DOI: 10.1002/cphc.200700131

Robust, Biomimetic Polymer Brush Layers Grown Directly from a Planar Mica Surface**

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Mica is unique in that it may be readily hand-cleaved to create large areas that are molecularly smooth (exposing a single {001} crystallographic plane, whose roughness over its entire area—up to several cm^2—is that of the lattice undulations alone, some 0.025 nm).[1] This property of planar mica surfaces has long been utilized in applications where sub-nanometric smoothness is essential; these include electron and scanning probe microscopies,[2] single-molecule force probes,[3] streaming-potential measurements,[4] and the surface force balance (SFB), where forces in a very wide range of conditions have been characterized.[5] This fact has made mica a paradigmatic "ideally smooth" substrate in research, and it is often coated with other species to modify its surface properties while retaining its atomically smooth topology. Macromolecular coatings, in particular, provide a wide scope for modifying surface characteristics,[6] but to date, in situ polymerization has only been achieved (at high temperatures) on mica powders;[7,8] these do not provide the advantages of planar mica, for which only physical adsorption or grafting have been reported. Herein, we report the direct in situ growth of biomimetic poly(zwitterion) brushes to demonstrate the feasibility of a grafting-from approach onto freshly cleaved planar mica, using atom-transfer radical polymerization (ATRP) from initiator groups attached to this surface. In particular, we characterize these brushes by using a wide range of chemical and physical approaches, which include X-ray photoelectron spectroscopy (XPS), multiple-beam interference, X-ray reflectometry, atomic force microscopy (AFM), and an SFB, to confirm the end-tethered structure of the layers and their robustness with respect to compression and shear. The in situ process provides clear advantages in terms of accessible surface density and robustness of the polymer coating, as demonstrated for other planar substrates,[9] while the versatility of ATRP[10] carries potential for a wide range of polymers to be grown onto planar mica.[11]

Freshly cleaved mica was primed for ATRP by attachment of a cationic macroinitiator, described earlier,[12] onto the mica from a 0.2% w/v aqueous solution (20 min incubation). This macroinitiator is comprised of about 80 mol% quaternized repeat units, which adsorb on the negatively charged mica surface, and 20 mol% 2-bromoisobutyryl ester initiator groups (Figure 1a). Its adsorption was confirmed by XPS, and its adsorbed amount and layer thickness were determined by neutron reflectometry on a corresponding silica surface under water and by XPS, which yielded a dry thickness of (0.4 ± 0.1) nm on the mica. Both measures indicate an essentially flat, quite densely packed adsorption of the macroinitiator on the surface, as sketched in Figure 1, with a mean area of (4.2 ± 1) nm^2 per bromo-initiator group.

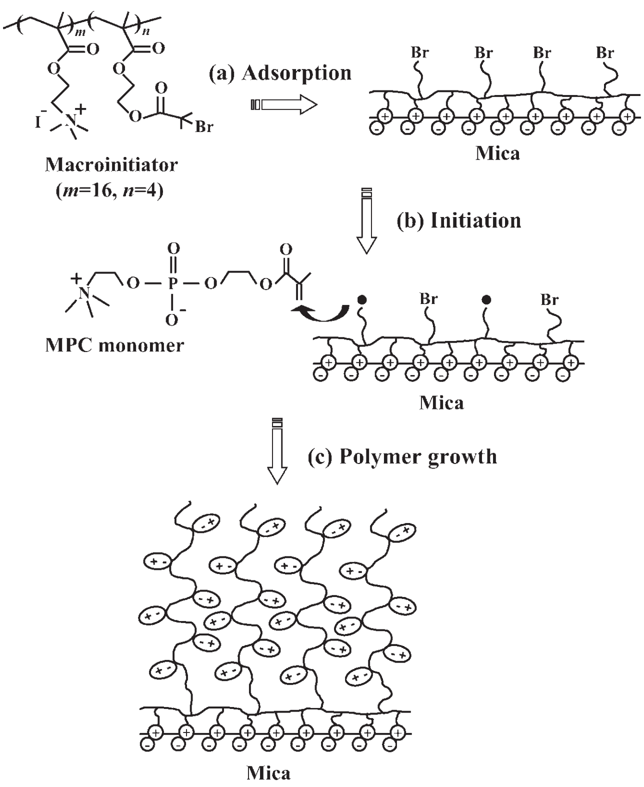

Figure 1. Polymerization of MPC: a) attachment of a cationic macroinitiator onto freshly cleaved mica, b) initiation of ATRP, and c) polymer growth (see text for details).

Polymerization of the biomimetic zwitterionic monomer, 2-(methacryloyloxy)ethyl phosphorylcholine (MPC, Figure 1b), was carried out on the pre-initiated mica described above, in an oxygen-free aqueous solution, by using ATRP at room temperature. Deoxygenated water was transferred via a Gastight syringe through a sealing septum to a pre-evacuated flask containing CuBr, CuBr$_2$, and 2,2′-bipyridine, and after thorough stirring and bubbling with nitrogen, part of this solution was transferred to dissolve the MPC monomer with further stirring and bubbling. The concentration in the final mixture was [MPC] = 1.33 mol L^{-1}, with the ratio [MPC]:[CuBr]:[CuBr$_2$]:[2,2′-bi-

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pyridine] = 60:0.9:0.1:2. The well-mixed and deoxygenated monomer/catalysts solution was then injected into a glass tube containing the macroinitiator-coated mica. After 1.5 h in a nitrogen atmosphere, the reaction was terminated by removing the mica from solution, rinsing thoroughly with water, and drying with nitrogen. The poly(MPC) layer prepared under these conditions is denoted 20–1.5 pMPC, which indicates 20 min macroinitiator incubation time and 1.5 h polymerization time. These times could be varied to control the grafting density and film thickness. X-ray reflectometry measurements (to be published) show that for a given initiator density, the polymer dry thickness increases with polymerization time (as expected), though the rate of such increase falls at longer times. The results below are for the 20–1.5 pMPC layer.

XPS measurements on the pMPC layer were carried out using a standard approach[13] in a Kratos AXIS-HS setup, with a monochromatic $Al_{K\alpha}$ source at 15 kV × 5 mA emission current. The base pressure was 1×10^{-9} torr, and angle-resolved spectra were recorded over a range of take-off angles. The data in Table 1 are for normal take-off angles. In the last two rows, the atomic concentrations are normalized with respect to phosphorus (= 1). The close agreement between the measured and stoichiometric atomic ratios (row 3 versus row 4 in Table 1) confirms the presence of the polymer on the surface. Evaluation of the polymer film thickness via attenuation of the photoelectron signal using a standard approach[13] yielded a thickness of 4 ± 0.5 nm. From this thickness, a number-average molecular weight ($M_n = 26{,}000 \pm 3{,}000$) of the 20–1.5 pMPC chains may be estimated.[14] Correspondingly higher values of M_n are achieved at longer polymerization times (a direct measure via GPC of the individual surface-grown polymer chains is difficult because of the multifunctional nature of the macroinitiator, which leads to graft copolymer formation).

The thickness of a bilayer of the 20–1.5 pMPC brushes was measured via interference fringes of equal chromatic order (FECO) in the mica SFB in a P_2O_5-dried SFB cell.[6] These results are shown in Figures 2a and b, revealing a thickness of (6.7 ± 0.3) nm per brush layer. X-ray reflectometry (XRR) of the 20–1.5 pMPC film on the mica was performed in ambient air[15] (Figure 3), yielding a thickness of 12.2 nm for the layer. We attribute the different thickness values measured by the different methods to the different hydration states of the pMPC. This polymer is known to be extremely hygroscopic,[16,17] with each monomer being hydrated by up to 15 or more water molecules. In the ultra-high-vacuum environment (10^{-9} torr) of the XPS chamber, most—if not all—of the water is removed (as confirmed directly by the XPS-measured oxygen concentration in the pPMC layer, see Table 1), so that the XPS-determined thickness [(4 ± 0.5) nm] is close to the true dry value. A simple estimate suggests that a hydration level corresponding to 15 water molecules per monomer for the 20–1.5 pMPC film would result in an increase from the dry film thickness of (4 ± 0.5) nm to (8.8 ± 0.5) nm. Therefore, the polymer layers studied via FECO in the SFB cell are likely (despite the P_2O_5-dried air) to have retained some of the hydration water taken up from the (undried) ambient atmosphere prior to being mounted in the cell; this uptake results in their partial swelling (to 6.7 nm). In the case of the XRR carried out in an (undried) ambient atmosphere, the even higher thickness (12.2 nm) may well be the result of uptake of humidity beyond just the hydration of the monomers, leading to the

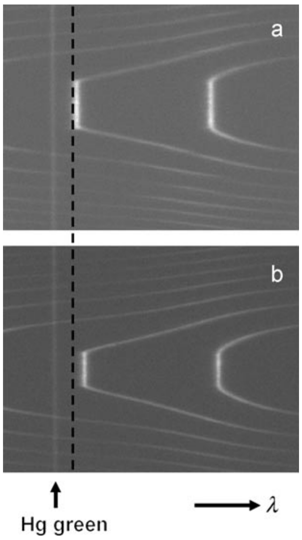

Figure 2. FECO fringes in P2O5-dried air before (a) and after (b) pMPC polymerization. The shift to the right of the fringes in (b) corresponds to a 6.7 nm pMPC layer on each mica surface. (Hg green is the mercury green emission line used to calibrate the wavelengths of the FECO frings.)

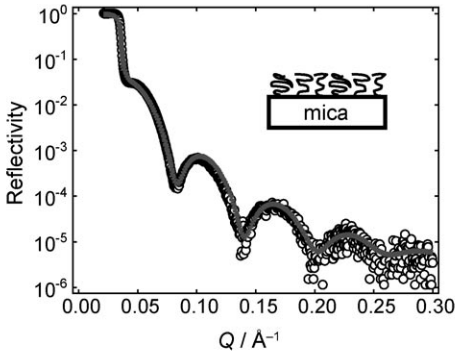

Figure 3. XRR data (○) in ambient air for 20–1.5 pMPC on mica. The fit to the data (——) corresponds to a 12.2 nm thick layer.

Table 1. XPS of 20–1.5 pMPC grown on mica.

Elements	P		C		N	O
		C–C	C–O/C–N	O=C–O		
binding energy [eV]	133.3	285.1	286–288	289.1	402.7	532.5
concentration [%]	5.3	16.4	37.7	6.07	5.32	29.2
measured ratio	1.0	3.1	7.12	1.15	1.0	5.52[a]
stoichiometric ratio	1	3	7	1	1	6

[a] Values in the range 5.5–6.1.

solvation and slight swelling of the pMPC brush, for which water is a good solvent. The AFM root-mean-squared (rms) roughness of such a film (0.43 nm, Figure 4) is closely comparable to that of similar pMPC films grown on silicon.[9]

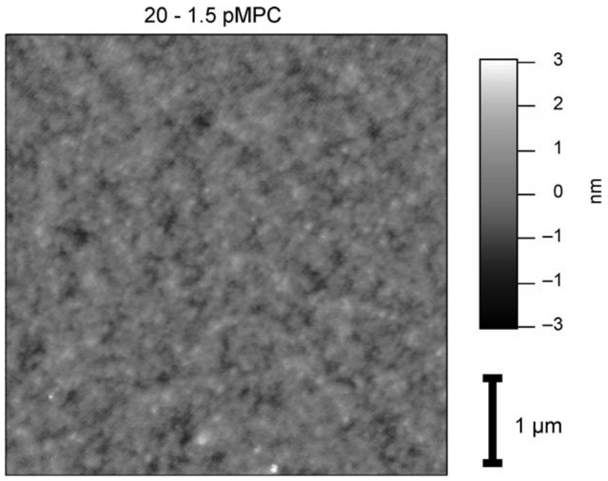

Figure 4. AFM image of 20–1.5 pMPC on mica in ambient air.

Finally, we carried out two control studies in the SFB. Force measurements between macroinitiator-coated mica surfaces (shown in Figure 5 a) revealed directly that the free pMPC homopolymer ($M_n = 22\,000$, $M_w/M_n = 1.3$) did not adsorb on the macroinitiator-coated mica from aqueous solution. This result shows that the pMPC layer subsequently grown from the surface formed true brushes in aqueous solution, that is, non-adsorbing pMPC chains tethered by one end only to the mica substrate. Indeed, normal force profiles in the SFB (such as Figure 5 b) revealed the extended nature of these brushes. In a separate SFB study, two such mica-attached 20–1.5 pMPC brushes were compressed against each other at pressures of up to 7.5 MPa (75 atmospheres) or more, and then sheared and made to slide past each other repeatedly. As seen in Figure 5 b, no evidence of any removal of the polymer from the surfaces was seen under these conditions [in contrast, for example, to the case where physically grafted (grafted-to) polyelectrolyte layers were completely sheared off mica surfaces under much milder pressures[18]]. This fact clearly demonstrates the robustness of the mica-grown brush layers and is attributed to the strong (covalent) bonding of the chains to the macroinitiator, together with the tenacious multipoint attachment of the macroinitiator itself to the oppositely charged mica surface.

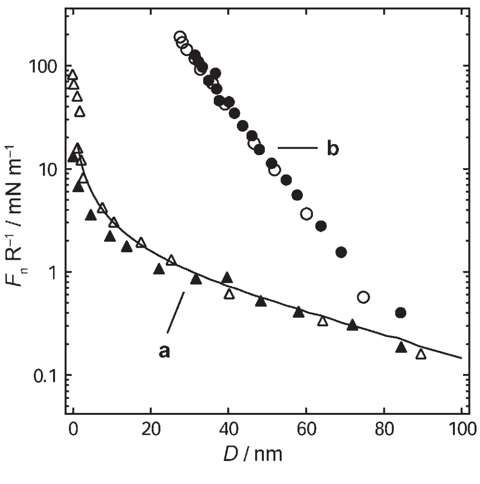

Figure 5. a) Profiles of normalized normal force $F_n R^{-1}$ versus separation D between macroinitiator-coated mica surfaces immersed in water (▲) and in 0.3% w/v MPC homopolymer solution (△). The continuous curve is a guide for the eye. b) Normalized force–distance profiles between 20–1.5 pMPC brushes in water before (●) and after (○) shear measurements at compressions up to 2 MPa.

In summary, using a range of chemical and physical characterization approaches, we have shown that polymers can be directly grown from a mica surface, on which initiator groups are fixed via a macroinitiator, to form robustly attached macromolecular surface layers. This finding has implications for modifying the surface of mica—the "ideally smooth" substrate—in a wide range of basic studies, which include those examining steric stabilization by surface-attached chains and the lubrication properties thereof.

Acknowledgements

We thank A. L. Lewis (Biocompatibles Ltd.) for kind donation of the MPC monomer, X. Y. Chen for synthesis of the macroinitiator, I. E. Dunlop, W. Feng, N. Harvey, S. Perkin, and R. K. Thomas for their valuable advice and help, and the EPSRC, the Israel Science Foundation, and the Petroleum Research Fund (grant 45694-AC7) for support of this work. S.P.A. is the recipient of a Royal Society Wolfson Research Award.

Keywords: interfaces · mica · polymerization · polymers · surface forces

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Received: February 21, 2007
Revised: April 2, 2007