

HIGHLY STRETCHED POLYMER BRUSHES WITH A LOW SWELLING CAPACITY

C. Devaux¹, F. Cousin², J-P. Chapel¹¹Laboratoire des Matériaux Polymères et des Biomateriaux, UMR CNRS 5627, Université Claude Bernard Lyon 1, ISTIL, 43, Boulevard du 11 Novembre 1918, 69622 Villeurbanne cedex, France}²Laboratoire Léon Brillouin, CEA-CNRS, CEA Saclay, 91191 Gif sur Yvette, France

Polymer chains in thin films are seen in a tremendous number of systems and devices of modern material science and technology. The need for controlled (thickness, Mw, conformations...), stable and reproducible thin films is then essential. We have developed an overall strategy to built-up chemisorbed thin films with tunable architectures grown directly from silica surface through controlled macromolecular chemistry [1]. The process is split in two distinct steps : (i) deposition of an initiator monolayer using "reactive" Langmuir-Blodgett deposition technique that allows the control of the chain lateral grafting density σ (up to 1.0 chain/nm²) (ii) the nitroxide mediated free radical polymerization of styrene that allows the control of chain length N. It induces a direct control of both brush thickness h and chain stretch S. The active chain ends enables to reinitiate the polymerization.

We describe here neutron reflectivity measurements performed on the EROS reflectometer on our controlled brushes in order to (i) test the homogeneity of the chains growth *during* the polymerization process and (ii) to measure the conformation of the brushes in good solvent. The brush preparation and characterization were achieved according to methods previously reported. The brush thicknesses were obtained in air through ellipsometric measurements with a 15-20 Å layer of native silica and a 10-15 Å layer of grafted initiator. All reflectivity curves have been fitted by model reflectivity curves calculated by the standard optical matrix method including SiO₂ and initiator layers. Best fits between calculated and experimental spectra were obtained by minimizing least squares χ^2 .

Homogeneity of the brushes

Taking profit from high neutronic contrast between deuterated and hydrogenated PS, we have designed a DPS/HPS copolymer brush to check *a posteriori* the homogeneity of the chain growth front *during* the polymerisation from the surface. It is linked to the width of the interdiffusion layer of the DPS/HPS interface. The bilayer was build up from two polymerization runs in a row a first one with deuterated styrene (N= 95) followed by a second

one with hydrogenated styrene (N=90). The DPS and (DPS+HPS) dry thicknesses obtained by ellipsometric measurements were respectively 230Å and 420Å. Neutron reflectivity measurements, carried out in the dry state, are presented on figure 1. There are irregular Kiessig Fringes arising from the three layers structure (HPS, DPS and the total PS layer). Best fits are obtained with a PSH and a PSD layer of 250Å and 180Å respectively with an interdiffusion layer of 25 Å. σ_{int} is get unambiguously from the progressive apparition or disappearance of the fringes when the interdiffusion layer is shifted shift from 0Å to 50Å. The value of 25Å for σ_{int} on a total layer of 430Å underline the homogeneity of the brush growth and the possibility to build multilayers with well defined interfaces.

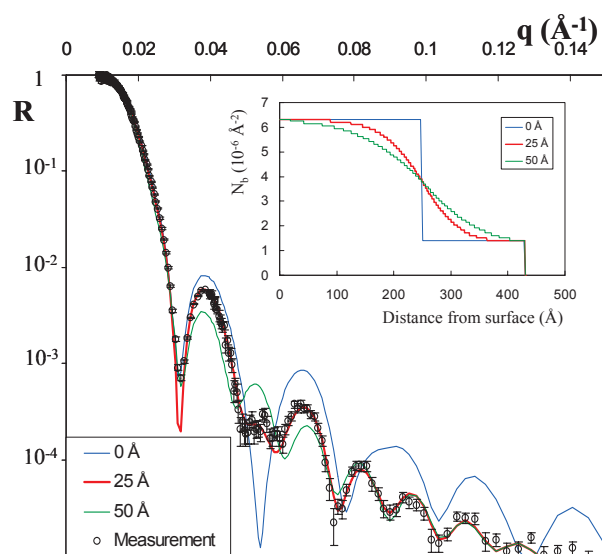


Figure 1. Reflected curve of the PDH/PSD layer. Fits correspond to the profiles showed in the insert.

Conformation of the brushes

Three samples were made with quite high grafting density in which we vary either σ test at constant N, either N at constant σ ($\sigma=0.5\text{chain/nm}^2$, N=120; $\sigma=1\text{chain/nm}^2$, N=120; $\sigma=1\text{chain/nm}^2$, N=270).

Figure 2.a presents the results obtained for dry layers. Fits have been realized with a zero roughness interface and with a polymeric volume

fraction Φ of 1. We get $h = 110 \text{ \AA}$, 220 \AA and 470 \AA respectively for the three layers. We check thus that thickness the thickness h scales linearly with either the chain length N and the grafting density σ ($h \propto N\sigma$) in bad solvent (air). As σ is quite high, the chains are then already extended in air.

Though the brush structure does not depend on N , we studied the influence of σ on swollen brushes for the samples with $N = 120$ in good solvent (deuterated toluene). The reflected curves are presented on figure 2.b where they are compared to the calculated ones obtained for the unswollen brushes. Three features enables to conclude qualitatively on the swollen brush conformations: (i) brushes are partially swelled. The polymer/solvent contrast has decreased as the reflectivity is weaker than in the unswollen case. (ii) The Kiessig fringes are still visible but less marked. The polymer layer has hence finite size but the density profiles are no longer step-like. (iii) The solvent has enlarged the thickness of the layers as the Kiessig fringes are shifted towards lower q . Their thickness is roughly the same as the fringes minima are located at the same q .

Reflected curves have been fitted by a continuous profile of swelled chains which ensures polymer conservation from dry to swollen state (divided in layers of 10 \AA). Profiles are shown in the insert. The thickness for which Φ reaches 0 is the same for both samples ($\approx 300 \text{ \AA}$). This value corresponds nearly to the fully extended PS chain (L_0). The volume fraction Φ_s at the surface ($z=0$) keeps for the highest grafting density the unusual value of 0.85, to our knowledge the highest value ever reported in literature. As the chains are already very stretched the dry state when increasing σ , the solvent has some difficulty to penetrate the layer leading to a somehow low swelling capacity.

This has a direct impact on the swelling laws. In a good solvent, the chains adopt an extended conformation consecutive to the solvent-polymer interactions determined by a balance between the interactions that promote stretching and the associated loss of chain conformational entropy [2]: h/N scales with $\sigma^{1/3}$ for moderate densities

($\sigma < 0.2 \text{ chain/nm}^2$) [3] as the chains adopt an extended conformation consecutive to the solvent-polymer interactions. But for our dense brushes, $h_s/N \propto \sigma^n$ with $n=0.5$, a result generally obtained in Θ conditions. The very high grafting density which reduces the brush swelling capacity as toluene is a good solvent of PS at room temperature.

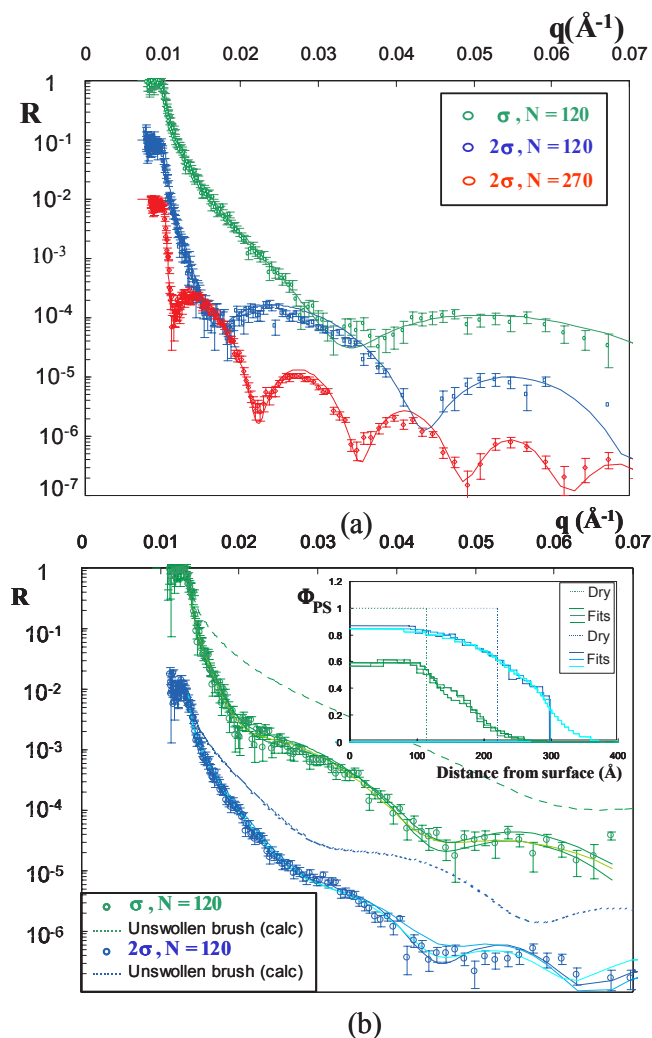


Figure 2. (a) Experimental reflected curves and corresponding fits for dry brushes. (b) Experimental reflected curves, corresponding fits for the swollen brushes and calculated curves for unswollen brushes. Insert present volume fraction profiles.

References

- [1] Devaux C., Beyou E., Chaumont P., Chapel JP., *Eur. Phys. J. E.*, 2002, 7(4), 345.
- [2] Brown H.R., Char K., Delin V.R., *Macromolecules*, 1990, 23, 3385.
- [3] Auroy P., Auvray L., Léger L., *Phys. Rev. Lett.*, 1991, 66, 719.