Soft Matter SUPPORTING INFORMATION

Polymer Pattern-Induced Patterned Self-Assembly of Inorganic Nanoparticles

Junfeng Wang,[a] *Bojin Zhu,*[a] *Yining Wang,*[a] *Yujian Hao,*[a] *Jun Zhang,*[a] *and Zhen Li**[a].

School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao 266580, Shandong, China.

CONTENTS

S1. Model details

S1.1. Modeling

The inorganic nanoparticles (NPs) are abstracted into an ideal sphere constructed by 480 DPD beads. The positions of beads are calculated by the DistMesh software[1]. The precise DPD model of the copolymer PGMA-*b*-PHPMA reported in our previous work is used in this work[2].

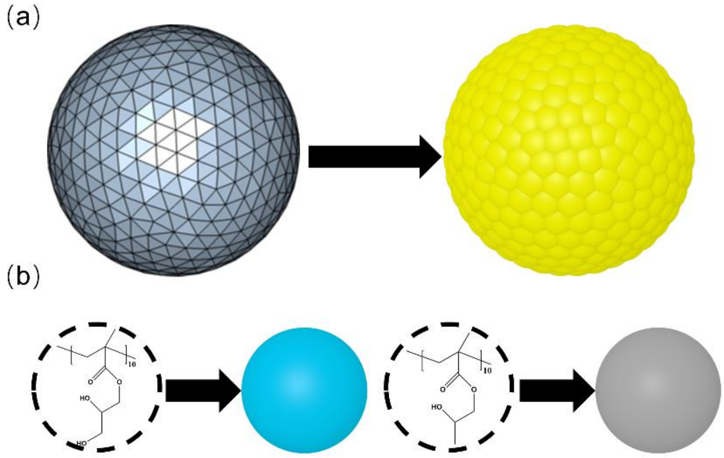


Fig S1. (a) The sketch map of modeling NP. (b) The molecular structure of the glycerol monomethacrylate (GMA) and 2-hydroxypropyl methacrylate (HPMA).

S1.2. Reaction Model

In 2006, Smith et al began to combine the Reaction Ensemble Monte Carlo with DPD to study polymer reaction in polymeric systems[3-5]. In 2015, Hiroshi Noguchi et al used a reaction model to study the self-assembly process induced by chemical reactions[6]. In 2016, Lin et al studied PISA of linear diblock copolymers[7]. After that, Alexey A. Gavrilov et al also used a reaction model to study the copolymerization of partially incompatible monomers[8]. As shown in **Fig S2**, when one monomer moves close to the active end with a reaction radio R (R=1.0r_c), this active end has certain possibility (Pr) to bond with the closest monomer. After this, the monomer transforms to be a solvophobic bead B. The reaction possibility Pr is controlled by series of random numbers. A random number from 0 to 1 is created by computer at every step. If one random number is smaller than the reaction possibility Pr, the active ends will be bonded with the closest monomers, so that the Pr can reflect the polymerization rate. The polymerization rate used in our previous work is adopted in this work, which Pr = 0.0001[9]. In all our simulation, the conversion of monomers is larger than 99%.

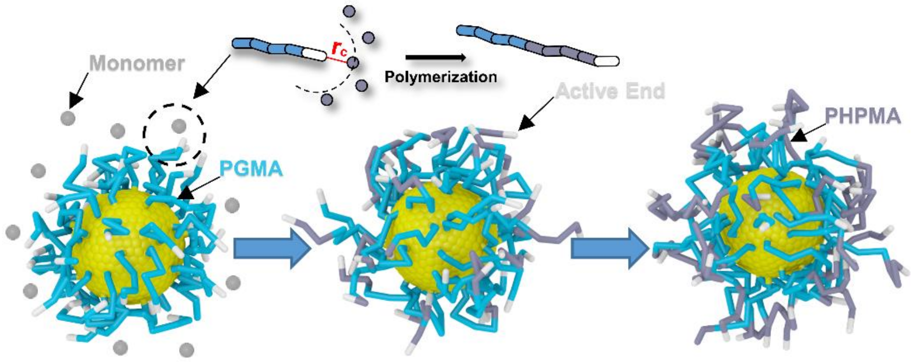
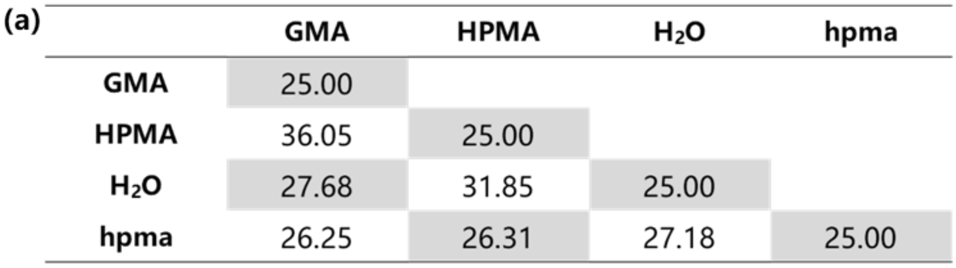


Fig S2. The sketch map of the reaction mode.

S2. Interaction parameters

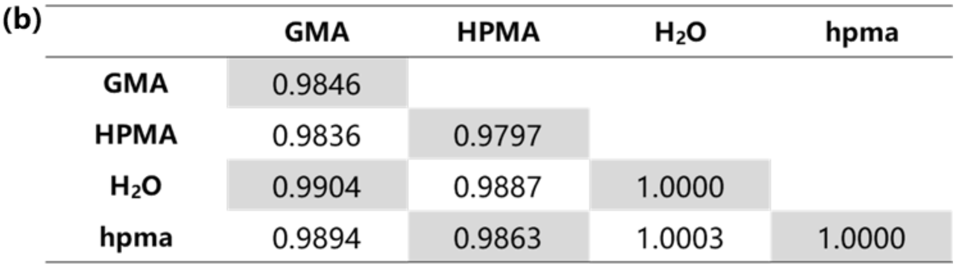
For grafting polymers onto the NPs, the surface of NPs is always treated by the acidification. Therefore, the repulsive interaction parameter between the surface of the NP and the aqueous solution is set to be 25. The interaction parameters of the PGMA-*b*-PHPMA are shown in **Table S1**. The “hpma” represents the HPMA monomers, and the “HPMA” represents one DPD bead of the PHPMA chain. **Fig S3** shows our simulation results and experimental results of PISA of PGMA-*b*-PHPMA, and our simulation results are well consistent with the experimental results[10].

Table S1. (a) Conservative Force Constants α_{ij} and (b) Interaction Cutoff used in DPD Simulations (PGMA-*b*-PHPMA)



(a)

	GMA	HPMA	H_2O	hpma
GMA	25.00			
HPMA	36.05	25.00		
H_2O	27.68	31.85	25.00	
hpma	26.25	26.31	27.18	25.00



(b)

	GMA	HPMA	H_2O	hpma
GMA	0.9846			
HPMA	0.9836	0.9797		
H_2O	0.9904	0.9887	1.0000	
hpma	0.9894	0.9863	1.0003	1.0000

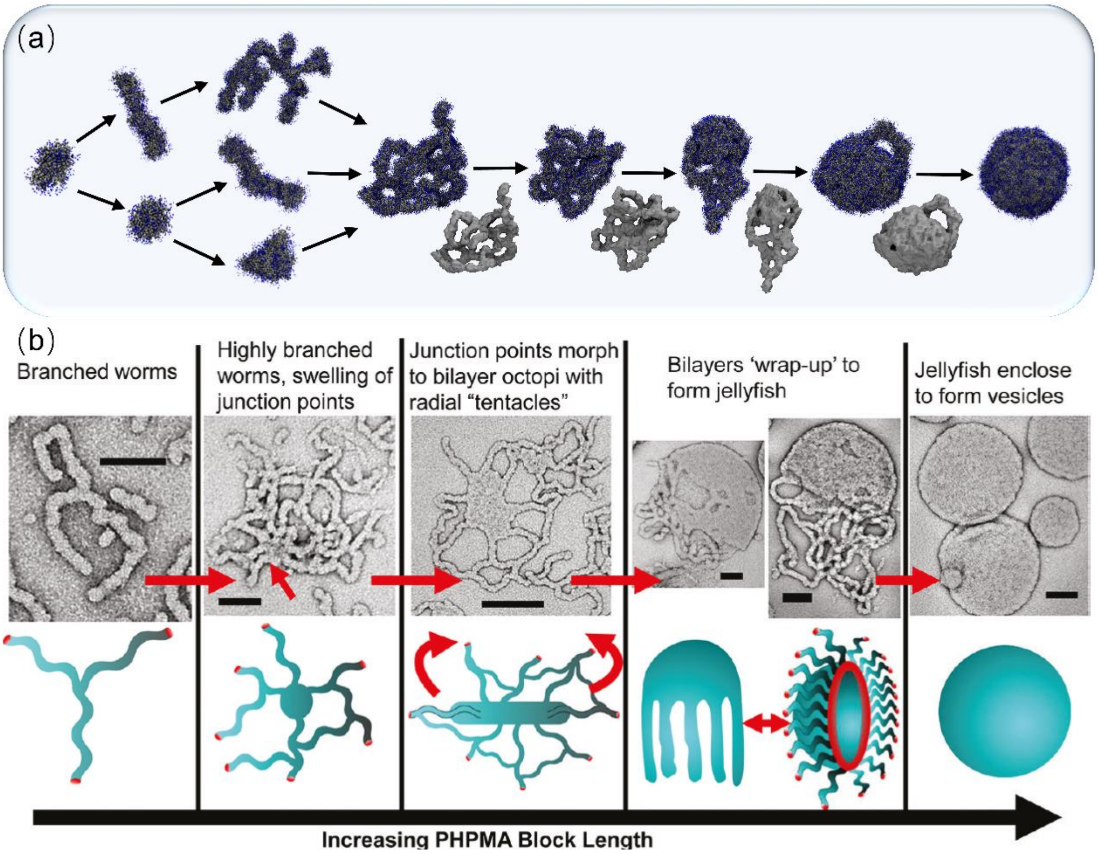


Fig S3. (a) The simulation results of the PISA of PGMA-*b*-PHPMA using our DPD models. (b) The experimental results of the PISA of PGMA-*b*-PHPMA reported by Armes et al. Reprinted from ref10 . Copyright 2011 American Chemical Society

S3. Details of restructuring

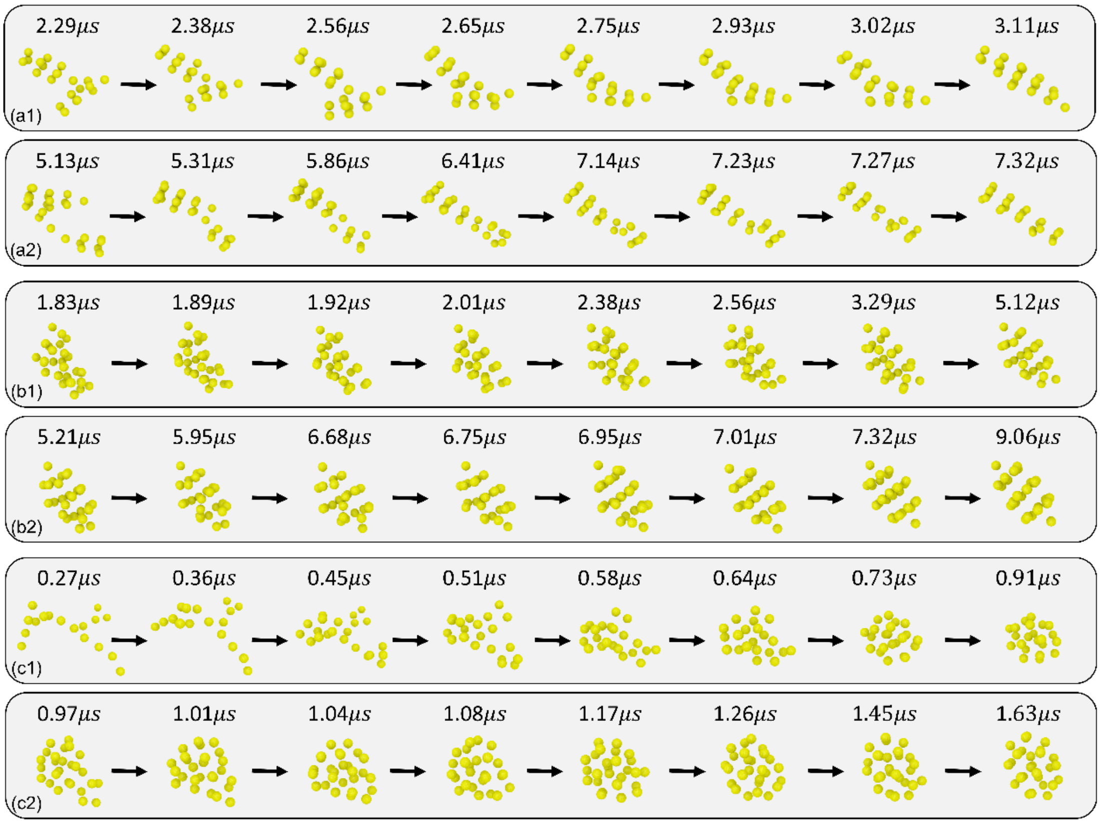


Fig S4. The details of the restructuring process of NPs.

S4. References

1. Burkardt, J., Distmesh: A simple mesh generator in matlab. **2011**.

2. Wang, J.; Fang, T.; Li, J.; Yan, Y.; Li, Z.; Zhang, J., Precise Mesoscopic Model Providing Insights into Polymerization-Induced Self-Assembly. *Langmuir* **2020,** 36, (27), 8009-8016.

3. Lísal, M.; Smith, W. R.; Nezbeda, I., Molecular simulation of multicomponent reaction and phase equilibria in MTBE ternary system. *AIChE journal* **2000,** 46, (4), 866-875.

4. Lísal, M.; Brennan, J. K.; Smith, W. R., Mesoscale simulation of polymer reaction equilibrium: Combining dissipative particle dynamics with reaction ensemble Monte Carlo. I. Polydispersed polymer systems. *The Journal of chemical physics* **2006,** 125, (16), 164905.

5. Lísal, M.; Brennan, J. K.; Smith, W. R., Mesoscale simulation of polymer reaction equilibrium: Combining dissipative particle dynamics with reaction ensemble Monte Carlo. II. Supramolecular diblock copolymers. *The Journal of chemical physics* **2009,** 130, (10), 104902.

6. Nakagawa, K. M.; Noguchi, H., Morphological changes of amphiphilic molecular assemblies induced by chemical reactions. *Soft matter* **2015,** 11, (7), 1403-1411.

7. Huang, F.; Lv, Y.; Wang, L.; Xu, P.; Lin, J.; Lin, S., An insight into polymerization-induced self-assembly by dissipative particle dynamics simulation. *Soft Matter* **2016,** 12, (30), 6422-6429.

8. Gavrilov, A. A.; Chertovich, A. V., Copolymerization of partly incompatible monomers: an insight from computer simulations. *Macromolecules* **2017,** 50, (12), 4677-4685.

9. Wang, J.; Li, J.; Wang, Y.; Li, Z.; Zhang, J., Polymerization-Induced Self-Assembly of Comb-like Amphiphilic Copolymers into Onion-like Vesicles. *Macromolecules* **2021**.

10. Blanazs, A.; Madsen, J.; Battaglia, G.; Ryan, A. J.; Armes, S. P., Mechanistic insights for block copolymer morphologies: how do worms form vesicles? *Journal of the American Chemical Society* **2011,** 133, (41), 16581-16587.