Macromolecules **2008**, *41*, 6641–6645

Superhydrophobic Poly(dimethylsiloxane) via Surface-Initiated Polymerization with Ultralow Initiator Density

Tongcheng Qian,[†] Yuefang Li,[‡] Yuanzi Wu,[†] Bo Zheng,[‡] and Hongwei Ma*,[†]

Department of Biomedical Engineering, College of Engineering, Peking University, Beijing 100871, P. R. China, and Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong

Received April 9, 2008; Revised Manuscript Received July 9, 2008

ABSTRACT: We reported herein a facile method that utilized surface-initiated polymerization (SIP) alone to produce superhydrophobic poly(dimethylsiloxane) (PDMS) surfaces, either flat or as the wall of microfluidic channels. In this so-called relayed SIP strategy, the first SIP was conducted from the initiator integrated PDMS (iPDMS) of varied initiator density, i.e., from 0.5iPDMS to 10^{-6}iPDMS, corresponding to surface density of 3.7×10^{-2} and 1.0×10^{-9} chains nm^{-2}, respectively, an estimation based on uniform distribution of feed initiator molecules. The monomer in use was oligo(ethylene glycol) methacrylate, resulting in poly(OEGMA) chains with terminal hydroxyl groups. The iPDMS substrates were then treated with bromoisobutyryl bromide as the initiation moiety, followed by the second SIP using monomer 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate (FMA). The resulting surface was covered with polymeric trees that had poly(FMA) as the branches and poly(OEGMA) as the central trunk. Only the iPDMS of ultralow initiator density, i.e., 10^{-3}iPDMS (1.0×10^{-5} chains nm^{-2}), produced a superhydrophobic surface with a contact angle of water at 155°. The impact of SIP duration and monomer in use was also studied. The results demonstrated that SIP from substrates of ultralow initiator density could also produce functional surfaces. Furthermore, because this method is compatible with the in situ modification of microfluidic channels, it also provides new opportunities for the field of microfluidics.

Introduction

Superhydrophobic surfaces have many important applications in naturally occurring systems and in artificial devices, which have inspired intensive research activities with regard to the preparation methods and theoretical modeling.[1−4] It is of particular interest to create superhydrophobic surface inside a microfluidic channel, which is important in a number of applications and fundamental studies, such as fluidic flow control in microfluidic devices[5,6] and fluidic behavior study.[7] As poly(dimethylsiloxane) (PDMS) is the most commonly used material in the fabrication of microfluidic devices,[8,9] superhydrophobic PDMS surfaces have attracted much research effort and have been produced by methods such as replicating from an artificial[10] or a natural mold (i.e., the lotus leaf),[11] laser etching,[12] and mechanical assisted self-assembled monolayer.[13] However, these methods cannot be applied to modifying the wall of preformed microfluidic channels. To address this issue, we report herein a facile method that utilizes surface-initiated polymerization (SIP) alone to produce superhydrophobic PDMS surfaces, either flat or as the wall of microfluidic channels.

SIP was generally conducted on substrates of high initiator concentration for the purpose of generating polymer brushes of extremely high density. Although high density of polymer chain led to many unique properties,[14] the increase of polymer chain density did not necessarily lead to superhydrophobicity. We believed, however, that SIP was advantageous not only for its ability to create high density polymer brushes but also for that SIP provided better structural control of the resulting coatings. We reasoned that polymer films prepared by SIP from a substrate of decreasing initiator density would undergo a transition from a continuous film, to a porous film, to separated polymer islands, and further to well-isolated single polymer chains. Since most superhydrophobic surfaces were a result of controlling both the surface topography and surface chemistry,[2,4,15−17] this transition in surface morphology may lead to superhydrophobicity. However, we have not seen such work.

Experimental Section

Materials. The vinyl-terminated initiator (v-initiator, undec-10-enyl 2-bromo-2-methylpropanoate) was obtained from HZDW (99%, Hangzhou, China). Oligo(ethylene glycol) methacrylate (OEGMA, 98%), 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate (FMA, 99%), methyl methacrylate (MMA, 99%), hydroxyethyl methacrylate (HEMA, 97%), and 2-bromoisobutyryl bromide (98%) were purchased from Aldrich and used as received.

SIP from iPDMS. Sylgard 184 was used as a model PDMS elastomer, which was commercially available from Dow Corning and consisted of liquid components A (a mixture of catalyst Pt and prepolymer dimethylsiloxane with vinyl groups) and B (prepolymer dimethylsiloxane with vinyl groups and Si−H groups). PDMS and initiator integrated PDMS (iPDMS) substrates (flat surface and as the walls of microfluidic channels) were prepared by thoroughly mixing the three components A, B (from Sylgard 184), and C (initiator) at a desired ratio (A:B:C = 10:1:C, C varied from 0.5 to 10^{-6}) and cured at 80 °C for 2 h. For SIP of OEGMA, the reaction mixture was prepared by thoroughly mixing two parts. Part 1 was a transparent, pale-blue solution, prepared by adding a specified amount of $CuCl_2$ (5.4 mg, 0.4 mmol), 2,2′-bipyridine (Bipy, 12.5 mg, 0.8 mmol, i.e., 1:2 mole ratio), and a fixed amount monomer to 5 mL of Milli-Q water. Part 2 was a colorless solution, prepared by adding a specified amount of ascorbic acid (AscA, 7.0 mg, 0.4 mmol) to 5 mL of Milli-Q water. After both solutions were deoxygenated, two parts were mixed together under nitrogen. The mixture was further deoxygenated, and the resulting mixture was red in color due to the reduction of the deactivator Cu(II)/Bipy complex to activator Cu(I)/Bipy complex. The resulting mixture had a mole ratio of monomer/$CuCl_2$/Bipy/AscA = 200/1/2/1, with a feed [$CuCl_2$] of 0.04 mM. This mixture was then transferred to a reaction setup under a nitrogen atmosphere, and SIP was initiated and continued for 120 min at ~25 °C. The polymerization was stopped when iPDMS was removed from the solution. Samples

---

* Corresponding author: Fax +86 10 62767142; e-mail hongwei@coe.pku.edu.cn.

[†] Peking University.

[‡] The Chinese University of Hong Kong.

10.1021/ma800784z CCC: $40.75

were thoroughly rinsed with methanol and Milli-Q water and dried under flowing nitrogen before further treatment.

After the first SIP, the iPDMS was functionalized with bromoisobutyryl bromide as the initiation moiety. Samples were immersed in *N*,*N*-dimethylformamide (DMF) (70 mL) at 0 °C, and Et_3N (1.16 mL, 7 mmol) was added dropwise; the concentration of Et_3N in DMF was kept at 0.1 M. After the mixture was stirred for about 10 min, we then added dropwise $BrCOC(CH_3)_2Br$ (0.88 mL, 7 mmol) into the mixture and stirred for another 30 min. The samples were then thoroughly rinsed with DMF, followed by the second SIP of FMA and surface characterization.

For the second SIP, 1.06 g of FMA (2 mmol) was added in 10 mL of DMF by drops and commixed by a magnetic bar under deoxygenating protection for 20 min. Then CuBr (28 mg, 0.2 mmol) and pentamethyldiethylenetriamine (PMDETA, 52 mg, 0.3 mmol) were added to the solution and mixed well, resulting in a homogeneous green solution. The resulting mixture had a mole ratio of monomer/CuBr/PMDETA = 200/2/3. After deoxygenated for 30 min, this mixture was then transferred to a reaction setup under a nitrogen atmosphere. SIP was initiated and continued for 120 min at ~25 °C. Details of the SIP condition for monomer HEMA and MMA can be found in a previous report.[18] For in situ modification of intact microfluidic channels, reaction solutions were pumped through the channel for a desired period of time.

X-ray Photoelectron Spectroscopy. XPS (AXIS Ultra by Kratos Analytical, UK) was used to characterize the surface chemistry of iPDMS before and after SIP modification. Monochromatic Al Kα X-rays (1486.7 eV) were employed. The X-ray source was 2 mm nominal X-ray spot size operating at 15 kV and 12 mA for both survey and high-resolution spectra. The neutralizer gun was on 1.85 A and 3.15 V. Survey spectra, from 0 to 1100 eV binding energy (BE), were recorded at 160 eV pass energy with an energy step of 1.0 eV and a dwell time of 200 ms. High-resolution spectra were recorded at 40 eV pass energy with an energy step of 0.1 eV and a dwell time of 500 ms, with a typical average of three scans. The operating pressure of the spectrometer was typically $\sim 10^{-7}$ Pa. All peaks were referenced to C 1s (CH_x) at 285 eV in the survey scan spectra and C 1s (CH_x) at 284.8 eV in the deconvoluted high-resolution C 1s spectra. All data were collected and analyzed using software provided by the manufacturer.

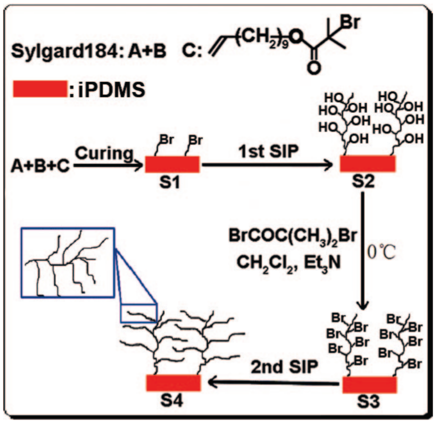
Scanning Electron Microscopy. A HITACH-S4800 scanning electron microscope was used to characterize iPDMS surfaces. The microscope was operated at 10.0 kV. Prior to measurements, the samples were coated with a thin gold film by means of a vacuum sputter to improve electrical conductivity.

Water Contact Angle. Water contact angles were measured on a Dataphysics OCA20 contact angle system at room temperature.

Results and Discussion

The initiator integrated PDMS (iPDMS) was prepared as previously reported.[19] Briefly, a vinyl-terminated initiator (referred to as component C, Scheme 1) was mixed with Sylgard 184 (Dow Corning), which consisted of liquid components A and B. The mixture was then cured at 80 °C for 2 h, resulting in an elastomer. This simple mixing procedure was compatible with replica molding, which was the key step in the fabrication of microfluidic devices. The resulting iPDMS elastomer presented initiator molecules on the surface and was ready for further surface modification via SIP (Scheme 1). The first SIP from iPDMS surfaces of varied initiator density was conducted using monomer oligo(ethylene glycol) methacrylate ($M_w = 526$, OEGMA). The resulting poly(OEGMA) chains had terminal hydroxyl groups for further functionalization. The iPDMS substrates were then treated with bromoisobutyryl bromide as the initiation moiety, followed by the second SIP using monomer 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate (FMA). The resulting surface was covered with polymeric trees that had the poly(FMA) as the branches and the poly(OEGMA) as the central trunk. After each modification step, the surfaces were characterized by XPS, SEM, and contact angle of pure water. We refer this three-dimensional growth of polymer as the relayed SIP method.

Scheme 1. Relayed Surface-Initiated Polymerization (Relayed SIP) from the Initiator Integrated PDMS (iPDMS) of Ultralow Initiator Density[a]



[a] S1 stands for step 1. Inset is a carton for the microstructure of polymer achieved by the second SIP.

Table 1. Contact Angle and XPS Results of the Initiator Integrated PDMS (iPDMS) Surfaces after Each Step of the Relayed Surface-Initiated Polymerization (with Oligo(ethylene glycol) Methacrylate and 1*H*,1*H*,2*H*,2*H*-Perfluorodecyl Methacrylate as the First and Second Monomer, Respectively)

			XPS[c]				
initiator (C)	status[a]	θ (deg)[b]	C 1s	O 1s	Si 2p	Br 3d	F 1s
0[d]	S1	106	49.4	27.2	22.4	0	
	S4	117	43.9	18.4	14.4	0	23.3
0.5	S1	106	50.4	22.8	26.7	0.1	0
	S2	57	28.5	66.4	5.1	0	
	S3[e]	74	63.9	16.4	9.5	4.6	
	S4	126	42.1	5.8	0.7	0.1	51.3
10^{-3}	S1	106	50.0	26.3	23.6	0	
	S2	99	52.0	27.4	20.6	0	
	S3	105	50.6	27.4	21.9	0.1	
	S4	155	41.5	5.2	0.4	0.1	52.9

[a] S1 stands for step 1; see Scheme 1 for details. [b] Average values from three different locations, SE < ±3°. [c] Atom % was based on the survey scan of Br 3d (71 eV), Si 2p (102 eV), C 1s (285 eV), O 1s (532 eV), and F 1s (690 eV). Average values from three different locations, SE < ± 0.4. [d] This sample was PDMS. [e] This sample had 5.6% N 1s (399 eV) due to Et_3N, which was used as catalyst in the S3.

The impact of initiator density was first tested as follows: iPDMS with five mass ratios of A:B:C were investigated, namely, 10:1:0.5, 10:1:10^{-1}, 10:1:10^{-2}, 10:1:10^{-3}, and 10:1:10^{-6}. In the rest part of this paper we refer to these five types of iPDMS as 0.5iPDMS (the surface density was estimated to be 3.7×10^{-2} chain nm^{-2}; see Supporting Information for detailed calculation), 10^{-1}iPDMS, 10^{-2}iPDMS, 10^{-3}iPDMS (surface density of 1.0×10^{-5} chain nm^{-2}), and 10^{-6}iPDMS. For a given SIP duration of 2 h for both the first and second SIP, only the 10^{-3}iPDMS yielded superhydrophobic surface. Thus, we reported only representative results from two iPDMS samples, namely 0.5iPDMS and 10^{-3}iPDMS, with fixed SIP duration of 2 h for both the first and second SIP.

Before the first SIP processes, XPS detected 0.1 atom % Br signal on the surface of 0.5iPDMS samples, which was consistent with our previous report that initiators were evenly distributed both on the iPDMS surface and within its body.[19] However, XPS indicated no detectable Br signal for the 10^{-3}iPDMS samples. We believed this was due to the limited sensitivity of XPS because the 10^{-3}iPDMS sample did initiate

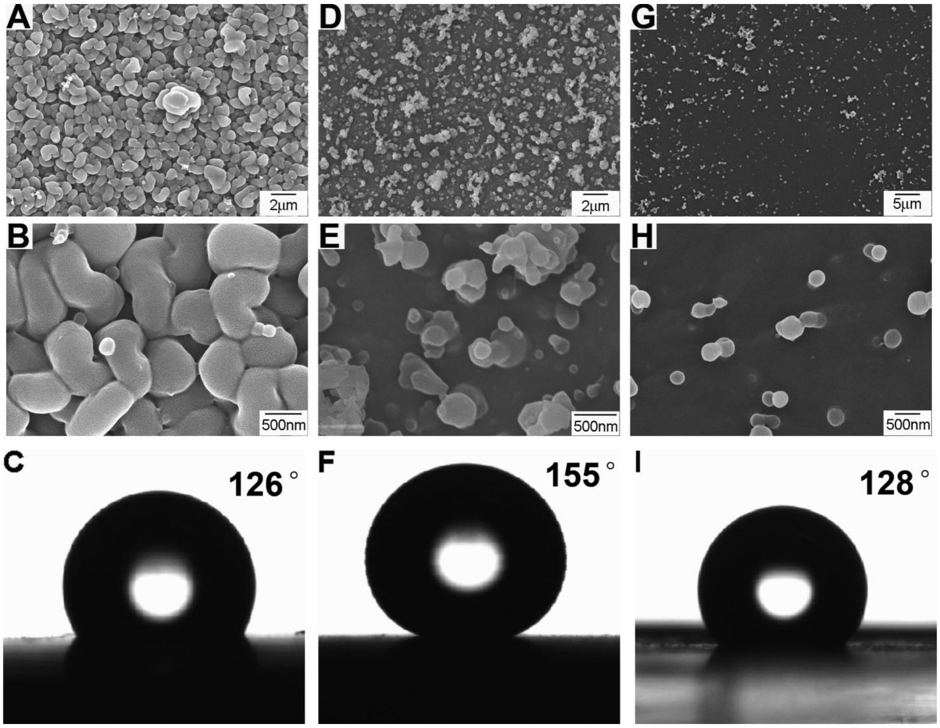


Figure 1. Scanning electron microscope and contact angle images of initiator integrated PDMS (iPDMS) surfaces after the relayed surface-initiated polymerization (A−F) and after only one time SIP (G−I): (A, B) surface morphology of iPDMS with a feed initiator ratio of 0.5 (0.5iPDMS); (C) water droplet on 0.5iPDMS; (D, E) surface morphology of iPDMS with a feed initiator ratio of 10^{-3} (10^{-3}iPDMS); (F) water droplet on 10^{-3}iPDMS. The sliding angle was ~1.5°; (G, H) surface morphology of 0.5iPDMS after only one time SIP of 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate (FMA); (I) water droplet on 0.5iPDMS after only one time SIP of FMA.

polymerization from its surface, which resulted in polymer that in turn acted as an amplification of the initiator and was detectable by XPS (see below and Table 1, 10^{-3}iPDMS, S4). XPS signals of C, O, and Si for the 10^{-3}iPDMS samples were reasonably close to those for the 0.5iPDMS (Table 1). Both the 10^{-3}iPDMS and 0.5iPDMS had the same contact angle as PDMS at ~106°. Although it was difficult to know the exact concentration of the initiator (component C) on the iPDMS surface, one could reasonably assume that the amount of initiator integrated into the network of iPDMS was proportional to the feed ratio of the starting components. This assumption was supported by the following data.

Figures 1A−F were representative SEM and contact angle images of 0.5iPDMS and 10^{-3}iPDMS after the relayed SIP surface modification. Although it was difficult to quantify, obvious was the density difference between these two samples. The 0.5iPDMS sample was covered with entangled polymer lines (~500 nm wide), while the 10^{-3}iPDMS sample was covered with individual dots sized from 100 to 500 nm in diameter, and the heights for these dots were up to 3 μm measured by a surface profiler (Figure 2). This initiator density difference was consistent with the contact angle results of the two iPDMS samples after the first SIP. The 0.5iPDMS sample had a contact angle at 57°, which agreed well with that of a poly(OEGMA) surface from a dense initiator surface.[20] The 10^{-3}iPDMS had a contact angle of 99°, close to that of PDMS, indicating a low density coverage of poly(OEGMA) chains. This poly(OEGMA) density difference was further supported by XPS characterization: the level of Br signal of the 10^{-3}iPDMS and 0.5iPDMS samples after addition of initiator moiety in S3 (Scheme 1) was 0.1 and 4.6 atom %, respectively. Note that the decrease of terminal Br signal in Table 1 after the first and second SIPs (0.1 to 0 atom % or from 4.6 to 0.1 atom %), this was a common phenomenon in SIP and was due to (1) the loss of Br groups during the SIP process and (2) the Br was buried underneath the top polymer layer and not detected by XPS.

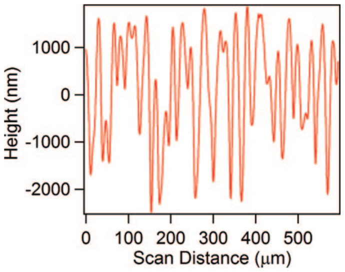


Figure 2. A representative profiler scan of a 10^{-3}initiator integrated PDMS surface after the relayed surface-initiated polymerization (after step 4 in Scheme 1, poly(1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate)); the height was up to 3 μm.

However, after the second run of SIP, the 10^{-3}iPDMS and 0.5iPDMS samples had very similar surface chemistry as determined by XPS (Table 1). This result was surprising, as we had expected a higher Si signal from the surface of 10^{-3}iPDMS sample since most of the surface was not covered by poly(FMA). Meanwhile, it was reasonable that the Si signal was greatly reduced (from 27 to 0.7 atom %) for the 0.5iPDMS sample as most of its surface was covered by poly(FMA) (Figure 1A). To better understand the unexpected XPS result from the 10^{-3} iPDMS, we applied the relayed SIP process to a control sample of PDMS without initiator and characterized the surface chemistry by XPS. The PDMS sample after the first and second SIP had a reduced Si signal (from 23 to 14 atom %) and increased F signal (from 0 to 23 atom %), which was attributed to the entrapment of monomer FMA into the PDMS networks by the minor swollen effect induced by dimethylformamide (DMF), the solvent used in the relayed SIP process. This might partially explain why the 10^{-3}iPDMS sample had such a low Si signal. Nevertheless, a superhydrophobic surface (with a static contact angle >150° and sliding angle at ~1.5°) was only created from 10^{-3}iPDMS after the second SIP although 10^{-3}iP-

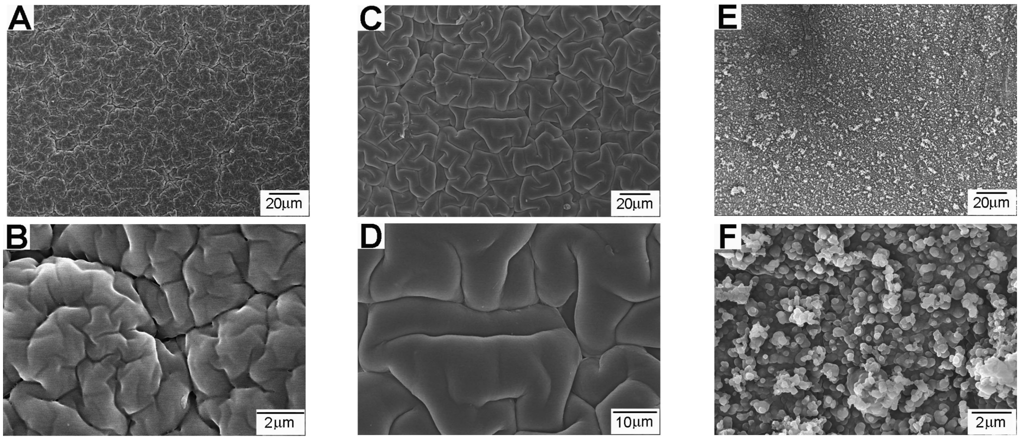


Figure 3. The contact angle was not sensitive to the change of the first and second surface-initiated polymerization duration. Representative scanning electron microscope images for samples after the relayed SIP. For all samples, oligo(ethylene glycol) methacrylate (OEGMA) and 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate (FMA) were used as the first and second monomer, respectively. For (A) and (B): 0.5iPDMS, 1 h of the first SIP time, 2 h of the second SIP time, $\theta = 130°$; for (C) and (D): 0.5iPDMS, 4 h of the first SIP time, 2 h of the second SIP time, $\theta = 130°$; for (E) and (F), 10^{-3}iPDMS, 2 h of the first SIP time, 6 h of the second SIP time, $\theta = 150°$.

DMS and 0.5 iPDMS after the second SIP showed similar XPS results. The 0.5iPDMS had a contact angle of 126°, close to that of poly(FMA) surface after one SIP.[17] Thus, the ultralow initiator density is one of the key conditions (i.e., 10^{-3}iPDMS but not the 10^{-6}iPDMS, which had a contact angle at 106° close to that of unmodified PDMS; see Supporting Information for the SEM image of 10^{-6}iPDMS after relayed SIP).

The relayed SIP strategy is also required to generate the superhydrophobicity on iPDMS. We carried out a control experiment by conducting SIP using FMA on 0.5iPDMS surface (Figures 1G−I). After 4 h of SIP, the surface was covered with individual dots similar to that in Figures 1D,E, but with smaller size, and was not superhydrophobic. Longer SIP duration (up to 8 h) resulted in similar surface morphology and contact angles, which was attributed to the difficulties in running SIP for longer duration.[18] In the relayed SIP process, the first SIP prepared a post to support the second SIP, which was a vertical direction growth. The second SIP provided an effective way to realized lateral expansion. The duration of the first and second SIP was, however, not critical as long as a decent (>200 nm laterally and >1000 nm vertically) tree size was achieved.

When the duration of the first and second SIP was varied from 1 to 8 h for all the five iPDMS samples, the surface morphology was very different, but we observed no conversion from a hydrophobic surface to a superhydrphobic surface. For example, Figure 3B, Figure 1B, and Figure 3D were SEM images for the 0.5iPDMS samples after the first SIP with different durations of 1, 2, and 4 h, respectively. Although the morphology was different, they all had a similar contact angle at 126° or 130°. Comparing Figure 1E with Figure 3F, we found that the density of poly(OEGMA−FMA) trees were increased as the second SIP duration increased from 2 to 6 h. However, these two 10^{-3}iPDMS samples also shared similar contact angles at 150° and 155°. Thus, we concluded that the effect of the SIP duration on the contact angles of water was rather limited.

The monomer FMA applied in the second SIP process was also critical in preparing superhydrophobic iPDMS surfaces. FMA acted both by lowering the surface energy with poly(FMA) and by generating a surface morphology with hierarchical scale roughness. For comparison, we applied three other monomers, namely, methyl methacrylate (MMA), OEGMA, and hydroxyethyl methacrylate (HEMA), as the monomer to replace FMA in the second SIP process while the conditions for S1 to S3 were maintained the same as before (Figure 4). Previously, the contact angles of surfaces with PMMA, PHEMA, and poly(OEGMA) polymer brushes were reported at 70°, 47°,[21] and ~57°,[20] respectively. We had the contact angles for the 0.5iPDMS samples covered with PMMA, PHEMA, and poly(OEGMA) at 85°, 39°, and 48°, respectively, which were all close to the previous reports.

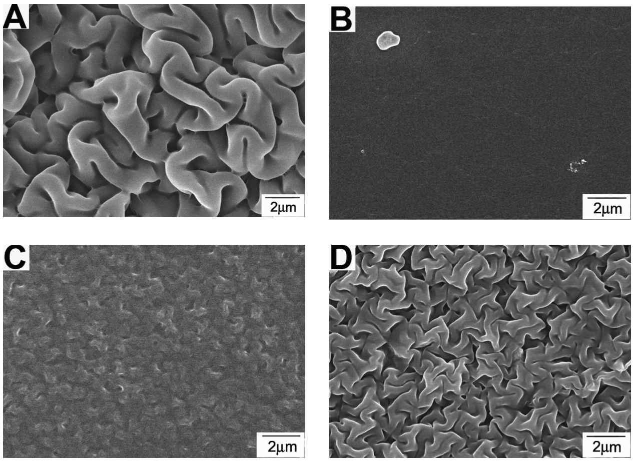


Figure 4. Scanning electron microscope images of initiator integrated PDMS (iPDMS) surfaces after the relayed surface-initiated polymerization (relayed SIP): (A) hydroxyethyl methacrylate (HEMA) as the second monomer for 0.5iPDMS; (B) HEMA as the second monomer for 10^{-3}iPDMS; (C) methyl methacrylate (MMA) as the second monomer for 0.5iPDMS; (D) OEGMA as the second monomer for 0.5iPDMS. The first monomer was OEGMA in all samples.

The patterns (or wrinkles) shown in Figures 4A,C,D were different from that in Figure 1A yet interesting and mysterious. The exact mechanism behind the pattern formation was not clear at this stage. We hypothesized that the mechanical stress induced by the tethered polymers might play a key role in pattern formation: different monomers resulted in distinctly different surface morphology (or wrinkle) for the 0.5iPDMS samples. These differences in surface morphology were believed to cause the unique behavior of Si signal detected by XPS after the relayed SIP. For example, with HEMA as the monomer in the second polymerization step, the surface of 10^{-3}iPDMS sample should have a lower surface coverage of PHEMA than the surface of 0.5iPDMS sample, but XPS showed a similar Si signal for these two samples: 10.7% and 11.8%, respectively. This was attributed to the fact that the 0.5iPDMS sample showed a rougher surface morphology than the 10^{-3}iPDMS sample, which led to more areas of PDMS surface exposed to XPS detection and consequently led to an increase of Si signal.

Table 2. Contact Angle and XPS Results of the Initiator Integrated PDMS (iPDMS) Surfaces with Different Monomers in the Second Surface-Initiated Polymerization (SIP) Process

			XPS[b]			
monomer	initiator (C)	θ (deg)[a]	C 1s	O 1s	Si 2p	F 1s
none[c]	0.5[d]	106	50.4	22.8	26.7	
	10^{-3}	106	50.0	26.4	23.6	
FMA[e]	0.5	126	42.1	5.8	0.7	51.3
	10^{-3}	155	41.5	5.2	0.4	52.9
MMA[e]	0.5	85	58.7	24.5	16.8	
	10^{-3}	82	63.4	24.9	11.7	
OEGMA[e]	0.5	48	59.2	28.9	11.9	
	10^{-3}	72	60.5	30.8	8.7	
HEMA[e]	0.5	39	61.2	27.0	11.8	
	10^{-3}	67	61.4	28.2	10.7	

[a] Average values from three different locations, SE < ±3°. [b] Atom % was based on the survey scan of Si 2p (102 eV), C 1s (285 eV), O 1s (532 eV), and F 1s (690 eV). Average values from three different locations, SE < ±0.4. [c] This sample was iPDMS before the first SIP process. [d] This sample had Br 3d (71 eV) intensity at 0.1 atom %. [e] FMA: 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate; MMA: methyl methacrylate; OEGMA: oligo(ethylene glycol) methacrylate; HEMA: hydroxyethyl methacrylate.

The 10^{-3}iPDMS sample covered with PMMA had a contact angle of 82°, close to that of 0.5iPDMS sample. However, we saw significant contact angle increase for the 10^{-3}iPDMS samples covered with PHEMA and poly(OEGMA) at 67° and 72°, respectively. The hydrophilicity of these three samples indicated the importance of surface chemistry brought by FMA. The monomer FMA was also unique in that the 10^{-3}iPDMS samples with FMA as the second monomer (Figure 1E) had a different surface morphology from the 10^{-3}iPDMS samples with the other three tested monomers (Figure 4B for HEMA; the surfaces of MMA and OEGMA were also featureless, data not shown).

In conclusion, we developed a simple SIP method to render the PDMS surface superhydrophobicity. Three factors, the ultralow initiator density, the relayed SIP strategy, and the monomer FMA, are all crucial to achieve the superhydrophobic PDMS surfaces. This relayed SIP method was highly reproducible and easy to scale up. The resulting coating was very robust. The iPDMS surfaces retained their superhydrophobicity even after rubbing against a rough floor, after incubation in 1 M HCl or in 1 M NaOH for 1 h at 50 °C. We have also accomplished the in situ modification of internal wall of microfluidic channels made from iPDMS (data not shown), and we are currently applying it to microfluidic studies. We also believe this method provides a unique set of surfaces/materials for sliding behavior study.[22] Besides the superhydrophobic effect, similar fluorinated copolymer had proved to be a protein resistant material.[23] Our preliminary evaluation indicated that the poly(OEGMA−FMA) superhydorphobic coating inhibited protein (fluorescently labeled bovine serum albumin) adsorption and small molecule (Rhodamine B) absorption to the level undetectable by fluorescent microscope, which were long-standing problems in microfluidics.[24−27] From these preliminary results we also expect this method to be applied to provide marine antifouling materials.[3]

Acknowledgment. The authors thank Mr. Dayong Yang (National Center for NanoScience & Technology, China) for SEM. This work was supported by the NSFC grant (50773001), RFDP (20060001014) grant to H.M., and the Research Grants Council of Hong Kong (404207) to B.Z.

Supporting Information Available: Table of density and surface density of initiator for iPDMS samples and figure showing SEM image of 10^{-6}iPDMS. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Zhang, X.; Shi, F.; Niu, J.; Jiang, Y.; Wang, Z. Q. *J. Mater. Chem.* **2008**, *18*, 621–633.
(2) Li, X. M.; Reinhoudt, D.; Crego-Calama, M. *Chem. Soc. Rev.* **2007**, *36*, 1350–1368.
(3) Genzer, J.; Efimenko, K. *Biofouling* **2006**, *22*, 339–360.
(4) Sun, T. L.; Feng, L.; Gao, X. F.; Jiang, L. *Acc. Chem. Res.* **2005**, *38*, 644–652.
(5) Gau, H.; Herminghaus, S.; Lenz, P.; Lipowsky, R. *Science* **1999**, *283*, 46–49.
(6) Takei, G.; Nonogi, M.; Hibara, A.; Kitamori, T.; Kim, H. B. *Lab Chip* **2007**, *7*, 596–602.
(7) Atencia, J.; Beebe, D. J. *Nature (London)* **2005**, *437*, 648–655.
(8) Whitesides, G. M. *Nature (London)* **2006**, *442*, 368–373.
(9) Psaltis, D.; Quake, S. R.; Yang, C. H. *Nature (London)* **2006**, *442*, 381–386.
(10) He, B.; Patankar, N. A.; Lee, J. *Langmuir* **2003**, *19*, 4999–5003.
(11) Sun, M. H.; Luo, C. X.; Xu, L. P.; Ji, H.; Qi, O. Y.; Yu, D. P.; Chen, Y. *Langmuir* **2005**, *21*, 8978–8981.
(12) Jin, M. H.; Feng, X. J.; Xi, J. M.; Zhai, J.; Cho, K. W.; Feng, L.; Jiang, L. *Macromol. Rapid Commun.* **2005**, *26*, 1805–1809.
(13) Genzer, J.; Efimenko, K. *Science* **2000**, *290*, 2130–2133.
(14) Tsujii, Y.; Ohno, K.; Yamamoto, S.; Goto, A.; Fukuda, T. In *Surface-Initiated Polymerization I*; Jordan, R., Ed.; Springer-Verlag GmbH: Berlin, 2006; Vol. 197, p 1.
(15) Erbil, H. Y.; Demirel, A. L.; Avci, Y.; Mert, O. *Science* **2003**, *299*, 1377–1380.
(16) Lafuma, A.; Quere, D. *Nat. Mater.* **2003**, *2*, 457–460.
(17) Yu, X.; Wang, Z. Q.; Jiang, Y. G.; Shi, F.; Zhang, X. *Adv. Mater.* **2005**, *17*, 1289–1293.
(18) He, J.; Wu, Y. Z.; Wu, J.; Mao, X.; Fu, L.; Qian, T. C.; Fang, J.; Xiong, C. Y.; Xie, J. L.; Ma, H. W. *Macromolecules* **2007**, *40*, 3090–3096.
(19) Wu, Y. Z.; Huang, Y. Y.; Ma, H. W. *J. Am. Chem. Soc.* **2007**, *129*, 7226–7227.
(20) Ma, H. W.; Li, D. J.; Sheng, X.; Zhao, B.; Chilkoti, A. *Langmuir* **2006**, *22*, 3751–3756.
(21) Shah, R. R.; Merreceyes, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L. *Macromolecules* **2000**, *33*, 597–605.
(22) Granick, S.; Zhu, Y. X.; Lee, H. *Nat. Mater.* **2003**, *2*, 221–227.
(23) Gudipati, C. S.; Finlay, J. A.; Callow, J. A.; Callow, M. E.; Wooley, K. L. *Langmuir* **2005**, *21*, 3044–3053.
(24) Huang, B.; Wu, H. K.; Bhaya, D.; Grossman, A.; Granier, S.; Kobilka, B. K.; Zare, R. N. *Science* **2007**, *315*, 81–84.
(25) Roman, G. T.; Hlaus, T.; Bass, K. J.; Seelhammer, T. G.; Culbertson, C. T. *Anal. Chem.* **2005**, *77*, 1414–1422.
(26) Toepke, M. W.; Beebe, D. J. *Lab Chip* **2006**, *6*, 1484–1486.
(27) Song, H.; Li, H. W.; Munson, M. S.; Van Ha, T. G.; Ismagilov, R. F. *Anal. Chem.* **2006**, *78*, 4839–4849.

MA800784Z