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Photopatternable Films of Block Copolymers Prepared through Double-Click Reaction†

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Patterned alignment of functional organic molecules on surfaces is increasingly investigated due to numerous promising applications in micro- and nanotechnology. Chemical surface patterning attracts particular importance in such fields of biotechnology in which a controlled surface immobilization of biomolecules like enzymes or proteins is desired,[1−4] e.g., for the development of biosensors.[5] For various applications, the controlled, site-specific positioning of molecules or functional nanoparticles on surfaces is indeed a critical prerequisite.[6,7] In particular, site-selective provision of functional groups is required for the reliable, site-specific attachment of functional molecules and, hence, the fabrication of regularly spaced functional arrays. Control over spatial distribution of chemical surface functionalities constitutes a major demand in diverse material applications, e.g., for the fabrication of DNA chips.[8] Therefore, in this Communication we introduce, synthesized by a double-click approach, photopatternable block copolymers films allowing to provide site-specific amino functions and covalent attachment specifically on gold surfaces.

Currently, a variety of surface patterning techniques exist in order to attain a controlled immobilization of nanoparticles,[6] biomolecules,[2] or polymers.[9] Those include photolithography,[10] microcontact printing,[11] nanoimprint lithography,[12,13] photocatalytic lithography,[14] dip-pen nanolithography,[15,16] and local oxidation via scanning probe lithography.[17] A promising approach that was developed in our group includes the preparation of photopatternable polymer films which can covalently be attached to silica or gold surfaces. Via selective UV irradiation of these films, a controlled release of functional groups was accomplished.[18−20] The possibility of a subsequent site-specific deposition of charged nanoparticles or biomolecules like DNA and proteins was demonstrated.[21,22]

Following the increasing demand for miniaturization in surface-based technologies, the utilization of self-assembling properties of block copolymers, which are able to form regular surface structures of mesoscopic dimensions, is a promising approach for the preparation of closer spaced functional arrays. The practicability of this approach has already been shown with patterned poly(styrene-*block*-methyl methacrylate) films[23,24] and poly(styrene-*block*-isoprene) surfaces,[25] where proteins were selectively adsorbed due to preferential interactions with one domain. However, short adsorption times and a limited protein concentration are requirements to achieve high selectivity. To avoid these limitations and for further utilization of such functional surfaces, e.g., in biochip applications, the molecules need to be attached reliably to the substrate. Furthermore, by combining surface patterning via self-assembly of block copolymers with a supplemental photostructuring, the fabrication of more complex functional surface pattern can be realized. Recently, such a hybrid structuring concept has been demonstrated by Bosworth et al. with the self-assembling block copolymer poly(α-methylstyrene-*block*-4-hydroxystyrene) that can be utilized as photoresist.[26,27]

With raising demands on the device performance, the requirements on the polymer systems increase similarly. Thus, the synthesis of polymer materials with highly defined architecture and specific functionality is needed. For that, suitable synthetic tools are necessary. In this regard, the use of controlled radical polymerization techniques allows preparation of block copolymers with adjustable block lengths, thus providing control over macromolecular architecture. Moreover, efficient postfunctionalization methods summarized under the term "click reactions" can be used to introduce specific functions into the polymer product.[28,29] Such efficient, robust, and orthogonal chemistries are increasingly utilized for the tailored synthesis of functional soft materials.[30] Moreover, Gupta et al. recently reported the fabrication of multifunctional microarrays by making use of the orthogonal reactivity of thiol−ene chemistry.[31]

In the present work, we report on the preparation of a novel functionalized block copolymer by a versatile and efficient synthetic approach that combines controlled radical polymerization with highly selective postfunctionalization techniques. The presented sequence of orthogonal chemistries allows a block-specific introduction of functional groups which fulfill different purposes like anchorage on gold surfaces and site-specific provision of amino functions by lithographic means. The resulting block architecture implies a specific arrangement of the polymer chains at a surface. The patterned grafting of functional materials to the films is demonstrated with fluorescent molecules or with initiators for ATRP. The latter allows the site specific growth of brushes tethered to the grafted block copolymer layer.

For the synthesis of the polystyrene-based precursor diblock copolymers (**BC1**) we used the reversible addition−fragmentation chain transfer polymerization (RAFT).[32] The general structure of **BC1** is displayed in Figure 1a. These polymers are composed of a poly(4-chloromethylstyrene-*co*-styrene) block (poly(CMS-*co*-S)) and a poly(4-propargyloxystyrene-*co*-styrene) block (poly(POS-*co*-S)). While in sample **BC1-a** both blocks are styrene-containing copolymers, in the samples **BC1-b** and **BC1-c** the designated anchor block is a poly(CMS) homopolymer. The RAFT polymerizations have been conducted using 2,2′-azobis(isobutyronitrile) (AIBN) as initiator and (S)-1-dodecyl-(S′)-(α, α′-dimethyl-α′′-acetic acid) trithiocarbonate (DDMAT) as chain transfer agent (CTA). The polymers were then used as macro-CTA to attach the second block obtaining the TMS-protected versions of the precursor polymers (**pBC1**). While in sample **pBC1-a** and **pBC1-c** the CMS-containing block was employed as macro-CTA to reinitiate the polymerization of TMSPOS and styrene, in the case of sample **pBC1-b** this sequence is reversed; i.e., the poly(TMSPOS-*co*-S) block was used as macro-CTA to polymerize CMS.

The lengths of both blocks could be adjusted, and thus, products of narrow molecular weight distributions were

† Dedicated to Prof. Oskar Nuyken on the occasion of his 70th birthday

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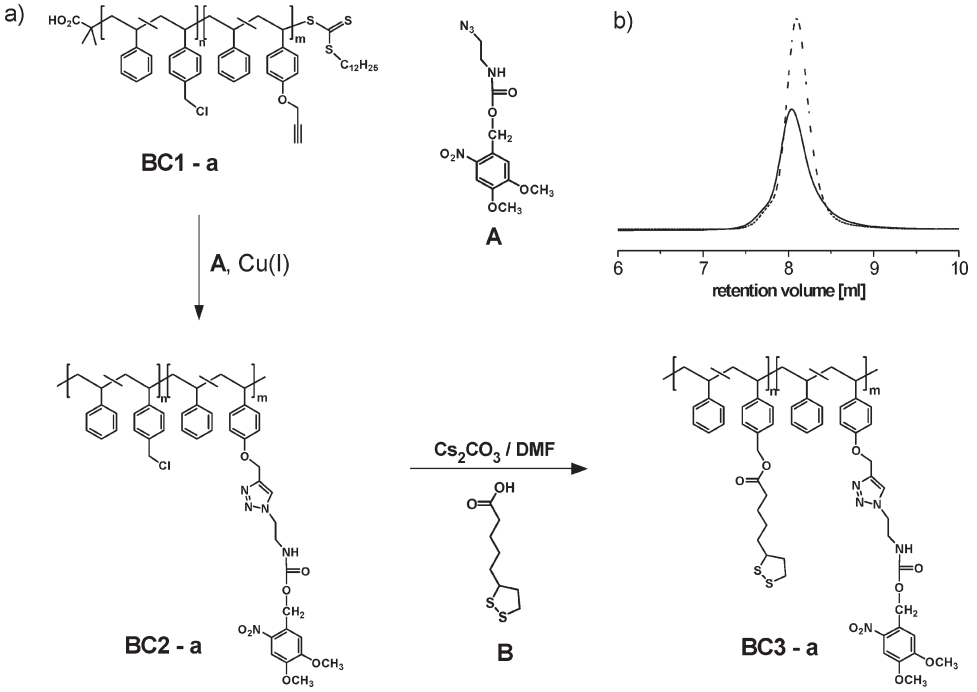

Figure 1. (a) Reaction sequence for the selective postfunctionalization of precursor polymer **BC1-a** and (b) GPC traces of polymer **BC3-a** (solid line; $M_{n,GPC(RI)}$: 18 100 g/mol; PDI: 1.25) and the corresponding precursor polymer **BC1-a** (dashed line; $M_{n,GPC(RI)}$: 16 500 g/mol; PDI: 1.17).

Table 1. Molar Masses, Block Ratios, and PDI of the Precursor Polymers

	poly(CMS-*co*-S) block			poly(TMSPOS-*co*-S) block			block copolymer (**pBC1**)				
polymer sample	$M_{n,GPC}$ [g/mol]	$M_{n,NMR}$ [g/mol]	monomer ratio CMS/S	$M_{n,GPC}$ [g/mol]	$M_{n,NMR}$ [g/mol]	monomer ratio[d] TMSPOS/S	$M_{n,GPC}$ [g/mol]	$M_{n,NMR}$ [g/mol]	PDI	monomer ratio[d] CMS/TMSPOS	block ratio[a,f] CMS-*co*-S/TMSPOS-*co*-S
pBC1-a	7700[b] 7000[c]	7900[e]	1/0.5[d]		10 600[f]	1/2.5	17 300[b] 17 700[c]	18 500	1.14[b] 1.15[c]	2/1	1/1.3
pBC1-b		2400[f]	1/0	19 000[b] 20 300[c]	23 100[e]	1/2.4	22 300[c]	25 500	1.14[c]	1/3	1/9.6
pBC1-c	8000[b] 7700[c]	9400[e]	1/0		24 400[f]	1/1.6	27 900[b] 26 900[c]	33 800	1.19[b] 1.17[c]	1/1	1/2.6

[a]Referring to the molar masses ($M_{n,NMR}$) of both blocks. [b] Determined with a light scattering (LS) detector. [c] Determined with a refractive index (RI) detector applying a polystyrene (PS) calibration. [d] Monomer ratio: determined by ^{1}H NMR. [e] Macro-CTA: determined by ^{1}H NMR via end-group method. [f] Second block and block ratio: determined from $M_{n,NMR}$ and monomer ratio of the macro-CTA and the monomer composition of the final diblock copolymer.

obtained. As shown in Table 1, block copolymers of different block ratios have been prepared (see samples **a**, **b**, and **c**). Since a short anchor block should be sufficient to attain a strong connection to the surface, the CMS-containing block, intended for the subsequent introduction of anchor units, was adjusted to be the shorter one in each sample. The monomer ratios within the blocks differ in the respective samples (Table 1).

By cleavage of the TMS-protecting groups, the reactive precursor polymers (**BC1**) have been obtained. Both polymer blocks of **BC1** are equipped with functional groups available for further functionalization. With respect to the intended use, the target polymers should exhibit two independent functions: in addition to the presence of photosensitive protected functional groups, making the polymer photopatternable, anchor units have to ensure a permanent connection of the polymer film to the substrate. Thus, the designated functional block was equipped with functional units (**A**) containing a photolabile protected amino group, where 6-nitroveratryloxycarbonyl (NVOC) is the protecting group. For that, the Cu(I)-catalyzed cycloaddition of alkynes with azides (known as the click reaction) was employed, leading to structure **BC2**. This chemistry has emerged as one of the most famous methods in terms of polymer modification[33] for both manipulation of the macromolecular architecture, e.g. by attachment of bulky side chains,[34,35] and the introduction of functional groups.[36] The click reaction with the functional unit **A** (Figure 1a) was accomplished at room temperature within 14 h, leading to a complete conversion. The subsequent introduction of anchor groups to the CMS-containing block was realized by converting polymer **BC2** with lipoic acid (**B**) containing a disulfide function capable of binding covalently to gold surfaces.[37] The reactions were carried out in the presence of cesium carbonate, which forms carboxylate intermediates that are very strong nucleophiles and that react quickly with the benzyl chloride groups. The exceptional high nucleophilicity of such carboxylates is described as the "cesium effect" and is used in organic chemistry for the performance of efficient reactions under mild conditions[38,39] but has not been employed in terms of polymer analogous modification so far. Both polymer analogous reactions carried out here were found to proceed under gentle conditions and to give a very high conversion. The reaction sequence leading to the target polymers (**BC3**) is displayed in Figure 1a for **BC3-a**.

By conducting GPC measurements of the products after each reaction, we found that the modification steps had only a small effect on the molecular weight distributions. This is demonstrated for polymer **BC3-a** and the corresponding precursor polymer

Table 2. Molar Masses and PDI of the Polymers BC1, BC2, and BC3

polymer sample	M_n[a] [g/mol]	PDI[a]	polymer sample	M_n[a] [g/mol]	PDI[a]	polymer sample	M_n[a] [g/mol]	PDI[a]
BC1-a	16 500	1.17	**BC2-a**	18 300	1.19	**BC3-a**	18 100	1.25
BC1-b	20 500	1.14	**BC2-b**	23 000	1.21	**BC3-b**	–[b]	–[b]
BC1-c	24 700	1.18	**BC2-c**	28 300	1.21	**BC3-c**	28 900	1.29

[a] Determined with a refractive index (RI) detector applying a polystyrene (PS) calibration. [b] Not measured.

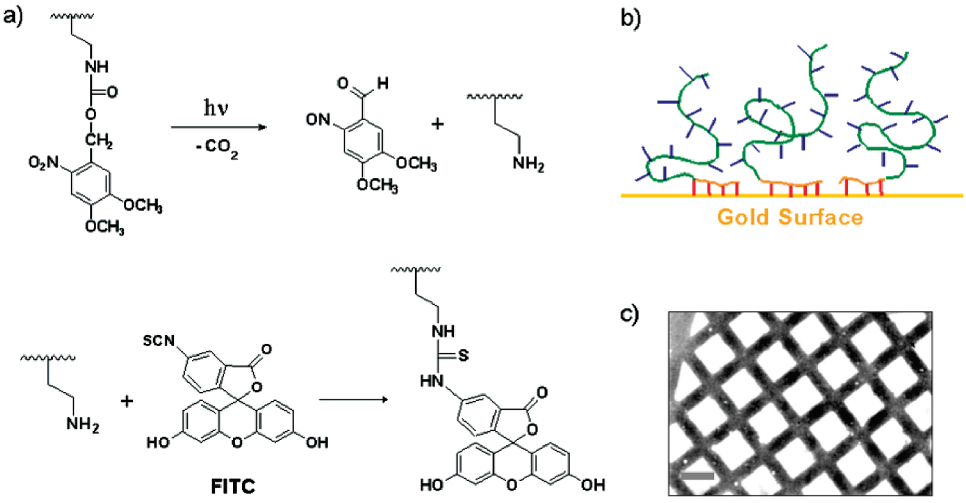

Figure 2. (a) Sequence for the cleavage of NVOC-protecting groups and binding of FITC to the released amino groups, (b) suggested arrangement of the polymer chains forming a monolayer attached to a gold surface, and (c) fluorescence microscopy image of a film of **BC3-a** after irradiation through a TEM grid and subsequent binding of FITC (scale bar: 40 μm).

BC1-a by their GPC curves (Figure 1b). Considering this fact together with the NMR analysis, we can presume that no appreciable side reactions took place during the polymer analogous modifications. ^{1}H and ^{13}C NMR spectra of the polymers **BC1-a**, **BC2-a**, and **BC3-a** together with complete signal assignments are shown in the Supporting Information (Figures SI2−SI4). The NMR signal integration confirmed that both the click reaction and the subsequent introduction of anchor groups proceeded quantitatively. Molar masses and PDI of the polymers **BC1**, **BC2**, and **BC3** determined via GPC (RI detector, PS calibration) are summarized for the samples **a**, **b**, and **c** in Table 2. While a considerable increase in molar mass can be observed from **BC1** to **BC2**, no significant molar mass difference was detected between **BC2** and **BC3** which can be explained by a similar hydrodynamic volume of the polymers. However, the complete conversion of **BC2** to **BC3** has been proved via NMR analysis.

Compared to the random NVOC-protected amino terpolymers prepared through free radical copolymerization,[19,20] the polymer analogous approach described here offers several important advantages. In our previous work, the NVOC groups were introduced via NVOC-containing methacrylate monomers. Radical copolymerizations of these monomers led to very limited molar masses due to the fact that the NVOC group acts as a scavenger. Thus, molar masses not higher than 4500 g/mol were obtained.[19] To circumvent this problem, the polymer analogous introduction of NVOC-protected amino groups via click chemistry was studied in our group and was shown to be practicable with random propargyloxystyrene-*co*-styrene copolymers.[36]

In the present work, the polymer analogous approach is realized with a block copolymer system, where the ratio of monomers carrying NVOC-protected amino groups in the functional block can be adjusted as required. The present designed multifunctional polymer system is thus distinguished by its block architecture. The two different functional groups are not randomly distributed along the polymer chain but are localized within the respective block. Figure 2b shows a schematic illustration of how the block copolymers are assumed to be arranged in a thin polymer film on a gold surface. While the anchor block is connected to the gold surface, the functional block is supposed to be nearly unrestricted in its dynamic motion and should provide a good accessibility of the functional groups. In addition, the suggested polymer orientation implies an increased number of functionalities per area unit compared to a random polymer system.

Thus, in this study, the consecutive block-specific introduction of different functional groups designed for specific purposes in a thin film is shown to be viable as a first step to introduce e.g. anchor groups in a selective block within a block copolymer system being capable of forming nanometer-sized structures in thin films via self-assembly. This fact will be addressed in further studies.

In the next step, thin films of the described block copolymers have been prepared on gold substrates and were demonstrated to be photopatternable in terms of functionality. The procedure involved the film preparation via spin coating followed by extraction of unattached polymer chains. Ellipsometric investigations of the resulting substrates revealed a thin layer of about 5 nm which remained constant with repeated extraction processes, indicating a strong attachment of the film to the gold substrate. Subsequently, the samples were irradiated through a TEM grid, acting as an optical mask by UV light, in order to attain a laterally patterned release of amino groups. The NVOC-protecting groups can be cleaved off by UV light of about 350 nm.[19,20] Next, the samples were carefully washed to remove the cleavage products and immersed into a solution of fluoresceine isothiocyanate (FITC) for 1−2 h followed by a thorough washing step. This fluorescent marker molecule is used as a model compound for the often used attachment of biomacromolecules onto amino-functionalized surfaces through isothiocyanate linkers. The reaction sequences for the light-mediated release of amino groups and the subsequent connection of FITC are displayed in Figure 2a.

The site-specific attachment of the fluorescence marker was confirmed via fluorescence microscopy (Figure 2c). While the

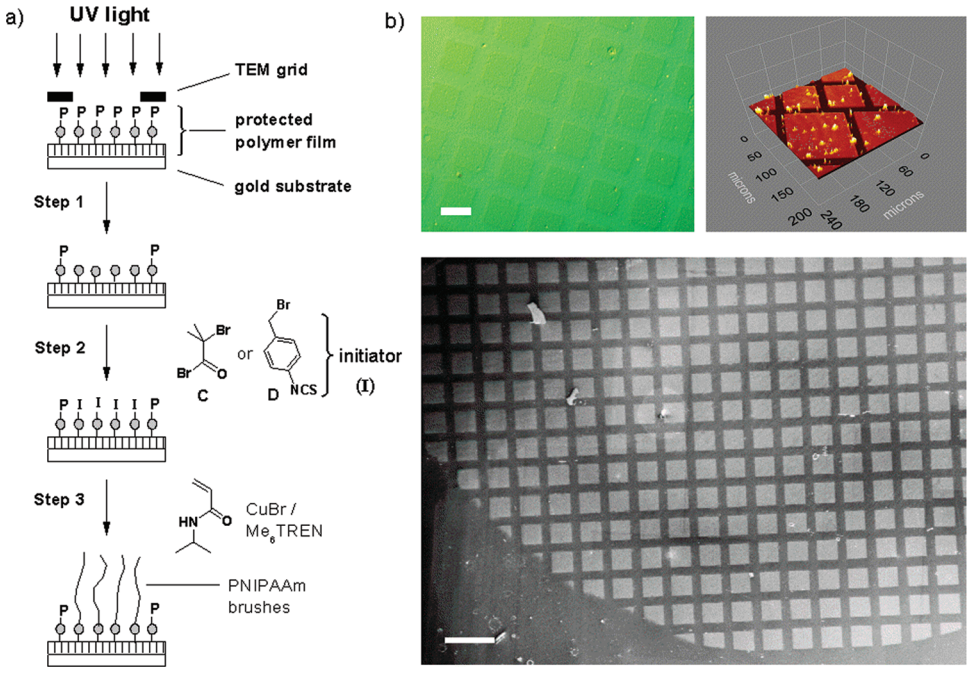

Figure 3. (a) Illustration of the applied procedure for initiation of the site-selective surface ATRP. (b) Images of samples after irradiation through a UV mask followed by binding of ATRP initiator and subsequent surface initiation of the ATRP of NIPAAm: (top left) light microscopy image (TEM grid: square 300 mesh; scale bar: 40 μm), (top right) ellipsometric contrast image (TEM grid: square 150−400 mixed mesh), (bottom) SEM image (TEM grid: square 300 mesh; scale bar: 100 μm).

previously irradiated squares appear bright, the bars remain dark since no amino groups are provided in these areas for the attachment of FITC.

In an alternative surface modification approach, immersion of the UV-patterned films into a solution of 2-bromoisobutyryl bromide (**C**) was used to accomplish a site-selective immobilization of initiators for atom transfer radical polymerization (ATRP)[40] to the surface. The exposure of these patterned films to ATRP conditions in presence of a suitable monomer leads to ATRP initiation selectively within the irradiated areas of the surface and, thus, to a site-specific formation of polymer brushes. Alternatively to the very reactive acid bromide (**C**), the films were also modified with an isothiocyanate (**D**) which reacts specifically just with amino groups.

Different techniques for a patterned growth of polymer brushes are described in the literature. Some allow the fabrication of brush arrays with nanoscopic features down to 20 nm.[41] In the present work, the surface-initiated polymerization is used as alternative method in order to demonstrate the tethered films being photopatternable. With a view to potential applications in sensor and actor technologies we used poly(*N*-isopropylacrylamide) (PNIPAAm) as a thermoresponsive brush material.

To demonstrate the ATRP initiation, first-prepared films were homogenously irradiated, washed, and immersed into a dichloromethane solution of **C**. After another thorough washing, the samples were exposed to a solution of *N*-isopropylacrylamide (NIPAAm) as well as copper bromide (CuBr) and tris-[2-(dimethylamino)ethyl]amine (Me_6TREN). After 6 h the samples were taken out and washed again exhaustively. Investigated by spectroscopic vis-ellipsometry, both samples showed a considerable increase in film thickness (from 5 to 98 nm, average values), indicating the presence of grafted PNIPAAm brushes at the surface. Since this result showed the general feasibility of the approach, in a second experiment the same procedure was applied to UV-patterned samples (Figure 3). The resulting surfaces were studied by light microscopy and scanning electron microscopy (SEM, see also Supporting Information Figure SI5). Furthermore, imaging ellipsometry was used as method of investigation which was demonstrated to be an efficient technique in order to study multilayer systems.[42]

Depending on the geometry of the used TEM grid, the corresponding surface pattern is visible by light microscopy, indicating the successful surface-initiated ATRP of NIPAAm at the irradiated areas. The comparison of the obtained film surfaces before and after the NIPAAm-ATRP confirms that the visible contrast is due to the accomplished surface polymerization (see Supporting Information, Figure SI6). The SEM reveals again a surface patterning according to the geometry of the used mask (Figure 3b, bottom) while the ellipsometric contrast image confirms a topographical patterning consistent with a specific polymer growth at the defined sites (Figure 3b, top right). The surface modifier **C** and **D** both turned out to bind specifically to the UV-irradiated films and to initiate the ATRP of NIPAAm efficiently since patterned surfaces as shown in Figure 3 have been obtained in both cases. Both the verification via fluorescence labeling and the detection by surface-initiated ATRP confirm that the synthesized block copolymers (**BC3**) are suitable for the fabrication of photopatternable functional surfaces.

Since the PNIPAAm brushes are thermoresponsive polymers, the obtained patterned surfaces are potentially interesting in sensor applications. Moreover, the presented approach offers the opportunity to further process the prepared surfaces: The still protected amino groups on the surface could also be released in a subsequent step, and by applying the same procedure as before, the growth of polymer brushes which are responsive to a different type of stimulus could be initiated at these sites. Thus, this approach might be suitable to provide the fabrication of patterned surfaces with different stimuli-responsive polymer brushes assembled in predefined surface areas.

In summary, we have demonstrated the synthesis of a novel photopatternable block copolymer by using a new synthetic approach that combines RAFT polymerization with a polymer analogous sequence of orthogonal high-efficiency chemistries. The styrene-based materials are distinguished by a highly defined architecture containing block-segregated specific functional groups.

The block copolymers were grafted to gold substrates via a dithiol-containing anchor block, and the tethered films were shown to be lithographically photopatternable through selective deprotection of the surface amino functions. The binding of ATRP initiators to the free amino groups allowed a subsequent site-specific growth of PNIPAAm brushes tethered to the grafted polymer. This approach constitutes a very simple and effective means of preparing micropatterned polymer brush arrays.

Forward looking, it seems likely that in these materials a microphase separation can be imparted by modification of the block copolymer structure. By exploiting the characteristic feature of block copolymers to form self-assembled structures in thin films combined with the photopatterning ability, the creation of functional surface pattern on two different levels is possible (hybrid structuring) and is presently under investigation.

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Supporting Information Available: Synthetic details, ^{1}H and ^{13}C NMR spectra with complete signal assignments, information to materials, film preparation, fluorescence labeling, surface-initiated ATRP of NIPAAm, additional SEM images, and detailed description of the characterization methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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