Dual-Brush-Type Amphiphilic Triblock Copolymer with Intact Epoxide Functional Groups from Consecutive RAFT Polymerizations and ATRP

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Introduction

Well-defined complex macromolecular architectures with controlled molecular weights are of particular interest when they can lead to new material properties. A large variety of macromolecules differing in topology of the bond skeletons and ordering of functional repeat units have been synthesized.[1,2] Polymer brushes are among the most intriguing macromolecular structures and can be synthesized by "grafting onto", "grafting through", and "grafting from" methods.[3−9]

Free radical polymerization is the most important industrial process for producing various vinyl polymers. However, conventional free radical polymerization techniques do not produce controlled molecular weights and molecular weight distributions because of the chain transfer and termination processes.[10] Thus, conventional radical polymerizations are precluded from the design and synthesis of well-defined polymers with narrow polydispersity and complex architecture. To achieve maximum control over the macromolecular structure, polydispersity, and composition, a controlled polymerization mechanism is highly desirable. Among the major controlled polymerization strategies developed, living radical polymerizations, atom transfer radical polymerization (ATRP) in particular, have become the most popular technique.[11−20] The ATRP process has good tolerance for a wide range of functional monomers and requires less stringent experimental conditions.[16,20] ATRP has been successfully applied to the preparation of well-defined polymer brushes in the "grafting from" approach.[21−29] In terms of chemical composition and molecular architecture, polymer brushes can be divided into homogeneous and heterogeneous (mixed) polymer brushes. A number of excellent works on the preparation of homogeneous polymer brushes have been reported.[30−34] In comparison, there have been fewer reports on the synthesis of heterogeneous polymer brushes. The synthesis of AB-type brush-*block*-brush amphiphilic copolymers via ATRP has been reported.[25,28] This paper presents a novel synthesis route, combining consecutive reversible addition−fragmentation chain transfer (RAFT) polymerizations and ATRP, for the preparation of heterogeneous dual-brush-type amphiphilic triblock copolymers.

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Experimental Section

Materials. The monomers, glycidyl methacrylate (GMA, 97%), 4-vinylbenzyl chloride (VBC, 90+%), and styrene (St, 99+%), were obtained from Aldrich Chemical Co. (Milwaukee, WI). After passing through inhibitor removing columns (Aldrich Chemical Co.), they were stored under an argon atmosphere at −10 °C. *N,N*-Dimethylformamide (DMF, analytical reagent) and tetrahydrofuran (THF, analytical reagent) were obtained from Fisher Scientific Co. (Leics, UK). Poly(ethylene glycol) methyl ether 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 an inhibitor removing 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 Figure 1), was synthesized according to procedures reported earlier.[35] The purity of CPDN was greater than 96% (Waters 515 HPLC; ^{1}H NMR ($CDCl_3$): 1.95 (s, 6H), 7.42 (m, 2H), 7.51 (m, 2H), 7.85 (m, 2H), and 8.10 (m, 1H)). The initiator α,α′-azobis(isobutyronitrile) (AIBN, 97%) was obtained from Kanto Chemical Co. (Tokyo, Japan) and was recrystallized in anhydrous ethanol. Copper(II) bromide ($CuBr_2$, 99+%), obtained from Aldrich Chemical Co., was dissolved in the deionized water, filtered, concentrated under reduced pressure at 30 °C, crystallized in a vacuum oven with P_2O_5, filtered, and dried. 2,2′-Bipyridyl (bpy, 99+%) was supplied by Aldrich Chemical Co. and was recrystallized in acetone. Copper(I) bromide (CuBr, 99+%) was supplied by Aldrich Chemical Co. All other solvents (reagent or HPLC grade) were obtained from Fisher Scientific Co. and used as received.

RAFT Polymerization of GMA Using CPDN as the RAFT Agent. Five mL (36.7 mmol) of GMA, 31.5 mg (0.183 mmol) of AIBN, and 159.7 mg (0.592 mmol) of CPDN were introduced into in a 10 mL dry glass tube. The light red homogeneous solution was purged with argon for ∼20 min to remove the dissolved oxygen. Then, the glass tube was sealed and placed in an oil bath at 60 °C to initiate the polymerization. At the end of the reaction (4.5 h), the glass tube was quenched in cold water and opened, diluted with THF, and precipitated into a large amount of methanol. The polymer, P(GMA), was dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained. The P(GMA) yield was about 4.45 g, and the conversion of GMA was about 88%. M_n of P(GMA) ∼ 6940 g mol^{-1}, as determined from gel permeation chromatography (GPC) results.

RAFT Polymerization of VBC Using P(GMA) as the Macro-RAFT Agent. The procedures used for the block copolymerization of VBC were similar to those used for the RAFT polymerization of GMA. 2.2 g (13.1 mmol) of VBC, 6.8 mg (0.040 mmol) of AIBN, and 1.0 g (0.149 mmol) of P(GMA) obtained above were dissolved in 2.0 mL of THF in a 10 mL dry glass tube under stirring. The homogeneous solution was purged with argon for ∼20 min. The glass tube was then sealed. Polymerization was carried out at 80 °C for 2 days. 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, P(GMA)-*b*-P(VBC), was dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained. The copolymer yield was about 2.1 g, and the conversion of VBC was about 60%. M_n of P(GMA)-*b*-P(VBC) ∼ 15700 g mol^{-1} from GPC results.

RAFT Polymerization of PEGMA Using P(GMA)-*b*-P(VBC) as the Macro-RAFT Agent. The procedures used for the RAFT polymerization of PEGMA were also similar to those used for the polymerization of GMA. 1.75 g (1.59 mmol) of PEGMA, 1.4 mg (0.008 mmol) of AIBN, and 0.5 g (0.031 mmol) of P(GMA)-*b*-P(VBC) obtained above were dissolved in

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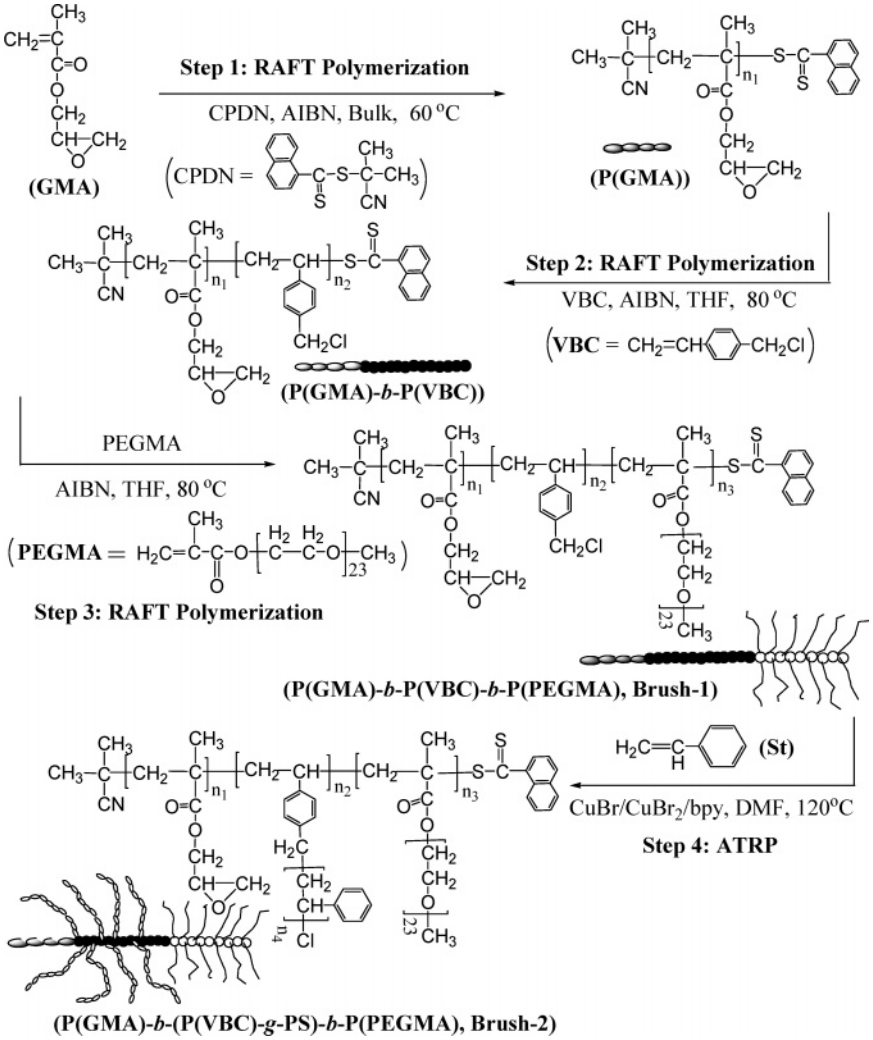

Figure 1. Schematic diagram illustrating the process for preparing the heterogeneous dual-brush-type amphiphilic triblock copolymer. GMA = glycidyl methacrylate; P(GMA) = poly(glycidyl methacrylate); AIBN = α,α′-azobis(isobutyronitrile); CPDN = 2-cyanoprop-2-yl 1-dithionaphthalate; VBC = 4-vinylbenzyl chloride; P(VBC) = poly(4-vinylbenzyl chloride); THF = tetrahydrofuran; PEGMA = poly(ethylene glycol) methyl ether methacrylate; P(PEGMA) = poly(poly(ethylene glycol) methyl ether methacrylate); St = styrene; PS = polystyrene; CuBr = copper(I) bromide; $CuBr_2$ = copper(II) bromide; bpy = 2,2′-bipyridyl; DMF = *N*,*N*-dimethylformamide; RAFT = reversible addition−fragmentation chain transfer; ATRP = atom transfer radical polymerization.

5.0 mL of THF in a 10 mL dry glass tube under stirring. The homogeneous solution was purged with argon for ∼20 min. The glass tube was then sealed. Polymerization was carried out at 80 °C for 26 h. 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 diethyl ether. The product was dried under reduced pressure at room temperature, transferred into methanol, precipitated into diethyl ether, centrifuged at 5000 rpm for 10 min, and filtered. The copolymer, P(GMA)-*b*-P(VBC)-*b*-P(PEGMA) or Brush-1, was dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained. The copolymer yield was about 1.18 g, and the conversion of PEGMA was about 40%. M_n of Brush-1 ∼ 36920 g mol^{-1} from ^{1}H NMR spectroscopy results.

ATRP of Styrene Using the VBC Units of Brush-1 as the Macroinitiators. The reaction mixture, containing 70 mg (0.116 mmol, based on the benzyl chloride units in Brush-1) of Brush-1, 1.0 mL of DMF, 1.0 mL (8.7 mmol) of St, 4.6 mg (0.032 mmol) of CuBr, 1.1 mg (0.005 mmol) of $CuBr_2$, and 15.4 mg (0.099 mmol) of bpy, was introduced into a 10 mL dry clean glass tube. The homogeneous solution was purged with argon for ∼20 min. The tube was then sealed. Polymerization was carried out at 120 °C under continuous stirring for 4 days. 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 40 mL of methanol, centrifuged at 5000 rpm for 10 min, and filtered. The Al_2O_3 column was flushed with excess (50 mL) THF to ensure complete elution of the copolymer. Elemental analysis of the resulting Al_2O_3 packing did not reveal any significant carbon content. The dual-brush-type amphiphilic triblock copolymer, P(GMA)-*b*-(P(VBC)-*g*-PS)-*b*-P(PEGMA) or Brush-2, was dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained. The copolymer yield was about 0.25 g, and the conversion of St was about 20%. M_n of Brush-2 ∼ 113 460 g mol^{-1} from ^{1}H NMR spectroscopy results.

Preparation of the Micelle Solution. Brush-2 (10 mg) was first dissolved in DMF (1 mL) to give a 10 mg mL^{-1} polymer solution. The polymer solution (0.50 mL) was added dropwise into deionized water (4.5 mL) under stirring. The micelle solution with a polymer concentration of about 1.0 mg mL^{-1} was used for the subsequent morphological studies by field emission scanning electron microscopy (FESEM).

Results and Discussion

Synthesis of the Triblock Copolymer with Amphiphilic Dual Brushes. RAFT polymerization is an alternative method for achieving controlled free radical polymerization in bulk polymerization,[36] solution polymerization,[37−42] and emulsion polymerization systems.[43] Brush-*co*-brush copolymers have been synthe-

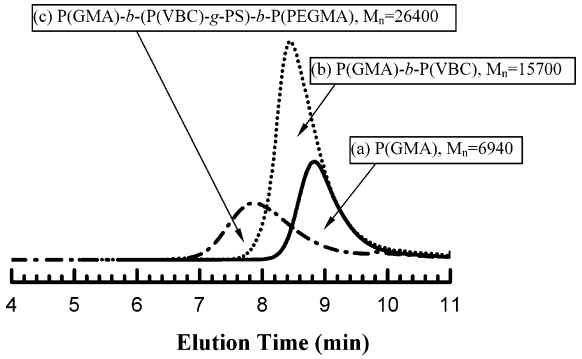

Figure 2. Gel permeation chromatography (GPC) traces of (a) P(GMA), synthesized by RAFT polymerization of GMA, using CPDN as the RAFT agent, (b) P(GMA)-*b*-P(VBC), synthesized by RAFT polymerization of VBC, using P(GMA) as the macro-RAFT agent, and (c) P(GMA)-*b*-(P(VBC)-*g*-PS)-*b*-P(PEGMA), synthesized by RAFT polymerization of PEGMA, using P(GMA)-*b*-P(VBC) as the macro-RAFT agent and subsequently ATRP of St using the VBC units in P(GMA)-*b*-P(VBC)-*b*-P(PEGMA) as the ATRP macroinitiators. GMA = glycidyl methacrylate; CPDN = 2-cyanoprop-2-yl 1-dithionaphthalate; VBC = 4-vinylbenzyl chloride; St = styrene; PEGMA = poly(ethylene glycol methyl ether methacrylate); P(GMA) = poly(glycidyl methacrylate); P(VBC) = poly(4-vinylbenzyl chloride); P(PEGMA) = poly(poly(ethylene glycol) methyl ether methacrylate); PS = polystyrene; RAFT = reversible addition−fragmentation chain transfer; ATRP = atom transfer radical polymerization.

sized by a combination of RAFT and ATRP techniques.[29] This paper presents the preparation of heterogeneous dual-brush-type triblock copolymers with intact epoxide functional groups by a combination of consecutive RAFT polymerizations and ARTP techniques. The synthetic pathway is shown in Figure 1. The process involves (i) synthesis of well-defined poly(glycidyl methacrylate), or P(GMA), via RAFT polymerization of glycidyl methacrylate (GMA), using 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN)[43] as the RAFT agent and α,α′-azobis(isobutyronitrile) (AIBN) as the initiator, (ii) synthesis of the diblock copolymer, poly(glycidyl methacrylate)-*b*-poly(4-vinylbenzyl chloride)) (P(GMA)-*b*-P(VBC)), via RAFT polymerization of 4-vinylbenzyl chloride (VBC), using P(GMA) as the macro-RAFT agent, (iii) synthesis of the triblock copolymer with hydrophilic brushes, poly(glycidyl methacrylate)-*b*-poly(4-vinylbenzyl chloride)-*b*-poly(poly(ethylene glycol) methyl ether methacrylate) (P(GMA)-*b*-P(VBC)-*b*-P(PEGMA) or Brush-1), via RAFT polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA), using the diblock copolymer (P(GMA)-*b*-P(VBC)) as the macro-RAFT agent, and (iv) synthesis of the heterogeneous dual-brush-type amphiphilic triblock copolymer, poly(glycidyl methacrylate)-*b*-(poly(4-vinylbenzyl chloride)-*g*-polystyrene)-*b*-poly(poly(ethylene glycol) methyl ether methacrylate) (P(GMA)-*b*-(P(VBC)-*g*-PS)-*b*-P(PEGMA) or Brush-2), via ATRP of styrene (St), using the benzyl chloride group of the VBC units in the P(VBC) block as the active ATRP macroinitiators. Details on the characterization of the polymer and copolymers are provided in the Supporting Information.

The size, structure, and composition of the polymer and copolymers were studied by gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy. Figure 2 shows the GPC traces of the P(GMA), P(GMA)-*b*-P(VBC), and Brush-2. The GPC traces of the three samples show a monomodal distribution. It should be noted that, arising from the limited resolution of the traces, the small changes in the elution time found for the copolymers may cover a substantial percentage of imperfect polymer in various mono-, di-, and triblocks. Figure 3 shows the ^{1}H NMR spectra of these polymers. The chemical shifts at $\delta = 3.23$ ppm (***a***) and $\delta = 2.63$ and 2.84 ppm (***b***) in Figure 3a−d can be assigned to the protons of the oxirane ring. The two protons labeled ***b*** are in different chemical environments and consequently give rise to two different resonances.[44] The results indicate that the epoxide groups remain intact in the polymer and copolymers throughout the RAFT polymerizations and ATRP. The chemical shifts at 7.44−8.14 ppm (***c***) in Figure 3a−c can be assigned to the aromatic protons of CPDN in the P(GMA) block.[44] The chemical shift at 4.52 ppm (***d*** in Figure 3b,c) is characteristic of the protons of $-CH_2Cl$ in the P(VBC) block. The chemical shifts at 6.15−7.03 ppm correspond to the aromatic protons (***e*** in Figure 3b,c) of the P(VBC) block. The chemical shifts at 3.38 and 3.64 ppm correspond to the protons of methoxyl group ($-OCH_3$, ***f*** in Figure 3c,d) and methylene protons ($-OCH_2-CH_2-$, ***g*** in Figure 3c,d) of the pendant poly(ethylene glycol) (PEG) brushes of P(PEGMA), respectively.[30,34,45,46] The chemical shifts at 6.38−7.07 ppm correspond to the aromatic protons (***e*** and ***h*** in Figure 3d) of the P(VBC) block and PS brushes. All these chemical shifts are consistent with the structures of the P(GMA) homopolymer, P(GMA)-*b*-P(VBC) diblock copolymer, Brush-1, and Brush-2.

The number-average molecular weights (M_n's) and the polydispersity indices (PDI's, PDI = M_w/M_n) of the corresponding polymer and copolymers are listed in Table 1. The M_n's and PDI's of polymer and copolymers were deduced from both GPC and ^{1}H NMR spectroscopy results. Entries 1 and 2 in Table 1 show the results for two linear polymers, P(GMA) and P(GMA)-*b*-P(VBC), respectively. The M_n's of 6940 and 6700 g mol^{-1}, deduced respectively from GPC and ^{1}H NMR spectroscopy (ratio of the aromatic protons of CPDN (***c*** in Figure 3a) to the protons of the oxirane ring (***a*** and ***b*** in Figure 3a)) for the P(GMA) homopolymer via the RAFT process are in fairly good agreement with the theoretical value of 7750 g mol^{-1} calculated from the mole ratio of the monomer to RAFT agent. Similarly, the M_n's of 15 700 and 16 020 g mol^{-1}, deduced respectively from GPC and ^{1}H NMR spectroscopy (ratio of the aromatic protons of VBC units in the P(VBC) block (***e*** in Figure 3b) to the protons of the oxirane ring (***a*** and ***b*** in Figure 3b)) for the diblock copolymer, P(GMA)-*b*-P(VBC), via the RAFT process are also in fairly good agreement with the theoretical value of 14 800 g mol^{-1}. Thus, based on M_n's estimated from the ^{1}H NMR spectroscopy results, the degrees of polymerization (DP's) are about 47 for P(GMA) and about 61 for P(VBC). Thus, the P(GMA) homopolymer is referred to as $P(GMA)_{47}$ and the diblock copolymer, P(GMA)-*b*-P(VBC), as $P(GMA)_{47}$-*b*-$P(VBC)_{61}$. The PDI's from GPC for $P(GMA)_{47}$ and $P(GMA)_{47}$-*b*-$P(VBC)_{61}$ remain less than 1.5.

However, from entries 3 and 4 in Table 1, the M_n's (17 000 and 26 400 g mol^{-1}) of Brush-1 and Brush-2 measured by GPC are much less than their corresponding theoretical values of 38 500 and 131 860 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 polystyrene standards. The ^{1}H NMR spectra were also used to estimate the molecular weights of these brush-type copolymers. For entries 3 and 4 in Table 1, the M_n's

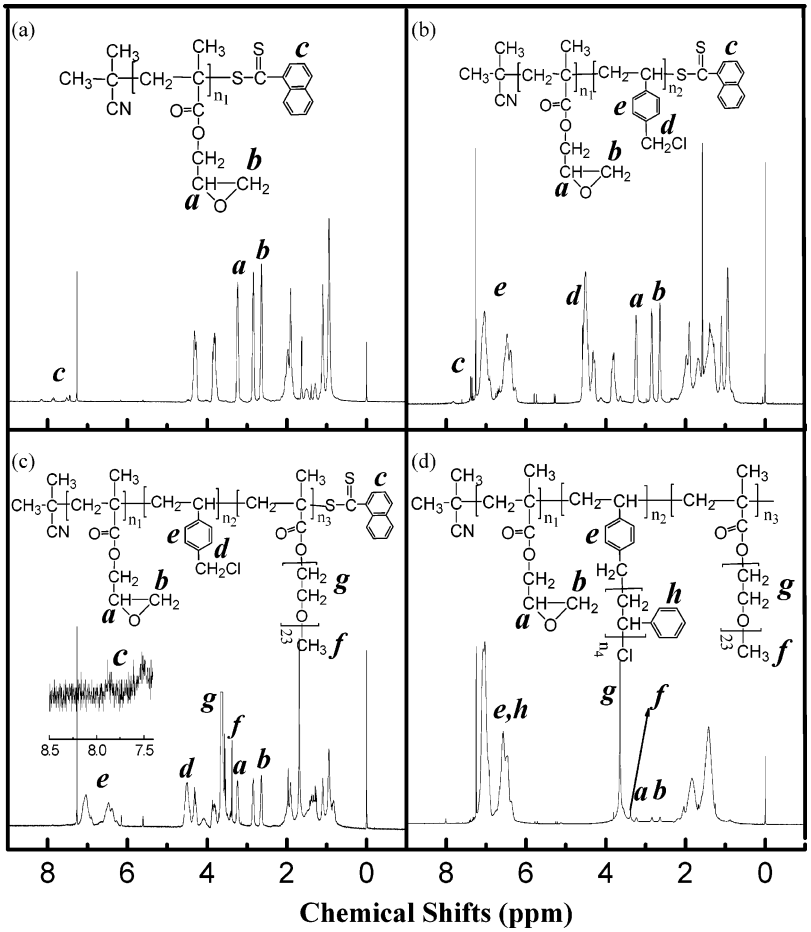

Figure 3. ^{1}H NMR of spectra of (a) P(GMA)$_{47}$, synthesized by RAFT polymerization of GMA, using CPDN as the RAFT agent, (b) P(GMA)$_{47}$-*b*-P(VBC)$_{61}$, synthesized by RAFT polymerization of VBC, using P(GMA)$_{47}$ as the macro-RAFT agent, (c) P(GMA)$_{47}$-*b*-P(VBC)$_{61}$-*b*-P(PEGMA)$_{19}$, synthesized by RAFT polymerization of PEGMA, using P(GMA)$_{47}$-*b*-P(VBC)$_{61}$ as the macro-RAFT agent, and (d) P(GMA)$_{47}$-*b*-(P(VBC)-*g*-PS$_{12}$)$_{61}$-*b*-P(PEGMA)$_{19}$, synthesized by ATRP of St using the VBC units in P(GMA)$_{47}$-*b*-P(VBC)$_{61}$-*b*-P(PEGMA)$_{19}$ as the ATRP macroinitiators. GMA = glycidyl methacrylate; CPDN = 2-cyanoprop-2-yl 1-dithionaphthalate; VBC = 4-vinylbenzyl chloride; St = styrene; PEGMA = poly(ethylene glycol methyl ether methacrylate); P(GMA) = poly(glycidyl methacrylate); P(VBC) = poly(4-vinylbenzyl chloride); P(PEGMA) = poly(poly(ethylene glycol) methyl ether methacrylate); PS = polystyrene; RAFT = reversible addition−fragmentation chain transfer; ATRP = atom transfer radical polymerization.

Table 1. Number-Average Molecular Weights (M_n's) and Polydispersity Indices (PDI's) of the Synthesized (Co)polymers

entry	sample	M_n,[a] g mol^{-1}	M_n,[b] g mol^{-1}	M_n,[c] g mol^{-1}	PDI[a]
1	P(GMA)	6 940	6 700	7 750	1.34
2	P(GMA)-*b*-P(VBC)	15 700	16 020	14 800	1.42
3	P(GMA)-*b*-P(VBC)-*b*-P(PEGMA)	17 000	36 920	38 500	1.50
4	P(GMA)-*b*-(P(VBC)-*g*-PS)-*b*-P(PEGMA)	26 400	113 460	131 860	2.00

[a] Number-average molecular weight determined from GPC results, calibrated with PS standards. PDI = M_w/M_n. [b] Number-average molecular weight calculated from ^{1}H NMR spectroscopy results. [c] 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. P(GMA) was synthesized by RAFT polymerization of GMA, using CPDN as the RAFT agent. P(GMA)-*b*-P(VBC) was synthesized by RAFT polymerization of VBC, using P(GMA) as the macro-RAFT agent. P(GMA)-*b*-P(VBC)-*b*-P(PEGMA) was synthesized by RAFT polymerization of PEGMA, using P(GMA)-*b*-P(VBC) as the macro-RAFT agent. P(GMA)-*b*-(P(VBC)-*g*-PS)-*b*-P(PEGMA) was synthesized by ATRP of St using the VBC units in P(GMA)-*b*-P(VBC)-*b*-P(PEGMA) as the ATRP macroinitiators. GMA = glycidyl methacrylate; CPDN = 2-cyanoprop-2-yl 1-dithionaphthalate; VBC = 4-vinylbenzyl chloride; St = styrene; PEGMA = poly(ethylene glycol methyl ether methacrylate); P(GMA) = poly(glycidyl methacrylate); P(VBC) = poly(4-vinylbenzyl chloride); P(PEGMA) = poly(poly(ethylene glycol) methyl ether methacrylate); PS = polystyrene.

of 36 920 g mol^{-1} (calculated from the ratio of the protons of methoxyl group in the P(PEGMA) brushes (***f*** in Figure 3c) to the protons of the oxirane ring (***a*** and ***b*** in Figure 3c)) for Brush-1 and 113 460 g mol^{-1} (calculated from the ratio of the protons of methoxyl group in the P(PEGMA) brushes (***f*** in Figure 3d) to the aromatic protons of the P(VBC) block and PS brushes (***e*** and *h* in Figure 3d)) for Brush-2 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. DP's of 19 for the P(PEGMA) and 12 for the 61 PS brushes were obtained. Benzyl chloride has a high initiation efficiency for the ATRP of styrene.[47] No benzyl chloride residue was discernible in the ^{1}H NMR spectrum of Brush-2 (Figure 3d). For Brush-1, the P(GMA)-*b*-P(VBC)-*b*-P(PEGMA) copolymer can be referred to as the P(GMA)$_{47}$-*b*-P(VBC)$_{61}$-*b*-P(PEGMA)$_{19}$ copolymer, and for Brush-2, the P(GMA)-*b*-(P(VBC)-*g*-PS)-*b*-P(PEGMA) copolymer as the P(GMA)$_{47}$-*b*-(P(VBC)-*g*-PS$_{12}$)$_{61}$-*b*-P(PEGMA)$_{19}$ copolymer. The C, H, N, and S elemental analysis results of the polymer and copolymers (Table S1, Sup-

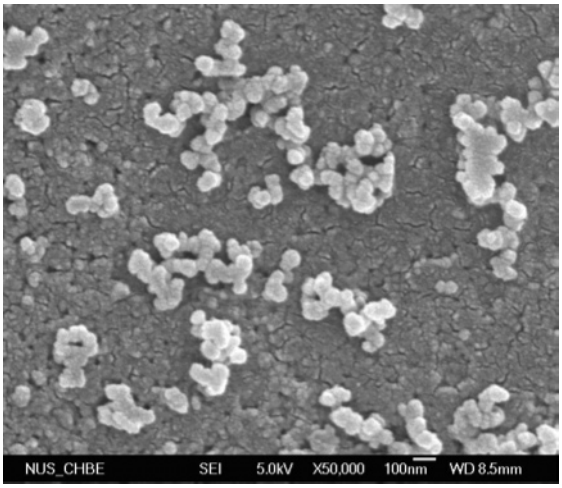

Figure 4. FESEM image of micelles of $P(GMA)_{47}$-*b*-(P(VBC)-*g*-$PS_{12})_{61}$-*b*-$P(PEGMA)_{19}$, or Brush-2, from self-assembly in deionized water at room temperature. Brush-2 was synthesized by RAFT polymerization of GMA, using CPDN as the RAFT agent, RAFT polymerization of VBC, using $P(GMA)_{47}$ as the macro-RAFT agent, RAFT polymerization of PEGMA, using $P(GMA)_{47}$-*b*-$P(VBC)_{61}$ as the macro-RAFT agent, and ATRP of St, using the VBC units in $P(GMA)_{47}$-*b*-$P(VBC)_{61}$-*b*-$P(PEGMA)_{19}$ as the ATRP macroinitiators. GMA = glycidyl methacrylate; CPDN = 2-cyanoprop-2-yl 1-dithionaphthalate; VBC = 4-vinylbenzyl chloride; St = styrene; PEGMA = poly(ethylene glycol methyl ether methacrylate); P(GMA) = poly(glycidyl methacrylate); P(VBC) = poly(4-vinylbenzyl chloride); P(PEGMA) = poly(poly(ethylene glycol) methyl ether methacrylate); PS = polystyrene; RAFT = reversible addition−fragmentation chain transfer; ATRP = atom transfer radical polymerization.

porting Information) are in reasonable agreement with the corresponding theoretical values based on molecular weights derived from NMR results. These results suggest that the molecular weights and composition of heterogeneous brush-type copolymers could be successfully controlled by the monomer to initiator feed ratios in combined RAFT and ATRP syntheses.

Aggregation Behavior of Brush-2 in Water. Depending on its architecture and chemical composition, linear amphiphilic block copolymer can self-assemble into micelles, vesicles, and a variety of other morphologies.[48−50] The self-assembly of homogeneous brush-type amphiphilic block copolymers in aqueous media has been reported.[30,34] Figure 4 shows the field emission scanning electron microscopy (FESEM) image of the micelles of Brush-2, the dual-brush-type block copolymer, from self-assembly in water. Aggregates of nanosized spherical micelles are discernible. The diameter of these spherical micelles was on the order of 80−90 nm. P(PEGMA) brushes are water-soluble, while PS brushes are hydrophobic. Thus, the self-assembled spherical micelles probably contain a hydrophobic PS core surrounded by a hydrophilic P(PEGMA) corona. Although the observed micelle structure in the present work is yet to be critically compared to that in the aqueous medium, the structures and aggregation morphologies of micelles from amphiphilic copolymers in aqueous media are known to be readily preserved for characterization by scanning and transmission electron microscopies.[51,52] The persistence of comparable proton signal intensities associated with the oxirane rings in the ^{1}H NMR spectrum of the micelles of Brush-2 suggested that, in the absence of a catalyst, the glycidyl groups did not undergo extensive reaction with water to form 1,2-diols during micelle formation.

In summary, a four-step process, combining consecutive RAFT and ATRP techniques, for synthesizing dual-brush-type amphiphilic triblock copolymer with intact epoxide functional groups was demonstrated. Well-defined macromolecular structure and composition could be obtained through the control of the monomer-to-initiator ratios in the combined living radical polymerizations.

Supporting Information Available: Detailed materials characterization by GPC, NMR, FESEM, and elemental analysis; tabulation of elemental analysis results. These materials are available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ambilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725−2828.
(2) Matyjaszewski, K. Advances in Controlled/Living Radical Polymerization. *ACS Symp. Ser.* **2003**, *854*, 161−179.
(3) Tsukahara, Y.; Tsutsumi, K.; Yamashita, Y.; Shimada, S. *Macromolecules* **1990**, *23*, 5201−5208.
(4) Schappacher, M.; Deffieux, A. *Macromolecules* **2000**, *33*, 7371−7377.
(5) Dziezok, P.; Sheiko, S. S.; Fischer, K.; Schmidt, M.; Moller, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2812−2815.
(6) Granville, A. M.; Brittain, W. J. *Polym. Brushes* **2004**, 35−50.
(7) Husseman, M.; Malmstro1m, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424−1431.
(8) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem. Soc. Rev.* **2004**, *33*, 14−22.
(9) Mori, H.; Müller, A. H. E. *Prog. Polym. Sci.* **2003**, *28*, 1403−1439.
(10) Matyjaszewski, K., Davis, T. P., Eds.; *Handbook of Radical Polymerization*; John Wiley & Sons: Hoboken, 2002.
(11) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 2689−3746.
(12) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.
(13) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615.
(14) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721−1723.
(15) Percec, V.; Narboiu, B. *Macromolecules* **1995**, *28*, 7970−7972.
(16) Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101*, 2921−2990.
(17) John, C. Y. K.; Frances, E.; Julia, K.; Jeffery, J.; Le, T. P.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.
(18) Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127−132.
(19) Otsu, T.; Yoshida, M.; Tazaki, T. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 133−140.
(20) Feng, W.; Brash, J.; Zhu, S. P. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2931−2942.
(21) Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. *Macromolecules* **1998**, *31*, 9413−9415.
(22) Borner, H. G.; Beers, K.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. *Macromolecules* **2001**, *34*, 4375−4383.
(23) Cheng, G. L.; Boker, A. A.; Zhang, M. F.; Krausch, G.; Müller, A. H. E. *Macromolecules* **2001**, *34*, 6883−6888.
(24) Börner, H. G.; Duran, D.; Matyjaszewski, K.; da Silva, M.; Sheiko, S. S. *Macromolecules* **2002**, *35*, 3387−3394.
(25) Qin, S. H.; Matyjaszewski, K.; Xu, H.; Sheiko, S. S. *Macromolecules* **2003**, *36*, 605−612.
(26) Zhang, M. F.; Breiner, T.; Mori, H.; Müller, A. H. E. *Polymer* **2003**, *44*, 1449−1458.
(27) Matyjaszewski, K.; Qin, S. H.; Boyce, J. R.; Shirvanyants, D.; Sheiko, S. S. *Macromolecules* **2003**, *36*, 1843−1849.
(28) Ishizu, K.; Satoh, J.; Sogabe, A. *J. Colloid Interface Sci.* **2004**, *274*, 472−479.
(29) Venkatesh, R.; Yajjou, L.; Koning, C. E.; Klumperman, B. *Macromol. Chem. Phys.* **2004**, *205*, 2161−2168.
(30) Holder, S. J.; Rossi, N. A. A.; Yeoh, C.-T.; Durand, G. G.; Boerakkerb, M. J.; Sommerdijk, N. A. J. M. *J. Mater. Chem.* **2003**, *13*, 2771−2778.

(31) Neugebauer, D.; Zhang, Y.; Pakula, T.; Sheiko, S. S.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 6746−6755.
(32) Neugebauer, D.; Zhang, Y.; Pakula, T.; Matyjaszewski, K. *Polymer* **2003**, *44*, 6863−6871.
(33) Ali, M. M.; Stöver, H. D. H. *Macromolecules* **2004**, *37*, 5219−5227.
(34) Bes, L.; Angot, S.; Limer, A.; Haddleton. D. M. *Macromolecules* **2003**, *36*, 2493−2499.
(35) Zhu, J.; Zhu, X. L.; Cheng, Z. P.; Liu, F.; Lu, J. M. *Polymer* **2002**, *43*, 7037−7042.
(36) Zhou, G.; Harruna. I. I. *Macromolecules* **2004**, *37,* 7132−7139.
(37) Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. A. *Macromolecules* **1999**, *32*, 2071−2074.
(38) Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. *Macromolecules* **2003**, *36*, 1505−1513.
(39) Loiseau, J.; Doerr, N.; Svau, J. M.; Egraz, J. B.; Llauro, M. F.; Ladaviere, C. *Macromolecules* **2003**, *36*, 3066−3077.
(40) Yusa, S.; Shimada, Y.; Mitsukami, Y.; Yamamoto, T.; Morishima, Y. *Macromolecules* **2003**, *36*, 4208−4215.
(41) Christopher, B.-K.; Davis, T. P.; Heuts, J. P. A.; Stenzel, M. H.; Vana, P.; Whittaker, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 365−375.
(42) Quinn, J. F.; Barner, L.; Rizzardo, E.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 19−25.
(43) Smulders, W.; Monteiro, M. J. *Macromolecules* **2004**, *37*, 4474−4483.
(44) Zhu, J.; Zhou, D.; Zhu, X. L.; Chen, G. J. *J. Polym. Chem., Part A: Polym. Chem.* **2004**, *42*, 2558−2565.
(45) Hester, J. F.; Banerjee, P.; Won, Y.-Y.; Akthakul, Acar, A. M. H.; Mayes, A. M. *Macromolecules* **2002**, *35*, 7652−7661.
(46) Chen, Y. W.; Wang, W. C.; Yu, W. H.; Kang, E. T.; Neoh, K. G.; Vora, R. H.; Ong, C. K.; Chen, L. F. *J. Mater. Chem.* **2004**, *14*, 1406−1412.
(47) Nakagawa, Y.; Miller, P. J.; Matyjaszewski, K. *Polymer* **1998**, *39*, 5163−5170.
(48) Förster, S.; Plantenberg, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 688−714.
(49) Fu, J.; Luan, B.; Yu, X.; Yang, C.; Li, J.; Pan, C. Y.; Han, Y. C.; Yang, Y. M.; Li, B. Y. *Macromolecules* **2004**, *37*, 976−986.
(50) Zhang, L. F.; Yu, K.; Eisenberg, A. *Science* **1996**, *272*, 1777−1779.
(51) Shen, H.; Eisenberg, A. *J. Phys. Chem. B* **1999**, *103*, 9473−9487.
(52) Vriezema, D. M.; Krus, A.; de Gelder, R.; Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M. *Macromolecules* **2004**, *37*, 4736−4739.

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