

SWELLING AND COLLAPSE OF A WEAK POLYELECTROLYTE AS A FUNCTION OF PH

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Progress in the application of soft condensed matter to areas of nanotechnologies depends in large part in the development of “smart” polymers with the capacity to respond to their environment. Weak polyacids and polybases contain no fixed charges along the chain and so present an interesting class of material in their own right as this absence of fixed charges allows a reasonable amount of control over the polymer conformation. We have synthesized polybase chains tethered to a silicon substrate using a “grafting from” method, in which the polymer chains grow from a self-assembled monolayer coated surface. (Diethylamino)ethyl methacrylate was grown directly from the functionalised surface using atom transfer radical polymerization (ATRP). Full details of the poly[(diethylamino)ethyl methacrylate] (PDEAEMA) synthesis are given elsewhere [1] and in a forthcoming publication.

Although polyelectrolyte brushes have been studied by a variety of techniques [2] including ellipsometry [3], neutron reflectometry is perhaps the technique most suited to studying their conformation. We have used this technique on the EROS reflectometer to study PDEAEMA grafted from silicon wafers. The PDEAEMA was immersed in deuterated water with small amounts of NaOH or HCl added to control the pH between 3 and 10. In acidic conditions, the PDEAEMA is stretched; Coulombic repulsion between charges located along the chain control the structure of the normally hydrophobic polymer. In the presence of added salt, charges are stripped from the brush, causing collapse of the now-hydrophobic chains.

In Figure 1 we show neutron reflectivity data for a PDEAEMA brush, which was measured to be 13 nm thick dry (in air). The data are plotted in the Porod form of k against $R.k^4$ in order to better reveal the quality of the fits (a variation of less than three orders of magnitude in comparison to six orders with a simple reflectivity plot). The data were fitted using a downhill simplex routine using a depth profile consisting of a trilayer structure. The fits are of a very high quality with $\chi^2 < 2$ in each case.

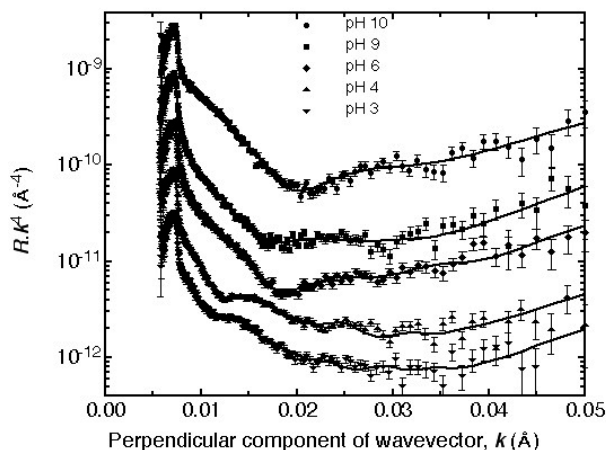


Figure 1. Reflectivity data and fits for a PDEAEMA brush in D₂O for various values of pH. The data for pH = 9, 6, 4, and 3 are staggered by factors of 3 for clarity.

Depth profiles (as a function of distance from the substrate) obtained from these data are shown in Figure 2.

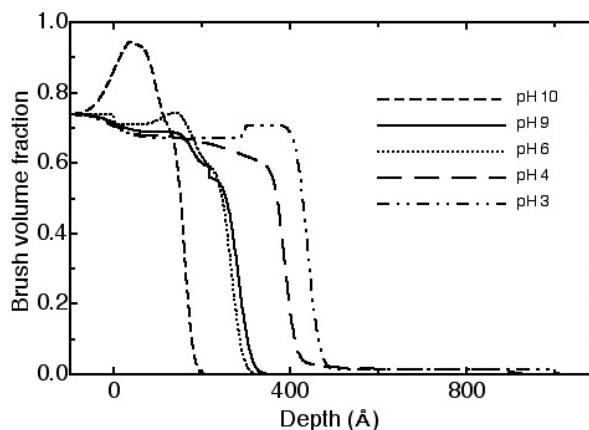


Figure 2. Volume fraction-depth profiles for a PDEAEMA brush as a function of pH (the fits are presented in Figure 1). A clear swelling of the brush with decreasing pH is visible. Note that initiator and oxide layer are not visible in these profiles; the k -range of the experiment was not sufficient to visualise these rather thin layers

In order to consider the effect of brush thickness on the conformation, we considered a thicker brush (28 nm dry thickness). In this case the brush

structure shows a more pronounced structure with a large depletion in the near-substrate region, with the brush swelling by a factor of four in comparison with a factor of a little over two in the depth profiles shown in Figure 2. These depth profiles are shown in Figure 3. The fits were of a similar quality to those in Figure 1, with χ^2 again less than 2 in all cases. It must be pointed out that in both cases there is a small amount of brush that is strongly extended. This effect is real because of the existence of short wavelength fringes in the neutron data, which must correspond to extended layers.

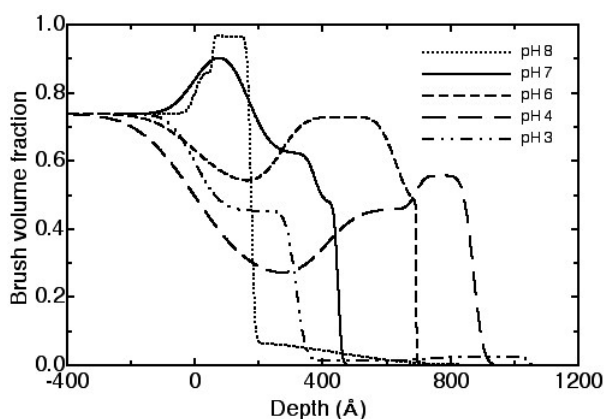


Figure 3. Volume fraction-depth profiles for a PDEAEMA brush as a function of pH. This brush exhibits more dramatic swelling than that shown in Figure 2.

Grafting densities for brushes of this nature are very difficult to experimentally determine [3], and we have been unable to determine the grafting density for these PDEAEMA brushes. Without this information, an explanation for the dramatically different profiles displayed in Figures 2 and 3 must remain speculative. Basic polymer physics would suggest that the thicker grafted layer (Figure 3) is in a “mushroom” conformation, whereby the brush stretches away from the surface before adopting a random walk conformation. We note that the

nomenclature “brush” is often used for grafted polymers, but is used uniquely to differentiate the polymer layer from the mushroom regime. Given that the polymer layer detailed in Figure 3 stretches significantly more than that in Figure 2, this polymer must be of a greater molecular weight if it is adopting a mushroom conformation.

We have performed scanning force microscopy measurements to examine the brush surface and observed that the brush does not completely cover the entire surface (in both samples); there were “holes” in the brush layer of typically $\sim 1 \mu\text{m}$ diameter. The consequence for the analysis of the neutron reflectometry data is that the brush can swell laterally, and the neutron depth profile does not necessarily constitute a lateral average of the total material. To obtain the best possible fits to the data, the requirement that the total brush mass be conserved was relaxed. In fact, a one parameter fit with conserved mass is provided elsewhere [1]. Although the fits are substantially weaker than those presented here, the conclusions are not significantly altered; the degree of swelling discussed here is still observed.

To summarise; we have used ATRP to study the swelling of a polyelectrolyte brush as a function of pH. The synthesis was capable of providing a reasonably uniform film over the large length scales necessary for neutron reflectometry measurements ($\sim 3 \text{ cm}$). The polymer swells to a thickness of around a factor of three from its dry thickness. Such brushes may have applications in technologies where pH responsive behaviour is particularly desirable such as controlled drug delivery.

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References

- [1] A. J. Ryan, C. J. Crook, J. R. Howse, P. Topham, R.A.L. Jones, M. Geoghegan, A. J. Parnell, L. Ruiz-Pérez, S. J. Martin, A. Cadby, A. Menelle, J. R. P. Webster, A. J. Gleeson, W. Bras, *Faraday Disc.* 128 in press.
- [2] J. Rühle, M. Ballauff, M. Biesalski, P. Dziezok, F. Gröhn, D. Johannsmann, Houbenov, N, Hugenberg, R. Konradi, S. Minko, M. Motornov, R. R. Netz, M. Schmidt, C. Seidel, M. Stamm, T. Stephan, D. Usov, H. Zhang, *Adv. Polym. Sci.* 165 (2004) 79.
- [3] M. Biesalski, D. Johannsmann, J. Rühle, *J. Chem. Phys.* 120 (2004) 8807.