

## Y-Shaped Polymer Brushes: Nanoscale Switchable Surfaces

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Received June 9, 2003. In Final Form: July 28, 2003

We report a first observation of nanoscale surface structures of segregated pinned micelles of grafted Y-shaped molecules and their reversible structural reorganization. We designed a novel type of Y-shaped molecules combining two highly incompatible polymer chains (arms) attached to a single focal point capable of chemical grafting to a functionalized silicon surface. We demonstrated that spatial constraints induced by a chemical junction of two dissimilar (hydrophobic and hydrophilic) polymer arms in such Y-shaped molecules lead to the formation of a novel type of segregated pinned micellar structures in chemically grafted brush layers. We propose a model of segregated pinned micelles and corresponding reverse micelles featuring different segregation states of polystyrene and poly(acrylic acid) arms. These arms are capable of local reversible rearrangements leading to reversible surface structural reorganization in different solvents.

### Introduction

Polymer brush layers composed of flexible polymer chains tethered to a solid substrate are the subject of intensive theoretical and experimental investigations.<sup>1</sup> Recent very sophisticated designs resulted in the formation of polymer layers with unique properties. For instance, reversible switching of surface properties has been recently observed for mixed, binary brush layers grafted to solid substrates suggested as the development of conventional brush polymer layers.<sup>2–4</sup> For these systems, conformational changes of dissimilar polymer chains A and B with relatively high molecular weights randomly tethered to a solid surface resulted in dramatic structural reorganization. It has been shown that the shifts in the balance of lateral and vertical phase separations of dissimilar polymer chains with segregated regions of 30–100 nm

across are responsible for this phenomenon.<sup>5,6</sup> However, to date, the type of surface structures formed in binary brushes under conditions of spatial constraints imposed by their chemical connection to a single grafting site (Y-shaped molecules) was not explored. According to theoretical considerations, such molecules with modest lengths of the arms should form a wide variety of segregated surface layers with pinned micellar structures controlled by the chemical attachment of chains A and B.<sup>7</sup> The formation of mixed, internally segregated and split micelles, as well as striped morphology, has been predicted for different grafting conditions.

In a search for this variety, we designed a novel type of Y-shaped molecules combining two dissimilar (hydrophobic and hydrophilic) polymer chains (arms) with a modest length attached to a single focal point capable of chemical grafting to a silicon surface (Figure 1). Here, we report a first observation of nanoscale surface structures representing internally segregated pinned micelles of grafted amphiphilic Y-shaped molecules and their reversible structural reorganization upon treatment with selective solvents.

### Results and Discussion

The preparation of novel Y-shaped molecules with different stem lengths required a multistep synthesis of hairpinlike block copolymers (Figure 1) as will be described in detail elsewhere.<sup>8</sup> The NMR analysis of designed molecules revealed that the polystyrene (PS) arm contained on average of 40 monomeric units and that of poly(*tert*-butyl acrylate) (PBA) had 30 units. The post-grafting hydrolysis of the PBA arms was conducted under acidic conditions (see Experimental Section). The final Y-shaped brush layers were composed of amphiphilic molecules with a volume ratio of PS and poly(acrylic acid) (PAA) arms of approximately 60:40 (Figure 1).

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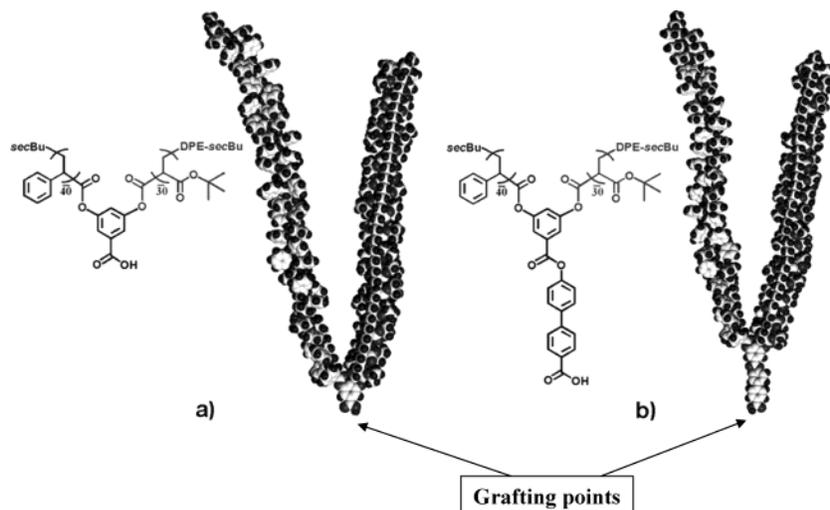
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**Figure 1.** Chemical structure and molecular graphics representation of Y-shaped block copolymers with short (a) and long (b) aromatic functional stem. Molecules **1** and **2** contain 40 and 30 monomeric units in the PS and PAA arms, respectively.

**Table 1. Properties of Y-Shaped PS–PAA Brush Layers**

molecule	film thickness (nm)	rms roughness (nm)	contact angle after toluene treatment (degrees)	contact angle after water treatment (degrees)	grafting density, <sup>a</sup> $\Sigma$ (chain/nm <sup>2</sup> )	grafting distance, <sup>a</sup> $D$ (nm)
<b>1</b>	1.35 ± 0.2	0.37 ± 0.02	81 ± 3	53 ± 1	0.10	3.6
<b>2</b>	1.96 ± 0.2	0.72 ± 0.02	76 ± 3	52 ± 2	0.15	3.0

<sup>a</sup> Estimated from the molecular weight and the grafted amount according to the known equations as discussed in a previous publication (ref 19).

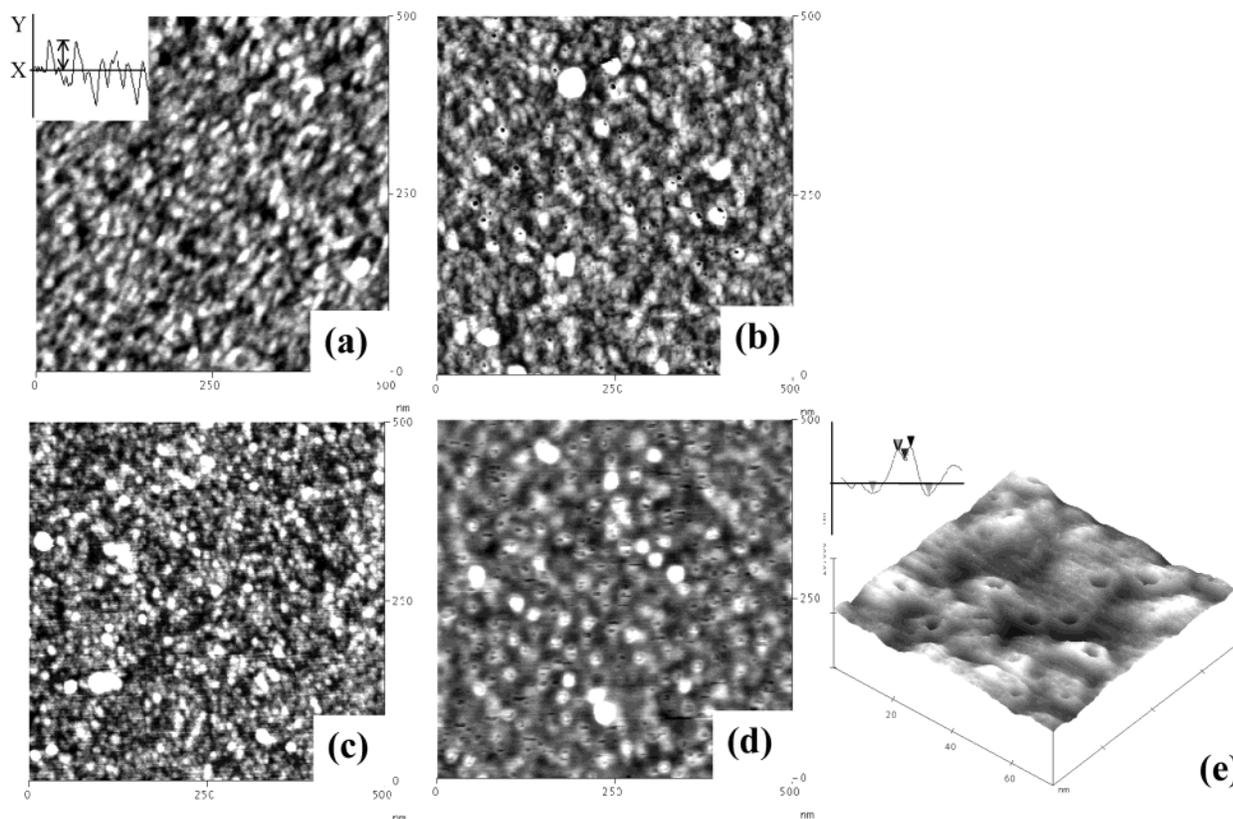
The evaluation of grafting parameters in the dry state shows that both brushes prepared from molecules **1** and **2** possess a medium grafting density with the average distance between the neighboring molecules of 3–4 nm (Table 1). Under these conditions, the flexible arms are collapsed with the vertical dimensions well below the contour length of both arms (~10 nm). Y-shaped brushes possess a very smooth surface on a microscale, unlike mixed binary brush layers from high-molecular-weight polymers with a well-developed segregated structure.<sup>2,4,5</sup> The surface microroughness estimated within a 1- $\mu\text{m}^2$  area remained below 1 nm even after the hydrolysis (Table 1). This indicates that the spatial constraints introduced by the chemical junction result in a homogeneous surface structure with a suppressed microphase separation usually developed for mixed binary brushes.

However, high-resolution atomic force microscopy (AFM) images demonstrate that Y-shaped molecules exhibit the lateral inhomogeneities expected for chemically connected, incompatible blocks. Parts a and b of Figure 2 show that both brush layers after toluene treatments possess a grainy surface topography. The surface is covered with densely packed islands with a lateral dimension close to 10 nm, as was estimated after correction for the tip dilation. The heights of these islands vary from 1.8 nm for molecule **1** and 2.5 nm for molecule **2**, as was estimated from the effective layer thickness and topographical cross sections (Table 1, Figure 2). Phase images (not shown) demonstrate a uniform surface composition with a low phase contrast. This morphology corresponds to internally segregated “pinned micelles” theoretically predicted for sparse brushes of Y-shaped copolymers containing incompatible arms.<sup>7</sup> Considering that toluene is a good solvent for PS and a bad solvent for PAA, we suggest that the topmost surface layer is predominantly composed of PS arms which form “coronas” of pinned micelles, whereas collapsed PAA arms constitute their “cores”. This suggested composition is also confirmed by contact angle measurements (Table 1). The

measured values of 73–76° are close to that expected for PS with some presence of PAA arms (about 27%, as was estimated from the Cassie–Baxter equation).<sup>9</sup>

Treatment of the brushes with water, which is a selective solvent for PAA arms, causes dramatic surface reorganization (Figure 2b,d,e). Remarkably, an array of *crater-shaped* small features is observed for both the short- and the long-stem Y-shaped molecules. The craters represent discrete objects whose rims are slightly elevated with respect to their surroundings (see the high-resolution three-dimensional image in Figure 2e). This morphology is found only under light tapping conditions and has not been previously observed in either mixed or diblock PS–PAA brushes. The average diameter of a crater is close to 8 nm for both the short-stem (Figure 2b) and the long-stem (Figure 2d) brushes, as was estimated by the averaging of at least 10 independent measurements for randomly selected craters. As known, the distance between the edges of a rim can be estimated correctly because it is not undisturbed by the tip dilation.<sup>10</sup> The depth of the craters is at least 0.5 nm, although it cannot be estimated accurately because of the tip dilation. Unfortunately, a precise estimation of the depth and the shape of the surface features via a deconvolution procedure cannot be conducted because of an unknown contribution of the tip–surface contact instabilities. This morphology is better defined for brushes prepared from molecule **2**, which is expected because of the higher grafting density facilitated by a longer stem (Table 1). We suggest that this characteristic surface structure is formed by a collapsed central core of PS arms surrounded by swollen PAA chains. For this structure, the surface exposure of PAA arms should increase the hydrophilicity that is, indeed, confirmed by decreasing the contact angle to 52°. This value indicates

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**Figure 2.** AFM topographical images ( $500 \times 500$  nm) of the Y-shaped PS–PAA brushes treated with toluene (a, c) and water (b, d). Images a and b show the surface of the short-stem brush, whereas images c and d show the surface of long-stem brush. The vertical scale is 5 nm. (e) High-resolution three-dimensional topographical image ( $70 \times 70 \times 10$  nm) showing the craterlike surface structures in the long-stem brush treated with water. Representative cross sections ( $30 \times 3$  nm) are shown.

that 65% of the surface has to be occupied by PAA arms, as was calculated from the Cassie equation. Therefore, only two-thirds of the entire brush surface is covered by hydrophilic arms with a certain amount of exposed PS arms. On the basis of these data, we suggest that the centers of the craters filled with collapsed PS chains.

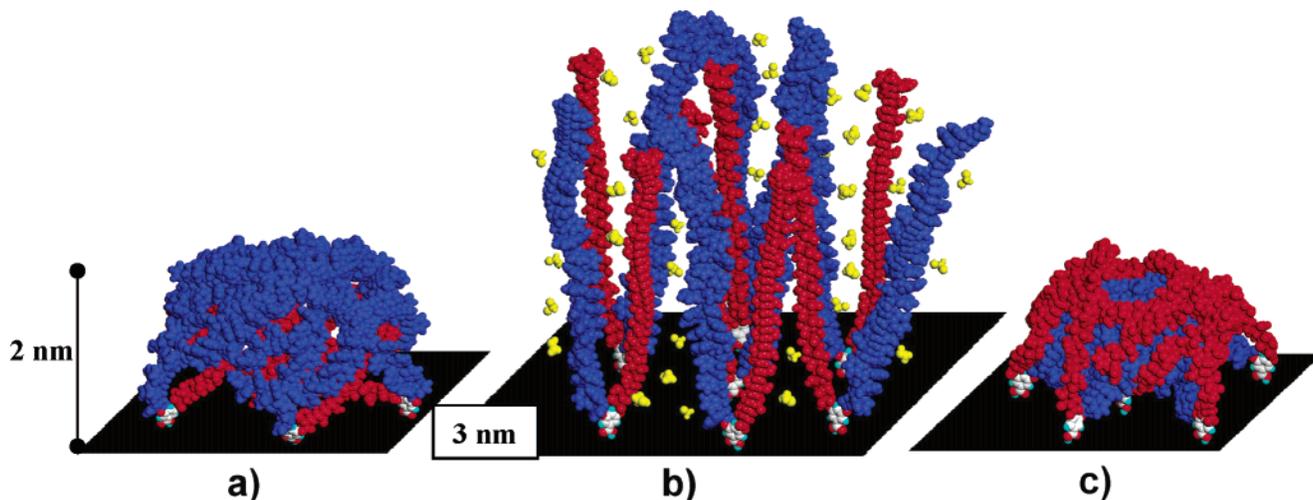
Such morphology has not been predicted theoretically for Y-shaped brushes.<sup>7</sup> It is also qualitatively different from the “dimple” morphology predicted and found in mixed binary brush layers, inasmuch as the observed craters are spatially isolated and do not fuse into a continuous matrix.<sup>11</sup> Several reasons may account for this unusual morphology. The smaller volume fraction of the PAA arms (40%) facilitates such clustering. Alternatively, the interactions between PAA and the hydrophilic silicon surface can be strong enough to prevent rearrangement of some arms and keep them permanently in the immediate vicinity of the substrate. The short length of both arms might contribute to such clustering. Finally, the Y-shaped molecular architecture may impose constraints limiting conformational reorganizations to localized surface areas. Regardless of what the origin of the craterlike morphology is, one simple conclusion is obvious. It exhibits structures with truly nanoscale lateral dimensions, which are much smaller than those found in mixed and diblock copolymer brushes, although with longer chains.<sup>2,4,12</sup>

Molecular modeling can provide additional insight into the structure of the Y-shaped brushes and verify our suggestions. Considering the experimental data for the grafting density and chemical composition, the molecular

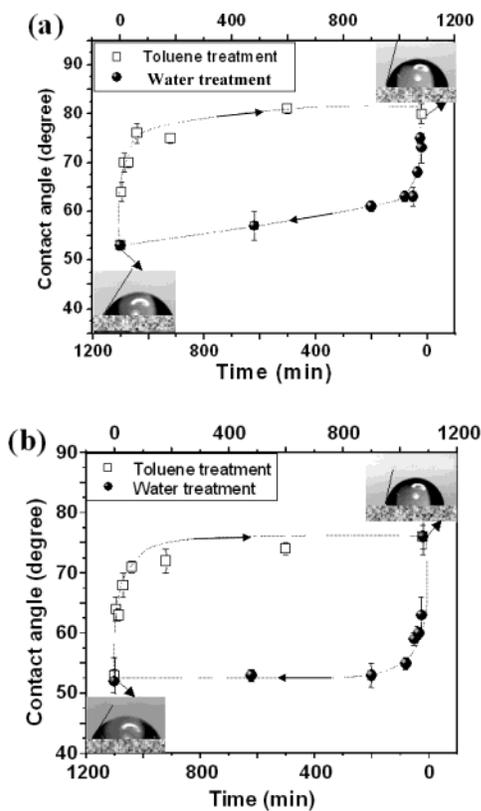
reconstruction can be conducted as illustrated in Figure 3. It is reasonable to expect that in the presence of a nonselective solvent, the molecules would adopt an extended conformation with all arms pointing outward from the substrate (Figure 3b). As the quality of the solvent for one type of the arms is reduced, they would collapse and form a core of a pinned surface micelle (Figure 3a). The total diameter of such a micelle estimated from cross sections collected for 10 randomly selected surface features is about 10 nm, and, thus, the area it occupies is close to  $75\text{--}80\text{ nm}^2$  as estimated assuming a circular shape. This allows us to estimate the average number of arms in one micelle because it can be expressed as  $N = A/s$ , where  $A$  is the area per micelle and  $s$  is the area per one arm.<sup>6</sup> Because the experimental grafting density of the short-stem Y molecules is  $0.1\text{ molecule/nm}^2$ , one micelle is composed of 7–8 grafted molecules as depicted in our model (Figure 3b). For the sake of simplicity, we consider seven molecules, six of which could be placed in the corners of a hexagon and one in its center. The collapse of seven PAA arms upon treatment with toluene should result in the formation of a dense core in the center of such a hexagon, whereas seven PS arms would form the micelle’s corona as represented in Figure 3b. Force field minimization of this structure with anchored ends reveals that the PS arm can cover nearly all the area occupied by the PAA core because the volume fraction of the PS arms reaches 60%. In contrast, when similar modeling is done for a reverse micelle (in a good solvent for PAA), the full coverage of the bulkier PS core with PAA arms cannot be completed. In this case, PAA arms could be primarily located on the outer walls of the micelle with a central, noncovered area revealing the PS core (Figure 3a). This model is consistent

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**Figure 3.** Molecular graphics representation of the proposed structural rearrangements in the Y-shaped brushes. (a) Internally segregated pinned micelle composed of seven grafted PS-PAA molecules spaced 3.5-nm apart. Upon treatment with toluene and subsequent drying, the PS arms (blue) form a corona covering the micelle's core consisting of seven PAA (red) arms. (b) Representation of the same seven molecules **1** swelled in a nonselective solvent (yellow). (c) Top-open craterlike structure containing seven collapsed PS arms partially covered by seven PAA chains.



**Figure 4.** Water contact angle as a function of the solvent treatment time for Y-shaped PS-PAA brushes with short (a) and long (b) stems. Each data point was obtained for the same specimen, which was rinsed and dried before the measurement followed by placing it back in the solvent for an additional period of time.

with the experimental data related to the surface microstructures, grafting parameters, and surface compositions of both Y-shaped brushes and verifies the feasibility of the proposed structural reorganization.

Finally, the dynamics of switching the surface properties was studied by observing reproducible changes of the water contact angle. Figure 4 shows the contact angle values for both brushes after toluene and water treatments as a function of time. The value of the contact angle after

toluene treatment gradually reached  $79 \pm 3^\circ$  within the first 100 min and stays virtually constant even after 10 h of solvent treatment. The contact angle decreases gradually to  $52 \pm 3^\circ$  after water treatment within several hours, completing a full cycle. These cycles are similar for both brushes and can be reproduced repeatedly.

In conclusion, we demonstrated that spatial constraints imposed by chemical junctions of two dissimilar (hydrophobic and hydrophilic) polymer chains in Y-shaped molecules cause the formation of a novel type of segregated pinned micellar structures in brush layers chemically grafted to the silicon surface. The formation of such surface features is obviously caused by chemical junctions of dissimilar arms to a single grafting point and can be affected by a relatively short length of the arms. We propose a model of segregated pinned micelles and reverse craterlike micelles featuring different segregation states of PS and PAA arms capable of structural reorganization in selective solvents. The switching of surface properties driven by changes in the local heterogeneous composition is of potential interest because the resulting patterned morphology can facilitate the assembly of inorganic nanoparticles, proteins, and nanotubes. Such surfaces hold a great promise in designing nanoelectromechanical, bioanalytical, and microfluidic devices with adaptive properties.<sup>4,13–18</sup>

## Experimental Section

We used 3,5-dihydroxybenzoic acid as an AB<sub>2</sub> anchoring moiety to which carboxyl-terminated PS and PBA have been attached in a stepwise manner using a protection–coupling–deprotection strategy. The resulting product had a very narrow polydispersity index (1.07), and the weight-average molecular weight of 7300 was determined by GPC. The NMR analysis revealed that the PS arm contained on average of 40 monomeric units and that of PBA had 30 units. The carboxyl group at the focal point of molecule **1** can be used for covalent grafting to epoxy-terminated silicon substrates by grafting from melt at an elevated temper-

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ature, as has been demonstrated earlier.<sup>19</sup> Molecule **2** with a longer stem was used to determine the influence of the stem's length on the properties of the Y-shaped brushes. Post-grafting hydrolysis was conducted under acidic conditions. The complete disappearance of *tert*-butyl groups was confirmed by <sup>13</sup>C NMR of copolymers obtained in solution under identical deprotection conditions. Thus, the Y-shaped molecules possess amphiphilic-nature hydrophobic PS and hydrophilic PAA arms. Molecular modeling was conducted using the Materials Studio Program.

For the fabrication of the brush layer, the "grafting to" approach from a polymer melt to an epoxy-terminated SAM has been used as discussed in detail in previous publications.<sup>19,20</sup> The polymers were spin-coated from a 1.5 wt % toluene solution onto the wafers functionalized with the epoxysilane self-assembled monolayers.<sup>21</sup> The thickness of the initial spin-coated film measured by ellipsometry was about  $30 \pm 3$  nm. The coated wafers were annealed at grafting temperatures ranging from 120 to 150 °C for 6 h to enable the end groups to graft to the substrate. The ungrafted polymer was removed by multiple washings with toluene and additional washing in an ultrasonic bath. Then, the grafted polymer brush was hydrolyzed in the mixture of 30%

tetrahydrofuran and 70% trifluoroacetic acid for 48 h. The hydrolyzed polymer brush was rinsed with Nanopure water and toluene followed by an ultrasonic bath. The samples were dried under a nitrogen atmosphere and kept in covered containers. Temporal changes of the contact angle were measured for a specimen, which was placed in the proper solution for different periods of time. Contact angle measurements were conducted with a sessile drop method. The film thickness was measured with ellipsometry (typical accuracy is  $\pm 0.1$  nm) using a COMPEL Automatic Ellipsometer (InOm Tech, Inc.). All the reported thickness values were averaged over six measurements from different locations on the substrate. AFM studies were performed on Dimension 3000 and Multimode microscopes (Digital Instruments, Inc.). Silicon or silicon nitride tips were used with a radius of 10–30 nm, as was tested on a gold nanoparticle reference sample. Tapping mode AFM was used according to the well-established procedure.<sup>22</sup>

**Acknowledgment.** We acknowledge support by the National Science Foundation, Grants CMS-0099868 and DMR-0308982, and Grant M01-C03 from DOC.

LA035007J

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