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Single Monomer for Multiple Tasks: Polymerization Induced Self-Assembly, Functionalization and Cross-Linking, and Nanoparticle Loading

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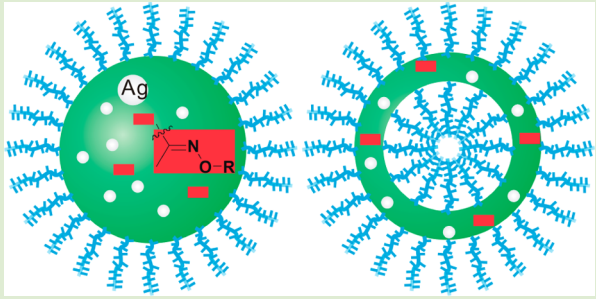
Supporting Information

ABSTRACT: Efficient preparation of multifunctional nano-objects with controlled morphologies in one step at high concentrations is synthetically challenging, yet is highly desirable, in a broad range of materials applications. Herein, we address this synthetic hurdle by introducing a single commodity monomer 2-(acetoacetoxy)ethyl methacrylate (AEMA) to realize multiple functions. Facile preparation of both nanospheres and vesicles via polymerization induced self-assembly at concentrations of 20−30% provided defined polymeric nanomaterials with reactive handles inherent to the AEMA units. High-yielding keto-alkoxylamine chemistry was utilized to decorate and cross-link the nano-objects. Nanoparticle loading into the designated location within both nano-objects was exemplified with in situ formation of silver nanoparticles. The concept of using a single monomer capable of both morphology control and multifunctionalization is expected to offer significant opportunities in functional nanomaterials.



Synthetic efforts toward the preparation of multifunctional polymeric nanomaterials of various morphologies are growing, aiming at applications in catalysis,[1] therapy,[2] imaging,[3] and sensing.[4] Self-assembly of block copolymers is an elegant, well-established strategy to afford nano-objects of a wide breadth of morphologies.[5−11] One major limitation, however, is the low polymer concentration (typically <1%) employed to generate these nano-objects via a secondary postpolymerization processing step involving, for example, solvent displacement. While the recently emerging polymerization induced self-assembly (PISA) strategy may potentially solve this problem by conducting a one-step polymerization to generate nano-objects with controllable morphologies at high concentrations,[12−24] it suffers from a general lack of functionality of the core-forming block.[25]

In traditional self-assembly of block copolymers, multifunctionality is generally introduced through copolymerization of comonomers bearing different reactive groups.[26] Typically, this requires tedious optimization of polymerization and is potentially limited by the compatibility of different reactive groups. In PISA, the introduction of functionality is rarely demonstrated, presumably due to the difficulties for functional core-forming polymers to effectively self-assemble under the in situ polymerization conditions. Moreover, cross-linking is employed when enhanced thermal, mechanical, and structural stability is required.[27] In situ cross-linking using bisfunctional monomers during PISA hinders morphology transition, and therefore, mild and efficient chemistry for postpolymerization cross-linking is highly desirable.

Inorganic-polymer composite nanoparticles are of great current interest, combining the best properties of both components.[28] Two general strategies for the preparation of composite nanoparticles include (1) coassembly of block copolymers and presynthesized inorganic nanoparticles,[29−32] and (2) in situ formation of inorganic nanoparticles within the matrix of presynthesized polymer nanoparticles.[33−38] While these approaches have been successful in generating diverse inorganic-polymer nanoparticles, effective synthesis of composite nanoparticles coupled with multifunctionality is generally lacking.

Herein, we introduce a "multitask" monomer concept to effectively address a number of synthetic limitations, wherein a single monomer is used in a one-step process to generate multifunctional nano-objects with controlled morphologies, thus minimizing synthetic efforts while maximizing gain in functionality (Scheme 1). Specifically, dispersion polymerization of AEMA produces nanospheres and vesicles bearing reactive β-ketoester groups. The keto group is functionalizable (cross-linkable) with alkoxylamine (bisalkoxylamine) to form oxime[39,40] under ambient conditions. Moreover, the β-ketoester can engage in metal complexation[41] and a subsequent reduction step produces silver nanoparticles within the nano-objects.

PISA of AEMA-based nanospheres and vesicles was conducted via RAFT (reversible addition−fragmentation

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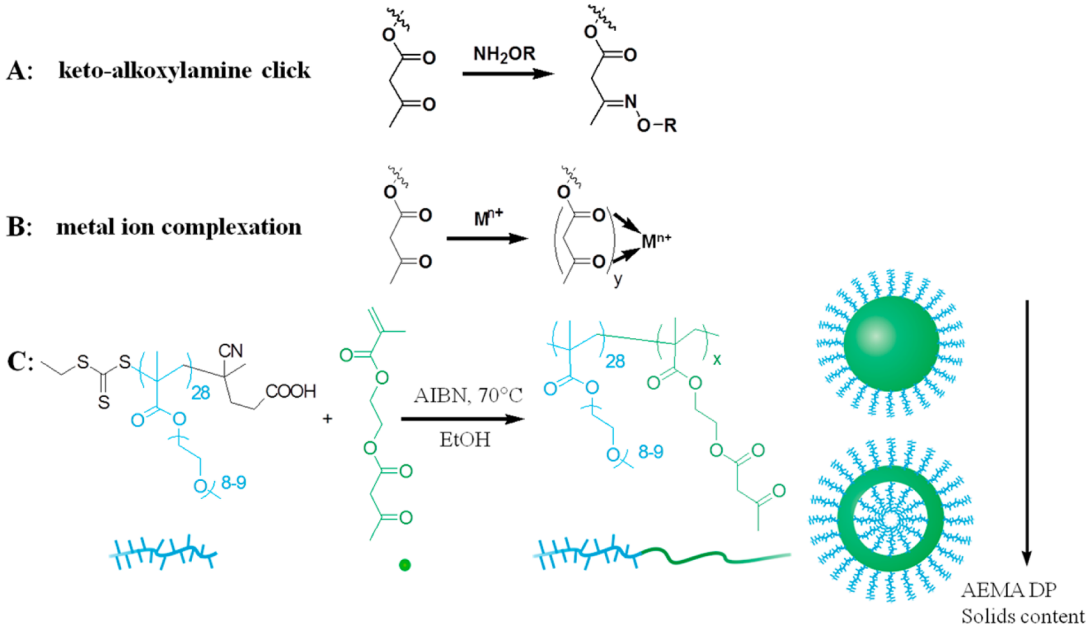
Scheme 1. (A) Reaction between the Keto Group of PAEMA and Alkoxylamine; (B) Metal Ion Complexation with the Ketoester Group of PAEMA; (C) PISA of AEMA in Ethanol Using PPEGMA as Macro-CTA to Prepare Nanospheres and Vesicles



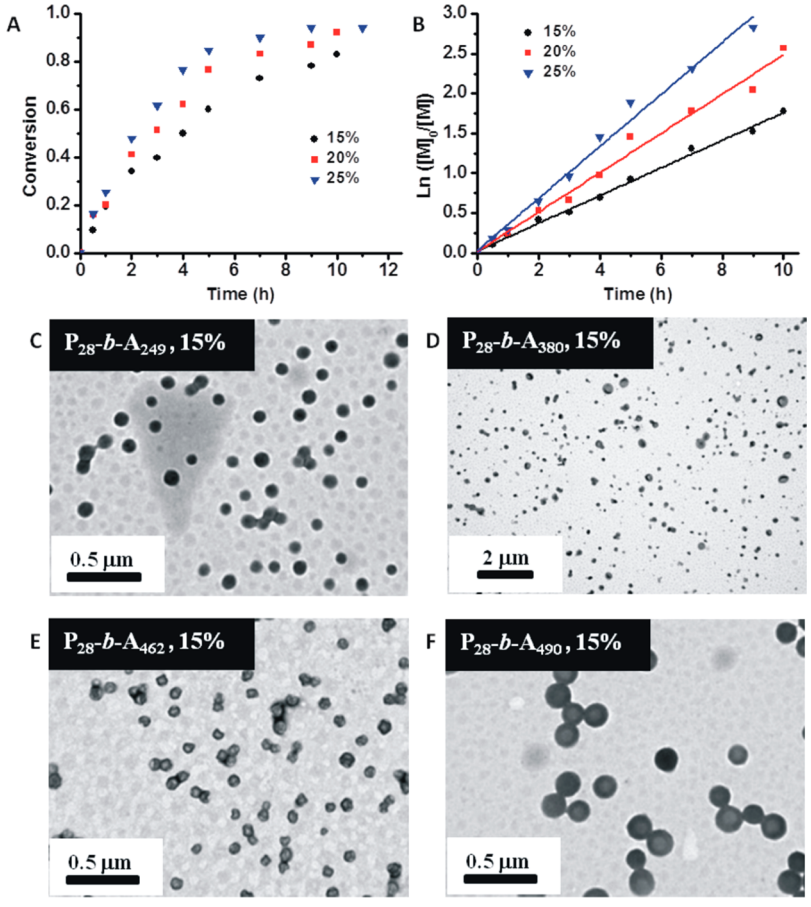


Figure 1. RAFT dispersion polymerization of AEMA targeting a DP of 300 at different solids contents of 15−25% w/v, [$PPEGMA_{28}$]/[AIBN] = 1:0.5, ethanol, 70 °C: (A) AEMA conversion vs polymerization time, (B) pseudo-first order polymerization kinetics. TEM images: $PPEGMA_{28}$-*b*-$PAEMA_x$ block copolymer nano-objects synthesized by RAFT dispersion polymerization at a solids content of 15% w/v, ethanol, 70 °C, where *x* corresponds to (C) 249 (nanospheres), (D) 380 (nanospheres + vesicles), (E) 462 (vesicles), and (F) 490 (vesicles; P-*b*-A denotes PPEGMA-*b*-PAEMA).

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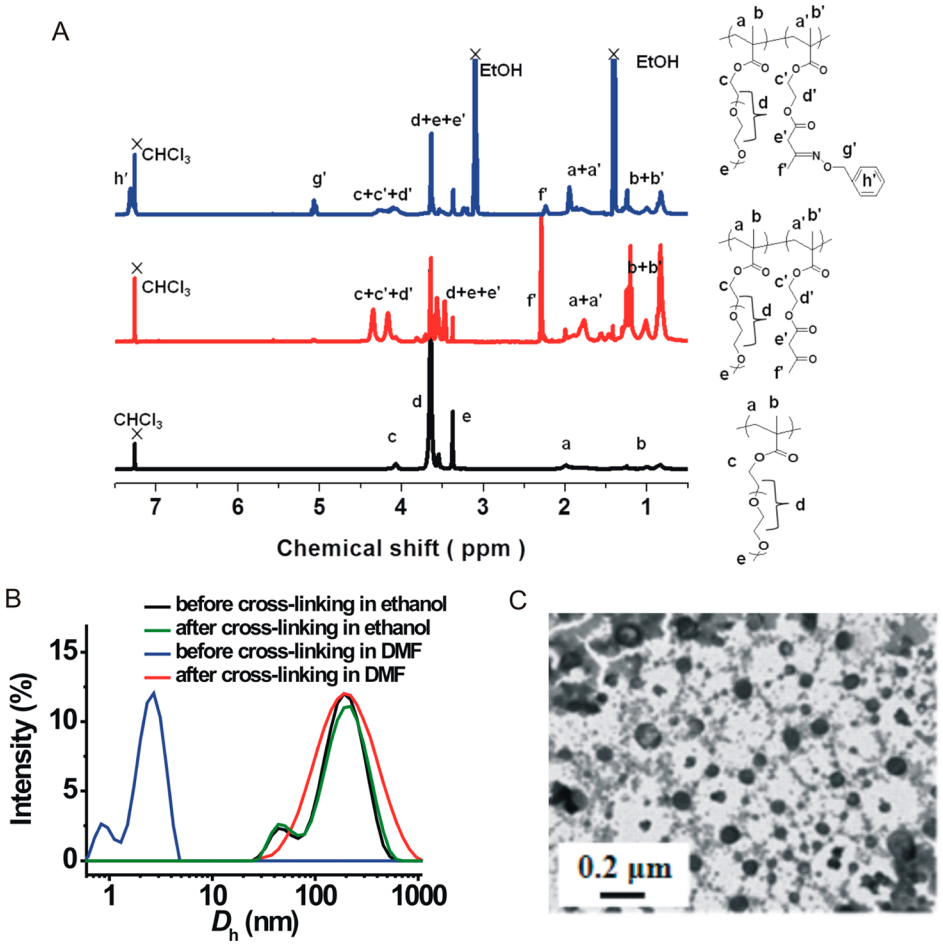

Figure 2. (A) ^{1}H NMR spectra in $CDCl_3$ of $PPEGMA_{28}$, $PPEGMA_{28}$-*b*-$PAEMA_{194}$, and *O*-benzyloxylamine functionalized $PPEGMA_{28}$-*b*-$PAEMA_{194}$. (B) DLS of $PPEGMA_{28}$-*b*-$PAEMA_{192}$ vesicles in ethanol and DMF before and after cross-linking. (C) TEM image of cross-linked $PPEGMA_{28}$-*b*-$PAEMA_{192}$ vesicles prepared from DMF dispersion.

chain transfer) dispersion polymerization in ethanol using poly(poly(ethylene glycol) methyl methacrylate) with a number-average degree of polymerization (DP) of 28 ($PPEGMA_{28}$) as the macromolecular chain transfer agent (Supporting Information, Figures S1,2), affording PPEGMA-*b*-PAEMA block copolymer nano-objects in one step. Both the DP (200−500) of AEMA and the total solids content (10−25%) were systematically adjusted to effect morphology transition (Supporting Information, Table S1). Typically, a high monomer conversion (~90%) was obtained within 12 h of polymerization, and the polymerization exhibited pseudo-first order kinetics, showing good RAFT control (Figures 1A,B and S3,4). As the DP of AEMA and the total solids content increased, the obtained nano-objects showed a morphology transition from nanospheres to vesicles (we did not observe worm[42] as the intermediate morphology in between). Representative TEM (transmission electron microscopy) images for increasing DP at a solids content of 15% are shown in Figure 1C−F. When the AEMA DP increased from 249 to 490, nanospheres were first observed at DP 249, both nanospheres and vesicles coexisted at DP 380, pure vesicles with a uniform size were evident at DP 462 and 490. The membrane thickness of the vesicles increased from 44 nm for DP 462 to 52 nm for DP 490, and the increased thickness showed a stronger mechanical support to the structure (wrinkled membrane for the former and smooth membrane for the latter). Solids content seemed to be more effective on inducing morphology transition than DP, with representative TEM images shown in Figure S6. Evolution of nanospheres to vesicles was also observed as the AEMA monomer conversion (thus DP) gradually increased during the same polymerization process targeting a DP of 500, at a 20% solids content (Figure S7).

Keto-alkoxylamine reaction was conducted using a slightly excess of benzyloxylamine (benzyloxylamine/AEMA unit = 1.05) on both nanosphere and vesicle samples in ethanol dispersion, and the conversion was ~90% for both samples. In a control experiment, a slightly higher conversion was obtained for the reaction conducted on molecularly dissolved block copolymers in THF (96%). After reaction, the nano-objects were characterized by TEM, DLS (dynamic light scattering), and ^{1}H NMR (proton nuclear magnetic resonance). Both TEM and DLS indicated that after reaction, the nano-objects maintained their dispersity with only a slight increase in diameter (Figures S8,9). By dissolving the nano-objects in $CDCl_3$, formation of oxime was confirmed by the appearance of the benzyl methylene group (g′) at 5.07 ppm and the aromatic ring protons (h′) at 7.32 ppm (Figure 2A). In addition, to generalize the functionality to other nano-objects by PISA, we demonstrated that AEMA can be copolymerized with other monomers suitable for PISA, such as benzyl methacrylate,[43] to provide functionalizable nano-objects that are unattainable with

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benzyl methacrylate alone (Supporting Information, Table S2, Figures S11−15).

This keto-alkoxylamine chemistry was also exploited to cross-link the nano-objects employing *O*,*O*′-1,3-propanediylbisoxylamine. Both nanosphere and vesicle samples were cross-linked similarly, which was confirmed by TEM and DLS. The nano-objects maintained their nanostructure in DMF (a good solvent) after cross-linking, while uncross-linked samples simply disintegrated into soluble polymers (Figures 2B,C and S10).

Silver nanoparticles were formed in situ in both nanospheres and vesicles by reduction using $NaBH_4$ after complexation of Ag^+ with the ketoester groups in the polymer nano-objects. The bluish colloidal polymer dispersion became brownish upon addition of $NaBH_4$ (Figure S16). The diameter of Ag nanoparticles was about 10 nm in both cases (Figure 3).

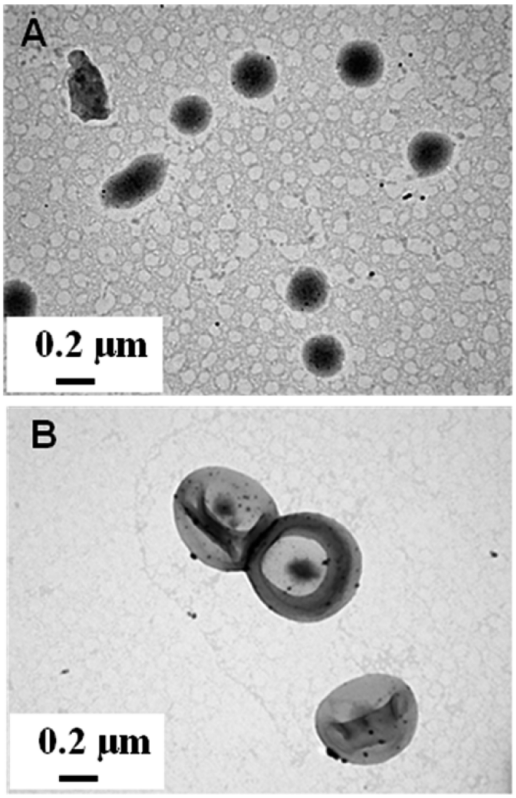

Figure 3. TEM images of (A) Ag nanoparticles in nanospheres ($PPEGMA_{28}$-*b*-$PAEMA_{200}$) and (B) Ag nanoparticles in vesicles ($PPEGMA_{28}$-*b*-$PAEMA_{192}$; $PPEGMA_{28}$-*b*-$PAEMA_{200}$ and $PPEGMA_{28}$-*b*-$PAEMA_{192}$ were synthesized at 15% and 30% solids, respectively; see Table S1).

Thermogravimetric analysis (TGA) suggested that the loading of Ag nanoparticles was 4% and 3.5% for the nanosphere and vesicle, respectively (Figure S17). Nanoparticle loading may be further increased by increasing the ratio of metal ion/AMEA units.

In conclusion, we demonstrate that PISA of AEMA produces block copolymer nano-objects with controlled morphologies in one step at high concentrations. The nano-objects undergo facile functionalization and cross-linking under mild conditions capitalizing on the keto-alkoxylamine chemistry. The versatility of the AEMA unit is further highlighted by loading silver nanoparticles into the AEMA-containing nano-objects. The use of a single monomer for simultaneous morphology control and generation of multifunctionality provides a strategy to minimize synthetic labor and facilitate scaleup of nanomaterial synthesis for a range of applications.

■ 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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