Supplementary Material

Nanoparticle’s selectivity for polydispersed ligand chains during the grafting-to process: a computer simulation study

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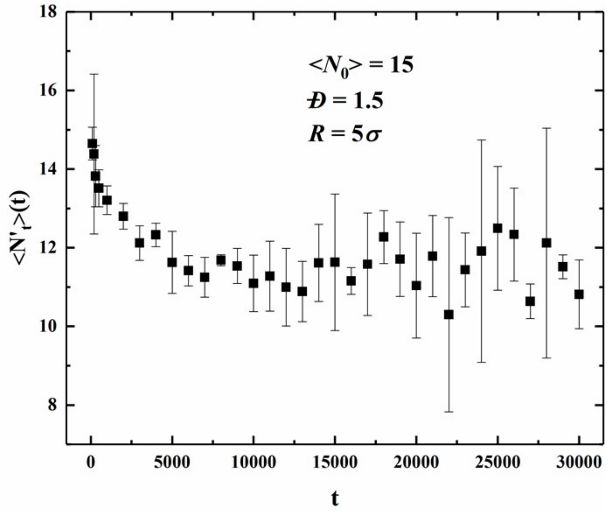

Fig. S1 Time evolution of the averaged chain length of newly bound grafts during the grafting-to process. It is obtained by comparing the continuous trajectories during the reaction. As compared to the last trajectory, all of the newly bound polymer chains are grouped together to calculate the average chain length, and it is labeled as $<N_t'>$(t) of this specific time *t.* $<N_t'>$(t) decays obviously as the reaction proceeds, indicating that in late stage more short chains are bound to be grafts. On the other hand, the large error bars in the late stage imply that a few long chains are still possible to be bound on the nanoparticle sites from specific directions with low steric repulsion. Three samples are conducted to calculate the mean values and the error bars.

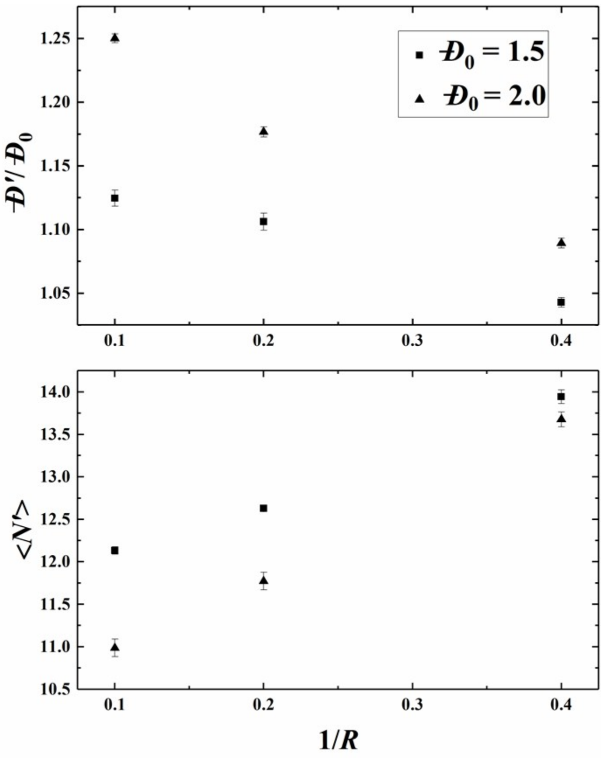

Fig. S2 The dependence of $Đ'/Đ_0$ and $<N'>$ on the surface curvature of the nanoparticles $1/R$ in both systems with $Đ_0$ =1.5 and 2.0. Clearly, for both systems $Đ'/Đ_0$ decays monotonically with the increase of surface curvature of nanoparticles. Besides, $Đ'/Đ_0$ in $Đ_0$ =2.0 is basically higher, implies a larger deviation of the grafts from the feeding polymer chains in this system. On the other hand, however $<N'>$ increases almost linearly with the increase of surface curvature, indicating that with higher surface curvature, the longer chains are relatively easier to be bound because of the weakened steric repulsion. $<N'>$ in $Đ_0$ =1.5 is slightly higher, which may be ascribed to that more longer chains are involved in the feeding polymers. With the same selectivity of nanoparticles of the same size, naturally more longer chains are possibly be bound. Three samples are conducted to calculate the mean values and the error bars.

Nanoparticle Model Construction

In our simulations, the nanoparticle (NP) is constructed by lumping *N*-type beads into a spherical structure. We first use the geodesic subdivision method[1] to get all the vertex positions of one NP. This method is actually a repeated subdivision procedure with triangles. Starting with an icosahedron inscribed in a sphere, we first find the midpoint of each edge, and then push 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 procedure will be helpful to find more vertices which can combine to represent the true spherical shell. Then each vertex position is occupied by an *N*-type bead. Alternatively, we can also first define the side length of the subdivision triangle (say, 0.7σ) and then locate the vertex positions with geodesic method, so that the resulted *N*-type beads 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_{out}-R_{in}=0.5σ). This two-layer surface model can well describe the hard NP sphere surface. After that, the geodesic subdivision is executed with radius R_{out} to determine the initiator sites on the outer shell. By slightly tuning the side length of the subdivision triangle, we can get near-uniformly distributed vertex positions with desired number to represent a predefined g_0 value on the NP sphere surface (the initial density of the reactive sites on the NP surface is initially set as Σ_i=$0.84/\sigma^2$, thus g_0 can be calculated as g_0=$4\pi R_{\mathrm{out}}^2\Sigma_i$). The beads with the amount of g_0 that occupy the vertices of this shell are labeled as the reactive sites in grafting-to reactions. At last, these three shells are combined together (with their sphere centers overlapped) to construct the hollow NP model with uniformly distributed reactive sites on the surface. This reasonably designed hollow NP model can largely reduce computational cost.

1. F. Lo Verso, S. A. Egorov, A. Milchev and K. Binder, *The Journal of Chemical Physics*, 2010, **133**, -.