

Supplementary Information

Polymer-grafted nanoparticles prepared by surface-initiated polymerization: the characterization of polymer chain conformation, grafting density and polydispersity correlated to the grafting surface curvature

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Model construction

In our model, the immobile frozen particles are used to construct the spherical surface template of the NP. For a specific NP with determined radius, we first use the geodesic subdivision method to get all the vertex positions. This method is a repeated subdivision process of triangles. Starting with an icosahedron inscribed in the sphere, we first find the midpoint of each edge, and then push

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it out to get a new vertex lying on the sphere. This protocol divides each original triangle into four smaller ones and increases the number of vertices. Repeating this process will be helpful to find more vertices which can combine to represent the true spherical shell. Then each vertex position is occupied by an unmovable frozen particle in our model. In another way, we can also first define the side length of the subdivision triangle (say, $0.7\sigma_{LJ}$) and then locate the vertex positions in this method, so that the resulted shell particles are densely packed to construct the near-smooth and impenetrable sphere surface. In practice, to make sure the shell is impenetrable, we generate an outer shell and an inner shell with slight radius difference (e.g., $R_{outer} - R_{inner} = 0.5\sigma_{LJ}$). This two-layer surface model can well describe the hard NP sphere surface. After that, the geodesic subdivision is executed with radius R_{outer} to determine the initiator sites on the outer shell. By slightly tuning the side length of the subdivision triangle, we can get the near-uniformly distributed vertex positions with desired number to represent a pre-defined initiator density on the NP sphere surface. The frozen particles occupying the vertices of this shell are labeled as the initiators in the simulations. At last, these three shells are combined together (with their sphere centers overlapped) to construct the hollow NP model with uniformly distributed initiator sites on the outer surface (a hollow NP model is used to reduce computational cost).

Defining the simulation box size

The simulation box size is not set constant in the systems with different NP sizes. Because a series of NP radii (R_{NP}) values are considered in the simulations, it is not rational to define a constant simulation box size, since the amount of free monomers (with the same density, determined by the free space except the NP) are with great differences in different NP size systems. Because the quantities of the reactants are not equal for them, the setting of constant simulation box size for all systems inevitably leads to it impossible to compare the grafting conversion between these systems. On the other hand, the box should be large enough so that during the polymerization the grafted chains touch other chains belonging to the NP in the periodic image box as less as possible. Considering the above factors, we define the simulation box as follows: we set the ratio

of original free monomer number (N_m) to the area of the NP surface ($S = 4\pi R_{NP}^2$) as constant for different NP size systems (i.e., for different NP size systems with the same initiator density, the ratio of N_m and number of initiators (N_i) is also constant), so that the simulation box sizes can be determined and the conversions of SIP are comparable with the same criteria (in practice, we find the ratio $k = N_m/S = 150$ is suitable to ensure the large enough free space of simulation box for the chain growth). Therefore, the cubic simulation box length L_d can be calculated by the following relationship:

$$k = N_m/S = \frac{(L_d^3 - 4/3\pi R_{NP}^3)\rho_n}{4\pi R_{NP}^2}. \quad (1)$$

For comparing the results with that grafted from the standard flat surface, we also add the flat-SIP simulations¹ with the same polymerization condition. As the reference flat-SIP system in the simulation, we first set the size of the grafting surface as $L_x = L_y = 50$, thus the height of the simulation box L_z can be defined by:

$$k = N_m/S = \frac{(L_x \times L_y \times L_z)\rho_n}{L_x \times L_y}. \quad (2)$$

Based on the above rule, the systems with different NP sizes in the series of simulations are listed in Table.1 in the manuscript.

Why do we choose the same period of polymerization for all of the systems?

In this manuscript, we describe the process as living polymerization, i.e., the chain termination is omitted. A living radical polymerization is commonly thought to be determined by a linear increase in the degree of polymerization (or number-average molecular weight) with conversion. Thus the polymer chains can continuously grow as the polymerization proceeds. Within the nanosecond time scale based on the simulation method, the chain growth should be the indefinite growth type in living polymerization. While for practical analysis, it is reasonable to compare the results with the same polymerization time after the reaction is switched on. First of all, based on the present

computational efficiency, the simulation box cannot be set too large (the GPU-accelerated simulations includes at most 4 million free particles in our study). Thus if the chains grow freely for longer time, they may become too long to be accommodated in the simulation box (i.e., the periodic boundary condition describes the very long chain with fake trajectory), as a result, it may affect our simulation results, e.g., the chain conformations. To avoid it, it is reasonable to only consider the first part of polymerization before the chains grow too long to exceed the border of the box. On the other hand, by comparing the conversion of the free monomers in polymerization, it is helpful for us to get some hints about the grafting efficiency, as described in Fig.3 of the manuscript. Therefore, we define the simulation box size as the rule described in the above section “Defining the simulation box size”, so that the conversion can be compared between different systems with different NP sizes. Therefore, for the sake of conversion comparison between systems, the results are obtained after the same period of polymerization.

For the above two reasons, in practice, we make all of the systems polymerize for 2000 MD time units, during which the grafted chains can grow long enough to obtain the real conformations and not too long to be accommodated in the simulation box, and besides the comparison of conversion of free monomers is also possible.

The influence of the choice of parameters on the results

The Lennard-Jones (LJ) well depth defines the interaction energy between the beads. A larger value of LJ well depth yields the stronger repulsion between beads, as a result, the effective concentration of the free monomers around the active chain end will be lower. Thus a slower chain growth process is expected with the same parameters in polymerization. As shown in Figure S1, we plot the mass distribution of the typical system with $R^{-1} = 0.100$ and $\sigma_i = 0.03$ but with different LJ well depth ϵ . It is clear that the system with $\epsilon = 0.5$ has a narrower distribution with a slightly larger peak position. While the mass distribution of $\epsilon = 2.0$ is much broader and its peak position is smaller. Based on the Poisson-like distribution of mass, the value of peak position should be close to the average chain length, which reflects the chain growth speed. Thus this result supports the

conclusion that the large LJ well depth yields a slower chain growth. Besides the polymerization, the direct influence of LJ well depth is the diffusion and distribution of monomers. In Figure S2 we plot the density profiles of the above systems. We can find the density value of each peak in the system with larger $\varepsilon = 2.0$ is higher. With the enhanced repulsion between beads from $\varepsilon = 0.5$ to $\varepsilon = 2.0$, this density profile is the result of crystal-trend arranging of grafted monomers.

The parameter temperature directly influences the diffusion of the free monomers. There are two dynamics in the system, including the diffusion dynamics of free particles and the reaction dynamics between monomers. We had indicated that the chosen parameters P_r and τ represent a relatively moderate reaction by our previous experiences. If the temperature is chosen to be a higher value, the diffusion dynamics is enhanced. At the later stage more unsaturated initiators should be induced, since the fast diffusion of free monomers will increase the opportunity of them to move closer and contact the unsaturated initiators on the NP surface. On the contrary, if the polymerization is simulated with a very low temperature, the free monomers may become unlike to move and nearly frozen. As a result, the effect governed by the so-called diffusion limited aggregation² may occur during the polymerization. In this condition, more initiators will become unsaturated ones. As shown the relationship between σ_i and σ_g in Figure S3, when the temperature is higher than the standard $T = 1.0$, e.g., $T = 1.5$ (the red plot), the plot gets closer to the reference dashed line (corresponding to initiation efficiency 100%), implying more initiators can be induced. While in the condition with $T = 0.5$ (the blue plot), the plot deviates from the reference line much more obviously, implying that the slowed diffusion of the free monomers yields more unsaturated initiators during polymerization. This figure well proves the above analysis.

References

- (1) H. Liu, M. Li, Z. Lu, Z. Zhang and C. Sun, *Macromolecules*, 2009, **42**, 2863–2872.
- (2) T. A. Witten, Jr and M. L. Sander, *Phys. Rev. Lett*, 1981, **47**, 1400–1403.

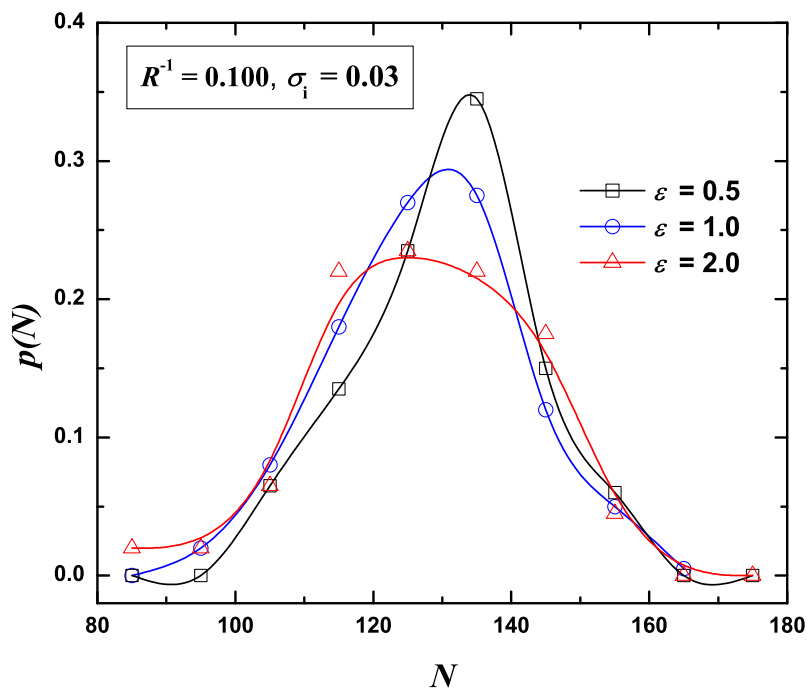


Figure S1: Mass distribution of the systems with $R^{-1} = 0.100$ and $\sigma_i = 0.03$ but with different LJ well depth.

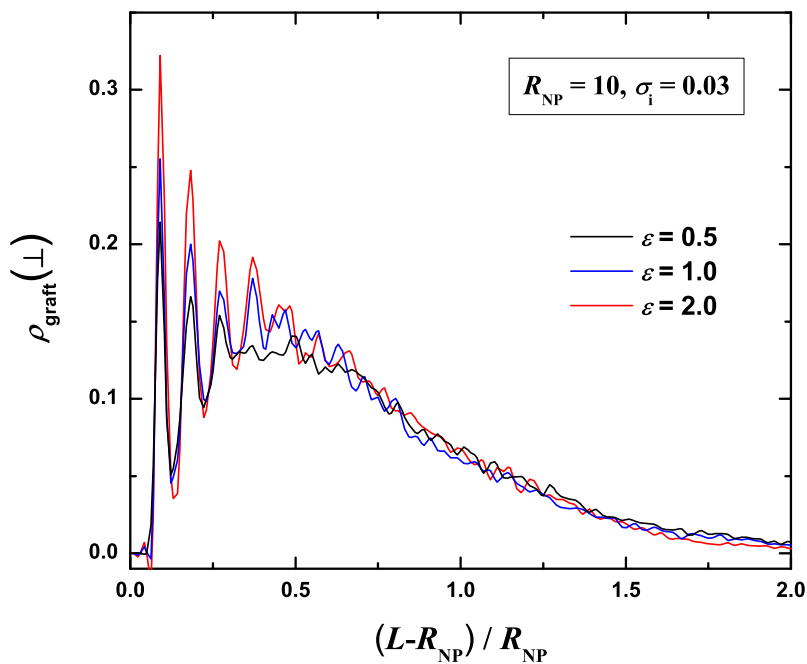


Figure S2: The grafted monomer density profile in the systems with $R_{\text{NP}} = 10$ ($R^{-1} = 0.100$) and $\sigma_i = 0.03$ but with different LJ well depth.

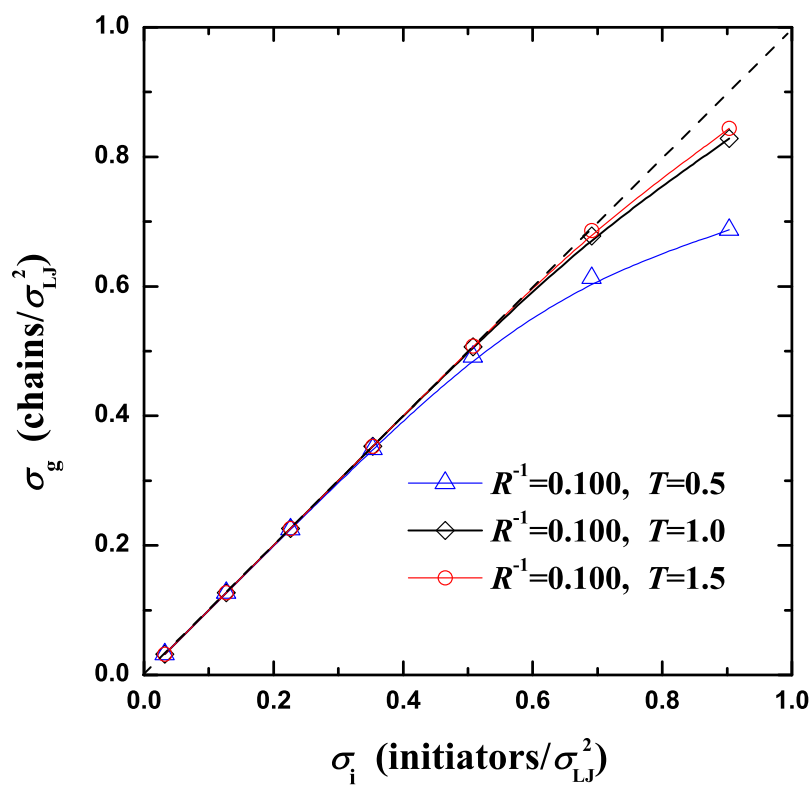


Figure S3: The relationship of the final grafting density σ_g versus the original initiator density σ_i in the systems with $R^{-1} = 0.100$ but with different simulation temperatures.