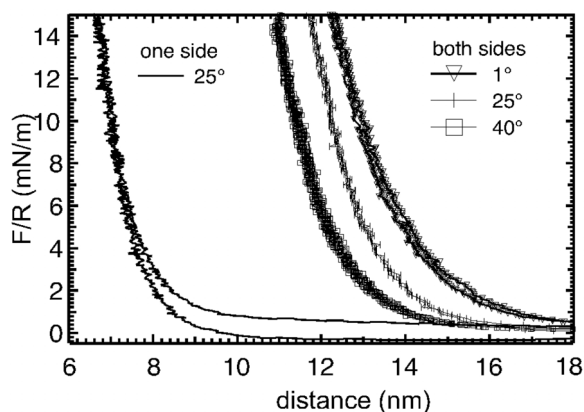


## MOLECULAR FORCES AND MORPHOLOGY OF AN ADSORBED POLY(L-LYSINE)-G-POLY(ETHYLENE GLYCOL) COPOLYMER

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**INTRODUCTION:** Polyethylene glycol (PEG) surface grafts are used as non-specific protein adsorption resistant surface coatings. In this work, films of PEG grafted to a cationic poly-lysine backbone (PLL-g-PEG) were investigated using the surface forces apparatus technique, which provides direct measurements of forces and refractive index using thin-film interferometry. Surface force isotherms were recorded for different molecular architectures and temperatures. The observed interaction force is predominantly repulsive, nearly elastic and can be described by polymer brush scaling theory and electrostatic double layer forces.

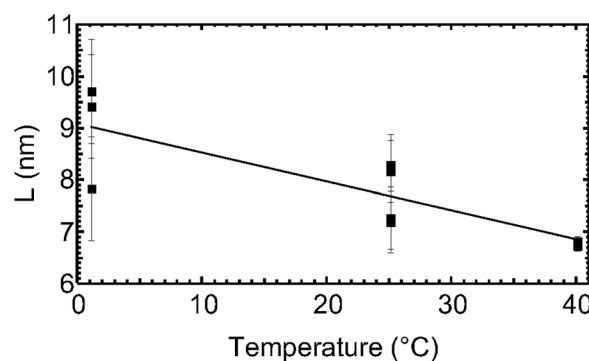


*Fig. 1: Compression isotherms of PLL(20)-g-[2,9]-PEG(2) adsorbed layers on one and on both mica surfaces. Loading and unloading tracks are shown.*

**METHODS:** The experimental data were obtained using the extended surface forces apparatus<sup>1,2</sup>. For preparing the mica surfaces, a cutting procedure with scissors was used in order to avoid the formation of nano-particles reported to occur for standard preparation procedure<sup>3-5</sup>. The poly(L-lysine)-g-poly(ethylene glycol) films were adsorbed from aqueous solution and HEPES buffer with 0.5 and 1 mg/ml concentration. Compression isotherms were measured in aqueous solution at controlled temperature for one surface (asymmetric) and two surfaces (symmetric) covered with the adsorbed polymer.

**RESULTS:** A strong exponential repulsive force appeared in the high load regime, caused by the steric repulsion of the PEG chains. In case of the asymmetric setup, a small hysteresis was observed for low loads, as well as transfer of polymers to the second surface at higher loads. The film thickness showed an inverse temperature dependence of  $-0.5\text{\AA}/\text{K}$ , which contradicts predictions from brush scaling theory, but is in agreement with the solubility behavior of the PEG molecule. Superimposed to the steric repulsion, discrete film

thickness transitions with a variable step size of 0.1 to 0.2 nm could be observed, which reveal the presence of long-lived load-bearing molecular structures of the hydrated PLL-g-PEG film.



*Fig. 2: Polymer brush length  $L$  obtained by fitting the compression isotherms of PLL(20)-g-[2,9]-PEG(2) with scaling theory as a function of temperature<sup>6</sup>.*

**DISCUSSION & CONCLUSIONS:** Surface force isotherms measured at high resolution reveal ubiquitous sub-nanometer film-thickness transitions suggesting the existence of equilibrium structures superimposed to the well-known steric repulsion.

**REFERENCES:** <sup>1</sup>M. Heuberger (2001) *Rev. Sci. Instr.* **72**(3):1700-1707. <sup>2</sup>M. Heuberger, et al (2001) *Rev. Sci. Instr.* **72**(9):3556. <sup>3</sup>S. Ohnishi et al (1999) *Langmuir* **15**:3312. <sup>4</sup>M. Kohonen et al (2003) *Langmuir* **19**(3):975. <sup>5</sup>M. Heuberger, M. Zäch (2003) *Langmuir* **16**(6):1943. <sup>6</sup>PG deGennes (1987) *Advances in Colloid and Interface Science* **27**:189.

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