

Three-stage switching of surface wetting using phosphate-bearing polymer brushes

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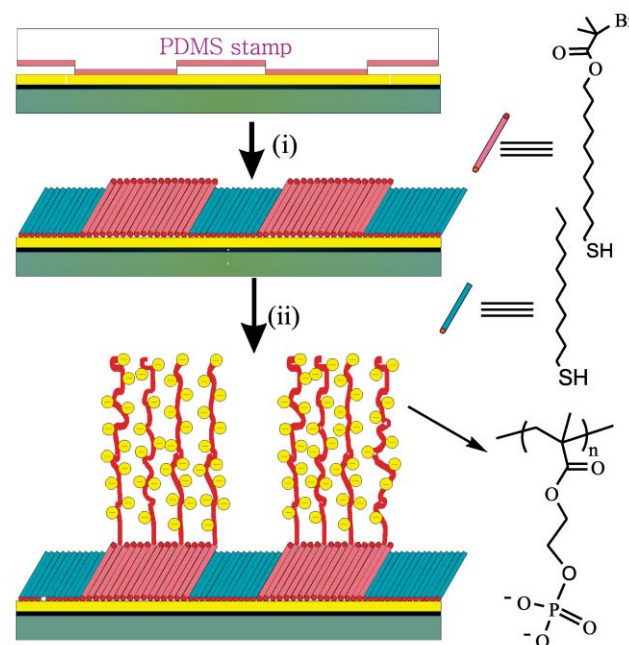
Surface initiated polymer brushes containing phosphate side groups have been used to reversibly switch wettability and hydration between three different states.

Polyelectrolyte brushes consist of surface grafted polymer chains containing charged monomers. The electrostatic interactions inside such brushes control the conformation of the polymer chains. The use of a variety of environmental triggers, for example, pH, salt concentration and temperature, to control the conformation of the chains and hence surface properties such as hydration and contact angle, has recently been explored by a number of groups.^{1–4} An especially complex system is presented by so-called “weak” polyelectrolyte brushes, in which the density of charge is not fixed but depends strongly on the pH and salt concentration.² Previously, the swelling and collapse of poly(methacrylic acid) brushes has been studied as a model system. To our knowledge, no publication on divalent weak polyelectrolyte brushes has been reported. In this communication, we report the use of phosphate group containing polymer brushes as a first example of divalent weak acid polyelectrolyte brushes. Phosphate containing polymers have found versatile uses as adhesion promoters, flame-retardant additives, complexing reagents to recover metal ions from effluents and industrial liquids, agents for controlling crystallization of CaCO₃ and use in tissue engineering and drug controlled release because of their biocompatibility and biodegradability.^{5,6} We therefore expect that the polymer brushes described in this study will not only show interesting responsive properties, but could also serve as model surfaces in some of the fields mentioned above.

Our strategy for the one-step synthesis of phosphate group containing methacrylic brushes follows our previous work^{7,8} on surface-initiated atom transfer radical polymerization (ATRP) and the reaction procedures are illustrated in Scheme 1. The complexation of the transition metal used in ATRP by the phosphate group can significantly influence the reaction. Recently, Huang and Matyjaszewski demonstrated synthesis of organophosphate group containing polymers *via* ATRP, but several side-reactions were reported.⁶ Direct grafting of poly[2-(methacryloyloxy)ethyl]phosphate (PMEP) brushes is very difficult because of the reactive nature of the monomer as well as the complexation of the catalyst by the growing brushes. Armes and co-workers demonstrated that acidic monomers in their salt form can be polymerized in aqueous solution *via* ATRP despite

relatively low reactivity and poor polydispersity.⁹ By using a similar strategy, we have previously succeeded in grafting polymethacrylate acid brushes.⁷ The MEP monomer was obtained from Aldrich and neutralized with NaOH solution to the di-sodium salt. The polymerization solution contained 20 ml of 3 mol l⁻¹ MEP aqueous solution (60 mmol monomer), CuBr (0.144 g, 1 mmol), CuBr₂ (0.011 g, 0.05 mmol) bipyridine (0.39 g, 2.5 mmol). The polymerization was performed at 60 °C for a range of reaction times.

Fig. 1 shows the evolution of brush thickness (as measured by ellipsometry in the dry state on a homogeneous brush surface) with the polymerization time on both gold and silicon substrates. The growth of the PMEPE brushes is very fast (but uncontrolled) in the first stage. The thickness can reach around 20 nm within 1 min. The fast polymerization can be sustained for about 10 min after which only a limited (but approximately linear) increase remained. Huang and Matyjaszewski⁶ also found fast termination with phosphorus-containing monomer and tentatively ascribed this to the complexation between the copper ion and monomer/polymer.



Scheme 1 Procedure for patterned polymer brush formation on gold substrates. (i) Microcontact printing of thiol initiator onto gold surface followed by backfilling with inert thiol (undecylthiol); (ii) polymer brush growth from initiator modified areas. Cations are not included for clarity. Polymerization conditions: [monomer] : [CuBr] : [bipy] : [CuBr₂] = 120 : 2 : 5 : 0.1. Temperature: 60 °C.

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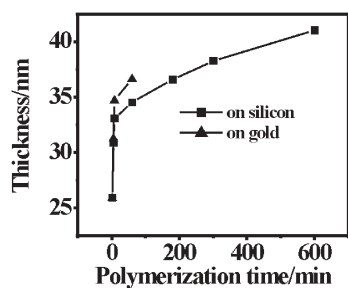


Fig. 1 Evolution of brush thickness with the polymerization time. The line was added to guide the eye.

Polymer brushes grafted from the gold surfaces were usually slightly thicker than those on silicon within the same polymerization time, presumably because of the higher density of initiators on gold. If the polymerization was carried out at room temperature, only very thin polymer brushes of less than 10 nm thickness were obtained. Although no completely linear growth of brush was found, PMEP brushes prepared within 1 min still can be used to further graft a second brush, indicating the initiator still remains on the end of polymer chain, which is partial proof of the ATRP nature of this polymerization. Table 1 lists some of the copolymer brushes prepared. Subsequent polymerization of methyl methacrylate from an 11 nm PMEP brush on gold resulted in a thickness increase of about 10 nm within 1 h and an increase of the contact angle to 74° which is characteristic of a PMMA surface. The formation of diblock copolymer brushes with HEMA, OEGMA, and NIPAM allows the formation of polymer brush surfaces with multiple responsive blocks (pH and temperature).

Our main aim in this paper is to explore the responsive nature of the PMEP brushes as a function of pH. Orthophosphoric acid is a diacid with pK_{a1} ranging from 1 to 2 and pK_{a2} about 6–7.¹⁰ Hence, in solutions with $pH < 1$, the phosphate groups are completely protonated (diacid); when $1 < pH < 7$ the brushes carry partly protonated groups (monoacid–monobasic) and when $pH > 7$ they will exist in their salt form (dibasic) (Fig. 2). The charges on the brush, the concentration of free counterions, and the degree of swelling can therefore all be tuned *via* the adjustment of the pH. The PMEP brushes as obtained after synthesis were first soaked in acid solution ($pH < 1$) and subsequently rinsed with Milli-Q water. The brushes were then immersed into three stock solutions of different pH. As can be seen from Fig. 2, after treatment with the $pH < 1$ solution the polymer brush is relatively hydrophobic

Table 1 Thickness change and static contact angle of copolymer brush

Copolymer brush	Thickness increase ^a /nm		Contact angle ($^\circ$)
	Silicon	Gold	
PMEP–PMMA	15 (18)	11 (21)	74
PMEP–PHEMA	15 (21)	12 (20)	44
PMEP–POEGMA	13 (20)	16 (36)	53
PMEP–PNIPAm	13 (25)	16 (29)	51

^a The thickness columns show the thickness of initial PMEP brushes from which the second block was grafted after 1 h polymerization time; the value in parentheses indicates the total thickness of copolymer brush. MMA: methyl methacrylate; HEMA: hydroxyethyl methacrylate; OEGMA: oligo(ethylene glycol) methacrylate, MW, 526; NIPAm: *N*-isopropyl acrylamide

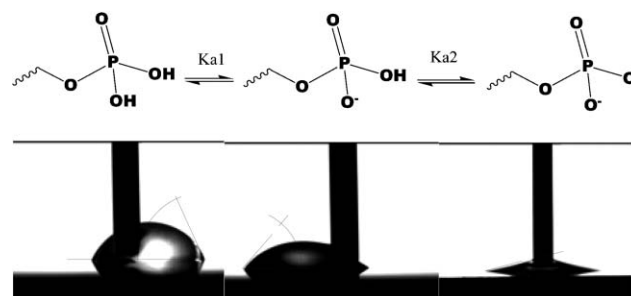


Fig. 2 Top: schematic of the association–dissociation equilibrium upon contact with solutions of different pH. Bottom: the advancing contact angle of a water droplet on the corresponding PMEP brush treated with different pH solutions (a) $pH < 1$, 65° (b) $pH = 4$, 49° , (c) $pH > 10$, 13° .

(advancing contact angle of 65°), presumably because of inter/intra molecular H-bonding between fully protonated groups. After immersing into a pH 4 solution, the brushes become more hydrophilic and the water advancing contact angle is decreased to 49° . Finally, when treated with base solution ($pH > 12$), the polyelectrolyte brushes yielded almost completely wetting surfaces with a lower static contact angles of 13° .

FTIR was used to trace the composition change within the brushes when treated with solutions of different pH values. Fig. 3 shows the FTIR spectra of PMEP brushes in different forms. The absorbance peak around 1732 cm^{-1} in all spectra is assigned to the carbonyl stretching vibration of the ester. The peaks at 1181 , 1077 , 1038 cm^{-1} ($\nu(\text{P}=\text{O})$ or $\nu(\text{P}-\text{O})$) and 1005 cm^{-1} ($\nu(\text{P}-\text{OH})$) correspond to P–O stretching vibrations. When treated with pH 4 and base solutions, the bands at 1038 and 1005 cm^{-1} disappeared and a new peak appeared at 973 cm^{-1} , that grew in intensity with increasing pH and was attributed to the symmetric stretching vibration of P–O in PO_3^{2-} . The other obvious change comes from the alternation of the relative intensities of asymmetric and symmetric vibrations of P–O at 1181 and 1077 cm^{-1} , attributed to the different forms of the phosphate group. It is likely that the ‘dry’ PMEP brushes in the dibasic form still contain a certain amount of water as deduced from the shoulder absorbance (1654 cm^{-1}) of water. FTIR spectra of PMEP brushes (acid form) show hardly any water present, whereas the brushes in their dibasic form show the presence of water even after drying in vacuum for 5 h.

Patterned polymer brushes allow the study of the responsive behavior using AFM. Fig. 4 shows the images of the patterned

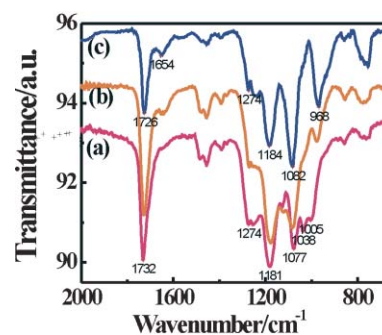


Fig. 3 FTIR of the PMEP brush (a) diprotonated acid (treated with $pH < 1$ solution), (b) monosodium salt obtained by immersing into pH 4 solution and (c) disodium salt obtained in pH > 10 solution.

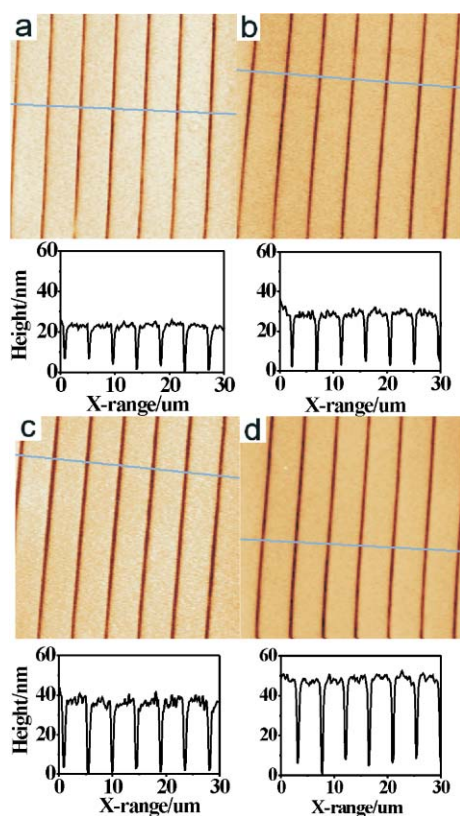


Fig. 4 Swelling behavior of a PMEP brush: (a) PMEP acid brush with saturated water vapour, (b) PNa₂MEP brush under dry nitrogen (c) PNa₂MEP brush in air with saturated water vapour and (d) PNa₂MEP brush under water. The corresponding cross-section profiles of these images are given below. Image scale: 30 × 30 μm.

PMEP acid brush under water vapour, and the PMEP-dianion brush in a “dry” state (continuous blow with nitrogen), under water vapour, and immersed in water. Comparing the images of the brushes in the acidic form (Fig. 4a) and the ‘dry’ brushes (Fig. 4b) it can be seen that the former are completely collapsed even in the presence of water vapour. This might be due to the strong H-bonding between phosphate groups, while the dry PNa₂MEP brushes are slightly larger than the acid brush, probably due to the absence of H-bonding. The anionic brushes are very sensitive to water, since the phosphonate groups lead to electrostatic repulsions between the chains. Even under water vapour, the brushes swell approximately 10 nm compared with

their dry thickness (Fig. 4c). Placing the brushes in water solution leads to an even larger swelling of more than 2 times their thickness in an acidic environment (Fig. 4d). Similar responsive behaviour in cationic brushes was recently reported by Biesalski and Ruehe.¹¹

In conclusion, we have demonstrated for the first time the synthesis of phosphate group containing polymer brushes *via* surface initiated atomic transfer radical polymerization on both gold surfaces and silicon wafers. These brushes exhibited three stage switching of wettability due to different chemical states derived from the association–dissociation equilibrium. Selectively grafting the patterned brush from microcontact-printed initiator proved to be quite successful. These phosphate containing polymer brushes represent diacidic/dibasic weak polyelectrolytes, and provide an ideal model for studying the collapse–swelling behavior under different pH or salt solutions. We hope to use these brushes as a model interface for studying bioprocesses because of the potential biocompatibility of the polymers used.

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Notes and references

- 1 J. Ruehe, M. Ballauff, M. Biesalski, P. Dziezok, F. Grohn, D. Johannsmann, N. Houbenov, N. Hugenberg, R. Konradi, S. Minko, M. Motornov, R. R. Netz, M. Schmidt, C. Seidel, M. Stamm, T. Stephan, D. Usov and H. Zhang, *Adv. Polym. Sci.*, 2004, **165**, 79.
- 2 M. Biesalski, D. Johannsmann and J. Ruehe, *J. Chem. Phys.*, 2002, **117**, 4988; M. Biesalski, D. Johannsmann and J. Ruehe, *J. Chem. Phys.*, 2004, **120**, 8807.
- 3 S. Moya, O. Azzaroni, T. Farhan, V. L. Osborne and W. T. S. Huck, *Angew. Chem., Int. Ed.*, 2005, **44**, 4578.
- 4 M. Biesalski and J. Ruehe, *Macromolecules*, 1999, **32**, 2309; M. Biesalski, J. Ruehe and D. Johannsmann, *J. Chem. Phys.*, 2000, **111**, 7029.
- 5 E. D. Weil, *Encycl. Polym. Sci. Eng.*, 1987, **11**, 96; K. Kaluzynski, J. Pretula, G. Lapienis, M. Basko, Z. Bartczak, A. Dworak and S. Penczek, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 955; Y. Iwasaki, C. Nakagawa, M. Ohtomi, K. Ishihara and K. Akiyoshi, *Biomacromolecules*, 2004, **5**, 1110.
- 6 J. Huang and K. Matyjaszewski, *Macromolecules*, 2005, **38**, 3577.
- 7 V. L. Osborne, D. M. Jones and W. T. S. Huck, *Chem. Commun.*, 2002, 1838.
- 8 A. Brown, N. S. Khan and W. T. S. Huck, *Eur. Polym. J.*, 2005, **41**, 1757; D. M. Jones and W. T. S. Huck, *Adv. Mater.*, 2001, **13**, 1256.
- 9 E. J. Ashford, V. Naldi, R. O'Dell, N. C. Billingham and S. P. Armes, *Chem. Commun.*, 1999, 1285.
- 10 J. R. Van Wazer, *Phosphorus and its compounds. Vol. I: Chemistry*, Interscience Publishers Ltd., London, 1958.
- 11 M. Biesalski and J. Ruehe, *Langmuir*, 2000, **16**, 1943.