Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material

# Polymer-grafted nanoparticles prepared via grafting-from strategy: a computer simulation study

Long Li, Cheng Han, Dan Xu, Ji-Yuan Xing, Yao-Hong Xue* and Hong Liu

## Stochastic Reaction Model

The grafting reaction, i.e., the grafting-from polymerization, is described by the generic stochastic reaction model proposed in our previous works[1, 2]. In this reaction model, we introduce the idea of reaction probability $P_\mathrm{r}$ to control the reaction process. In each reaction time interval $\tau$, if an active end meets several reactable beads (free monomers) in the reaction radius, firstly it randomly chooses one of the reactable beads as a reacting object. Subsequently, another random number $P$ is generated, then by checking if it is smaller than the preset reaction probability $P_\mathrm{r}$, we decide whether the chosen reactable bead will connect with the active end or not. This judging process in one reaction step is schematically illustrated in Fig. S1. If the bond can be formed between the active end and the reacting object, we record the connection information and update the spring forces between them.

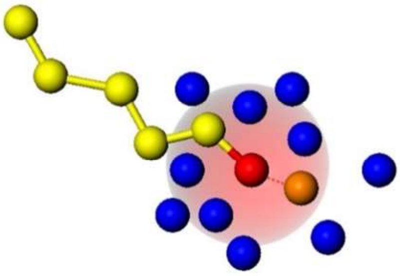

Fig. S1. Illustration of the reaction process controlled by the reaction probability in grafting-from reactions. When the active end (the red ball) of the chain (the connected yellow balls) meets several free monomers (the blue balls and the orange one) in its capture radius (the semitransparent sphere), it randomly chooses one of the monomers as a reacting object (e.g., the orange ball). Then whether the bond between the red ball and the orange ball can be generated is decided by the preset reaction probability.

This idea of reaction is especially suitable for the design of polymerization-type reactions. During the polymerization, the newly connected monomers then turn to be the growth centres in the next propagation step of the same chain to connect other free monomers, so that the active end is transferred forward. This generic stochastic reaction model had been successfully used to describe the polymerizations in different conditions, such as polymerization induced phase separation[1] and surface-initiated polymerization on the flat substrate[2], on the concave surface[3] and on the convex NP surface[4]. This generic reaction model had also been used to describe other types of reactions. For example, it had been used to describe curing reactions in epoxy resin systems[5]. In a recent paper, we proposed an updated reaction model that is easier to be handled technically. For example, it has lower perturbation on the MD simulations, so that the adoption of thermostat turns to be unimportant[6]. More details on reaction kinetics of this reaction[6] and simulation protocols for grafting-from[4] can be found in our previous papers.

### 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[7] 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, $0.7\sigma$) 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., $R_{out}-R_{in}=0.5\sigma$). 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 $\Sigma_i=0.84/\sigma^2$, thus $g_0$ can be calculated as $g_0=4\pi R_{out}^2\Sigma_i$). 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, as shown in Fig. S2.

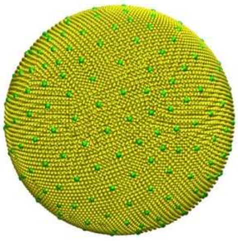

Fig. S2. Schematic illustration of an NP structure in simulations. Two shells of yellow beads are used to represent near-smooth and impenetrable NP surface (the inner shell is not visible). The green beads in the outer shell represent the reactive sites.

## The method of calculating the potential of mean force

In the molecular modeling studies, the free energy of the system is always the most concerned issue. Different works had been performed to find the methods which are efficient and credible to calculate the free energy. Torrieet al.[8] applied a kind of umbrella sampling method to promote the sampling efficiency, in which they introduced a biased potential to obtain the trend of the free energy changing along a determined coordination route. Commonly, the harmonic spring type potential is often introduced as the biased potential, i.e.,

$$w_i(\xi) = \frac{1}{2}K(\xi - \xi_i)^2 . \tag{1}$$

It is possible to obtain the unbiased free energy changing along a determined route $\xi$ by using the biased probability $P_i^b(\xi)$. Namely, the potential of mean force (PMF)[8],

$$A_i^u(\xi) = -\frac{1}{\beta}\ln P_i^b(\xi) - w_i(\xi) + F_i \quad (\beta = \frac{1}{k_B T}) . \tag{2}$$

Notably, in the umbrella integration algorithm used in our study[9], the PMF is obtained by calculating $\partial A^u / \partial \xi$ instead of directly calculating $A^u$, so that it is no need to calculate the unknown quantity $F_i$, i.e.,

$$\frac{\partial A_i^u}{\partial \xi} = -\frac{1}{\beta}\frac{\partial \ln P_i^b(\xi)}{\partial \xi} - \frac{dw_i}{d\xi} . \tag{3}$$

We further assume that the samples in each window approximately obey the Gaussian distribution, i.e.,

$$P_i^b(\xi) = \frac{1}{\sigma_i^b\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\xi - \overline{\xi_i^b}}{\sigma_i^b}\right)^2\right]. \tag{4}$$

Thus we can obtain that in their window, the form of $\partial A^u / \partial\xi$ is,

$$\frac{\partial A_i^u}{\partial\xi} = \frac{1}{\beta}\frac{\xi - \overline{\xi_i^b}}{\left(\sigma_i^b\right)^2} - K(\xi - \xi_i). \tag{5}$$

For combining the results of different windows, we divide the reaction coordination into X parts of the same size *bin*. For each part the center position is labeled as $\xi_{bin}$. The windows are combined by a weighted average as,

$$\left.\frac{\partial A(\xi)}{\partial\xi}\right|_{\xi_{bin}} = \sum_i^{windows} p_i(\xi_{bin})\left(\frac{\partial A_i^u(\xi)}{\partial\xi}\right)_{\xi_{bin}}, \tag{6}$$

with the weighting function $p_i(\xi) = N_i P_i^b(\xi) \Big/ \sum_i N_i P_i^b(\xi)$.So the Eqs. (5) and (6) are the equations used to calculating PMF via the umbrella integration algorithm.

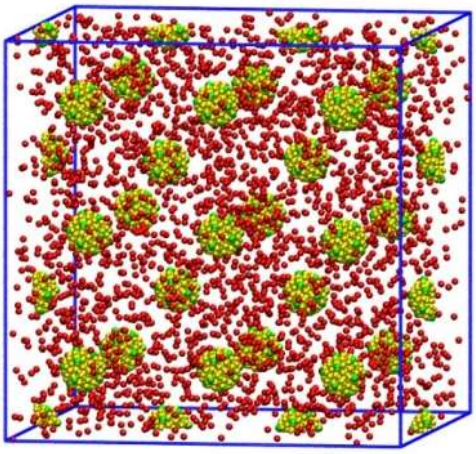

Fig. S3. Typical snapshot of the initial configuration in grafting-from reaction. The free monomers (red) are randomly distributed among the NPs (yellow spheres) with reactive sites (green) on the surface. The grafting-from reaction takes place as a chain growth process starting from the green sites on the NPs.

Table. S1.The side length of the simulation box for the systems bases on that they possess almost the same packing fraction value $f_{\mathrm{p}}$.

| $f_{\mathrm{p}}$<br>Radius | 0.155 | 0.098 | 0.065 | 0.034 | 0.019 |
|---|---|---|---|---|---|
| 2.5 | 30 | 35 | 40 | 50 | 60 |
| 5 | 45 | 52.4 | 60 | 75 | 90 |
| 10 | 60 | 70 | 80 | 100 | 120 |

## References:

1. H. Liu, H.-J. Qian, Y. Zhao and Z.-Y. Lu, *Journal of Chemical Physics*, 2007, **127**, 144903.
2. H. Liu, M. Li, Z. Y. Lu, Z. G. Zhang and C. C. Sun, *Macromolecules*, 2009, **42**, 2863-2872.
3. H. Liu, Y.-L. Zhu, J. Zhang, Z.-Y. Lu and Z.-Y. Sun, *ACS Macro Letters*, 2012, **1**, 1249-1253.
4. Y.-H. Xue, Y.-L. Zhu, W. Quan, F.-H. Qu, C. Han, J.-T. Fan and H. Liu, *Physical Chemistry Chemical Physics*, 2013, **15**, 15356-15364.
5. H. Liu, M. Li, Z.-Y. Lu, Z.-G. Zhang, C.-C. Sun and T. Cui, *Macromolecules*, 2011, **44**, 8650-8660.
6. H. Liu, Y.-L. Zhu, Z.-Y. Lu and F. Müller-Plathe, *Journal of Computational Chemistry*, 2016, **37**, 2634-2646.
7. F. Lo Verso, S. A. Egorov, A. Milchev and K. Binder, *The Journal of Chemical Physics*, 2010, **133**, -.
8. G. M. Torrie and J. P. Valleau, *Chemical Physics Letters*, 1974, **28**, 578-581.
9. J. Kästner and W. Thiel, *The Journal of Chemical Physics*, 2005, **123**, 144104.