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Synthesis of Miktoarm Dumbbell-Like Amphiphilic Triblock Copolymer by Combination of Consecutive RAFT Polymerizations and ATRP

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Summary

A novel synthetic route, combining three reversible addition-fragmentation chain transfer (RAFT) and one atom transfer radical polymerization (ATRP) processes, for the preparation of a miktoarm dumbbell-like amphiphilic triblock copolymer, poly(poly(ethylene glycol) methyl ether methacrylate)-*b*-polystyrene-*b*-(poly(4-vinyl-benzyl chloride)-*g*-polystyrene) (PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS)), was developed using 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) as a RAFT agent, and the benzyl chloride group of the VBC units in the PVBC block as active ATRP macroinitiators, respectively. The structures of the obtained (co)polymers were characterized by ^{1}H NMR spectroscopy. The obtained PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS) amphiphilic triblock graft copolymer could self-assemble into spherical micelles with 100-300 nm diameters in a selective solvent.

Introduction

These polymers with complex macromolecular architectures, such as star polymers [1], hyperbranched, or highly branched polymers [2], usually exhibit very different chemical and physical properties as well as special performances as compared with the corresponding linear analogues [3]. Generally, the use of macromonomers is a convenient method for preparing branched polymers. However, graft copolymers obtained by conventional radical copolymerization of macromonomers often exhibit poorly control over molecular weights and high polydispersities as well as large compositional heterogeneities from chain-to-chain. In contrast, recent progress in "living"/controlled radical polymerization involve reversible addition-fragmentation chain transfer (RAFT) [4] polymerization and atom transfer radical polymerization (ATRP) [5] has facilitated the precise synthesis of novel and complex macromolecular architectures with controlled molecular weights and low polydispersities. The advantages of using RAFT and ATRP techniques in the building of these structures are not only the controlled main chain, graft chain and block lengths, but also the flexibility

of introducing specific properties resulting from various functional groups due to their tolerance of a very wide range of functionality in monomers [6].

Since Roovers and Toporowski synthesized the H-shaped polystyrenes via anionic polymerization techniques [7] in 1981, great deal of works were devoted to the studies of this type of complex macromolecular architectures. Such well-structured copolymers with controlled main chain, graft chain, and block lengths have been synthesized mainly by living ionic polymerizations, except for several recent examples [8,9]. Among them, the A_xBA_x-type block-graft copolymer, coined as dumbbell [8c] or pom-pom [8d] copolymers are much more interesting. Ohno and Matyjaszewski reported the synthesis of an A_xAA_x-type block-graft poly(n-butyl acrylate) [poly(BA)], consisting of BA in the middle and outer graft chains, via copper-mediated atom transfer radical block copolymerization of BA and the poly(BA) macromonomer [9d]. Quite recently, Kamigaito and coworkers synthesized a series of well-defined A_xBA_x-type dumbbell-like copolymer consisting of soft middle (PDMA) and hard outer graft chains (PMMA) from the ruthenium-catalyzed sequential ATRP techniques [9e]. However, the design and synthesis of A_xBC_y-type dumbbell-like or miktoarm dumbbell-like copolymer have still been an important challenge. We recently reported a dual-brush-type or AB_xC_y-type amphiphilic triblock copolymer via a combination of consecutive RAFT polymerizations and ATRP [10]. To the best of our knowledge, there have been no any reports on the synthesis of A_xBC_y-type dumbbell-like triblock amphphilic copolymers. This paper first presents a novel synthesis route, combining consecutive RAFT polymerizations and ATRP, for the preparation of miktoarm dumbbell-like triblock amphiphilic copolymers, poly(poly(ethylene glycol) methyl ether methacrylate)-b-polystyrene-b- (poly(4-vinylbenzyl chloride)-g-polystyrene) (PPEGMA-b-PS- b-(PVBC-g-PS)). The obtained copolymer can self-assemble into spherical micelles in a selective solvent.

Experimental section

Materials

The monomers, 4-vinylbenzyl chloride (VBC, 90+%) and styrene (St, 99+%), were obtained from Aldrich Chemical Co.. After passing through a neutral Al_2O_3 column, they were stored under an argon atmosphere at -10°C. Poly(ethylene glycol)methylether methacrylate (PEGMA, 97%, M_n = 1100 g.mol^{-1}, containing 23 ethylene glycol units (n = 23)) was obtained from Aldrich Chemical Co. It was dissolved in THF and passed through a neutral Al_2O_3 column, concentrated in a rotary evaporator and then dried under reduced pressure. The RAFT agent, 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN, structure shown in Scheme 1), was synthesized according to procedures reported earlier [11]. The initiator α,α'-azobisisobutyronitrile (AIBN, 97%) was obtained from Kanto Chemical Co. (Tokyo, Japan) and was recrystallized in anhydrous ethanol. Copper(I) chloride (CuCl, 99+%) and *2,2'*-bipyridyl (bpy, 99+%) obtained from Aldrich Chemical Co. and used as received. Copper(II) bromide (CuBr$_2$, 99+%), obtained from Aldrich Chemical Co. and used as received. *N,N*-dimethyl-formamide (DMF) (analytical reagent), tetrahydrofuran (THF) (analytical reagent) and all other chemicals were obtained from Shanghai Chemical Reagents Co. and used as received unless mentioned. The dialysis tubing cellulose membrane (cellulose tubing with cutoff molecular weight of 2000 g/mol) was obtained from Shanghai Supermed Co. (Shanghai, China).

RAFT polymerization of PEGMA using CPDN as the RAFT agent

A typical polymerization procedure for RAFT polymerization was as follows: 5 g (4.517 mmol) of PEGMA, 24.8 mg (0.151 mmol) of AIBN, 162.3 mg (0.6 mmol) of CPDN and 5 mL of anisole were introduced into a 20 mL dry glass tube. The light-red homogeneous solution was purged with argon for approximately 20 min to remove the dissolved oxygen. Then, the glass tube was sealed, placed in an oil bath at 90°C to initiate the polymerization. At the end of the reaction (5 d), the glass tube was quenched in cold water and opened. The reaction mixture was dialyzed against methanol for 3 days to remove anisole and the residual PEGMA. The dialysate was exchanged every 8 h. The polymer, PPEGMA, was dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained. The conversion of PEGMA was about 86%. M_n of the PPEGMA, as determined from gel permeation chromatography (GPC) results, was 7770 g.mol^{-1}.

RAFT polymerization of St using PPEGMA as the macro-RAFT agent

The procedures used for the block copolymerization of St were similar to those used for the RAFT polymerization of PEGMA. 1.0 mL (8.74 mmol) of St, 2.4 mg (0.0146 mmol) of AIBN, and 0.5 g (0.0494 mmol) of PPEGMA obtained above were dissolved in 2.0 ml of anisole in a 5 mL dry glass tube under stirring. The homogeneous solution was purged with argon for approximately 20 min. The glass tube was then sealed. Polymerization was carried out at 90°C for 5 d. At the end of the polymerization reaction, the glass tube was quenched in cold water and opened, diluted with THF and precipitated into a large amount of methanol. The block copolymer, PPEGMA-*b*-PS, was dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained. The conversion of St was about 77%. M_n of the PPEGMA-*b*-PS, as determined from GPC results, was 17000 g.mol^{-1}.

RAFT polymerization of VBC using PPEGMA-b-PS as the macro-RAFT agent

The procedures used for the RAFT polymerization of VBC were also similar to those used for the polymerization of St. 0.5 g (0.0202 mmol) of PPEGMA-*b*-PS obtained above, 0.9 mg (0.0055 mmol) of AIBN, and 0.35 mL (0.031 mmol) of VBC were dissolved in 1.5 mL of anisole in a 5 mL dry glass tube under stirring. The homogeneous solution was purged with argon for approximately 20 min. The glass tube was then sealed. Polymerization was carried out at 80°C for 3 d. At the end of the polymerization reaction, the glass tube was quenched in cold water and opened, diluted with THF and precipitated into a large amount of methanol. The triblock copolymer, PPEGMA-*b*-PS-*b*-PVBC, was dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained. The conversion of VBC was about 40%. M_n of the PPEGMA-*b*-PS-*b*-PVBC, as determined from GPC results, was 17200 g.mol^{-1}.

ATRP of styrene using the VBC units of PPEGMA-b-PS-b-PVBC as the macroinitiators

The reaction mixture, containing 161 mg of PPEGMA-*b*-PS-*b*-PVBC obtained above, 1.0 mL of DMF, 1.5 mL (13.0 mmol) of St, 4.0 mg (0.04 mmol) of CuCl, 0.4 mg (0.0018 mmol) of CuBr$_2$ and 18.7 mg (0.12 mmol) of bpy were introduced into a 5 mL dry clean glass tube. The mixture was purged with argon for approximately 20 min. The tube was then sealed. Polymerization was carried out at 110°C under continuous stirring

for 2 d. At the end of the polymerization reaction, the glass tube was quenched in cold water and opened, diluted with 2 mL of THF, passed through Al_2O_3 to remove the copper salts, concentrated by rotary evaporation, precipitated into 100 mL of methanol. The miktoarm dumbbell-like amphiphilic triblock copolymer, PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS), was dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained. The conversion of St was about 68%. M_n of the PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS), as determined from GPC results, was 42800 g.mol^{-1}.

Preparation of the micelle solution

The PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS) dumbbell-like copolymer obtained above (130 mg) was first dissolved in DMF (5 mL), a common solvent for both PS and PPEGMA blocks, and subsequent addition of deionized water to the solution under stirring to induce aggregation of the PS blocks. After a predetermined water content (5.5 wt%) had been reached to give a 2.5 wt% polymer solution, the water addition was stopped for 5 days. After the aggregate solutions had been stirred for a period of 5 days, more water was added dropwise to freeze the aggregate structures. Finally, aqueous solutions of the aggregates were obtained by dialyzing the resulting colloidal solution against water to remove DMF. The obtained colloidal solution was used for the subsequent morphological studies by transmission electron microscopy (TEM).

Characterization

The number-average molecular weight ($M_{n,GPC}$) values and molecular weight distribution (M_w/M_n) values of the polymers were determined using Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector (Waters 2414), using HR 1, HR 2 and HR 4 (7.8×300 mm, 5 μm beads size) columns with molecular weights ranged $10^2 \sim 5 \times 10^5$ g/mol. THF was used as an eluent at a flow rate of 1.0 mL/min and 30°C. The GPC samples were injected using a Waters 717 plus autosampler and calibrated with poly(methyl methacrylate) or polystyrene standards from Waters. ^{1}H NMR spectra was recorded on an Inova 400 MHz nuclear magnetic resonance (NMR) instrument using CDCl$_3$ as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. TEM was recorded on a Tecnai G^2-20 TEM at a 200 kV accelerating voltage. The samples were prepared by mounting a drop of the micelle solution (~ 50 μL) on the carbon-coated Cu grids and allowing the samples to dry in air.

Results and discussion

*Synthesis of miktoarm dumbbell-like amphiphilic triblock copolymer*

Scheme 1 shows the synthetic pathway for the synthesis of A$_x$BC$_y$-type dumbbell-like triblock amphphilic copolymers. The process involves (i) synthesis of PPEGMA hydrophilic brushes via RAFT polymerization of PEGMA, using 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) as the RAFT agent and α,α'-azobis-(isobutyronitrile) (AIBN) as the initiator, (ii) synthesis of the diblock copolymer, PPEGMA-*b*-PS, via RAFT polymerization of styrene, using PPEGMA obtained above as the macro-RAFT agent, (iii) synthesis of the amphiphilic triblock copolymer PPEGMA-*b*-PS-*b*-PVBC via RAFT polymerization of 4-vinylbenzyl chloride, using the brush-type diblock

copolymer PPEGMA-*b*-PS as the macro-RAFT agent, and (iv) synthesis of the miktoarm dumbbell-like amphiphilic triblock copolymer PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS) via ATRP of styrene, using the benzyl chloride group of the VBC units in the PVBC block as the active ATRP macroinitiators.
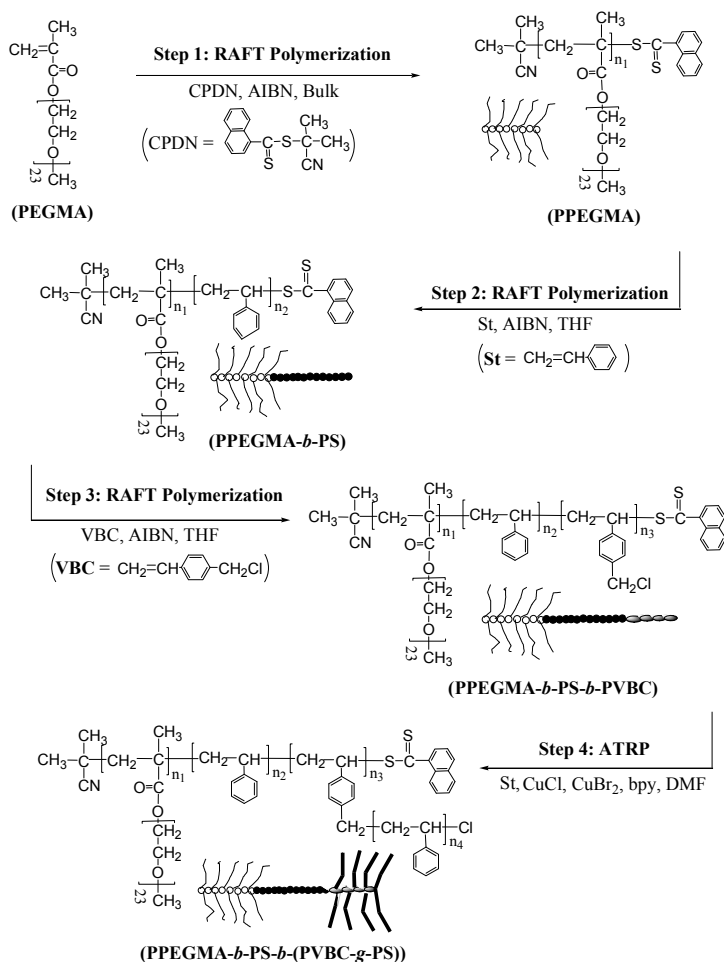
Scheme 1. Schematic diagram illustrating the process for preparing the miktoarm dumbbell-like amphiphilic triblock copolymer.

The size, structure and composition of the homopolymer and copolymers were studied by gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy. Figure 1 shows the GPC traces of the PPEGMA, PPEGMA-*b*-PS, PPEGMA-*b*-PS-*b*-PVBC and PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS). The GPC traces of the four samples show a monomodal distribution. However, there is a shoulder for the GPC trace of the PPEGMA-*b*-PS-*b*-PVBC copolymer, which should result from a small part of dead chains of the PPEGMA-*b*-PS sample.
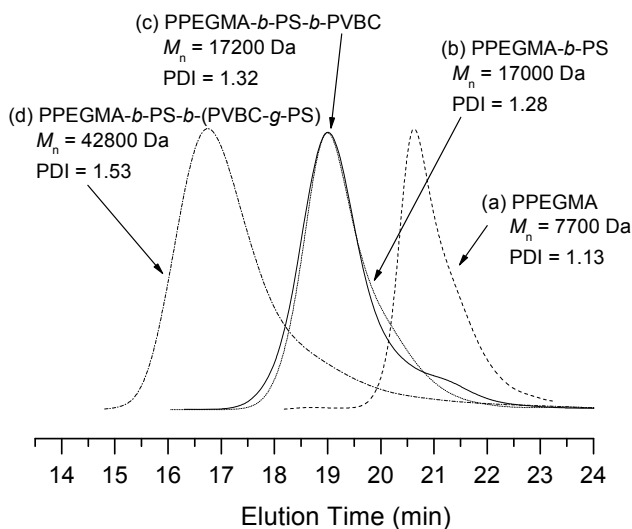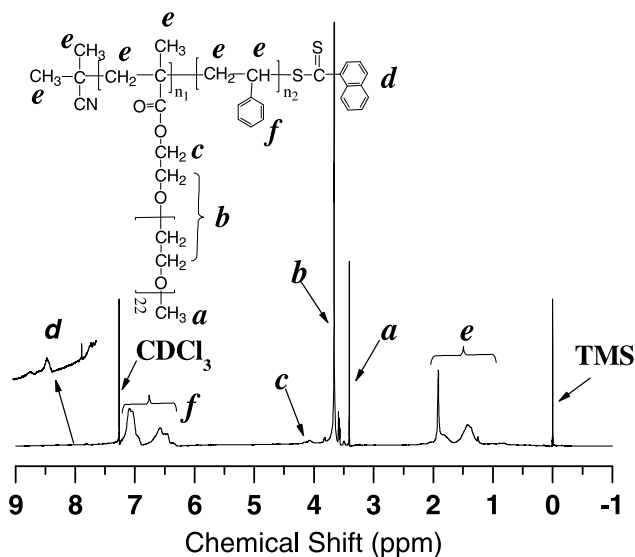
Figure 1. GPC traces of (a) PPEGMA, synthesized by RAFT polymerization of PEGMA, using CPDN as the RAFT agent, (b) PPEGMA-*b*-PS, synthesized by RAFT polymerization of St, using PPEGMA as the RAFT agent, (c) PPEGMA-*b*-PS-*b*-PVBC, synthesized by RAFT polymerization of VBC, using PPEGMA-*b*-PS as the macro-RAFT agent and (d) PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS) , synthesized by ATRP of St using the VBC units in PPEGMA-*b*-PS-*b*-PVBC as the ATRP macroinitiators.

Figure 2 shows the ^{1}H NMR spectrum of the PPEGMA homopolymer. The chemical shifts at δ = 3.38 ppm (*a)* and δ = 3.6-4.2 ppm (*b, c*) can be assigned to the protons of methoxyl group (-OCH$_3$) and methylene protons (-OCH$_2$-CH$_2$-) of the pendant poly(ethylene glycol) (PEG) brushes of PPEGMA, respectively [12]. The chemical shifts at 7.44-8.14 ppm (*d*) can be assigned to the aromatic protons of CPDN in the PPEGMA homopolymer [13]. The chemical shifts at 1.02-1.92 ppm (*e*) can be assigned to the methyl and methylene protons in the main chains of PPEMA homopolymer. Figure 3 shows the ^{1}H NMR spectrum of the PPEGMA-*b*-PS diblock brush-type amphiphilic copolymer. Besides the characteristic chemical shifts (*a*, *b* and *c*) of block PPEGMA, the chemical shifts at δ = 6.37- 7.09 ppm (*f*) correspond to the aromatic protons of block PS. From Figure 4, the chemical shift at δ = 4.5 ppm (*g*) is characteristic of the protons of –CH$_2$Cl in the PVBC block [14]. The benzyl chloride groups of the PVBC block in the triblock copolymer PPEGMA-*b*-PS-*b*-PVBC obtained from three consecutive RAFT processes can served as the active ATRP macroinitiators to initiate the polymerization of styrene via Cu(I)-mediated ATRP process using bpy as a ligand, resulting in the formation of the expected miktoarm dumbbell-like amphiphilic triblock copolymer. Figure 5 shows the ^{1}H NMR spectrum of the final polymer, miktoarm dumbbell-like amphiphilic triblock copolymer PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS) synthesized by combining three RAFT processes and one ATRP process. Similarly, besides the characteristic chemical shifts (*a*, *b* and *c*) of block PPEGMA, the chemical shifts at 6.38-7.09 ppm correspond to the aromatic protons (*f*) of the PS and PVBC blocks as well as PS brushes. It is mentioned that the characteristic chemical shift (4.5 ppm) of benzyl chloride groups has completely disappeared after ATRP process, indicating high initiator efficiency of macroinitiators. All these chemical shifts

are consistent with the structures of the PPEGMA homopolymer, PPEGMA-*b*-PS brush-type diblock copolymer, PPEGMA-*b*-PS-*b*-PVBC brush-type triblock copolymer and PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS) miktoarm dumbbell-like amphiphilic triblock copolymer.
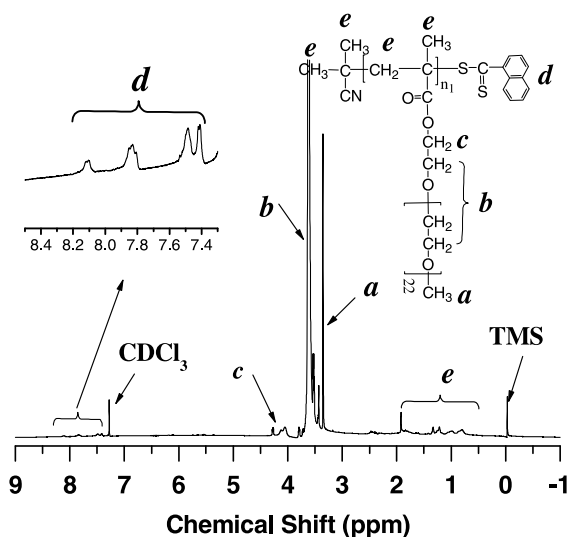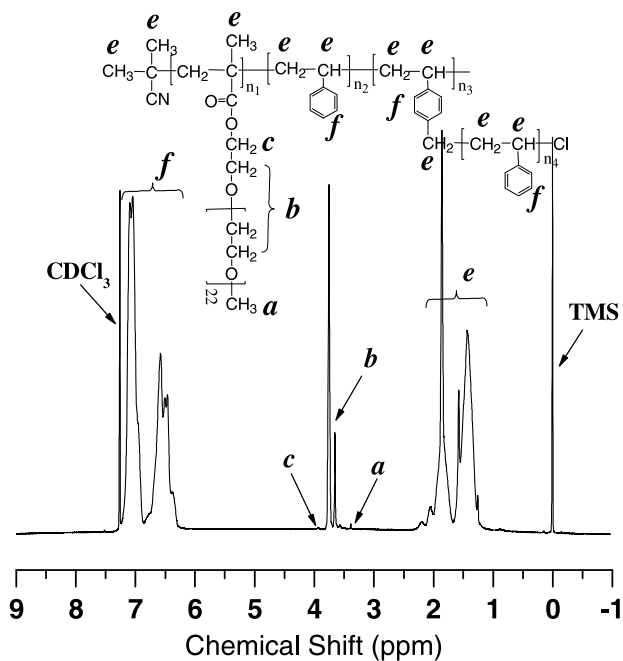

Figure 2. ¹H NMR of spectrum of PPEGMA synthesized by RAFT polymerization of PEGMA, using CPDN as the RAFT agent. $M_{n,NMR}$ = 10120 g/mol, PDI = 1.13.

Figure 3. ¹H NMR of spectrum of PPEGMA-*b*-PS synthesized by RAFT polymerization of St, using PPEGMA as the macro-RAFT agent. $M_{n,NMR}$ = 24780 g/mol, PDI = 1.28.
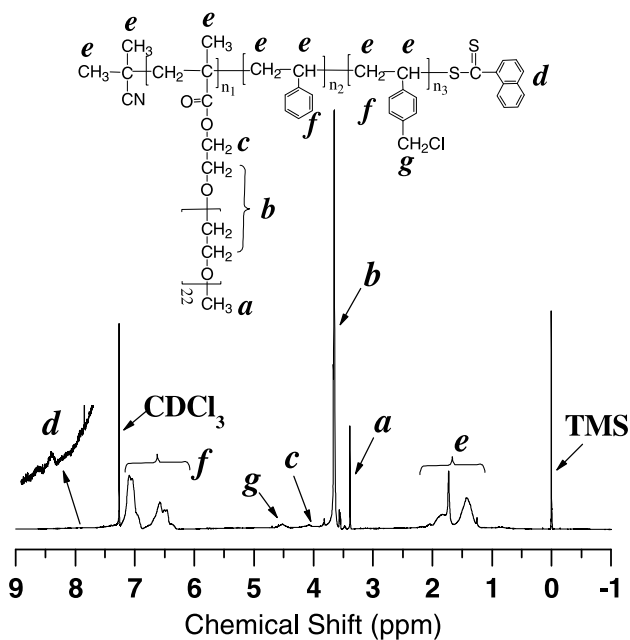
Figure 4. ^{1}H NMR of spectrum of PPEGMA-*b*-PS-*b*-PVBC synthesized by RAFT polymerization of VBC, using PPEGMA-*b*-PS as the macro-RAFT agent. $M_{n,NMR}$ = 26460 g/mol, PDI = 1.32.

Figure 5. ^{1}H NMR of spectrum of PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS) synthesized by ATRP of St using the VBC units in PPEGMA-*b*-PS-*b*-PVBC as the ATRP macroinitiators. $M_{n,NMR}$ = 151160 g/mol, PDI = 1.53.

Table 1. Number-average molecular weight (M_n) values and polydispersity index (PDI) values of the synthesized (co)polymers

Entry	Sample	$M_{n,GPC}$[a] g.mol^{-1}	$M_{n,th}$[b] g.mol^{-1}	$M_{n,NMR}$[c] g.mol^{-1}	PDI[a]
1	PPEGMA	7700	7450	10120	1.13
2	PPEGMA-*b*-PS	17000	24100	24780	1.28
3	PPEGMA-*b*-PS-*b*-PVBC	17200	30030	26460	1.32
4	PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS)	42800	175800	151160	1.53

[a]Number-average molecular weight determined from GPC results, calibrated with PMMA standards.
[b]Theoretical number-average molecular weight calculated from the molar ratio of monomer to reversible addition–fragmentation chain transfer (RAFT) agent for the RAFT process or from the molar ratio of the monomer to initiator for the atom transfer radical polymerization (ATRP) process.
[c]Number-average molecular weight calculated from ^{1}H NMR spectroscopy results.

The number-average molecular weight (M_n) values and the polydispersity index (PDI, PDI = M_w/M_n) values of the corresponding homopolymer and copolymers are listed in Table 1. The M_n values and PDI values of the polymers and copolymers were deduced from both GPC and ^{1}H NMR spectroscopy results. Entry 1 in Table 1 shows the results for the PPEGMA homopolymer. The M_n's of 7700 and 10120 g.mol^{-1}, deduced, respectively, from GPC and ^{1}H NMR spectroscopy (ratio of the aromatic protons of CPDN (*d* in Figure 2) to the protons of methoxyl group (-OCH$_3$) (*a* in Figure 2) for the pendant poly(ethylene glycol) (PEG) brushes of PPEGMA via the RAFT process) are in fairly good agreement with the theoretical value of 7450 g.mol^{-1} calculated from the mole ratio of the monomer to RAFT agent. However, from Entries 2-4 in Table 1, the M_n's (17000 g.mol^{-1}, 26400 g.mol^{-1} and 42800 g.mol^{-1}) of the diblock copolymer PPEGMA-*b*-PS, the triblock copolymer PPEGMA-*b*-PS-*b*-PVBC and the miktoarm dumbbell-like amphiphilic triblock copolymer PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS) measured by GPC are much less than their corresponding theoretical values of 24100 g.mol^{-1}, 30030 g.mol^{-1} and 175800 g.mol^{-1}. The deviations were probably caused by the fact that the hydrodynamic volumes of the brush-type copolymers probably differ substantially from that of the linear PMMA standards. The ^{1}H NMR spectra were also used to estimate the molecular weights of these brush-type copolymers. From Entries 2-4 in Table 1, the M_n's of 24780 g.mol^{-1} (calculated from the ratio of the aromatic protons of the PS block (*f* in Figure 3) to the protons of methoxyl group in the PPEGMA brushes (*a* in Figure 3) for the PPEGMA-*b*-PS copolymer, 26460 g.mol^{-1} (calculated from the ratio of the protons of methoxyl group in the P(PEGMA) brushes (*a* in Figure 4) to the protons of –CH$_2$Cl (*g* in Figure 4) in the PVBC block for the PPEGMA-*b*-PS-*b*-PVBC copolymer, and 151160 g.mol^{-1} (calculated from the ratio of the protons of methoxyl group (-OCH$_3$) and methylene protons (-OCH$_2$-CH$_2$-) of the pendant poly(ethylene glycol) (PEG) brushes of PPEGMA (*a*, *b* and *c* in Figure 5) to the aromatic protons of the PS and PVBC blocks (*f* in Figure 5) for the PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS) dumbbell-like copolymer are in reasonable agreement with their corresponding theoretical values. Thus, the molecular weights of the brush-type copolymers deduced from ^{1}H NMR spectroscopy results were adapted. The degrees of polymerization (DP's) of 9 for the PPEGMA, 141 for the PS block, 11 for the PVBC block and 109 for the PS brushes were obtained. Thus, for the obtained miktoarm

dumbbell-like amphiphilic triblock copolymer PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS) can be referred to as the PPEGMA$_9$-*b*-PS$_{141}$-*b*-(PVBC-*g*-PS$_{109}$)$_{11}$ copolymer. These results suggest that the molecular weights and composition of miktoarm dumbbell-like amphiphilic triblock copolymer could be successfully controlled by the monomer to initiator feed ratios in combined RAFT and ATRP techniques.

Micellization of the miktoarm dumbbell-like amphiphilic triblock copolymer in
Water/DMF mixtures containing 5.5 wt % water
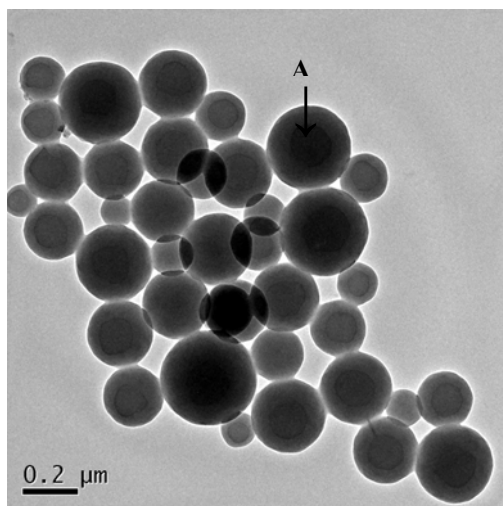
Figure 6. TEM images of the self-assembled micelles in water/DMF solution from the miktoarm dumbbell-like amphiphilic triblock copolymer, PPEGMA$_9$-*b*-PS$_{141}$-*b*-(PVBC-*g*-PS$_{109}$)$_{11}$. $M_{n,NMR}$ = 151160 g/mol, PDI = 1.53; polymer concentration = 2.5 wt%; water/(DMF + water) = 5.5 wt%.

It is well known that the amphiphilic copolymers can self-assemble into micelles in a suitable selective solvent. The aggregated morphology depends on many factors, including the chemical structure of copolymers, the block sequence, the relative lengths of the hydrophobic and hydrophilic blocks, and the nature of solvents [15]. Figure 6 shows the TEM image of the micelles of the miktoarm dumbbell-like amphiphilic triblock copolymer formed from self-assembly in water/DMF mixture containing 5.5 wt% water. Aggregates of nano-sized spherical micelles with 100-300 nm diameters are discernible. PPEGMA brushes are water-soluble, while PS brushes are hydrophobic. DMF is common solvent for both the hydrophobic PS brushes and hydrophilic PPEGMA brushes. In DMF solution, the entire copolymer spread well, when the deionized water was added into the solution, the hydrophobic segment is prone to pack together and reduce the contact area with DMF, which minimized the surface tension and the interaction with the environment. Thus, the self-assembled spherical micelles probably contain a hydrophobic PS core (the deep black spherical centre A in Figure 6) surrounded by a hydrophilic PPEGMA corona.

Conclusions

A four-step process, combining consecutive RAFT and ATRP techniques, for synthesizing miktoarm dumbbell-like amphiphilic triblock copolymer was demonstrated. Well-defined macromolecular structure and composition could be obtained through the control over ratios of the monomer to initiator in the combined living radical polymerizations. The obtained PPEGMA-*b*-PS-*b*-(PVBC-*g*-PS) copolymer could self-assemble into spherical micelles with 100-300 nm diameters in water/DMF mixture.

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