Polymerization-Induced Self-Assembly (PISA) Using ICAR ATRP at Low Catalyst Concentration

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Supporting Information

ABSTRACT: Polymerization-induced self-assembly (PISA) was achieved by conducting an initiators for continuous activator regeneration atom transfer radical polymerization (ICAR ATRP) at low ppm of copper catalyst concentration. A poly(oligo(ethylene oxide) methyl ether methacrylate)50 (POEOMA50) macroinitiator and stabilizer was synthesized by an aqueous ICAR ATRP using CuIICl2/tris(pyridin-2-ylmethyl)amine (TPMA) complex. Subsequently, the dispersion polymerization of benzyl methacrylate (BnMA) in ethanol was realized with a CuIIBr2/TPMA complex either at room temperature or at 65 °C using V-70 or AIBN as radical initiators, respectively. The effect of catalyst concentration, radical initiators, targeted degree of polymerization (DP) of PBnMA, solids content, and temperature on the molecular characteristics and self-assembly behavior of block copolymers POEOMA−PBnMA was evaluated by gel permeation chromatography (GPC), transmission electron microscopy (TEM), and dynamic light scattering (DLS). Block copolymers assembled into spheres, wormlike aggregates, and vesicles with diameters ranging from 100 to 600 nm, depending on the temperature, solids content, and the DP of PBnMA. The effect of the temperature on the polymerization behavior and morphological evolution was attributed to the temperature-dependent plasticization of the core-forming PBnMA block above and below its glass transition temperature (Tg = 54 °C).

INTRODUCTION

Over the past several years, polymerization-induced self-assembly (PISA) has been developed as a versatile route to prepare phase-separated nano-objects. Unlike the conventional strategy to self-assemble block copolymers by postpolymerization process, the essence of PISA is that the self-assembly is simultaneously accomplished and modulated during polymerization. Highly dilute conditions are often required (<1% w/w) for conventional solution self-assembly procedures in order to afford the controlled self-assembly of nanostructures. However, PISA can be readily realized at high solids content up to 40–50% w/w. A range of morphologies, such as spheres, worms/rods, lamellae, toroids, and vesicles, can be selectively produced in a PISA process. The polymeric nano-objects can be potentially used as templates, coatings, gel, and elastomers as well as in nanotechnology. Thus, PISA can present an important advancement in the technological utilization of self-assembly processes.

In a typical aqueous PISA procedure, a selected water-soluble macroinitiator is simultaneously used as a stabilizer and a surfactant. It is chain extended via a controlled/“living” polymerization process by a water-soluble monomer which forms a water-insoluble polymer. PISA can also be carried out in organic solvents, employing the same solubility/insolubility strategy. In a PISA, there is a transition from a homogeneous to a heterogeneous system with increasing monomer conversion. Micelles are formed by the chain extension from the soluble macroinitiator at a certain critical monomer conversion. This contrasts with conventional polymerization in dispersed media (such as suspension or emulsion) where micelles are formed at the beginning of the polymerization. In principle, all controlled/“living” polymerization mechanisms can be applied to PISA, such as nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), reversible addition–fragmentation chain transfer (RAFT) polymerization, living anionic polymerization, or ring-opening metathesis polymerization (ROMP). However, to date, PISA has been predominantly demonstrated using the RAFT
mechanism. Only few attempts have been reported on PISA via normal ATRP mechanism. One major barrier for the application of normal ATRP in this interesting emerging field is the significant concentration of copper catalyst that presents challenges for purification and application of final materials. In order to extract the large amount of copper catalyst used in these systems by dialysis, a cross-linker was always copolymerized at the beginning of polymerization. This requirement placed constraints on both the control of morphologies and the viability of the process. Another challenge for the ATRP-based PISA lies in the unique transition metal complex catalyst.

PISA was successfully carried out at room temperature using various solvents under either diminished copper catalyst concentration. Recently, RAFT polymerization. This can strongly affect ATRP-based PISA. Recently, employing a reversible activation and deactivation equilibrium catalyzed by transition-metal redox-active complexes, the normal ATRP process has been improved by using lower concentration of catalyst and higher tolerance to impurities and air. These procedures include reverse ATRP, simultaneous reverse and normal initiation (SR&NI) ATRP, activator generated by electron transfer (AGET) ATRP, initiators for continuous activator regeneration (ICAR) ATRP, activators regenerated by electron-transfer (ARGET) ATRP, supplemental activators and reducing agent (SARa) ATRP, electrochemically mediated ATRP (eATRP), and photoinitiated ATRP. A large range of monomers can be polymerized by ATRP in various solvents under either homogeneous or heterogeneous conditions over a wide temperature range. With the advantage of producing pure copolymers without homopolymer contamination, ATRP has been successfully used for the synthesis of polymers with various complex architectures and advanced materials.

Herein, we presented a new methodology to harness the recent advances in ATRP to accomplish a PISA process with diminished copper catalyst concentration. Recently, RAFT PISA was successfully carried out at room temperature using poly(oligo(ethylene oxide) methyl ether methacrylate) (POLMA) as macrorinitiator/stabilizer and poly(benzyl methacrylate) (PBnMA) as core-forming block. A similar system was adopted for PISA by ATRP at room temperature and at 65 °C. Aiming to minimize contamination of the final products with the copper catalyst and to simplify the experimental procedure, ICAR ATRP techniques at low ppm of copper catalyst concentration were selected (Scheme 1). The effect of the concentration of CuBr and TPMA, radical initiators, targeted degree of polymerization (DP) of PBnMA, solids content, and temperature on the morphological evolution of nano-objects was systematically monitored.

**EXPERIMENTAL SECTION**

**Materials.** Cupric bromide (CuBr, 99%, Aldrich), cupric chloride (CuCl2, 99%, Aldrich), azobis(isobutyronitrile) (AIBN, 98%, Aldrich), 2,2′-azodi((2,4-dimethyl-4-methoxyvaleronitrile) (V-70, Wako), and 2,2′-azobis(2-methylpropionamide) dihydrochloride (VA-044) were used as received. Benzyl methacrylate (BnMA, 98%, Alfa Aesar) and oligo(ethylene oxide) methyl ether methacrylate (OEOMA, average molecular weight 300, Aldrich) were purchased and passed over a column of basic alumina to remove inhibitor prior to use. Tris(pyridin-2-ylmethyl)amine (TPMA) and 2-hydroxyethyl 2-bromoisobutyrate (HEBiB) were prepared as previously reported in the literature. All other chemicals were used as received unless otherwise specified.

**Synthesis of POEOMA Macrorinitiator and Stabilizer by ICAR ATRP.** The POEOMA macrorinitiator and stabilizer was prepared by ICAR ATRP of OEOMA monomer by the following procedure. NaCl (3.5064 g, 60 mmol), OEOMA (40 mL, 140 mmol), HEBiB (0.51 mL, 3.5 mmol), VA-044 (0.2263 g, 0.7 mmol), CuCl2 (0.0059 g, 0.044 mmol), and TPMA (0.1016 g, 0.35 mmol) were dissolved in water (160 mL). The mixture was added into a 250 mL round-bottomed flask and purged with nitrogen for 30 min, and then the flask was placed in an oil bath set at 45 °C. After 12 h, the polymerization was terminated and poured into a large amount of dichloromethane (CH2Cl2). The remaining monomers and catalyst were removed by washing with water, and the product was recovered from CH2Cl2 after the evaporation of the solvent. The obtained POEOMA was further purified by thrice precipitation into hexane and dried under vacuum for 24 h. Mw,GPC = 10 600, Mn/Mw = 1.34, Mw,MALLS = 15 100.

**ICAR ATRP PISA for Diblock Copolymer POEOMA–PBnMA.** The following representative protocol was used for the synthesis of the diblock copolymer POEOMA–PBnMA at solids content of 20% w/w using BnMA as monomer and POEOMA as both macrorinitiator and stabilizer. POEOMA (0.3000 g, 2.0 × 10−2 mmol), TPMA (0.0028 g, 9.6 × 10−3 mmol), CuBr2 (0.0005 g, 2.4 × 10−3 mmol), BnMA (1.02 mL, 6.0 mmol, targeted DP = 300), and AIBN (0.0039 g, 2.4 × 10−2 mmol) were dissolved in 6.9 mL of ethanol in a 25 mL Schlenk flask. After the system was degassed by three freeze–pump–thaw cycles, the flask was purged with nitrogen and placed in an oil bath set at 65 °C to start the polymerization. The polymerization was quenched by exposure of the flask to air after 48 h. For the kinetic studies, the aliquots were periodically taken for analysis by GPC and 1H NMR measurements. The systematical variation of targeted DP of PBnMA and solids content allowed different PISA dispersion systems to be realized.

Replacing the AIBN in the above procedure with V-70 allowed ICAR ATRP PISA to be carried out at room temperature.

**Characterization.** Molecular weight (MW) and molecular weight distribution (MWD) values were determined by gel permeation chromatography (GPC). The apparent MW and MWD were measured by GPC equipped with a Waters 515 HPLC pump and Waters 2414 refractive index detector using PSS columns (SDV 10^5, 10^4, and 10^3 Å) with tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min at 35 °C. The sample was diluted with THF and injected with toluene as the flow marker. The apparent MW and MWD were calculated using linear poly(methyl methacrylate) (Mw = 800–1 820 000) standards and WinGPC 7.0 software. The absolute MW was measured by GPC equipped with a Waters 515 HPLC pump and
RESULTS AND DISCUSSION

Synthesis and Characterization of POEOMA Macroinitiator and Stabilizer. The POEOMA macroinitiator and stabilizer was synthesized by ICAR ATRP of OEOMA in an aqueous solution using a hydrophilic initiator HEBiB and a Cu[II]/TPMA catalyst complex (Scheme 1). In order to suppress the loss of deactivator by dissociation of Br–Cu[II] bond,\textsuperscript{21} the polymerization was carried out in the presence of an excess of NaCl, as discussed in previous reports.\textsuperscript{13,14}

In order to provide consistency throughout the study, a large batch of POEOMA macroinitiator and stabilizer with an apparent molecular weight (MW, based on linear PMMA standards) (\(M_n\text{GPC} = 10\,600\)) and a relatively narrow molecular weight distribution (MWD) (\(M_w/M_n = 1.34\)) was synthesized (Figure 1a). The \(^1\text{H NMR}\) spectrum of POEOMA displayed the characteristic resonance signals of methylene protons (\(-\text{CH}_2\text{CH}_2\text{OCO}\)–) close to ester bond in monomer unit at 4.0 ppm, methylene protons (\(-\text{CH}_2\text{CH}_2\text{O}\)–) in the monomer unit at 3.6 ppm, and methyl protons (\(\text{CH}_3\text{O}-\)) at 3.3 ppm (Figure S1). However, the signal of the residual initiator overlapped with oligo(ethylene oxide) signals and could not be used to analyze the absolute MW of POEOMA. Accordingly, the \(dn/dc\) value was measured as 0.0430 mL/g in \(N,N\)-dimethylformamide (DMF) solvent at 50 °C, and the absolute MW (\(M_w\text{MALLS} = 15\,100\)) was determined by GPC equipped with a MALLS detector. This value agrees with the theoretical MW based on quantitative initiation and monomer conversion. The average DP was calculated as 50, and this macroinitiator was labeled as POEOMA\(_{50}\) in the following sections.

ICAR ATRP PISA for Diblock Copolymer POEOMA\(_{50}\)–PBnMA. In an ICAR ATRP, the Cu[Br]–TPMA ligand, AIBN or V-70 initiators, ethanol solvent, and BnMA monomer were all added at the very beginning of the polymerization. The polymerization rate can be readily modulated by the rate of decomposition of radical initiators. First, using V-70 (\(T_{1/2} = 30 \text{ °C}\)) as radical initiator, the polymerization was carried out at room temperature. The minimal amount of the required [Cu[Br]\(_2\)] was studied. As shown in Figure 1a, in the case of 10% w/w solids content, the experiments for targeted DP = 225 and 300 of PBnMA were successfully carried out with [Cu[Br]\(_2\)] = 3200 ppm. However, the use of [Cu[Br]\(_2\)] = 1600 ppm resulted in a loss of polymerization control and GPC traces with broad MWDs. Thus, the [Cu[Br]\(_2\)] = 1600 ppm could only be successfully used for experiments with targeted DP ≥ 225 of PBnMA (Figure 1b). For 5% w/w solids content, the polymerization for all the targeted DP ≤ 300 of PBnMA required a minimal [Cu[Br]\(_2\)] = 3200 ppm. When 20% w/w solids content was examined, the
[CuIIBr2]0 = 1600 ppm was sufficient for targeted DP of PBnMA from 75 to 225, but [CuIIBr2]0 = 3200 ppm was still required for targeted DP ≥ 300 of PBnMA. When solids content was 30% w/w, a [CuIIBr2], solids content, and targeted DP of PBnMA is illustrated in Figure 1c. In the PISA ICAR ATRP process at room temperature, the minimal amount of catalyst depends on both the targeted DP of PBnMA and the solids content. Next, the effect of the amount of V-70 on the polymerization was studied (Figure S3). The molar ratio [CuIIBr2]:[V-70] of 1:2.5 resulted in no polymerization, and the molar ratio of 1:5:0 led to the GPC traces with multiple peaks and broad MWDs. Molar ratios of 1:7.5, 1:10, and 1:20 were used to mediate a successful polymerization. With the optimized [CuIIBr2]0 and molar ratio [CuIIBr2]:[V-70], a series of experiments were designed for different targeted DP of PBnMA and solids content (Table S1).

To further reduce the amount of required catalyst, ICAR ATRP PISA was conducted at elevated temperature (T = 65 °C) using AIBN as radical initiator (Tobs = 65 °C). Again, the minimal amount of [CuIIBr2], in the polymerization was first optimized. As shown in Figure 2, at [CuIIBr2]0 ≤ 200 ppm, MWD showed bimodal GPC traces, indicating a loss of polymerization control. At [CuIIBr2]0 ≥ 300 ppm, all the polymerizations were well controlled and symmetrical GPC traces with narrow MWDs were achieved. Additionally, the effects of molar ratio [CuIIBr2]:[TPMA] (1:2, 1:4, 1:6, and 1:8) and [CuIIBr2]:[AIBN] (1:2.5, 1:5.0, 1:10, and 1:20) on polymerization were studied. The GPC results indicated that the polymerizations were well controlled in all cases (Figures S4 and S5). Thus, these results confirmed that the ICAR ATRP PISA can be successfully realized at elevated temperatures using low copper catalyst concentrations.

To realize a better control and a faster polymerization, a 400 ppm of [CuIIBr2]0 and a molar ratio [CuIIBr2]:[TPMA]:[AIBN] = 1:4:10 were adopted in the following series of experiments at 65 °C. The kinetics of the ICAR ATRP PISA process was followed while targeting a DP = 300 of PBnMA at solids content of 10% w/w (Figure 3a). The MW of the synthesized diblock copolymers POEOMA50−PBnMAx progressively shifted to the higher MW region with increasing of monomer conversion. The GPC traces were symmetrical with relatively narrow MWDs (Mw/Mn ≤ 1.50) in all cases. These results indicated that the ICAR ATRP PISA proceeded in a controlled manner. The semilogarithmic kinetic plot in Figure 3b showed two stages (at 10% w/w solids content). The first stage can be assigned to a slow polymerization period in homogeneous solution. The AIBN was gradually decomposed.
and CuIBr/TPMA was reduced to CuIBr/TPMA activator. The polymerization was triggered by the generated CuIBr/TPMA, and the ATRP equilibrium was established. In the second stage, after the PBnMA block was chain extended to a certain length and the micelles were formed by the aggregation of diblock copolymer POEOMA50−PBnMAx. The remaining monomers predominantly migrated into the micelles, and the local high monomer concentration accelerated the polymerization rate at this stage. The inflection point between these two stages corresponded to a monomer conversion of 24%. This phenomenon was similar to the RAFT PISA process reported in the literature. All the semilogarithmic kinetic plots displayed two stages with similar inflection points as the solids content was varied between 5% w/w and 20% w/w. However,

Figure 5. TEM images of representative nano-objects formed from diblock copolymer POEOMA50−PBnMAx by the ICAR ATRP PISA system at room temperature: (a) spheres prepared at 20% w/w solids content; (b, c) short wormlike aggregates prepared at 20% w/w solids content; (d) spheres prepared at 30% w/w solids content; (e, f) short wormlike aggregates prepared at 30% w/w solids content. Spheres prepared at (g) 5% w/w and (h) 10% w/w solids content. (i) DLS volume-weighted size distribution for diblock copolymers POEOMA50−PBnMAx (x = 300, 375, and 450) at 20% w/w and 30% w/w solids content, respectively.

Figure 6. Structure map (“phase diagram”) for the ICAR ATRP PISA of BnMA monomer using POEOMA50 macroinitiator: (a) polymerization carried out at room temperature; (b) polymerization carried out at 65 °C.
further increasing the solids content resulted in an increase in the polymerization rate. A series of experiments were designed and performed in order to systematically investigate the effect of targeted DP of PBnMA and solids content on the ICAR ATRP PISA process (Table S2). For example, Figure 3c shows the GPC results of diblock copolymers POEOMA50−PBnMAx prepared with different targeted DP of PBnMA (x = 75, 150, 225, 300, 375, and 450) at 20% w/w solids content. All the GPC showed narrow MWDs as well as a "tail" in the low molecular eight regions that was independent of the target DP of PBnMA. The latter can be attributed to a partial loss of bromide chain-end functionalities in the macroinitiator POEOMA rather than the early termination in PISA procedures which would be expected to increase the number of dead chains with increasing targeted DP of PBnMA. In order to follow the PISA system with accurate measurement of composition and solids content of diblock copolymer POEOMA50−PBnMAx, monomer conversion was monitored by 1H NMR to almost 100% in all cases (Figure S2).

The distinct effects of [CuIBr2]0 and [AIBN]0 or [V-70]0 on the ICAR ATRP PISA can be explained as illustrated in Figure 4. The glass transition temperature (Tg) of PBnMA is 54 °C.22 Thus, at 65 °C, the core-forming PBnMA block should be more easily plasticized. This should give rise to increased mass transport of the BnMA monomer, CuBr2/TPMA and CuBr/TPMA complexes, and AIBN between the external and internal region of the formed micelles during the polymerization. The polymerization can, therefore, be well controlled at lower amount of CuBr2/TPMA with less dependence on the molar ratio [CuBr2]:[AIBN]. However, for the ICAR ATRP PISA at room temperature, the mass transport between the external and internal region of the formed micelles can only proceed during the initial stage of the chain extension (when Tg of the core-forming PBnMA block in micelles was low). As the monomer conversion increased, the PBnMA block gradually vitrified and reduced mass transport between the monomer-swollen PBnMA core and ethanol-soluble POEOMA shell. Thus, under these conditions, the polymerization in micelles can be only mediated by the V-70, CuBr2/TPMA, and CuBr/TPMA complex initially located in the micelles. A larger amount of CuBr2/TPMA and V-70 was required for a successful ICAR ATRP PISA at room temperature.

Morphological Evolution of Nano-Objects Formed in an ICAR ATRP PISA Process. The morphology of self-assembled products in the ICAR ATRP PISA process was found to sensitively depend on temperature and composition of

Figure 7. TEM images of representative nano-objects formed from diblock copolymer POEOMA50−PBnMAx by the ICAR ATRP PISA at 65 °C: (a, b) spheres prepared at 10% w/w solids content; (c) mixture of spheres and short wormlike aggregates prepared at 10% w/w solids content; (d, e) mixture of spheres and long wormlike aggregates prepared at 10% w/w solids content. Mixture of spheres and long wormlike aggregates prepared at (f) 5% w/w, (g) 20% w/w, and (h) 30% w/w solids content. (i) DLS volume-weighted size distribution for diblock copolymers POEOMA50−PBnMAx (x = 75, 150, 225, 300, 375, and 450) at 10% w/w solids content.
the reaction system. As revealed by the TEM images shown in Figure 5a and Figure S6 for ICAR ATRP PISA procedure at room temperature, large spheres (300 nm) were observed for diblock copolymers with targeted DP ≤ 225 of PBnMA at 20% w/w solids content, and short wormlike aggregates with an aspect ratio ca. 10 were formed for targeted DP ≥ 300 of PBnMA (Figure 5b,c). It was also interesting to note that the structures of the wormlike aggregates exhibited a fractal-type connected-bead morphology rather than a uniform individual cylindrical shape. Fractal-type structures were commonly observed in diffusion-limited aggregation and growth processes and were indicative of random collision events between aggregating subunits (here spherical nano-objects).23 We therefore hypothesized that the mechanism of formation of anisotropic structures involved the aggregation and fusion of spherical nano-objects that formed as the primary aggregate structure during the PISA process. When the solids content was increased to 30% w/w solids content, short wormlike aggregates with an aspect ratio ca. 6 were observed at the targeted DP ≥ 300 of PBnMA (Figure 5e,f). However, the hydrodynamic diameters (Figure 5i, measured by DLS) of the formed nano-objects at 20% w/w solids content were always larger than those formed at the 30% w/w system. For targeted DP ≤ 225 of PBnMA at solids content of 30% w/w, DLS analysis revealed a bimodal population of spherical nano-objects (with diameters of 300 and 100 nm) (Figure 5d and Figure S6). At lower level of solids content (5% w/w and 10% w/w), only large spherical morphology (400 nm) was formed even when the higher DP = 300 and 450 of PBnMA was targeted (Figure 5g,h). Based on the above results, the structure map for ICAR ATRP PISA at room temperature was depicted as Figure 6a. In summary, our results suggest the existence of two levels of structure formation during room temperature ICAR ATRP PISA. In a first step, primary spherical nano-objects were formed by organization of block copolymers. In a second step, anisotropically assembled structures were formed by diffusion limited aggregation and growth.

For ICAR ATRP PISA procedure at 65 °C, a distinctly different self-assembly behavior during ICAR ATRP PISA was observed. As shown in Figure 7, increasing the targeted DP of PBnMA from 75 to 450 at solids content of 10% w/w, the morphology of the formed nano-objects systematically changed from spheres to wormlike aggregates. For the diblock copolymer POEOAMA50–PBnMA75, spheres with weak electron density contrast were observed (Figure 7a). There was a systematic discrepancy between aggregate sizes determined from TEM (300 nm) and DLS (100 nm) analysis (Figure 7i). The larger aggregate size observed in TEM images suggested that aggregate structures underwent a transition during TEM sample preparation. We interpreted this more dynamic behavior as a consequence of the meltlike state of the PBnMA block and the more extensive solvent swelling at higher temperature of 65 °C. In further confirmation of this assumption, the differential scanning calorimetry (DSC) measurement of diblock copolymer POEOAMA50–PBnMA75 was performed, revealing a glass transition temperature of $T_g$ = 16.5 °C (Figure S8). We hypothesized that the softness of the diblock copolymers is responsible for the deviation between the particle sizes observed in electron imaging and in light scattering. This could be due to capillary forces that occur during solvent evaporation that can significantly alter the shape and increase the size of soft aggregates.

When the targeted DP of PBnMA was increased to 150, the solubility of the PBnMA block in ethanol-insoluble decreased, and thus more dense spherical structures (150 nm) with a solid core were formed (Figure 7b). A higher fraction of short wormlike aggregates structure was observed when the target DP of PBnMA was increased to 225 (Figure 7c). For the targeted DP ≥ 300 of PBnMA, the dominant morphology was long wormlike aggregates mixed with a few spheres (Figure 7d,e), and both have similar diameters close to 150 nm. The progression of microstructure formation was also evidenced in the continuous change of hydrodynamic diameters that was revealed in Figure 7i. At solids content of 5% w/w, 20% w/w, and 30% w/w, a mixture of long wormlike aggregates and spheres were also prepared with targeted DP = 450 of PBnMA (Figure 7f–h). The morphology transition from spheres to wormlike aggregates for these solids content had the same tendency as those at 10% w/w system (Figure S7). The self-assembly behavior of the ICAR ATRP PISA system at 65 °C is summarized in Figure 6b. The diagram highlighted that structure formation was determined by the MW of PBnMA (and hence polymer composition) rather than the solids content. The reason can be attributed to the use of a longer POEOOMA50 macroinitiator and stabilizer. A similar correlation between solids content and morphology was reported previously for poly(glycerol monomethacrylate)$_2$-poly(2-hydroxpropyl methacrylate), (PGMA$_{75}$–PHMA$_{25}$).24

In a PISA process, the morphology of the formed nano-objects was predominantly determined by the solids content and DP of the core-forming block and macroinitiators.7 In the present work, temperature was also confirmed to have a significant effect on morphological evolution in the ICAR ATRP PISA process. We interpreted the effect of temperature on structure formation in ICAR ATRP PISA to be a consequence of both thermodynamic and kinetic parameters. At temperature above the $T_g$ (54 °C) of PBnMA, the core-forming PbNMA block was in a meltlike state during the PISA process and more susceptible to plasticization through solvent swelling. The swelling should promote the fusion of spherical

Figure 8. Illustration of the morphological evolution during the ICAR ATRP PISA: (a) at 65 °C, (b) at room temperature, and (c) nano-objects formed at room temperature after heating treatment at 65 °C.
aggregate structures which formed at the primary organization stage. In contrast, at room temperature, the PBnMA block was in the glassy state and hence would exhibit more hard-sphere-type interactions that prevent fusion processes. Only short wormlike aggregates were thus formed at the higher targeted DP of PBnMA and higher solids content. The proposed effect of temperature on aggregate growth and morphological evolution is illustrated in Figure 8. Previously, acetonitrile (MeCN)/ethanol were used as cosolvent to improve the plasticization of the core-forming POEOMA block at room temperature.9h,i Our work demonstrated that temperature can—through softening and change of solvation behavior—exert a similar influence on the structure formation processes in PISA systems.

**Morphological Transformations of Nano-Objects Formed in an ICAR ATRP PISA Process.** To better understand the equilibrium characteristics of the observed nanostructures as well as the role of kinetics, the structure evolution during heating treatment was evaluated. As discussed above, only large spheres (400 nm) were generated from diblock copolymer POEOMA$_{50}$−PBnMA$_{300}$ prepared at 10% w/w solids content (Figure 5). However, after thermal annealing at 65 °C for 3 h, the spheres changed to wormlike aggregate structures with a diameter of 150 nm (Figures 9a and 9a’). Similarly, the short wormlike aggregates formed by the diblock copolymer POEOMA$_{50}$−PBnMA$_{300}$ at 20% w/w and 30% w/w solids content (Figures 5b and 5c) were transformed into vesicles with a diameter of 600 nm (Figures 9b and 9b’, 9c and 9c’). For the POEOMA$_{50}$−PBnMA$_{450}$ at 20% w/w solids content, some nano-objects with a diameter of 500 nm with a hollow cavity and a thick corona were generated after a similar heat treatment (Figures 9d, 9d’). In RAFT PISA process at temperatures higher than $T_g$ of the core-forming block, the preformed higher order wormlike aggregates could reversibly transform to spheres by changing temperature.25 In contrast, in the system studied here, the lower order spheres were transformed into the higher order morphologies of wormlike aggregates or vesicles. We interpret the irreversible transformation as a consequence of the increased mobility of the core-forming block, which accelerated the reorganization of diblock copolymers to more equilibrium type structures. If the microstructures would represent thermodynamically stable state, the nano-objects directly formed from ATRP PISA at 65 °C and those transformed from ATRP PISA at room temperature should have the same morphologies. However, the above results revealed some difference between these two cases, which might be attributed

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**Figure 9.** TEM images of nano-objects formed from diblock copolymer POEOMA$_{50}$−PBnMA$_{300}$ prepared by ICAR ATRP PISA process at room temperature and subjected to a heating treatment at 65 °C for 3 h: (a, a’) wormlike aggregates prepared at 10% w/w solids content; (b, b’) vesicles prepared at 20% w/w solids content; (c, c’) vesicles prepared at 30% w/w solids content; (d, d’, d”), nano-objects with a hollow cavity and a thick corona prepared at 30% w/w solids content.
ICAR-ATRP was shown to facilitate the controlled fabrication of nanostructures using PISA of POEOMA-PBnMA at low ppm of copper catalyst concentration. Reaction process and structure formation sensitively depend on the polymerization temperature. In ICAR ATRP PISA at room temperature, the minimal \([\text{CuBr}_2]_0\) needed for a controlled polymerization depends on the solids content and targeted DP of PBnMA. With \([\text{CuBr}_2]_0\) as low as 400 ppm and the molar ratio of \([\text{CuBr}_2]_0[\text{TPMA}]_0[\text{AIBN}]_0 = 1:4:10\), ICAR ATRP PISA at 65 °C was successfully carried out. The kinetics showed that the polymerization could be divided into two stages: the initial slow polymerization in homogeneous solution and subsequent faster polymerization in micelles at the later stage. For ICAR ATRP, the structure formation at room temperature was attributed to the initial plasticization ability of the core-forming PBnMA block of PISA. The di block copolymer aggregates via polymerization-induced self-assembly and reorganization.

**CONCLUSIONS**

ICAR-ATRP was shown to facilitate the controlled fabrication of nanostructures using PISA of POEOMA-PBnMA at low ppm of copper catalyst concentration. Reaction process and structure formation sensitively depend on the polymerization temperature. In ICAR ATRP PISA at room temperature, the minimal \([\text{CuBr}_2]_0\) needed for a controlled polymerization depends on the solids content and targeted DP of PBnMA. With \([\text{CuBr}_2]_0\) as low as 400 ppm and the molar ratio of \([\text{CuBr}_2]_0[\text{TPMA}]_0[\text{AIBN}]_0 = 1:4:10\), ICAR ATRP PISA at 65 °C was successfully carried out. The kinetics showed that the polymerization could be divided into two stages: the initial slow polymerization in homogeneous solution and subsequent faster polymerization in micelles at the later stage. For ICAR ATRP, the structure formation at room temperature was attributed to the initial plasticization ability of the core-forming PBnMA block of PISA. The di block copolymer aggregates via polymerization-induced self-assembly and reorganization.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b01966.

1H NMR spectra of POEOMA50 and diblock copolymer POEOMA50−PBnMA375, GPC traces of copolymers obtained with different formulations, TEM images at different solids content and targeted DP of BnMA, tables for experimental data (PDF)

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**REFERENCES**


Macromolecules


