Tuning Polymerization Rate Program Block Copolymer Assemblies in PISA: A Simulation Study

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Abstract. As a powerful tool of controlled preparation of polymeric nanomaterials, polymerization-induced self-assembly (PISA), has been developed and extensively studied in the past decade. In this work, the RAFT polymerization system of P4VP as chain transfer agent and St as monomer in methanol was modelled and their PISA process was simulated by dissipative particle dynamics. Different morphologies of P4VP-b-PS was obtained at tuning polymerization rate. The morphology evolution at high conversation was investigated in detail and it was found that the appearance of worm-like micelles was a key point to determine the self-assemblies was vesicles or tubes. In addition, the PISA behavior at low conversion was also studied. The final morphologies was different with that at 100% conversion, but these results were well agreed with experiments. This simulation studies identified polymerization rate as the key factors on tuning morphology in PISA and broadens its research method.

1. Introduction
Polymeric nano-objects have gained great interest due to their versatile applications in self-healing, nanocatalyst carrier, nanoparticles or drug controlled release, and cancer treatment and diagnosis[1]. In preparation of these nano-objects, polymerization induced self-assembly (PISA) has shown great advantages over conventional self-assembly in the selective solution (SA) by virtue of uniform morphology, one-pot facial synthesis route and high solids, which makes the scale-up production of polymeric nano-materials possible[2].

In the past decade, some strategies have been developed to tune the morphologies in PISA. For example, Wan et al tuned block length and feed ratio to synthesize a series of assemblies of poly(4-vinylpyridine)-b-polystyrene (P4VP-b-PS), such as sphere, rod, worm, vesicle and yolk/shell structure[3]. Armes group has made great contribution to the morphology control in PISA, the spherical micelle, worm-like micelle, vesicle and oligolamellar vesicle of poly(ethylene glycol)-b-poly(2-hydroxypropyl methacrylate) diblock copolymer were successfully achieved though regulating on degree of polymerization (DP)[4]. In addition, unique jellyfish and frambooidal vesicle were yielded by using poly(glycerol monomethacrylate)-b-poly(2-hydroxypropyl methacrylate) and poly(glycerol monomethacrylate)-b-poly(2-hydroxypropyl methacrylate)-b-poly(benzyl methacrylate)[5]. Zhang et al prepared compartmentalized vesicle by employing the blends of AB/BAB block copolymer[6]. An et al demonstrated that star polymer architecture could promote the morphology transformation in PISA[7].

In short, PISA developed from SA has shown many efficient strategies to control morphology, but the in-depth understanding of underlying growth origin like we do in self-assembly still needs more efforts.
Compared with SA, the major difference in PISA is the self-assembly happens along with a simultaneous polymerization. Hence, polymerization rate (Pr) plays an important role in the PISA behavior. One example is that different morphologies, vesicles in PISA and nanotubes in SA were prepared using P4VP-b-PS in methanol[8], which suggests that the polymerization in PISA affects the self-assemblies morphology. So, processing an in-depth discussion on the dynamic self-assembly process and uncover the roles of Pr on the morphology regulation has great promise for the development of PISA, especially to develop a feasible route to tune morphology of self-assemblies.

Here, employing the dissipative particle dynamic (DPD) simulation and reaction model[9], which was first used by Lin et al to study the PISA behavior[10], we designed a series of simulations to investigate the effects of Pr on self-assembly morphology.

In this work, the PISA behavior in RAFT polymerization of styrene (St) in methanol with P4VP as the macromolecular chain transfer agent (macro-CTA) was examined. In all simulations, initial concentration of P4VP and St kept constant (1.5 w/w% for P4VP, 10.5w/w% for St). To probe the Pr effect, the reactive probability of bonding between monomers and active end of P4VP denotes Pr, which was set to 0.00001, 0.000025, 0.0001, 0.0002, 0.0004, respectively. Notably, the morphology evolution at different Pr was exhibited when the conversion was almost 100%. Besides that, PISA processes at lower conversion (~ 64%) were also studied, which is closer to the experimental condition. Our study suggested that Pr was one primary factor dominating the self-assembly behavior, and provided a versatile approach to tune self-assembly morphologies for definite functionalized applications.

2. Results and discussion

Figure 1 (a)-(e) showed self-assemblies obtained from PISA at different P_r. With increase of P_r from 0.00001 to 0.000025, 0.0001, 0.0002, 0.0004, lamellar vesicle, vesicle, peanuts-like vesicle and nanotube were produced, respectively. In Figure 1 (f)-(j), P4VP-b-PS with various chain lengths in self-assemblies were shown by different colors. And it was obvious that the distribution of the copolymers with various lengths on the five micelles was uniform. In simulations, all monomer conversations achieved 100% at five P_r, and the total polymerization time was 1.3 x 10^7 \tau \text{ at } P_r = 0.00001, 5 \times 10^6 \tau \text{ at } P_r = 0.00025, 1.3 \times 10^6 \tau \text{ at } P_r = 0.0001, 6.5 \times 10^5 \tau \text{ at } P_r = 0.0002, 3 \times 10^5 \tau \text{ at } P_r = 0.0004. Figure 2 (a) showed ln(M_0/M) and conversion versus normalized time in PISA at five P_r. These curves have similar variation tendency, and indicate that polymerization behavior at different P_r are identical, except that the polymerization time is expanded at lower P_r. On the other hand, from Figure 2 (b), the length distribution of copolymers was almost identical at five different P_r. So in this case, the versatile morphologies obtained at five different P_r was not due to the polymerization behavior or copolymer composition, it might be ascribed to different growth rate of chain, which was further confirmed as follow.

![Figure 1](image)

**Figure 1.** Self-assembly morphologies obtained at varied Pr, (a) Pr = 0.00001 (b) Pr = 0.000025 (c) Pr = 0.0001 (d) Pr = 0.0002 (e) Pr = 0.0004; (f-j) Spatial distribution map of copolymer in micelles with
different chain length, corresponding to the upside micelles, the long and short chain are shown in red and blue, respectively.

The SA of P4VP-b-PS in methanol, which is the self-assembly progress without the polymerization was also studied. The amphiphilic copolymer system was modelled and their molecular weight and molecular weight distribution were set as Figure 2 (b). Long nanotube was obtained from sphere-vesicle-tube transition as shown in Figure 3 (f). Firstly, the spherical micelles were formed by aggregation of dispersive amphiphilic copolymers due to the solvophobic effect of PS. Then the spherical micelles fused to lamellar structure, which curled to small vesicles with similar size. Finally, the vesicles fused along one direction to form a long nanotube.

![Figure 2](image-url)  
**Figure 2.** (a) The profile of \( \ln(M_0/M) \) over time, \( M_0 \) is the initial monomer concentration, \( M \) is the monomer concentration at a certain time; the inset shows the conversion of the monomers with the normalized time. (b) The probability distribution of copolymer with different chain length in micelles obtained at different Pr.

![Figure 3](image-url)  
**Figure 3.** Self-assembly progress of the PISA of five Pr and the SA versus time and the corresponding conversion. Hiding the hydrophilic block and sectional view were used to show the details. For the PISA, when \( Pr = 0.0004 \), the 63.6% of monomers polymerized at \( 6.0 \times 10^4 \tau \) and spherical micelles appeared in Figure 3 (e). Then similar sphere-vesicle-tube transition occurred, and a short
nanotube was obtained at 100% conversation. Thus, polymerization at the high Pr didn’t affect self-assembly process, because it arrived almost 100% conversion in a short time ($2.4 \times 10^5 \tau$). When Pr = 0.0002, similar nanotube was obtained. It is worthy to note that worm-like micelles turned out during sphere-vesicle transition. However, the worms existed in seconds and they transformed into lamella quickly. When Pr = 0.0001, the chain growth rate was further slowed down, so the worms existed for longer time to grow longer and partly crosslink. Then crosslinked worm transformed to a large vesicle, and other short worms curled into small vesicles. Finally, these vesicles with different sizes fused into a peanut-like vesicle because of the different curvature. When Pr decreased to 0.000025, worms crosslinked into a 2D porous structure and then transformed into a large vesicle. When Pr = 0.00001, low polymerization rate led to long time for self-assembly, the worms had enough time to fully crosslink and a porous clew-like sphere was formed. As the chain growth, the holes were filled and the layer was formed from the outer to the inner, finally a multilamellar vesicle was appeared. Therefore, at high Pr, polymerization finished in seconds and weakly affected the self-assembly, that is why PISA behavior at Pr = 0.0004 and the SA is similar. With Pr decreasing, chain growth was slowed down, and transition between spheres to vesicle became slower. The worm-like micelle, which is intervening morphology between spheres to vesicle, turned out. At Pr = 0.0002, worms was transitory and nanotube was formed. With further decrease of Pr, worms existed enough time to grow longer and crosslink, and vesicles with varying architecture were observed. Therefore, changing Pr controlled the existing time of worm-like micelle, which is the key to tune the final morphology to be vesicle or nanotube.

Figure 4. The number of micelles versus time from the PISA of five different Pr and the SA. Inset: An enlarged view of the bottom-left corner.

Figure 5. (a) Morphologies when the polymerization was terminated at 64% conversion and (b) final morphologies after continuous evolution.

To further uncover the process of PISA, the number of micelles ($N_{mic}$) varies over time were studied as shown in Figure 4. $N_{mic}$ declined over time both in PISA and SA, due to the fusion of self-assemblies and morphology transition. In PISA, when Pr was increasing, fast growing of hydrophobic block caused $N_{mic}$ to decrease more quickly, and the $N_{mic}$ curves of PISA was increasingly close to that of SA. Based on self-assembly process of PISA and SA, we could draw a conclusion that the SA in selective solvent could be regarded as a particular case of the PSIA when Pr is infinite.

In fact, the high conversion is hard to be realized in practical experiments of PISA, especially in organic solvent[3, 10]. The low conversion led to the formation of shorter chain and continuous
transformation of morphologies by self-assembly after chain termination. So we also simulated the PISA progress in real experimental condition by terminating the polymerization at ~60% conversion. As shown in Figure 5, at $Pr = 0.0004$, and 0.0002, vesicles were formed, but these vesicles can’t further transfer into tubes with expanding time. These results are well agreed with the vesicles prepared in experiments from PISA of the P4VP-b-PS when the conversion is about 60% to 70%. Therefore, the low conversion hindered the further transformation of morphology from vesicle to tube. In addition, we adjusted $Pr$ to 0.00015 and the nanotube were successfully synthesized, which showed that the appropriate $Pr$ was the key point to obtain nanotubes even when the conversion was low. However, the region of $Pr$ where nanotubes appeared was relatively narrow, we assumed this is the reason why it is rarely reported about nanotubes obtained in experiments.

3. Conclusion
In summary, PISA of P4VP-b-PS were studied, various morphologies, multilamellar vesicle, peanut-like vesicle, and nanotube, were obtained by tuning $Pr$. It was found that $Pr$ affected the final morphology no matter the conversion is high (100%) or low (64%). During the PISA, existing time of worm-like micelle as a key point to determine the final morphology is vesicle or tube. Through comparison with PISA, based on the morphologies and their evolution, SA in selective solvent could be regarded as a special case of PISA where $Pr$ is infinite. The application of DPD simulations in PISA strengthens the understanding of PISA and accelerates its further development.

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