

Supplementary Materials

Decreasing Polymer Flexibility Improves Wetting and Dispersion of Polymer Grafted Particles in a Chemically Identical Polymer Matrix

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I. Methodology Details

A. Model

We model polymer grafted spherical nanoparticles in a polymer matrix using a generic coarse-grained model, where the nanoparticles are modeled as a rigid-body of several $d=1\sigma$ beads ($\sigma \approx 1\text{nm}$), and the polymers as bead-spring chains. The nanoparticle consists of surface beads to preserve the excluded volume of the particle and grafting sites to anchor the grafted chains. The surface and grafting site beads overlap in the rigid body of the particle, with the grafting site beads isotropically located in the spherical particle surface. Each grafted or matrix polymer is modeled as a bead-spring chain¹, with each bead of size $d=1\sigma$ representing a group of monomers on the polymer chain, and harmonic springs linking the beads having a force constant of $k_{\text{bond}}=50 k_B T/\sigma^2$ and a bond rest length of $r_0=1\sigma$, mathematically represented as

$$U_{\text{bond}}(r) = \frac{1}{2} k_{\text{bond}} (r - r_0)^2 \quad (1)$$

where r is the center to center distance between the bonded beads.

We model decreasing flexibility in the graft and matrix polymers through a harmonic angle potential with varying force constant of $K=0-10 k_B T/\text{radians}^2$, and a rest angle of $\theta_0=\pi$ radians, mathematically represented as²

$$U_{\text{angle}}(r) = \frac{1}{2} K_X (\theta - \theta_0)^2 \quad (2)$$

where X is graft or matrix, and θ is the angle between the two bond vectors that define the potential. Polymer chains with the values of K studied here would have persistence lengths³ as shown in the Table S1 using three different calculation methods³:

$$\left\{ \begin{array}{l} L_{p1} = \frac{\langle \vec{R}_{ee} \cdot \vec{b}_1 \rangle}{\langle b \rangle} \\ \frac{\langle \vec{b}_i \cdot \vec{b}_1 \rangle}{\langle b \rangle^2} = \exp\left(-\frac{i}{L_{p2}}\right) \\ \langle R_{ee}^2 \rangle = 2L_{p3}N_X - 2L_{p3}^2 \left(1 - \exp\left(-\frac{N_X}{L_{p3}}\right)\right) \end{array} \right. \quad \begin{array}{l} (3a) \\ (3b) \\ (3c) \end{array}$$

where L_{pn} is the persistence length calculated using method n, \vec{R}_{ee} is a chain end-to-end vector, \vec{b}_1 is the bond vector for the first bond (from bead 0 to 1) of a chain, $\langle b \rangle$ is the average bond length where $\langle \rangle$ denotes ensemble averages over 200 independent snapshots and all grafted or matrix chains, \vec{b}_i is the i^{th} bond vector (from bead $i-1$ to i) of a chain, $\langle R_{ee}^2 \rangle$ is the mean-square end-to-end distance (calculation described below), and N_X ($X=\text{graft or matrix}$) is the chain length. While Equation 3a can be solved directly for L_{p1} , in Equation 3b L_{p2} is solved for by linearly interpolating to find when the LHS is equal to e^{-1} (i.e. when L_{p2} is equal to i), and Equation 3c must be iteratively solved for L_{p3} . Using three estimates for L_p allows us to assess the effects of the specific assumptions in Equation 3a ($N \rightarrow \infty$), Equation 3b (fixed bond angle), and Equation 3c (worm-like chain model).

Table S1: Expected persistence lengths L_p , (in units of σ), of graft and matrix chains at given grafting density and chain lengths calculated using three methods described in Supplementary Information.

					Grafts (units of σ)			Matrix (units of σ)		
K_{graft}	K_{matrix}	Grafting Density (chains/ σ^2)	N_{graft}	N_{matrix}	L_{p1}	L_{p2}	L_{p3}	L_{p1}	L_{p2}	L_{p3}
5	5	0.65	20	60	7.1	6.1	5.7	5.8	4.1	5.3
10	10	0.65	20	60	9.9	10.1	10.3	10.9	9.1	9.4

We model a purely athermal system where all pairs of coarse-grained beads, including grafted, matrix, and surface beads, interact via the Weeks-Chandler-Andersen⁴ (WCA) potential.

$$\begin{cases} U_{WCA}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \varepsilon & r < r_{cut} \\ U_{WCA}(r) = 0 & r > r_{cut} \end{cases} \quad (4)$$

where $\varepsilon=1$ (in units of $k_B T$), $\sigma=1$ and $r_{cut}=\sigma*2^{1/6}$

In this study the nanoparticle size is maintained at 5σ , grafting density is varied from 0.25 to 0.65 chains/ σ^2 , the matrix polymer length is varied from 20-100 coarse-grained beads, the graft polymer length is varied from 10-40 beads, and the angle potential force constant is varied from 0 to 10 $k_B T/\text{radians}^2$, with the majority of the results shown for 0 and 5 $k_B T/\text{radians}^2$. For single particle simulations, we use 60,000 matrix beads and for multi particle simulations we use 120,000 matrix beads. The simulation box volume for single particle simulations is about $68 \times 68 \times 68 \sigma^3$, and for multi particle simulations is about $91 \times 91 \times 91 \sigma^3$. The total occupied volume fraction in the simulation box is maintained to be 0.1 for all systems and the number of grafted particles is varied from 1 to 20 particles.

B. Simulation Method

Using the model described above, we conduct Brownian dynamics (BD) simulations in the canonical ensemble using the graphical processing unit based HOOMD-blue package.^{5, 6} We first create an initial configuration in the following manner: We generate a particle of a desired diameter with isotropically distributed graft points, with the chains extending radially from these graft points embedded on the particle surface. In order to make it easier to insert the grafted particle into the simulation box, a short simulation with strong Lennard-Jones monomer-monomer and monomer-particle attraction is then run to compress the grafted chains from these

extended conformations. We note that this is the only time we use attractive non-bonded interactions in our simulation, as the study is focused on a system with athermal interactions. Copies of this one compressed grafted nanoparticle are then randomly placed in a large cubic box to achieve the desired number of particles along with the desired number of matrix chains. This initial configuration is then integrated using a Brownian dynamics integrator for 0.5e6 time steps to both mix and relax the grafted and matrix chains. The box is then compressed to the desired volume fraction over 0.5e6 steps, and then mixed again for 0.5e6 steps at the compressed state. Using this relaxed initial configuration at the appropriate packing fraction at reduced temperature $T^*=1$, we finally conduct the production simulation runs for at least 40 million time steps where snapshots of the system are saved every 0.1e6 time steps.

C. Analysis

We calculate a number of structural features (e.g. monomer concentration profiles, radii of gyration, graft and matrix end-end distances) and thermodynamic information (e.g. mixing entropy). Data is calculated from 200 independent uncorrelated snapshots, with the error bars calculated as the standard error between these 200 data points.

We quantify monomer concentration profiles of the grafted and matrix chains from the particle surface as follows:

$$C_X(r) = \frac{\langle n_X(r) \rangle}{4\pi r^2 \Delta r} \quad (5)$$

where $C_X(r)$ (X =graft or matrix) is the monomer concentration profile, in units of $\sigma^{(-3)}$, as a function of r , the distance between the particle surface and the monomer bead, and $\langle n_X(r) \rangle$ is the average number of beads of type X that are within a shell of thickness Δr at distance r .

The brush height defines the effective thickness of the grafted layer of the grafted particle and is calculated as the root mean square of the distance of the grafted beads from the surface of the particle.

$$\langle H_B^2 \rangle^{0.5} = \sqrt{\frac{1}{(n_P * n_G)} \sum_{i=1}^{n_G} r_i^2} \quad (6)$$

where $\langle H_B^2 \rangle^{0.5}$ is the brush height in units of σ , r_i is the distance of the i^{th} graft bead from the surface of the particle the graft belongs to, n_P is the total number of grafted particles, and n_G is the total number of graft beads in the system (across all grafted particles).

The average end-to-end distance of the polymer chain is calculated by averaging the distance between the first and last bead of each matrix chain over the number of matrix chains in the system:

$$\langle R_{ee}^2 \rangle = \frac{1}{n_{MC}} \sum_{i=1}^{n_{MC}} (r_{i,n} - r_{i,1})^2 \quad (7)$$

where $\langle R_{ee}^2 \rangle$ is the average squared end to end distance of the matrix chains, in units of σ^2 , n_{MC} is the number of matrix chains, and $r_{i,n} - r_{i,1}$ is the distance between the first and last beads of the i^{th} chain.

The average radius of gyration of the grafted chains quantifies the size of the grafted chain conformations averaged over all of the grafted chains in the system.

$$\langle R_g^2 \rangle = \left(\frac{1}{n_{GC} * N_G} \right) \sum_{i=1}^{n_{GC}} \sum_{j=1}^{N_G} (r_{i,j} - r_{i,com})^2 \quad (8)$$

where $\langle R_g^2 \rangle$ is the average squared radius of gyration, in units of σ^2 , n_{GC} is the number of grafted chains in the system (across all particles), N_G is the length of the grafted chains, $r_{i,j}$ is the position of bead j on chain i , and $r_{i,com}$ is the center of mass of chain i .

The wet matrix bead percentage quantifies the degree of wetting of the grafted layer by matrix beads, and is calculated as:

$$\text{wet matrix \%} = \frac{n_{M,wet}}{n_M} (100\%) \quad (9)$$

where n_M is the total number of matrix beads in the system and $n_{M,wet}$ is the number of matrix beads that are within the brush height ($\langle H_B^2 \rangle^{0.5}$) i.e. the number of matrix beads that have wet the grafted layer of any particle.

We also calculate the particle-particle pair correlation function, $g_{PP}(r)$, which describes the extent of aggregation/dispersion of the grafted particles in the polymer matrix, by quantifying the correlation between the particle centers⁷. This is calculated only for the systems with multiple grafted particles.

We also estimate the total gain in mixing entropy upon the matrix chains wetting the grafted layer, ΔS_{wet} , as shown below in Equation 10. We calculate this quantity using

$$\Delta S_{wet} = -\frac{k_B}{N_M} \sum_{n_{M,wet}=1}^{\langle n_{M,wet} \rangle} \ln \frac{\phi_{M,wet}}{\phi_{M,unwet}} \quad (10)$$

$$\phi_{M,wet} = \frac{n_{M,wet}}{n_{M,wet} + n_{G,wet}}, \quad \phi_{M,unwet} = \frac{n_M - n_{M,wet}}{n_M + n_G - (n_{M,wet} + n_{G,wet})}$$

where ΔS_{wet} is the total gain in mixing entropy, k_B is Boltzmann's constant, N_M is the length of the matrix chains, $\phi_{M,wet}$ is the volume fraction of matrix beads that have wet the grafted layer, and $\phi_{M,unwet}$ is the volume fraction of matrix beads that are outside the grafted layer. Since the volumes of the individual matrix and grafted beads are equal, the volume fractions can be calculated as number fractions, where n_M is the total number of matrix beads in the system, $n_{M,wet}$ is the number of wet matrix beads, n_G is the total number of graft beads in the system, and $n_{G,wet}$ is the number of wet graft beads. We calculate the number fractions in two separate ways: (a)

explicitly counting graft and matrix beads in the simulation that are within the brush height and averaging that over snapshots and independent trials or (b) assuming that $\langle n_{G,wet} \rangle$ is approximately $0.6n_G$, based on our observations for number of grafted beads within grafted layer, and calculating $\langle n_{M,wet} \rangle$ by assuming the density of the matrix beads in the grafted layer is equal to the bulk density:

$$\langle n_{M,wet} \rangle = \frac{4}{3}\pi \left[\left(\langle H_B^2 \rangle^{0.5} + \frac{D}{2} \right)^3 - \left(\frac{D}{2} \right)^3 \right] \rho_{M,bulk} \quad (11)$$

where $\rho_{M,bulk}$ is the bulk density of matrix beads in the simulation, $\langle H_B^2 \rangle^{0.5}$ is the brush height or grafted layer thickness, and D is the diameter of the particle. Method (b) is intended to be a crude check for trends found with method (a) as it involves less information from the simulation, and allows us to decouple the entropy estimations from the simulation data more than method (a)

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II. Additional Results

A. Effect of polymer flexibility on wetting of the grafted polymer layer by matrix polymers:

Table S2 (see next page): Average end-end distance of the matrix polymers for varying matrix and graft lengths, grafting densities, and flexibilities. The graft and matrix end-to-end distances are defined as the average over all of the graft and matrix chains respectively. The “wet matrix” end-to-end distance is defined as the average over any chain that has any bead within the grafted layer “brush” height, $\langle H_B^2 \rangle^{0.5}$, and the “unwet matrix” end-to-end distance is the average over the remainder of the chains. The standard deviation of the independent snapshots is shown.

(See next page)

n_p	K_{graft}	K_{matrix}	Grafting Density (chains/ σ^2)	N_{graft}	N_{matrix}	Graft $\langle R_{\text{end-end}}^2 \rangle^{0.5}$ (units of σ)	Stdev Graft $\langle R_{\text{end-end}}^2 \rangle^{0.5}$ (units of σ)	Matrix $\langle R_{\text{end-end}}^2 \rangle^{0.5}$ (units of σ)	Stdev Matrix $\langle R_{\text{end-end}}^2 \rangle^{0.5}$ (units of σ)	Wet Matrix $\langle R_{\text{end-end}}^2 \rangle^{0.5}$ (units of σ)	Stdev Wet Matrix $\langle R_{\text{end-end}}^2 \rangle^{0.5}$ (units of σ)	Unwet Matrix $\langle R_{\text{end-end}}^2 \rangle^{0.5}$ (units of σ)	Stdev Unwet Matrix $\langle R_{\text{end-end}}^2 \rangle^{0.5}$ (units of σ)
1	0	0	0.65	20	60	8.3	1.9	12.6	4.5	12.9	4.3	12.6	4.5
1	0	5	0.65	20	60	8.2	1.9	24.3	7.9	24.5	8	24.3	8.3
1	5	0	0.65	20	60	12.8	2.7	12.6	4.5	13	4.7	12.6	4.5
1	5	5	0.65	20	60	12.9	2.6	24.3	7.9	24.9	8.1	24.2	8.3
1	10	10	0.65	20	60	15.2	2.2	32.5	7.6	32.8	9.1	32.4	9.2
1	0	0	0.25	20	60	7.3	2	12.6	4.5	12.9	4.7	12.6	4.5
1	5	5	0.25	20	60	12.6	2.8	24.2	7.9	24.9	8.2	24.2	8.3
1	0	0	0.65	20	20	8.3	1.9	6.7	2.1	6.9	2.1	6.7	2.1
1	5	5	0.65	20	20	12.9	2.7	12.4	2.9	12.5	2.8	12.4	2.9
1	0	0	0.65	10	60	5.1	1.1	12.6	4.5	13	4.5	12.6	4.5
1	5	5	0.65	10	60	7.4	1	24.2	7.9	24.8	8.4	24.2	8.3
1	0	0	0.65	40	60	12.6	3.2	12.6	4.5	13	4.6	12.6	4.5
1	5	5	0.65	40	60	20.3	5.6	24.2	7.9	24.9	8.2	24.1	8.3
1	0	0	0.65	20	40	8.3	1.9	10	3.5	10.2	3.4	10	3.5
1	5	5	0.65	20	40	12.9	2.7	19.2	6	19.7	5.9	19.2	6
1	0	0	0.65	20	100	8.2	1.9	16.7	6.1	17.2	6	16.7	6.1
1	5	5	0.65	20	100	12.8	2.7	32	8.2	32.4	11.8	32	11.8
20	0	0	0.65	20	100	8.3	1.9	16.6	6.1	17.1	6.2	16.6	6.1
20	5	5	0.65	20	100	12.9	2.7	31.9	11.8	32.6	11.8	31.3	11.7

Table S3: Average radii of gyration of the graft chains. The standard deviation for all values is $<0.1\sigma$

n_p	K_{graft}	K_{matrix}	Grafting Density (chains/ σ^2)	N_{graft}	N_{matrix}	$\langle R_g^2 \rangle^{1/2}$ (σ)
1	0	0	0.65	20	60	3.0
1	0	5	0.65	20	60	2.9
1	5	0	0.65	20	60	4.5
1	5	5	0.65	20	60	4.5
1	10	10	0.65	20	60	5.0
1	0	0	0.25	20	60	2.8
1	5	5	0.25	20	60	4.4
1	0	0	0.65	20	20	3.0
1	5	5	0.65	20	20	4.5
1	0	0	0.65	10	60	1.9
1	5	5	0.65	10	60	2.6
1	0	0	0.65	40	60	4.4
1	5	5	0.65	40	60	7.4
1	0	0	0.65	20	40	3.0
1	5	5	0.65	20	40	4.5
1	0	0	0.65	20	100	2.9
1	5	5	0.65	20	100	4.5
20	0	0	0.65	20	100	3.0
20	5	5	0.65	20	100	4.5

B. Effect of polymer flexibility on trends of varying grafting density and varying matrix and graft polymer length on wetting/dewetting:

For flexible graft and matrix polymers, where the matrix length is greater than graft length, as grafting density increases, wetting of the grafted layer decreases due to increased crowding in the grafted layer⁸. As the flexibility of graft and matrix polymer chains is reduced, we see that the effect of changing the grafting density on grafted layer wetting seems qualitatively unaltered, as seen in Figure S1a and S1b. However, the percent change in the number of matrix beads that have wet the grafted layer with increasing grafting density, normalized by the lower grafting density, shows a 70% drop for $K=0$ and a 33% drop for $K=5$. This suggests that the effect of increasing grafting density on wetting of the grafted layer is reduced with decreasing flexibility. We justify this trend as follows: For flexible grafted polymers at low grafting densities, the brush height is small because the grafted chains adopt mushroom conformations on the particle. As the grafting density increases, the grafted chains adopt extended conformations and the brush height increases. In contrast, for grafted polymers with reduced flexibility, at low grafting densities, the grafted chain conformations are extended to some degree, resulting in a larger brush height than the corresponding flexible grafted polymer, and therefore significantly improved wetting. As the grafting density increases, the change in brush height for grafted chains with reduced flexibility (Figure S1b) is lower than that for flexible grafted chains (Figure S1a). This is also confirmed by the change in average radius of gyration of grafted polymer chains with increasing grafting density being smaller for semiflexible polymers than flexible polymers (Table S3). In short, decreasing the flexibility reduces the effect of grafting density on the graft conformations, brush height, and wetting behavior.

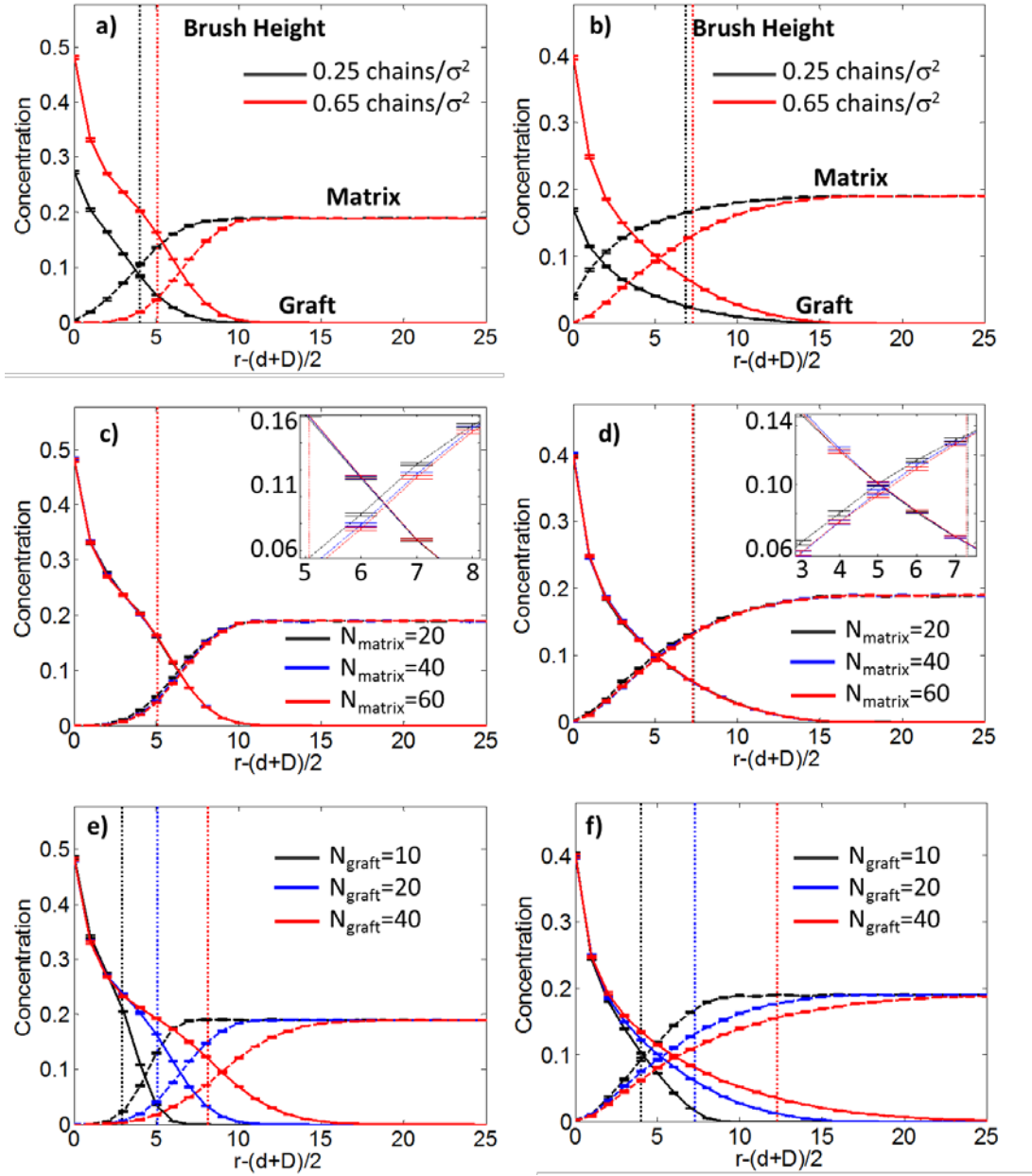


Figure S1: Graft (solid) and matrix (dashed) monomer concentration profile for single polymer grafted particle with particle diameter 5nm for $K_{\text{graft}} = K_{\text{matrix}} = 0$ (left column) and $K_{\text{graft}} = K_{\text{matrix}} = 5$ (right column) for varying polymer grafting density $= 0.25$ (black) and 0.65 (red) chains/ σ^2 with $N_{\text{graft}} = 20$ and $N_{\text{matrix}} = 60$ (in subplots a and b), varying matrix length $= 20$ (black), 40 (blue) and 60 (red) with $N_{\text{graft}} = 20$ and grafting density $0.65 \text{ chains}/\sigma^2$ (in subplots c and d) and varying graft length $= 10$ (black) and 20 (red) with $N_{\text{matrix}} = 60$ and grafting density $0.65 \text{ chains}/\sigma^2$ (in subplots e and f). The brush heights, $(H_B^2)^{0.5}$, are shown with dotted lines. The insets in subplots c) and d) have the same axes as the main figure.

In the case of flexible polymers, it is known that as the *matrix* polymer chain length increases at constant graft length, the wetting of the grafted layer by the matrix chains decreases. In Figure S1c and S1d, despite the different shapes of the graft and matrix monomer concentration profiles with decreasing flexibility, we see that decreasing flexibility does not alter how the wetting of the grafted layer by the matrix chains changes with increasing matrix chain length, both visually as well as quantitatively (using data in Table 1 of main manuscript). Our reasoning for this is as follow. In the flexible polymers case, the loss in conformational entropy of the matrix chain upon wetting the grafted layer is expected to increase slightly as the matrix polymer chain length increases (at constant graft length). Even though we know that as the flexibility decreases the matrix polymer conformational entropy decreases, both in the unwet and wet states, the trend of increasing loss in conformational entropy of the matrix chain upon wetting with increasing matrix length is likely the same as that in the completely flexible case.

In the case of flexible polymers, it is known that as the *graft* polymer length increases, at constant matrix length, the wetting of the grafted layer by matrix chains increases. While this trend is true for semi-flexible polymers as well (Figure S1e and S1f) we find quantitative differences between flexible and semi-flexible cases. Using the data in Table 1 of main manuscript, for semi-flexible polymers and $N_{\text{matrix}}=60$, going from graft length of 10 to 20, the wetting increases approximately 7 times and going from graft length of 10 to 40 the wetting increases about 35 times. In contrast for flexible polymers, going from graft length of 10 to 20, the wetting increases 10 times and going from 10 to 40 the wetting increases 77 times. This suggests that with decreasing flexibility of graft and matrix polymers, the effect of increased graft length on wetting of the grafted layer is reduced. This is likely because the wetting of the grafted layer by the matrix chain is large even at short graft length, for semi-flexible polymers

(esp. as we approach chains length close to persistence lengths), that increasing the graft length does not change the wetting as much as it does for flexible polymers.

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