Polyelectrolytes

DOI: 10.1002/anie.200701796

Controlling Network–Brush Interactions to Achieve Switchable Adhesion**

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Polyelectrolytes are remarkable molecules because of their smart behavior. By altering the environmental pH value, polyelectrolytes can undergo conformational transitions, which, if controlled, enable a wide range of applications. Herein, we describe experiments whereby a polyacid gel and a polybase grafted to a silicon substrate can be used as a means of demonstrating reversible switching adhesion in aqueous solution. By changing the environmental pH value, we can control in situ whether the gel adheres to the grafted layer or whether it dissociates. Such control over adhesion may have applications in actuators, microfluidics, drug delivery, personal-care products, or even in the understanding of biological materials.

If we consider nonpolyelectrolytic polymers, the adhesion between a grafted polymer layer (polymer brush) and a polymer network in the molten state is due to enthalpic interactions that force the brush into the gel as well as the entropy of the brush as it maximizes its conformations by forming a random or self-avoiding walk structure. As the brush is entangled between fixed cross-links, the only way for the brush and the network to come apart and disentangle is for the brush to diffuse along its own contour.[1–4] This is prohibited, all the more so given that all of the other grafted polymers would have to perform the same disentanglement at the same time. The only way to remove the adhesion is therefore to break bonds, leaving the system unusable.

Polyelectrolytes in aqueous solution, however, often undergo a transition from a hydrophobic state, where they can collapse and fall out of solution, to an extended hydrophilic state. This property makes them useful as nanoactuators when they are attached to a surface.[5,6] The properties of hydrogels in good solvent conditions are perhaps even more dramatic, with swellings greater than an order of magnitude than in their dry state routinely observed.[7]

We present herein a means of using the responsiveness to the pH value of polyelectrolytes to create reversible adhesion of two surfaces by studying the interaction of a poly[2-(dimethyl amino)ethyl methacrylate] (PDMAEMA, a polybase) brush-modified surface with a poly(methacrylic acid) (PMAA) gel. The brush and gel were equilibrated in water (initially at pH 7), then brought into contact, where it was found that there was good adhesion between the brush and the gel, a result previously obtained for two oppositely charged polyelectrolyte gels.[8] (The gel will not adhere to a silicon substrate without the brush at any pH value.) At equilibrium, the PMAA gel is partially charged and swollen to 112 % of its collapsed mass at pH 2 (approximately 300 % of its dry mass). There is also expected to be some charge on the PDMAEMA[9] brush, the free polymer of which has a pK_a value of approximately 7. The two components of the system should be oppositely charged at the pH value at which equilibrium was achieved (pH 5.8). However, even at pH values of between 3 and 7, there is good adhesion between the brush and the gel, with stronger adhesion at higher pH values. At a pH value less than 2, the adhesion fails and the gel and brush disconnect.

To quantify the level of adhesion, experiments were performed by using a modified Johnson–Kendall–Roberts (JKR) experiment. The experimental setup is shown in Figure 1. The JKR technique provides a means of directly probing the adhesion at the interface, whereas other methods, such as tack and peel tests measure the adherence, which is also dependent on bulk-material properties.[10] The gel, formed in a hemispherical mould, is placed in contact with the brush-coated substrate. By compressing the gel with different forces, we can vary the contact radius. This radius, before, after, and during loading is noted at equilibrium. On unloading, the energy required to open the interface may be determined, yielding the work of adhesion, G (specifically, G is the static crack propagation energy, which is the energy required to separate the gel from the substrate). The JKR equation is shown below.[11]

$$a^3 = \frac{R}{K}\left(P + 3\pi GR + \sqrt{6\pi GRP + (3\pi GR)^2}\right) \quad (1)$$

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[**] We acknowledge financial support from the European Community's "Marie-Curie Actions" under contract MRTN-CT-2004-504052 [POLYFILM] and from the Engineering and Physical Sciences Research Council (GR/R74383/01). We thank Liliane Léger and Costantino Creton for invaluable discussions.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

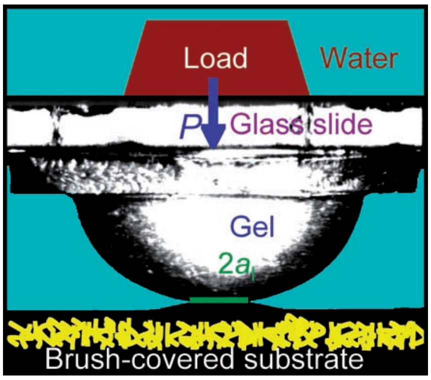

Figure 1. Schematic diagram of the experimental setup incorporating a photograph of the gel in contact with the surface. Note that in the present experiment, the contact radius is measured in profile, rather than imaging through the gel from above.[22] The advantage of our approach is that it allows better contrast in aqueous media for hydrogels. The contact diameter during loading, $2a_l$, in the photograph is 0.93 mm.

In Equation (1), a is the contact radius of the lens on the brush, R is the radius of curvature of the gel, K is the bulk modulus of the lens, and P is the load on the gel. These measurements are made as a function of load and pH value, which affects the ionization within the gel and brush. If the pH value is changed, the bulk properties (swelling and modulus) of the gel change. The modulus of the gel is obtained as a function of the pH value by using the Hertz equation (Equation (2)).[12]

$$PR = Ka^3 \tag{2}$$

Herein we examine the surface contact radius for the gel on an uncoated silicon substrate, where there is negligible adhesion. In the absence of adhesion, Equation (1) reduces to Equation (2), which can be used to measure the modulus.

The use of the JKR equation (Equation (1)) with our separate explicit measurements of the modulus of the gel allow us to directly probe the interaction between the gel and the substrate at the interface. The energy required to separate the gel from the substrate remains a function of the applied load, which suggests that the work of adhesion is pressure sensitive. A better means of displaying the data is to take into account this pressure effect by plotting the work of adhesion as a function of the compressive stress (i.e. the pressure) at the point where the JKR measurement determines the adhesion, which is the circular contact line (final radius a_f) that the gel relaxes to when the load is removed.[13] This stress is given by Equation (3).

$$\sigma(a_f) = \sqrt{\frac{3a_l K G_0}{2\pi(a_l^2 - a_f^2)}} - \frac{3K\sqrt{a_l^2 - a_f^2}}{2\pi R} \tag{3}$$

In Equation (3), G_0 is the work of adhesion measured before any load is applied and a_l is the equilibrium contact radius after the load is applied. In Figure 2, we show the work of adhesion as a function of stress for two different loads at three different values of pH. The work of adhesion varies by a factor of 30. Indeed, the largest value measured, 442 mN m^{-1}, is less than an order of magnitude smaller than values obtained from JKR measurements of an epoxy with a silanated glass[14] and is comparable with results on model soft adhesives.[15]

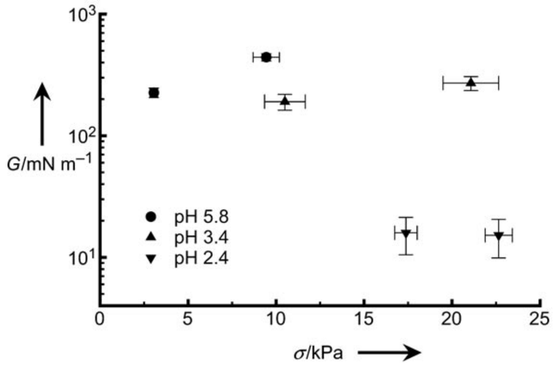

Figure 2. Work of adhesion G as measured from the JKR equation (Equation (1)) as a function of surface stress σ measured at pH values of 2.4, 3.4, and 5.8 after loads of 32 and 60 mN were applied for 15 minutes. The dry brush thickness is approximately 20 nm here, except for the smallest stress (applied at pH 5.8), where the brush is approximately 16 nm thick.

To demonstrate that the system exhibited switchable behavior, we measured the contact area as a function of time whilst altering the pH value. In this case, when the pH value is lowered from 3.4 to 2.4 (see Figure 3), the contact diameter does not change. When the pH value is further lowered to 1.1, the contact diameter decreases. At this pH value, the gel may be safely removed from the brush without damaging either the gel or the brush, allowing reuse. This measurement clearly demonstrates that, although the interaction between the gel and the brush depends on its history, adhesion will be removed if the pH value is low enough. After adhesion and disconnection, the gel and brush can be readhered by simply bringing them in contact with solution at a pH value greater

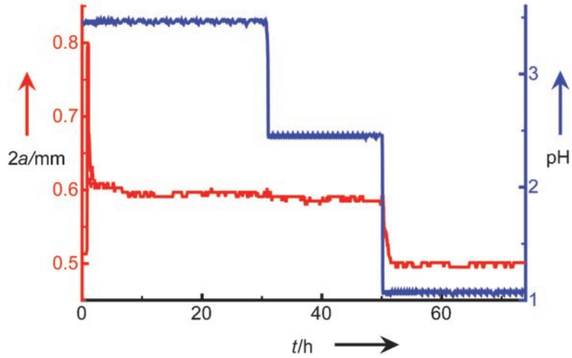

Figure 3. Contact diameter ($2a$, red) and pH value (blue) for a PMAA gel placed in contact with a PDMAEMA brush of a dry thickness of approximately 16 nm as a function of time t after removing a load of 32 mN. The contact diameter does not change as a function of the pH value until the gel disconnects from the brush at pH 1.1.

than approximately three. This process may be repeated several times.

When the larger load is applied, the time taken to detach the gel from the brush at low pH values is very long; in the case of the largest work of adhesion measured at pH 5.8, the gel took up to three days at pH 1.1 to dissociate compared with 7 h for the smaller load. It is clear therefore that smaller loads improve the switchability of the system.

To examine further the nature of the interaction between the brush and the gel, neutron reflectometry[16] experiments were performed on brushes lightly pressed into contact with gels at pH 7. In this case, the brush was synthesized from a deuterated monomer to provide contrast with the nondeuterated gel and the solution in H_2O. In Figure 4, we show the reflectivity data and the brush-volume-fraction–depth profile. The depth profile is remarkably similar to that of swollen poly[2-(diethyl amino)ethyl methacrylate] (PDEAEMA) brushes in good solvent,[17] and in fact, the depth profile of the brush at pH 7 without gel present is also very similar (also shown in Figure 4). We therefore believe that at small loads there is no interpenetration of the gel by the brush, and we therefore tentatively suggest that the origin of the adhesion is a mixture of electrostatic interactions between opposite charges as well as hydrogen bonding between the amine groups of the PDMAEMA and the carboxylic groups of the PMAA. This suggestion is also supported by the adhesion being reversible. Hydrogen bonding between proton donor and proton acceptor species has been previously demonstrated as a useful means of controlled adhesion,[18] and the switchability and reversibility in situ described in this manuscript represents a valuable means of controlling adhesion without any interim substrate treatment. It is very possible that, for larger loads, a significant contribution to the adhesion may arise from interpenetration between the brush and the gel, which might help explain the extended recovery times at low pH values after the gel has been adhered.

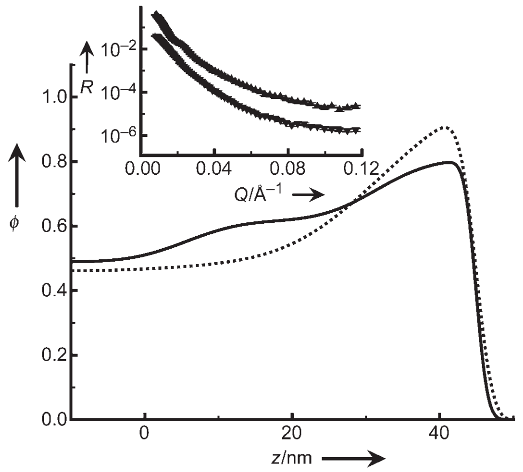

Figure 4. The volume-fraction–depth profile $\phi(z)$ for a deuterated PDMAEMA brush in contact with a PMAA gel at pH 7 reveals that the brush is not extended at its extremity, but rather has a sharp interface with the gel. Although it would be difficult to eliminate the possibility that the brush is also entangled within the gel, the profile for the brush without the gel is also shown and is similar, which suggests that the dominant contribution to the interaction between the brush and the gel is at the interface between them. In the inset the corresponding reflectivity R data and fit as a function of the neutron momentum transfer wavevector Q for a deuterated PDMAEMA brush in contact with a PMAA gel at pH 7 are shown. The quality of the fit is excellent with a χ^2 value of approximately 1. Adhesion with gel: —— (▲ for inset), brush conformation in water: ----- (▼ for inset).

Experimental Section

PDMAEMA brushes were synthesized by using atom-transfer radical polymerization (ATRP) on a silicon substrate by using a similar procedure to that described previously for PDEAEMA brushes.[19] In this case, however, $Cu^{II}Br_2$ was added at the beginning of the reaction to induce a more controlled ATRP. The [11-(2-bromo-2-methyl) propionyloxy]undecyl trichlorosilane initiator layer was allowed to equilibrate on the surface of a toluene solution overnight to maximize surface coverage. Although we have not measured directly the brush molecular weight, we can estimate it by assuming a grafting density of 0.5 brushes nm^{-2}, which is reasonable for our experimental conditions,[20,21] and a monomer density of 0.93 $g\,cc^{-1}$ (Aldrich). We then obtain, for a 20-nm film, a molecular mass of 22.4 kDa. This molecular mass scales linearly with brush thickness. For a uniform distribution of molecular initiatior, a low polydispersity is assured when the films are of uniform thickness, as is the case in the present experiments.

PMAA gels were synthesized by the free radical cross-linking 32% (w/w) methacrylic acid with 0.5% (w/w) *N,N′*-methylene bisacrylamide by using 0.6% (w/w) 2,2′-azobis(2-methylpropionamidine) dihydrochloride as the catalyst in aqueous solution. The gels are highly cross-linked with a factor of 123 more methacrylic acid monomers to methylene bisacrylamide cross-linker in the solution. If the cross-linking were perfect, this would correspond to an average of 62 monomers between cross-links and the gel would be highly heterogeneous.

Neutron reflectometry measurements were performed by using the reflectometer CRISP of the ISIS pulsed neutron and muon source at the Rutherford Appleton Laboratory. The gel was gently pressed onto the brush in a specially designed perspex sample cell. Care was taken to avoid contact with the cell during alignment of the beam. In these experiments, the neutrons were incident on the brush through the silicon substrate. This was necessary because thr neutrons incident on the brush layer through the gel and water would have been very strongly scattered owing to the large incoherent scattering of water. The disadvantage of our sample geometry is that, for such a thin brush layer, there is no total reflection ($R=1$) in the data, which is a useful means of normalizing the data. We circumvented this problem by comparing the data acquisition with that with a D_2O interface in the same sample cell. The brush volume fraction profiles were obtained by optimizing an increasing series of layers to minimize χ^2.[17] The brush was also characterized in the dry state and revealed a uniform layer with a Gaussian surface roughness of 1.5 nm.

Received: April 23, 2007

Keywords: adhesion · gels · interfaces · polyelectrolytes · polymers

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