Core Size Dispersity Dominates The Self-Assembly of Polymer-Grafted Nanoparticles in Solution

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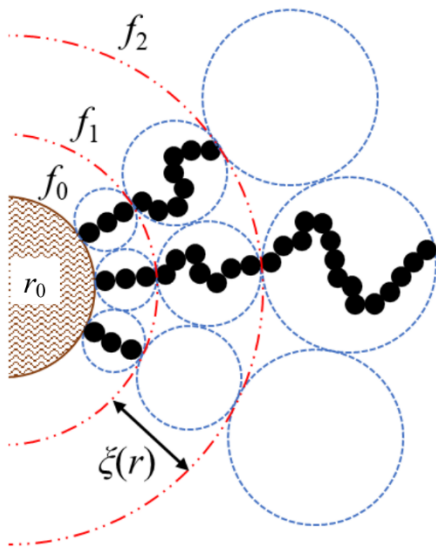[2]Department of Chemical Engineering, Columbia University, New York, New York 10025, USA

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Abstract

In polymer grafted nanoparticles (PGN), covalent tethering of apolar polymer chains to a polar inorganic nanoparticle (NP) core induces the formation of self-assembled aggregates. Since the nature of these aggregates determine bulk mechanical and transport properties, it is of importance to understand the factors that determine the underlying assembly processes. In the literature, the solution assembly of PGNs has been understood in analogy to small molecule amphiphiles. However, in any experimental realization, PGNs are invariably characterized by additional structural complexity, such as the distributions in the inorganic core size and in the grafted chains. These strongly influence the assembly of amphiphilic PGNs. We have previously demonstrated that dispersity in core size qualitatively affects the structure of PGN aggregates, and Jayaraman *et al.* have demonstrated the effect of grafted chain length dispersity. The combined effects of dispersity in the size of the core and grafted chains has not been explored previously. Here, we develop a model that builds on the work of Daoud and Cotton to explore a wide parameter space of PGN with dispersity simultaneously in core size and grafted chain length. We demonstrate that dispersity in core size is the dominant factor affecting the self-assembled solution structure of PGN aggregates. Our work suggests the importance of focusing on synthetic strategies for control of core size dispersity to control aggregate structure in PGN.

TOC:

Introduction: Controlling nanoparticle (NP) miscibility in a polymer matrix has been of considerable interest over the last two decades. This topic is particularly germane since optimal spatial filler dispersion can yield significantly improved behaviour, e.g., mechanical[1,2] and optical properties,[3] and enhanced gas permeation[4,5]. Both experiment[6,7] and theory[6,8,9] have demonstrated that grafting polymer chains onto the NPs improves their miscibility in solvents and in polymer matrices, providing a synthetic route for control of structure in NP/polymer systems. Akcora *et al.*,[6] for example, demonstrated that polymer grafted nanoparticles (PGNs) in a polymer matrix self-assembled to form a variety of aggregate structures. These workers identified the grafting densities for chains on the nanoparticle surface (ρ_g) and the ratio of the grafted chain molecular weight (M_w) to the matrix chain M_w as the two key parameters that controlled the aggregate structure. Systematic variation of these parameters afforded rational control of aggregates in a homopolymer matrix, ranging from three-dimensional, disordered structures to completely dispersed individual particles. Asai *et al.*[10] theoretically rationalized the experimental phase diagram of Akcora *et al.*[6] by invoking concepts similar to Israelachvili's geometric packing parameter. They modelled[10] PGNs as nanoparticles whose surfaces were "covered" with patches of grafted polymer chains and were able to predict the different self-assembled structures obtained experimentally.

Initial theoretical studies were on idealized PGN systems[11,12] comprised of NPs of a single core size grafted at a given grafted density with monodisperse chains in a matrix of monodisperse polymers. However, such ideal systems are not representative of experiments. Real systems are characterized by distributions in the length of grafted chains, in core NP size, in graft density on the NP surface and in chain length of the matrix polymer. Recently, it has become clear that such dispersity effects play an important role in determining the miscibility of NPs and the matrix polymer and on the self-assembled structures that form. This has implications for the properties of the nanocomposite. For example, recent studies show that nanocomposites containing PGNs with a bimodal distribution of grafted chains exhibit enhanced thermomechanical[13,14] and optical properties[15]. Therefore, there is renewed interest in predicting the effect of dispersity on self-assembly in PGNs. Jayaraman *et al.*[16–20] demonstrated using Monte Carlo simulations that increasing the dispersity of grafted chains increases the contact repulsion between monodisperse NPs, thereby improving miscibility in a polymer matrix. Bachhar *et al.*[9] demonstrated that the distribution in NP size (comparable to that observed in experiments), strongly affects NP dispersion in polymer matrices and in solvent. In particular, they showed that NP dispersity governed the formation of a variety of self-

assembled structures including dispersed NPs, strings of NPs, etc. The distribution of the number of grafted chains on NP cores has typically been modelled[21,22] as a Poisson distribution, analogous to the treatment for micelles[23,24]. However, Hakem et al.[25] established that the Poisson distribution does not accurately model the grafting process and provided a more accurate theoretical description. Bachhar et al.[9] have however demonstrated that the distribution in the number of grafted chains (comparable to that reported in the literature[25,26]) played only a secondary role, relative to the core size dispersity, in PGN assembly.

Investigations that consider dispersity simultaneously in NP size, graft density and graft chain size have not been attempted in the past, since suitable theoretical frameworks were unavailable and since such simulations were computationally very expensive. In this work we demonstrate that a direct extension of the Daoud and Cotton[27] (DC) theory, combined with a previously reported model[9] allows us to describe the assembly state of dispersions of polymer grafted nanoparticles in solution, accounting for effects of dispersity in both NP core size and grafted chain length. We use DC theory to estimate the size of a grafted polymer chain that forms the corona around a given NP core. This is subsequently coupled with the model of Bachhar et al.[9] to systematically account for dispersity in NP core size and in graft chain length. Our results establish that the assembly/miscibility of PGNs in solution is dominated by the size dispersity of the NP cores and that the dispersity in grafted chain length plays a secondary role.

Theory: We extend DC theory to obtain the mean size of the corona formed by polydisperse chains grafted on an NP core, which is dispersed in a good solvent. The DC model[27,28] considers a star polymer having f_0 arms, each having a statistical step length (monomers) of size a. This model has been generalized by Ohno et al.[29] for chains grafted to a NP of radius $r_{c,0}$ (where the chain grafting density, $\rho_g = f_0/4\pi r_{c,0}^2$). We modify DC theory to account for a distribution of grafted chain lengths as follows. We consider N_k as the number of monomers in the kth grafted chain and assume that N_k is normally distributed. (Other N_k distributions can be employed as appropriate.) We divide the star-like grafted chain into radial shells such that the shell at a distance r from the centre of the NP contains $f(r)$ blobs (arms) of size $\xi(r)$. Thus, unlike the original DC theory (Fig. 1a), the number of arms, f is no longer constant, but varies with r and is given as:

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

Since the chains are polydisperse, longer grafted chains extend further from the NP surface

than shorter chains. This is represented in terms of a "surviving" number of star arms that decreases progressively from f_0 at the NP surface to 0 at large r (Fig. 1b). We define this survival function for each grafted chain as the complementary cumulative distribution function

$$\left(\Phi_N^c(N_i) = \frac{1}{2}\left[1 - \text{erf}\left(\frac{N_i - \mu_n}{\sqrt{2}\sigma_n}\right)\right] \right) \text{ for the number of monomers from the current monomer to}$$

the free end of the polymer. This function decreases radially as short chains reach their chain ends before longer chains. Following DC theory,[27,28,30] the grafted chain thus comprises three regions, an inner melt-like region $\left(r \leq r_2, \text{ where } r_2 \sim af_0^{1/2}\right)$, a second intermediate semi-dilute region $(r_2 < r \leq r_1)$ where the blobs are ideal, and a third outer region $(r_1 < r \leq R)$ where the blobs are swollen. The monomer volume fraction, $\phi(r)$, follows,

$$\left.\begin{aligned}
\phi(r) &\sim 1, & r &< af_0^{1/2} \\
\phi(r) &\sim (r/a)^{-1} f(r)^{1/2}, & af_0^{1/2} &< r < af(r_1)^{1/2}(v/a^3)^{-1} \\
\phi(r) &\sim (r/a)^{-4/3} f(r)^{2/3}(v/a^3)^{-1/3}, & af(r_1)^{1/2}(v/a^3)^{-1} &< r < R
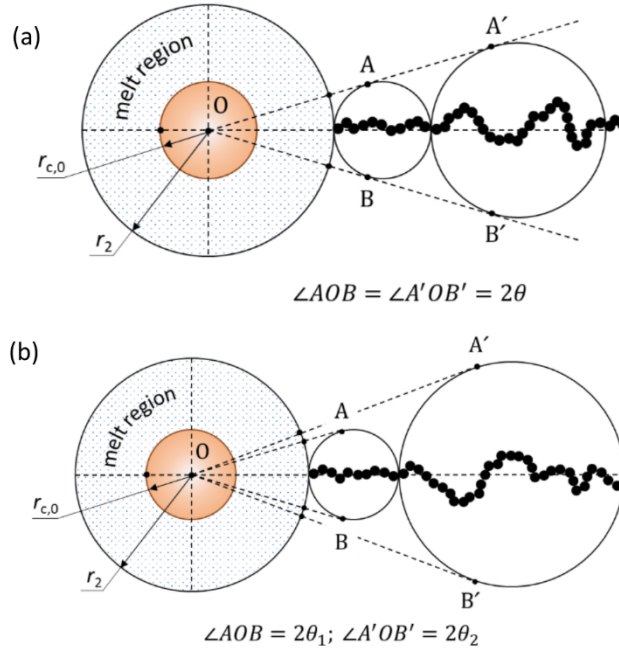\end{aligned}\right\} \quad (2)$$

Figure 1. Representation of the model. (a) DC theory without modification, the blob size for constant number of grafts f_0. (b) Modified DC theory, for polydisperse grafted chains. Short chains terminate with increasing radial distance from the NP core. Therefore, at these distances, the blob size for the longer chains increases such that $2\theta_2 > 2\theta_1$

According to DC theory, chains that radiate from a central core are modelled as blobs of radially increasing size. Here, we additionally account for the change in the number of grafted

chains at a distance r, from the centre. For $r \leq r_2$, we assume that there is no attrition in the number of chains, i.e., all f_0 grafted chains survive in the inner melt region. For $r > r_2$; $f(r)$ changes with radial distance r. From Fig. 1b, we observe that the radial distance to the centre of the first blob in region 2 is $r_2 + \xi_1/2$. The area subtended by the blob is $\sim (\xi_1/2)^2$ and the surface area of the shell is $\sim (r_2 + \xi_1/2)^2$. Thus, from Fig. 1b we can write,

$$\left(\frac{\xi_1/2}{r_2 + \xi_1/2} \right)^2 \sim f_0^{-1} \tag{3}$$

Eq. 3 is consistent with the modified DC theory described in eq. 1and can be generalized as the chain radiates outwards to yield:

$$\left(\frac{\xi_i/2}{r_2 + \sum_{j=0}^{i-1} \xi_j + \xi_i/2} \right)^2 \sim f_i^{-1} \tag{4}$$

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

Thus, we iteratively calculate f_i from eqs (3) and (4), and obtain the survival function at the ith shell. Since we know the form of the survival function, we can obtain the number of monomers in the ith shell (see Supplementary Information for detailed derivation). The survival function decays to 0 at $r = R$.

From eq. 2, one can estimate the total volume fraction (ϕ_T, which is the total volume fraction including all three regimes) of monomers in the corona as:

$$\phi_T \sim \frac{3}{R^3} \int_{r_2}^{R} \phi(r) r^2 dr \tag{5}$$

The brush height follows: $h_t = R - r_{c,0}$. We calculate h_t for an ensemble of NPs and define α (= $h_t/r_{c,0}$). The probability distribution, $P(\alpha)$, can be obtained from the h_t-distribution over the ensemble of particles. We follow Bachhar et al.[9] and Asai et al.[10] to obtain the "morphology diagram" for the PGN aggregates as a function of α. Briefly, these previous workers model PGNs as patchy particles with the patchiness defined by the number of chains grafted on the

NP core and the brush height. Interparticle interactions between PGNs are then obtained by invoking a geometric model, similar in spirit to that of Israelachviili.[31] Asai *et al.*[10] demonstrated that α represents a geometric measure for the interaction between PGNs. An increase in α promotes steric hindrance between PGNs resulting in well-dispersed, miscible PGNs in the matrix. They were able to demonstrate that a "morphology diagram" that delineates the boundaries of the self-assembled PGN clusters could be obtained in this manner. Bachhar *et al.*[9] generalized the model of Asai *et al.*[10] and demonstrated that dispersity in NP cores resulted in a distribution of self-assembled structures in polymeric matrix or in different solvents. Here, we use the method strategy developed by Bachhar *et al.*[9] and obtain the distribution of different aggregates from $P(\alpha)$. For dispersity in both the NP core size and grafted chain length, $P(\alpha)$ is obtained as the joint probability of $P_{r,h}(r_{c,0}|h_t)$ and $P_h(h_t)$, where $P_{r,h}(r_{c,0}|h_t)$ represents a conditional probability. We note that the introduction of dispersity in brush height or in core size does not change the underlying mechanism of particle assembly, as elucidated by Asai *et al.*[10] We investigate PGNs at fixed ρ_g – thus, dispersity in the size of the NP core results in varying f. The joint probability of $P(\alpha)$ and $P(f)$ represents the bivariate probability of both α and f.[9] By integrating the bivariate probability in each phase, we estimate the fraction of different types of self-assembled aggregates.
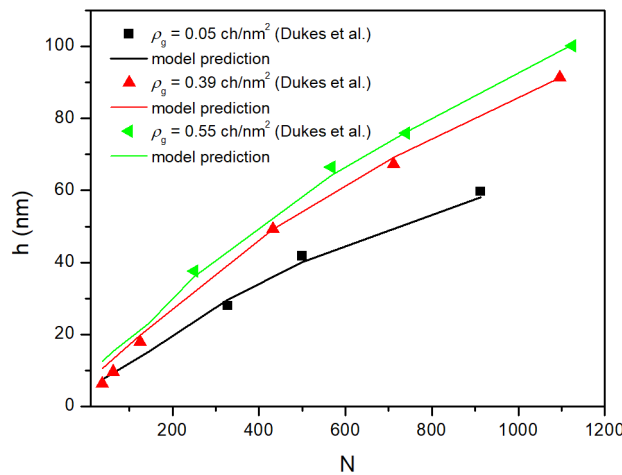

Figure 2. Comparison of prediction from the modified DC model with the experimental data of Dukes et al. for various grafted chain lengths (with known dispersity) and for different grafting density on a NP core radius =10 nm.

Results and Discussion: We validate the modified DC model by comparison with the experimental brush height data reported by Dukes *et al.*[32] (Fig. 2). For dilute dispersions of polystyrene grafted silica particles in good solvent (benzene), our model accurately describes

the experimentally obtained corona size ($h_t = R- r_{c,0}$), as long as the excluded volume parameter, v, varies with M_w (Fig S2, SI). This idea is consistent with literature[32] and we use this purely as a phenomenological parameter in our model. We note that the modified DC model is inapplicable for short chains, i.e., when the chain size is smaller than a blob. This is evident since in DC theory, short chains (viz. $f^{1/2} > N$) are in a melt state with $\phi(r) = 1$. When radially propagating grafted chains are polydisperse, short chains terminate at lower radial distances. Thus, long chains ($< f^{1/2}$) that survive beyond the short chains will not have $\phi(r) = 1$ even in regime 1. Thus, the model fails. Therefore, we are constrained to investigations where $N \gg f^{1/2}$. Following this, we limit our estimates to $N > 144$ (corresponding to $M_w > 15$ kDa).

Dispersity of grafted chain length for fixed core particle size: We now examine how dispersity in grafted chain-length affects NP self-assembly for monodisperse particle cores. Here, we implicitly assume that the NP core is solvophobic, while the chains are in good solvent. Therefore, the aggregation of the polymer grafted NPs is determined by a balance between core-core attraction and steric repulsion provide by the grafted polymer. Depletion attraction between the NPs, in the spirit of the venerable ideas of Asakura and Oosawa,[33,34] is not considered. We consider the case of PGNs in solvent and therefore, we do not consider the effect of the grafted brush on the entropy of the matrix chains as in the case of Martin *et al.*[17] Thus, our results cannot be directly compared with their work.

We assume that polydisperse chains are grafted on a NP of radius ($r_{c,0}$). The resulting effective radius of the NP includes a corona of height $= h_t$. Using the central limit theorem, we assumem , that the mean number of monomers per grafted polymer will have a normal distribution with mean μ_n and with standard deviation, $\sigma \left(\sim \sigma_n/\sqrt{f} \right)$. We note that for a given dispersity in grafted chain length and for monodisperse NP cores, each particle has the same corona size (h_t). Variations in the corona size arise only when the NP core size is varied (SI, Table S1).
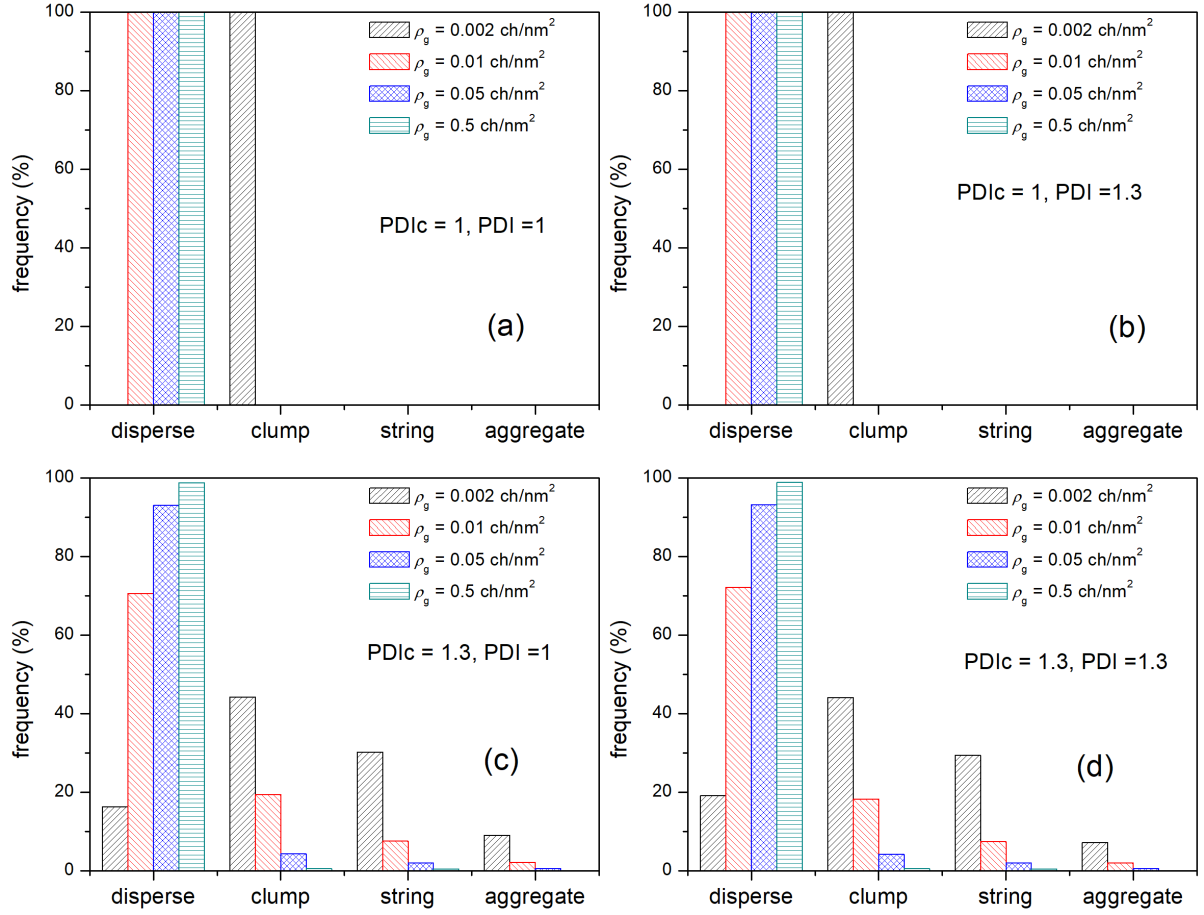
Figure 3. Distributions of self-assembled aggregate structures for variations in core NP dispersity (PDIc) and in grafted chain dispersity (PDI). (a) PDIc = 1 (μ_c = 10nm, σ_c = 0) and PDI = 1, (b) PDIc = 1 (μ_c = 10nm, σ_c = 0) and PDI = 1.3, (c) PDIc = 1.3 (μ_c = 10nm, σ_c = 5) and PDI = 1 and (d) PDIc = 1.3 (μ_c = 10nm, σ_c = 5) and PDI = 1.3. We present data at different grafting densities, namely 0.002, 0.01, 0.05 and 0.5 chains/nm^2. The y-axis represents the % fraction of NPs in various self-assembled aggregates.

We now obtain $P(\alpha)$ from the h_t-distribution. Following Bachhar *et al.*[9] we define different types of NP aggregate structures through the coordination number (CN) of the NPs, *viz.* disperse (isolated NPs, CN= 0), clumps (small aggregates, with CN= 1-3), strings (one-dimension linear aggregate, CN = 2), and aggregates (two or three-dimensional disordered aggregates, CN >3). We note that this measure cannot differentiate between sheet like two-dimensional structures and three-dimensional aggregates. We estimate the "amounts" of different phases by integrating $P(\alpha)$ over each morphology. The morphology diagram reported by Asai *et al.*[10] shows that, as α and f increase, the assemblies change from disordered 3-dimensional aggregates to sheets (2-dimensions), to strings (1-dimension), to small clumps and finally to completely dispersed particles. To examine the role of the dispersity of grafted chain lengths (PDI) we chose two PDIs, namely 1.0 and 1.3, respectively. A comparison between

Figs. 3a and 3b clearly shows that varying the grafted chain dispersity has no substantial effect on the distribution of self-assembled structured formed over the range of grafting densities investigated. We observe no effect even at low grafting densities where the system is in a mildly aggregated state.

Polydisperse grafted chains on polydisperse NP cores: We now study the combined effect of particle size distribution and grafted chain dispersity on the aggregation behaviour of the NPs. Therefore, our system is now characterized by dispersity in the NP core size (PDI$_c$) and in the grafted chain size (PDI). The dispersity in grafted chain-length remains the same as previously reported in Table S1. We assume that the core radius ($r_{c,0}$) can be described by a normal distribution quantified by mean radius ($\mu_c = 10$nm) and standard deviation (σ_c). We define the NP core dispersity in the same language as the grafted chain length PDI, as $PDIc = \dfrac{\sum_n N_i r_i^2 \big/ \sum_n N_i r_i}{\sum_n N_i r_i \big/ \sum_n N_i}$. We investigate systems with PDIc = 1.0 and 1.3 (details in Table S1). We note that the corona size, h_t is determined by the NP core size, since varying $r_{c,0}$ results in variations in the number of grafted chains, f_0 for constant graft density, ρ_g. We note that the breadth of the corona size distribution (σ_p) is obtained from the variation in h_t for the $r_{c,0}$ distribution. As explained earlier, we obtain $P(\alpha) = P_{r,h}(r_{c,0}|h_t)P_h(h_t)$ and then obtain the joint probability of $P(\alpha)$ and $P(f)$. We obtain the fraction of different self-assembled aggregates from this bivariate probability. Representative phase diagrams for two different grafting densities are reported in Fig S3 in SI.

Since α in the phase-diagram is affected by the core-size and chain-length dispersity we examine the effect of individually varying PDI and PDIc on α. Using our present model, we have estimated the α-distribution for PDI (from 1 to 1.3) and PDIc (from 1 to 1.3) at three different grafting densities, e.g. 0.01, 0.05 and 0.5 chains/nm^2 (Fig. 4). We observe that varying the grafted chain dispersity, PDI from 1 to 1.3 has only a minor influence on the α-distribution. In contrast, varying the core dispersity, PDIc from 1.0 to 1.3 significantly changes the α-distribution. We attribute this to the strong dependence of h_t on $r_{c,0}$. This is also apparent from a comparison between Figs. 3c and 3d. Thus, at the same PDI$_c$, the effect of varying PDI does not significantly affect the distribution of self-assembled aggregate structures. We note that, in our model, we account for the effect of solvent quality on the brush height through the fitted excluded volume parameter, *v*. The quantitative value of h_t is determined by the value of *v*,

Further, we also observe that as ρ_g decreases, the effect of PDI is enhanced. This is consistent with our expectations from the DC model, since $\sigma \sim f^{-1/2}$ which means σ also scales with $\rho_g^{-1/2}$
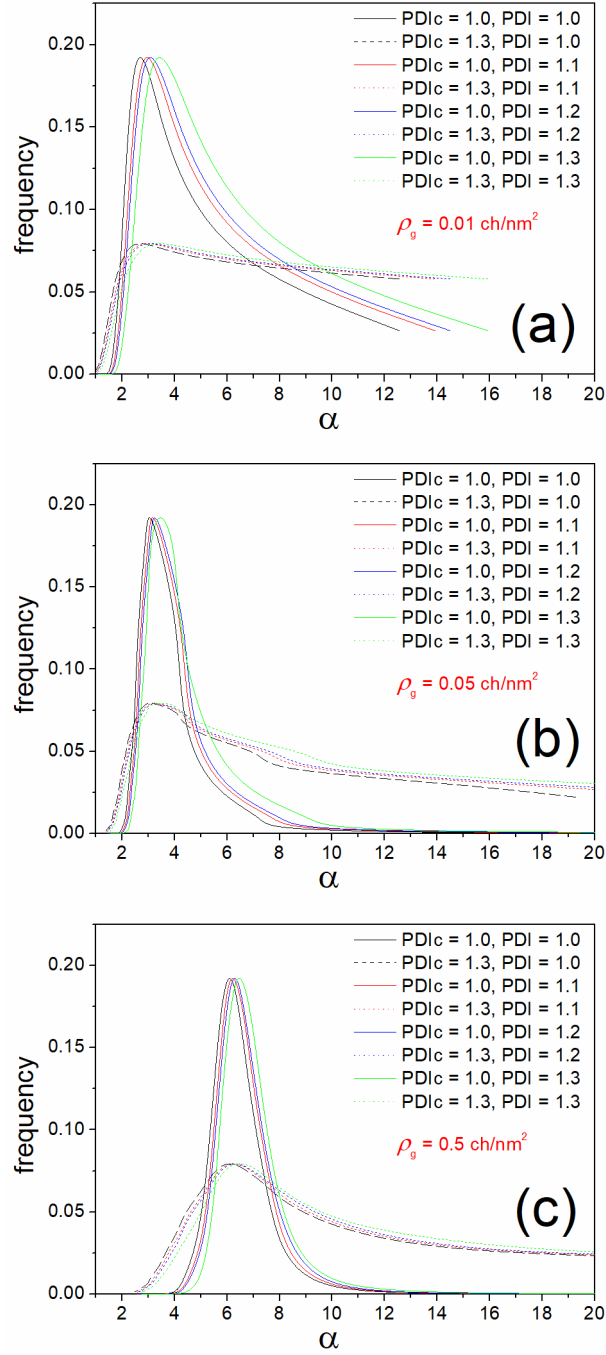

Figure 4. Effect of both grafted-chain dispersity (PDI) and core-size dispersity (PDIc) on α for different grafting densities (ρ_g): (a) $\rho_g = 0.01$ ch/nm², (b) $\rho_g = 0.05$ ch/nm² and (c) $\rho_g = 0.5$ ch/nm².

Following the same trend, we see a significant change in self-assembled structures when we change PDIc from 1 to 1.3 (Figs. 2 and 4). The system evolves from a highly aggregated state to well-dispersed PGNs by increasing the grafting density of the tethered polymer. There is a small increase in the dispersed fraction for PDIc = 1.3 (shown in SI, Fig S4) with an increase in PDI from 1 to 1.3 – however, it is clear that the effect of PDIc is dominant. This is the main result of our paper.
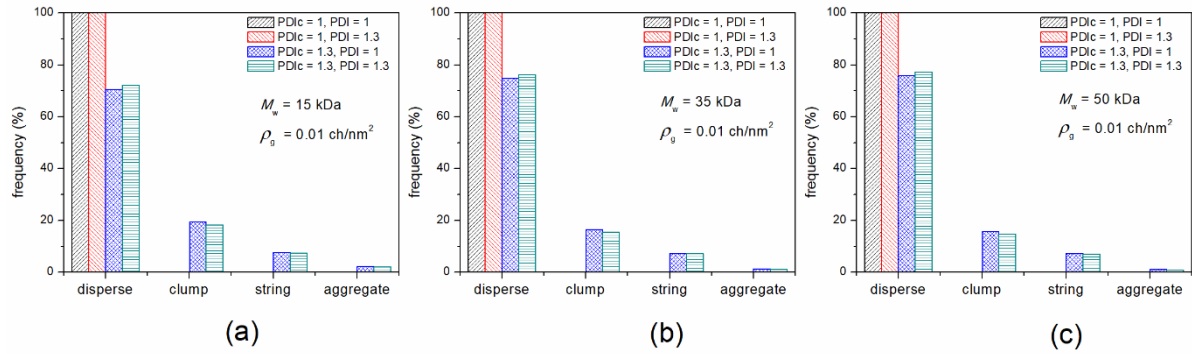

Figure 5. The effect of molecular weight (M_w) on the fraction of various self-assembled aggregates for a grafting density of 0.01 ch/nm^2. The different hashed bars represent different PDIc and PDI combinations.: (a) M_w = 15kDa, (b) 35kDa and (c) 50kDa.

Fig. 5 presents the effects of both core nanoparticle size ($r_{c,0}$) distribution (PDIc) and grafted chain length (N) distribution (PDI) on the self-assembly of PGNs across a range of graft chain lengths. We see that as we increase the dispersity of grafted chains, the dispersed fraction increases, consistent with the findings of Jayaraman *et al.*[16,17,35] However, we continue to reiterate that NP core dispersity (PDIc) strongly determines the fraction of dispersed PGNs, and this effect dominates over the effect of grafted chain dispersity. This conclusion is robust to changes in the shape of the core size distribution. For example, we have modeled a system where the nanoparticle core is characterized by a log normal distribution (as compared with the normal distribution for which results have been presented in this work). Specifically, we use a mean NP core size = 10 nm with standard deviations of 2.0 nm, 2.6 nm and 5 nm, matched with the data presented in Figures 3 and 5. We note that for a log normal distribution of core size, these standard deviations correspond to dispersities of PDIc = 1.45, 2.33 and 4.62, respectively. We observe that varying the grafted chain dispersity, PDI, has only a marginal effect on the shape of the self-assembled aggregates (Supporting Information, Fig. S5, S6). However, changing the core dispersity, PDIc qualitatively changes the nature of the self-

assembled aggregates (Supporting Information, Fig. S5, S6).

Our results suggest that to obtain a specific desired self-assembled state, it would be more profitable to focus on synthetic strategies aimed at controlling the size distribution of the inorganic nanoparticles used in PGN nanocomposites, rather than in control of grafted chain length dispersity. We note that there have been significant advances in synthetic methodologies to obtain highly monodisperse metal nanoparticles.[36,37] These systems are amenable to surface grafting using thiol-terminated polymer chains. Our results indicate that exploration of composites synthesized using such materials could represent an interesting future experimental direction.

We reiterate that the results presented here are for dispersions of PGN in a good solvent for the grafted chains. Therefore, effects that are relevant in polymeric matrices, such as, for example, the effect of the grafted chains on matrix chain conformations are not considered here, precluding a direct comparison of our results with the literature on PGNs in polymer melt matrices. It is possible to extend[27] the modified DC model for melt matrices – this is a promising avenue for future work.

Conclusions:

In this work, we present a direct extension of the Daoud and Cotton[27,28] model for star polymers that allows us to investigate a wide parameter space for PGNs. We investigate the effect of dispersity simultaneously in the core NP size and grafted chain lengths for dispersions of PGNs in solvent. Our results indicate that NP dispersion can be improved by increasing the dispersity in grafted chain length, consistent with the previous work of Martin *el al*.[17] However, we show that increasing the dispersity in core nanoparticle size distribution strongly diminishes the enhancement in dispersion due to chain-length dispersity. We conclude that well-dispersed GNPs in solution can be obtained by reducing particle dispersity and enhancing chain dispersity. The structure of self-assembled GNP aggregates is determined primarily by the dispersity in core NP size.

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