Supplementary Information

Polydisperse homopolymer grafts stabilize dispersions of nanoparticles in a chemically identical homopolymer matrix: An integrated theory and simulation study

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I. Additional details about the method

A. Model

We model polymer grafted spherical nanoparticle as a hard spherical nanoparticle of diameter D with N_{graft} freely jointed homopolymer chains permanently attached symmetrically on the particle surface, and model the matrix chain as a freely jointed homopolymer chain. The polymer chains (grafted and matrix) consist of monomer beads of diameter d chosen to mimic a Kuhn segment of a linear synthetic polymer. While chains in the Monte Carlo (MC) simulations have a constant bond length, monomers in the Brownian Dynamics (BD) simulations are connected together with harmonic bonds with force constant k=30 and bond rest length $r_0=1.4d$:

$$V_H(r) = \frac{1}{2}k(r - r_0)$$
 (1)

where k is the force constant, r is the center to center distance between the bonded beads, and r_0 is the bond rest length. The grafted chains are either monodisperse, with chains of equal length (or number of monomers), or polydisperse with a log normal distribution or bidisperse with equal number of short and long chains. In the case of polydisperse grafted chains, we quantify the polydispersity via the polydispersity index (PDI):

$$PDI = \frac{E[(N_{graft})^2]}{E[N_{graft}]^2} = \frac{\overline{N}_{graft,w}}{\overline{N}_{graft,avg}} \quad (2)$$

where $E[(N_{graft})^n]$ is the nth moment of the distribution of N_{graft} , $\overline{N}_{graft,w}$ is the weight average molecular weight of the graft length distribution, and $\overline{N}_{graft,avg}$ is the number average molecular weight. For systems with graft PDI>1, we fit the chain lengths to a log-normal distribution with minimum and number average graft lengths $N_{graft,min}=8$ and $N_{graft,avg}=20$. The probability density function for the log-normal distribution is:

$$P(N_{graft}) = \frac{1}{N_{graft}\sigma\sqrt{2\pi}}\exp\left(-\frac{\left(\ln N_{graft} - \mu\right)^2}{2\sigma^2}\right)$$

where μ and σ are the mean and standard deviation of $\ln(N_{graft})$. We generate our desired chain distribution by first solving the following linear system for the log-normal distribution parameters using PDI, $N_{graft,avg}$, and $N_{graft,min}$ as inputs.

$$\mu + \frac{1}{2}\sigma = \ln(\overline{N}_{graft,avg} - N_{graft,min})$$

$$\mu + \sigma = \frac{1}{2}\ln\left[PDI(\overline{N}_{graft,avg})^2 - 2(N_{graft,min})(\overline{N}_{graft,avg}) + (N_{graft,min})^2\right]$$

The μ and σ are then used with the above equation to generate a distribution of chain lengths with the desired properties.

Supplementary Figure 1 shows the distribution of chain lengths for the system whose results are presented in Figure 1 in main manuscript.



Figure S1: Chain length distributions of polydisperse chains grafted on nanoparticles (D=5d) at $\sigma=0.1$ chains/ d^2 (a), $\sigma=0.25$ chains/ d^2 (b), $\sigma=0.65$ chains/ d^2 (c), and PDI= 1.5 (squares), 2.0 (upward facing triangles), and 2.5 (downward facing triangles) with $N_{g,avg}=20$ and $N_{g,min}=8$

II. Characterizing the distribution of grafted monomers and matrix monomers in Brownian Dynamics simulations:

In Supplementary Figure 2 - 4 we present the total monomer concentration profiles for grafted chains and matrix chains, distribution of average radius of gyration of matrix chains, end-monomer concentration profiles, respectively.



Figure S2: Total monomer concentration profiles (in units of d^{-3}) versus distance from particle surface, r-(D+d)/2 (in units of d), between grafted (filled symbols) or matrix chains (open symbols) and grafted nanoparticles (D=5d) at σ =0.65, 0.25, 0.10 chains/ d^2 and PDI= 1.0 (circles), 1.5 (squares), 2.0 (upward facing triangles), and 2.5 (downward facing triangles) with $N_{g,avg}$ =20, in a dense solution (η =0.1) of monodisperse homopolymer matrix chains with N_{matrix} =40 (top) and N_{matrix} =10 (bottom).

This figure shows that with increasing polydispersity in the grafted chains we see increasing penetration of the grafted layer by the matrix chains. The grafted chain concentration profile also shows changes with increasing polydispersity. We do not see differences near the particle surface. We see lower graft monomer concentration at intermediate distances from the particle surface for higher PDI attributed to the reduced monomer crowding brought about by polydispersity. At farther distances from particle surface we see higher graft monomer concentration at high PDI due to the presence of longer chains in the highly polydisperse distribution.



Figure S3: Average radius of gyration of the monodisperse matrix chains as a function of distance of center of mass of matrix chain from particle surface, r-(D+d)/2 (in units of d) for grafted monomers at varying polydispersity of grafted chains on nanoparticles have diameter D=5d at grafting density $\sigma=0.65$ chains/ d^2 in a dense solution ($\eta=0.1$) of monodisperse homopolymer matrix chains with $N_{matrix}=40$ (a) or $N_{matrix}=10$ (b). For both plots, the symbols correspond to the polydispersity of the grafted chains as: PDI = 1.0 (circles), 1.5 (squares), 2.0 (upward triangles), and 2.5 (downward triangles). The solid symbols represent the mean value while the open symbols represent the upper and lower limits of the error bar.

This figure characterizes the matrix conformations as a function of distance of matrix chain from the particle surface. In both cases of matrix chain lengths equal to 10 and 40 segments the error bars are large enough that we do not expect there to be a significant differences in matrix conformations as a function of distance. However we do note the slight increase in the mean matrix chain radius of gyration as the matrix chains approach the particle surface. This could be expected as the matrix chains might have to stretch while penetrating a densely grafted polymer layer.



Figure S4: End monomer concentration profiles (in units of d^{-3}) versus distance from particle surface, r-(D+d)/2 (in units of d), between grafted (filled symbols) or matrix chains (open symbols) and grafted nanoparticles (D=5d) at σ =0.65, 0.25, 0.10 chains/ d^2 and PDI= 1.0 (circles), 1.5 (squares), 2.0 (upward facing triangles), and 2.5 (downward facing triangles) with $N_{g,avg}$ =20, in a dense solution (η =0.1) of monodisperse homopolymer matrix chains with N_{matrix} =40 (top) and N_{matrix} =10 (bottom).

This figure characterizes the distribution of the end monomers of the grafted chains within the grafted layer as a function of polydispersity index. As seen in prior work by Dodd and Jayaraman where the polymer grafted nanoparticles were in an implicit matrix, we see a shift of the end monomer distribution closer to the surface and becomes narrower with increasing PDI.

III. Additional results from PRISM-MC



A. Potential of mean force (PMF) at PDI between 1 and 1.5

Figure S5: PMF (in units of kT) versus inter-particle distance, r-D (in units of d), between grafted nanoparticles (D=5d) at σ =0.65 chains/d² and PDI= 1 – 1.5 with N_{g,avg}=20, in a dense solution (η =0.1) of monodisperse homopolymer matrix chains with and N_{matrix}=40.

In the main paper at 0.65 chains/d² and $N_{matrix} > N_{g,avg}$ (open symbols in Figure 1a) the attractive well of ~0.1kT at intermediate distances seen in monodisperse systems is completely eliminated at PDI of 1.5 and above. The above figures shows additional calculations at smaller PDI (1.05-1.4) demonstrating that there is a minimum PDI needed to eliminate the attractive well. Since this minimum PDI needed to remove this attraction is dependent on the strength of the mid-range attraction (which is a function of grafting density, particle size and average graft and matrix lengths) we expect this minimum PDI to be a function of grafting density, particle size and average graft and matrix length.

B. PMF for systems with really long matrix lengths

While we only show results for $N_{matrix}=10$ and 40 in the main manuscript we have confirmed at the monodisperse graft limit that as N_{matrix} increases the attractive well at intermediate distances deepens thereby increasing particle aggregation (parts a and b), in agreement with past studies.



Figure S6: PMF (in units of kT) versus inter-particle distance, r-D (in units of d), between grafted nanoparticles (D=5d) at σ =0.65 chains/d² in a polymer solution (η =0.1) (top row) or melt-like (η =0.3) (bottom row) matrix of monodisperse homopolymer chains. Parts a and b are for monodisperse grafts of length 20 and monodisperse homopolymer matrix of N_{matrix}=10 (triangles), N_{matrix}=40 (circles), N_{matrix}=80 (squares). Parts c and d are for polydisperse grafts with PDI=2.0 and monodisperse homopolymer matrix with N_{matrix}=10 (solid circles), 40 (squares), 100 (upward triangles), 200 (downward triangles), 300 (open circles). The insets have the same axes labels as the main plots.

Parts c and d show that with grafts of polydispersity PDI=2 the mid-range attraction is weakened for all matrix lengths, and completely removed for lower matrix lengths where the mid-range attraction at the monodisperse limit (a and b) are weaker than the longer matrix lengths. This figure supports the comment in the main manuscript that as the matrix length increases we would need larger PDI to remove the tendency of the grafted particles to aggregate. In other words, larger PDI is needed to induced wetting of the grafted layer by longer matrix chains.



C. Effect of increasing matrix packing fraction on penetration depth

Figure S7: Penetration depth (in units of d) of the matrix chains into the grafted layer of nanoparticles (D=5d) with polydisperse chains $(N_{g,avg}=20)$ at $\sigma=0.10$ chains/ d^2 (circles) and $\sigma=0.25$ chains/ d^2 (triangles) in a dense solution ($\eta=0.3$) with (a) $N_{matrix}=10$ and (b) $N_{matrix}=40$.



D. Polydisperse distribution versus Bidisperse distribution

Figure S8: (left) PMF (in units of kT) versus inter-particle distance, r-D (in units of d) and graft monomer concentration profile (right) for grafted nanoparticles (**D**=5d) with monodisperse homopolymer grafts with PDI= 1.0 (blue line), polydisperse homopolymer grafts PDI=1.5 (maroon line), and bidisperse homopolymer grafts PDI=1.5 (green line), all with $N_{g,avg}$ =20 and grafting density σ =0.65 chains/d² in a in a dense solution (η =0.1) of monodisperse homopolymer matrix with N_{matrix} =40. The insets have the same axes labels as the main plots.