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ORIGINAL PAPER

Secondary self-assembly behaviors of PEO-*b*-P*t*BA-*b*-PS triblock terpolymers in solution

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Abstract A series of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_x ($x = 42$, 84, 165) triblock terpolymers were synthesized by the atom transfer radical polymerization and characterized by size exclusion chromatography and ^{1}H NMR. Their self-assemblies were conducted by a two-step hierarchical self-assembly method and a one-step dialysis method and the self-assembly behaviors were investigated. The morphologies, sizes, and size distributions of micelles produced by the self-assembly were determined by transmission electron microscopy and dynamic light scattering. The secondary self-assembled structure of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_x obtained by the two-step hierarchical self-assembly could be controlled by tuning the length of PS block, the core forming block. The micelles were uniform with diameters of 20–25 nm and their size distributions, except for that of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{165}, were narrow with particle size distribution indexes ranging from 0.014 to 0.246. The one-step dialysis of the triblock terpolymers produced vesicular micelles with distinct vesicle walls that exhibited similar thicknesses. The vesicles did not show significant aggregation. The size distribution of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{42} vesicle was the narrowest with a particle size distribution index value of 0.135. The PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{165} vesicles tended to overlap with each other.

Keywords Triblock terpolymers · PEO-*b*-P*t*BA-*b*-PS · Hierarchical self-assembly · Block length

Introduction

Block copolymers can self-assemble into a variety of controllable nanostructures in bulk or in solution (Chen 2012; Wyman and Liu 2013). In particular, linear ABC triblock terpolymers can self-assemble and form more diverse and more complex nanostructures (Cui et al. 2007) in both bulk and solution phases due to the interactions between component blocks and the interactions between each block and the solvent (Wyman and Liu 2013). Therefore, the self-assembly of ABC linear triblock terpolymers into multi-compartment micelles and their applications in soft matter nanoscience have attracted considerable attentions in recent years (Wu et al. 2015; Gröschel et al. 2012b). Linear ABC triblock terpolymers with different block sequences can form spherical or cylindrical multicompartmentalized micelles under optimized self-assembly conditions (Dou et al. 2010; Fustin et al. 2005; Hadjichristidis et al. 2005; Huo et al. 2014; Moughton et al. 2012; Wu et al. 2015; Wyman and Liu 2013). The further aggregation of these micelles can produce a secondary self-assembled structure (Erhardt et al. 2001, 2003; Gao et al. 2012; Gröschel et al. 2012a). For example, Müller group. prepared controllable Janus Particles by the two-step hierarchical self-assembly of linear ABC triblock terpolymers and proposed a stepwise self-assembly mechanism (Erhardt et al. 2001, 2003; Gröschel et al. 2012a, b; Löbling et al. 2016; Schacher et al. 2009a, b, c; Walther et al. 2010; Wolf et al. 2011). The mechanism that they described provided a general concept of homogeneous populations of multicompartment micelles

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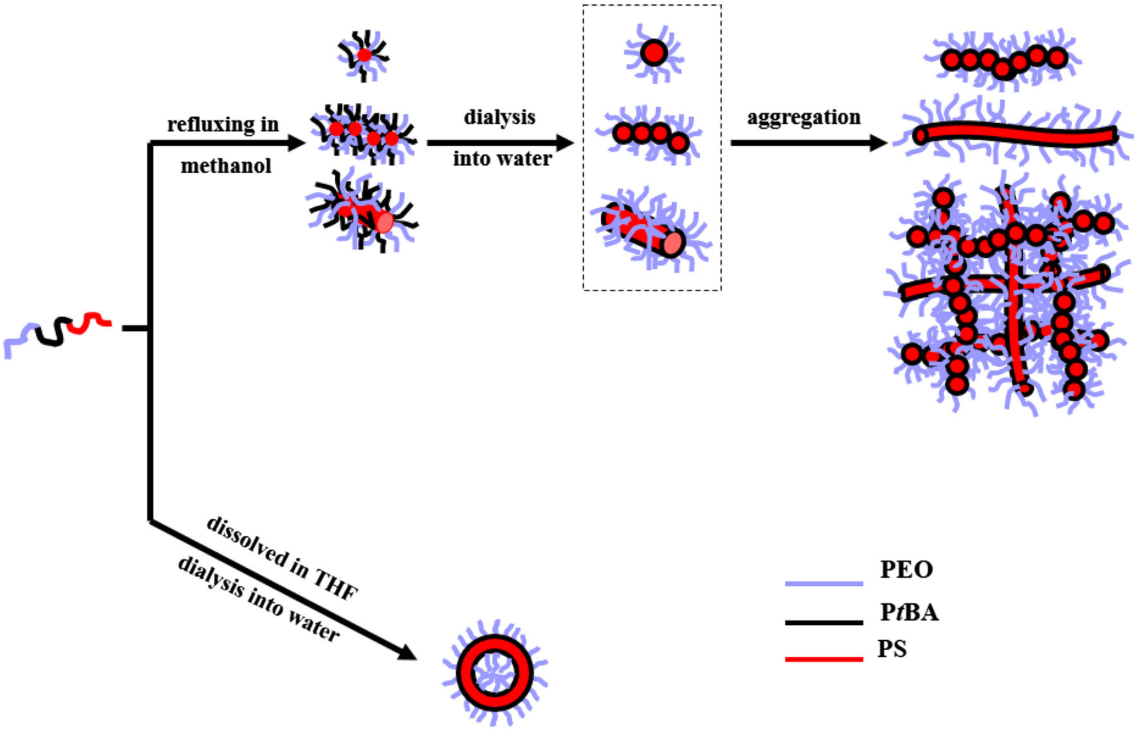
in step-wise self-assembly processes (Gröschel et al. 2012b). They also pointed out that only few self-assembly approaches were reliable to obtain particles with narrow particle size distributions (Gröschel and Müller 2015). It remained challenging to fabricate controllable patchy particles in the desired size regime and gain a more comprehensive understanding about how to target the self-assembly behaviors of ABC triblock terpolymers to obtain compartmentalized micelles (Gröschel and Müller 2015; Gröschel et al. 2013).

The self-assembly of amphiphilic ternary block copolymers is rarely studied (Marsat et al. 2011). Especially, only a few extensive studies have been carried on the step-wise hierarchical self-assembly behaviors of linear ABC triblock terpolymers with poly(ethylene oxide) (PEO) and polystyrene (PS) as the terminal blocks in solution (Hadjichristidis et al. 2005; Wyman and Liu 2013; Cheng et al. 2014; Fustin et al. 2005; Moughton et al. 2012). Most of those studies were focused on the primary self-assembly in aqueous solutions and demonstrated that many factors, such as the block length ratio, temperature, pH, solvent, block sequence, external stimuli-factors, and so on, can affect the self-assembly structures of block copolymers (Hadjichristidis et al. 2005; Wyman and Liu 2013). For example, the position of the core forming block decides the exposing area of the ABC triblock terpolymer to the solvent (Wyman and Liu 2013) and thus influences its self-assembly behavior. However, the effects of the length of core forming block of ABC triblock terpolymers on their self-assembly have been rarely reported. In addition, the self-assembly behaviors of linear ABC triblock terpolymers in solution remain unexplored (Kubowicz et al. 2005).

To determine the hierarchical self-assembly behaviors of triblock terpolymer in the stepwise self-assembly process, the hydrophobic blocks should have a high degree of mutual immiscibility (Cui et al. 2007). Therefore, a series of ABC triblock terpolymers PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_x ($x = 42, 84, 165$) with two incompatible hydrophobic blocks were prepared in the present work. The effects of the length of PS block on the self-assembly behaviors of the triblock terpolymers were then investigated. Micelles with a narrow particle size distribution were obtained by the stepwise self-assembly. Schematic diagram of formation process of micelles given in scheme 1. We previously prepared poly(*tert*-Butyl acrylate)-*b*-polystyrene-*b*-poly(2-vinylpyridine) (P*t*BA_{154}-*b*-PS_{300}-*b*-$P2VP_{240}$) and investigated its two-step hierarchical self-assembly behaviors (Muslim et al. 2015a). The present work focused on the factors, such as the block length of the core forming segment, affecting the self-assembly behaviors. The replacement of P2VP block with PEO block could broaden the application of block copolymers due to the unique properties of PEO, such as good biocompatibility and biodegradability, high hydrophilicity, and so on (Goren and Lennox 2001). Although both PEO and P2VP can form micelle corona in non-solvent of P*t*BA and PS, P2VP can



Scheme 1 Schematic diagram of formation process of micelles

Table 1 Synthesis conditions of triblock copolymers

Sample	Equivalents of feed					Reaction conditions	
	PEO_{45}-P*t*BA_{53}-Br	PMDETA	St	CuCl	[a]Toluene (g)	[b]τ (h)	[c]*T* (°C)
PEO_{45}-P*t*BA_{53}-PS_{42}	1	1	200	1	0.72	4.5	90
PEO_{45}-P*t*BA_{53}-PS_{84}	1	1	300	1	2.57	5	90
PEO_{45}-P*t*BA_{53}-PS_{165}	1	1	300	1	0.23	10	90

[a] The mass ratio to feed, 20–30%

[b] Reaction time

[c] Reaction temperature

only form the micelle shell in a specific pH range, which makes the self-assembly very complicated. In contrast, the formation of micelle shell with PEO is not affected by pH. The self-assembly of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_x ($x = 42$, 84, 165) was conducted by a two-step hierarchical self-assembly method and a one-step dialysis method. For the two-step self-assembly method, the non-solvent feeds were added slowly to fabricate thermodynamically equilibrated uniform multicompartment nano structure (Gröschel and Müller 2015). The triblock terpolymer was refluxed in MeOH and dialyzed against water to achieve polymer aggregates with hierarchical structures. For the one-step dialysis method, the THF solution of the triblock terpolymer was dialyzed against water directly. The morphologies of the self-assembly structures by the two-step self-assembly method evolved from sphere to string micelles and small amount of cylinder micelles and eventually to tangled into reticular structure with the increase of PS block length. The one-step dialysis produced polymer vesicles. The formation mechanism of these different structures were proposed.

Experimental

Materials

CuBr and CuCl were washed with acetic acid and ethanol and vacuum dried. Styrene (St) was dried over CaH_2 and distilled under reduced pressure. *tert*-Butyl acrylate (*t*BA) (99%, Alfa Aesar) was purified by vacuum distillation. *N,N*-Dimethylformamide (DMF) was dried over anhydrous $MgSO_4$ and distilled under reduced pressure. *N,N,N',N",N"*-pentamethylenetriamine (PMDETA) (98%, Aldrich), $CDCl_3$ (99.8%, J&K Chemicals) and other reagents were used as received.

Characterization

The M_n and M_w/M_n of polymers were determined using a SEC system equipped with a Waters 515 pump, a Waters 2414 refractive index detector and Waters HT2, HT4, and HT5 styragel columns. DMF at a flow rate of 1.0 mL/min was used as mobile phase, column temperature was set to 50 °C. PS standards were used for the calibration. Nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker DMX400 spectrometer using $CDCl_3$ as the solvent. A drop of micelle solution was deposited on a carbon-coated copper grid and evaporated in air for the transmission electron microscopy (TEM) imaging on a TECNAI $G^2$20 TEM at 200 kV. The samples were filtered through a 0.45-μm membrane and analyzed on a Zetasizer dynamic light scattering (DLS) instrument (Nano Series, Malvern Instruments, UK) at the scattering angle of 173° using a wavelength of 633.0 nm. The data were fitted by the cumulated fitting method.

Synthesis of PEO_{45}-*b*-P*t*BA_{53} diblock copolymer

The macromolecular initiator PEO-Br was synthesized as described in the literatures (Du and Chen 2004). 1 g PEO_{45}-Br, 84 mg PMDETA, 4.39 g *t*BA, and 0.6 g acetone were added into a 20-mL flask and degassed by three freeze–pump–thaw cycles. CuBr (70 mg) was added into the flask and degassed by two the freeze–pump–thaw cycles. The flask was sealed under vacuum and heated in an oil bath at 60 °C for 2 h. The resulted crude product was cooled to room temperature, diluted with CH_2Cl_2, passed through a column filled with neutral alumina to remove the catalyst, dried by rotary evaporation, dissolved in benzene, and freeze-dried.

Synthesis of PEO_{45}-*b*-PtBA_{53}-*b*-PS_x ($x = 42, 84, 165$) triblock terpolymers

PEO_{45}-*b*-P*t*BA_{53}-Br, PMDETA, St, and toluene were mixed in a 20-mL flask at certain equivalent ratios as listed in Table 1 and degassed by three freeze–pump–thaw cycles. A certain amount of CuCl was added into the flask and degassed by two freeze–pump–thaw cycles. The flask was sealed under vacuum and heated in an oil bath at 90 °C for several hours. The resulted crude product was cooled to

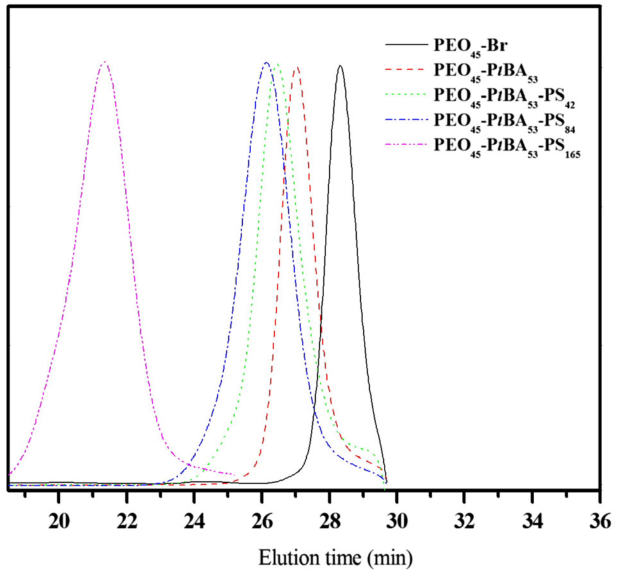


Fig. 1 SEC profiles of block copolymers

slow the polymerization, diluted with THF, passed through a column filled with neutral alumina and precipitated with a large amount of petroleum ether three times. The final product was dried under vacuum to a constant mass.

The self-assembly behaviors of PEO_{45}-*b*-$PtBA_{53}$-*b*-PS_x ($x = 42, 84, 165$) in solution

The self-assembly of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_x ($x = 42$, 84, 165) triblock terpolymers in solution were carried out by a two-step hierarchical self-assembly and a one-step dialysis method. For the two-step hierarchical self-assembly process, 20 mg PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_x was refluxed in 20 mL methanol at 80 °C overnight for the primary self-assembly. 5 mL of the primary self-assembled sample was dialyzed against deionized water. For the one-step dialysis process, 7.6 mL deionized water was added to 0.4 mL 1 mg/mL PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_x ($x = 42$, 84, 165) solution in THF dropwise and 3 mL of the mixture was dialyzed against deionized water.

Results and discussion

Synthesis of the block copolymers

Diblock and triblock copolymers were synthesized by ATRP as shown in Scheme 2 and characterized by SEC and ^{1}H NMR.

Figures 1 and 2 are the SEC profiles and ^{1}H NMR spectra of PEO-Br, PEO_{45}-*b*-P*t*BA_{53}, PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{42}, respectively. Both PEO-*b*-P*t*BA and PEO-*b*-P*t*BA-*b*-PS exhibited one single symmetrical SEC peak. No macro initiator residue was observed. The elution times of block polymers were in the order of PEO-Br > PEO_{45}-*b*-P*t*BA_{53} > PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{42}, indicating that polymers were successfully synthesized. M_n, M_w/M_n, and molecular weights calculated from the ^{1}H NMR spectra of the polymers are listed in Table 2. All copolymers exhibited narrow molecular weight distributions. The molecule weights of the copolymers calculated from ^{1}H NMR spectra are consistent with the theoretical values, further indicating that target copolymers were successfully prepared.

The degree of polymerization (DP) of *t*BA in PEO_{45}-*b*-P*t*BA_{53} was calculated by the peak area ratio between the peaks at $\delta = 3.4$ ppm and $\delta = 2.2$ ppm that were, respectively, assigned to the –CH_3 group in PEO block and the –CH– in P*t*BA block. The DP of PS in PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_x triblock terpolymers were calculated as 42, 84, 165, respectively, from the peak area ratio between the peaks at $\delta = 2.2$ ppm and $\delta = 6$–7.5 ppm that were assigned to the H on benzene ring in PS block. These results indicated that a series of triblock terpolymers with the same AB block length and different C block length were successfully synthesized.

Scheme 2 Synthesis mechanism of block copolymer

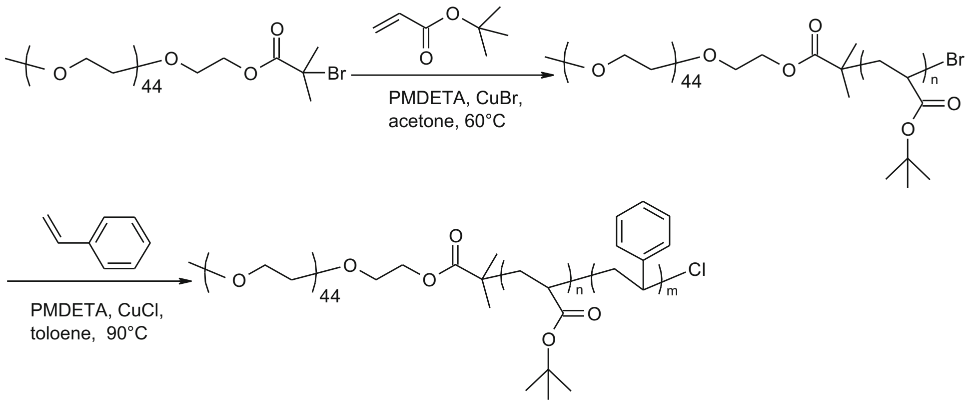


Fig. 2 ^{1}H NMR spectra of block copolymers

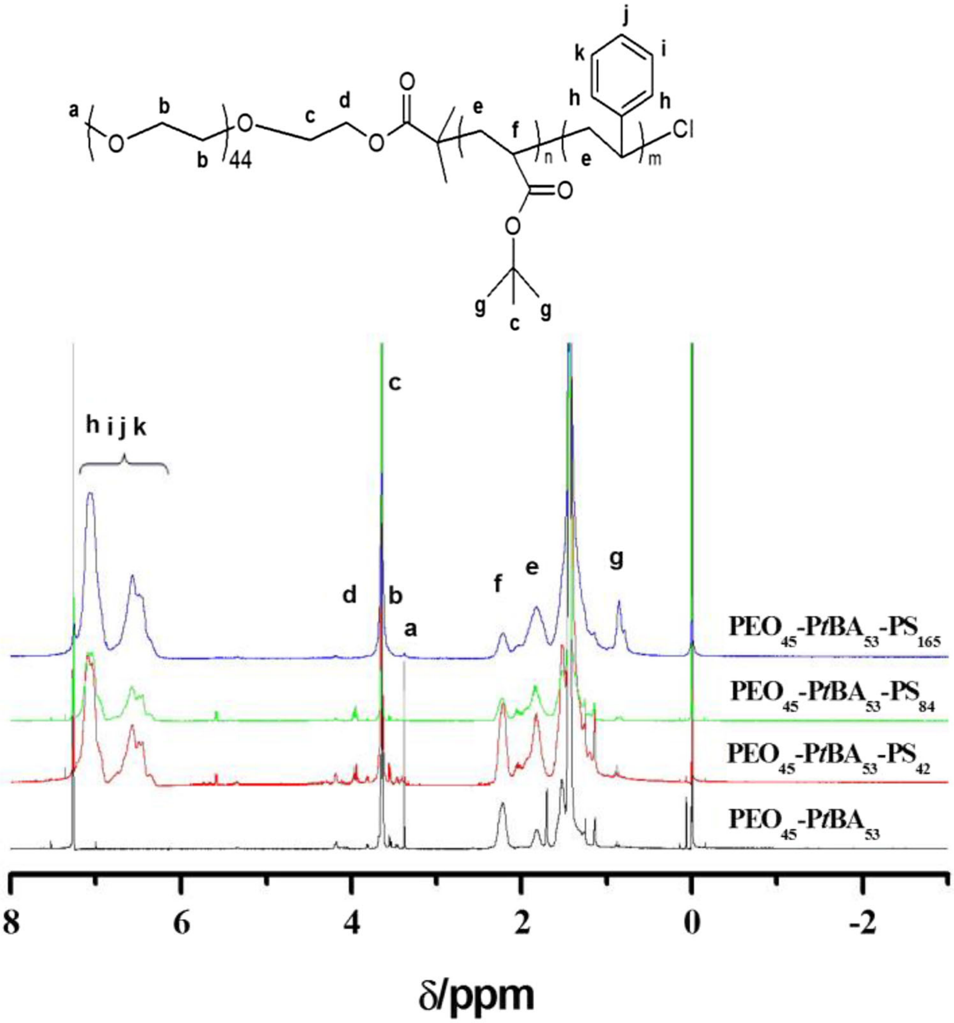


Table 2 Characterization data of copolymers by SEC and ^{1}H NMR

Sample	$^{a}M_{\mathrm{H\ NMR}} \times 10^4$	$^{b}M_n \times 10^4$	M_w/M_n
PEO$_{45}$-*b*-P*t*BA$_{53}$	0.88	2.98	1.07
PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_{42}$	1.32	3.28	1.12
PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_{84}$	1.75	4.43	1.16
PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_{165}$	2.59	7.31	1.20

[a] Calculated by the formula of $2000 + 128 \times 53 + 104x$ ($x = 42$, 84, 165)

[b] Obtained by SEC

Self-assembly behaviors of PEO$_{45}$-*b*-PtBA$_{53}$-*b*-PS$_x$ (x = 42, 84, 165)

The self-assembly of PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_x$ ($x = 42$, 84, 165) were carried out by a two-step hierarchical self-assembly method and a one-step dialysis method.

For the two-step hierarchical self-assembly process, 20 mg PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_x$ was refluxed in 20 mL methanol at 80 °C overnight and cooled naturally. Figure 3 shows the TEM images of PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_x$ ($x = 42$, 84, 165). The self-assembly of P*t*BA$_{53}$-*b*-PS$_{42}$ formed uniformly dispersed spherical micelles (Fig. 3a). As the DP of PS increased to 84, in addition to the spherical micelles, a small amount of cylindrical micelles was observed and the spherical micelles were close to each other and tended to aggregate into short string and cylindrical micelles (Fig. 3b). Further increasing the DP of PS to 165 caused the string and cylindrical micelles entangled into a raspberry-like network structure (Fig. 3c).

Solvent is critical for the solution self-assembly of ABC triblock terpolymers (Dupont et al. 2009). Methanol is a non-solvent for PS, but a good solvent for other two blocks. PS has a high glass transition temperature ($T_g = 89.8$ °C) and in glassy state at room temperature (Gao et al. 2014). Its microphases are in thermodynamic metastability in methanol and the micelles can be activated by the refluxing process, which promotes the self-assembly (Muslim et al. 2015b). As refluxed in methanol, the triblock terpolymer

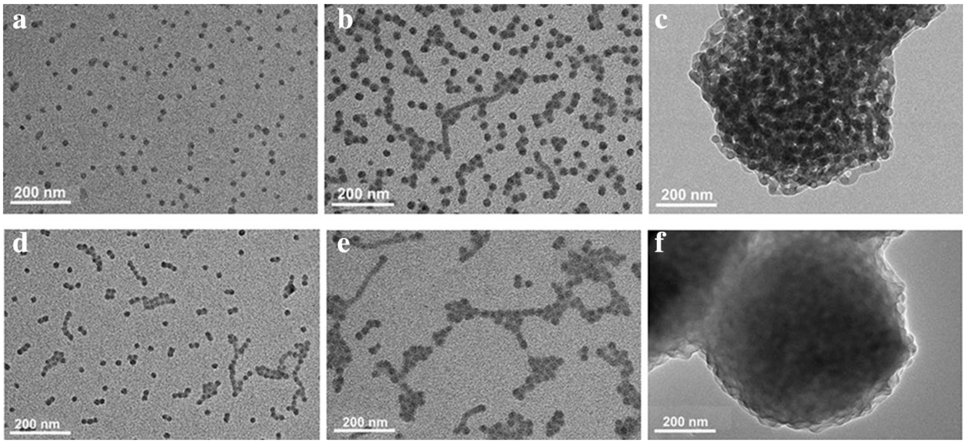


Fig. 3 TEM images of micelles obtained by the two-step hierarchical self-assemblies of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{42} before dialysis (**a**), PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{42} after dialysis (**d**), PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{84} before dialysis (**b**), PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{84} after dialysis (**e**), PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{165} before dialysis (**c**), and PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{165} after dialysis (**f**)

self-assembled and formed core-corona compartmentalized micelles with PS as the core and P*t*BA and PEO as the corona. Both P*t*BA and PEO were solvable in methanol and completely covered the short PS core (Fig. 3a). The spherical micelles cannot get close to each other and thus are well and uniformly dispersed in the solution (Gröschel et al. 2012b). The core of the micelles became larger with the increase of PS block length and the corona became incapable to cover the core. The increases in micelle size enhanced the collision possibilities of the micelles. To minimize the system energy, the spherical micelles tended to get closer to each other and transformed into a cylindrical structure, and eventually entangled and formed a reticular structure (Fig. 3b, c).

The secondary self-assembly was conducted by dialyzing 5 mL of the primary self-assembled triblock terpolymer against water. The spherical micelles of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{42} formed in first step (Fig. 3a) were aggregated into strings (Fig. 3d). The short string of the spherical PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{84} micelles obtained in the first step (Fig. 3b) turned into longer strings and cylindrical particles (Fig. 3e). The reticular structure of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{165} formed in first step (Fig. 3c) further aggregated during the second self-assembly step (Fig. 3f). P*t*BA and PS are insoluble in water. Therefore, the P*t*BA corona collapsed on the surface of PS core during the dialysis. The corona-compartmentalized micelles turned into core-compartmentalized micelles. The collapse of P*t*BA made it difficult for PEO alone to drag the micelles into solvent. However, the collapse also increased the core size and lowered the coverage of the swollen corona on the PS core. These changes increased the vibration between the compartmentalized core and PEO corona. The hydrophilic block lost the ability to keep the micelles dispersed in the solvent system as spheres. The micelle structure tended to transforming into the structures with lower free energies to release the extra energy (Njikang et al. 2008). No significant difference was observed between the diameters of the particles formed in the first and second steps of the hierarchical self-assembly process (Table 3). However, the hydrodynamic diameters of the particles of the first and second steps were significantly different, indicating the intermicellar population occurred in the second step due to the reduced distance between the spherical micelles by the collapse of P*t*BA. The variation between the average diameters measured by TEM and DLS was caused by the states measured. The particle size was measured by TEM using dry samples and particles were analyzed in solution. Therefore, the particle size measured by TEM was smaller than that obtained by DLS. In addition, the self-assembly reticular structure of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{165} is consistent with the core-compartmentalized micelle structure reported in the literature (Wyman and Liu 2013).

Our results clearly demonstrated that the self-assembly of ABC triblock terpolymers, PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_x, by the two-step hierarchical self-assembly method could be controlled by tuning the length of the core-forming PS block. The diameters of the particles formed in both steps were in the range of 20–30 nm. As mentioned above, the micelles stayed close to and even entangled with each other with the increase of the length of PS block. As a result, the distribution of the particle size became wider. As showed in Fig. 4, the particle size distribution index (PDI) of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{42} was 0.014 in the first step of the two-step hierarchical self-assembly, indicating that the particles were uniformly distributed. When the length of PS block increased to 84, the PDI was increased accordingly. Kubowicz et al. (2005) reported that broad particle size distributions might be related to high M_w/M_n ratio, which, in addition to intermicellar aggregation, might explain the increase of PDI with the increase of PS block length.

The one-step dialysis of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_x ($x = 42$, 84, 165) solutions in THF against water was conducted and the produced structures were imaged by TEM. As shown in Fig. 5, PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{42} self-assembled into micelles of two connected spheres with PS

Table 3 The morphology characteristics of triblock terpolymers

Samples	Morphology			[a]Average diameter (nm)			[b]Average hydrodynamic diameter (nm)		
	Two-step hierarchical self-assembly		One-step dialysis	Two-step hierarchical self-assembly		One-step dialysis	Two-step hierarchical self-assembly		One-step dialysis
	First step	Second step		First step	Second step		First step	Second step	
PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{42}	Sphere	String	Vesicle	20	21	70	31	53	107
PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{84}	Sphere/ string	Sphere/ string	Vesicle	23	24	99	53	90	191
PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{165}	Reticular	Reticular	Vesicle	[c]25	[d]–	155	[d]–	[d]–	[e]–

[a] Measured from TEM images. The data of the one-step dialysis are referred to the outer diameter of the vesicles

[b] Determined by DLS

[c] Measured from the margin of the particle

[d] Indeterminable due to the formation of raspberries of closely packed cylindrical micelles

[e] Indeterminable due to the formation of cotton-like or granular precipitates

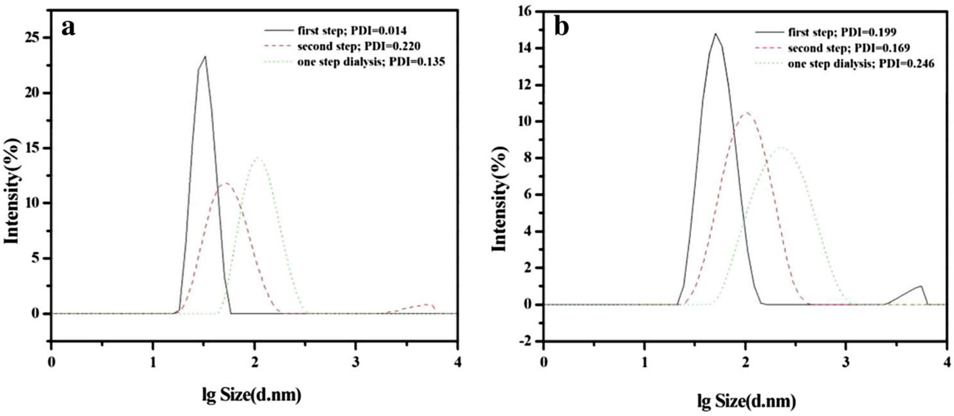


Fig. 4 Sizes and size distributions of micelles formed by the two-step hierarchical self-assemblies and one-step dialysis of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{42} (**a**) and PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{84} (**b**)

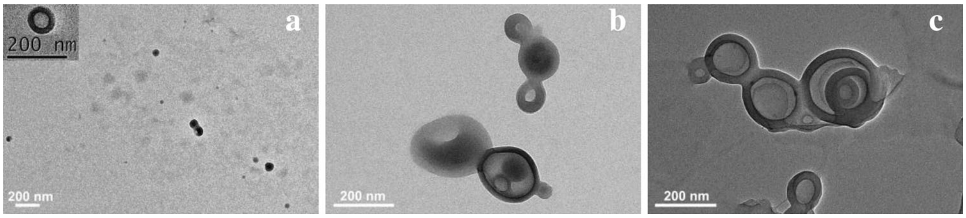


Fig. 5 TEM images of the self-assembled PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{42} (**a**), PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{84} (**b**), and PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_{165}(**c**) by the one-step dialysis

block as the core, P*t*BA block as the shell and PEO block as the corona. A small amount of vesicles was also observed (Fig. 5a). The outer diameter of both core–shell-corona micelles and vesicles was ~70 nm. All other PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_x ($x = 84$ and 165) triblock terpolymers self-assembled into vesicles (Fig. 5b, c). Although the sizes of these vesicles differed from each other, they all exhibited distinct vesicle walls with similar thicknesses. The amount of the vesicle increased with the length of PS block. It can be explained that all three blocks of PEO_{45}-*b*-P*t*BA_{53}-*b*-PS_x ($x = 84$ and 165) are soluble in THF. Both PS and P*t*BA collapsed and a compartmental core structure was formed with PEO as the corona as the triblock terpolymer THF solution dialyzed against water. As THF gradually dialyzed away, the core-compartmentalized micelles aggregated into vesicles with PS and P*t*BA as the compartmentalized vesicle wall. The PEO scattered on the inner or outer surfaces of vesicle wall formed a corona. The micelle size increased with the increase of PS block length, which promoted the possibility of collision between the cores and accelerated the formation of vesicle walls. The distance between vesicles was reduced to maintain a steady status. These results are consistent with TEM and DLS results (Figs. 4, 5). The particle size distributions of vesicles produced by the one-step dialysis of all PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_x$ triblock terpolymers were all broad (Fig. 4), which might be caused by the irregular aggregation of the vesicles. In addition, the aggregation increased with the increase of PS block length except for PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_{165}$ (Fig. 5). The majority of PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_{165}$ vesicles overlapped with each other. Gröschel et al. (2012b) reported that the self-assembly of triblock terpolymers was uncontrollable and formed polydispersed multicompartmental micelles. However, the vesicles of PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_{42}$ formed by the one-step dialysis were uniform and exhibited narrow size distributions with a particle size distribution index of 0.135 (Fig. 4a) and the vesicles of PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_{84}$ showed no obvious aggregation, indicating that the length of core forming block could not significantly affect the self-assembly structure of ABC triblock terpolymers.

In all, the secondary self-assembled structure of PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_x$ triblock terpolymer was controllable by tuning the length of PS block for the two-step hierarchical self-assembly. However, the length of PS block that was the core forming block exhibited no significant effect on the self-assembly structure of PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_x$ formed by the one-step dialysis. It has been reported that the morphologies of the self-assembled micelles of diblock polymers change from spherical to cylindrical, and eventually to vesicular as the volume fraction of corona forming block is reduced (Wyman and Liu 2013). Similar morphology evolution was observed during the two-step hierarchical self-assembly of PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_x$ ($x = 42$, 84) in the present work. It can be explained that the micelle size gradually changed with the length of PS block and the P*t*BA block slowly collapsed during the dialysis. These changes gradually weakened the swelling capability of the hydrophilic PEO block. Therefore, the morphological variation of the system catered the general self-assembly tendency of block copolymers in solution. The raspberry-like structure of PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_{165}$ was in a metastable state between cylinders and vesicles. For the one-step dialysis of the triblock terpolymer against water, the secondary self-assembled structure might have already formed during the dropwise addition of deionized water to the THF solution of the polymer. The dialysis enhanced the aggregation trend of the micelles to reduce the overall free energy of the system.

Conclusions

A series of PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_x$ ($x = 42$, 84, 165) triblock terpolymers were synthesized by ATRP and characterized by SEC and ^{1}H NMR. Their two-step hierarchical self-assembly and one-step dialysis self-assembly behaviors were investigated. The morphologies, sizes, and size distributions of the self-assembled micelles of the triblock terpolymers were determined by TEM and DLS. The morphology of the micelles produced by the two-step hierarchical self-assembly changed from sphere to string or cylinder, and eventually to the tangled reticular structure with the increase of the length of core forming PS block. The self-assembled micelles of the triblock terpolymers, except for PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_{165}$, were uniform with narrow particle size distributions. The one-step dialysis of the triblock terpolymer produced vesicular micelles with distinct vesicle walls. The vesicle walls had similar thicknesses and the vesicles exhibited no severe aggregation. PEO$_{45}$-*b*-P*t*BA$_{53}$-*b*-PS$_{165}$ self-assembled into overlapped vesicles. Although the length of core forming block showed no significant effect on the morphology of the self-assembled aggregates of the one-step dialysis, shorter PS block resulted in narrower particle size distributions of the aggregates.

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