Supplemental Information:

Core Size Dispersity Dominates Self-assembly of Polymer-Grafted Nanoparticles in solution

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Theory:

Here, we provide a complete description of the development of the modified DC model, described in brief in the main manuscript.

We assume a polymer grafted nanoparticle with $f_0$ chains grafted on the NP core. The monomers size is $a$. Unlike the description in DC theory, all the arms are not identical. We assume a normal distribution of the number of monomers per chain. $N_i$ is the number of monomers on the $i$-th grafted chain, $\mu_n$ and $\sigma_n$ are the mean and standard deviation, respectively, of chain lengths. We allow a maximum number of monomers in a chain = $N_0$.

The complementary cumulative distribution function (CCDF) of the chains provides a “survival” probability of the chains as they radiate out from the NP core. This accounts for the polydispersity in the grafted chains and the shorter chains terminate at a smaller radial distance from the NP core relative to the longer chains. The CCDF for chains with a normal distribution is given as:

$$
\Phi^c_N(N_i) = \frac{1}{2} \left[ 1 - \text{erf} \left( \frac{N_i - \mu_n}{\sqrt{2}\sigma_n} \right) \right]
$$  (1)

In the modified DC model, we account for grafted chain polydispersity as follows. As we move radially outward from the NP core, the short chains terminate. Therefore, the number of chains grafted to the NP core that survive to a radial distance $r$ is given as $f(r)$. In contrast, in the original DC model comprising a star with monodisperse arms, the number of arms, $f_o$, is not a function of $r$ since all arms extend out to the same radial distance. In the modified DC model, we can then divide the corona into shells that, at a radial distance $r$, contain $f(r)$ blobs of size $\xi(r)$. $f(r)$ decreased radially from $f_0$ at the NP core to 0, as the number of monomers to the grafted chain end decreases following $\Phi^c_N$.

Therefore, in the spirit of the original model, the modified DC theory\textsuperscript{2,3} yields:

$$
\xi(r) = r f(r)^{-1/2}
$$  (2)

Following DC theory, the blob-size $\xi(r)$ can be given as:

$$
\xi(r) \sim an(r)^{3/5} \left( \frac{v}{a^3} \right)^{1/5}
$$  (3)

where $n(r)$ is the number of monomers per blob and, the non-dimensional monomer volume fraction is given as:

$$
\phi(r) \sim \left( \frac{r}{a} \right)^{-4/3} f(r)^{2/3} \left( \frac{v}{a^3} \right)^{-1/3}
$$  (4)

Eq. 4 explicitly assumes, $\xi(r) > l_c$, where $l_c$ is a thermal blob $\sim a(v/a^3)^{-1}$. Therefore, eqs. 3 and 4 are valid for the outer part of the star, where $r \geq r_i$ with
\[ r_1 \sim af(r_1)^{3/2} \left( \frac{v}{a^3} \right)^{-1} \]  

(5)

For \( r < r_1 \), the DC theory models each arm as a succession of growing ideal spherical blobs. Therefore, the blob size \( \xi(r) \) can be given as,

\[ \xi(r) \sim an(r)^{1/2} \]  

(6)

For \( r \leq r_1 \), the monomer volume fraction can be given as,

\[ \phi(r) \sim n(r) / \xi(r)^3 \sim (r/a)^{-1} f(r)^{1/2} \]  

(7)

Closer to the NP core, for radial distances \( r < r_2 \), the polymer chains are in a melt state, viz. monomer volume fraction is unity (\( \phi \sim 1 \)). Therefore, from eq. 7 we get,

\[ r_2 \sim af(r_2)^{1/2} \]  

(8)

This can only be realized at the highest grafting density. Therefore, we rewrite the eq. 8 as:

\[ r_2 \sim af_0^{1/2} \]  

(8.a)

In summary, a PGN with sufficiently long grafted chains characterized by a polydispersity embodied in the survival function, \( \Phi_N^c(N_i) \) consists of three regions. The inner-most region is melt-like (\( r \leq r_2 \)), and is followed by an intermediate region (\( r_2 < r \leq r_1 \)) where the blobs are ideal, and finally an outer region (\( r_1 < r \leq R \)) where the blobs are swollen. In these three regions the monomer volume fraction can be given as,

\[ \begin{align*}
\phi(r) & \sim 1, & r < af_0^{1/2} \\
\phi(r) & \sim (r/a)^{-1} f(r)^{1/2}, & af_0^{1/2} < r < af(r_1)^{1/2} (v/a^3)^{-1} \\
\phi(r) & \sim (r/a)^{-4/3} f(r)^{2/3} (v/a^3)^{-1/3}, & af(r_1)^{1/2} (v/a^3)^{-1} < r < R
\end{align*} \]  

(9)

Now, to relate the blob size to the number of monomers in that blob, we use the growing blob model postulated in the DC theory and modify this to account for the change in number of grafted chains at a distance \( r \) from the NP core. For \( r \leq r_2 \), the chain is in a melt state at the original graft density; thus, the number of grafted polymers is \( f_0 \). For \( r > r_2 \); \( f(r) \) changes with the radial distance \( r \). The diameter of the \( i \)-th blob is \( \xi_i \) (Fig. 1a, main manuscript). The radial distance to centre of the first blob is \( r_2 + \xi_1/2 \) and the surface area of the shell at that distance is \( \sim (r_2 + \xi_1/2)^2 \). The area of the blob is \( \sim (\xi_1/2)^2 \). Thus, as is evident from Fig. 1b we can write:
\[
\left( \frac{\xi / 2}{r_2 + \sum_{j=1}^{i-1} \xi_j + \xi_i / 2} \right)^2 \sim f_i^{-1}
\]

(10)

Eq. 10 is consistent with the modified DC theory described in eq. 2.

Upon generalizing eq. 10 we can write,

\[
\left( \frac{\xi / 2}{r_2 + \sum_{j=1}^{i-1} \xi_j + \xi_i / 2} \right)^2 \sim f_i^{-1}
\]

(11)

where, \( f_i = f_0 \Phi_N \left( N_{\text{min}} + \sum_{k=1}^{i-1} n_k \right) \). Here, \( \Phi_N \) is the survival function of the chain, \( N_{\text{min}} \) is the number of monomers in the inner melt region and \( n_k \) is the number of monomers in the \( k \)th shell.

Now, \( n(r) \sim \xi(r)^3 \phi(r) \), which for the range, \( af_0^{1/2} < r < af(r_1)^{1/2} (v/a^3)^{-1} \) can be written as, \( n(r) \sim \left( r / a \right)^2 f(r)^{-1} \). For the 1st blob, we have \( f_1 = f_0 \Phi_N \left( N_{\text{min}} \right) \sim f_0 \). Hence, we can write,

\[
n(r_2 + \xi_1 / 2) \sim \left( r_2 + \xi_1 / 2 \right)^2 f_0^{-1}
\]

(12)

Using eq. 12 we can iteratively estimate \( f_i \) for the \( i \)-th blob, for the range, \( af_0^{1/2} < r < af(r_1)^{1/2} (v/a^3)^{-1} \) as:

\[
n \left( r_2 + \sum_{j=1}^{i-1} \xi_j + \xi_i / 2 \right) \sim \left( \frac{1}{a} \left( r_2 + \sum_{j=1}^{i-1} \xi_j + \xi_i / 2 \right) \right)^2 f_i^{-1}
\]

(13)

Similarly, for the range, \( af(r_1)^{1/2} (v/a^3)^{-1} < r < R \), we have \( n(r) \sim \left( r / a \right)^{5/3} f^{-5/6} (v/a^3)^{-1/3} \). This can be generalized as:

\[
n \left( r_2 + \sum_{j=1}^{i-1} \xi_j + \xi_i / 2 \right) \sim \left( \frac{1}{a} \left( r_2 + \sum_{j=1}^{i-1} \xi_j + \xi_i / 2 \right) \right)^{5/3} f_i^{-5/6} (v/a^3)^{-1/3}
\]

(14)

We note that in the dilute regime, due to the rapid decrease in concentration at the free end of the chain, the last blob behaves like a Gaussian coil where, \( \xi_{\text{end}} \sim an_{\text{end}}^{3/5} (v/a^3)^{1/5} \).

This provides a general description of the grafted chains in PGNs. However, we note that, depending on the value of \( r_{c,0} \) all 3 regions described in Eq. 9 might not be present. For
example, if \( r_{c,0} > r_2 \), the innermost melt region will not be present. Similarly, if \( r_{c,0} > r_1 \), the semi-dilute region will not be present.

We now calculate the effect of chain-length distribution on the size of the polymer corona around the nanoparticle core.

Using eq. 9, one can estimate the total volume fraction (\( \varphi \)) of polymer arms (or grafted chains) in the corona, as:

\[
\varphi \sim \frac{3}{R^3} \int_{r_2}^{R} \phi(r)r^2 \, dr
\]  

(15)

The brush height can be written as, \( h_c = R - r_{c,0} \)

While here we focus on PGNs dispersed in solvent, we note that for a star polymer melt, the penetration depth (\( \lambda \)) of the matrix polymer can be obtained by a scaling approximation as,

\[
\lambda \sim (1-\varphi)^{1/3}
\]  

(16)

Thus, the penetration depth can be physically understood as a proxy of the local volume fraction of chains in the corona. Therefore, a comparison of PDI dependence of \( \lambda \), with our results, viz. the PDI dependence of \( h_t \) (Fig. S1 d) suggests that our results are in qualitative agreement with the detailed simulations of Martin et. al.\(^4\) We note that a direct comparison of our results with those of Martin et. al. cannot be made since we model PGNs in solution. However, it is encouraging that our results qualitatively match the trends that they have reported.
Table S1. A set of representative parameters for the modified DC theory for PGN dispersion in solvent. These parameters are used to obtain the data in Fig. S1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Grafted chain polydispersity</th>
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<tbody>
<tr>
<td>$a$ (nm)</td>
<td>0.7</td>
</tr>
<tr>
<td>$r, \mu_c$ (nm)</td>
<td>10</td>
</tr>
<tr>
<td>$\sigma_c$ (nm)</td>
<td>\begin{align*} PDI_c &amp;= 1.00 \quad &amp; 2 \ PDI_c &amp;= 1.10 \quad &amp; 2.6 \ PDI_c &amp;= 1.3 \quad &amp; 5 \end{align*}</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>500</td>
</tr>
<tr>
<td>$\sigma_n$ (nm)</td>
<td>\begin{align*} PDI &amp;= 1.00 \quad &amp; 10 \ PDI &amp;= 1.10 \quad &amp; 159 \ PDI &amp;= 1.2 \quad &amp; 241 \ PDI &amp;= 1.3 \quad &amp; 350 \end{align*}</td>
</tr>
<tr>
<td>$\rho_g$ (ch/nm$^2$)</td>
<td>\begin{align*} &amp;0.002 \ &amp;0.01 \ &amp;0.05 \ &amp;0.5 \end{align*}</td>
</tr>
</tbody>
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* depending on the molecular weight the values of standard deviation of polymer chain polydispersity is varied to match the polydispersity, PDI.
Figure S 1. (a) Normal distribution of monomers in the grafted polymers, characterized by different PDI (viz. 1.0, 1.1, 1.2 and 1.3) (b) Complementary cumulative density function (CCDF) for different PDI, (c) The volume fraction of monomers at different radial distances and (d) $\lambda$ vs. PDI & $h_t$ vs. PDI showing both $\lambda$ and $h_t$ increases as PDI increases.
Figure S 2. Phenomenological variation in the excluded volume parameter with molecular weight, fitted with a power-law. This is consistent with the treatment in the literature.\(^5,6\) The underlying reason for the molecular weight dependence of the excluded volume parameter is not currently understood and remains an open question. This fit is used for the results presented in Fig. 3 in the main manuscript.
Figure S3. Phase diagram of different self-assembled structure. The different phase boundaries are shown by dotted lines and the contour represents the bi-variate probability distribution on the phase diagram for mean polymer chains of 35 kDa, and PDIcon = 1.3 and PDI = 1.3. for different grafting density (a) 0.05 ch/nm² and (c) 0.01 ch/nm².
Figure S4. Distribution of different self-assemblies for PDiC = 1.3 and grafted chain polydispersity (PDI) having PDiC = 1 and 1.3 for grafting density (a) 0.002 ch/nm², (a) 0.01 ch/nm², (a) 0.05 ch/nm² and (a) 0.5 ch/nm².
Figure S 5. The effect of log-normal core size distribution on self-assembly of PGN for three different core size polydispersity (a) PDIc = 1.45, (b) PDIc = 2.33 and (c) PDIc = 4.62. The grafted chain mean molecular weight (M_w) is 15 kDa with grafting density of 0.01 ch/nm². The different hashed bars represent different PDI combinations.
Figure S 6. Log-normal distribution of core-size having mean of 10 nm and standard deviation of 2.0 nm (PDIc = 1.45), 2.6 nm (PDIc = 2.33) and 5 nm (PDIc = 4.62), respectively.

References:


