

Direct preparation of vesicles from one-pot RAFT dispersion polymerization

Chuan-Qun Huang, Cai-Yuan Pan*

Department of Polymer Science and Engineering, CAS Key Laboratory of Soft Matter Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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ABSTRACT

Various morphologies including spherical micelles, nanowires and vesicles have been prepared by reversible addition-fragmentation chain transfer (RAFT) dispersion polymerization of styrene (St) in methanol using S-1-dodecyl-S-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (TC)-terminated poly(ethylene oxide) (PEO-TC) and 2,2'-azobis(isobutyronitrile) (AIBN) as chain transfer agent and initiator, respectively. GPC, ^1H NMR, TEM and laser light scattering (LLS) were used to track the polymerization. The results showed that the block copolymers PEO-*b*-polystyrene (PEO-*b*-PS) were formed firstly in homogenous polymer solution, and then the spherical micelles were produced via polymerization-induced self-assembling. Continuous polymerization of the PS blocks induced the transition of spherical micelles into other morphologies. The polymerization-induced self-assembling and reorganization (PISR) were induced by chain length ratio increase of PS to PEO blocks. The concentration of St in methanol is also important factor to influence the formation of morphologies.

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1. Introduction

Vesicular nanostructural materials have exhibited various promising applications in a variety of fields such as in cosmetic, biomedical, catalysis, and food industries [1–6]. So their preparation attracted considerable attention in recent years, and general strategy for preparation of the vesicles is self-assembling of the amphiphilic block copolymers in a selective solvent, which is performed by slowly adding a nonsolvent of the hydrophobic blocks into a polymer solution for inducing micellization followed by dialysis for removal of good solvent resulting in freeze of the assemblies [7–11]. So, the solvent parameter (δ) is essentially variable, and the block copolymers used have fixed molecular weight, polydispersity index and chain length ratio in this process. However, this strategy is performed in low concentration, is time-consuming and needs multiple steps; these restrict their commercialization and further applications. So finding a novel and convenient method for solving these problems is one of the challenging and desired aims for polymer chemists. One approach relies on controlled radical polymerization in a selective solvent, which is so-called polymerization-induced self-assembling, but in most cases only spherical micelles were formed [12–15]. Very recently, we developed a simple and facile strategy for one-pot synthesis of multiple morphologies besides vesicles via controlled radical polymerization in high concentration [16–18]. Various

morphologies, such as spherical micelles, vesicles, nanorods have been conveniently prepared via reversible addition-fragmentation chain transfer (RAFT) polymerization of St in methanol using trithiocarbonate-terminated poly(4-vinylpyridine) as chain transfer agent.

Dispersion polymerization is a useful technique for preparation of micron and submicron particles with narrow size distribution and has been extensively studied [19–22]. In a dispersion polymerization, all reaction ingredients are dissolved in a reaction medium at initial polymerization. With proceeding of the polymerization, the formed polymer chains aggregate to form the spherical particles stabilized by steric stabilizer, and then the polymerization takes place mainly in the monomer-swollen droplet, and at last, a stable polymer latex is formed. The stabilizer used in the dispersion polymerization system could be low molecular weight reagents, polymers, or macromonomers [23,24]. When the hydrophilic macro agents replace these stabilizers, the dispersion polymerization of hydrophobic monomers forms diblock copolymer at first, and then phase separation occurs when the hydrophobic block chains grow gradually past a critical value. The resulting morphologies are determined by the chain length ratio of hydrophobic to hydrophilic block [25,26]. Based on these results, we designed a dispersion polymerization for preparation of multiple morphologies, where the RAFT polymerization of St was performed in methanol using trithiocarbonate-terminated poly(ethylene oxide) (PEO-TC) as macro RAFT agent and stabilizer. Since PEO can dissolve in both St and methanol, it stabilizes the morphologies formed in the polymerization. The methanol ($\delta = 29.7$) is nonsolvent, but the St ($\delta = 19.0$) is solvent of PS

* Corresponding author.

E-mail address: pcy@ustc.edu.cn (C.-Y. Pan).

($\delta = 16.6\text{--}20.3$), so, high content of St was applied to improve the solubility of PS in the polymerization media for keeping the growth rate of PS chains in the cores of micelles.

PEO-TC was selected as macro RAFT agent because PEO is a well-known hydrophilic, nontoxic and biocompatible polymer, and has been extensively applied in the synthesis of block copolymers [27–30]. To the best of our knowledge, using PEO-TC as RAFT agent in the dispersion polymerization for formation of various morphologies has not been reported yet. Herein, we report our study on the formation of vesicles through PISR in the polymerization.

2. Experimental

2.1. Materials

Styrene (St, Shanghai Chem. Co.) was distilled under reduced pressure prior to use. The 2,2'-azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol and dried under vacuum. Poly(ethylene oxide) monomethyl ether (PEO-OH) with $M_n = 5000$ and $M_w/M_n = 1.01$ was purchased from Aldrich, and further freed of water by azeotropic distillation in anhydrous benzene. All other reagents with analytical grade were purified by standard procedures or used as received.

2.2. Characterization

^1H NMR spectra were recorded on a Bruker DRX-300 nuclear magnetic resonance (NMR) instrument with CDCl_3 as solvent and tetramethylsilane (TMS) as internal standard. The molecular weight and molecular weight distribution were determined on a Waters-150C gel permeation chromatograph (GPC) equipped with micro-styragel columns (500, 10^3 and 10^4 Å) at 30°C . Narrow polystyrene standards were used in the calculation of molecular weights. THF was used as eluent at a flow rate of 1.0 mL/min. The transmission electron microscope (TEM) observation was performed on a Hitachi H-7650 transmission electron microscope at an accelerating voltage of 100 kV. The samples for TEM observation were prepared by depositing a drop of the diluted polymer solution in methanol on copper grids. A commercial laser light scattering (LLS) spectrometer (Zetasizer Nano ZS90, Malven Instruments Ltd., Malvern, UK) equipped with a He-Ne Laser (4.0 mW, 633 nm) was used. All the dynamic light scattering measurements were carried out at 25°C with scattering angle of 90° .

2.3. Synthesis of S-1-dodecyl-S-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (TC)

TC was synthesized in yield of 50% according to Refs. [31,32]. ^1H NMR, δ (TMS, ppm): 0.90 (t, 3H, $-\text{CH}_3$), 1.37–1.47 (m, 20H, $-(\text{CH}_2)_{10}-$), 1.75 (s, 6H, 2- CH_3), 3.42 (t, 2H, $-\text{CH}_2\text{S}$), 13.05 (s, 1H, $-\text{COOH}$).

2.4. Synthesis of TC-terminated poly(ethylene oxide) (PEO-TC)

TC (3.64 g, 10 mmol) and oxalyl chloride (4.3 mL, 50 mmol) were added into dry CH_2Cl_2 (20 mL) and stirred at room temperature until gas evolution stopped. Excess reagents were then removed under vacuum, and the residue was redissolved in dry CH_2Cl_2 (40 mL), followed by addition of PEO-OH (10 g, 2 mmol, in 50 mL of CH_2Cl_2). The reaction was carried out for 24 h at room temperature, and then the contents were concentrated before precipitation from an excess of cold diethyl ether. The crude polymer obtained by filtration was purified by redissolving the resulting product in

CH_2Cl_2 , precipitated in diethyl ether again, and dried under vacuum overnight. The PEO-TC was obtained in 80% yield.

^1H NMR, δ (TMS, ppm): 0.85 (t, 3H, $-\text{CH}_3$), 1.20–1.47 (m, 20H, $-(\text{CH}_2)_{10}-$), 1.75 (s, 6H, 2- CH_3), 3.24 (t, 2H, $-\text{CH}_2\text{S}$), 3.36 (s, 3H, $-\text{OCH}_3$), 3.62 (m, 450H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 4.23 (t, 2H, $-\text{CH}_2\text{OCO}-$).

2.5. RAFT polymerization of St using PEO-TC as macro chain transfer agent

A typical procedure is as follows. The PEO-TC (20 mg, 3.8×10^{-3} mmol), St (0.784 g, 7.5 mmol), AIBN (0.062 mg, 3.7×10^{-4} mmol) and methanol (7 g) were successively added into a 10 mL glass tube with a magnetic bar. The tube was sealed under vacuum after 3 cycles of freeze-pump-thaw, and the sealed tube was immersed in an oil bath at 80°C while stirring. After the polymerization was performed for 24 h, the tube was cooled to room temperature with ice-water. The polymer was precipitated by pouring the polymer solution in methanol into excess petroleum ether while stirring. The precipitate obtained by filtration was dried in a vacuum oven at room temperature overnight before analyzed by ^1H NMR and GPC.

For preparation of the vesicles and testing the kinetics of RAFT dispersion polymerization, the PEO-TC (100 mg, 1.9×10^{-2} mmol), St (19.622 g, 0.189 mol), and AIBN (0.3 mg, 1.9×10^{-3} mmol) with their feed molar ratio = 1:10,000:0.1 were dissolved in methanol (10 g). The resultant solution was equally divided into 10 portions and every portion was placed in a 5 mL glass tube, respectively. The polymerization was carried out under the same conditions mentioned above, and then stopped at 0.5 h, 1 h, 2 h, 3h, 4 h, 6 h, 8 h, 12 h and 24 h, respectively. After the polymerization, the solution was treated with the same procedure mentioned above, and the white powder products were obtained. GPC traces of the block copolymers obtained at different times and the relationship of molecular weights with polymerization time are shown in Figs. 2 and 3.

2.6. Measurement of critical selective solvent content for the polymer solution

10 mg of the block copolymer, PEO₁₁₃-*b*-PS₂₆₄ (subscript number is DP, $M_w/M_n = 1.14$) was dissolved in a common solvent (St, 10 g). Then the methanol was gradually added into W_1 g of the solution until the clean solution became slightly cloudy suddenly. The solution formed was weighted (W_2). The content of methanol in the solution at the onset turbidity is defined as critical selective solvent content (csc), and the csc was calculated according to $\text{csc} = (W_2 - W_1)/W_2$. The 1 mg/g copolymer solution was diluted with St to yield solutions with concentrations of 0.5, 0.1 and 0.05 mg/g. Their csc values were measured using the same method and the plot of critical methanol content versus logarithm of the polymer concentration for PEO₁₁₃-*b*-PS₂₆₄ is shown in Fig. 5.

3. Results and discussion

3.1. Dispersion polymerization of styrene in methanol

Since PEO-TC, St and AIBN are soluble in the polymerization media, the initial dispersion polymerization was carried out homogeneously, and the block copolymers, PEO-*b*-PS were formed. The phase separation occurred to yield spherical micelles after the PS block passed a critical chain length. Generally, the chain length ratio of PS to PEO at phase separation met the requirement of spherical micelles, so, the polymerization-induced self-assembling in the controlled polymerizations produced always spherical micelles [12–15]. As we know, the morphologies formed via self-

assembly of the block copolymers are mainly determined by a force balance involving the stretching of the core chains, the surface tension between the core and outside solvent, and repulsion among the corona chains [25,26]. The chain length ratio change of the PS to PEO blocks should accomplish transition of the spherical micelles into other morphologies. Thus, a feasible strategy for preparation of various morphologies is to keep propagation rate of the core PS block chains even after the formation of spherical micelles. When the molar ratio of PS to PEO increases significantly, the transition of spherical micelles to other morphologies can be achieved. Therefore, we firstly studied the dispersion polymerization of St in methanol, a selective solvent of PEO-*b*-PS.

The PEO-TC was prepared by esterification reaction of PEO-OH with TC. To ensure one RAFT transfer site in every PEO chain, excess of TC was used in the reaction, and the residual TC was removed during the precipitation in diethyl ether. Fig. 1A represents a typical ¹H NMR spectrum of PEO-TC, and we can see a new signal of ester methylene protons at $\delta = 4.23$ (c), the signal at $\delta = 3.62$ (b) corresponding to the methylene protons in the PEO chain and other four new signals at 3.24 (e), 1.75 (d), 1.20–1.47 (f) and 0.85 (g) ppm are ascribed to the protons of TC. The integral ratio of proton signals c:d are 2:6, which indicates that all terminal hydroxyl groups of PEO-OH were capped with TC. The molecular weight was calculated based on the integration ratio of signal at 1.75 (d) ppm to that at 3.62 (b) ppm. The PEO-TC with $M_n(\text{NMR}) = 5314$ g/mol, $M_w/M_n = 1.01$ was applied in the following study except specially mentioned.

After the dispersion polymerization of St was carried out in methanol using AIBN and PEO-TC as initiator and RAFT agent, respectively, the results obtained are listed in Table 1. For determining structure of the resultant polymers, their ¹H NMR spectra were measured, and Fig. 1B and C are ¹H NMR spectra of the PEO-*b*-PS obtained from polymerization with feed molar ratio of PEO-TC/St/AIBN = 1/10,000/0.1 for 1 h and 8 h, respectively. The signals at $\delta = 3.62$ and 6.3–7.2 ppm are ascribed to ether methylene protons of PEO and the phenyl protons of PS, respectively. So, the block copolymers, PEO-*b*-PSs were produced after considering their unimodal GPC curves (Fig. 2). The chain length of PS block obtained at different reaction times can be calculated based on the integration ratio of the signals at $\delta = 6.3\text{--}7.2$ ppm to the signal at $\delta = 3.6$ ppm and degree of polymerization (DP) of PEO. The

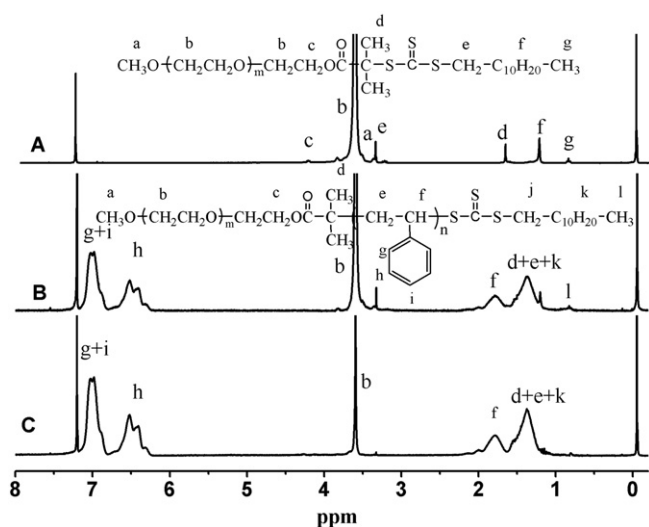


Fig. 1. ¹H NMR spectra of A: PEO-TC; Block copolymers, PEO-*b*-PS, were prepared by RAFT polymerization of styrene with PEO-TC/St/AIBN = 1/10,000/0.1 (St: 1.9 g; methanol: 1 g) in methanol at 80 °C for 1 h (B) and 8 h (C).

Table 1

Results and conditions for RAFT dispersion polymerization of St using PEO-TC as chain transfer agent.^a

No.	St/PEO-TC/AIBN (molar ratio)	M_n (GPC) ^b	M_w/M_n ^b	M_n (NMR) ^c	Morphology
1	2000/1/0.1	40,300	1.06	26,100	Nanowires and vesicles
2	5000/1/0.1	52,270	1.09	40,350	Vesicles
3	10,000/1/0.1	89,210	1.12	72,600	Vesicles
4	15,000/1/0.1	88,430	1.13	70,610	Vesicles

^a St was polymerized at 80 °C in methanol, St concentration is 66 wt% except 53 wt% for sample 1. The polymerization time is 24 h.

^b Obtained from GPC measurements.

^c Calculated according to Eq. (1).

number-average molecular weight, M_n (NMR) of the block copolymer was calculated according to Eq. (1).

$$M_n(\text{NMR}) = (4 \times 113/5) \times 104 \times (I_{6.3-7.2}/I_{3.6}) + 5314 \quad (1)$$

Here, 104, 113 and 5314 are the molecular weight of St, the DP and molecular weight of PEO-TC, $I_{6.3-7.2}$ and $I_{3.6}$ are the integral values of the proton signals at $\delta = 6.3\text{--}7.2$ ppm and at 3.6 ppm, respectively. From Table 1, we can see that the M_n (NMR)s of PEO-*b*-PSs enhanced with the increase of feed molar ratio of St/PEO-TC below the feed ratio of 10,000, but when this ratio was above 10,000, the molecular weight of the copolymer obtained wouldn't increase continuously. The GPC curves of the polymers obtained from different polymerization times are shown in Fig. 2, all the curves are unimodal and symmetrical, and are continuously shifted to less elution time with increase of polymerization time, which indicates the molecular weights increase of the resulting copolymers with evolution of the polymerization. This result was also supported by the $M_n(\text{NMR})$ results shown in Fig. 3, which displays $M_n(\text{NMR})$ s increase with the evolution of polymerization. These results showed that continuous chain length increase of the PS block is possible even after the phase separation. Thus we studied the morphologies formed in the RAFT polymerization of St using PEO-TC as transfer agent and stabilizer in methanol.

Before discussion on PISR of PEO-*b*-PS in the polymerization, we studied the composition variation in the polymerization media and its effect on the phase separation. St is a monomer, and also acts as a solvent of the formed PEO-*b*-PS before its polymerization. Since St is a common solvent for both blocks of the PEO-*b*-PS, methanol is

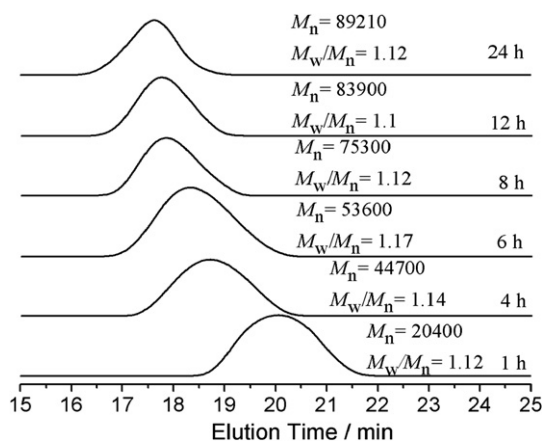


Fig. 2. GPC traces of the block copolymers obtained from RAFT polymerization with a feed molar ratio of PEO-TC/St/AIBN = 1/10,000/0.1 in methanol (St: 1.9 g; methanol: 1 g) for different polymerization times.

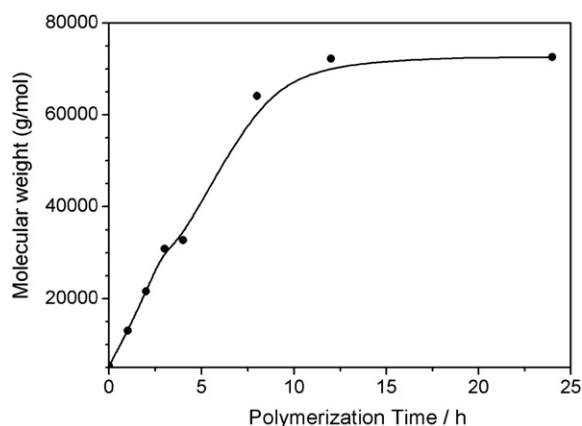


Fig. 3. The relationship of M_n (NMR) with the polymerization time at 80 °C. Feed molar ratio: PEO-TC/St/AIBN = 1/10,000/0.1 (St: 1.9 g; methanol: 1 g).

a good solvent of PEO, but is a nonsolvent of PS block, it is expected that the phase separation should occur at critical chain length ratio of PS to PEO as we mentioned. Theoretically, other factor influencing the phase separation is the relative content of the methanol and St, which is varied in the polymerization. The relationship of the methanol contents with the polymerization time is shown in Fig. 4, and the result showed slight change (34.6–36.1%) of the methanol content in the polymerization with feed molar ratio of PEO-TC/St/AIBN = 1/10,000/0.1 (St: 1.9 g; methanol: 1 g). In order to understand the phase separation in this polymerization, the critical selective solvent (methanol) content (csc) values at phase separation were measured for various concentrations of the block copolymer, PEO-*b*-PS. Fig. 5 demonstrates a typical relationship of polymer concentration with csc for the PEO₁₁₃-*b*-PS₂₆₄. We can see that the phase separation occurred at different csc in the mixture of St and methanol for polymer concentrations from 0.05 to 1 mg/g, for example, the concentration of polymer and csc for the PEO₁₁₃-*b*-PS₂₆₄ were 1 mg/g and 24% of methanol, respectively. In the RAFT polymerization of St, the growth of PS blocks must lead to the increase of polymer concentration, thus phase separation should occur for the polymerization in the concentration range of methanol from 34.6% to 36.1% because the concentration of polymer formed was much higher than 1 mg/g.

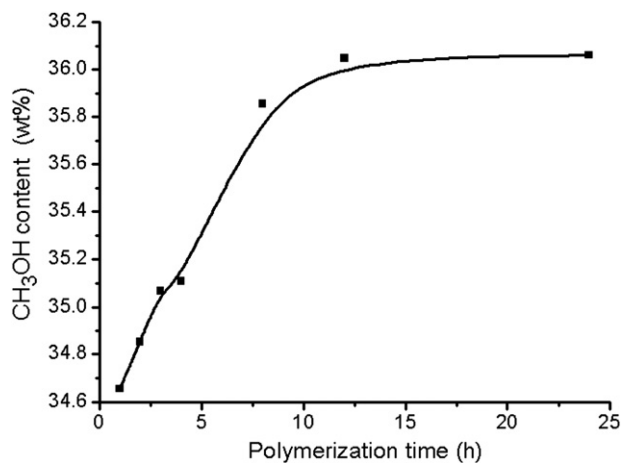


Fig. 4. The relationship of methanol content with the polymerization time for the RAFT polymerization at 80 °C with feed molar ratio of PEO-TC/St/AIBN = 1/10,000/0.1 (St: 1.9 g; methanol: 1 g).

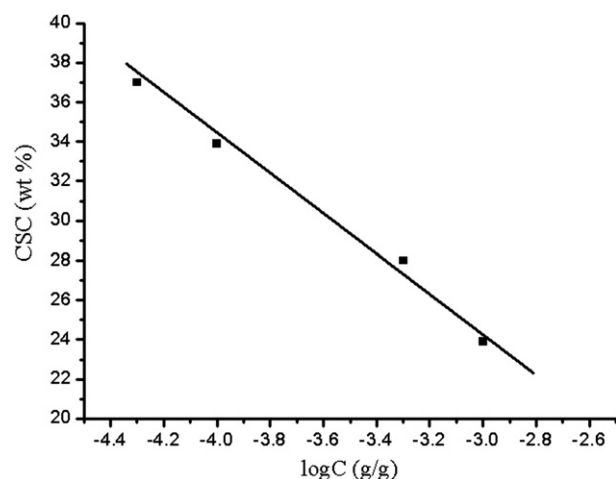


Fig. 5. Plot of critical methanol content versus logarithm of the polymer concentration in the mixture of St and methanol for the diblock copolymer, PEO₁₁₃-*b*-PS₂₆₄ (measured at room temperature).

3.2. Formation of vesicles and other morphologies

Theoretically, chain length ratio of the PS to PEO blocks is one of the determining factors for formation of the morphologies. As discussed above, in this dispersion polymerization, the ratios of PS to PEO chain length increased gradually with evolution of the polymerization. When the PS chain length increased past a critical value, the phase separation occurs to form spherical micelles with PS core and PEO corona. We observed the same results in this study. When RAFT polymerization with a feed molar ratio of St/PEO-TC/AIBN = 2000/1/0.1 was carried out in methanol (concentration of St was 10 wt%), the opalescent polymerization solution kept consistently throughout the whole polymerization process (Fig. 6A), and only the spherical micelles with D of ~50 nm were observed even if the polymerization lasted to 24 h (Fig. 6B).

For the polymerization with a feed molar ratio of St/PEO-TC/AIBN = 2000/1/0.1, the PS chain lengths at phase separation and at 24 h showed very slight increase (less than 5%) due to diffusion restriction of the monomer from the solution into spherical micelles [12]. To solve this problem, one convenient method is to swell the PS cores with St monomer because St acts as monomer

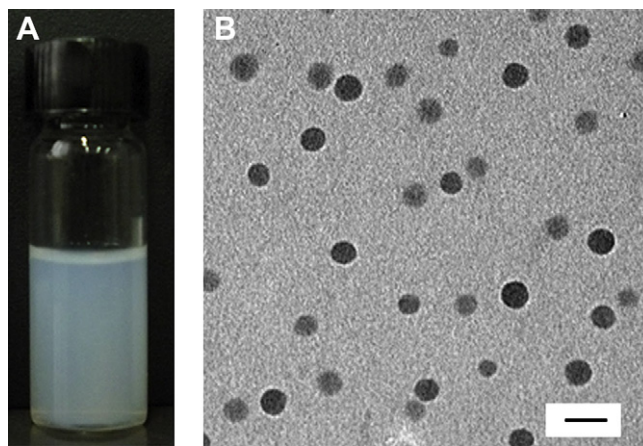


Fig. 6. (A) Optical digital photo of the polymer solutions. (B) TEM image of the aggregates formed from the RAFT polymerization at 80 °C with feed molar ratio of St/PEO-TC/AIBN = 2000/1/0.1 in methanol (St: 0.78 g; CH₃OH: 7.0 g). Reaction time: 24 h. Scale bar: 100 nm.

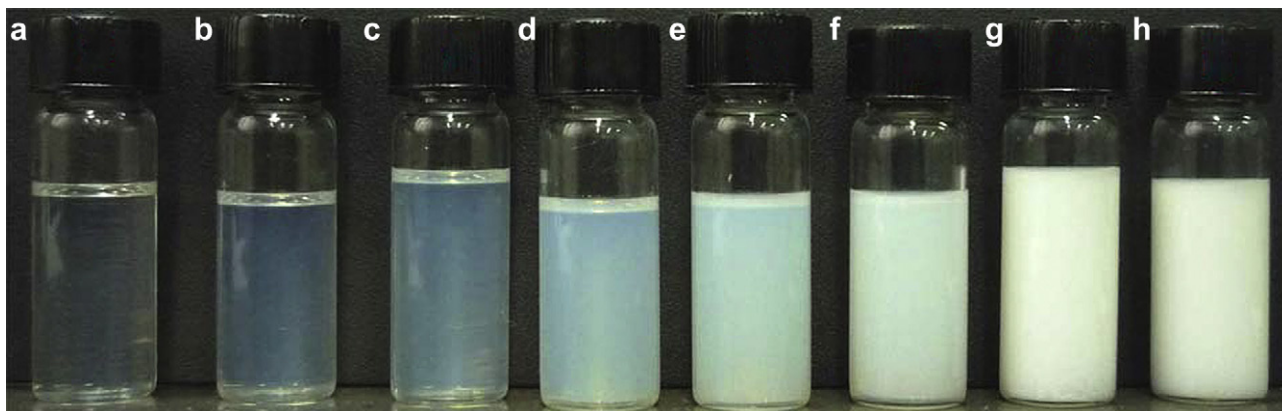


Fig. 7. Optical digital photos of the polymer solutions obtained from RAFT polymerization in methanol at 80 °C with feed molar ratio of PEO-TC/St/AIBN = 10/10,000/1 (St: 1.9 g; methanol: 1 g) for 0.5 h (A), 1 h (B), 2 h (C), 3 h (D), 4 h (E), 6 h (F), 8 h (G) and 24 h (H).

and a good solvent of PS before its polymerization. So, high concentration of St was used in the following polymerization system. The RAFT polymerization of St with a feed molar ratio of St/PEO-TC/AIBN = 10000/1/0.1 was performed in methanol (concentration of St was 66 wt%) at 80 °C, apparent changes of the reaction solution at different polymerization times were obviously different from that observed in Fig. 6. We can see that the solution at 0.5 h of polymerization kept transparency (Fig. 7A), and then the polymerization solution became pale blue at 1 h (Fig. 7B), which demonstrated the beginning of phase separation. When the polymerization lasted to 2 h, to 3 h and to 4 h, transition of the resulting polymer solution to opalescence took place (Fig. 7C–E). With continuous polymerization, the polymer solution was turned to milk-white as shown in Fig. 7F–H. The milky dispersion was quite stable and no precipitation was observed when standing at room temperature for at least one month.

In order to illustrate the phase separation and reorganization of the spherical micelles, TEM was used to follow the polymerization with the feed molar ratio of St/PEO-TC/AIBN = 10,000/1/0.1 and 66 wt% of St concentration. The TEM images of the aggregates formed at 2, 4, 6, 8 and 24 h are shown in Fig. 8. No particle was observed for the specimen obtained at 0.5 h of polymerization, only the block copolymers were formed, and their average composition was PS₃₈-*b*-PEO₁₁₃, which was calculated based on the M_n (NMR) data. Before 1 h of polymerization, the block copolymers were soluble in the polymerization media, so the polymerization solution is transparent (Fig. 7A). When the polymerization lasted to 1 h, the chain length ratio of PS to PEO blocks increased to 0.65 (PS₇₄-*b*-PEO₁₁₃), the phase separation occurred (Fig. 7B). Fig. 8A shows that the aggregates formed at 2 h are spherical micelles with an average D of ~30 nm. After PS blocks propagated for 4 h, the chain length ratio of PS to PEO blocks enhanced to 2.37 (PS₂₆₈-*b*-PEO₁₁₃). Based

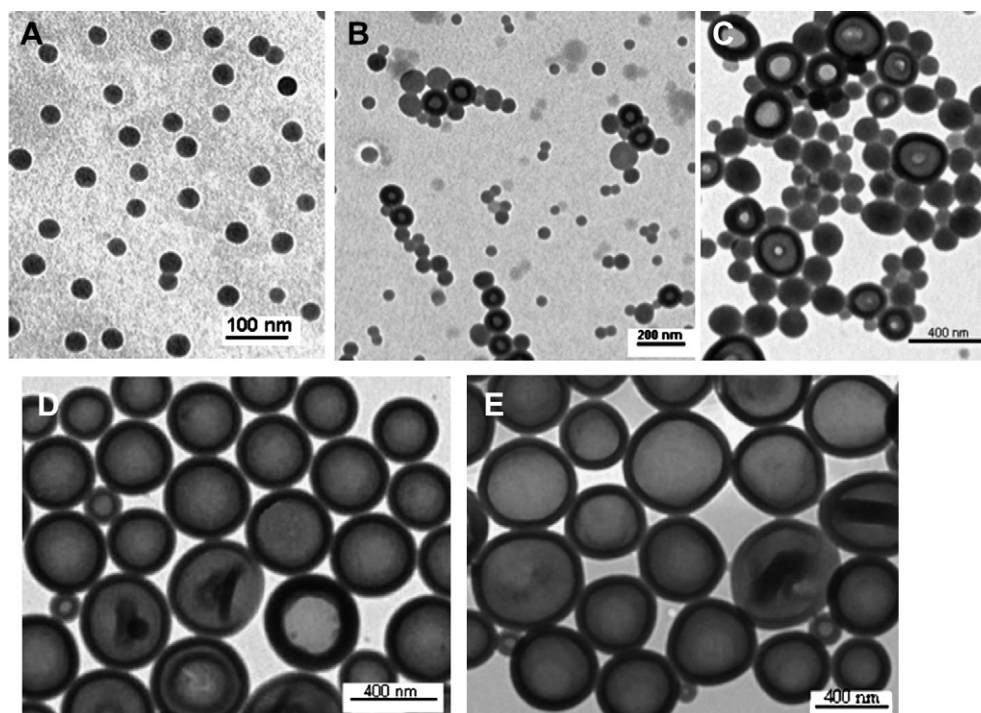


Fig. 8. TEM images of the morphologies formed from RAFT polymerization with feed molar ratio of St/PEO-TC/AIBN = 10,000/1/0.1 (St: 1.9 g; methanol: 1 g) for different polymerization times: (A) 2 h, (B) 4 h, (C) 6 h, (D) 8 h and (E) 24 h.

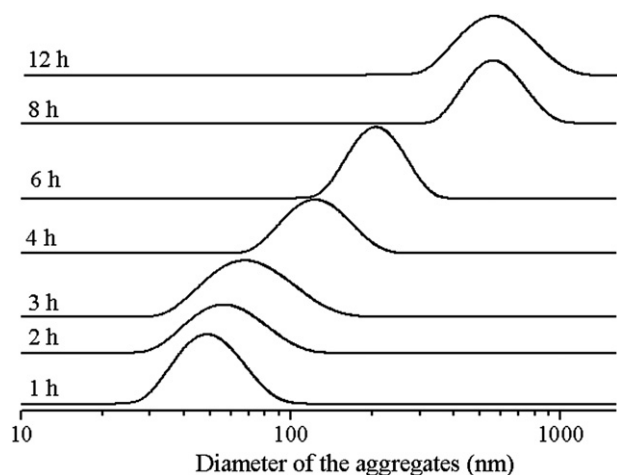


Fig. 9. LLS results of the PEO-*b*-PS block copolymer aggregates obtained from RAFT polymerization with feed molar ratio of St/PEO-TC/AIBN = 10,000/1/0.1 (St: 1.9 g; methanol: 1 g) for different polymerization times.

on the general concept in determining the shape of molecular assemblies [33–35], the increased PS chain length resulted in the increased packing parameter, leading to the decreased curvature of the molecular assemblies. When the chain length of PS block increased to 268, the spherical micelles with big curvature became unstable, they began to coagulate and fuse forming more stable and large size vesicles because their curvature was decreased. We can see a few vesicles coexisting with a large amount of spherical micelles. The D and wall thickness are ~ 100 nm and ~ 30 nm, respectively, at the same time, the size of spherical micelles increased also ($D = \sim 50$ nm) (Fig. 8B). With continuous propagation of PS blocks, the chain length ratio became 3.7 and the block copolymer, PS₄₁₈-*b*-PEO₁₁₃ was formed. This made more spherical micelles fusing, and more vesicles with D of ~ 200 nm and wall thickness of ~ 54 nm were produced as shown in Fig. 8C. Complete transition of the spherical micelles into the vesicles took place at ~ 8 h of polymerization, the D and wall thickness of the vesicles formed are ~ 350 nm and ~ 75 nm, respectively (Fig. 8D). The composition of the block copolymers obtained was PS₅₆₄-*b*-PEO₁₁₃. When the polymerization was prolonged to 24 h, the morphology of vesicles unchanged, but their D increased to ~ 450 nm (Fig. 8E). Here, one point we emphasize is that the solubility parameter (δ) of the polymerization media changed slightly (from $\delta = 22.93$ to 23.07), the morphology transition from micelles to vesicles is

mainly induced by significant increase of the chain length ratio of the PS to PEO (from 0 to 5). It is completely different from the general self-assembly of the amphiphilic block copolymers in a selective solvent for preparation of various morphologies, where δ changes tremendously.

For further verifying formation process of the vesicles observed by TEM, LLS was also used to trace the same polymerization, and the results are shown in Fig. 9. The polymerization solution formed at 1 h of polymerization displayed one peak at 48 nm, indicating the occurrence of phase separation and this is consistent with the observation shown in Fig. 7B. For the polymer solution obtained at 2 h and 3 h of polymerization, the spherical micelles grew slowly from D of 48 nm–57 nm, to 68 nm. It is understandable that the D measured by LLS is larger than that obtained from TEM because TEM measured the size of dried aggregates. With chain growth of the PS blocks, LLS result of the polymerization solution obtained at 4 h of polymerization displayed a peak at 121 nm, such D value was the result of spheres coexisting with vesicles. When more spheres transformed to the vesicles, average size of the aggregates increased continuously, as we can see that the D of aggregates formed at 6 h was 207 nm. TEM results in Fig. 8 showed complete transition of the spherical micelles into the vesicles occurred at 8 h of polymerization, it is reasonable that the average size of the aggregates increased significantly (from 207 nm to 543 nm). Continuous polymerization to 12 h did not change the size of vesicles formed as shown in Fig. 9. Thus, the coagulation and fusion of the spherical micelles took ~ 4 h and continued until complete transition of spherical micelles to vesicles. With size increase of the vesicles, the wall of vesicles expanded from 30 nm at 4 h to 54 nm at 6 h, and to 75 nm at 8 h of polymerization via rearrangement and continuous growth of the PS chains in the wall of vesicles.

Except the effect of feed molar ratio on the formation of morphologies, all factors influencing the polymerization of St, such as concentration of St in methanol, affected the morphologies formed. When the same feed molar ratio of St/PEO-TC/AIBN = 2000/1/0.1 was applied in RAFT polymerization, and the concentration of St in methanol varied from 10 wt% to 49 wt%, to 53 wt%, we can see the morphologies changed from spherical micelles (Fig. 6B) to nanowires coexisting with small amount of spherical micelles (Fig. 10A), to nanowires coexisting with vesicles (Fig. 10B). In the polymerization with low concentration of St (10 wt%), mobility of the core PS chains is highly restricted, thus the propagation of PS chains decreased significantly leading to transition of spheres to other morphologies impossible [12–15]. When the PS cores are swollen by an appropriate solvent, such as St, for enhancing the mobility of PS chains, the propagation of core PS leads to alter the ratio of PS to PEO blocks, so, transition of the

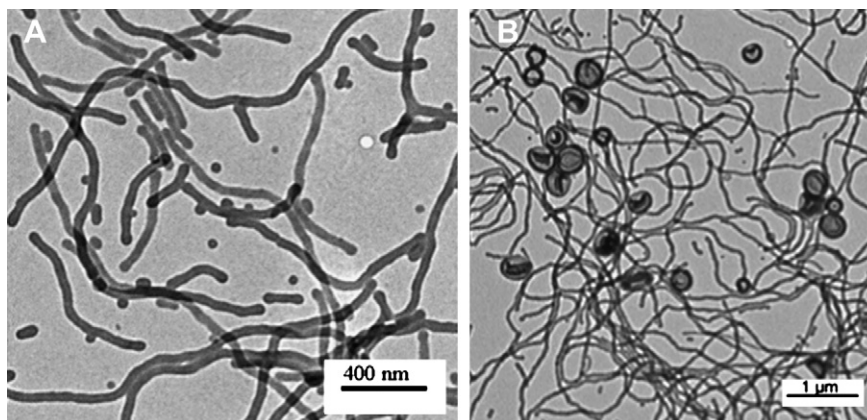


Fig. 10. TEM images of the aggregates formed from RAFT polymerization at 80 °C for 24 h with different concentrations of St with same feed molar ratios of St/PEO-TC/AIBN = 2000/1/0.1, (A) St: 0.78 g, CH₃OH: 0.8 g; (B) St: 0.78 g, CH₃OH: 0.68 g.

morphology becomes possible. For 49 wt% of St concentration, we can observe most of the spherical micelles were transformed to nanowires (Fig. 10A), but for 53 wt% of St concentration, the complete transition of the spherical micelles occurred, most of them were transformed to nanowires, small amount of spheres became vesicles (Fig. 10B). Thus various morphologies can be prepared just by changing the feed ratio and the polymerization conditions.

4. Conclusions

The PS-*b*-PEO vesicles have been successfully prepared by RAFT dispersion polymerization of St in methanol using PEO-TC and AIBN as macro RAFT agent and initiator, respectively. During the polymerization, the spherical micelles were formed firstly via polymerization-induced self-assembling, and then the spherical micelles were transformed to the vesicles via polymerization-induced reorganization. The determining factor for morphology transition is the chain length ratio increase of PS to PEO blocks. By changing the feed molar ratio and concentration of St in methanol, the spherical micelles, nanowires and vesicles can be prepared. Thus we provide a feasible and facile strategy for preparation of multiple morphologies in large scale.

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