

# Stimuli responsive surfaces through recognition-mediated polymer modification†

Hao Xu, Tyler B. Norsten,‡ Oktay Uzun, Eunhee Jeoung§ and Vincent M. Rotello\*

Received (in Columbia, MO, USA) 5th July 2005, Accepted 29th August 2005

First published as an Advance Article on the web 20th September 2005

DOI: 10.1039/b509572g

Specific three-point hydrogen bonding between diamidopyridine (DAP) and thymine (Thy) was employed to reversibly anchor “brush-like” Tri-DAP end-functionalized polystyrene onto Thy-modified silica surfaces.

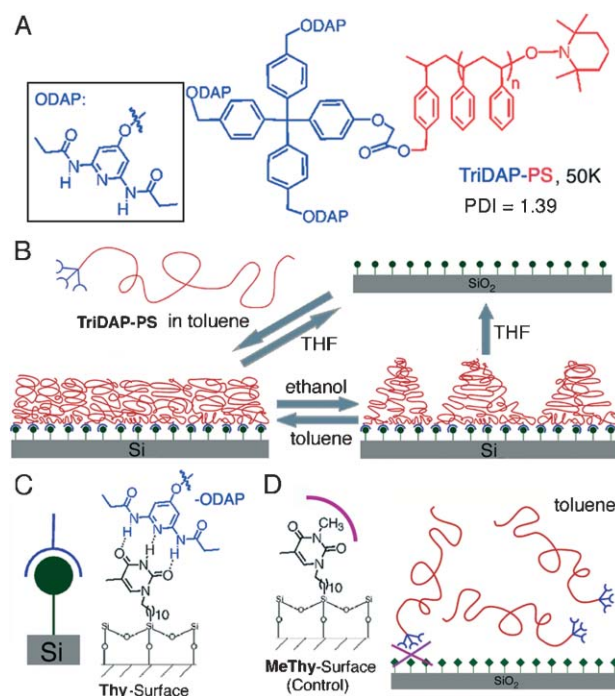
Fabricating polymers onto solid substrates is a versatile technique not only to prepare new composite and functional materials but also to provide artificial materials with “smart” surface behavior.<sup>1</sup> These surfaces are capable of responding to environmental stimuli such as temperature,<sup>2a</sup> pH,<sup>2b</sup> light,<sup>2c</sup> and solvents.<sup>2d</sup> In these systems, subtle changes in surrounding environment result in large macroscopic responses due to structural reorganization of the grafted layers. This mobility permits external stimuli-induced modulation of surface structures and on–off switching of their respective functions in a broad range of technologies, including colloidal stabilization,<sup>3a</sup> tailoring interfaces’ adhesion and wetting properties,<sup>3b</sup> chemical gating,<sup>3c</sup> and drug delivery.<sup>3d,e</sup>

The ability to renew immobilized polymers with concomitant recovery of initial surface properties is an important issue in such areas as sensor/column regeneration and efficient recycling of catalysts.<sup>4</sup> Covalent attachment, which has been extensively investigated,<sup>5</sup> renders polymers permanently immobilized to the surface so that other weaker non-covalent interactions must be employed to provide the reversible binding process.<sup>6</sup> By combining both multi-point and multiple cooperative hydrogen bonding interactions, the overall stability of the resulting structures are substantially increased while the reversible nature of H-bonding yields well behaved renewable systems.<sup>7</sup> Additionally, in contrast to non-specific physisorption,<sup>6a</sup> the specificity provided by multi-point hydrogen-bonding recognition dyads can ultimately lead to orthogonal surface modification employing the rich diversity of synthetic recognition elements.<sup>8</sup>

Recently, we demonstrated the reversible adsorption/desorption of block copolymers on gold self-assembled monolayers (SAMs) using a thymine–diamidopyridine (Thy–DAP) three-point-hydrogen-bonding motif.<sup>9</sup> In these studies, the binding elements were decorated along the polymer backbone. This strategy results in high affinity between the polymer and substrate, and therefore

requires harsh conditions (extended rinsing in boiling ethanol–chloroform) for desorption of the polymer, limiting this method’s practical application in terms of sequential testing and multiple analyses. To overcome this limitation and make the surface modification readily reversible, we have explored polymers terminated by multiple recognition units using Hawker’s alkoxyamine LFR (Living Free Radical) initiators,<sup>10</sup> which result in simple desorption process at very mild conditions (THF at room temperature). Herein we report the easily renewable tri-DAP end-functionalized polystyrene (**triDAP-PS**) on modified silica surfaces (Fig. 1). Moreover, the “brush-like” polymer we created displays similar solvent induced morphology changes to previously reported covalent attached polymer brushes, with the added benefit of renewability.

End-functionalized polymer **triDAP-PS** in toluene (15  $\mu$ M) was selectively adsorbed onto thymine-silane derivatized silica surfaces



**Fig. 1** (A) Chemical structure of tri-DAP end-functionalized polystyrene (**TriDAP-PS**). (B) Schematic illustration of reversible adsorption–desorption of **TriDAP-PS** to/from the thymine-functionalized silicon substrate (Thy-surface) and solvent-induced morphology changes. (C) Specific interaction between DAP (on polymer) and Thy-surface; (D) The control MeThy-surface, in which the methyl group disrupts the specific Thy–DAP interaction, so that the MeThy-surface shows no adsorption of polymers under identical conditions.

Department of Chemistry, University of Massachusetts, Amherst, MA, USA. E-mail: rotello@chem.umass.edu; Tel: (+1) 413-545-2058

† Electronic supplementary information (ESI) available: Synthesis and characterization of the TriDAP initiator, preparation of silica surfaces, and surface characterization data, including XPS, AFM, ellipsometry and contact angle measurements. See <http://dx.doi.org/10.1039/b509572g>

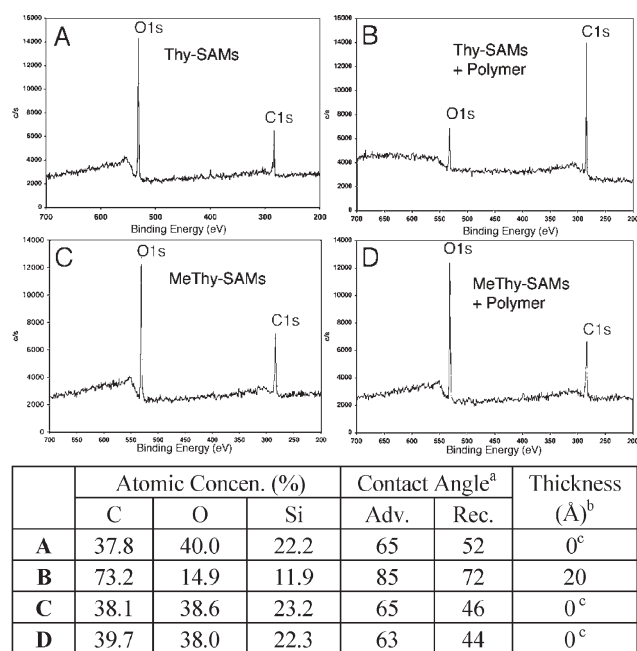
‡ Current address: National Research Council of Canada, ICPET-Polymeric Materials Group, 1200 Montreal Road, Ottawa, Ontario, KIA 0R6 Canada.

§ Current address: Department of Chemistry, Kangnung National University, 123 Jibyeon-dong, Gangneung, Gangwondo, 210-702, Korea.

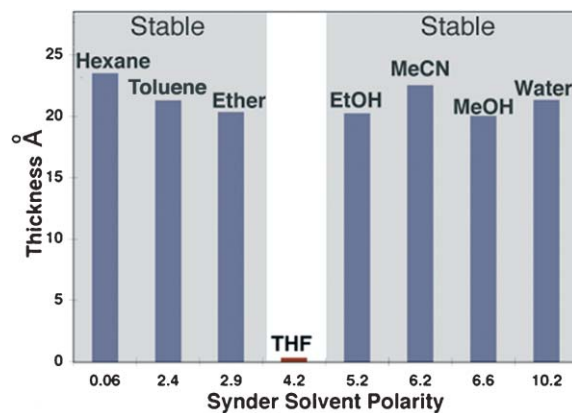
(Thy-surface) (experimental details and corresponding characterization are provided in the ESI†). X-Ray photoelectron spectroscopy (XPS) was used to study the specificity associated with the DAP–Thy three-point H-bonding interaction. At 15° take-off angle, XPS provides the information of the topmost layer (around 2 nm thickness). Fig. 2 shows that the intensity of carbon signal of Thy-surfaces increased due to the formation of an overlayer of carbon-rich polystyrene. In contrast, MeThy-surfaces showed little uptake of polymer under identical conditions, demonstrated by the unchanged intensity of carbon, oxygen and silicon signals. This selectivity was also verified by ellipsometry and water contact angle analysis. Formation of a ~2 nm polymer overlayer was observed on Thy-surfaces and the advancing water contact angle increased up to 85°, while MeThy-surfaces showed no change in either contact angle or film thickness.

The modified silica surfaces were treated with various solvents to test the stability of grafted polymer layers. Ellipsometry data (Fig. 3) show that toluene and diethyl ether, which are well known to dissolve and rinse off spin-coated PS films, have no effect on the immobilized polymer layer due to the multiple cooperative H-bonding. Not surprisingly, the polymer film can also survive polar solvent conditions, such as ethanol, acetonitrile and water, because, as poor solvents for PS, they cannot penetrate through the polymer layer to disrupt the interfacial DAP–Thy interactions.

The surface morphology of the polymer films can be controlled by dipping modified surfaces into ethanol or toluene, based on their different solvating ability of PS. According to previous

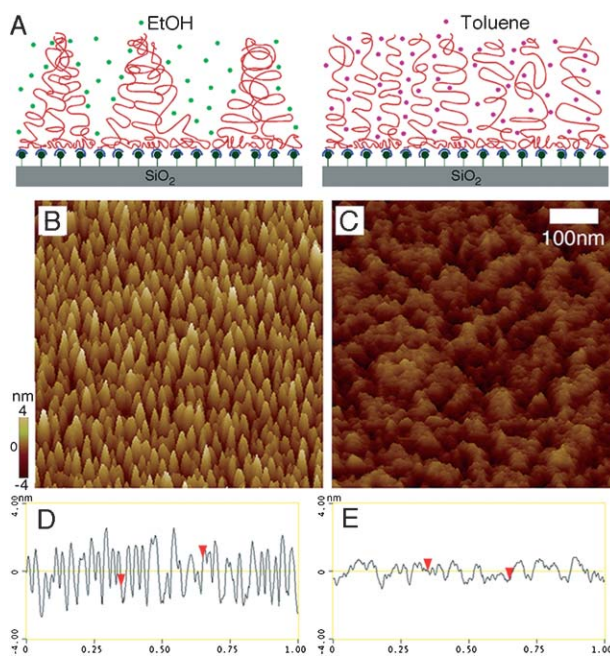


**Fig. 2** XPS survey scans of the Thy-surface (A, B) and MeThy-surface (C, D) before and after being immersed in the toluene solution of triDAP-PS for 2 h, followed by thorough rinse with fresh toluene to remove physisorbed polymers. Corresponding atomic concentration (from XPS), advancing (Adv.)/receding (Rec.) water contact angle and ellipsometric thickness analysis of the four surfaces (A–D). <sup>a</sup>Values reported here are an average of ten separate measurements and in the range of ±1–2°. <sup>b</sup>Values for film thickness represent an average of five measurements at different positions on the surfaces and in the range of ±1 Å. <sup>c</sup>No polymer films detected.

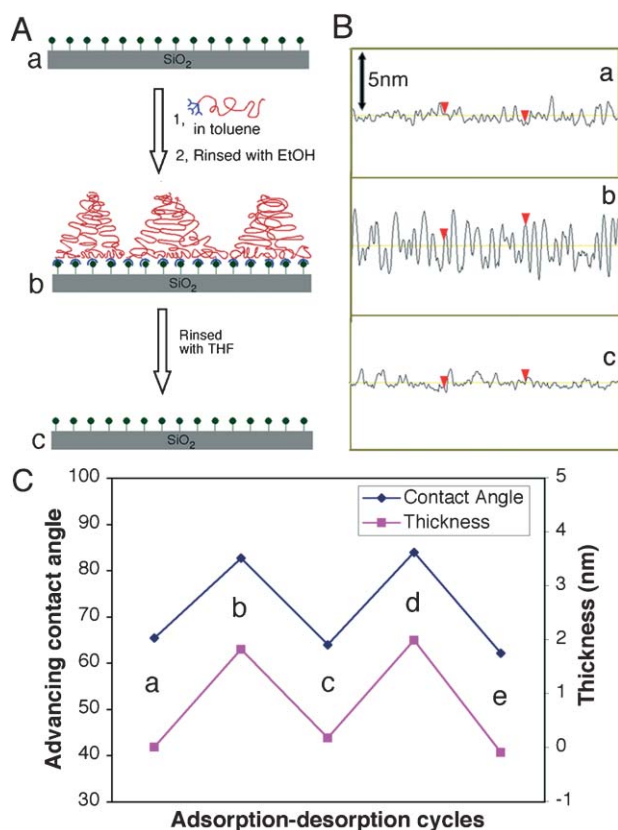


**Fig. 3** Ellipsometric analysis of thickness changes of modified surfaces upon rinsing with different solvents. The captions on top of each bar indicate which solvent was employed.

theoretical discussion<sup>11</sup> and reports on covalent tethered polymer brushes,<sup>5a,b</sup> in the presence of solvents, polymers confined near surfaces reorganize into regular structures and show different morphologies as a function of the interplay between polymer, interface and solvent interactions. In an ethanolic solution, the PS blocks collapse and aggregate with neighbors to form a core, minimizing the contact with the non-solvent environment, resulting in an array of surface-immobilized micelles with the domain shape. This nanomorphology is retained upon slow evaporation of ethanol as shown by atomic force microscopy (AFM). However, toluene, a “good” solvent, results in a uniform PS layer and relatively smoother interface (Fig. 4). An increase in surface roughness is observed in ethanol-treated surfaces compared with the surfaces treated by toluene (from 0.52 to 1.32 nm). The solvent induced morphology change was verified using XPS (see



**Fig. 4** Schematic illustration of solvent-induced morphology change (A), and AFM images and corresponding height profiles of ethanol (B, D) and toluene (C, E) treated surfaces.



**Fig. 5** Schematic illustration (A), AFM height profiles (B), and thickness and contact angle changes (C), following (a) SAMs, and subsequent (b) adsorption, (c) desorption, (d) readsorption, (e) redesorption of polymer layer. See ESI† for more detailed AFM information, including the second adsorption–desorption cycles.

Fig. S6 in ESI†) The relative intensity of Si 2s and O 1s, compared to C 1s, increased after the surface was treated with ethanol due to the collapse of the uniform PS layer, which allowed the emitted Si and O photoelectrons (from the substrate) more opportunity to escape the polymer layer.

An important attribute of supramolecular chemistry is the reversible binding process that can be employed to recover the original surface. Although the modified surfaces were stable under most solvent conditions, rinsing with THF (a good solvent for PS and a competitive solvent for H-bonding) can efficiently remove the adsorbed polymer layers. The resulting surfaces show the same thickness as the original SAMs and the advancing contact angles decreased from 83 to 65° as a result of the top layer switching from the hydrophobic PS backbone to more hydrophilic Thy-surfaces. AFM images indicate the removal of the polymer layer as the surface becomes smooth and all the micelles were erased, displaying similar features to the original SAMs. This renewable modification displays good cyclability as the regenerated surface was found to perform similar functions multiple times without affecting its recognition ability (Fig. 5).

In summary, we demonstrated the reversible functionalization of silica surfaces *via* specific H-bonding interaction using

“brush-like” TriDAP-PS. The topographic structures together with adsorption and desorption of the polymer film can be readily controlled by appropriate choice of solvent systems. This study provides new directions in corresponding fields in terms of renewability based on the reversible nature of hydrogen bonding, and orthogonal modification associated with the specific recognition interaction. Furthermore, the Tri-DAP unit can be easily incorporated into other functional polymers to impart desired mechanical, optical, electronic or biological properties onto various substrates. The investigations are underway and will be reported in due course.

This research was supported by the National Science Foundation (US) CHE-0518487. We thank Prof. Thomas J. McCarthy’s group for help in surface analysis. T. B. N acknowledges NSERC (Canada) for a postdoctoral fellowship.

## Notes and references

- (a) S. T. Milner, *Science*, 1991, **251**, 905; (b) B. Zhao and W. J. Brittain, *Prog. Polym. Sci.*, 2000, **25**, 677; (c) I. Luzinov, S. Minko and V. V. Tsukruk, *Prog. Polym. Sci.*, 2004, **29**, 635; (d) T. P. Russell, *Science*, 2002, **297**, 964; (e) Y. Nagasaki and K. Kataoka, *Trends Polym. Sci.*, 1996, **4**, 59; (f) Y. Liu, L. Mu, B. Liu and J. Kong, *Chem. Eur. J.*, 2005, **11**, 2622.
- (a) S. Khongtong and G. S. Ferguson, *J. Am. Chem. Soc.*, 2002, **124**, 7254; (b) R. R. Netz and D. Andelman, *Phys. Rep.*, 2003, **380**, 1; (c) K. Ichimura, S. K. Oh and M. Nakagawa, *Science*, 2000, **288**, 1624; (d) D. Julthongpiput, Y. H. Lin, J. Teng, E. R. Zubarev and V. V. Tsukruk, *J. Am. Chem. Soc.*, 2003, **125**, 15912.
- (a) G. Sharma and M. Ballauff, *Macromol. Rapid Commun.*, 2004, **25**, 547; (b) S. Minko, M. Muller, M. Motornov, M. Nitschke, K. Grundke and M. Stamm, *J. Am. Chem. Soc.*, 2003, **125**, 3896; (c) Y. Ito, Y. Ochiai, Y. S. Park and Y. Imanishi, *J. Am. Chem. Soc.*, 1997, **119**, 1619; (d) M. Ornatka, S. E. Jones, R. R. Naik, M. O. Stone and V. V. Tsukruk, *J. Am. Chem. Soc.*, 2003, **125**, 12722; (e) M. C. Woodle, *Adv. Drug Deliv. Rev.*, 1998, **32**, 139.
- R. Chen, R. P. J. Bronger, P. C. J. Kamer, P. van Leeuwen and J. N. H. Reek, *J. Am. Chem. Soc.*, 2004, **126**, 14557.
- (a) B. Zhao, W. J. Brittain, W. S. Zhou and S. Z. D. Cheng, *J. Am. Chem. Soc.*, 2000, **122**, 2407; (b) B. Zhao, R. T. Haasch and S. MacLaren, *J. Am. Chem. Soc.*, 2004, **126**, 6124; (c) M. Husemann, D. Mecerreyes, C. J. Hawker, J. L. Hedrick, R. Shah and N. L. Abbott, *Angew. Chem., Int. Ed.*, 1999, **38**, 647; (d) X. G. Liu, S. W. Guo and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2003, **42**, 4785.
- (a) G. Fytas, S. H. Anastasiadis, R. Seghrouchni, D. Vlassopoulos, J. B. Li, B. J. Factor, W. Theobald and C. Toprakcioglu, *Science*, 1996, **274**, 2041; (b) P. Brandani and P. Stroeve, *Macromolecules*, 2003, **36**, 9492.
- (a) L. J. Prins, D. N. Reinhoudt and P. Timmerman, *Angew. Chem., Int. Ed.*, 2001, **40**, 2383; (b) R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. Hirschberg, R. F. M. Lange, J. K. L. Lowe and E. W. Meijer, *Science*, 1997, **278**, 1601; (c) F. H. Beijer, H. Kooijman, A. L. Spek, R. P. Sijbesma and E. W. Meijer, *Angew. Chem., Int. Ed.*, 1998, **37**, 75; (d) E. A. Fogelman, W. C. Yount, J. Xu and S. L. Craig, *Angew. Chem., Int. Ed.*, 2002, **41**, 4026.
- J. M. Pollino, L. P. Stubbs and M. Weck, *J. Am. Chem. Soc.*, 2004, **126**, 563.
- (a) T. B. Norsten, E. Jeoung, R. J. Thibault and V. M. Rotello, *Langmuir*, 2003, **19**, 7089; (b) A. Sanyal, T. B. Norsten, O. Uzun and V. M. Rotello, *Langmuir*, 2004, **20**, 5958; (c) A. Ulman, *Chem. Rev.*, 1996, **96**, 1533.
- J. Dao, D. Benoit and C. J. Hawker, *J. Polym. Sci. Polym. Chem.*, 1998, **36**, 2161.
- E. Zhulina and A. C. Balazs, *Macromolecules*, 1996, **29**, 2667.