Polydispersity for Tuning the Potential of Mean Force between Polymer Grafted Nanoparticles in a Polymer Matrix

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We present an integrated theory and simulation study of polydisperse polymer grafted nanoparticles in a polymer matrix to demonstrate the effect of polydispersity in graft length on the potential of mean force between the grafted nanoparticles. In dense polymer solutions, increasing polydispersity in graft length reduces the strength of repulsion at contact and weakens the attractive well at intermediate interparticle distances, completely eliminating the latter at high polydispersity index. The reduction in contact repulsion is attributable to polydispersity relieving monomer crowding near the particle surface, especially at high grafting densities. The elimination of the midrange attractive well is attributable to the longer grafts in the polydisperse graft length distribution that introduce longer range steric repulsion and alter the wetting of the grafted layer by matrix chains. Dispersion of the grafted particles is stabilized by increased penetration or wetting of the polydisperse grafted layer by the matrix chains. This work demonstrates that at high grafting densities, polydispersity in graft length can be used to stabilize dispersions of grafted nanoparticles in a polymer matrix at conditions where monodisperse grafts would cause aggregation.

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Controlling the morphology of nanoscale additives in a polymer matrix is critical for tuning the macroscopic properties of the resulting polymer nanocomposite. One way to manipulate the morphology is by grafting the nanoparticle surface with polymers that are compatible with the matrix polymer and, as a result, tuning the interactions between the grafted nanoparticles and the polymer matrix. A recent comprehensive review by Green [1] presents the extensive theoretical and experimental work that has shown that the molecular weights of the grafted and matrix polymer play a critical role in dictating the interparticle interactions, both at high and low grafting density [Ref. [1], and references therein]. At high grafting density, where the grafted chains are in the "strong brush" regime, nanoparticles disperse (aggregate) if the graft molecular weight is higher (lower) than matrix molecular weight with dispersion and aggregation being driven by wetting and dewetting of the grafted layer by matrix chains, respectively [1]. At low grafting density, larger graft molecular weight chains can better shield nanoparticles from direct particle-particle contacts and lead to dispersion of grafted particles in the polymer matrix [2]. Additionally, by tailoring the graft and matrix molecular weights along with the grafting density, one can further tune the shape of particle aggregation in the nanocomposite [3]. Despite the importance of graft molecular weight for controlling the morphology, experimental and theoretical studies on polymer grafted nanoparticles have not investigated how polydispersity in the grafted chains affects the morphology of the particles in a polymer matrix.

Past studies have shown that polydispersity in chain lengths grafted on flat surfaces [4,5] can alter chain conformations and the overall height of the grafted layer on these surfaces (with no curvature). Star polymers with polydisperse arms can be thought of as polydisperse polymers grafted on a nanoparticle with infinitely large curvature. The effective force F between polydisperse star polymers in a good solvent has been shown to have a drastically different expression as compared to monodisperse star polymers [6,7]. While these past studies justify further exploration of polydispersity effects, they do not predict the behavior of polydisperse polymers grafted on spherical hard nanoparticle surfaces with finite curvature in the presence of an explicit polymer matrix. Recently, using Monte Carlo (MC) simulations [8], Dodd and Jayaraman studied a single spherical polymer grafted nanoparticle with polydisperse grafted chains, in an implicit solvent, at a purely athermal limit, for varying polydispersity indices (PDI $>$ 1–2.5), particle diameter, and grafting density. Dodd and Jayaraman showed that the conformations of the grafted chains in a polydisperse system deviates significantly from the monodisperse counterpart and approaches that of a single chain grafted on the same particle size because of polydispersity-induced relief in monomer crowding. Specifically, the radius of gyration of the short chains was lower at PDI > 1 than at PDI $= 1$ (monodisperse), and the long chains were less stretched at distances away from the particle surface at PDI > 1 than at PDI $= 1$. These observations demonstrate that the chain conformations on hard nanoparticles with finite curvature are significantly affected by polydispersity in the grafted chain lengths. This leads to the question: Is the effect of polydispersity on grafted chain conformations large enough to alter how matrix chains wet, dewet, or deplete the grafted layer? If yes, is this change in matrix wettability of the grafted layer predictable so that one could deliberately introduce polydispersity as a design knob to tailor interparticle interactions? In this Letter, we answer these questions by exploring how polydispersity in polymer chains grafted on nanoparticles affects the potential of mean force (PMF) between the polymer grafted nanoparticles at varying grafting densities (e.g., low, intermediate, and high), in a dense solution of matrix polymers and melt-like polymer matrix at varying matrix lengths (e.g., less than and greater than average graft length) using a combined polymer reference interaction site model (PRISM) theory–Monte Carlo simulation approach. One of the key results is that, at high grafting density, polydispersity in the grafted polymers can stabilize dispersions in a monodisperse polymer matrix at conditions where corresponding monodisperse polymer grafted particles would exhibit aggregation.

We use a self-consistent PRISM theory–MC simulation approach to calculate the PMF for a system of a polymer matrix (dense solution and melt) with polymer grafted particles (filler) at infinitely dilute filler concentration. The details of the PRISM-MC method, including the choice of closures for the PRISM part and the limitations of the method are presented in Ref. [9], where this approach is reviewed in detail, and applied to study polymer grafted nanoparticles in polymer matrix. An overview of this method is presented in the Supplemental Material [10]. In this work, polydispersity in the grafted chains is modeled using a log-normal distribution of chain lengths to achieve a target polydispersity index (PDI) while maintaining the average graft length, $N_{g,\mathrm{avg}}$, constant at 20 Kuhn segments and minimum graft length of 8 Kuhn segments (or "monomers"). The particle diameter (D) is maintained as either 5 or 8 times the monomer diameter (d). We vary the grafting density σ in the range 0.1–0.65 chains/d^2, the matrix chain length N_{matrix} from 10 to 80 monomers, and total packing fraction η of the nanocomposite from 0.1 to mimic the matrix as a dense solution to 0.3 to mimic melt-like polymer matrix. We model all pairwise interactions in the system to be hard sphere (athermal) interactions to capture the purely entropic effects of introducing polydispersity. These athermal interactions are also appropriate to mimic experimental systems where the graft and matrix monomers have similar chemistry, and particle-monomer interactions are negligible.

First, we present the PMF between polymer grafted nanoparticles, calculated as $\mathrm{PMF} = -k_B T \ln[g_{\text{particle-particle}}(r)]$, for particle size $D = 5d$ at $\sigma = 0.1$ chains/d^2 placed in a dense solution ($\eta = 0.1$) of monodisperse polymer matrix [Fig. 1(a)]. When $N_{\mathrm{matrix}} = 10$ (solid symbols) and graft PDI $= 1.0$ (monodisperse), the PMF exhibits repulsion at contact and no attractive well at intermediate interparticle distances, which is in agreement with past experiments and theoretical studies for these lightly grafted systems (see review articles [1,11]). As the graft PDI increases, the PMF becomes slightly less repulsive at contact and slightly more repulsive at larger distances [Fig. 1(a), inset]. When $N_{\mathrm{matrix}} =$ 40 (open symbols) and graft PDI $= 1.0$, the PMF is repulsive

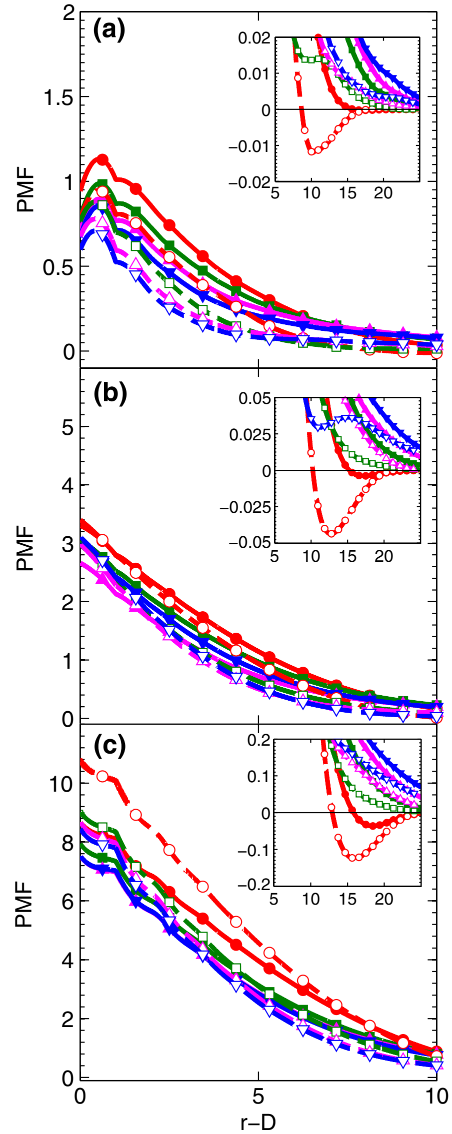

FIG. 1 (color online). PMF (in units of kT) versus interparticle distance, r-D (in units of monomer diameter d), between grafted nanoparticles ($D = 5d$) at $\sigma = 0.1$ (a), 0.25 (b), and 0.65 (c) chains/d^2 and PDI $= 1.0$ (circles), 1.5 (squares), 2.0 (upward facing triangles), and 2.5 (downward facing triangles) with $N_{g,\mathrm{avg}} = 20$, in a dense solution ($\eta = 0.1$) of monodisperse homopolymer matrix chains with $N_{\mathrm{matrix}} = 10$ (solid symbols) and $N_{\mathrm{matrix}} = 40$ (open symbols). The insets have the same axes labels as the main plots.

at contact and exhibits a weak attractive well at intermediate lengths. As graft PDI increases, the PMF loses the weak attractive well completely and exhibits purely repulsive PMF [Fig. 1(a), inset]. Additionally, for both matrix lengths as PDI increases, the repulsive tail in the PMF increases in strength and extends to larger interparticle distances. The decrease in repulsion at contact is driven by the polydisperse grafted polymers relieving some monomer crowding near the particle surface by causing a change in grafted chain conformations to maximize overall conformational entropy upon introduction of polydispersity, as seen in a recent study [8]. That study also showed that the effect of polydispersity on chain conformations is relatively minor at low grafting densities and more drastic at higher grafting densities where chain crowding is strong at the monodisperse limit. Therefore, one can expect that the attractive well at intermediate interparticle distances, which was negligible at 0.1 chains/d^2 [Fig. 1(a)], could be more significant at higher grafting densities and that the elimination of the attractive well could be more pronounced at higher grafting densities when polydispersity is introduced than seen at 0.1 chains/d^2.

At higher grafting densities of $\sigma = 0.25$ [Fig. 1(b) and 0.65 chains/d^2 [Fig. 1(c)], as expected from prior theoretical and experimental work on monodisperse grafts [1], we see that the repulsion at contact and attraction at intermediate distances increase in strength significantly compared to low grafting density, especially when N_{matrix} is larger than $N_{g,\mathrm{avg}}$. While we only show $N_{\mathrm{matrix}} = 10$ and 40 here, we have confirmed as N_{matrix} increases the attractive well at intermediate distances deepens (Supplemental Material [10]). We note that, for a few systems at the highest grafting density (0.65 chains/d^2) only, where matrix chains are expected to deplete or dewet large regions in the grafted layer near the particle surface, the choice of Percus-Yevick closure leads to negative values in $g_{\mathrm{matrix\text{-}particle}}(r)$ at low r [where $g_{\mathrm{matrix\text{-}particle}}(r)$ should be 0], owing to numerical issues. We also add that, for these specific systems, all other pair correlation functions are devoid of this issue and do not exhibit any negative values. Despite this issue, we note that PRISM-MC simulations correctly predict all known (qualitative and some quantitative) trends in monodisperse systems: (a) with increasing grafting density the midrange attractive well deepens and shifts to higher interparticle distances (Fig. 1); (b) with increasing matrix chain length the attractive well depth deepens (Supplemental Material [10]); (c) the value of the well depth seen at 0.65 chains/d^2 is of the same order of magnitude (~0.3–0.5 kT in Supplemental Material [10]) as that seen for similar systems in recent simulation studies [12,13] on systems with graft length of 10 monomers and matrix lengths of 10–70 monomers, and particle sizes approximately 10 times monomer size at high grafting density (~0.76 chains/nm^2). The ability of PRISM-MC simulations to predict the same qualitative trends as other theoretical methods [14], and, in certain cases quantitative agreement with prior simulations [12,13], for monodisperse grafts suggests that this approach is capable of predicting correct qualitative trends for the polydisperse polymer grafted nanoparticles as well.

Continuing our discussion of higher grafting densities, as PDI increases the repulsion at contact is reduced more significantly at 0.65 chains/d^2 for $N_{\mathrm{matrix}} = 40$ [Fig. 1(c)] than at smaller grafting densities. This is because, at higher grafting densities, increasing polydispersity relieves the higher monomer crowding in the grafted layer at the monodisperse limit. This is confirmed by the end-monomer concentration profiles that show larger values near the particle surface with increasing polydispersity, implying higher accessibility of the particle surface (Supplemental Material [10]). The higher accessibility of the particle surface by end monomers is because of the shorter chains in the distribution as well as the changes in chain conformations attributable to reduced monomer crowding resulting from a wider grafted chain length distribution [8].

Most interestingly, at 0.65 chains/d^2 and $N_{\mathrm{matrix}} > N_{g,\mathrm{avg}}$ [open symbols in Fig. 1(c)] the attractive well of $\sim$0.1 kT at intermediate distances seen in monodisperse systems is completely eliminated at PDI of 1.5 and above. Additional calculations at smaller PDI (1.05–1.4) (Supplemental Material [10]) found that there is a minimum PDI needed to eliminate the attractive well, and we expect this minimum PDI to be a function of grafting density, particle size, and average graft length. The attractive well is eliminated at higher PDI because the longer chains in the polydisperse chain length distribution (a) sterically repel the longer chains on the other grafted particle, and (b) shift the entropic contributions more heavily toward the grafted chains than matrix chains, thus driving matrix chains to wet the grafted layer. The latter is confirmed from increasing penetration depth of the matrix chains into grafted layer, λ, (Fig. 2) with increasing PDI. Since λ is a measure of the average distance the matrix chains penetrate the grafted layer on the surface (Supplemental Material [10]), Fig. 2 implies increased matrix wetting of the grafted layer with increasing PDI. Since the midrange attractive well has been shown to drive the nanoscale additives in

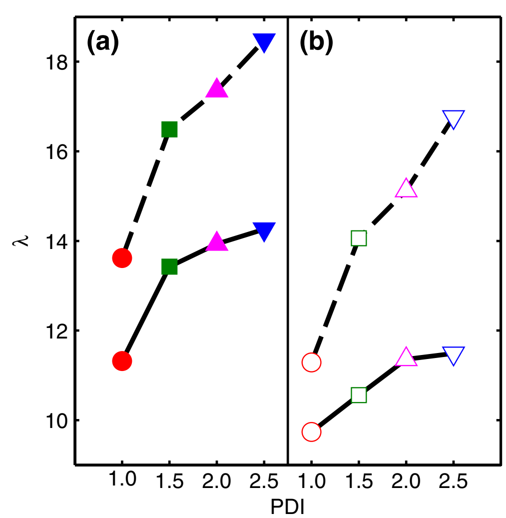

FIG. 2 (color online). Penetration depth, λ (in units of d), of matrix chains into grafted layer on nanoparticles ($D = 5d$) grafted with polydisperse chains with $N_{g,\mathrm{avg}} = 20$ at $\sigma = 0.10$ chains/d^2 (solid lines) and $\sigma = 0.25$ chains/d^2 (dashed lines) in a dense solution ($\eta = 0.1$) of monodisperse homopolymer matrix chains with $N_{\mathrm{matrix}} = 10$ (filled symbols) and $N_{\mathrm{matrix}} = 40$ (open symbols).

polymer nanocomposites toward aggregation, eliminating the attractive well because of increased wetting of the grafted layer suggests the exciting possibility of using polydispersity as a means to stabilize dispersions in systems where monodisperse grafts would drive aggregation.

To ensure that our choice of a specific discretized chain length distribution, which mimics a continuous log-normal distribution, does not bias the above results, we calculated the PMF for five different chain length distributions (all log-normal) for a select number of systems and found no significant change in PMF in either the repulsion at contact or the attractive well (Supplemental Material [10]) in dense solutions. In contrast, when we compare PMFs from particles grafted with a log-normal chain length distribution to those grafted with a bidisperse chain length distribution at the same PDI, we observe some differences in both low-r repulsion and midrange attraction (Supplemental Material [10]), and is the subject of our ongoing investigation.

All the results presented so far are at a total packing fraction of $\eta = 0.1$, which is characterized as a dense solution rather than a melt through calculations of the compressibility from the structure factor $S(k)$ as $k \to 0$ [15]. At a melt-like packing fraction of $\eta = 0.3$, the matrix polymers have been shown to induce depletion like attractions between both bare and polymer grafted nanoparticles at infinitely dilute concentrations. This matrix-induced depletion-like attraction at low grafting densities shows up in the PMF as an attraction at contact [Fig. 3(a)] and, at high grafting densities, significantly reduces the steric repulsion at contact [Fig. 3(b)] and deepens the mid-range attractive well [inset of Fig. 3(b) versus Fig. 1(c)]. At low grafting density [Fig. 3(a)], the effects of polydispersity are reduced for $\eta = 0.3$, as compared to $\eta = 0.1$, as the values of attraction at contact ($\sim$3 kT) dominate at all PDI. Therefore in these conditions, polydispersity in grafted chains cannot overcome the matrix-induced aggregation of the particles. At high grafting density [Fig. 3(b)], comparing $\eta = 0.3$ and $\eta = 0.1$, the repulsion at contact is less sensitive to PDI for $\eta = 0.3$, and a larger PDI is needed to eliminate the stronger attractive well at intermediate distances at $\eta = 0.3$ [inset of Fig. 3(b)]. These results lead us to conclude that, for melt-like polymer matrices, one can stabilize dispersions using polydispersity only at high grafting densities, and the extent of polydispersity needed to stabilize dispersions is higher as compared to dense polymer solutions.

Past studies have shown that the relative graft length to particle diameter is an important parameter driving dispersion or aggregation in a polymer matrix [2,16]. Higher D or lower curvature leads to increased monomer crowding, especially at high grafting densities. At PDI = 1.0 and at $\sigma = 0.1$ chains/d^2 the repulsion at contact and midrange attraction is higher in the PMF for $D = 8d$ than in the corresponding PMF for $D = 5d$. This is in accordance with previous studies of monodisperse grafts [2,16] that showed that decreasing curvature increases the monomer crowding near the particle surface and decreases the propensity of matrix wetting the grafted layer. We see that at low grafting densities varying polydispersity of grafts on $D = 8d$ brings about approximately the same effect as that seen for $D = 5d$ (Supplemental Material [10]). A detailed study of how curvature affects the polydispersity-induced stabilization at a range of parameters is the subject of ongoing work.

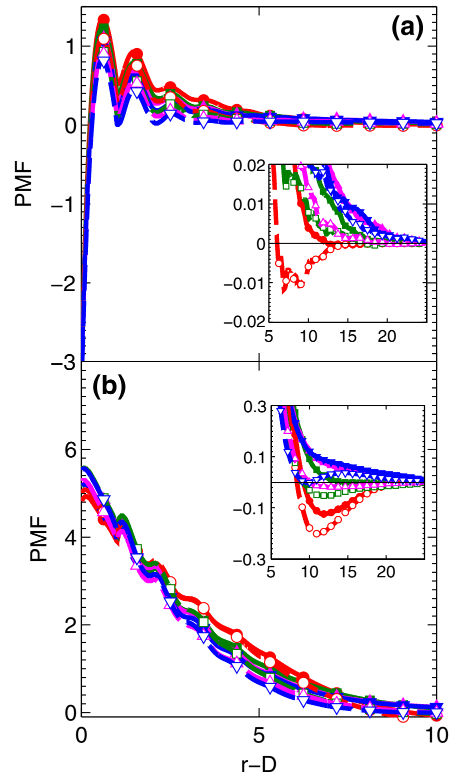

FIG. 3 (color online). PMF (in units of kT) versus r-D (in units of monomer diameter d) between nanoparticles ($D = 5d$) at PDI = 1.0 (circles), PDI = 1.5 (squares), PDI = 2.0 (upward facing triangles), and PDI = 2.5 (downward facing triangles) and $N_{g,\mathrm{avg}} = 20$ at (a) $\sigma = 0.1$ and (b) 0.65 chains/d^2 in a monodisperse meltlike matrix ($\eta = 0.3$) with $N_{\mathrm{matrix}} = 10$ (solid symbol) and $N_{\mathrm{matrix}} = 40$ (open symbol). The insets have the same axes labels as the main plots.

In summary, this is one of the first studies demonstrating how increasing polydispersity in polymers grafted on spherical nanoparticles affects the PMF between homopolymer grafted nanoparticles in a homopolymer matrix. The effect of polydispersity is greatest at high grafting densities where polydispersity in grafted chain lengths has the largest effect on chain conformations [8] and the midrange attraction is eliminated with increasing polydispersity. The implications that polydispersity can stabilize dispersions, even when the average graft molecular weight is lower than the matrix molecular weight, conditions that cause particle aggregation for monodisperse grafts, are exciting since much of the polymer synthesis community has been striving to achieve low polydispersity. This study motivates synthetic efforts to be directed toward obtaining controlled polydispersity in chain lengths as a design tool to program interparticle interactions in a polymer matrix.

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