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Communication

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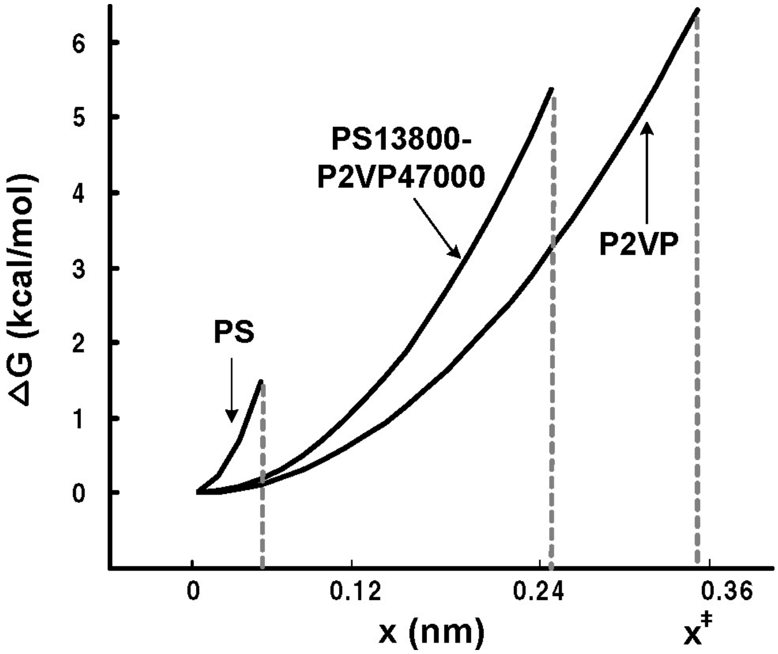

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Quantifying Adhesion Bond Parameters to Distinguish Interactions of Hydrophilic and Hydrophobic Blocks of Polystyrene−Poly-2-vinylpyridine with a Silicon Nitride Surface

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An analysis of the loading rate dependence of the forces required to rupture an AFM tip from a block copolymer surface is reported that provides insight into the structure of the surface−macromolecule contact, differentiation of the block contacting the tip, a measure of the polymer−surface binding energy, and the rigidity of the contact. In a poor solvent, a macromolecule may be driven entirely into contact with a surface if the interaction with the surface is favorable, while in a good solvent, the chain dissolves or at least exhibits large fractions extended into solution.[1] Macromolecular adhesion to surfaces is at the foundation of numerous polymer-based technologies and natural biomaterial interfaces,[2] yet adhesion bond measurements to compare with predictive models have often proven elusive.

Molecular force spectroscopy,[3−12] which probes conformational transitions as a function of structural loading rate, potentially provides the ability to examine the structure of macromolecule−surface bonds directly. The unloading rate dependence of the adhesion between the AFM tip and the molecule should provide information that is significantly beyond adhesion strength. The force required to rupture a polymer chain from an interacting molecular force probe is illustrated in the inset of Figure 1. In a simple model initially proposed by Bell and Evans,[13] each linear region seen in a plot of the transition force versus the logarithm of the loading rate corresponds to a barrier traversed by the system in the direction of applied force. From the slopes and intercepts of each linear region, information about barrier heights, barrier positions for bond breaking, as well as rates of reaction can be calculated. Recently, a more accurate method was proposed by Hummer and Szabo.[14] Here, we report experimental rupture data, analyzed by the Hummer model, to characterize the diblock copolymer interactions with a silicon nitride AFM tip. This paper provides a description of the surface unbinding of individual polymer blocks under conditions where a specific solvent−polymer−surface structure is expected.

Films of the named polymers were spun cast from THF solution onto glass substrates and examined under 10 mM sodium acetate solution, as described previously.[15] The surface topography of the block copolymers is irregular with occasional features about 100 nm tall. Smaller (∼50 nm wide, 5 nm high), more ordered structures, which appear micellar in nature,[15−17] are also visible (see Supporting Information). These micellar structures are not visible in the homopolymer studies. In the ample areas (∼1 μm^2) that are devoid of height features greater than 15 nm, force−distance plots were then collected. The magnitude of the rupture force as a function of the loading rate was then obtained.

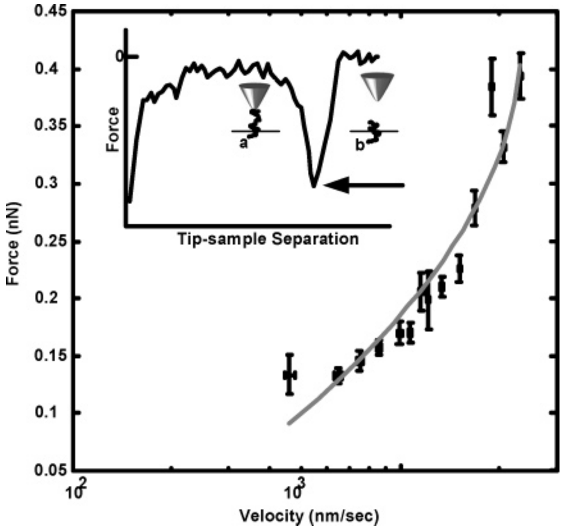

Figure 1. (Inset) Force−extension data for a polymer chain (a) being stretched away from the surface by the AFM tip. After the rupture of the adhesive bond (arrow), the interaction force falls to zero (b). (Outset) A fit of the Hummer model (gray line) to the polystyrene−surface bond rupture force as a function of the velocity of the separation of the two surfaces.

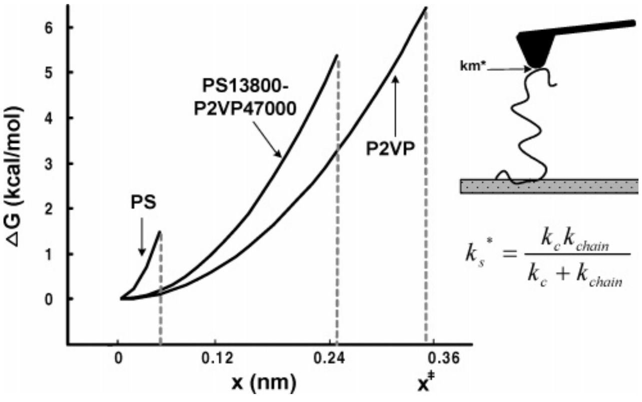

Figure 2. (Left) Free energy surfaces and transition positions in the bond extension coordinate shown for polystyrene (PS), poly-2-vinylpyridine (P2VP), and a block copolymer separating from a silicon nitride tip in aqueous buffer. ΔG offsets between curves are unknown. (Upper right) Scheme of polymer−AFM tip bond being loaded, broken, and analyzed. Stiffness of polymer−tip surface bond is k_m*. (Lower right) Bond is loaded by a spring of stiffness, k_s*, comprised of cantilever and polymer chain springs.

These data were analyzed using Hummer's method to characterize the adhesion reaction surface (see Figure 2). In the Hummer model, the bond is loaded by a flexible chain,[18] and the bond is characterized by a harmonic potential with a cutoff at a critical barrier position and height where the loaded bond ruptures. The

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Table 1. Thermodynamic and Kinetic Parameters Obtained for PS, P2VP, and Their Diblock Copolymers Detaching from a Silicon Nitride Surface

molecule	k_m* (N/m)	$x^‡$ (nm)	$\Delta G^‡$ (kcal/mol)	$k_{off}(0)$ (s^{-1})	k_{chain} (N/m)	D (nm^2/s)
PS29100	6.4	0.06	1.5	83	0.62	0.80
P2VP50000	0.75	0.35	6.5	0.4	0.03	69
PS7800−P2VP10000	0.82	0.34	6.9	0.12	0.14	41
PS13800−P2VP47000	1.2	0.25	5.4	1.6	0.08	31
PS60100−P2VP46900	0.91	0.25	4.0	7.2	0.04	19

molecular spring constant, k_m*, illustrates the stiffness of the adhesive bond, and free motion on the reaction surface is characterized by a diffusion coefficient, D.[19]

An analysis for rupturing different PS and P2VP adhesion bonds with a silicon nitride surface is summarized in Table 1. The fits themselves and a description of the fitting process can be found in Supporting Information. It can be seen that the stiffness of the adhesion bond for pure polystyrene is nearly 10 times that of pure P2VP and the diblock copolymers, while the barrier to breaking the adhesion bond is nearly 6 times smaller. From these data, we infer that the P2VP block of the diblock copolymers is preferentially exposed to the aqueous solution. This is reasonable given the polar nature of P2VP and the nonpolar nature of PS. In addition, we observe that the distance to the barrier is significantly greater for rupturing the P2VP−surface bond compared with that for rupturing the PS−surface bond. This, we speculate, is due to two different characteristic polymer−Si_3N_4 surface bonds. In the case of PS, it appears that a tight bond, probably caused by a direct van der Waals attraction with a neutral region of the AFM tip's surface, is present. By way of crude comparison, in an approximation neglecting stochastic behavior of the bond breakage, one may roughly locate the inflection point of a Lennard-Jones potential for two interacting atoms where the maximum adhesive force can be found; this is 0.04 nm beyond the equilibrium interatom separation. The similarity with our obtained value is probably fortuitous, but the order of magnitude similarity is stimulating.[20] The surface charge density on a silicon nitride tip at pH 7 is -0.03 e/nm^2, determined by measuring the surface feature's apparent height at different electrolyte concentrations, which provides free space for polymer binding to neutral regions.[21] On the other hand, P2VP would be expected to bind preferentially to surface silanols. The far greater distance to the barrier and the softness of the effective spring suggest the P2VP−surface bond occurs through another surface intermediate, perhaps a water molecule bound to a surface silanol.

This description of an indirect interaction between a pyridine ring and silica surface is consistent with observations from other researchers, though our work may provide the first direct evidence. Yoon and co-workers[22] found by AFM that the hydration force between a silicon nitride tip and silica surface remains unchanged in 2% pyridine in water. Matzner et al.[23] determined the standard free energy of adsorption (ΔG°_{ads}) for pyridine binding to silica is -14 kJ/mol. Since this value is smaller than the heat of adsorption of water vapor on silica (52 kJ/mol),[24] it was suggested that pyridine may adsorb on silica in such a way that the water molecules are not displaced from the first (few) adsorption layer(s). Upon adsorption to a silica surface, only weak perturbation of pyridine's Raman spectrum was observed.[23] Rivera and Harris[25] found that pyridine bound via waters bound to surface silanols of silica sol−gels with a free energy of adsorption of 13.0 ± 2.5 kJ/mol.

The fitted diffusion coefficients for PS on silicon nitride are about 25−75 times smaller than that of P2VP. These values are comparable to those previously obtained by other means (0.02−0.26 nm^2/s).[26]

In this work, it is not determined how many individual "contact points" there are between a chain and the surface at rupture, though the heights of the barriers to unbinding are consistent with a single contact. If the number of contacts is different between the polymer blocks and the surface, then the rupture process might not be viewed as breaking a single contact, which could affect the molecular interpretation of the barrier positions obtained by the Hummer model, though a full discussion of this effect is beyond the scope of this paper.

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Supporting Information Available: Force versus velocity plots, an AFM image, and details on experiment/modeling are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) In the model, the free energy surface is harmonic with a cutoff $\beta V_o(x) = 1/2 k_m x^2$ for ($x < x^‡$) and $\beta V_o(x) = -\infty$ for ($x > x^‡$) Here, k_m is the molecular spring constant, and x is a good reaction coordinate if the dynamics of the other degrees of freedom are sufficiently fast. $\beta = k_B T$. $\beta k_m = k_m$* and $\beta k_s = k_s$*. The average rupture force versus velocity data are then fit by $\beta F = k_m x^‡ - [2k \ln \{k_{off}(0) \exp(\gamma + k_m (x^‡)^2/2)/k_s \upsilon x^‡ (k_m/k)^{3/2}\}]^{1/2}$. Here, $k = k_m + k_s$, where k_s is the pulling spring constant and reflects the properties of the cantilever and polymer chain linker. The loading rate was obtained directly from our force plots using four data points prior to the cantilever's point of maximum extension. The velocity is then calculated using the loading rate and spring constant of the system. Therefore, a factor of $\{1 + (k_c k_m + k_c k_{chain})/(k_m k_{chain})\}$ was multiplied to υ in the above equation to account for the tip's velocity.
(20) In this rough estimate, the A and B parameters of the Lennard-Jones potential for two atoms are taken to be roughly 10^{-77} J m^{-6} and 10^{-134} J m^{-12}, respectively. The equilibrium separation of the atoms is $(2B/A)^{1/6}$ (or 0.355 nm), and the separation where the adhesive force is maximum is $(26B/7A)^{1/6}$ (or 0.395 nm).
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