Well-Defined Polymer−Germanium Hybrids via Surface-Initiated Atom Transfer Radical Polymerization on Hydrogen-Terminated Ge(100) Substrates

F. J. Xu, Q. J. Cai, E. T. Kang,* and K. G. Neoh

Department of Chemical and Biomolecular Engineering, National University of Singapore, Kent Ridge, Singapore 119260

C. X. Zhu

Department of Electrical and Computer Engineering, National University of Singapore, Kent Ridge, Singapore 117576

Received November 22, 2004

Summary: UV-induced hydrogermylation of 4-vinylbenzyl chloride (VBC) on the hydrogen-terminated Ge(100) (Ge−H) surface provided a stable Ge−C bonded initiator monolayer (the Ge−VBC surface) for the surface-initiated atom transfer radical polymerization (ATRP). Well-defined polymer−Ge hybrids, consisting of covalently tethered functional polymer brushes, were prepared via surface-initiated ATRP from the Ge−VBC surfaces. Surface-initiated block copolymerization studies revealed that the chain growth from the functionalized germanium surface was a controlled process.

Introduction

Covalently bonded organic molecules on group IV semiconductor surfaces are of crucial importance to the development of new semiconductor-based hybrid materials and devices.[1−7] Germanium is an important semiconductor for a number of technologies and has other potential applications due to its high electron mobility, twice that of silicon.[1,4,8] In contrast to a wide range of chemical reactions involving silicon surfaces,[1,5] the formation of organo-germanium hybrids remains scarcely studied. Pioneering studies on the formation of organic monolayers on germanium surfaces have involved halogenation, alkylation, and hydrogermylation.[1,4,5,9] Tethering of polymer brushes on a solid substrate is an alternative and effective method for increasing the spatial density of functional groups on the surface, as well as for modifying the surface properties of a substrate.[6,10,11] Atom transfer radical polymerization (ATRP) is a recently developed “living” or “controlled” radical polymerization method.[12−14] It is possible to prepare well-defined or nearly monodispersed graft chains on various substrate surfaces via surface-initiated ATRP.[15−19]

In this work, we report on the surface modification of (100)-oriented single crystal germanium by covalently bonded polymer brushes from surface-initiated ATRP. The simple approach of UV-induced hydrogermylation of 4-vinylbenzyl chloride (VBC) on the hydrogen-terminated Ge(100) surface (Ge−H surface) provided a stable Ge−C bonded initiator monolayer (the Ge−VBC surface) for the subsequent surface-initiated ATRP (Figure 1). Well-defined polymer−Ge hybrids, consisting of covalently tethered polymer brushes of pentafluorostyrene (PFS), (2-dimethylamino)ethyl methacrylate DMAEMA), and PFS-DMAEMA diblock copolymers, were prepared.

Results and Discussion

Exposure of pristine germanium chips (Ge(100) single crystals) to 10 vol % HF for 10 min gave rise to uniform hydrogen-terminated (Ge−H) surfaces with a surface roughness on the order of 3−4 nm.[1,5] The static water contact angle increased from about 19° for the pristine Ge(100) surface to about 71° for the Ge−H surface (Table 1). The initiators were immobilized via UV-induced hydrogermylation[5] of VBC on the Ge−H surface to give rise to a stable initiator monolayer via the Ge−C bonds. The vigorous washing/extraction procedures ensured the complete removal of adhered and physically adsorbed VBC after UV irradiation (see Experimental Section). From the comparison of the X-ray photoelec-

---

* To whom all correspondence should be addressed. Tel: +65-6874-2189. Fax: +65-6779-1936. E-mail: cheket@nus.edu.sg.

(1) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1272.
(2) Lu, X.; Zhu, M. P.; Wang, X. L. *J. Phys. Chem. B* **2004**, *108*, 7359.
(3) Jamers, R. J.; Coulter, S. K.; Ellison, M.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P. *Acc. Chem. Res.* **2000**, *33*, 617.
(4) He, J. L.; Lu, Z. H.; Mitchell, S. A.; Wayer, D. D. *J. Am. Chem. Soc.* **1998**, *120*, 2660.
(5) Choi, K.; Buriak, J. M. *Langmuir* **2000**, *16*, 7737.
(6) Yu, W. H.; Kang, E. T.; Neoh, K. G. *J. Phys. Chem. B* **2003**, *107*, 10198.
(7) Hanrath, T.; Korgel, B. A. *J. Am. Chem. Soc.* **2004**, *126*, 1566.
(8) Colace, L.; Masini, G.; Galluzzi, F.; Assanto, G. *Nucl. Instrum. Methods A* **2001**, *457*, 212.
(9) Cullen, G. W.; Amick, J. A.; Gerlich, D. *J. Electrochem. Soc.* **1962**, *109*, 124.
(10) Kato, K.; Uchida, E.; Kang, E. T.; Uyama, Y.; Ikada, Y. *Prog. Polym. Sci.* **2003**, *28*, 209.
(11) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31.
(12) Rio, I. D.; Koten, G. V. *Organometallics* **2000**, *19*, 361.
(13) Wang, J. S.; Matayjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(14) Coessens, V.; Pintauer, T.; Matayjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337.
(15) Zhao, B.; Brittain, W. J. *J. Am. Chem. Soc.* **1999**, *121*, 3557.
(16) Kizhakkedathu, J. N.; Raymond, N. J.; Brooks, D. E. *Macromolecules* **2004**, *37*, 734.
(17) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem. Soc. Rev.* **2004**, *33*, 14.
(18) Werne, T. V.; Patten, T. E. *J. Am. Chem. Soc.* **1999**, *121*, 7409.
(19) Sill, K.; Emrik, T. *Chem. Mater.* **2004**, *16*, 1240.

10.1021/om049095u CCC: $30.25

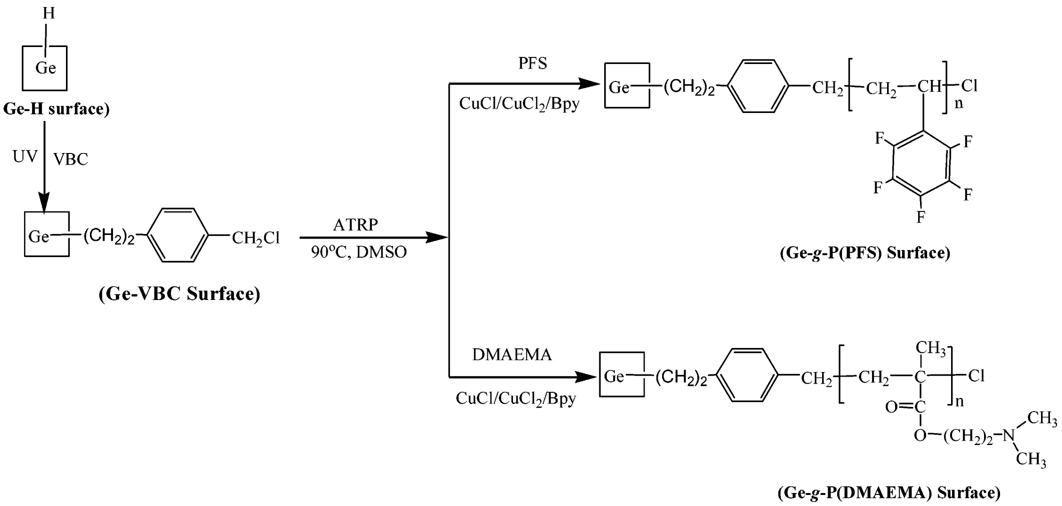

Figure 1. Schematic diagram illustrating the process of surface-initiated graft polymerization via ATRP from the Ge−VBC surface.

Table 1. Layer Thickness, Static Water Contact Angle, and Degree of Polymerization of the Polymer−Ge Hybrids Prepared via Surface-Initiated ATRP

sample[a]	layer thickness[b] (nm)	static water contact angle (±3°)[c]	degree of polymerization (DP)[d]
Ge−*g*-P(PFS)	13	97	120
Ge−*g*-P(DMAEMA)	19	56	160
Ge−*g*-P(PFS)−*b*-P(DMAEMA)	21	58	67
Ge−*g*-P(DMAEMA)−*b*-P(PFS)	25	92	53

[a] Reaction conditions: [monomer]:[CuCl]:[$CuCl_2$]:[Bpy] = 100:1:0.2:2 in DMSO at 90°C for 4 h. [b] Determined by ellipsometry. The thickness value of the Ge−VBC surface was about 0.4 nm. [c] Static water contact angles for the pristine Ge(100) and Ge−H surfaces are about 19° and 71°, respectively. [d] Based on the VBC monolayer thickness of about 0.4 nm, VBC density of 1.08 g/cm^3, VBC molecular weight of 153 g/mol, and an average cross-sectional area of about 2 nm^2 for the polymer chain. The surface initiator density (SID) and initiator efficiency (IE) for the Ge−VBC surface were estimated to be about 1.6 units/nm^2 and 30%, respectively. The average DP was calculated from the ratio of the surface polymer density (SPD) to SID and IE. The SPD, in turn, was obtained from the respective graft layer thickness, the density of the graft polymer, and the molecular weight of the monomer. For the diblock copolymer brushes, the DP refers to that of the second block.

tron spectroscopy (XPS) wide scan and Cl 2p core-level spectra of the Ge−H surface in Figure 2a and those of the Ge−VBC surface in Figure 2b, it is unambiguous that a new Cl 2p spectrum at the binding energy (BE) of about 200 eV, characteristic of covalently bonded Cl,[20] has appeared on the Ge−VBC surface. The intensity of the C 1s signal has increased significantly, while those of the Ge 3d (BE ∼29 eV), Ge 3p (BE ∼122 eV), and Ge 3s (BE ∼181 eV) signals[20] have decreased, after the immobilization of VBC on the Ge−H surface. The presence of a weak O 1s signal in the wide scan spectrum of the Ge−H surface (Figure 2a) suggests that the Ge−H surface has been oxidized to a small extent, even though the hydride-terminated surface is stable in air for up to 1 h.[1] Hydrogermylation of VBC only gives rise to a marginal increase in the extent of the surface oxidation (Figure 2b).

In a control experiment on hydrogermylation, the Ge−H substrate was soaked in neat VBC for the same period of time, albeit in the absence of UV irradiation. No VBC molecules were detected on the Ge−H surface after the substrate was rinsed briefly with acetone and subjected to surface analysis by XPS. The fact that the [Cl]/[C] ratio (∼0.10), determined from the sensitivity-factor-corrected Cl 2p and C 1s core-level spectral area ratio, for the Ge−VBC surface is close to the theoretical ratio of 0.11 for the VBC molecule suggests that UV-induced formation of benzyl radical (C−Cl cleavage) during hydrogermylation has occurred only to a small extent. A further increase in water contact angle to 87° for the Ge−VBC surface, from that of the Ge−H surface, is consistent with the presence of a hydrophobic VBC layer on the Ge−H surface. Thus, the benzyl chloride groups have been successfully immobilized on the Ge−H surface to cater to the subsequent surface-initiated ATRP from the Ge−VBC surface. On the basis of the VBC monolayer thickness of about 0.4 (± 0.1) nm,[21] VBC density of 1.08 g/cm^3, and VBC molecular weight of 153 g/mol, the initiator density of the Ge−VBC surface was estimated to be about 1.4 (± 0.4) units/nm^2.

Two functional monomers, viz., PFS and DMAEMA, were selected as the model monomers for the preparation of polymer−Ge hybrids via surface-initiated ATRP. Fluoropolymers are promising materials for interlayer dielectric applications because of their low dielectric constants and good chemical and thermal stability.[22,23] The DMAEMA polymer (P(DMAEMA)) is both temperature- and pH-sensitive. Well-defined P(DMAEMA) brushes can be used to prepare stimuli-responsive surfaces on a nanometer scale.[6] Addition of either a free (sacrificial) initiator or a Cu(II) complex to the ATRP

---

(20) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. In *X-ray Photoelectron Spectroscopy*; Chastain, J., Ed.; Perkin-Elmer: Eden Prairie, MN, 1992; p 40, 47, 62, 92.

(21) Xu, F. J.; Cai, Q. J.; Li, Y. L.; Kang, E. T.; Neoh, K. G. *Biomacromolecules,* published online Jan. 8, 2005.

(22) Fu, G. D.; Kang, E. T.; Neoh, K. G. *Adv. Mater.* **2004**, *16*, 839.

(23) Sacher, E. *Prog. Surf. Sci.* **1994**, *47*, 273.

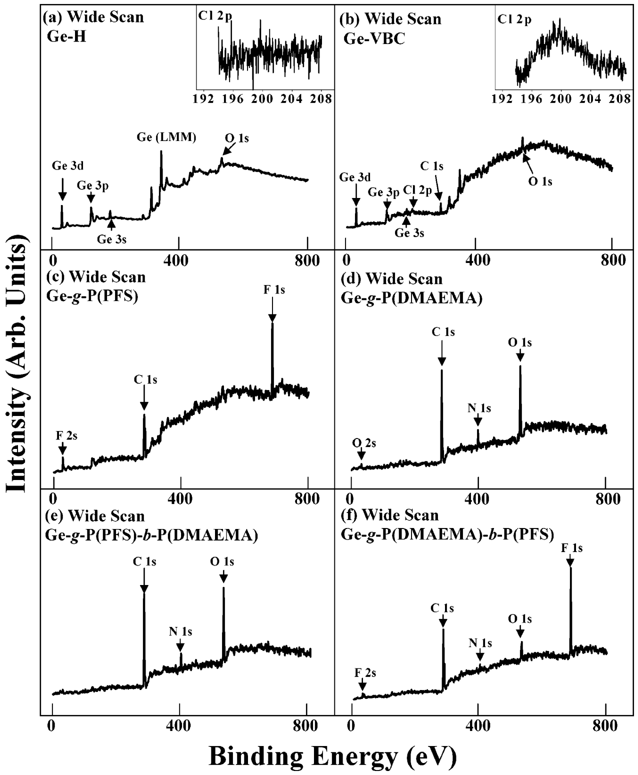

Figure 2. Wide scan spectra of the (a) Ge−H, (b) Ge−VBC, (c) Ge−*g*-P(PFS), (d) Ge−*g*-P(DMAEMA), (e) Ge−*g*-P(PFS)−*b*-P(DMAEMA), and (f) Ge−*g*-P(DMAEMA)−*b*-P(PFS) surfaces. (Reaction conditions are given in Table 1.)

reaction mixture allows the control of the deactivating Cu(II) complex concentration. In comparison to the approach of addition of a Cu(II) complex, addition of a sacrificial initiator can give rise to the formation of free polymers, leading to a reduction in film thickness.[24] Thus, in this work, the method of addition of a Cu(II) complex ($CuCl_2$) was chosen to control the concentration of the deactivating Cu(II) complex during the surface-initiated ATRP process on the Ge−VBC surface. The ratio of [monomer]:[CuCl (catalyst)]:[$CuCl_2$ (deactivator)]:[Bpy (ligand)] was controlled at 100:1:0.2:2.

The presence of grafted PFS polymer (P(PFS)) and P(DMAEMA) on the Ge−VBC surfaces was confirmed by XPS analysis and ellipsometry measurement. These surfaces are referred to as the Ge−*g*-P(PFS) and Ge−*g*-P(DMAEMA) surfaces, respectively. The appearance of an F 1s signal at the BE of about 685.8 eV, as well as the presence of an enhanced C 1s signal at the BE of about 285 eV,[20] in the wide scan spectrum of Figure 2c indicates that P(PFS) has been immobilized on the Ge−VBC surface. The presence of prominent C 1s (BE ~285 eV), N 1s (BE ~399 eV), and O 1s (BE ~530 eV) signals[20] in the wide scan spectrum of Figure 2d suggests that P(DMAEMA) has been successfully grafted on the Ge−VBC surface. The disappearance of the Ge signals in the wide scan spectra of Figures 2c and 2d is consistent with the fact that the thickness of the P(PFS) brushes (about 13 nm after 4 h of ATRP) and the P(DMAEMA) brushes (about 19 nm after 4 h of ATRP) on the germanium surface is larger than the sampling depth of the XPS technique (about 7.5 nm in an organic matrix).[25] The corresponding water contact angles of the Ge−*g*-P(PFS) and Ge−*g*-P(DMAEMA) surfaces are about 97° and 56°. Since the average cross-sectional areas of poly(methyl methacrylate)[26] and polystyrene[27] chains prepared by "living" radical polymerization are about 2 nm^2 and the surface initiator density is about 1.4 unit/nm^2, the surface initiator efficiency of the present system is estimated to be about 30%. The average degrees of polymerization (DPs) for the grafted P(PFS) and P(DMAEMA) brushes obtained after 4 h of ATRP are thus estimated to be about 120 and 160, respectively (Table 1). In the absence of an added (free) initiator for homopolymerization, and as about 2 g of monomer was used in the reaction mixture for surface-initiated ATRP on a Ge substrate of about 1.2 cm × 1.2 cm (see Experimental Section), the monomer conversion was negligible and it remained in large excess throughout the reaction.

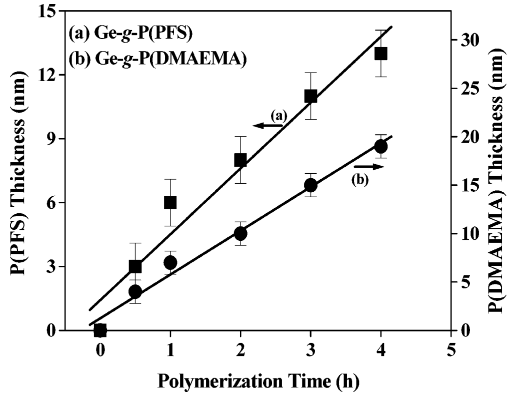

Figure 3. Dependence of thickness of (a) the grafted P(PFS) layer on the Ge−*g*-P(PFS) surface and (b) the grafted P(DMAEMA) layer on the Ge−*g*-P(DMAEMA) surface on the surface-initiated ATRP time.

An approximately linear increase in thickness of the grafted P(PFS) and P(DMAEMA) brushes on the Ge−VBC surfaces with polymerization time is observed, as shown by lines a and b, respectively, in Figure 3. The results suggest that the chain growth from the Ge−VBC surface was consistent with a "controlled" process. The root-mean-square surface roughness values, as derived from the atomic force microscope (AFM) images, of the Ge−*g*-P(PFS) and Ge−*g*-P(DMAEMA) surfaces at the ATRP time of 4 h are on the order of 1−2 nm. Thus, the surface-initiated ATRPs have proceeded uniformly on the Ge surfaces. No increase in organic layer thickness was discernible on the pristine Ge(100) and Ge−H surfaces when the two substrates were subjected to the "surface-initiated" ATRP of the two monomers under similar reaction conditions. Benzyl halides are useful ATRP initiators for the polymerization of styrene and its derivatives due to their structural similarity to styrene. However, they fail to polymerize the methacrylate monomers.[28] The fact that DMAEMA can be easily

---

(24) Jeyaprakash, J. D.; Samuel, S.; Dhamodharan, R.; Rühe, J. *Macromol. Rapid Commun.* **2002**, *23*, 277.

(25) Tan, K. L.; Woon, L. L.; Wong, H. K.; Kang, E. T.; Neoh, K. G. *Macromolecules* **1993**, *26*, 2832.

(26) Shah, R. R.; Merreceyes, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L. *Macromolecules* **2000**, *33*, 597.

(27) Husseman, M.; Malmstrom, E. E.; Mcnamara, M.; Mate, M.; Mecerreves, D.; Benoit, D. G.; Hedrick, J. J.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J.*Macromolecules* **1999**, *32*, 1424.

(28) Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101,* 2921.

graft polymerized from the Ge−VBC surface in surface-initiated ATRP readily suggests that the Ge−C bonded VBC has a much higher reactivity than its molecular counterpart.

Surface-initiated “nonliving” radical polymerization may indeed give rise to similar dependence of the film thickness on reaction time.[29] The molecular weight distribution of the surface-grafted polymer cannot be determined with sufficient accuracy without the cleavage of grafted chains from a sufficiently large surface area of the substrate (>1 m^2).[30] However, one of the unique characteristics of the polymers synthesized by ATRP is the preservation of active groups at the chain ends.[31] To confirm the existence of active chain ends, surface-initiated ATRP is again used to synthesize the P(PFS)−*b*-P(DMAEMA) (or P(DMAEMA)−*b*-P(PFS)) diblock copolymer brushes from the germanium surface, using the grafted P(PFS) (or P(DMAEMA)) brushes as the macroinitiators and in the absence of any added initiators. The formation of block copolymer brushes was confirmed again by XPS and ellipsometry. After an ATRP time of 4 h, the appearance of strong N 1s (BE ~399 eV) and O 1s (BE ~530 eV) signals[20] in the wide scan spectrum of the resulting Ge−*g*-P(PFS)−*b*-P(DMAEMA) surface suggests that DMAEMA has been successfully block-copolymerized on the Ge−*g*-P(PFS) surface (Figure 2e). The thickness of the P(DMAEMA) layer (about 8 nm) is larger than the sampling depth of the XPS technique.[25] As a result, the F signals from the underlying P(PFS) layer are no longer discernible in the wide scan spectrum. On the other hand, for the PFS block-copolymerized Ge−*g*-P(DMAEMA) surface, the appearance of the F 1s signal (BE ~685.8 eV) and F 2s signal (BE ~30 eV)[20] in the wide scan spectrum of the Ge−*g*-P(DMAEMA)−*b*-P(PFS) surface (Figure 2f) indicates that P(PFS) has been immobilized on the Ge−*g*-P(DMAEMA) surface. As the P(PFS) block thickness (about 6 nm) of the Ge−*g*-P(DMAEMA)−*b*-P(PFS) surface is less than the XPS sampling depth,[25] the N 1s (BE ~399 eV) and O 1s (BE ~530 eV) signals[20] from the underlying P(DMAEMA) layer are still discernible in Figure 2f. The DPs of the P(DMAEMA) and P(PFS) blocks were estimated to be about 67 and 53, respectively (Table 1). The above results confirmed that the dormant sites at the end of the grafted P(PFS) and P(DMAEMA) chains on the germanium surfaces allowed reactivation during the subsequent block copolymerization process, resulting in the formation of P(PFS)−*b*-P(DMAEMA) and P(DMAEMA)−*b*-P(PFS) diblock copolymer brushes.

In conclusion, a simple one-step process for the covalent immobilization of an ATRP initiator monolayer on the Ge−H surface has been demonstrated. The process was based on the direct UV-induced hydrogermylation of VBC on the Ge−H surface to give rise to the Ge−VBC surface. Well-defined polymer−Ge hybrids could be readily prepared via surface-initiated ATRP on the Ge−VBC substrates. The linear increase in polymer film thickness with polymerization time suggested that the chain growth of the fluoropolymer and the N-containing polymer from the functionalized germanium surface was consistent with a “controlled” process. The active chain ends on the graft-modified germanium surface could be used as macroinitiators for further functionalization of the hybrid surfaces via block copolymerization.

Experimental Section

The Ge(100) wafer was sliced into square chips of about 1.2 cm × 1.2 cm in size. The pristine germanium chips were immersed in 20 mL of 10 vol % HF in individual Teflon vials for 10 min to give rise to a uniform H-terminated Ge(100) surface (the Ge−H surface).[5] The initiators were immobilized via UV-induced coupling of VBC with the Ge−H surface for 10 min under an atmosphere of dry argon to give rise to a covalently bonded (Ge−C bonded) monolayer (the Ge−VBC surface). The Ge−VBC substrate was immersed in about 200 mL of acetone (a good solvent for VBC) for about 24 h. The solvent was stirred continuously and changed every 8 h. The substrate was subsequently rinsed with copious amounts of fresh acetone to ensure the complete removal of the adhered and physically adsorbed VBC.

For the preparation of the Ge−*g*-P(PFS) and Ge−*g*-P(DMAEMA) hybrids, the reaction was carried out using a [monomer (2 mL)]:[CuCl]:[CuCl$_2$]:[Bpy] molar feed ratio of 100:1:0.2:2 in 2 mL of DMSO at 90°C in a Pyrex tube containing the Ge−VBC substrate for a predetermined period of time. After the reaction, the polymer−Ge hybrids were washed and extracted thoroughly with DMSO and acetone (for the Ge−*g*-P(PFS) hybrids), and doubly distilled water and ethanol (for the Ge−*g*-P(DMAEMA) hybrids). The hybrids were subsequently immersed in large volumes of their respective solvent system for about 48 h to ensure the complete removal of the adhered and physically adsorbed polymer, if any. The solvents were stirred continuously and changed every 8 h. The chemical composition of the modified germanium surfaces was determined by X-ray photoelectron spectroscopy (XPS). The static water contact angles were measured by the sessile drop method, using 3 μL water droplets, in a telescopic goniometer. The thickness of the polymer brushes was determined by ellipsometry.

OM049095U

---

(29) Prucker, O.; Rühe, T. *Macromolecules* **1998**, *31*, 602.

(30) Biesalski, M.; Rühe, J. *Macromolecules* **2004**, *37*, 2196.

(31) Husseman, M.; Malmstrom, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424.