

ADSORPTION OF CATIONIC, ANIONIC, AND HYDROPHOBICALLY MODIFIED POLYACRYLAMIDES ON SILICA SURFACES

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ABSTRACT

Cationic, anionic and hydrophobically modified polyacrylamides with varying charge density and degree of hydrophobisation were studied in order to determine the factors controlling the adsorption of modified polyacrylamides. The influence of the presence of surfactants was also analysed.

Hydrophilic silicon layers grown on polished silicon wafers at 900° C were used as substrates for the adsorption studies. Samples were studied by ellipsometry at a wavelength of 4015Å and at an angle of incidence of 68°. Measurements were taken when pseudoequilibrium was reached. The results of ψ and Δ were interpreted within the framework of an optical four-layer model, assuming isotropic media and planar interfaces.

For the complete range of polyacrylamides used in this study, the adsorption isotherms were of high-affinity type. The slope of the Γ vs. time curves changes from solution to solution, suggesting different affinities of the polymers towards the surface.

The thickness of the adsorbed layer and the adsorbed amount of Γ neutral polyacrylamides are lower than those observed for hydrophobically modified and cationic polyacrylamides. Possible causes for the adsorption of neutral polyacrylamides are hydrogen bonding, the additional gain of entropy caused upon the release of water molecules into the bulk solution when the polymer attaches to the surface and promotion through residual surfactant. Cationic polyacrylamides adsorb extensively onto the negatively charged silica surface. At the highest density of hydrophobic moieties and the highest charge density, the adsorbed amount is significantly lower. Further, unmodified and anionic polyacrylamides also adsorb, suggesting the presence of non-electrostatic interactions between the polymers and the surface.

For cationic polymers further modified with hydrophobic groups, the adsorbed amount tends to decrease with the increase in hydrophobic groups. The thickness of the adsorbed interfacial layers for these polymers is generally higher than in the absence of these hydrophobic groups. It is likely that the balance between solvency and affinity to the surface governs the distribution of the segments in the interfacial layer. This could lead to increases in the local concentration of hydrophobic groups near the surface where the high chain segment density favours segment-segment contacts and hydrophilic groups in the outer region where polymer loops protrude into the liquid phase where segment-solvent contacts are more probable. It is possible, that the hydrophobic microdomains block part of the surface sites available for electrostatic interaction with the cationic segments, leading to a drop in the adsorbed amount for cationic hydrophobically modified polyacrylamides.

Despite unfavourable electrostatic interactions, adsorption of anionic polyacrylamides does occur, pointing to a non-electrostatic attraction between the polymer and the surface. However, the amount adsorbed is quite low and similar to the adsorption of non-charged polyacrylamide. Further, an increase in the adsorbed amount was observed when the number of charged segments was decreased. In the presence of residual non-ionic surfactant (undialysed samples), the adsorbed amount of polymer increases. This is especially the case for polymers that, in the absence of surfactant, adsorb at relatively low values. However, for polymers showing a good ability to adsorb on silica, the addition of surfactant has no significant effect on

the adsorbed amount. For all samples, more material was observed at the interface for polymers having residual surfactant.