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

Supporting Info for: Microscopic Characteristics of Janus Nanoparticle Prepared via Grafting-From Reaction at Immiscible Liquid Interface

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1. The order parameter RC.

An order parameter RC is defined to describe the regularity of chains that have grafted from the nanoparticle,

$$RC(M) = \sum_{i=1}^{M-1} RC(i), \tag{1}$$

$$RC = \frac{\sum_M RC(M)}{M-1}. \tag{2}$$

To calculate RC, firstly the obtained Janus nanoparticle (JNP) after simulation is divided into several bins along the x axis (i.e., the interface normal direction). As shown in the schematic diagram in Figure 2(b) in our manuscript, the nanoparticle is divided into several parts by white dash lines; the width of each bin equals to 0.5. Then we count each monomer

type in every chain that has grafted from the JNP in each bin, M denotes the chain length, and i denotes the i-th bead in each chain (i ranges from 1 to M − 1). If the i-th and (i + 1)-th monomers are of the same type (both A or both B), then RC(i) = 1; if the i-th and (i + 1)-th monomers are of different types (A and B), then RC(i) = −1. The sum of all RC(i) in this chain is RC(M), which describes the regularity of this chain. RC is the average of all chains RC(M) in each bin. As the regularity of chains in this bin decreases, the RC value will also decrease.

2. The simulations of multi-nanoparticle system.

In the beginning of simulation, we put four nanoparticles at the solvent interface in the middle of box with equal distance between them in Y and Z directions. Other simulation conditions and interaction parameters are consistent with those for reporting the blue line in Figure 2(a) in the manuscript. After simulation we use the order parameter RC to describe the regularity of the chains that have grafted from the nanoparticle surface.

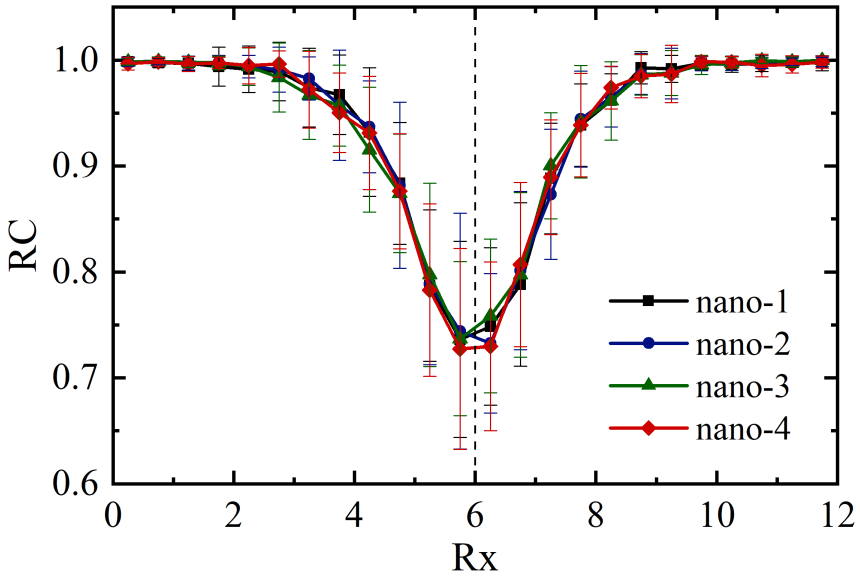

Figure 1: The order parameter RC of grafted chains on four JNPs in each bin. Vertical line shows the mass center of each JNP. Nano-i represents the index of nanoparticle i (i = 1,2,3 and 4).

SI Figure 1 shows that four curves are overlapping and the trend reflected by the curves

is consistent with that of the single nanoparticle system (blue line in Figure 2(a) in the manuscript). This result indicates that the conclusion we obtained in the manuscript is also applicable to the high NP concentration system.

3. The simulations with $\alpha = 100$.

In the simulations we only change the interaction parameter α_{WO} to 100, while other interaction parameters and simulation conditions are consistent with those for reporting Figure 2(a) in the manuscript. After simulations we also use the order parameter RC to describe the regularity of the chains that have grafted from the nanoparticle surface. The results are shown in SI Figure 2.

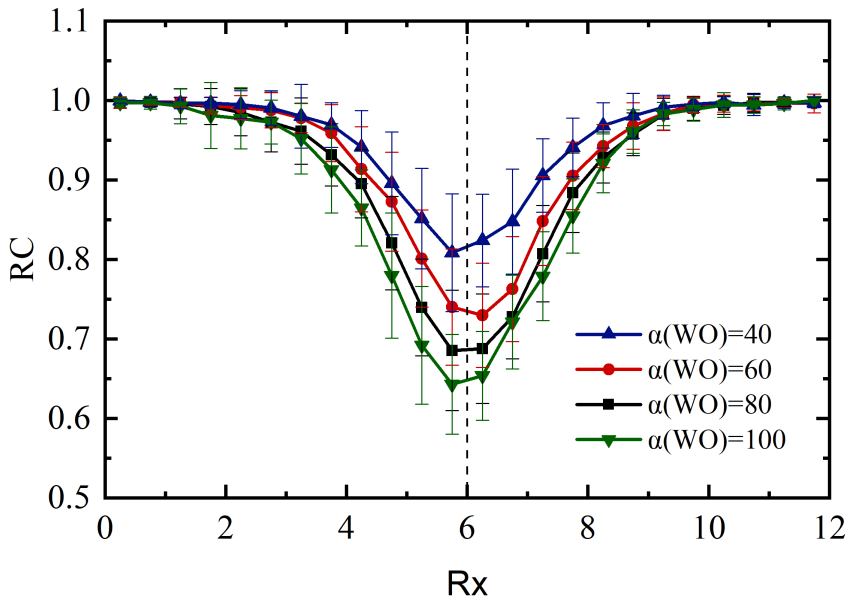

Figure 2: The order parameter RC of grafted chains on JNPs in each bin in cases of different interaction parameters for the solvent mixtures. Vertical line shows the mass center of the JNP.

The curve with $\alpha_{WO} = 100$ in SI Figure 2 is similar to those with $\alpha_{WO} = 40/60/80$, except that for the case with $\alpha_{WO} = 100$ the regularity of the chains at interfacial region is poorer. This result indicates that the conclusion drawn in the manuscript could be applicable to a large number of solvent pairs available in experiments.

4. The simulations with different Pr.

Here we set reaction probability Pr(AA) = 0.05, Pr(AB) = 0.02, Pr(BA) = 0.01, and Pr(BB) = 0.005. The results of RC are shown in SI Figure 3, in which the results for the system with same Pr = 0.05 (i.e., the black line in Figure 2(a) in the manuscript) are shown for comparison.

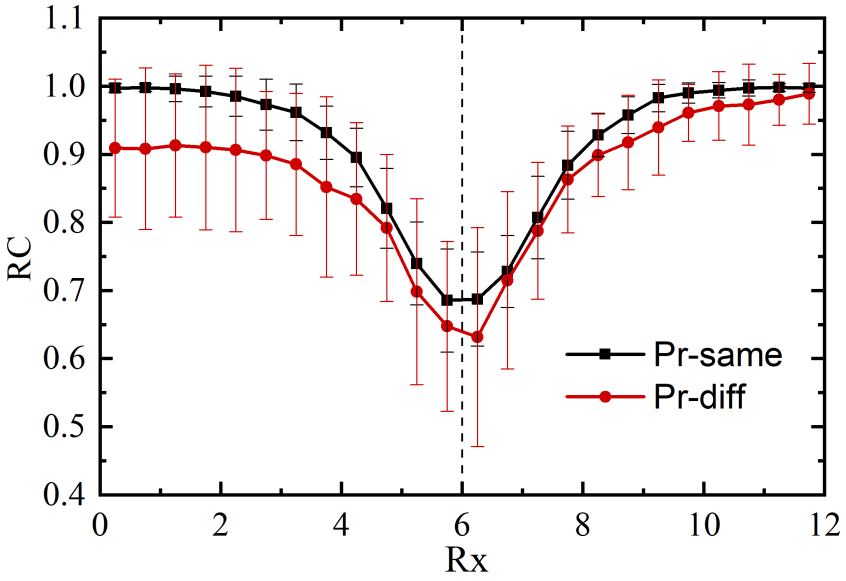

Figure 3: The order parameter RC of grafted chains on JNPs in each bin in cases of same Pr (black curve) and different Pr (red curve). Vertical line shows the mass center of JNP.

From SI Figure 3 we can find that using different Pr takes effect on the grafted chain regularity. In this system, Pr(AB)/Pr(BA) is higher than Pr(BB), i.e., it is easier to form copolymers AB or BA than homopolymers BB. This reaction probability setup is to represent a type of inactive monomer B in copolymerization systems. Therefore, it is easier to form copolymers on the surface of nanoparticle in the initial stage of simulation. In addition, there are few chains grafted on the nanoparticle surface at the beginning of grafting from reaction so that the nanoparticle can rotate more freely at the interface, which leads to a large proportion of the surface of nanoparticle being covered by copolymers. When the chains A grow longer, the nanoparticle cannot rotate freely because chain A "hates" the oil phase, and then more A-type and B-type homopolymers are generated on the nanoparticle

surface in both phases. However, the copolymer composition at the NP surface still leads to a reduction in RC, as illustrated by the red curve in SI Figure 3. For comparison, in the system with the same Pr, the homopolymerization proceeds fast enough in both oil and water phases. There will be no apparent copolymer composition at the nanoparticle surface, thus the effect of the copolymer on the RC of the outermost part of the nanoparticle is rather weak.

5. The simulations with the bond-breaking process.

Following experiments,[1,2] in simulations we design a two-step reaction process. The first step is the atom transfer radical polymerization (ATRP) and the second step is the bond-breaking process under stress. Specifically, the bond S-A connecting the initiator S and the homopolymer A has the possibility to be broken in the second reaction. We will stop the bond-breaking reaction when the number of dissociated chains is about half of the total number of chains (about $6 * 10^5$ steps). Then we calculate the regularity of chains that have grafted from the nanoparticle surface in different cases.

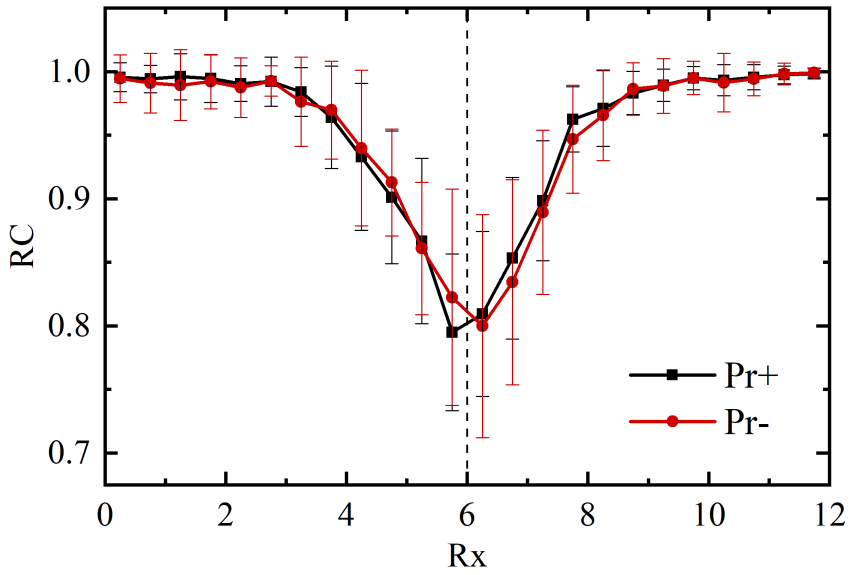

Figure 4: The order parameter RC of grafted chains on JNPs in each bin in cases of ATRP step (Pr+, black curve) and the bond-breaking step (Pr-, red curve). Vertical line shows the mass center of JNP.

From SI Figure 4 we can find that the bond-breaking process will not influence the profile of RC but it can cause the nanoparticle move into the oil phase (favoring component B) slightly. This is because with the reduction of the A chains, there is residue pulling force resulted from the solvation of more B chains in oil phase. It is in consistence with the result that when the molar ratio of one component is reduced, the nanoparticle will move into another phase favoring the other component gradually.[3]

References

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(2) Lyu B, Cha W, Mao T, et al. Surface confined retro Diels-Alder reaction driven by the swelling of weak polyelectrolytes. ACS Applied Materials & Interfaces, 2015, 7(11): 6254-6259.

(3) Zhao S, Zhan B, Hu Y, et al. Dynamics of Pickering emulsions in the presence of an interfacial reaction: a simulation study. Langmuir, 2016, 32(49): 12975-12985.