

# Aqueous Polymerization-Induced Self-Assembly for the Synthesis of Ketone-Functionalized Nano-Objects with Low Polydispersity

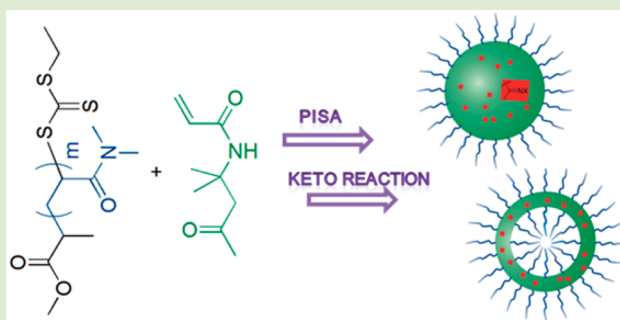
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## Supporting Information

**ABSTRACT:** Efficient synthesis of functionalized, uniform polymer nano-objects in water with controlled morphologies in one step and at high concentrations is extremely attractive, from perspectives of both materials applications and industrial scale-up. Herein, we report a novel formulation for aqueous reversible addition–fragmentation chain transfer (RAFT) dispersion polymerization based on polymerization-induced self-assembly (PISA) to synthesize ketone-functionalized nanospheres and vesicles. Significantly, the core-forming block was composed entirely of a ketone-containing polymer from a commodity monomer diacetone acrylamide (DAAM), resulting in a high density of ketone functionality in the nano-objects.

Producing uniform vesicles represents another challenge both in PISA and in the traditional self-assembly process. Aiming at producing uniform nano-objects, especially vesicles, in such a highly efficient aqueous PISA process, we devised strategies to allow sufficient time for the in situ generated polymers to relax and reorganize into vesicles with a remarkably low polydispersity. Specifically, both reducing the radical initiator concentration and lowering the polymerization temperature were shown to be effective for improving the uniformity of vesicles. Such an efficient, aqueous PISA to produce functionalized and uniform nano-objects with controlled morphologies at solid contents up to 20% represents important progress in the field.



Self-assembly of block copolymers<sup>1,2</sup> in solution is an elegant and well-established strategy for the preparation of polymer nano-objects with wide-ranging morphologies, including spheres,<sup>3</sup> worms,<sup>4–6</sup> lamellae,<sup>7,8</sup> vesicles,<sup>9,10</sup> toroids,<sup>11,12</sup> multi-compartment micelles,<sup>13,14</sup> and hexagonally packed rods,<sup>15</sup> among others. This powerful technique has enabled the preparation of nanomaterials with tailored composition, functionality, and structure, providing a versatile material basis for a number of nanotechnologies such as catalysis,<sup>16</sup> therapy,<sup>17</sup> imaging,<sup>18</sup> sensing,<sup>19</sup> and nanoreactors.<sup>20</sup> However, despite great success having been achieved, block copolymer self-assembly suffers from low efficiencies by using low copolymer concentrations (<1%), multistep syntheses, and postpolymerization processing procedures.<sup>21</sup>

Alternatively, the recently emerging polymerization-induced self-assembly (PISA) strategy is promising for producing nano-objects with controllable morphologies, albeit in a more efficient manner via simultaneous polymerization and in situ self-assembly at high polymer concentrations.<sup>22–24</sup> The key to the success of PISA is the employment of controlled radical polymerization techniques,<sup>25,26</sup> particularly RAFT, in heterogeneous media.<sup>27–40</sup> The ability to produce PISA-generated nano-objects in water is appealing for economic and environmental reasons. We have been interested in aqueous RAFT dispersion polymerization because of its facile and robust nature: the homogeneous starting solution is easy to manipulate, the diameter of the nanoparticles is readily tunable,

and stimuli-responsive nanoparticles can be effectively prepared. However, examples of successful aqueous RAFT dispersion polymerization formulations have been limited due to the special requirement for a soluble monomer that produces an insoluble polymer in water;<sup>24</sup> current demonstrations include *N*-isopropylacrylamide,<sup>41–43</sup> *N,N*-diethylacrylamide,<sup>44</sup> 2-methoxyethyl acrylate,<sup>45,46</sup> oligo(ethylene glycol) methyl ether methacrylate,<sup>47</sup> and 2-hydroxypropyl methacrylate.<sup>48,49</sup> Therefore, developing new aqueous dispersion polymerization formulations for PISA is essential to expand the scope of this unique approach, which may be aided via rational monomer/polymer structure–property analysis and potentially via design of new monomer/polymer pairs guided by computation.

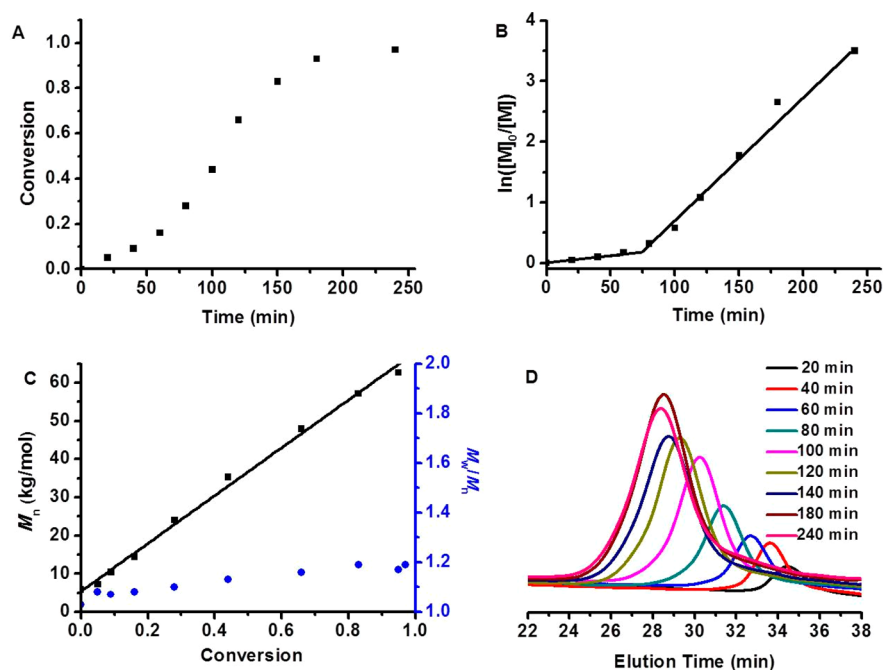
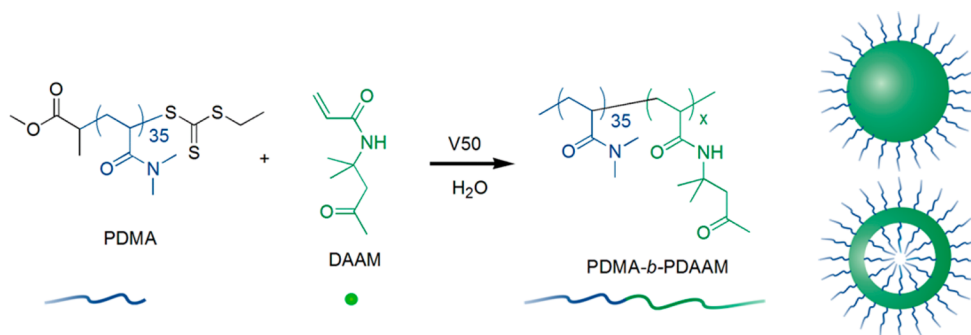
Although the field of PISA is rapidly growing, the core polymer of PISA-generated nano-objects generally lacks functionality. The nano-objects based on 2-hydroxypropyl methacrylate contain secondary alcohol in the core, but derivatization has not been demonstrated.<sup>31,32,49</sup> Only in a few cases, functionality was introduced by copolymerization of a small fraction of functional monomers with the major nonfunctional monomer.<sup>50,51</sup> The generation of nano-objects with an entirely functionalized core via PISA represents another

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Scheme 1. Schematic Representation of Aqueous RAFT Dispersion Polymerization of DAAM to Prepare Nanospheres and Vesicles



**Figure 1.** RAFT dispersion polymerization of DAAM using PDMA<sub>35</sub> at 70 °C, [DAAM]/[PDMA]/[V-50] = 300:1:0.03, solids content = 10%: (A) conversion vs polymerization time, (B) polymerization kinetics, (C) PDMA-*b*-PDAAM molecular weight and dispersity vs conversion (the intercept corresponds to the  $M_n$  of PDMA), and (D) evolution of GPC traces of PDMA-*b*-PDAAM.

important challenge. We envisaged that PISA-generated nano-objects comprising a pure functionalized polymer core are advantageous for a more efficient functionalization step and to produce a high density of functionality in the nano-objects, which should be beneficial for many applications. In addition, aqueous PISA to produce nano-objects with an entirely functionalized core should be more desirable than alcoholic PISA.<sup>52</sup>

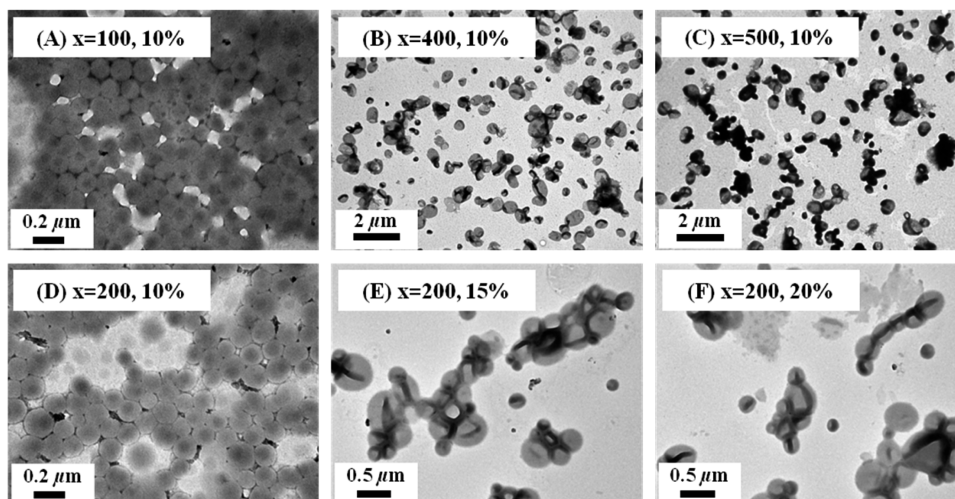
The application of polymer nano-objects is often impeded by the broad size distribution, especially for polymer vesicles or polymersomes. Efforts have been devoted to improving the uniformity of vesicles produced by traditional self-assembly of block copolymers.<sup>10,53,54</sup> This drawback in the uniformity of vesicles inevitably applies to PISA. In a recent report, Armes et al. utilized a binary mixture of short and long stabilizer blocks to reduce the polydispersity of vesicles in ethanolic PISA.<sup>55</sup>

Bearing the above challenges in PISA in mind, herein we report (1) a novel aqueous dispersion polymerization formulation based on a commodity monomer, (2) nano-objects comprising a ketone-functionalized core, and (3) new

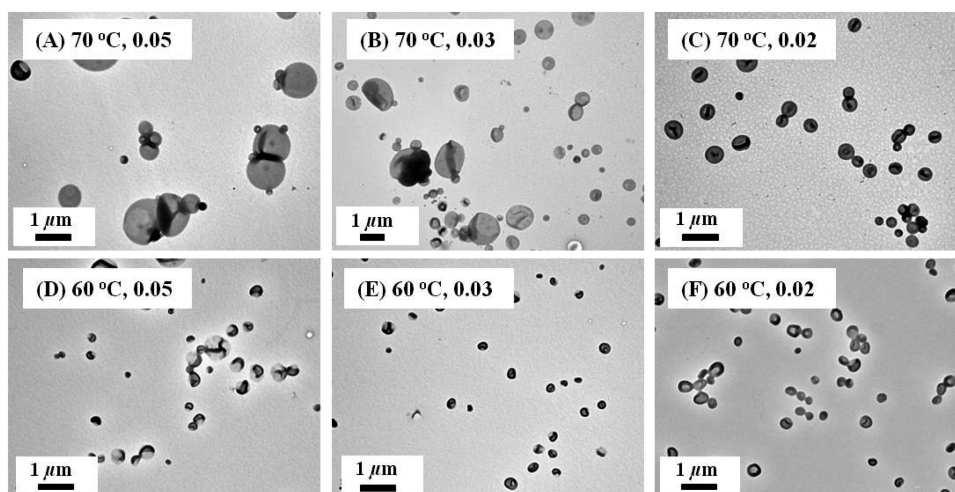
strategies to improve the uniformity of vesicles produced by PISA.

As shown in Scheme 1, aqueous RAFT dispersion polymerization of DAAM was conducted using poly(*N,N*-dimethylacrylamide) (PDMA) as the stabilizing block and 2,2'-azobis(2-methylpropionamide) dihydrochloride (V-50) as the radical initiator. Near-quantitative conversion was routinely achieved within 3 h of polymerization at 70 °C (Figure 1A and Supporting Information). Kinetics analysis of  $\ln([M]_0/[M])$  vs time revealed that this dispersion polymerization proceeded via two stages: the first stage corresponding to initial solution polymerization had a slower polymerization rate and the second stage corresponding to polymerization in monomer-swollen particles had a polymerization rate more than 7 times higher (Figure 1B). Such an enhancement in polymerization rate was observed to varying degrees depending on the polymerization conditions.

The onset of turbidity at around 60 min (~16% conversion) indicated the formation of nanoparticles self-assembled from block copolymers with a critical composition of PDMA<sub>35</sub>-*b*-PDAAM<sub>48</sub>, when the polymerization was conducted targeting a



**Figure 2.** Representative TEM images of PDMA<sub>35</sub>-*b*-PDAAM<sub>x</sub> nano-objects synthesized at different solid contents,  $[V-50]/[PDMA] = 0.03$ , 70 °C.



**Figure 3.** TEM images of PDMA<sub>35</sub>-*b*-PDAAM<sub>300</sub> vesicles synthesized at 70 or 60 °C, 20% solids, using different molar ratios of  $[V-50]/[PDMA]$ .

number-average degree of polymerization (DP) of 300 at a solid content of 10%. The molecular weight of the block copolymers scaled linearly with conversion, and the dispersity ( $\bar{D}$ ) remained below 1.2 up to near-quantitative conversion (Figure 1C). The gel permeation chromatography (GPC) traces showed a gradual shift toward high molecular weights as the conversion increased, indicating successful block copolymer formation (Figure 1D). Taken together, these results suggest that the dispersion polymerization of DAAM was well controlled by the RAFT process when employing PDMA as the stabilizer. Well-defined block copolymers were obtained in all cases when targeting DAAM DPs in the range of 100–500 at various solids (Figure S2 and Table S1, Supporting Information).

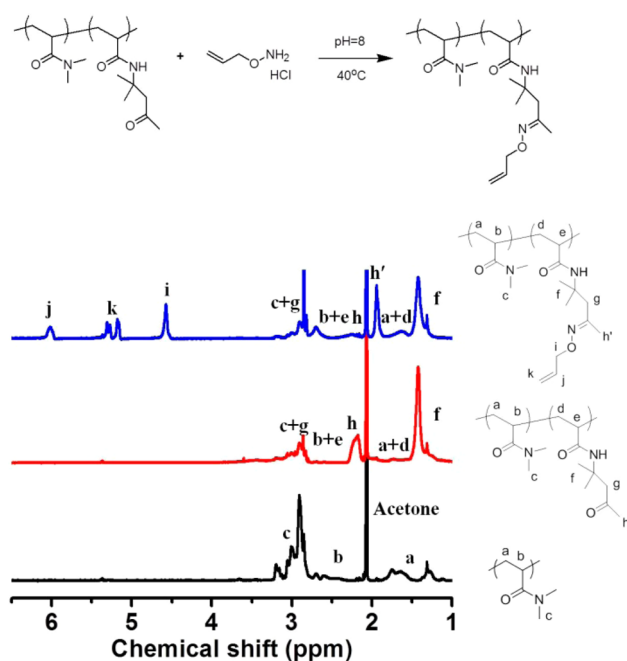
PISA formation of PDMA<sub>35</sub>-*b*-PDAAM<sub>x</sub> copolymer nano-objects was investigated by systematically adjusting the targeting DAAM DP (translating into block volume ratio after polymerization) and the solid content (translating into copolymer concentration after polymerization), and the results are summarized in Table S1 (Supporting Information). The size of the nano-objects was affected by several factors including target DP, solid content, and initiator concentration. As the target DP and solid content were increased, a nano-object morphology transition from solid nanospheres to vesicles was

observed. When the DPs were lower than 200, only solid nanospheres were obtained up to 20% solids. Pure vesicles were obtained for DPs 200 and 300 at solid contents  $\geq 15\%$ . For larger DPs of 400 and 500, pure vesicles were formed at a lower solid content (10%). Representative TEM (transmission electron microscopy) images are shown in Figure 2.

Experimentally, PISA is quite simple and readily conducted in one step. Mechanistically, PISA is a rather complex process involving simultaneous polymerization, self-assembly, and reorganization steps. The coexistence of multiple processes implies that the in situ formed block copolymers often have insufficient time (on the time scale of polymerization) to relax to their thermodynamically favorable conformations such that some of the morphologies may merely represent kinetically frozen states rather than thermodynamically equilibrated states. Indeed, rapid polymerization quickly depletes the monomers in the monomer-swollen particles and simultaneously increases the chain length, which results in a combined effect in immobilizing the polymer chains, especially for polymers having a high glass transition temperature. As a consequence, some higher-order morphologies, e.g., vesicles, may have a high polydispersity index (PDI) due to insufficient time for the copolymers to fully relax and completely reorganize from the lower-order morphologies. We surmised that lowering the

polymerization rate to allow a slower growth of the polymer chains such that the polymer chains (swollen by monomers to a higher degree) could have more time to adjust their conformations and reorganize would be a feasible strategy to improve the uniformity of vesicles. We have attempted to lower both the polymerization temperature and the concentration of the radical initiator. The polymerization rate was suppressed in such a way that near-quantitative conversion was still achieved within an acceptable period of time (10 h) (Figure S3, Supporting Information). To our delight, reducing the polymerization rate indeed improved the uniformity of the vesicles, as confirmed by both TEM (Figure 3) and dynamic light scattering (DLS) (Figures S5 and S6, Supporting Information). At 70 °C, when the molar ratio of [V-50]/[PDMA] (at a constant [PDMA]) was lowered from 0.05 to 0.03 to 0.02, remarkably uniform vesicles ( $D_h$  510 nm and PDI 0.08 by DLS) were obtained using the lowest initiator concentration (Figure 3C), which were in direct contrast to the highly polydisperse vesicles obtained using higher initiator concentrations (Figures 3A and B), for which the PDI was 0.20 and 0.15, respectively. In the series of vesicles prepared at 60 °C, the same effect was also discernible: the vesicles prepared using 0.05 equiv of initiator had a PDI of 0.13 (Figure 3D), while the other two samples prepared using 0.03 and 0.02 equiv of initiator had a similarly low PDI of 0.08–0.09 (Figures 3E and F). Interestingly, when comparing the samples prepared at these two different temperatures, it was clear that the vesicles prepared at 60 °C using 0.05 and 0.03 equiv of initiator were more uniform than those prepared at 70 °C, suggesting that lowering the polymerization rate by polymerizing at a lower temperature is equally effective to reduce the PDI of the vesicles.

Functionalization such as fluorescent labeling or drug conjugation is often employed when applying nano-objects in biomedical fields. With PDAAM as the core polymer, we anticipated that these nano-objects could be efficiently functionalized using oxime or hydrazone chemistry.<sup>56–58</sup> To illustrate this aspect, *O*-allyl hydroxylamine was chosen as a representative hydroxylamine to functionalize the nano-objects in phosphate buffer (pH = 8) at 40 °C. For functionalization to PDMA<sub>35</sub>-*b*-PDAAM<sub>100</sub> nanospheres ( $D_h$  = 428 nm), 1.3 equiv (relative to DAAM units) of *O*-allyl hydroxylamine resulted in 62% ketone groups being converted to oxime; this number increased to 82% when 2 equiv of hydroxylamine was used. As shown in Figure 4, the methyl group (h) adjacent to the ketone group was initially at 2.29–2.13 ppm, which shifted to 2.0–1.85 ppm for the methyl group (h') adjacent to the formed oxime group in the functionalized polymer. In addition, three sets of protons from the allyl group appeared at 6.08–5.96 ppm (j), 5.35–5.13 ppm (k), and 4.64–4.49 ppm (i) in the functionalized polymer. While functionalization using 1.3 equiv of hydroxylamine (62% conversion) only slightly increased the size of the nanospheres with a negligible effect on the PDI, broadening of size distribution was observed when using 2 equiv of hydroxylamine (82% conversion). PDMA<sub>35</sub>-*b*-PDAAM<sub>300</sub> vesicles ( $D_h$  = 346 nm) could be similarly functionalized. The stability of vesicles was more sensitive to the functionalization conditions. The use of 1.3 equiv of hydroxylamine (53% conversion) increased the PDI from 0.087 to 0.177, while the use of 2 equiv of hydroxylamine caused precipitation of the vesicles. We also used fluorescein-5-thiosemicarbazide to label nanospheres via hydrazone chemistry, which resulted in a colloidal solution with a strong green



**Figure 4.**  $^1\text{H}$  NMR spectra in  $\text{CD}_3\text{COCD}_3$  of PDMA, PDMA-*b*-PDAAM, and *O*-allyl hydroxylamine-functionalized PDMA-*b*-PDAAM.

fluorescence. The labeling was calculated to result in one fluorescent molecule per 640 polymer chains.

In summary, we have developed a novel aqueous RAFT dispersion polymerization formulation based on the DAAM/PDAAM pair. Both nanospheres and vesicles with a ketone-functionalized core were produced via PISA by systematically adjusting the DP and the solid content. Significantly, the uniformity of the vesicles could be improved by lowering the polymerization temperature and the concentration of the radical initiator, both of which reduced the polymerization rate such that the in situ generated block copolymers could have sufficient time to relax and reorganize, thus improving the uniformity of the vesicles. The ketone-containing nanospheres and vesicles could be efficiently functionalized via oxime and hydrazone chemistry. Such unique features make these aqueous PISA-generated nano-objects well-suited for various applications. The principle demonstrated herein to improve the uniformity of vesicles may be well extended to other PISA formulations to synthesize uniform higher-order nano-objects.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental details and supplementary data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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