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Supplementary Information

Responsive polymer brushes for controlled nanoparticle exposure

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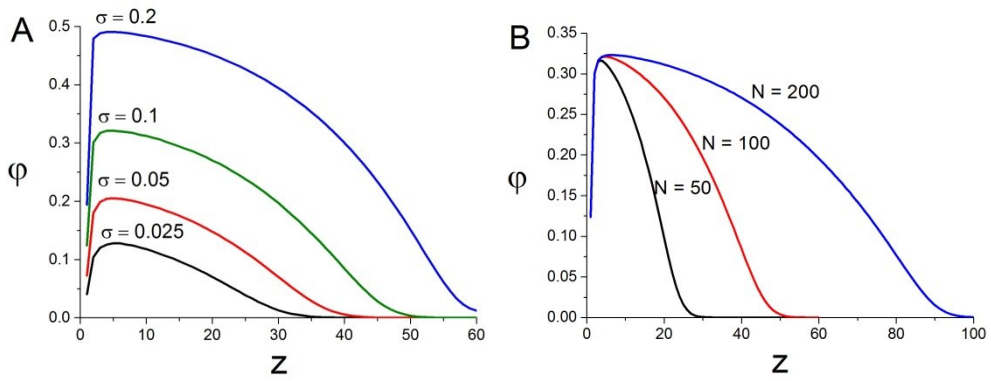
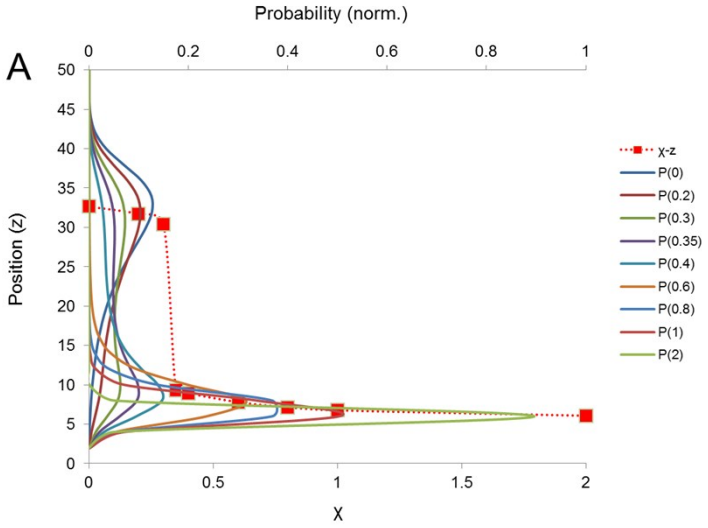
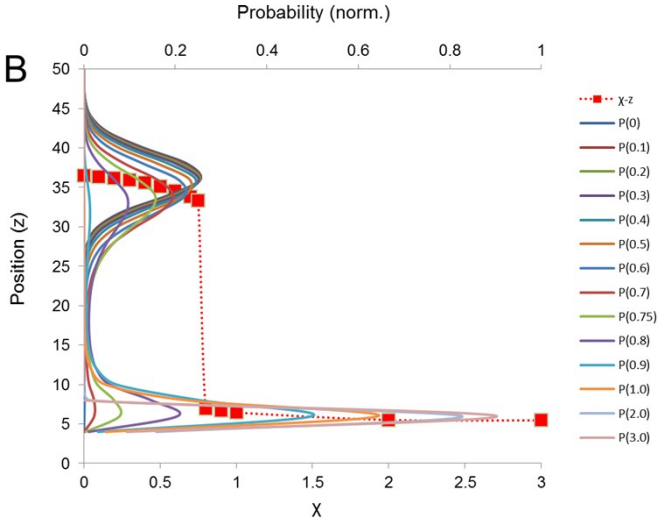


Figure S1. (A) Brush density (ϕ) as a function of distance from the grafting interface (Z) at grafting densities of $\sigma = 0.025$, $\sigma = 0.05$, $\sigma = 0.1$ and $\sigma = 0.2$. $N = 100$. (B) Brush density (ϕ) as a function of distance from the grafting interface (Z) at chain lengths of $N = 50$, $N = 100$ and $N = 200$. $\sigma = 0.1$.

In Figure S1A, we show polymer density in a brush as a function of distance from the surface (Z) for different grafting densities. Here we kept the chain length constant at $N = 100$ and gradually varied the grafting density from $\sigma = 0.025$ to $\sigma = 0.2$ in units of number of chains per lattice site. Increasing the grafting density will also increase the osmotic pressure in the brush leading to chains that are more strongly stretched away from the grafting interface. The polymer density thus increases but at the same time the height of the brush also increases.

In Figure S1B we show the polymer density in a brush as a function of distance from the surface (Z) for different chain lengths. Here we have kept the grafting density constant at $\sigma = 0.1$ and varied the chain length from $N = 50$ to $N = 200$. An increase in chain length leads to an identical brush but with twice the height. These results are well-known and have been investigated theoretically and experimentally. At the same time we do show these results as they show so clearly that the grafting density and chain length are key parameters for the brush composition [1, 2]. Furthermore, the results with these exact grafting densities and chain length provide a benchmark for the discussion of the results.


A
Probability (norm.)
0
0.2
0.4
0.6
0.8
1
Position (z)
50
45
40
35
30
25
20
15
10
5
0
0
0.5
1
1.5
2
X
χ-z
P(0)
P(0.2)
P(0.3)
P(0.35)
P(0.4)
P(0.6)
P(0.8)
P(1)
P(2)


B
Probability (norm.)
0
0.2
0.4
0.6
0.8
1
Position (z)
50
45
40
35
30
25
20
15
10
5
0
0
0.5
1
1.5
2
2.5
3
X
χ-z
P(0)
P(0.1)
P(0.2)
P(0.3)
P(0.4)
P(0.5)
P(0.6)
P(0.7)
P(0.75)
P(0.8)
P(0.9)
P(1.0)
P(2.0)
P(3.0)

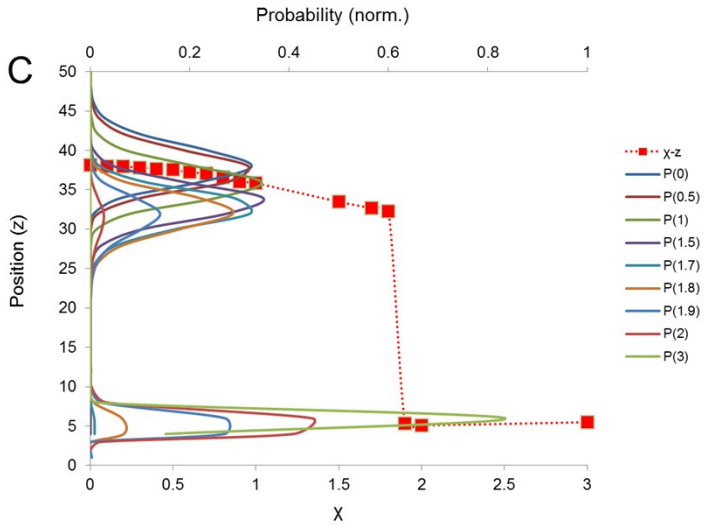

C
Probability (norm.)
0
0.2
0.4
0.6
0.8
1
Position (z)
50
45
40
35
30
25
20
15
10
5
0
0
0.5
1
1.5
2
2.5
3
X
χ-z
P(0)
P(0.5)
P(1)
P(1.5)
P(1.7)
P(1.8)
P(1.9)
P(2)
P(3)

Figure S2. Probability distributions of nanoparticles with different sizes being either inside and/or outside of a polymer brush as function of the interaction parameter, χ. A) 1 × 3 LS; B) 3 × 3 LS; C) 5 × 3 LS. $N = 100$ and $\sigma = 0.1$.

Furthermore, these results in Figure 5 were supported by the probability analysis of particle with different sizes being either outside or (deep) inside of the brush. The overall conditions for the brush were kept fixed at an experimentally relevant values of $\sigma = 0.1$ chains per surface lattice site and chain length $N = 100$. We observe that when interaction energy between a small particle and a brush is very small, the particle tends to stay outside of the brush however, there is very high chance that the particle may also penetrate into the denser parts of the brush (Fig. S2A). Although there is no fast switching predicted from outside to inside of the brush, higher the interaction energy ($\chi \geq 0.6$) will easily push the particle close to the grafting interface. This phenomenon is different when the particle size is bigger: in the same brush conditions, when the particle size is higher (3 × 3 LS, Fig. S2B), at low interaction parameters, the probability of being at the outside of the brush is much higher because of the less binodal contributions in the system. However, increasing the particle size to 5 × 3 LS will cost more energy to penetrate inside, thus it will remain outside of the brush and may compress the system from a distance $Z = 38$ to $Z = 32$ (Fig. S2C). Consequently, this biggest particle will reach much closer to the grafting interface at very high interaction parameter ($\chi \approx 2.0$).

References

1. T. Wu, K. Efimenko, P. Vlček, V. Šubr and J. Genzer, *Macromolecules*, 2003, **36**, 2448-2453.
2. G. Sudre, D. Hourdet, C. Creton, F. Cousin and Y. Tran, *Macromolecular Chemistry and Physics*, 2013, **214**, 2882-2890.