfect agreement with the IRRAS experiments showing that the adsorption layer thickness is constant on the plateau region.

The X-ray reflectivity data obtained for the Fe₃O₄@MEO₂MA NP layers formed on the 1M NaCl subphase are shown in Figure 2. Adding 1M NaCl to the subphase changes the electron density of the subphase from 0.334 e⁻/Å³ (water) to 0.345 e⁻/Å³ (1M NaCl). The derived electron density profile (Figure 2B) shows that the adsorbed polymer chains are similarly stretched and packed as on the water surface, suggesting a pancake-like conformation. This is in good agreement with the IRRAS data showing very similar spectra at lateral pressures below the critical one on water as well as on the salt solution. Above the critical surface pressures, the monolayer is intact and no multilayers are formed at high salt concentrations. The increased electron density in the part underneath the polymer adsorption layer shows that the contrast between the subphase and the particle layer is enhanced, indicating that the collapsed polymer chains are strictly localized between the particles (mushroom-like structure of the copolymer).

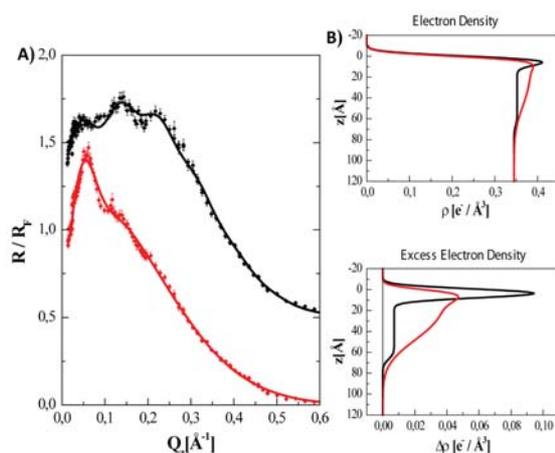


Figure 2: A) Measured reflectivity (symbols) and fits (lines) of the Fe₃O₄@MEO₂MA NP layers on the 1M NaCl subphase at 20 °C (15 mN/m – black curve (shifted for clarity), 31 mN/m – red curve) and B) the respective electron density profile (top) and the excess electron density profile (bottom) of the NP layers.

The different behaviour of the Fe₃O₄@MEO₂MA NPs below and above the LCST is due to conformational changes of the copolymer chains, which occur upon variation of the temperature or the ionic strength of the aqueous subphase and only as a consequence of lateral compression of the film to surface pressures above the characteristic critical surface pressure.

References

- [1] C. Stefaniu, M. Chanana, D. Wang, D. V. Novikov, G. Brezesinski and H. Möhwald, *ChemPhysChem* **11**, 3585 (2010).
- [2] C. Stefaniu, M. Chanana, D. Wang, D. V. Novikov, G. Brezesinski and H. Möhwald, *Langmuir* **27**, 1192 (2011).
- [3] X. Zou and S. W. Barton, *Langmuir* **10**, 2866 (1994).