Communication

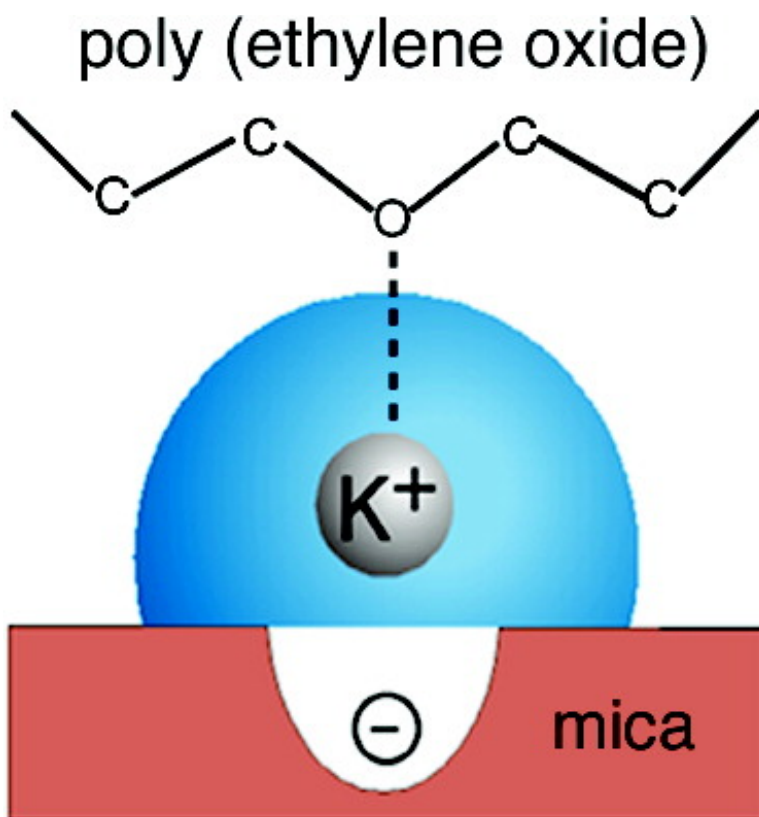# Role of Ion Ligands in the Attachment of Poly(ethylene oxide) to a Charged Surface

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Role of Ion Ligands in the Attachment of Poly(ethylene oxide) to a Charged Surface

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Poly(ethylene oxide), $-(CH_2-CH_2-O)_N-$ (PEO), is almost unique in being a nonionic polymer that is highly soluble in both aqueous and organic solvents.[1] This, together with its relative biocompatibility,[1] has made it not only a popular model polymer but also a widely used material in both technological and particularly biomedical areas: these range from zeolite templating,[2] to controlled drug release,[3] to modifying the adhesion and spreading of cells on surfaces.[4] The modification of surface properties by PEO, and its adsorption to various organic and inorganic surfaces, have been well investigated.[5,6] Here we report that high-molecular-weight (M) PEO, which is known to adsorb strongly onto mica surfaces from aqueous salt solution,[5] surprisingly does not adsorb on it from water in the absence of added salt. An analysis of the charge state of the mica in these two limits, together with its known complexation with alkali metal ions,[7] suggests that the hydrated metal cation in the salt solution (K^+) may act as a ligand in binding the PEO to the negatively charged mica. This sheds light on the molecular mechanism of PEO adsorption and may have interesting implications for its control.

To establish the adsorbance of the PEO (weight averages $M = 150\,000$ and $170\,000$, and polydispersity PD = 1.02; Polymer Laboratories, UK), we used a surface force balance[8] (SFB) to measure normal and shear interactions between molecularly smooth mica surfaces in the following four configurations: (a) across purified water (Milli-Q gradient system, resistivity ≥ 18.2 MΩ, and total organic content 3−4 ppb) with no added salt or polymer; (b) across purified water with added PEO; (c) across aqueous 0.1 M KNO$_3$ solution with no added polymer (KNO$_3$, Aldrich 99.999%); and (d) across aqueous 0.1 M KNO$_3$ solution with added PEO. Figure 1 shows the profiles of the normalized normal forces $F_n(D)/R$ between the curved mica surfaces (mean radius of curvature $R \approx 1$ cm in the standard crossed-cylinder configuration) a closest distance D apart. Profiles are shown for both polymer-free water and water with PEO, as in configurations (a) and (b) above. Within the scatter, profiles with and without PEO (both M values) are identical and resemble earlier profiles for mica across water with no added salt.[9] Mica in water ionizes, losing K^+ ions from its surface, to develop a net negative charge. This results in the weak long-ranged repulsion seen in Figure 1, arising from the osmotic pressure of the trapped counterions (predominantly hydrated protons, H_3O^+), followed by a jump into adhesive contact from ca. 6 ± 1 nm. At this point, counterions condense into the negatively charged mica surface sites and the attractive van der Waals force dominates,[9,10] resulting in the jump at the instability point when $\partial F_n(D)/\partial D = K_n$, the normal spring constant (inset to Figure 1). The facts that the presence of the polymer makes no discernible difference to the force profiles, and that they jump into mica−mica contact both with and without the polymer in solution, indicate that the PEO is not adsorbing onto the mica. This is a qualitatively
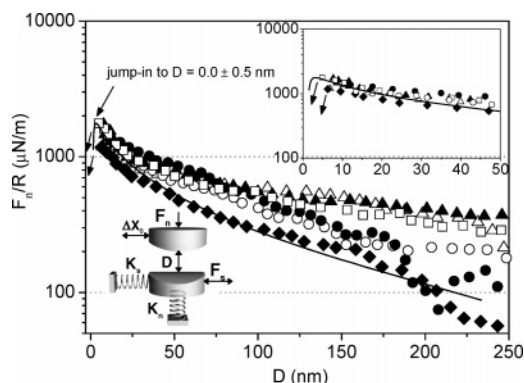
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Figure 1. Normalized force profiles $F_n(D)/R$ between curved mica surfaces across water (no added salt) in the absence (empty symbols) and in the presence (full symbols) of added PEO ($M = 150\,000$, $170\,000$; 150 µg/mL), measured using an SFB (schematic inset). Different symbols represent different contact points and different experiments. Fits to profiles[12] (solid line) yield Debye screening lengths in the range 94−242 nm, corresponding to effective monovalent salt concentrations $1.6 \times 10^{-6}-1 \times 10^{-5}$ M (scatter due to variance in trace salt presence) and surface potentials 150 ± 10 mV. Inset shows region of jump-in on an expanded scale.

surprising result, insofar as it is well established that PEO of high (though not low[11]) M adsorbs strongly onto mica from aqueous salt solutions.[5]

To confirm this nonadsorbance, we carried out also shear force measurements between the mica surfaces in pure water with and without added PEO. In these, the upper mica surface moves laterally past the lower surface and the shear force transmitted across the gap between them is monitored with great sensitivity[8] by the bending of the lateral springs K_s (schematic inset in Figure 1). This approach can, in principle, reveal the presence of weakly adsorbed polymer through its effect on the shear forces, even when its effect on the normal forces may be swamped by counterion osmotic pressure, and when the jump into contact may mask the presence of any weak adsorption by squeezing the polymer out during the jump. In Figure 2, we show shear force traces across water with and without added PEO, when the surfaces are some nanometers apart, approaching slowly (under thermal drift) and jumping into contact from the instability point. In both cases, as evidenced also by a frequency analysis of the transmitted force (not shown), there is no shear force (above the noise level) between the surfaces either prior to or during the jump-in. This confirms the essentially total absence of any PEO adsorption.

In contrast, as shown in the normal force profiles of Figure 3, PEO adsorbs strongly when mica surfaces are immersed in PEO solution in aqueous 0.1 M KNO$_3$. Figure 3 shows both the short-range repulsion between the mica surface in polymer-free aqueous 0.1 M KNO$_3$ and the long-range repulsion following addition of the PEO, as in configurations (c) and (d) above. Both sets of profiles are closely similar to literature values[5] and demonstrate the clear adsorption of the PEO in the presence of the salt.
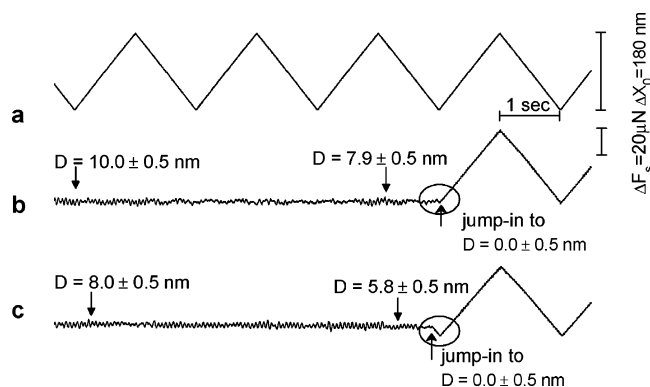
Figure 2. Typical time traces of shear forces transmitted across water (no added salt) in the absence (trace c) and presence (trace b) of added PEO ($M = 150\,000$, $170\,000$; $150\,\mu g/mL$), in response to lateral motion ΔX_0 of the upper mica surface (inset to Figure 1 and trace a), at separations D close to jump-in as shown. No shear force is detected above the noise in either trace b or c.
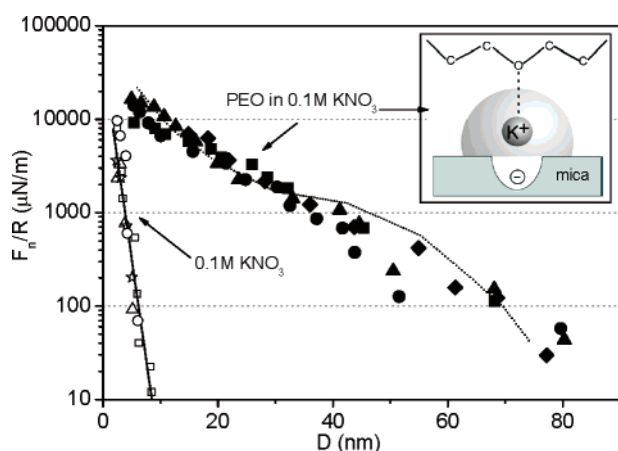

Figure 3. Normalized surface interactions between mica surfaces across aqueous 0.1 M KNO$_3$ (empty symbols) and in the presence of 150 μg/mL PEO (full symbols). Different symbols represent different contact points and different experiments. Fits to profiles[12] (solid line) across the polymer-free salt solution yield surface potentials 90 ± 30 mV. The dotted line is the literature profile for a similar KNO$_3$/PEO system.[5] The inset illustrates the proposed ligand action.

Why does the presence of salt lead to attachment of the PEO from water? The attachment from solution of polymers onto solid surfaces arises from their net preference for the polymer segments rather than for the solvent molecules.[13,14] The mean net change in interaction energy per segment attaching to the surface, $-\delta k_B T$ (where k_B and T are Boltzmann's constant and the temperature), depends on the balance between segment, solvent, and surface interactions.[14] In the present PEO/water vs PEO/aqueous KNO$_3$ case, the water/PEO segment interaction is closely similar to the aqueous KNO$_3$/PEO segment interaction: both are good solvents for the polymer,[15] while dynamic light-scattering measurements of the PEO hydrodynamic radius R_H show that $R_H = 12.9 \pm 0.3$ nm in pure water and 12.6 ± 0.3 nm in aqueous 0.1 M KNO$_3$, indicating segment/solvent interaction parameters that are equal within the scatter. The origin of the PEO adsorption from the salt solutions is thus likely to be in the different PEO segment/mica interactions between the two cases.

Attachment of nonionic polymers, including PEO, to solid surfaces is in general largely driven by van der Waals attraction[14,16] or, for PEO, by H-bonding of the backbone $-O-$ to surface $-OH$ groups.[2,17] An analysis of the $F_n(D)/R$ profiles, however, suggests that this is not the case in the present study: these (Figures 1 and

3) yield potentials ψ_0 at the ionized mica surfaces of 150 ± 10 and 90 ± 30 mV for water and 0.1 M KNO$_3$, respectively.[18] From the Grahame equation for the corresponding effective charge density σ, $\sigma = \sqrt{8\epsilon\epsilon_0 k_B T}\sinh((e\psi_0/2k_B T))\sqrt{[K^+]_\infty}$ (where ϵ and ϵ_0 are the dielectric constant and the free space permittivity, e is the electronic charge, and $[K^+]_\infty$ is the bulk salt concentration,[19] or its monovalent equivalent for the pure water, which from the measured Debye lengths, Figure 1, is ca. 6×10^{-6} M), we find surface charge densities of ca. 0.002 and 0.1 C/m^2 for the pure water and the aqueous 0.1 M KNO$_3$, respectively. That is, far more of the charged mica surface lattice sites are neutralized in the pure water case. Since the $-O-$ atom on the PEO backbone carries a slight net negative charge, its van der Waals-driven attachment to the surface is likely to be less favorable from the salt solution, where the mica is more negatively charged relative to pure water. The fact that PEO nonetheless adsorbs from the salt solution but not from pure water suggests therefore another mechanism. We propose, in analogy with the known complexation of PEO with alkali metal ions in organic and aqueous solvents,[6,7] that the oxy-ethylene segments bind to the negatively charged mica via an interlayer of hydrated or partly hydrated potassium ions, as schematically shown in the inset in Figure 3. Such a ligand configuration immediately accounts for the propensity of the PEO to bind to the ostensibly more repulsive surface (whose higher charge density results also in a higher density of the counterions available for ligand formation at the surface) and may have interesting implications also for controlling PEO attachment to other negatively charged surfaces, both in synthetic and in biological contexts.

References

(1) Harris, J. M. *Poly(ethylene glycol) Chemistry: Biotechnical and Biomedical Application*; Plenum Press: New York, 1992.
(2) Blin, J.-L.; Léonard, A.; Yuan, Z.-Y.; Gigot, L.; Vantomme, A.; Cheetham, A. K.; Su, B. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 2872.
(3) Maggi, L.; Segale, L.; Torre, M. L.; Machiste, E. O.; Conte, U. *Biomaterials* **2002**, *23*, 1113.
(4) Ryan, P. L.; Foty, R. A.; Kohn, J.; Steinberg, M. S. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 4323.
(5) Klein, J.; Luckham, P. F. *Macromolecules* **1984**, *17*, 1041.
(6) Kuhl, T. L.; Berman, A. D.; Hui, S. W.; Israelachvili, J. N. *Macromolecules* **1998**, *31*, 8258.
(7) Cross, J. *Nonionic surfactants*; Marcel Dekker: New York, 1987.
(8) Klein, J.; Kumacheva, E. *J. Chem. Phys.* **1998**, *108*, 6996.
(9) Pashley, R. M. *J. Colloid Interface Sci.* **1981**, *80*, 153.
(10) Raviv, U.; Laurat, P.; Klein, J. *J. Chem. Phys.* **2002**, *116*, 5167.
(11) Geke, M. O.; Shelden, R. A.; Caseri, W. R.; Suter, U. W. *J. Colloid Interface Sci.* **1997**, *189*, 283.
(12) Chan, D. Y. C.; Pashley, R. M.; White, L. R. *J. Colloid Interface Sci.* **1980**, *77*, 283.
(13) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(14) Fleer, G. J.; Cohen-Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman and Hall: London, 1993.
(15) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; John Wiley & Sons: New York, 1999.
(16) Raviv, U.; Tadmor, R.; Klein, J. *J. Phys. Chem. B* **2001**, *105*, 8125.
(17) Pattanayek, S. K.; Juvekar, V. A. *Macromolecules* **2002**, *35*, 9574.
(18) We note that, since PEO is neutral, these different surface potentials would not affect its energy on approaching the mica surface.
(19) Israelachvili, J. N. *Intermolecular and Surfaces Forces*, 2nd ed.; Academic Press Ltd.: London, 1992.

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