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Tuning transition properties of stimuli-responsive brushes by polydispersity

Shuanhu Qi,[1, 2] Leonid I. Klushin,[3, 4] Alexander M. Skvortsov,[5] Mingjie Liu,[1] Jiajia Zhou,[1, *] and Friederike Schmid[2]
[1] *Key Laboratory of Bio-inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry, Beihang University, Beijing 100191, China*
[2] *Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudingerweg 7, D-55099 Mainz, Germany*
[3] *Department of Physics, American University of Beirut, P. O. Box 11-0236, Beirut 1107 2020, Lebanon*
[4] *Institute for Macromolecular Compounds RAS, Bolshoi pr. 31, 199004 St. Petersburg, Russia*
[5] *Chemical-Pharmaceutical Academy, Professora Popova 14, 197022 St. Petersburg, Russia*

A new design for sensors and switches based on polymer brushes including a small fraction of end-grafted adsorption-active minority chains was proposed recently. The switching transition is controlled by temperature or solvent composition changes and is linked to a sharp change from a flattened adsorbed conformation to a stretched conformation. Two characteristics are most important for the switch performance: the sharpness of the transition affecting the switch sensitivity, and the response time. We use Monte Carlo simulations to study the effects of brush polydispersity on the main properties of the switching transition. The chain length distribution is taken to be of Schulz-Zimm type, and different values of the polydispersity index are considered. Contrary to intuitive expectations, polydispersity enhances the performance of the switch, in particular by reducing the activation barrier controlling the response time. Polydispersity also dramatically increases the robustness of the switch with respect to modifications of the adsorption-active switch chains.

I. INTRODUCTION

The ability to adjust surface properties dynamically in response to variations in the environment is a distinct feature of biological objects, and it is also essential to sustain life and maintain biological functions [1]. Through million years of evolution, nature has optimized the apparatus to near perfection: the surface properties can be varied with only tiny changes of the external stimuli, and the transition can happen quickly. Only recently, synthetic polymer systems with similar attributes start to emerge [2]. These systems are grouped under the name "stimuli-responsive polymers" and are capable of strong conformational or chemical responses to variations of the environmental temperature, pH, electric fields, etc. These materials have applications in the field of biomedical and material engineering, e.g., for the design of smart surfaces [3–8]. Multicomponent polymer brushes are recognized as particularly promising candidates for stimuli-responsive surfaces [2, 9].

We have recently proposed a class of brush-based switches, which rely on a radical conformational change of individual adsorption-active minority chains in an otherwise inert monodisperse brush [10, 11]. In contrast to more conventional responsive brushes, which involve highly cooperative chain rearrangements and hence are generally quite slow [3, 4], our proposed switches are fast and efficient because only local conformation changes are involved in the switching process. In this design, the minority chains must be slightly longer than the matrix brush chains in order to guarantee a sharp and fast conformational transition.

The basic constituent of the switch is a polymer chain with one end grafted to a surface, while the other end is modified by attaching specific groups that provide the sensor action. In the presence of moderately attractive interactions between the surface and the polymer, one can induce an adsorption-desorption transition by tuning the temperature or the solvent composition. In the adsorbed state, the sensor group is very close to the surface, and in the desorbed state, it is far away [12]. For an isolated polymer chain, the adsorption transition is continuous [13] and therefore too smooth to be useful for switch design. However, if the active chain is surrounded by a relatively dense but otherwise inert polymer brush that effectively acts as a long-range repulsive field, the adsorption transition can change its nature. It becomes of first-order type and hence much sharper. In the desorbed state, the active chains are now strongly stretched due to crowding and the active groups may be exposed outside the brush edge triggering designed chemical reactions in the solution. For example, if the polymers are grafted to medical implants or nanoparticle drug carriers, they could be exploited to selectively trigger immune responses. Yet another type of sensoring activity can be achieved if the chain end is modified by attaching a fluorophore. A grafting surface with appropriate optical absorption spectrum can effectively quench the fluorescence through the well-known non-radiative Förster energy transfer mechanism [14], when the active chain is in the adsorbed state. The rate of the non-radiative energy transfer decays as r^{-6} as a function of distance between fluorophore and the substrate, so that the quenching essentially disappears if the active chain is stretched. The sensoring mechanism based on fluorescence quenching does not depend on whether the end-group is fully exposed outside the brush or not: Only the change in the distance to the surface matters.

In the work cited above [10, 11], we have considered monodisperse polymer brushes. However, in practice, producing monodisperse polymers is very difficult, and

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[*] jjzhou@buaa.edu.cn

all synthetic polymer materials are polydisperse. Strictly monodisperse polymer brushes have special features that cannot be expected in experimentally available samples [15, 16]. Polydispersity is thus an important factor [17–25] which is often overlooked in theoretic studies. Specifically, the switch mechanism proposed in [10, 11] is only effective if the length of the switch chain is close to the length of brush chains (in fact, slightly higher), which raises the question whether it still persists in realistic polydisperse brushes.

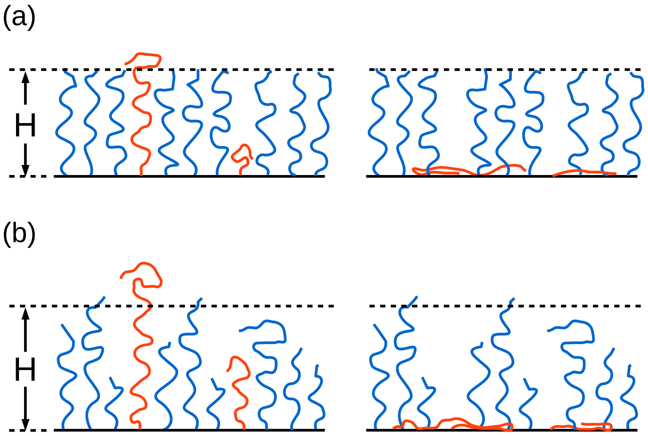

FIG. 1. Cartoon illustrating the switching transition of the adsorption-active minority chain in an inert monodisperse (a) or a polydisperse (b) brush of height H. In a monodisperse brush, shorter minority chains are not stretched in the desorbed state, whereas long desorbed minority chains are strongly stretched with exposed chain ends. In a polydisperse brush, desorbed minority chains are always stretched irrespective of the active chain length.

The purpose of the present work is thus to investigate the effect of brush polydispersity on the functioning of the proposed switching sensors. Contrary to what one might expect intuitively, we find that polydispersity enhances the switch characteristics and makes it more robust with respect to variations of the switch chain. Our main findings are illustrated in the cartoon of Fig. 1. The switching transition is associated with an adsorption-desorption transition of the adsorption-active switch chain, which is smooth on a bare substrate. The surrounding brush polymers can force desorbed switch chains to stretch away from the substrate. In such cases, the associated stretching energy generates a free energy barrier between the adsorbed and the desorbed state. The transition then turns into a sharp switching transition. In monodisperse brushes, this mechanism is effective for active chains that are longer than the brush chains. However, shorter active chains are fully immersed inside the brush where the monomer density varies only slowly, hence the brush has a similar effect than a homogeneous solvent and does not induce stretching. In polydisperse brushes, on the other hand, the brush monomer density varies more rapidly, desorbed chains are always stretched, and the transition is always sharp.

Furthermore, we find that polydispersity also improves the properties of the switch sensors at a quantitative level. Since they work on the basis of phase transitions (which are rounded due to the finite length of the polymers), the sensors can be characterized by the properties of the corresponding transition. The most relevant indicators are the transition width and transition barrier. The former describes the sensitivity, while the latter controls the response time. For stimuli-responsive brushes, the transition width and the response time determine the quality of the switching sensors and are important for practical applications. They depend sensitively on the properties of the brush and the switch chain. For example, a small change of the chemical properties of the active chain may shift the transition point and greatly change the response time. We will show below that brush polydispersity can significantly reduce the response times for switches with otherwise comparable properties.

In the present paper, we present extensive Monte Carlo (MC) simulations of coarse-grained model [11, 26] for polydisperse brushes with a single immersed adsorption-active minority chain. We study brushes with small, moderate and high polydispersity. The transition properties of the minority chain are studied and the effect of polydispersity is highlighted by the comparison with that of the monodisperse brushes.

II. MODEL DESCRIPTION AND MC SCHEME

We consider systems composed of a dense polymer brush and a single adsorption-active minority chain in a volume $V = L_x L_y L_z$. The brush chains and the minority chain are of the same type; the only difference is that the minority chain can interact with the substrate. Periodic boundary conditions are applied in the x and y directions, while impenetrable boundary walls are placed at $z = 0$ and $z = L_z$. The polymer chains are composed of beads connected by elastic springs, with a spring constant $3k_\mathrm{B}T/2a^2$. The statistical bond length is denoted by a, and $k_\mathrm{B}T$ is the product of Boltzmann constant and the temperature. In the following, all lengths and energies are scaled by a and k_BT, respectively. Each brush chain is grafted with one end onto a flat substrate located at z_0. To account for nonbonded interactions, we introduce soft interactions that are based on the local monomer density. The explicit form of the Hamiltonian has an Edwards-type form [27–29]

$$\mathcal{H}/k_{\mathrm{B}}T = \frac{3}{2a^2}\sum_{\alpha=1}^{n_b}\sum_{j=1}^{N_\alpha-1}\Big(\mathbf{R}_{\alpha j}-\mathbf{R}_{\alpha,j-1}\Big)^2 + \frac{3}{2a^2}\sum_{j=1}^{N-1}\Big(\mathbf{R}_j-\mathbf{R}_{j-1}\Big)^2 + \frac{\nu}{2}\int \mathrm{d}\mathbf{r}\hat{\phi}_t^2(\mathbf{r}) + \int d\mathbf{r}U_{\mathrm{ads}}(\mathbf{r})\hat{\phi}_m(\mathbf{r}). \tag{1}$$

The first and the second term account for the bonded interactions of the brush chain and the switch chain, respectively. Here, n_b is the total number of chains, N_α the chain length for α-th chain, $\mathbf{R}_{\alpha j}$ the position of the j-th bead in the α-th chain, and the index α runs over all brush chains. For the single minority chain, N is the chain length and $\mathbf{R}_j$ is the position of j-th bead. The third term represents the nonbonded effective monomer-monomer interactions, where ν is the excluded volume interaction parameter characterizing the interaction strength. In the present work, we choose $\nu = 1$, which corresponds to the athermal solvent condition. The microscopic density of total monomers is defined as $\hat{\phi}_t = \sum_{\alpha=1}^{n_b}\sum_j \delta(\mathbf{r}-\mathbf{R}_{\alpha j})$ and $\hat{\phi}_m = \sum_j \delta(\mathbf{r}-\mathbf{R}_j)$. In actual MC simulations, local densities are extracted from the position of the beads by using the first order Particle-to-Mesh technique [30]. The last term describes the interaction between the substrate and the minority chain. The interaction is assumed to be attractive and has the functional form

$$U_{\mathrm{ads}} = \begin{cases} -\varepsilon & 0 \leqslant z \leqslant a \\ 0 & \text{otherwise} \end{cases} \tag{2}$$

The brush is polydisperse and the chain lengths are distributed according to the Schulz-Zimm (SZ) distribution, which is often used to model the polydispersity of realistic polymer samples [17, 20, 24]. The continuous SZ distribution is characterized by two parameters: the number-averaged chain length N_{n}, and a parameter k which is related to the polydispersity index. The explicit form is

$$P(N) = \frac{k^k N^{k-1}}{\Gamma(k) N_{\mathrm{n}}^k}\exp\Big(-k\frac{N}{N_{\mathrm{n}}}\Big) \tag{3}$$

where $\Gamma(k)$ is the Gamma function. In the limit of $k \to \infty$, the distribution is a δ-function and corresponds to the monodisperse case. For $k = 1$, it reduces to a simple exponential. The weight-averaged chain length can be expressed in terms of N_{n} and k and one obtains the polydispersity index $N_{\mathrm{w}}/N_{\mathrm{n}} = (k+1)/k$.

This system is studied by Monte Carlo (MC) simulations and - in some cases - numerical self-consistent field (SCF) calculations, using the methods described in Ref. [11]. Specifically, we have simulated a series of polydisperse brushes with $k = 1; 7; 50$ together with a strictly monodisperse brush, corresponding to the polydispersity index $N_{\mathrm{w}}/N_{\mathrm{n}} = 2; 1.15; 1.02$, and 1. In a simulation, we have a finite number of polymer chains that depends on the size of the system as well as the grafting density. Chain lengths are sampled according to the SZ distribution with the additional requirement that the first, second and third chain length moments of the sampled chains could match those predicted by the continuous SZ chain length distribution within small errors (less than 1%). We checked the density profiles obtained by MC simulations for a pure brush with chain lengths sampled according to the SZ distribution by comparing with those obtained by SCF calculations using the corresponding continuous SZ distribution. Figure 2 shows the density profiles for a pure brush with grafting density $\sigma = 0.2$ for both MC simulations and one dimensional numerical SCF calculations [31–33]. It can be seen that the density profiles are approximately parabolic in the case of low polydispersity $k = 50$, linear in the case of moderate polydispersity $k = 7$, and concave parabolic in the case of high polydispersity $k = 1$. The density profiles obtained from MC and SCF are similar. In the present study, the number averaged chain length is fixed at $N_{\mathrm{n}} = 100$, and the grafting density at $\sigma = 0.2$, while the polydispersity index is varied. The grafting points of the chains on the substrate were fixed on a regular square lattice. The system size was chosen $L_x = 60$, $L_y = 60$, and $L_z = 150$.

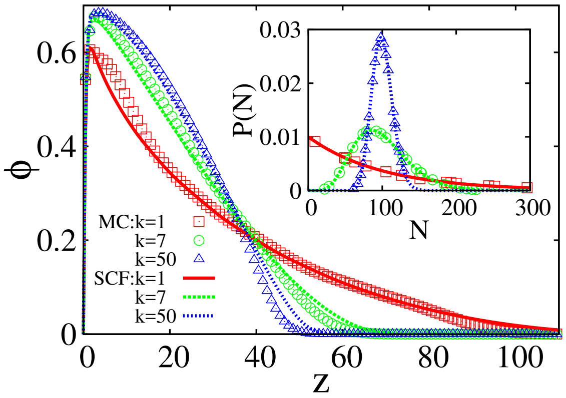

FIG. 2. Density profiles of mono- and polydisperse brushes with SZ chain length distributions (shown in the inset with the same color-coding). The average number of chain units in all brushes is $N_n = 100$. All data obtained by MC simulations and SCF calculations at grafting density $\sigma = 0.2$.

III. RESULTS AND DISCUSSION

A. Equilibrium conformation of minority chains

The basic mechanism of the switching transition has been illustrated in the introduction in Fig. 1. As discussed there, the transition can be exploited by attaching appropriate functional groups to the chain ends. Although one would expect that such separate groups interact differently with the surface than the rest of the switch chain, we will neglect this possibility in the present work. We follow the position of the functional groups by monitoring the position of the free end of the switch chain. It is clear that the average distance between this end and the substrate is a very important parameter characterizing the switching transition,

$$Z_{\rm e} = \langle z_{\rm N} \rangle, \tag{4}$$

where $z_{\rm N}$ is the distance between the chain free end and the grafted substrate, and $\langle \cdots \rangle$ denotes the ensemble average. Figure 3(a) shows a typical profile for the average distance $Z_{\rm e}$ as a function of the adsorption strength. The brush is monodisperse and composed of polymer with fixed chain length $N_b = N_n = 100$. The curves for different minority chain length show similar features: The distance $Z_{\rm e}$ decreases with increasing adsorption strength. This corresponds to the transition from the desorbed state to the adsorbed state. The chain length N of the minority chain determines the width of the transition. When the minority chain is longer than the length of the monodisperse brush, $N > N_n$, the distance $Z_{\rm e}$ is almost constant when the adsorption strength is either very small or very big, with a sharp transition at the intermediate value. For short minority chains $N < N_n$, the transition is relatively smooth. This can be related to the different types of phase transition [10]. (The transition becomes a sharp phase transition in the limit $N, N_n \to \infty$). For $N > N_n$, the phase transition is first-order, and a free energy barrier separates the desorbed and adsorbed states. For $N < N_n$, the minority chain is always immersed inside the brush chains, the influence of the brush potential on the adsorption process is too small to change the nature of the phase transition, and the phase transition is continuous.

Figure 3(b) shows similar curves as Fig. 3(a), but for a polydisperse brush with $k = 1$. Here, even short chains (e.g. $N < N_n = 100$) exhibit sharp transitions. This is because in polydisperse brushes, the monomer density is more diffuse in comparison to the monodisperse case (see Fig. 2), indicating that the excluded volume interactions are not effectively screened in the range close to the size of the minority chain. Therefore, the minority chain still exhibits a sharp conformational change, which is the signature of a first-order phase transition.

The effect of polydispersity on the conformations of the minority chain is demonstrated in Fig. 3(c) and (d). Here we show the distance $Z_{\rm e}$ for different values of the polydispersity parameter. In Fig. 3(c), the minority chain is shorter than the number average length of the brush $N_{\rm n}$. With increasing polydispersity (k decreases), the profile $Z_{\rm e}$ moves upwards with a plateau appearing at small values of $-\varepsilon$ and a sharp transition region. In a polydisperse brush, chains of different lengths form "sub-brush" layers of different height. A minority chain with a specific chain length will always be repelled and stretched by "sub-brushes" with shorter chain lengths. Therefore a continuous transition happening in a monodisperse brush could become a first-order transition in a polydisperse brush.

When the minority chain length is longer than the number average length of the brush, $N > N_{\rm n}$, the change of polydispersity does not change the type of the transition [see Fig. 3(d)]. The formation of "sub-brushes" in a polydisperse brush increases the height of the brush due to the existence of long chains, and the brush potential widens and becomes more diffuse (Fig. 2). This leads to a shift of the transition point to large values of the adsorption strength, and at the same time the average distance $Z_{\rm e}$ decreases for the desorbed states.

To further characterize the conformations of the minority chain, we analyze the distribution of its free end position. We consider the distribution P_z, which represents the probability density to find the free end in a layer with its z coordinate ranging from z to $z + {\rm d}z$. The average distance of the free end can also be evaluated from the distribution function as $Z_{\rm e} = \int_0^{L_z} {\rm d}z\, z P_z$, where P_z has been normalized to unity.

Close to a switching transition, the distribution P_z has a bimodal structure The two maxima are well-separated; the adsorbed state is represented by a maximum located at $z \simeq 0$ and the extended state corresponds to the maximum away from the surface. We define the transition point ε^* from the condition that the two maxima in the probability distribution P_z have the same height.

Figure 4(a) and (b) presents the free end distribution of the minority chain at the corresponding transition points for chain lengths $N = 80$ and $N = 110$, respectively, in brushes with different polydispersity. For a short minority chain ($N = 80$) in a monodisperse brush, P_z is a rather flat but monotonically decreasing function, showing that there is only one state at the transition point and no switching occurs, as one expects from a continuous transition. With increasing brush polydispersity, the extended state localizes around $z \simeq 20$, this position depending only weakly on the polydispersity. The adsorbed state and the extended state are well separated in the case of moderate or high polydispersity. This indicates that the polydispersity changes the intrinsic nature of the transition, i.e. from a continuous transition to a first-order type.

For long minority chains at the transition point, P_z has two maxima with equal height, indicating a coexistence of an adsorbed and an extended states irrespective of the brush polydispersity, see Fig. 4(b). Therefore, the polydispersity does not change the first-order type of the switching transition in this case. However, the location of the maximum corresponding to the stretched state moves towards the substrate with increasing polydispersity index, and its width increases.

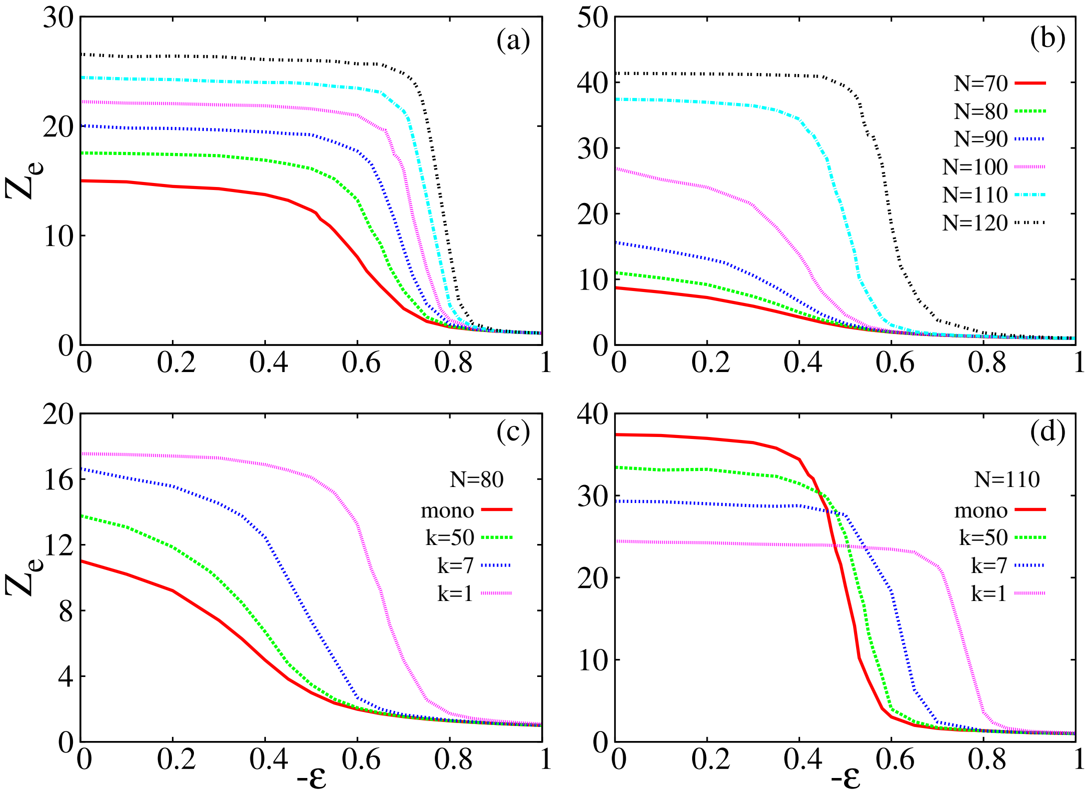

FIG. 3. Average free end height, Z_e, of adsorption-active minority chains chains as a function of the adsorption energy, ε in monodisperse (a), and strongly polydisperse brush with k=1 (b) for minority chains of different length N, and in brushes of varying polydispersity for minority chains of length $N = 80$ (c) and $N = 100$, as obtained from MC simulations. The number averaged length of brush chains is $N_n = 100$ and the grafting density is $\sigma = 0.2$.

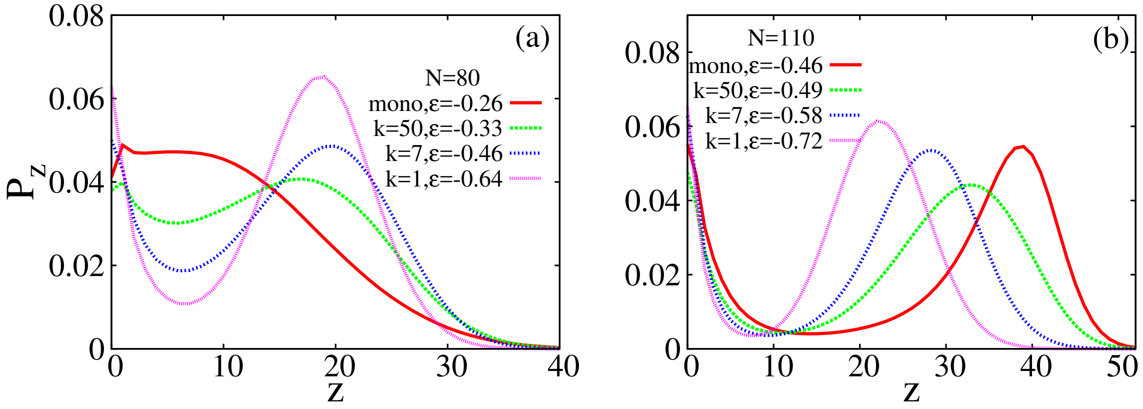

FIG. 4. Probability distribution of the free end minority chains in brushes with different polydispersity right at adsorption transition for minority chains of length $N = 80$ (a) and $N = 110$ (b). Data were obtained from MC simulations at $N_n = 100$, $\sigma = 0.2$.

B. Effect of polydispersity on the transition properties

To study the effect of polydispersity on the transition properties, we focus on three quantities: The transition point ε^*, the transition width (width) $\delta\varepsilon$, and the transition barrier U_{barrier}. The transition width is defined from the profile of Z_e v.s. $-\varepsilon$ as follows: We first find the point where Z_e has the maximum slope and calculate this slope as l. Subsequently, we draw a line through this maximum slope point with the slope l and find its intersection with the abscissa and with the line parallel to the abscissa that crosses the point $(0, Z_e(\varepsilon = 0))$. The absolute value of the difference of the adsorption strength at these two intersection points defines the transition width, $\delta\varepsilon = |\frac{Z_e|_{\varepsilon=0}}{l}|$. The transition barrier U_{barrier} is determined from the free end distribution $P_z(Z_e)$, which defines an effective potential for the free end via $U(Z_e) = -\ln P_z(Z_e)$. It is the difference between the value of U at the two minima corresponding to the coexisting states and the maximum in between.

Figure 5(a) shows the transition width as a function of the length of the minority chain. Independent of the polydispersity, the transition width becomes sharper for longer minority chains. One might expect that in the thermodynamic limit $N \to \infty$, $\delta\varepsilon$ goes to 0, indicating a true classical phase transition. This seems to be the case for minority chains in a monodisperse brush, where $\delta\varepsilon$ keeps decreasing quickly. However, for $k = 1$, the width $\delta\varepsilon$ seems to converge to a finite value at $N \to \infty$. In this case, both N and N_n presumably have to be infinite to obtain a sharp transition.

Polydispersity affects the width in different ways for short and long minority chains. For short chains, the transition becomes sharper if the polydispersity is higher, while for long chains, it becomes broader. Thus polydispersity increases the sensitivity of the switch if the minority chain is short, and decreases it if the minority chain is long. The width of the transition is determined by the response of the adsorbed state to variation of the adsorption strength [11]. From the point of view of statistical physics, the extensive variable that is conjugate to ε is the average number of contact to the substrate, therefore the width of the transition is directly related to the average number of monomers in the adsorption layer at the transition point.

Figure 5(b) shows the height of the transition barrier, U_{barrier}, as a function of the minority chain length in brushes with different polydispersity parameters. This quantity determines the transition time τ between the two states. A simple Arrhenius estimate would predict $\tau \sim \exp(U_{\text{barrier}})$. In reality, the dependence is more complex [10], but τ still increases roughly exponentially with U_{barrier}. The transition barrier is directly related to the ratio of maximum and minimum values in the free end distribution. As discussed earlier, for short minority chains, P_z gradually becomes bimodal with increasing polydispersity, and the dip between the two maxima deepens, hence the transition barrier increases. In contrast, for long minority chains, the peak in the free end distribution corresponding to the extended state moves towards the substrate for increasing polydispersity, and becomes wider. As a consequence, the difference between the maximum and minimum values in the curve of P_z becomes smaller, and the transition barrier decreases. In general, to be useful in a switch, the transition barrier should neither be too small (larger than 1, otherwise the two states are not well separated), nor too large (otherwise the switching times are too long). In polydisperse brushes, the range of minority chain lengths where the height of the transition barrier takes interesting values between 1 and 5 is much larger than in monodisperse brushes, hence the design of good switches should be easier when using polydisperse brushes.

Comparing Fig. 5(a) and (b), one can see that the effects of polydispersity on the transition barrier and the transition width are opposite. This is probably because they have different physical origin: the former is directly related to the number of contact in the adsorption layer, while the latter is determined by the free end distribution function. For practical applications, it is desirable to have both small transition widths (i.e., high sensitivity) and low barriers (i.e., fast switching times). Both the polydispersity of the brush and the length of the minority chain can be used to manipulate these two parameters, but there is a trade-off: Either one decreases the transition width at the cost of having a higher transition barrier, or one decreases the transition barrier at the cost of having a larger transition width. To study whether polydisperse brushes can be used to improve the quality of switches, one must therefore plot the height of the transition barrier versus the transition width. This is done in Fig. 5(c). Indeed, we find that for a given small transition width ($\delta\varepsilon = 0.1 - 0.15$), the height of the free energy barrier can be reduced significantly by using strongly polydisperse brushes.

C. Theoretical predictions and comparison to simulations

An analytical theory describing the transition properties of an adsorption-active minority chain in a monodisperse brush was proposed in [10, 11]. It is based on on the concept of two states: an adsorbed state, with the free end situated in the immediate vicinity of the grafting surface, and a desorbed state having no monomer contacts with the solid substrate. The chain conformations in the two states are described by well-known Green's functions [34]. For the adsorbed state not too close to the critical adsorption point, they read [35]

$$G_{\text{ads}}(N,\ Z_e) = 2\sqrt{-6\mu\left(\varepsilon\right)}\,\mathrm{e}^{N(-\phi_0-\mu(\varepsilon))-\sqrt{-6\mu(\varepsilon)}Z_e}. \quad (5)$$

where N is the chain length of the adsorption-active chain, Z_e is the coordinate of the free end, $\mu\left(\varepsilon\right)$ is the free energy of adsorption per monomer, and

$$\phi_0 = \frac{3}{2}\left(\frac{\pi\sigma}{2}\right)^{2/3} \quad (6)$$

is the mean-field potential produced by the brush density profile at the grafting surface.

The Green's function of the desorbed stretched state is determined by the parabolic shape of the monodisperse brush density profile [36],

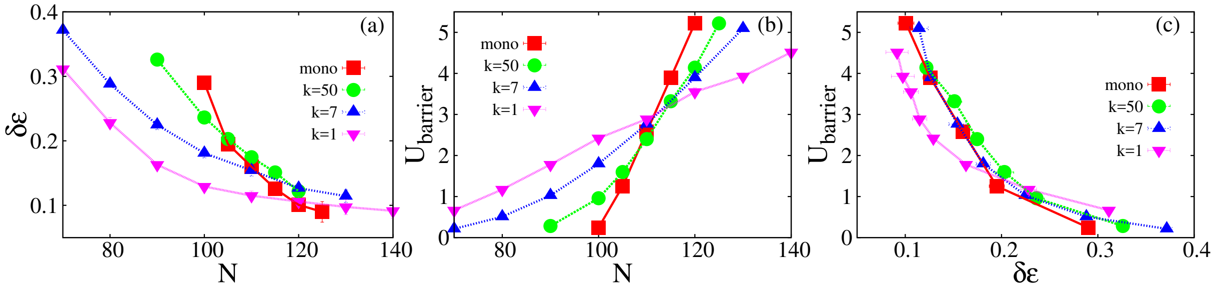

FIG. 5. Transition width $\delta\varepsilon$ (a) and barrier height U_{barrier} between coexisting states at the transition point (b) vs. the minority chain length N, and (c) U_{barrier} vs. $\delta\varepsilon$, for brushes with different polydispersity. Data obtained by MC simulations at $N_n = 100$, $\sigma = 0.2$.

$$G_{\mathrm{str}}(z,N) = \frac{\pi}{2}\left[\frac{3}{N_n \sin\left(\frac{\pi N}{2N_n}\right)}\right]^{3/2} z e^{-N\phi_0 - \frac{3\pi}{4N_b}\cot\left(\frac{\pi N}{2N_n}\right)z^2}. \tag{7}$$

A detailed theoretical analysis shows that if the adsorption-active minority chain is shorter than the chains forming the monodisperse brush, $N < N_n$, the desorbed conformation is a weakly deformed coil. Hence the adsorption transition is smooth and continuous, closely resembling the standard situation of an isolated chain grafted to a solid attractive substrate. However, for longer minority chains, $N > N_n$, the situation is quite different. The desorbed state becomes strongly stretched, with the free end exposed outside the brush edge. The two competing states are well separated and the transition becomes much sharper resembling a first-order phase transition albeit smoothed by finite-size effects. The case of $N = N_n$ is intermediate with no clear separation between the adsorbed and the stretched states. The qualitative difference in the transition for shorter and longer minority chains is clearly seen in Fig. 3(a).

The integration of the Green's function over Z_e in the vicinity of the respective equilibrium end position gives the partition functions for the two competing states. The transition point is defined by equating the two partition functions. The apparent width of the transition, $\delta\varepsilon$, is determined from the analysis of the rate of change of the free energy of the adsorbed state with ε in the vicinity of the transition point. Finally, the free energy barrier separating the two competing states at the transition is estimated by analyzing the Green's function of partially adsorbed states with the desorbed tail of varying length. The analytical theory suggests that the barrier height, U_{barrier} is determined by two parameters: The chain length difference, $N - N_{\mathrm{n}}$, and the brush grafting density, σ. Specifically, it was proposed in [11] that the barrier height is given by a scaling combination

$$U_{\mathrm{barrier}} \sim \sigma(N - N_{\mathrm{n}}) \tag{8}$$

The MC simulations results support the suggested scaling very well as illustrated in Fig. 6(a).

The analytical theory can be extended to cover the case of a moderately polydisperse brush with a linearly decreasing density profile. The adsorbed state is still described by the Green's function of Eq. 5. The desorbed conformation is affected by the linear profile of the self-consistent brush field with the slope

$$f = \phi_0/H = \frac{9}{8}\left(\frac{\pi}{2}\right)^{4/3}\frac{\sigma^{1/3}}{N_n} \tag{9}$$

which has the meaning of a mean force acting on each monomer. Since the force does not depend on the coordinate, it is similar to a uniform gravitational field. The Green's function of a chain in a uniform field is well known [37, 38]

$$G_{\mathrm{str}}(z,N) = \left(\frac{2\pi N}{3}\right)^{-1/2} \times \exp\left[-\phi_0 N + \frac{f^2 N^3}{18} - \frac{3}{2N}\left(z - \frac{f\,N^2}{6}\right)^2\right] \tag{10}$$

In contrast to the case of a monodisperse brush, the adsorbed and desorbed states are always separated by a barrier, irrespective of whether the minority adsorption-active chain is shorter or longer than N_n. Hence the transition follows the first-order scenario and is always relatively sharp. Qualitatively, this applies also to the case of strongly polydisperse brushes for which the transition profiles are shown in Fig. 3(b). The analysis of the transition point, the apparent transition width and the barrier height follows the logic outlined above for the monodisperse brush case under the condition $N > N_n$. In particular, the barrier height is predicted to scale as

$$U_{\mathrm{barrier}} \sim \frac{N^3}{N_n^2}\sigma^{2/3} \tag{11}$$

This suggested scaling agrees excellently with the MC simulations data as shown in Fig. 6(b).

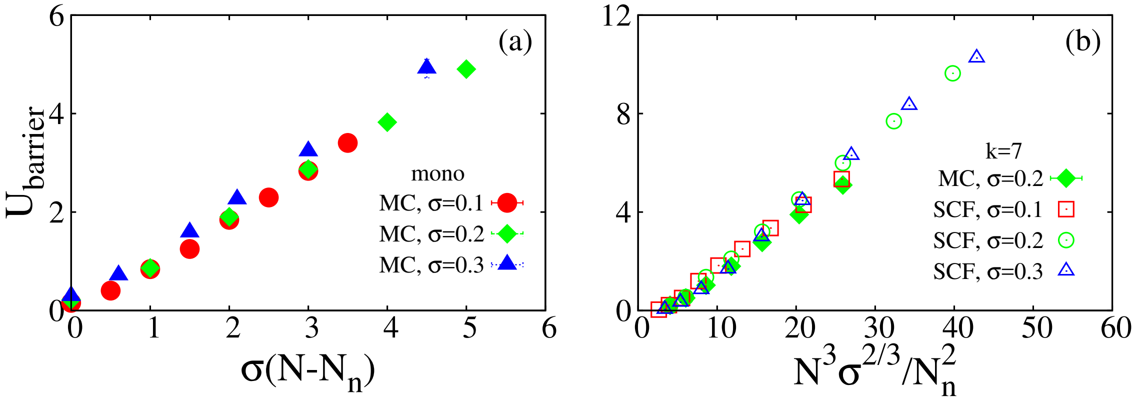

FIG. 6. Scaling plots of the barrier height, $U_{\rm barrier}$, for minority chains with lengths in the range $N = 100 - 135$ in monodisperse brushes (a), and for minority chains in the range $N = 70 - 140$ in a moderately polydisperse brush with $k = 7$; (b). Data were obtained by MC simulations and SCF calculations at different grafting densities as indicated and $N_{\rm n} = 100$.

IV. CONCLUSION

To summarize, we have investigated in detail the effect of polydispersity on the conformation and transition properties of a new type of adsorption-responsive polymer brushes, where the minority chain is used as the switch sensor, using particle-based MC simulations. We also proposed a theoretical description for such switches. The theory is valid for the moderate polydisperse case where the density profile in the brush is approximately linear. To verify the theory, we performed additional one dimensional SCF calculations. The scaling predictions of the analytic theory are in reasonable agreement with the results from SCF calculations. Depending on the length of the minority chain, the polydispersity has a different effect on transition properties of the minority chain. The difference originates from the differences in the conformations of short and long chains in response to the potential generated by the polydisperse brush.

We have adopted the SZ distribution to model the distribution of chain lengths in the brush, since this distribution is commonly used to represent molecular weight distributions of realistic polymers. In industry and experimental studies, one usually uses the polydispersity index ($N_{\rm w}/N_{\rm n}$) to describe the dispersity of the material. This raises the question whether the conformation and transition properties are uniquely determined by the polydispersity index of the polymer brush. The answer is no. In fact, these properties of the minority chain are directly related to the brush potential, i.e., the monomer density of the brush. To accurately determine the monomer density profile, one must know the full chain length distribution. The knowledge of the first and second moment is not sufficient. Quantitatively, the effect of polydispersity will thus depend on the the explicit form of the chain length distribution. Qualitatively, however, it can be expected to be similar for different chain length distributions.

In the present study, we found that short chains immersed in a polydisperse polymer brush can exhibit sharp transitions. A sharp transition is a type of transition where a minor changes of the control parameters at the transition point leads to dramatic changes in the properties of the material. The existence of a sharp transition is a prerequisite for a material to be useful for the design of efficient switch sensors. A material which can undergo a first-order phase transition is a good candidate for such a purpose. In monodisperse brushes, switch chains can exhibit a sharp transition if they are long enough to be able to form a crown structure outside of the brush. Shorter "switch" chains exhibit only smooth continuous transitions, hence they cannot be used as switch sensors. The present study suggests a way to design switch sensors with short switch chains that are immersed inside the brush and not in contact with objects outside the brush. Such switches could be used to trigger reactions on or inside the grafting surface, for example, intracellular immune signaling.

The main issues when designing switch sensors are the sensitivity and the switch time. Usually people seek for switch sensors with sharp transitions and short switch times, i.e., quick response and fast switch. Our study shows that polydispersity has a noticeable effect on the switch properties, and that this finding may be exploited to improve the performance of the switch sensors. In Fig. 5(c), it is demonstrated that in polydisperse brushes, the transition barrier can be reduced by an amount of order $k_B T$ while keeping the same sensitivity (transition width). This would roughly correspond to a speedup by a factor three in switching times according to a simple Arrhenius estimate.

Our study also shows that the switch is not only more efficient in polydisperse brushes, but also more robust with respect to chemical modifications of the switch chain, since the switching mechanism works for minority chains of all lengths.

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