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ARTICLE

A Model of a Homopolymer Brush as a Switch

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ABSTRACT: We present a simple model of a densely grafted homopolymer brush with a small fraction of chains extended with solvent-responsive monomers that acts as a switch. On the basis of a simple free energy description, we describe the "*on*" and "*off*" states of the switch brush, where the switch between states is driven by a change in solvency for the solvent-responsive monomers. These solvent-responsive monomers reside at the brush surface, exposed to solvent, in an *on* state but are sequestered within the dense brush, sheltered from solvent contact, in an *off* state. The model considers persistent-*on* states where the responsive monomers form globules, micelles, and pancake layers at the brush surface under poor solvent conditions. These persistent-*on* states decrease the sensitivity of the switch to solvent, but they also increase the signal when the switch is activated. We describe the *on* and *off* states, as well as the switch sensitivity and signaling, over design parameters that include the size of the homopolymer chains and solvent-responsive blocks, and the fraction of chains appended with these responsive monomers.

Introduction

Responsive surfaces are capable of reversibly changing their properties in response to external stimuli.[1−3] Polymer brushes have been explored as ideal candidates for the chemical design of responsive surfaces. A polymer brush is a surface to which linear chains are end-grafted at such high densities that the chains stretch away from the grafting surface. These chains still retain sufficient conformational freedom to allow a significant conformational response to environmental conditions, such as temperature, solvency, and pH.[1−3] Such responsive brushes can be broadly classed into two categories: homopolymer brushes and complex brushes containing two or more types of monomers.[4] Simple homopolymer brushes already exhibit some intriguing responsive behaviors. For example, brushes made of thermosensitive Poly(NIPAAM) have been shown to change from hydrophobic to hydrophilic with small changes in temperature;[5] brushes made of polyelectrolyte chains may swell or shrink as pH is changed, potentially serving as actuators, sensors[6] or microvalves that control the flow of microfluid;[7] particles grafted with polyelectrolyte brushes exhibit promising properties for the uptake and release of drugs with changes in local pH.[8] Complex polymer brushes that contain multicomponents have even more design potential as they provide additional parameters for switch operation and surface properties to switch.

Recent investigations focus upon the reversible switching of mixed polymer brushes, i.e. brushes comprised of chains of different chemical components, and block copolymer brushes, where the relative solvency of two or more different components can be tuned. Minko et al.[9] and Vyas et al.[10] experimentally demonstrated that different components of a mixed brush can be selectively exposed to the interface by treating with suitable solvents, and this enables them to control the surface properties, such as wettability, adhesion, roughness, friction coefficients, among others. Similarly, Zhao et al. showed that block copolymer brushes exhibit switching behavior by suitable solvent treatment.[11] The changing of surface morphologies under different solvent treatments has also been utilized to move colloidal particles on surfaces.[12] The responsive mechanism in these brushes essentially is that one component shields the less compatible component from the solvent.

The development of new synthetic techniques allows us to produce a wide array of complex polymer brushes[4] but only a limited number of design parameters that determine switchability have been investigated experimentally. For example, the effect of the relative size of blocks in a diblock copolymer brush is studied via fabricating a brush with the size of the top block varying gradually,[13] while that of the grafting density of the two components in a mixed polymer brush is investigated by creating a gradient of the grafting density ratio of the two polymers.[14] Searching for an optimum parameter window for switching is a fundamental step toward application of these stimuli-responsive brushes.

Recently, Merlitz et al. proposed a novel system comprised of a high-density grafted homopolymer brush with a small fraction of ends extended by a responsive monomer of variable size that is sensitive to external conditions.[15] Using molecular dynamics, they demonstrated that such a brush is "switchable", as the responsive monomers may reversibly (i) hide within the brush body or (ii) be exposed at the brush surface or tip by tuning temperature, or equivalently, solvent condition. The switching is a result of a competition between the responsive monomers' unfavorable interactions with the solvent and the energy penalty for the chains to stretch in order to shield these responsive ends. If the stretching penalty is smaller, then the ends will be buried and the brush is said to "switch". However if the stretching penalty is larger, then the end monomer will remain at the tip and the brush will not "switch". The balance of this competition depends on a number of parameters: the fraction of chains having responsive ends, the size of the homopolymer and the responsive monomer extensions, as well as the grafting density of the brush. While the molecular dynamics (MD) method of Merlitz et al. produces quantitative detail of an equilibrium brush and can potentially explore the dynamics of the switching process, it is also quite a time-intensive method. As such, MD and experimental synthesis are not feasible techniques for mapping out the phase diagram of

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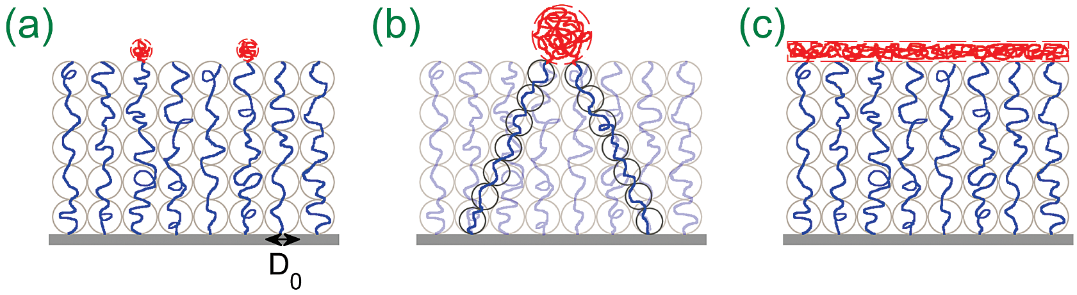

Figure 1. Different morphologies for the persistent-*on* state, where responsive monomers remain at the tip of the brush under poor solvent conditions: (a) Globule phase where each responsive block collapses into isolated globules of close-packed monomers. D_0 is the grafting distance between neighboring chains. (b) Micelle phase where responsive blocks fuse into micelles at the surface, akin to octopus micelles, where the first N monomers of minority chains serve as octopus arms which stretch to accommodate the fusion of k blocks of N_w monomers to form the octopus body. (c) Pancake phase where the responsive blocks fuse into a continuous layer, exposed at the tip of the brush.

switchability. Such a phase diagram specifies under what parameters (grafting density, fraction of monomer appended chains, *etc.*) the brush will switch.

Inspired by Merlitz et al.,[15] we present here an equilibrium phase diagram of the switchability of a high density, grafted homopolymer brush with a fraction of chains ends extended with a block of responsive monomers. We construct a qualitative prediction of the phase diagram of switchability using a free energy description *a la* the Alexander−deGennes brush description,[16,17] which includes persistent-*on* states. These persistent states occur when the responsive monomers alternatively form collapsed globules, micelles or pancakes at the brush surface, rather than bury within the body of the brush. As such, these persistent-*on* states diminish the sensitivity of the switch to changes in solvent quality. However when these persistent-*on* states are eventually switched *off*, the change in responsive monomer contact with solvent is greatest, leading to an enhanced switch signal.

The Responsive Brush Model

The responsive brush model is fashioned after Merlitz et al.: we consider a homopolymer brush comprised of solvent-insensitive chains of N monomers of size a, where a minority fraction, f, of the chains have a solvent-responsive block appended to their free end. The brush is assumed to be grafted at such a high grafting density, σ, that solvent molecules are effectively excluded from the brush. Under these conditions, we can invoke several concepts of the Alexander−deGennes (A−deG) brush model, including the concept of correlation blobs. Repulsive interchain excluded volume interactions give rise to chain stretch away from the grafting plane. Such chain stretching disrupts the intrachain monomer−monomer correlations above a length scale, D, and this is the basis of the correlation blob construct, where each chain, uniformly and homogeneously stretched, is modeled as a sequence of uniform blobs of size D. Within each blob, the monomers retain their unperturbed statistics, which we take as Gaussian or ideal $D \sim g_b^{1/2}a$, where g_b is the number of monomers in the correlation blob, and the stretching energy per chain[18] is $k_BT \times$ the number of blobs per chain, $k_BT \times N/g_b$, or k_BTNa^2/D^2. The A−deG model assumes the chain ends are at the tip of the brush so that the brush height is the end-to-end distance of the chain of blobs, or $L \sim N/g_b \times D$ or Na^2/D. When the brush grafting density is moderate, the stretching rate is not uniform over the contour of the chain and the chain ends are located throughout the brush body, as detailed by self-consistent field (SCF) calculations. However, under strong or large grafting densities, the assumption of chain ends located at the tip of a homopolymer brush is reasonably accurate. It is also an accurate assumption under polydisperse brushes, i.e., brushes where a minority of the chains are longer, as the osmotic pressure pushes these extended ends beyond the tip region.[19,20] Consequently, in our Merlitz-based model, the solvent-sensitive block of N_w monomers, appended to a small fraction of the chains, is also located at the tip when the solvent interactions are favorable.

The location of the solvent-sensitive block of N_w monomers indicates the state of the brush: if the block is located at the tip or brush surface, then the brush is said to be *on*. When, the solvent is made poor for the block, the block may bury or embed itself in the brush body, shielding itself from the solvent—in this case the brush is said to be in an *off* state. The switchability can be disrupted by alternative configurations which retain the responsive blocks at the tip while minimizing responsive monomer−solvent contact; we refer to these as persistent-*on* states. For example, if, under poor solvent, the fraction of chains with responsive blocks is too large, the brush can persist in an *on* state, as the responsive blocks will alternatively arrange to form a collapsed layer or "pancake" at the brush-solvent interface. Here we qualitatively map out the window of switchability by considering the free energy of simplistic brush configurations. Our energy descriptions are based upon simple perturbations to the homogeneous chain stretching assumption in A−deG and characterization of the solvency of the responsive block by a surface tension, $\gamma = ck_BT/a^2$, which is large for poor solvency and small for good solvency.

The *Off* State. In the spirit of the A−deG model, we consider that the *off* state perturbs the uniform and homogeneous stretching of the brush in the simplest way. We consider here only two simplistic scenarios: one shown in Figure 2a where chains stretch uniformly along their contour, but differently depending upon whether they are majority chains or minority chains with solvent-sensitive blocks, and another scenario pictured in Figure 2b where all chains stretch uniformly, but the stretch rate differs at the tip so as to allow burial of the responsive block. In the latter scenario we assume two distinct stretching rates which can be extended to variable stretching rate using more detailed calculations. However, these different scenarios result in the same energy scaling.

In the first case, Figure 2a, the majority chain stretches more, with its blob size decreasing from D_0 to D_{maj}, while the minority chains stretch less, with blob size increasing from D_0 to D_{min}. The cross section of the brush bisects blobs of $1-f$ majority chains and f minority chains and as the cross sectional area is unchanged upon switching,

$$(1-f)D_{\mathrm{maj}}^2 + fD_{\mathrm{min}}{}^2 = D_0^2 \tag{1}$$

Furthermore, the end-to-end distance of the minority chains, L_{min}, is a few (e.g., m) blob sizes smaller than the end-to-end distance from monomer 1 to N of the majority chains or L_{maj},

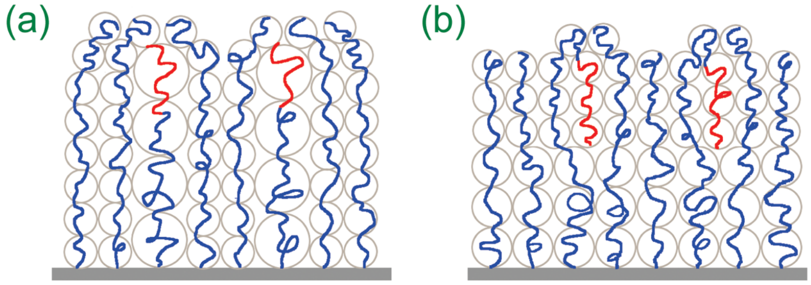

Figure 2. Different morphologies for the *off* state, where responsive monomers are sheltered from poor solvent contact through burial in the body of the brush. (a) Uniform stretching of all chains with majority chains stretching more to shelter the responsive blocks of minority chains from solvent. The extra stretching of the majority chains is reflected in a blob size shrink from D_0 to $D_{\rm maj}$, allowing minority chains to relax, as reflected in a blob size increase from D_0 to $D_{\rm min}$. (b) Discontinuous stretching of all chains to accommodate a top and bottom layer of uniformly stretched chains. The top layer stretches more to shield responsive blocks of minority chains from solvent, as reflected by blob sizes $D_{\rm top} < D_{\rm bottom}$. The reader is referred to the MD simulation snapshots of Merlitz et al., showing an analogous *off* state to part a, where a single responsive monomer of variable size is buried in a high density grafter homopolymer brush.

which is to ensure that the top of responsive blobs is covered by a layer of homopolymer blobs, sheltering the responsive monomers from solvent:

$$L_{\rm maj} = L_{\rm min} + mD_{\rm maj} \tag{2}$$

The cross sectional area of responsive blobs should equal to that of the m shielding, homopolymer blobs:

$$fD^2_{\rm min} = (1-f)D^2_{\rm maj}m \tag{3}$$

Equations 1−3 yield an expression for m:

$$\left(\frac{Na^2}{D_{\rm maj}{}^2} - m\right)D_{\rm maj} = \frac{(N+N_w)a^2}{D_{\rm min}{}^2}D_{\rm min}$$

$$\left(\frac{Na^2}{D_{\rm maj}{}^2}D^2_{\rm min} - mD^2_{\rm min}\right) = (N+N_w)a^2\frac{D_{\rm min}}{D_{\rm maj}}$$

$$m\left(Na^2\frac{1-f}{f} - D^2_{\rm min}\right) = (N+N_w)a^2\sqrt{\frac{1-f}{f}m}$$

$$m = \frac{(N+N_w)^2\dfrac{f}{1-f}}{\left(1-\dfrac{D^2_{\rm min}}{Na^2(1-f)/f}\right)}$$

As $f \ll 1$ and the blob size of the minority chain is smaller than the dimensions of a tension-less chain or $D_{\rm min}{}^2/Na^2 \ll 1$, then $m = (N + N_w)^2 f/(1 - f)$. The stretching energy of a polymer chain is proportional to the number of blobs;[18] therefore, the total energy penalty for this scenario is

$$\frac{F_{\rm off,1}}{k_{\rm B}T} = \frac{N+N_w}{D^2_{\rm min}/a^2}\sigma f + \frac{N}{D^2_{\rm maj}/a^2}\sigma(1-f) - \frac{N}{D_0^2/a^2}\sigma$$
$$\approx N_w\sigma^2 f\left[1+(1-f)\frac{r(2+r)}{1+r}\right] \tag{4}$$

where we set $r = N_w/N$. The assumption of m shielding blobs is useful for understanding the concept, but it is not required in the derivation of the free energy: because of the high grafting density (or small blob size, D_0) the same energy penalty results if we assume uniform chain stretching, *i.e.* $L_{\rm maj} = L_{\rm min}$ instead of eqs 2 and 3.

The other *off* scenario is that responsive blocks bury their heads inside the brush body, forming two layers: a top (or tip) layer of effective grafting density of $(1+f)\sigma$ and a bottom (or root) layer of grafting density σ. Within each layer, the stretching is uniform so that the correlation blob size of the top and bottom layers is $D_{\rm top}{}^2 = a^2/(\sigma(1+f))$ and $D_{\rm bottom}{}^2 = a^2/\sigma$, respectively. As the last N_w monomers of the majority chains are located in the top layer, the number of blobs per majority chain is $N_w(1+f)\sigma + (N - N_w)\sigma$ and the number of blobs per minority chain is $2N_w(1+f)\sigma + (N - N_w)\sigma$. This gives the number of blobs per grafting area of $\{(1-f)[N_w(1+f)\sigma + (N - N_w)\sigma] + f[2N_w(1+f)\sigma + (N - N_w)\sigma]\}\sigma$ as compared with $N\sigma^2$ blobs per grafting area. The free energy penalty is thus

$$\frac{\Delta F_{\rm off,2}}{k_{\rm B}T} = N_w\sigma^2 f(2+f) \tag{5}$$

Comparing eq 4 and eq 5, we see that bidisperse stretching increases the free energy, but retains the form of the energy scaling: $F_{\rm off} \sim N_w\sigma^2 f$. This is consistent with the MD snapshots of Merlitz et al.[15] where the *off* state is due to inhomogeneous stretching among minority and majority chains.

The Persistent *On* State. When plunged into poor solvent, the responsive blocks may not necessarily be sheltered within the brush body, but can remain in a persistent *on* state, adopting morphologies at the brush surface which minimize, but not exclude, solvent contact. Each of these *on* states has an energy penalty for formation, and it is the comparison of the lowest energy *on* states with that of the *off* state which determines the switchability. The simplest persistent-*on* state is one where each responsive block collapses into an isolated globule, Figure 1a. In this isolated globule regime, the size of the globule of responsive monomers, R, is smaller than the distance between grafted minority chains,

$$D = a/\sqrt{\sigma f}$$

Thus,

$$aN_w{}^{1/3} < a/\sqrt{\sigma f}$$

and isolated globules are possible for responsive blocks when $N_w < (\sigma f)^{-3/2}$. When $N_w = (\sigma f)^{-3/2}$, the isolated globules start touching, and there is no distinguishable difference in energy penalty for formation of globules and for formation of a pancake of responsive monomers at the brush-solvent interface. Hence, the globules are replaced by pancakes as N_w increases beyond $(\sigma f)^{-3/2}$. The energy penalty associated with per grafting area is

$$\frac{F_{\mathrm{on,G}}}{k_{\mathrm{B}}T} \sim \frac{\gamma R^2}{k_{\mathrm{B}}T} \times \sigma f \sim c N_w^{\,2/3} \times \sigma f \qquad (6)$$

for the globules and for the pancakes, it is $F_{\mathrm{on,P}}/k_BT = c$, where $c = \gamma a^2/k_BT$. However, if N_w is sufficiently large or the grafting density significantly high, then neighboring minority blocks aggregate to form larger globules that minimize the surface energy penalty, Figure 1b. These aggregated surface micelles are similar to the octopus micelles that form on grafted surfaces[21,22] where end-grafted chains aggregate by forming stretched tethers (octopus arms) which reach to a collapsed micelle or globule (the octopus body). Our configuration corresponds to octopus micelles that occur at the solvent-brush interface: each octopus arm consists of N monomers of a minority chain and the octopus body is comprised of the N_w solvent-sensitive monomers from several minority chains. Suppose that on average k minority chains fuse into one octopus micelle, then the density of octopus micelles is $\sigma f/k$. There are kN_w monomers per micelle body. The radius of micelle body is $\sim a[kN_w]^{1/3}$, so the surface energy associated with it is $E_{\mathrm{surf}} \sim \gamma a^2[kN_w]^{2/3} \times \sigma f/k = ck_BT\,[kN_w]^{2/3} \times \sigma f/k$.

To determine the stretching penalty in micelle formation, we need to determine the blob size characterizing the stretched octopus arms (the minority chains) as well as the majority chains. In order for the micelle to form, the minority chains must stretch within the body of the brush. As L_{maj} and $L_{\min}$ are the end-to-end distance of majority and minority chains, then the octopus arms, of length $L_{\min}$, must satisfy

$$L_{\min}^2 = \Delta^2 + L_{\mathrm{maj}}^2 = \frac{a^2\,k}{4\,\sigma f} + L_{\mathrm{maj}}^2$$

where

$$\Delta = \frac{a}{2}\sqrt{\frac{k}{\sigma f}}$$

is half the distance between octopus micelles. Recasting L in terms of blob size D

$$\frac{1}{D_{\min}^2} = \delta^2 + \frac{1}{D_{\mathrm{maj}}^2} \qquad (7)$$

where we let $\delta^2 = (\Delta/(Na^2))^2$. Equation 7 along with conservation of cross-sectional area, eq 1, are used to eliminate blob size in the expression for the energy penalty associated with stretching the first N monomers of every chain, which is

$$\frac{Na^2}{D_{\min}^2}\sigma f + \frac{Na^2}{D_{\mathrm{maj}}^2}\sigma(1-f) - \frac{Na^2}{D_0}\sigma$$

to give the stretching penalty per unit grafting area for octopus micelle formation as

$$\frac{k^2}{16\sigma^2 N^3 f}$$

The free energy penalty per unit grafting density of forming octopus micelles includes the unfavorable interaction energy between the solvent and the octopus body and is

$$\begin{aligned}\frac{F}{k_{\mathrm{B}}T} &= \frac{k^2}{16\sigma^2N^3f} + c[kN_w]^{2/3} \times \frac{\sigma f}{k}\\ &= \frac{k^2}{16\sigma^2N^3f} + c\sigma f N_w^{\,2/3} k^{-1/3}\end{aligned}$$

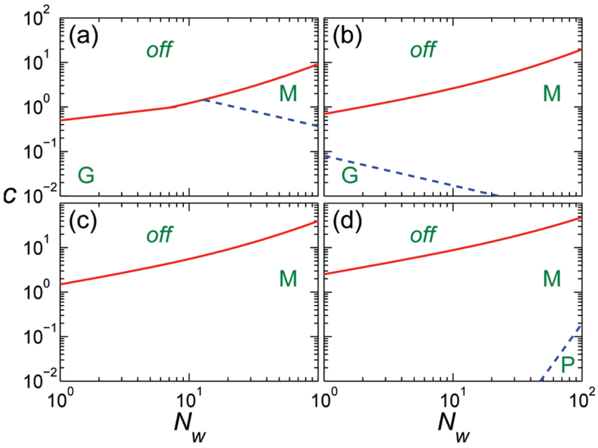

Figure 3. Phase diagram showing switchability for solvent quality, c, versus the number of monomers in the solvent-responsive block, N_w, for a homopolymer brush of $N = 100$, $\sigma = 0.5$ and the fraction of chains appended with responsive blocks is (a) $f = 0.001$, (b) 0.01 (c) 0.1, and (d) 0.5. The heavy (red) line is the transition line between persistent-*on* and *off* states. Above the transition line, the brush is in an *off* state. Below the transition line, the brush in a persistent-*on* state, where the solvent responsive blocks persist at the tip of the brush as either isolated globules (G), fused micelles (M), or a continuous pancake layer (P).

The brush will adopt a micelle size, or an average number of responsive blocks per micelle, k, that minimizes F ($\partial F/\partial k = 0$ and $\partial^2F/\partial k^2 > 0$) or

$$k = \left[\frac{8c\sigma^3 f^2 N_w^{\,2/3} N^3}{3}\right]^{3/7}$$

and the free energy penalty for surface micellization in the *on* state is, accordingly

$$\begin{aligned}\frac{F_{\mathrm{on,M}}}{k_{\mathrm{B}}T} &= \left(\frac{3}{8}\right)^{1/7}\frac{7}{6}c^{6/7}\sigma^{4/7}f^{5/7}N_w^{\,4/7}N^{-3/7}\\ &\approx c^{6/7}\sigma^{4/7}f^{5/7}N_w^{\,4/7}N^{-3/7} \qquad (8)\end{aligned}$$

Note that the free energy of these persistent-*on* states (globules, micelles, and pancakes) do not depend solely upon the size of the responsive block relative to that of the homopolymer, or N_w/N, but depend upon N_w. This is important as both N and N_w are then tunable parameters for switch design.

Results and Discussion

To determine the switchability, we compare the energy penalty for each of the persistent-*on* states, i.e., where the solvent-sensitive blocks form isolated globules, fused micelles, or a continuous pancake at the brush-solvent surface, with that of the *off* state, where the solvent-sensitive blocks are buried in the brush. To demonstrate qualitatively the results of this simple model, we consider the switchability of homopolymer chains of $N = 100$ and grafted at a high density of $\sigma = 0.5$, and examine the phase behavior as a function of the fraction of chains, *f*, appended with a block of N_w solvent-sensitive monomers. The phase diagrams shown in Figure 3 are presented over a continuous range of $N_w \leq N$ and solvent quality for the responsive blocks, quantified by the dimensionless surface tension *c*. The red line demarcates the *on*−*off* states of the brush: below the line, the brush is *on* as the responsive block remains at the brush surface forming globules, micelles, or pancakes while above the line the brush is *off* as the solvent sensitive monomers are buried. The brush demonstrates switchability when solvent is changed from good to poor for the solvent-sensitive monomers: that is the switch is driven by an increase in dimensionless surface tension *c*. Our simple model predicts that any brush can be driven from *on* to *off* with a significant enough change in solvent condition, characterized by *c*.

The surface tension *c* at which the brush first switches, (the red line), reflects the sensitivity of the responsive brush: a lower value means that the brush is easier to switch and more sensitive to solvent. Let us start our description with brushes of low fractions of minority chains ($f = 0.001$), where the minority chains are far apart, Figure 3a. When N_w is small, these chains are effectively isolated from one another as a very high stretching penalty is required for neighboring responsive blocks to fuse into micelles. Thus, the switch depends upon the competition between globule phase and the *off* state. But as N_w increases, the homopolymer chains need to stretch more in order to accommodate the responsive blocks in an *off* state. Thus, the surface tension must be higher in order to overcome the increased stretching penalty to attain an *off* state, or the transition boundary increases to higher *c* with larger solvent-sensitive blocks.

As responsive blocks become large enough, it is easier for them to fuse into micelles, decreasing their surface contact with solvent. Then the switchability of the brush involves an energy competition between the micelle phase and the *off* state. Since the surface energy of the micelle is lower than that of globules, the driving force required to switch the brush must be greater: the brush becomes harder to switch and requires solvents of higher surface tension, *c*. Thus, the slope of the transition line between the micelle phase and the *off* phase is steeper compared to that between the globule phase and *off* phase. As *f* is increased (see Figure 3b where $f = 0.01$), the distance between responsive blocks is closer, which makes it easier for responsive blocks to fuse into micelles. Within the range of N_w we consider, the brush must pass through the micelle phase before switching *off*. At high enough *f*, the responsive blocks are so close to each other, that they collapse into a pancake at the brush surface. At the largest value of *f* shown, $f = 0.5$, the formation of a pancake phase is predicted at $N \sim N_w$, however, not as the precursor phase to an *off* state.

The size of the homopolymer chains or *N* has a dramatic effect upon the switchability of the brush in this simplified model. Longer homopolymer chains reduce stretching penalties, suggesting that, since it is easier to bury responsive blocks, longer homopolymers make more sensitive brush switches. However, the lowering of the stretching penalty also facilitates the formation of micelles in a persistent-*on* state, with the net effect, shown in Figure 4, that a brush of longer homopolymers switches at higher values of *c*, or is less sensitive to solvent.

A switchable brush which is most sensitive or responsive to solvent quality, is one that switches at smaller values of *c*. Figures 3 and 4 show that the most responsive brushes are predicted to be those with minimal fraction of chains and the shortest responsive blocks (or both *f* and N_w small). (Notice that when $f = 1$, our model reduces to a diblock coploymer brush and that, as switches, these brushes are least sensitive to solvent.) While we can state that the transition from *on* to *off* occurs most readily at the smallest values of *f* and N_w, if the number of solvent-sensitive monomers is too small, we would not detect the change of states. Indeed, any responsive brush should be designed to maximize both sensitivity (and here it is solvent sensitivity) as well as signal. If we assume reasonably that the signal from *on* to *off* states is proportional to the change in the contact area between the solvent and the solvent-sensitive monomers, then we can estimate qualitatively a switch signal. Because there is minimal contact between solvent and solvent-sensitive monomer in the *off* state, the signal is determined by the persistent-*on* states, namely, the surface area of the individual globules (G), micelles (M), and pancake (P). The signal change per unit grafting area for $G \rightarrow off$ is $N_w^{2/3} f\sigma$, while the signal change for $M \rightarrow off$ is $N_w^{2/3} f\sigma/k^{1/3}$, and for $P \rightarrow off$ it is a constant value of 1, irrespective of chain parameters. Here you see that the maximum signal could arise when, under poor solvent conditions, a collapsed pancake is formed at the surface so that the surface tension must be driven exceptionally high in order for the brush to switch. So while the switch signal is maximal, the brush is not very sensitive; conversely, where the brush is very sensitive, the signal is minimal. This is a common optimization problem in designing sensors. It is important to emphasize, that the *on*−*off* switch in Merlitz's computer simulation was not designed for persistent-*on* states, and therefore could not demonstrate intermediate globule, micelle, and pancake phases. Consequently, their simulated switch had maximum solvent-sensitivity and a switch signal that was dictated by the size of the responsive monomer that was appended to a fraction of the chains.

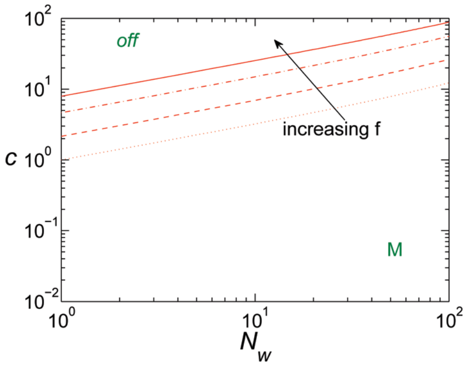

Figure 4. Phase diagram of switchability for solvent quality, *c*, versus the number of monomers in the solvent-responsive block, N_w, for a homopolymer polymer brush at $N = 1000$ and $\sigma = 0.5$. The transition line between persistent-*on* and *off* states is shown for four different values of *f*, the fraction of homopolymer chains appended with the responsive block. The arrow indicates the direction of increasing *f* from $f = 0.001$, 0.01, and 0.1 to 0.5. Comparison with Figure 3 shows that an increase in the size of the homopolymer increases the transition line to larger values of *c*, at any given N_w. That is, an increase in the size of the homopolymer chain, *N*, decreases the solvent sensitivity of the brush switch.

A brush that exhibits persistent-*on* states just prior to the switch to *off*, has potentially a stronger switch signal, albeit at the expense of sensitivity. However, our simple, qualitative model has parameter restrictions that limit any discussion of maximal switch signal. First, our treatment of stretching penalties requires the size of the responsive block to be less than the homopolymer size, $N_w \leq N$. Under that restriction, it is not possible to produce a pancake phase prior to the switch transition. Second, we also considered grafting densities comparable to Merlitz's simulation, which in our model is sufficiently large that the *on* state just prior to switch transition must be a persistent-*on* state of either isolated globules or micelles. The transition from globule to micelle phase at the switch transition occurs when, by scaling arguments, $N_w/N > (\sigma^4 f^2 N^4)^{-1}$. That is, by increasing the size of the responsive block relative to the homopolymer, or increasing either the grafting density, the fraction of appended chains, or the size of the homopolymer chain, the formation of the micelle phase as a persistent-*on* state is enhanced, and the switch signal is increased.

Conclusions

In summary, we presented a simple free energy scaling model of a high grafted homopolymer brush with a small fraction of chains appended with a block of solvent-responsive monomers. This model, while only qualitative, demonstrates the utility of persistent-*on* states, i.e., states where the brush remains *on,* despite poor solvent conditions, due to an excessive energy penalty for shielding the responsive block in the brush body. These persistent-*on* states consist of either collapsed, isolated globules of the responsive blocks, fused micelles of several neighboring responsive blocks, of a continuous pancake layer of responsive monomers, all residing at the tip of the brush. These persistent-*on* states decrease the sensitivity of the switch to solvent: the brush will switch *off* however only under stronger driving force from solvency condition. However these persistent-*on* states are also expected to impart a larger signal when the switch is set *off*. Our simple Alexander−deGennes style model suggests that increasing the homopolymer chain size, the fraction of chains appended with solvent-sensitive blocks, and the size of these solvent-sensitive blocks, the switch is made less sensitive to solvent, but provides a larger signal upon switch.

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