Mixing–Demixing Transition in Polymer–Grafted Spherical Nanoparticles

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Polymer-grafted nanoparticles can provide property profiles that cannot be obtained individually by polymers or nanoparticles. Here, we have studied the order–disorder transition of symmetric copolymer melts of polymer-grafted nanoparticles with spherical nanoparticles by means of coarse-grained molecular dynamics simulation and a theoretical model. We find that larger size of nanoparticles leads to higher stability for given number of grafted chains and chain length reaching a point where demixing is impossible. Our results also suggest that there is a transition region, where the steric interactions of the core particles are shielded by a growing effective attractive core of the tethered polymer chains with a nontrivial dependence. We anticipate that our study will open new doors in the understanding of these systems with implications in materials science and medicine.

Introduction. Inorganic nanoparticles (NPs) dispersed in polymer hosts have attracted much attention over the last decades in multiple technological areas, such as electronics, medicine, and others.1,2 In these applications, nanocomposite materials have property profiles that cannot be obtained by using polymers or NPs alone, for example, NPs in a polymer host must avoid aggregation. However, creating homogeneous mixtures of NPs and polymers turns out to be challenging, due to the attractive van der Waals forces between NPs and the polymer-mediated depletion interactions.4,5 A possible solution to this problem is NPs grafted with polymer chains,6,7, known as polymer-grafted or polymer-tethered NPs (PGNPs), which can be self-suspended with homogeneous particle dispersion in the absence of any solvent.8,9 Density functional theory has indicated that the phase stability is due to the space-filling constraint on the grafted corona chains, which leads to an effective attraction of entropic origin between NPs, which is also mediated by the attached polymer chains. In this case, the Flory–Huggins parameter may be larger and more negative.11,12 Another reason for the steric stabilization of the NPs may be the absence of the solvent and the presence of incompressible polymer chains. This results in the suppression of long wavelength fluctuations that induces an effective attraction between the particles.10,13,14 The constraints on the corona imposed by space-filling have been in the centre of attention of recent work, and in particular, the dependence on the core particle size,15,17 chain length,18,19,21 grafting density,22,23 and temperature.24

A theoretical description of the phase behavior for PGNP mixtures based on arguments of the Flory–Huggins theory25 is challenging, even for the most symmetric cases in composition and molecular architecture. This is due to the fact that the theoretical assumptions related to a necessary effective parameter that describes systems of PGNPs require extensive testing and validation with experimental and simulation results. This effective parameter would correspond to an effective chain length of effective polymer chains, which is also mediated by the attached polymer chains. In this case, the Flory–Huggins parameter may be larger and more negative. Another reason for the steric stabilization of the NPs may be the absence of the solvent and the presence of incompressible polymer chains. This results in the suppression of long wavelength fluctuations that induces an effective attraction between the particles. The constraints on the corona imposed by space-filling have been in the centre of attention of recent work, and in particular, the dependence on the core particle size, chain length, grafting density, and temperature. Recently, there has been also studies of PGNPs in blends with chemically distinct polymers focusing on the physical properties, structure, and underlying dynamics of these systems. This latter work has been corroborated with theoretical results that allowed the estimation of the heat of mixing of the PGNP blends as a function of the volume fraction of the system.
standing towards the design of PGNPs structures, useful for advanced applications in materials science, medicine, and beyond.

**Molecular Dynamics Simulations.** We implemented MD simulations of a standard bead-spring model in the NPT ensemble by using the large-scale atomic/molecular massively parallel simulator (LAMMPS) [29]. The pressure and temperature of the system was fluctuating around predefined values during the course of the simulation. In our case, the temperature was $T = 0.8\epsilon/k_B$ with $\epsilon$ being the unit of energy and $k_B$ the Boltzmann constant, while the pressure, $P$, corresponded to the ambient pressure. Each simulated PGNPs copolymer melt consists of 500 molecules placed in a cubic simulation box with periodic boundary conditions applied in all Cartesian directions. Each molecule is composed of a spherical core particle with diameter, $D$, which are labelled in our model with the index ‘c’. Here, we have considered the cases $D = 1, 4$, and 7, which are suitable for our simulations [9,12]. Linear polymer chains of either type A or B monomers are grafted to each core NP with grafting density $d_g = A_c/N_g$, where $A_c = \pi D^2/4$ is the surface area of the core particle, and $N_g$ is the number of grafted chains. The number of grafted chains, which is the same for all PGNPs in the melt, ranges in this study from 5 to 40 when $D = 4, 7$, while for $D = 1$ the maximum possible number of grafted chains is $N_g = 15$, due to the small size of the core NP. A previous study has determined that the maximum number of grafted chains for the $D = 1$ case is $N_g = 16$ [9]. Moreover, grafted polymer chains are homogeneously distributed on the NP’s surface by using the Fibonacci lattice (Fig. 1, upper left panel). The length of the polymer chains is $N$, which ranges from 5 to 40. Thus, our melts are symmetric in architecture and composition, namely each NP has the same number of polymer chains with the same length, while half of these PGNPs have type A polymer chains and the other half has tethered polymers of type B. Beads of type $c$, $A$, and $B$ interact by means of the Lennard–Jones (LJ) potential

$$U_{LJ} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right],$$  

where $r_{ij}$ is the distance between any beads of type $i$ and $j$. The potential is cut and shifted with the cutoff distance for the interactions between polymer beads being $r_c = 2.5\sigma_{ij}\sigma$, where $\sigma$ is the unit of length. The cutoff distance between any pair of interactions that involve the core particle is set to $21/6\sigma_c\sigma$. The potential parameters in our case are $\sigma_{AA} = \sigma_{BB} = \sigma$ and $\epsilon_{AA} = \epsilon_{BB} = \epsilon$. In our study, the size of the spherical NPs varied, namely we explored the cases $D = \sigma_{cc} = \sigma, 4\sigma$ and $7\sigma$. Also, the cross-interaction $\epsilon_{AB}$ between A and B beads, which is used to cross the order–disorder transition, typically varied between 0.5$\epsilon$ and 1.0$\epsilon$. Hence, the degree of incompatibility between type A and B polymer chains is introduced by varying $\epsilon_{AB}$ [26]. Polymer chains are fully flexible and they are connected by harmonic bonds, namely $V_h = k(r - r_0)^2$, where $r_0 = \sigma$ is the equilibrium bond length and $k = 10000\epsilon/\sigma^2$ is a constant. Grafted beads are immobile on the surface of the core NP. Depending on the particular parameters, we run our simulations up to $10^9$ MD times steps, with each time step corresponding to $\delta t = 0.005\tau$, where $\tau = \sigma(m/\epsilon)^{1/2}$ is the natural time unit. Each simulation at a lower $\epsilon_{AB}$ is a continuation of a previous simulation at higher $\epsilon_{AB}$. This procedure was employed for different initial snapshots.

**Results and Discussion.** Our results obtained by MD simulations are summarised in Fig. 2 where the phase diagrams for two different cases are illustrated ($D = 1$ and 4) as a function of the polymer chain length $N$ and the number of grafted chains $N_g$. The color bar indicates the value of the parameter $\epsilon_{AB}$ for which PGNPs with different type of grafted polymer chains can separate adopting morphologies such as the ones shown in Fig. 1 (right panel). Lower values of $\epsilon_{AB}$ indicate higher demixing difficulty, whereas larger values of $\epsilon_{AB}$ indicate much easier demixing of the PGNPs. Figure 1 also illustrates examples of mixed (disordered, middle panel) and demixed (ordered, right panel) states. Therefore, the value of $\epsilon_{AB}$ relates to the ODT of our systems. The phase diagram for $D = 7$ is not presented here, as no phase separation between PGNPs with chains of type A and B could be achieved within the available simulation time for the range of $N$ and $N_g$ values considered.
In the case of $D = 7$, we were able to detect only disordered configurations such as the ones illustrated in Fig. 1 (middle bottom panel). Overall, we have found that the increase of the core particle hinders the phase separation of the systems for given $N$ and $N_g$. Moreover, our results suggest that there is a threshold for the size of the core particle that prevents demixing of the PGNPs. For a given size of the core particle, the dependence on $N_g$ and $N$ is not trivial, and will be discussed below for two different cases of NP diameter $D$, namely for the cases $D = 1$ and 4.

The case $D = 1$ (Fig. 2, upper panel) indicates that the phase separation takes place easier when the length of the polymer chains is small (e.g., $N = 5$). In this case, values of $\epsilon_{AB} \approx 0.98$ can induce a phase separation between PGNPs with polymer chains of different type. Hence, a very small incompatibility between the different chemical beads of the grafted polymer chains leads to PGNPs segregation. Moreover, differences in the grafted density seem to play a minor role in the ODT for small chain length $N$, which indicates that PGNPs behave like small LJ beads with a similar effective diameter for the range of $N_g$ considered here. However, as the chain length $N$ increases the dependence on $N_g$ is more pronounced and the resulting behavior varies, depending on the value of $N$. For example, in the case of $N = 20$ an increase of the grafting density $N_g$ leads to a much easier demixing, a trend which is opposite for $N = 40$. This is an effect of the interplay between $N_g$ and $N$, which also leads to a crossover from branched polymer to NP behavior [30].

In the case of $D = 4$ (Fig. 2, lower panel), we observe that a small grafting density ($N_g$), which exposes the steric interaction between the core particles (Fig. 1) and minimizes the interaction between the grafted polymer chains of different type, hinders the demixing of PGNPs. For example, PGNPs with $N_g = 5$ and chain lengths as long as $N = 40$ cannot shield the steric interaction between the NP cores (Fig. 1). Hence, for $N_g = 5$ no phase separation occurs for any of the $N$ values considered in this study. In general, for each $N_g$ the dependence on $N$ is rather monotonic. In contrast, the most interesting behavior is observed when we keep $N$ constant and vary $N_g$ as the tethered polymer chains start to occupy the NP’s surface with attractive beads. If we consider the case $N = 5$, then $N_g = 10$ indicates easy segregation of the PGNPs. However, further increase of $N_g$ leads to an increase of the effective steric core interaction of the PGNPs [30], which eventually results in more difficult demixing. In the case of $N = 10$, the change in behavior with increasing $N_g$ takes place within a broader range of $N_g$ values, due to the higher value of the chain length $N$. As we increase the chain length $N$, the dependence on increasing values of $N_g$ is similar. A detailed analysis of our data provides the following key-points: On one hand, the increase of the grafting density results in an effective increase of the NP’s size, which in turn hinders the phase separation of the NPs. Still large grafting densities and small chain lengths $N$ can transform the PGNPs in attractive Lj-like beads. On the other hand the increase of the chain length favors phase separation. The interplay between these effects determines the value of $\epsilon_{AB}$ where segregation of A and B type PGNPs will take place.

We have explained the above effect via a mean-field theoretical approach, which combines the hard-core NP interactions and the soft effective-core interactions that result from the increase of the grafting density. The latter interactions can be described by the potential

**FIG. 2: Phase diagrams of PGNPs for the case $D = 1$ (star polymers, upper panel) and $D = 4$ (lower panel) as a function of the chain length $N$ and the number of grafted chains $N_g$. Open squares indicate a disordered phase for all $\epsilon_{AB}$ values explored in this work. The color bar denotes the ODT by means of the potential interaction $\epsilon_{AB}$.**
\( \varphi_{ij}(r) = \varepsilon_{ij} \exp \left( -r^2/R_{ij}^2 \right) \),

(2)

where \( i \) and \( j \) index the species in the melt, and the strength and range parameters, \( \varepsilon_{ij} \) and \( R_{ij} \), correspond to \( N_g \) and \( N \), respectively. The “wrapping” of the polymer chains around the core of the hard-sphere part is modeled using the Percus-Yevick equation of state, which we model as a hard-sphere of radius \( R \)

\[ \varphi_{hs}(r) = \begin{cases} 0, & \text{if } r > R \\ \infty, & \text{if } r \leq R. \end{cases} \]

(3)

Higher grafting densities correspond to larger radii. The local aggregation of the polymer chains around the core of radius \( R \) may cause additional soft repulsion interactions

\[ \tilde{\varphi}_{ij}(r) = E_{ij} \exp \left( -r^2/R \right). \]

(4)

The resulting bulk free energy per particle of the mixture as a function of the molar fraction \( x \) and total density \( \rho \) is given by the following expression

\[ f(x, \rho) = f_{id}(x, \rho) + f_{hs}(x, \rho) + f_{mf}(x, \rho), \]

(5)

where the ideal part \( f_{id}(x, \rho) \) is defined as

\[ f_{id}(x, \rho) = k_B T (x \log x + (1 - x) \log (1 - x) + \log \rho - 1), \]

(6)

the hard-sphere part is modeled using the Percus-Yevick equation of state, which in our case is independent of \( x \), due to symmetry

\[ f_{hs}(x, \rho) = T \left( \frac{3(2 - \eta)\eta}{2(1 - \eta)^2} \log (1 - \eta) \right), \quad \eta = \frac{4}{3} \pi R^3, \]

(7)

and the soft repulsive part via the mean-field expression

\[ f_{mf}(x, \rho) = \frac{1}{2} \rho \left( (1 - x)^2 V_{11} + 2x(1 - x) V_{12} + x^2 V_{22} \right), \]

(8)

with \( V_{ij} \) being the total integrated strength of the potential.

We assume that increasing the grafting density, in turn increases the effective radius of the hard core by an additional soft repulsion. This is modeled by coupling \( V_{ij} \) with \( R \):

\[ V_{ij} = \pi^{3/2} \left( R_{ij}^3 \varepsilon_{ij} + R^3 E_{ij} \right), \]

where again due to symmetry we can set \( E_{11} = E_{22} = 1 \), leaving us with \( E_{12} = E \) as the coupling parameter. We further chose a system of units where \( R_{11} = R_{22} = 1 \) and \( \varepsilon_{11} = \varepsilon_{22} = 1 \). To ensure phase separation at small values of \( R \), we fix \( \varepsilon_{12} = 1.2 \varepsilon_{11} \), and in order to enhance the repulsive effects even further we set \( T = 0.4 \varepsilon_{11} \).

The picture of phase coexistence is summarized in Fig. 3(a). Here the densities and molar fractions of the coexisting mixed phases are found as the intersections of the binodal curve (blue) with the isochores \( \rho(x) \) (red). The transition is accessible above the critical pressure \( P_{\text{crit}} \). In addition, we show the boundaries of stability of the demixed phases – the spinodal (black curve). A qualitative agreement with the results in Fig. 2 is expressed by the dependence of the critical pressure on the hard core radius \( R \), plotted in Fig. 3(b) for several values of the coupling parameter. There are three possible scenarios which \( P_{\text{crit}}(R) \) may follow. For weak and strong coupling (\( E = 1.25 \) and \( E = 1.75 \)), the dependence \( P_{\text{crit}}(R) \), is monotonic. This means that increasing \( N_g \) should make the transition respectively less and more accessible. Notice the existence of the intermediate regime at \( E = 1.50 \), where \( P_{\text{crit}}(R) \) has a local minimum. In this case, increasing \( N_g \) initially facilitates phase separation (by reducing \( P_{\text{crit}}(R) \)), but further increase of \( N_g \) actually inhibits phase separation, as \( P_{\text{crit}} \) starts to grow.

We have analyzed various structural properties from MD simulations that contain information on the interplay between the growing with \( N_g \) effective core size and the growing with \( N \) effective chain length of the polymers. All our results are for the case \( \epsilon_{AB} = 1.0 \) in order to isolate the structural components that play a role in the phase separation of PGNPs. Figure 4 presents re-
results for the end-to-end distance of the polymer chains, i.e., the distance between the bead attached onto the core NP and the free end of each polymer chain, \( \langle R_{ce}^2 \rangle^{1/2} \). An average over all chains for each PGNP and an ensemble average is taken. Results for the most interesting case \( D = 4 \) are presented in Fig. 4. Our results suggest that the chain size is smaller in the case of systems that undergo easier demixing, which means that grafted polymer chains are closer to the NPs and an increase in the number of neighbors is also seen (Fig. 5). \( \langle R_{ce}^2 \rangle^{1/2} \) is a property that correlates very well with the phase diagrams of Fig. 2. Larger variation with \( N_g \) is observed for \( \langle R_{ce}^2 \rangle^{1/2} \) in the case of larger values of the chain length \( N \). The smaller dimensions of the chains appear for intermediate values of \( N_g \), also, leading to an increase in the average number of neighbors for each PGNP, \( \langle M_{AB} \rangle \) (Fig. 5). Here, PGNPs are considered as neighbors when at least one of the beads belonging to different PGNPs interact. While \( \langle M_{AB} \rangle \) overall decreases for each \( N \) when \( N_g \) increases, a peak is formed for small \( N \). This peak is less pronounced beyond a grafting density \( N_g > 20 \), which indicates that the effective NP size plays a smaller role for large grafting densities, when the NP core is covered by the grafted chains.

**Concluding Remarks.** We have studied the mixing–demixing behavior of molecularly and compositionally symmetric melts with spherical NPs with different chemical types of grafted chains by using MD simulations of a coarse-grained model. The size of the NP, the grafting density, and the length of the side chains were varied in order to investigate the phase behavior of these complex systems. Our results indicate that the increase of the NP size hinders the phase separation. Moreover, the system cannot separate beyond a certain NP size for given grafting density and length of polymer chains. The phase behavior of intermediate NP sizes (i.e., \( D = 4 \)) indicates a transition region as the grafting density increases and the steric repulsions are occupied by an attractive core with larger effective diameter, which is formed by the tethered polymer chains. We have explained these effects and provided an analytical description by means of a mean-field theory model. We anticipate that our results will provide further insight into the phase behavior of PGNPs, guided by the interplay phenomena between the NP size, the chain length, and the grafting density as illustrated in this work, with implications in materials science and medicine.

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